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Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry

Point Source Category

Vol. I

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DEVELOPMENT DOCUMENT for INTERIM FINAL AND PROPOSED EFFLUENT LIMITATIONS GUIDELINES and NEW SOURCE PERFORMANCE STANDARDS for the ORE MINING AND DRESSING POINT SOURCE CATEGORY

VOLUME I - SECTIONS I - VI

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ABSTRACT

This document presents the findings of an extensive study of the ore mining and dressing industry, for the purpose of developing effluent limitations guidelines for existing point sources and standards of performance and pretreatment standards for new sources, to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1551, 1314, and 1316, 86 Stat. 816 et. seq.) (the "Act").

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available (BPCTCA) and the degree of effluent reduction attainable through the application of the best available technology economically achievable (BATEA) which must be achieved by existing point sources by July 1, 1977, and July 1, 1983, respectively. The standards of performance and pretreatment standards for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

Based upon the application of the best practicable control technology currently available, 14 of the 41 subcategories for which separate limitations are suggested can be operated with no discharge of process waste water. With the best available technology economically achievable, 21 of the 41 subcategories for which separate limitations are proposed can be operated with no discharge of process waste water to navigable waters. No discharge of process waste water pollutants is also achievable as a new source performance standard for 21 of the 41 subcategories.

Supporting data and rationale for development of the proposed effluent limitation guidelines and standards of performance are contained in this report (Volumes I and II).

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FIGURES (cont.)

SECTION I

CONCLUSIONS

To establish effluent limitation guidelines and standards of performance, the ore mining and dressing industry was divided into 41 separate categories and subcategories for which separate limitations were recommended. This report deals with the entire metal-ore mining and dressing industry and examines the industry by ten major categories: iron ore; copper ore; lead and zinc ores; gold ore; silver ore; bauxite ore; ferroalloy-metal ores; mercury ores; uranium, radium and vanadium ores; and metal ores, not elsewhere classified (ores of antimony, beryllium, platinum, rare earths, tin, titanium, and zirconium). The subcategorization of the ore categories is based primarily upon ore mineralogy and processing or extraction methods employed; however, other factors (such as size, climate or location, and method of mining) are used in some instances.

Based upon the application of the best practicable control technology currently available, mining or milling facilities in the 14 of 41 subcategories for which separate limitations are proposed can be operated with no discharge of process waste water. With the best available technology economically achievable, facilities in 21 of the 41 subcategories can be operated with no discharge of process waste water to navigable waters. No discharge of process waste water is also achievable as a new source performance standard for facilities in 21 of the 41 subcategories.

Examination of the waste water treatment methods employed in the ore mining and dressing industry indicates that tailing ponds or other types of sedimentation impoundments are the most commonly used methods of suspended-solid removal, and that these impoundments provide the additional benefit of reduction of dissolved parameters as well. Tailing impoundments also serve to equalize flow rates and concentrations of waste water parameters.

It is concluded that, for areas of excess water balance, the practices of runoff diversion, segregation of waste streams, and reduction in the use of process water will assist in the attainment of no discharge for the specified subcategories. Effective chemical-treatment methods which will result in significant improvement in discharge-water quality and pollutant waste loads beyond those attained by the application of impoundment and settling are identified in this report.

SECTION II

RECOMMENDATIONS

The recommended effluent limitation guidelines based on the best practicable control technology currently available (BPCTCA) are summarized in Table II-1. Based on information contained in Sections III through VIII, it is recommended that facilities in 14 of the 41 subcategories achieve no discharge of process waste water.

The recommended effluent limitation guidelines based upon the best available technology economically achievable (BATEA) are summarized in Table II-2. Of the 41 subcategories listed for which separate limitations are recommended, it is recommended that facilities in 21 subcategories achieve no discharge of process waste water by 1983.

The new source performance standards (NSPS) recommended for operations begun after the proposal of recommended guidelines for the ore mining and dressing industry are summarized in Table II-3. With the exception of four subcategories, new source performance standards are identical to BPCTCA and BATEA recommended effluent limitations.

TABLE II-1. SUMMARY OF RECOMMENDED BPCTCA EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 1 of 2)

CATEGORY/SUBCATEGORY		ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
IRON ORES			
Mines			IX-1
Mills	Physical/Chemical Separation		IX-2
	Magnetic and Physical Separation	X	
COPPER ORES			
Mines	Open-Pit, Underground, Stripping		IX-3
	Hydrometallurgical (Leaching)	X	
Mills	Vat Leaching	X	
	Flotation		IX-4
LEAD AND ZINC ORES			
Mines			IX-5
Mills			IX-6
GOLD ORES			
Mines			IX-7
Mills	Cyanidation Process	X	
	Amalgamation Process		IX-8
	Flotation Process		IX-9
	Gravity Separation		IX-10
SILVER ORES			
Mines			IX-11
Mills	Flotation Process		IX-12
	Cyanidation Process	X	
	Amalgamation Process		IX-13
	Gravity Separation		IX-14
BAUXITE ORE			
Mines			IX-15

TABLE II-1. SUMMARY OF RECOMMENDED BPCTCA EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 2 of 2)

CATEGORY/SUBCATEGORY		ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
FERROALLOY ORES			
Mines	> 5,000 metric tons[†]/year		IX-16
Mines/Mills	< 5,000 metric tons[†]/year		IX-17
Mills	> 5,000 metric tons[†]/year by Physical Processes		IX-18
	> 5,000 metric tons[†]/year by Flotation		IX-19
	Leaching		IX-20
MERCURY ORES			
Mines			IX-21
Mills	Gravity Separation	X	
	Flotation Process	X	
URANIUM, RADIUM, VANADIUM ORES			
Mines			IX-22
Mills	Acid or Acid/Alkaline Leaching	X	
	Alkaline Leaching	X	
ANTIMONY ORES			
Mines			IX-23
Mills	– Flotation Process	X	
BERYLLIUM ORES			
Mines		X	
Mills		X	
PLATINUM ORES			
Mines or Mine/Mills			IX-24
RARE-EARTH ORES			
Mines		X	
Mills	– Flotation or Leaching	X	
TITANIUM ORES			
Mines			IX-25
Mills	Electrostatic/Magnetic and Gravity/Flotation Processes		IX-26
	Physical Processes with Dredge Mining		IX-27

[†] 5,000 metric tons = 5,512 short tons

TABLE II-2. SUMMARY OF RECOMMENDED BATEA EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 1 of 2)

CATEGORY/SUBCATEGORY		ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
IRON ORES			
Mines			X-1
Mills	Physical/Chemical Separation		X-2
	Magnetic and Physical Separation	X	
COPPER ORES			
Mines	Open-Pit, Underground, Stripping		X-3
	Hydrometallurgical (Leaching)	X	
Mills	Vat Leaching	X	
	Flotation	X	
LEAD AND ZINC ORES			
Mines			X-4
Mills		X	
GOLD ORES			
Mines			X-5
Mills	Cyanidation Process	X	
	Amalgamation Process	X	
	Flotation Process	X	
	Gravity Separation		(Same as BPCTCA)
SILVER ORES			
Mines			X-6
Mills	Flotation Process	X	
	Cyanidation Process	X	
	Amalgamation Process	X	
	Gravity Separation		(Same as BPCTCA)
BAUXITE ORE			
Mines			X-7

TABLE II-2. SUMMARY OF RECOMMENDED BATEA EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 2 of 2)

CATEGORY/SUBCATEGORY	ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
FERROALLOY ORES		
Mines > 5,000 metric tons†/year		X-8
Mine/Mills < 5,000 metric tons†/year		(Same as BPCTCA)
Mills – > 5,000 metric tons†/year by Physical Processes		X-9
Mills – > 5,000 metric tons†/year by Flotation		X-10
Mills – Leaching		X-11
MERCURY ORES		
Mines		X-12
Mills – Gravity Separation	X	
Mills – Flotation Process	X	
URANIUM, RADIUM, VANADIUM ORES		
Mines		X-13
Mills – Acid or Acid/Alkaline Leaching	X	
Mills – Alkaline Leaching	X	
ANTIMONY ORES		
Mines		(Same as BPCTCA)
Mills – Flotation Process	X	
BERYLLIUM ORES		
Mines	X	
Mills	X	
PLATINUM ORES		
Mines or Mine/Mills		(Same as BPCTCA)
RARE-EARTH ORES		
Mines	X	
Mills – Flotation or Leaching	X	
TITANIUM ORES		
Mines		(Same as BPCTCA)
Mills – Electrostatic/Magnetic and Gravity/Flotation Processes	X	
Mills – Physical Processes with Dredge Mining		(Same as BPCTCA)

TABLE II-3. SUMMARY OF RECOMMENDED NSPS EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 1 of 2)

CATEGORY/SUBCATEGORY		ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
IRON ORES			
Mines			(Same as BATEA)
Mills	Physical/Chemical Separation		(Same as BATEA)
	Magnetic and Physical Separation	X	
COPPER ORES			
Mines	Open-Pit, Underground, Stripping		(Same as BATEA)
	Hydrometallurgical (Leaching)	X	
Mills	Vat Leaching	X	
	Flotation	X	
LEAD AND ZINC ORES			
Mines			(Same as BATEA)
Mills		X	
GOLD ORES			
Mines			(Same as BATEA)
Mills	Cyanidation Process	X	
	Amalgamation Process	X	
	Flotation Process	X	
	Gravity Separation		(Same as BPCTCA)
SILVER ORES			
Mines			(Same as BATEA)
Mills	Flotation Process	X	
	Cyanidation Process	X	
	Amalgamation Process	X	
	Gravity Separation		(Same as BPCTCA)
BAUXITE ORE			
Mines			(Same as BPCTCA)

TABLE II-3. SUMMARY OF RECOMMENDED NSPS EFFLUENT LIMITATIONS BY CATEGORY AND SUBCATEGORY – ORES FOR WHICH SEPARATE LIMITATIONS ARE PROPOSED (Sheet 2 of 2)

CATEGORY/SUBCATEGORY		ZERO DISCHARGE	EFFLUENT LIMITATIONS RECOMMENDED IN TABLE
FERROALLOY ORES			
Mines	> 5,000 metric tons[†]/year		XI-1
Mine/Mills	< 5,000 metric tons[†]/year		XI-2
Mills	> 5,000 metric tons[†]/year by Physical Processes		
	> 5,000 metric tons[†]/year by Flotation		XI-3
	Leaching		(Same as BATEA)
MERCURY ORES			
Mines			(Same as BPCTCA)
Mills	Gravity Separation	X	
	Flotation Process	X	
URANIUM, RADIUM, VANADIUM ORES			
Mines			XI-4
Mills	Acid or Acid/Alkaline Leaching	X	
	Alkaline Leaching	X	
ANTIMONY ORES			
Mines			(Same as BPCTCA)
Mills –	Flotation Process	X	
BERYLLIUM ORES			
Mines		X	
Mills		X	
PLATINUM ORES			
Mines or Mine/Mills			(Same as BPCTCA)
RARE-EARTH ORES			
Mines		X	
Mills –	Flotation or Leaching	X	
TITANIUM ORES			
Mines			(Same as BPCTCA)
Mills	Electrostatic/Magnetic and Gravity/Flotation Processes	X	
	Physical Processes with Dredge Mining		(Same as BPCTCA)

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

The United States Environmental Protection Agency (EPA) is charged under the Federal Water Pollution Control Act Amendments of 1972 with establishing effluent limitations which must be achieved by point sources of discharge into the waters of the United States.

Section 301(b) of the Act requires the achievement, by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement, by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants. Section 304(b) of the Act requires the Administrator to publish, within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operating methods and other alternatives.

The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the Ore Mining and Dressing Industry point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performance for new sources within such categories. Section 307 of the Act requires the Administrator to propose pretreatment standards for new sources simultaneously with the promulgation of standards of performance under Section 306. The Administrator published, in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of an amended list will constitute announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the ore mining and dressing industry, and under Section 307, pretreatment standards. The list will be amended when proposed regulations for the Ore Mining and Dressing Industry are published in the Federal Register.

The subgroups of the metal mining industries are identified as major group 10 in the Standard Industrial Classification (SIC) Manual, 1972, published by the Executive Office of the President (Office of Management and Budget). This industry category includes establishments engaged in mining ores for the production of metals, and includes all ore dressing and beneficiating operations, whether performed at mills operating in conjunction with the mines served or at mills operated separately. These include mills which crush, grind, wash, dry, sinter, or leach ore, or perform gravity separation or flotation operations.

The industry categories covered by this report include the following:

SIC 1011 - Iron Ores
SIC 1021 - Copper Ores
SIC 1031 - Lead and Zinc Ores
SIC 1041 - Gold Ores
SIC 1044 - Silver Ores
SIC 1051 - Bauxite Ores
SIC 1061 - Ferroalloy Ores
SIC 1092 - Mercury Ores
SIC 1094 - Uranium/Radium/Vanadium Ores
SIC 1099 - Metal Ores, Not Elsewhere Classified

The guidelines in this document identify, in terms of the chemical, physical, and biological characteristics of pollutants, the level of pollutant reduction attainable through application of the best practicable control technology currently available, and best available technology economically achievable. Standards of performance for new sources and pretreatment are also presented. The guidelines also consider a number of other factors, such as the costs of achieving the proposed effluent limitations and nonwater quality environmental impacts (including energy requirements resulting from application of such technologies).

SUMMARY OF METHODS USED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES AND STANDARDS OF TECHNOLOGY

Scope

The effluent limitations guidelines and standards of performance proposed herein were developed in a series of systematic tasks. The Ore Mining and Dressing Industry was first studied to determine whether separate limitations and standards would be appropriate for different SIC categories. Development of reasonable industry categories and subcategories and establishment of effluent guidelines and treatment standards require a sound understanding and knowledge of the Ore Mining and Dressing Industry, the mining techniques and milling processes involved, the mineralogy of the ore deposits, water use, waste water generation and characteristics, and the capabilities of existing control and treatment technologies.

Approach

This report describes the results obtained from application of the above approach to the mining and beneficiating of metals and ore minerals for the ore mining and dressing industry. The survey and sampling and analysis covered a wide range of processes, products, and types of wastes. In each SIC category, slightly different evaluation criteria were applied initially, depending upon the nature of the extraction processes employed, locations where mining activities occur, mineralogical differences, treatment and control technology employed, and water usage in the industry category. The following discussion illustrates the manner in which the effluent guidelines and standards of performance were developed.

Data Base

Each SIC category was first examined to determine the range of activities incorporated by the industry classification.

Information used as a data base for detailed examination of each category was obtained from a wide variety of sources including published data from journals and trade literature, mining industry directories, general business publications, texts on mining/milling technology, texts on industrial waste water control, summaries of production of the particular metals of interest, U.S. Bureau of Mines annual summaries, U.S. Environmental Protection Agency publications, U.S. Geological Survey publications, surveys performed by industry trade associations, NPDES permits and permit applications, and numerous personal contacts. Additional information was supplied by surveys of research performed in the application of mining, extractive processing, and effluent control technology. Various mining company personnel, independent researchers, and state and federal environmental officials also supplied requested information. In addition, Environment Canada provided information on current practices within the Canadian Mining and Dressing Industry.

Categorization and Waste Load Characterization

After assembly of an extensive data base, each SIC code group or subgroup was examined to determine whether different limitations and standards would be appropriate. In several categories, it was determined that further subdivision was unnecessary. In addition, after further study and site visits, subcategory designations were later reduced within a category in some instances. Where appropriate, subcategorization consideration was based upon whether the facility was a mine or a concentrating facility (mill), and further based upon differences such as raw material extracted or used, milling or concentration process employed, waste characteristics, treatability of wastes, reagents used in the process, treatment technology employed, water use and balance, end products or byproducts. Other factors considered were the type of mine (surface or underground), geographic location, size, age of the operation, and climate.

Determination of the waste water usage and characteristics for each subcategory as developed in Section IV and discussed in Section V included: (1) the source and volume of water used in the particular process employed and the source of waste and waste waters in the plant, and (2) the constituents (including thermal) of all waste waters, including pollutants, and other constituents which result in taste, odor, and color in water or aquatic organisms. Those constituents discussed in Section V and Section VI which are characteristic of the industry and present in measurable quantities were selected as pollutants subject to effluent limitation guidelines and standards.

Site Visits and Sampling Program

Based upon information gathered as part of the assembly of a data base, examination of NPDES permits and permit applications, surveys by trade associations, and examination of texts, journals, and the literature available on treatment practices in the industry, selection of mining and milling operations which were thought to embody exemplary treatment practice was made for the purpose of sampling and verification, and to supplement compiled data. All factors potentially influencing industry subcategorization were represented by the sites chosen. Detailed information on production, water use, waste water control, and water treatment practices was obtained. As a result of the visits, many subcategories which had been tentatively determined were found to be unnecessary. Flow diagrams were obtained indicating the course of waste water streams. Control and treatment plant design and detailed cost data were compiled.

Sampling and analysis of raw and treated effluent streams, process source water, and intermediate process or treatment steps were performed as part of the site visits. *In-situ* analyses for selected parameters such as temperature, pH, dissolved oxygen, and specific conductance were performed whenever possible. Historical data for the same waste streams was obtained when available.

Raw waste characteristics were then identified for each subcategory. This included an analysis of all constituents of waste waters which might be expected in effluents from mining and milling operations. In addition to examination of candidate control parameters, a reconnaissance investigation of some 55 chemical parameters was performed upon raw and treated effluent for each site visited. Additionally, limited sampling of mine waters for radiological parameters was accomplished at selected sites. Raw and treated waste characterization during this study was based upon a detailed chemical analysis of the samples and historical effluent water quality data supplied by the industry and Federal and State regulatory agencies.

Cost Data Base

Cost information contained in this report was obtained directly from industry during plant visits, from engineering firms, equipment suppliers, and from the literature. The information obtained from these sources has been used to develop general capital, operating and overall costs for each treatment and control method. Where data was lacking, costs were developed parametrically from knowledge of equipment required, processes employed, construction, and maintenance requirements. This generalized cost data plus the specific information obtained from plant visits was then used for cost effectiveness estimates in Section VIII and wherever else costs are mentioned in this report.

Treatment and Control Technologies

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each control and treatment technology, including both in-plant and end-of-process technologies, which is existent or capable of being designed for each subcategory. It also included an identification of the amounts and the characteristics of pollutants resulting from the application of each of the control and treatment technologies. The problems, limitations, and reliability of each control and treatment technology were also identified. In addition, the nonwater-quality environmental impact--such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise, and radiation--was also identified. The energy requirements of each of the control and treatment technologies were identified, as well as the cost of the application of such technologies.

Selection of BPCTCA, BATEA, and New Source Standards

All data obtained were evaluated to determine what levels of treatment constituted "best practicable control technology currently available" (BPCTCA), "best available technology economically achievable" (BATEA), and "best demonstrated control technology, processes, operating methods, or other alternatives." Several factors were considered in identifying such technologies. These included the application of costs of the various technologies in relation to the effluent reduction benefits to be achieved through such application, engineering aspects of the application of various types of control techniques or process changes, and nonwater-quality environmental impact. Efforts were also made to determine the feasibility of transfer of technology from subcategory to subcategory, other categories, and other industries where similar effluent problems might occur. Consideration of the technologies was not limited to those presently employed in the industry, but included also those processes in pilotplant or laboratory-research stages.

SUMMARY OF ORE-BENEFICIATION PROCESSES

General Discussion

As mined, most ores contain the valuable metals, whose recovery is sought, disseminated in a matrix of less valuable rock, called gangue. The purpose of ore beneficiation is the separation of the metal-bearing minerals from the gangue to yield a more useful product--one which is higher in metal content. To accomplish this, the ore must generally be crushed and/or ground small enough so that each particle contains either the mineral to be recovered or mostly gangue. The separation of the particles on the basis of some difference between the ore mineral and the gangue can then yield a concentrate high in metal value, as well as waste rock (tailings) containing very little metal. The separation is never perfect, and the degree of success which is attained is generally described by two numbers: (1) percent recovery and (2) grade of the concentrate. Widely varying results are obtained in beneficiating different ores; recoveries may range from 60 percent or less to greater than 95 percent. Similarly, concentrates may contain less than 60 percent or more than 95 percent of the primary ore mineral. In general, for a given ore and process, concentrate grade and recovery are inversely related. (Higher recovery is achieved only by including more gangue, yielding a lower-grade concentrate.) The process must be optimized, trading off recovery against the value (and marketability) of the concentrate produced. Frequently, depending on end use, a particular minimum grade of concentrate is required, and only limited amounts of specific gangue components are acceptable without penalty.

Many properties are used as the basis for separating valuable minerals from gangue, including: specific gravity, conductivity, magnetic permeability, affinity for certain chemicals, solubility, and the tendency to form chemical complexes. Processes for effecting the separation may be generally considered as: gravity concentration, magnetic separation, electrostatic separation, flotation, and leaching. Amalgamation and cyanidation are variants of leaching which bear special mention. Solvent extraction and ion exchange are widely applied techniques for concentrating metals from leaching solutions, and for separating them from dissolved contaminants. All of these processes are discussed in general terms--with examples--in the paragraphs that follow. This discussion is <u>not</u> meant to be all-inclusive; rather, its purpose is to discuss the primary processes in current use in the ore mining and milling industry. Details of processes used in typical mining and milling operations are provided, together with process flowcharts, under "General Description of Industry By Ore Category."

Gravity-Concentration Processes

General. Gravity-concentration processes exploit differences in density to separate valuable ore minerals from gangue. Several techniques (jigging, tabling, spirals, sink/float separation, etc.) are used to achieve the separation. Each is effective over a somewhat limited range of particle sizes, the upper bound of which is set by the size of the apparatus and the need to transport ore within it, and the lower bound, by the point at which viscosity forces predominate over gravity and render the separation ineffective. Selection of a particular gravity-based process for a given ore will be strongly influenced by the size to which the ore must be crushed or ground to separate values from gangue, as well as by the density difference and other factors.

Most gravity techniques depend on viscosity forces to suspend and transport gangue away from the (heavier) valuable mineral. Since the drag forces on a particle depend on its area, and its weight on its volume, particle size as well as density will have a strong influence on the movement of a particle in a gravity separator. Smaller particles of ore mineral may be carried with the gangue, despite their higher density, or larger particles of gangue may be included in the gravity concentrate. Efficient separation thus depends on a feed to the process which contains a small dispersion of particle sizes. A variety of classifiers--spiral and rake classifiers, screens, and cyclones--is used to assure a reasonably uniform feed. At some mills, a number of sized fractions of ore are processed in different gravity-separation units.

Viscosity forces on the particles set a lower limit for effective gravity separation by any technique. For sufficiently small particles, even the smallest turbulence suspends the particle for long periods of time, regardless of density. Such slimes, once formed, cannot be recovered by gravity techniques and may cause very low recoveries in gravity processing of highly friable ores, such as scheelite (calcium tungstate, $CaWO_4$).

Jigs. Jigs of many different designs are used to achieve gravity separation of relatively coarse ore (generally, a secondary crusher product between 0.5 mm and 25 mm--up to 1 in.--in diameter). In general, ore is fed as a thick slurry to a chamber in which agitation is provided by a pulsating plunger or other such mechanism. The feed separates into layers by density within the jig, the lighter gangue being drawn off at the top with the water overflow, and the denser mineral, at a screen on the bottom. Often, a bed of coarser ore or iron shot is used to aid the separation; the dense ore mineral migrates down through the bed under the influence of the agitation within the jig. Several jigs are most often used, in series, to achieve both acceptable recovery and high concentrate grade.

Tables. Shaking tables of a wide variety of designs have found widespread use as an effective means of achieving gravity separation of finer ore particles (0.08 to 2.5 mm--up to 0.1 in.--in diameter). Fundamentally, they are, as the name implies, tables over which water carrying ore particles flows. A series of ridges or riffles, approximately perpendicular to the water flow, traps heavy particles, while lighter ones are suspended by shaking the table and flow over the obstacles with the water stream. The heavy particles move along the ridges to the edge of the table and are collected as concentrate (heads), while the light material which follows the water flow is generally a waste stream (tails). Between these streams is generally some material (termed "middlings") which has been diverted somewhat by the riffles, although less than the heads. These are often collected separately and returned to the table feed. Reprocessing of either heads or tails, or both, and multiple stages of tabling are not uncommon. Tables may be used to separate minerals differing relatively little in density, but uniformity of feed becomes extremely important in such cases.

Spirals. Humphreys spiral separators provide an efficient means of gravity separation for large volumes of material between 0.1 mm and 2 mm (up to approximately 0.01 in.) in diameter and have been widely applied--particularly, in the processing of heavy sands for ilmenite ($FeTiO_3$) and monazite (a rare-earth phosphate). They consist of a helical conduit (usually, of five turns) about a vertical axis. A slurry of ore is fed to the conduit at the top and flows down the spiral under gravity. The heavy minerals concentrate along the inner edge of the spiral, from which they may be withdrawn through a series of ports. Wash water may also be added through ports along the inner edge to improve the separation efficiency. A single spiral may, typically, be used to process 0.5 to 2.4 metric tons (0.55 to 2.64 short tons) of ore per hour; in large plants, as many as several hundred spirals may be run in parallel.

Sink/Float Separation. Sink/float (heavy media separation) separators differ from most gravity methods in that buoyancy forces are used to separate the various minerals on the basis of density. The separation is achieved by feeding the ore to a tank containing a medium whose density is higher than that of the gangue and less than that of the valuable ore minerals. As a result, the gangue floats and overflows the separation chamber, and the denser values sink and are drawn off at the bottom--often, by means of a bucket elevator or similar contrivance. Because the separation takes place in a relatively still basin and turbulence is minimized, effective separation may be achieved with a more heterogeneous feed than for most gravity-separation techniques. Viscosity does, however, place a lower bound on particle size for practicable separation, since small particles settle very slowly, limiting the rate at which ore may be fed. Further, very fine particles must be excluded, since they mix with the separation medium, altering its density and viscosity.

Media commonly used for sink/float separation in the ore milling industry are suspensions of very fine ferrosilicon or galena (PbS) particles. Ferrosilicon particles may be used to achieve medium specific gravities as high as 3.5 and are used in "Heavy-Medium Separation." Galena, used in the "HuntingtonHeberlein" process, allows the achievement of somewhat higher densities. The particles are maintained in suspension by a modest amount of agitation in the separator and are recovered for reuse by washing both values and gangue after separation.

Magnetic Separation

Magnetic separation is widely applied in the ore milling industry, both for the extraction of values from ore and for the separation of different valuable minerals recovered from complex ores. Extensive use of magnetic separation is made in the processing of ores of iron, columbium and tantalum, and tungsten, to name a few. The separation is based on differences in magnetic permeability (which, although small, is measurable for almost all materials) and is effective in handling materials not normally considered magnetic. The basic process involves the transport of ore through a region of high magnetic-field gradient. The most magnetically permeable particles are attracted to a moving surface, behind which is the pole of a large electromagnet, and are carried by it out of the main stream of ore. As the surface leaves the high-field region, the particles drop off--generally, into a hopper or onto a conveyor leading to further processing.

For large-scale applications--particularly, in the iron-ore industry--large, rotating drums surrounding the magnet are used. Although dry separators are used for rough separations, these drum separators are most often run wet on the slurry produced in grinding mills. Where smaller amounts of material are handled, wet and crossed-belt separators are frequently employed.

Electrostatic Separation

Electrostatic separation is used to separate minerals on the basis of their conductivity. It is an inherently dry process using very high voltages (typically, 20,000 to 40,000 volts). In a typical implementation, ore is charged to 20,000 to 40,000 volts, and the charged particles are dropped onto a conductive rotating drum. The conductive particles discharge very rapidly and are thrown off and collected, while the non-conductive particles keep their charge and adhere by electrostatic attraction. They may then be removed from the drum separately.

Flotation Processes

Basically, flotation is a process whereby particles of one mineral or group of minerals are made, by addition of chemicals, to adhere preferentially to air bubbles. When air is forced through a slurry of mixed minerals, then, the rising bubbles carry with them the particles of the mineral(s) to be separated from the matrix. If a foaming agent is added which prevents the bubbles from bursting when they reach the surface, a layer of mineral-laden foam is built up at the surface of the flotation cell which may be removed to recover the mineral. Requirements for the success of the operation are that particle size be small, that reagents compatible with the mineral to be recovered be used, and that water conditions in the cell not interfere with attachment of reagents to mineral or to air bubbles.

Flotation concentration has become a mainstay of the ore milling industry. Because it is adaptable to very fine particle sizes (less than 0.001 cm), it allows high rates of recovery from slimes, which are inevitably generated in crushing and grinding and which are not generally amenable to physical processing. As a physico-chemical surface phenomenon, it can often be made highly specific, allowing production of high-grade concentrates from very-low-grade ore (e.g., over 95-percent MoS_2 concentrate from 0.3-percent ore). Its specificity also allows separation of different ore minerals (e.g., CuS, PbS, and ZnS), where desired, and operation with minimum reagent consumption, since reagent interaction is typically only with the particular materials to be floated or depressed.

Details of the flotation process--exact suite and dosage of reagents, fineness of grinds, number of regrinds, cleaner-flotation steps, etc.--differ at each operation where it is practiced and may often vary with time at a given mill. A complex system of reagents is generally used, including five basic types of compounds: pH conditioners (regulators, modifiers), collectors, frothers, activators and depressants. Collectors serve to attach ore particles to air bubbles formed in the flotation cell. Frothers stabilize the bubbles to create a foam which may be effectively recovered from the water surface. Activators enhance the attachment of the collectors to specific kinds of particles and depressants prevent it. Frequently, activators are used to allow flotation of ore depressed at an earlier stage of the milling process. In almost all cases, use of each reagent in the mill is low (generally, less than 0.5 kg--approximately 1 lb--per ton of ore processed), and the bulk of the reagent adheres to tailings or concentrates.

Sulfide minerals are all readily recovered by flotation using similar reagents in small doses, although reagent requirements and ease of flotation do vary throughout the class. Sulfide flotation is most often carried out at alkaline pH. Collectors are most often alkaline xanthates having two to five carbon atoms--for example, sodium ethyl xanthate ($NaS_2COC_2H_5$). Frothers are generally organics with a soluble hydroxyl group and a "non-wettable" hydrocarbon. Sodium cyanide is widely used as a pyrite depressant. Activators useful in sulfide-ore flotation may include cuprous sulfide and sodium sulfide. Other pyrite depressants which are less damaging to the environment may be used to replace the sodium cyanide. Sulfide minerals of copper, lead, zinc, molybdenum, silver, nickel, and cobalt are commonly recovered by flotation.

Many minerals in addition to sulfides may be, and often are, recovered by flotation. Oxidized ores of iron, copper, manganese, the rare earths, tungsten, titanium, and columbium and tantalum, for example, may be processed in this way. Flotation of these ores involves a very different suite of reagents from sulfide flotation and has, in some cases, required substantially larger dosages. Experience has shown these flotation processes to be, in general, somewhat more sensitive to feed-water conditions than sulfide floats; consequently, oxidized ores are less frequently run with recycled water. Reagents used include fatty acids (such as oleic acid or soap skimmings), fuel oil, and various amines as collectors; and compounds such as copper sulfate, acid dichromate, and sulfur dioxide as conditioners.

Leaching

General. Ores can be leached by dissolving away either gangue or values in aqueous acids or bases, liquid metals, or other special solutions. The examples which follow illustrate various possibilities.

(1) Water-soluble compounds of sodium, potassium, and boron which are found in arid climates or under impervious strata can be mined, concentrated, and separated by leaching with water and recrystallizing the resulting brines.

(2) Vanadium and some other metals form anionic species (e.g., vanadates) which occur as insoluble ores. Roasting of such insoluble ores with sodium compounds converts the values to soluble sodium salts (e.g., sodium vanadate). After cooling, the water-soluble sodium salts are removed from the gangue by leaching in water.

(3) Uranium ores are only mildly soluble in water, but they dissolve quickly in acid or alkaline solutions.

(4) Native gold which is found in a finely divided state is soluble in mercury and can be extracted by amalgamation (i.e., leaching with a liquid metal). One process of nickel concentration involves reduction of the nickel by ferrosilicon at a high temperature and extraction of the nickel metal into molten iron. This process, called skip-ladling, is related to liquid-metal leaching.

(5) Certain solutions (e.g., potassium cyanide) dissolve specific metals (e.g., gold) or their compounds, and leaching with such solutions immediately concentrates the values.

Leaching solutions can be categorized as strong, general solvents (e.g., acids) and weaker, specific solvents (e.g., cyanide). The acids dissolve certain metals present, which often include gangue constituents (e.g., calcium from limestone). They are convenient to use, since the ore does not have to be ground very fine, and separation of the tailings from the value-bearing (pregnant) leach is then not difficult. In the case of sulfuric acid, the leach is cheap, but energy is wasted in dissolving unsought-for gangue constituents.

Specific solvents attack only one (or, at most, a few) ore constituent(s), including the one being sought. Ore must be ground finer to expose the values. Heat, agitation, and pressure are often used to speed the action of the leach, and considerable effort goes into separation of solids--often, in the form of slimes--from the pregnant leach.

Countercurrent leaching, preneutralization of lime in the gangue, leaching in the grinding process, and other combinations of processes are often seen in the industry. The values contained in the pregnant leach solution are recovered by one of several methods, including precipitation (e.g., of metal hydroxides from acid leach by raising pH), electrowinning (which is a form of electroplating), and cementation. Ion exchange and solvent extraction are often used to concentrate values before recovery.

Ores can be exposed to leach in a variety of ways. In vat leaching, the process is carried out in a container (vat), often equipped with facilities for agitation, heating, aeration, and pressurization (e.g., Pachuca tanks). *In-situ* leaching takes place in the ore body, with the leaching solution applied either by plumbing or by percolation through overburden. The pregnant leach solution is pumped to the recovery facility and can often be recycled. *In-situ* leaching is most economical when the ore body is surrounded by impervious strata. When water suffices as a leach solution and is plentiful, *in-situ* leaching is economical, even in pervious strata. Ore or tailings stored on the surface can be treated by heap or dump leaching. In this process, the ore is placed on an impervious layer (plastic sheeting or clay) that is furrowed to form drains and launders (collecting troughs), and leach solution is sprinkled over the resulting heap. The launder effluent is treated to recover values. Gold (using cyanide leach), uranium using (sulfuric acid leach), and copper (using sulfuric acid or acid ferric sulfate leach), are recovered in this fashion.

Amalgamation. Amalgamation is the process by which mercury is alloyed with some other metal to produce an amalgam. This process is applicable to free milling precious-metal ores, which are those in which the gold is free, relatively coarse, and has clean surfaces. Lode or placer gold/silver that is partly or completely filmed with iron oxides, greases, tellurium, or sulfide minerals cannot be effectively amalgamated. Hence, prior to amalgamation, auriferous ore is typically washed and ground to remove any films on the precious-metal particles. Although the amalgamation process has, in the past, been used extensively for the extraction of gold and silver from pulverized ores, it has, due to environmental considerations, largely been superseded, in recent years, by the cyanidation process.

The properties of mercury which make amalgamation such a relatively simple and efficient process are: (a) its high specific gravity (13.55 at 20 degrees Celsius, 68 degrees Fahrenheit); (b) the fact that mercury is a liquid at room temperature; and (c) the fact that it readily wets (alloys) gold and silver in the presence of water.

In the past, amalgamation was frequently implemented in specially designed boxes containing plates (e.g., sheets of metal such as copper or Muntz metal (Cu/Zn alloy), etc.) with an adherent film of mercury. These boxes, typically, were located downstream of the grinding circuit, and the gold was seized from the pulp as it flowed over the amalgam plates. In the U.S., this process has been abandoned to prevent stream pollution.

The current practice of amalgamation in the U.S. is limited to barrel amalgamation of a relatively small quantity of high-grade, gravity-concentrated ore. This form of amalgamation is the simplest method of treating an enriched gold- or silver- bearing concentrate. The gravity concentrate is ground for several hours in an amalgam barrel (e.g., a small cylinder batching mill) with steel balls or rods before the mercury is added. This mixture is then gently ground to bring the mercury and gold into intimate contact. The resulting amalgam is collected in a gravity trap.

Cyanidation. With occasional exceptions, lode gold and silver ores now are processed by cyanidation. Cyanidation is a process for the extraction of gold and/or silver from finely crushed ores, concentrates, tailings, and low-grade mine-run rock by means of potassium or sodium cyanide, used in dilute, weakly alkaline solutions. The gold is dissolved by the solution according to the reaction:

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4NaAu(CN)_2 + 4NaOH$$

and subsequently sorbed onto activated carbon ("Carbon-in-Pulp" process) or precipitated with metallic zinc according to the reaction:

$$2NaAu(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Au$$

The gold particles are recovered by filtering, and the filtrate is returned to the leaching operation.

A recently developed process to recover gold from cyanide solution is the Carbon-in-Pulp process. This process was developed to provide economic recovery of gold from low-grade ores or slimes. In this process, gold which has been solubilized with cyanide is brought into contact with 6 x 16 mesh activated coconut charcoal in a series of tanks. The pulp and enriched carbon are air lifted and discharged on small vibrating screens between tanks, where the carbon is separated and moved to the next adsorption tank, countercurrent to the pulp flow. Gold enriched carbon from the last adsorption tank is leached with hot caustic cyanide solution to desorb the gold. This hot, high-grade solution containing the leached gold is then sent to electrolytic cells, where the gold and silver are deposited onto stainless steel wool cathodes. The cathodes are then sent to the refinery for processing.

Pretreatment of ores containing only finely divided gold and silver usually includes multistage crushing, fine grinding, and classification of the ore pulp into sand and slime fractions. The sand fraction then is leached in vats with dilute, well aerated cyanide solution. The slime fraction, after thickening, is treated by agitation leaching in mechanically or air agitated tanks, and the pregnant solution is separated from the slime residue by thickening and/or filtration. Alternatively, the entire finely ground ore pulp may be leached by countercurrent decantation processing. Gold or silver is then recovered from the pregnant leach solutions by the methods discussed above.

Different types of gold/silver ore require modification of the basic flow scheme presented above. At one domestic operation, the ore is carbonaceous and contains graphitic material, which causes dissolved gold to adsorb onto the carbon, thus causing premature precipitation. To make this ore amenable to cyanidation, the refractory graphitic material is oxidized by chlorine treatment prior to the leaching step. Other schemes which have been employed include oxidation by roasting and blanking the carbon with kerosene or fuel oil to inhibit adsorption of gold from solution.

Other refractory ores are those which contain sulfides. Roasting to liberate the sulfide-enclosed gold and preconditioning by aeration with lime of ore containing pyrrhotite are two processes which allow conventional cyanidation of these ores.

The cyanidation process is comparatively simple, and is applicable to many types of gold/silver ore, but efficient low-cost dissolution and recovery of the gold and silver are possible only by careful process control of the unit operations involved. Effective cyanidation depends on maintaining and achieving several conditions:

(1) The gold and silver must be adequately liberated from the encasing gangue minerals by grinding and, if necessary, roasting or chemical oxidation.

(2) The concentration of "free" cyanide and dissolved oxygen in the leaching solution must be kept at a level that will enable reasonably fast dissolution of the gold and silver.

(3) The "protective" alkalinity of the leach solution must be maintained at a level that will minimize consumption of cyanide by the dissolution of other metal-bearing minerals.

(4) The leach residues must be thoroughly washed without serious dilution to reduce losses of dissolved values and cyanide to acceptable limits.

Ion Exchange and Solvent Extraction

These processes are used on pregnant leach solutions to concentrate values and to separate them from impurities. Ion exchange and solvent extraction are based on the same principle: Polar organic molecules tend to exchange a mobile ion in their structure--typically, Cl^-, NO_3^-, HSO_4^-, or CO_3^{--} (anions) or H^+ or Na^+ (cations)--for an ion with a greater charge or a smaller ionic radius. For example, let R be the remainder of the polar molecule (in the case of a solvent) or polymer (for a resin), and let X be the mobile ion. Then, the exchange reaction for the example of the uranyltrisulfate complex is:

$$4RX + (UO_2(SO_4)_3) \rightleftarrows R_4UO_2(SO_4)_3 + 4X^-$$

This reaction proceeds from left to right in the loading process. Typical resins adsorb about ten percent of their mass in uranium and increase by about ten percent in density. In a concentrated solution of the mobile ion (for example, in N-hydrochloric acid), the reaction can be reversed, and the uranium values are eluted (in this example, as hydrouranyl trisulfuric acid). In general, the affinity of cation-exchange resins for a metallic cation increases with increasing valence:

$$Cr^{+++} > Mg^{++} > Na^{+}$$

and, because of decreasing ionic radius, with atomic number:

$$92U > 42Mo > 23V$$

and the separation of hexavalent 92U cations by ion exchange or solvent extraction should prove to be easier than that of any other naturally occurring element.

Uranium, vanadium, and molybdenum (the latter being a common ore constituent) almost always appear in aqueous solutions as oxidized ions (uranyl, vanadyl, or molybdate radicals), with uranium and vanadium additionally complexed with anionic radicals to form trisulfates or tricarbonates in the leach. The complexes react anionically, and the affinity of exchange resins and solvents is not simply related to fundamental properties of the heavy metal (U, V, or Mo), as is the case in cationic exchange reactions. Secondary properties, including pH and reduction/oxidation potential, of the pregnant solutions influence the adsorption of heavy metals. For example, seven times more vanadium than uranium was adsorbed on one resin at pH 9; at pH 11, the ratio was reversed, with 33 times as much uranium as vanadium being captured. These variations in affinity, multiple columns, and control of leaching time with respect to breakthrough (the time when the interface between loaded and regenerated resin arrives at the end of the column) are used to make an ion-exchange process specific for the desired product.

In the case of solvent extraction, the type of polar solvent and its concentration in a typically nonpolar diluent (e.g., kerosene) affect separation of the desired product. The ease with which the solvent is handled permits the construction of multistage, cocurrent and countercurrent, solventextraction concentrators that are useful even when each stage effects only partial separation of a value from an interferent. Unfortunately, the solvents are easily polluted by slimes, and complete liquid/solid separation is necessary. Ionexchange and solvent-extraction circuits can be combined to take advantage of the slime resistance of resin-in-pulp ion exchange and of the separatory efficiency of solvent extraction (Eluex process).

GENERAL DESCRIPTION OF INDUSTRY BY ORE CATEGORY

The ore groups categorized in SIC groups 1011, 1021, 1031, 1041, 1044, 1051, 1061, 1092, 1094, and 1099 vary considerably in terms of their occurrence, mineralogy and mineralogical variations, extraction methods, and end-product uses. For these reasons, these industry areas generally are treated separately except for groups SIC 1061, Ferroalloys (members of which are differently occurring ore minerals but are classed as one group), and SIC 1099, Metal Ores, Not Elsewhere Classified (a grouping of ore minerals whose mining and processing operations bear little resemblance to one another).

Iron Ore

American iron-ore shipments increased from 82,718,400 metric tons (91,200,000 short tons) in 1968 to 92,278,180 metric tons (101,740,000 short tons) in 1973, an increase of 11.56% (Reference 1). In this period, the shipments of agglomerates, most of which were produced by processing low-grade iron formations, increased by 19.1%. Total consumption of iron ore in the United States in 1973 was 139,242,640 metric tons (153,520,000 short tons), with 76.5% produced domestically. Domestic agglomerates accounted for 66,256,350 metric tons (73,050,000 short tons), or 47.6% of United States consumption. A summary of U.S. iron-ore shipments is shown in Table III-1. A breakdown of crude iron-ore production in the U.S. is shown in Table III-2. A breakdown of U.S. iron-ore shipments by producing company is given in Supplement B to this document. Except for a very small tonnage, iron ores are beneficiated before shipping.

Beneficiation of iron ore includes such operations as crushing, screening, blending, grinding, concentrating, classifying, briquetting, sintering and agglomerating and is often carried on at or near the mine site. Methods selected are based on physical and chemical properties of the crude ore. A noticeable trend has been developing in furthering efforts to use lower-grade ores. As with many other natural resources, future availability will largely be a matter of cost rather than of absolute depletion as these lower-grade ores are utilized. Benefication methods have been developed to upgrade 20-30% iron 'taconite' ores into high-grade materials.

TABLE III-1. IRON-ORE SHIPMENTS FOR UNITED STATES

a. QUANTITIES SHIPPED BY REGION

REGION	AMOUNT SHIPPED					
	1968		1969		1970	
	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS
Great Lakes	65,093,239	64,065,185	72,534,630	71,389,050	70,180,666	69,072,263
Northeastern	3,602,705	3,545,805	3,453,486	3,398,943	3,043,857	2,995,784
Southern	3,474,203	3,419,333	4,733,087	4,658,335	5,022,369	4,943,048
Western	10,566,860	10,399,972	10,454,364	10,289,252	10,544,782	10,378,242
TOTAL U.S.	82,736,905	81,430,195	91,175,567	89,735,580	88,791,674	87,389,337

REGION	AMOUNT SHIPPED					
	1971		1972		1973	
	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS
Great Lakes	62,766,873	61,775,561	65,759,357	64,720,783	77,504,865	76,280,787
Northeastern	2,859,973	2,814,804	2,362,067	2,324,762	2,405,456	2,367,465
Southern	4,240,720	4,173,744	4,032,651	3,968,961	3,923,518	3,861,552
Western	8,253,243	8,122,895	7,397,815	7,266,471	8,462,579	8,328,925
TOTAL U.S.	78,120,810	76,887,004	79,537,152	78,280,977	92,296,418	90,838,729

b. SHIPMENTS FROM GREAT LAKES REGION AS PERCENTAGES OF TOTAL U.S. SHIPMENTS

YEAR	GREAT LAKES SHIPMENTS AS PERCENTAGE OF TOTAL U.S. SHIPMENTS	AGGLOMERATES AS PERCENTAGE OF GREAT LAKES SHIPMENTS	GREAT LAKES AGGLOMERATES AS PERCENTAGE OF TOTAL U.S. SHIPMENTS
1968	78.7	61.9	48.7
1969	79.6	63.6	50.6
1970	79.0	66.2	52.3
1971	80.4	70.1	56.3
1972	82.7	74.8	61.8
1973	84.0	73.5	61.7

c. PERCENTAGES OF TOTAL U.S. SHIPMENTS

CATEGORY	YEAR					
	1968	1969	1970	1971	1972	1973
Direct Shipping	8.2	7.0	5.0	4.3	2.0	2.4
Coarse Ores					12.8	12.9
Fine Ores					11.9	12.9
Screened Ores	3.2	3.1	2.7	3.1		
Concentrates	28.3	27.5	28.2	23.7		
Agglomerates	60.3	62.4	64.1	68.9	73.3	71.8
	100.0	100.0	100.0	100.0	100.0	100.0

SOURCE: **Reference 1**

TABLE III-2. CRUDE IRON-ORE PRODUCTION FOR U.S.

a. QUANTITIES PRODUCED

YEAR	PRODUCTION BY REGION					
	GREAT LAKES		NORTHEASTERN		SOUTHERN	
	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS
1968	159,349,027	156,832,339	10,236,712	10,075,038	7,743,542	7,621,244
1969	169,328,525	166,654,225	9,728,661	9,575,011	9,135,951	8,991,662
1970	172,799,898	170,070,772	9,173,800	9,028,913	10,542,987	10,376,387
1971	161,947,509	159,389,781	7,774,210	7,651,428	9,414,016	9,265,335
1972	158,183,907	155,685,620	6,721,672	6,615,513	9,333,043	9,185,641
1973	186,627,840	183,680,322	6,915,338	6,806,120	8,629,278	8,492,991

YEAR	PRODUCTION BY REGION			
	WESTERN		TOTAL U.S. PRODUCTION	
	METRIC TONS	LONG TONS	METRIC TONS	LONG TONS
1968	19,671,003	19,360,328	197,000,285	193,888,949
1969	19,270,778	18,966,424	207,463,916	204,187,322
1970	19,981,771	19,666,188	212,498,366	209,142,260
1971	18,422,861	18,131,898	197,558,596	194,438,442
1972	13,347,447	13,136,643	187,586,069	184,623,417
1973	18,080,995	17,795,432	220,253,451	216,774,865

b. PERCENTAGE OF U.S. CRUDE IRON-ORE PRODUCTION

REGION	YEAR					
	1968	1969	1970	1971	1972	1973
Great Lakes	80.9	81.6	81.3	82.0	84.3	84.7
Northeastern	5.1	4.7	4.3	3.9	3.6	3.2
Southern	4.0	4.4	5.0	4.8	5.0	3.9
Western	10.0	9.3	9.4	9.3	7.1	8.2
	100.0	100.0	100.0	100.0	100.0	100.0

SOURCE: Reference 1

In most cases, open-pit mining is more economical than conventional underground methods. It provides the lowest cost operation and is employed whenever the ratio of overburden (either consolidated or unconsolidated) to ore does not exceed an economical limit. The depth to which open pit mining can be carried depends on the nature of the overburden and the stripping ratio (volume of overburden/crude ore). Economic stripping ratios vary widely from mine to mine and from district to district, depending upon a number of factors. In the case of direct shipping ores, it may be as high as 6 or 7 to 1; in the case of taconite, a stripping ratio of less than 1/2 to 1 may become necessary. Stripping the overburden necessitates continually cutting back the pit walls to permit deepening of the mine to recover ore in the bottom. Power shovels, draglines, power scrapers, hydraulicking, and hydraulic dredging are used to recover ore deposits. Drilling and blasting are usually necessary to remove consolidated overburden and to loosen ore banks directly ahead of power shovels. Iron ore is loaded into buckets ranging in size from 0.75 to 7.5 cubic meters (1 to 10 cubic yards). The ore is transported out of the pit by railroad cars, trucks, truck trailers, belt conveyors, skip hoists, or a combination of these. It is then transferred to a crushing plant for size reduction, to a screening plant for sizing, or to a concentrating plant for treatment by washing (wet size classification and tailings rejection) or by gravity separation.

Special problems are associated with the mining of taconite. The extreme hardness of the ore necessitates additional drilling/blasting operations and specialized, more rugged equipment. The low iron content makes it necessary to handle two or four times as much mined material to obtain a given quantity of iron as compared to higher grade ore deposits.

Water can cause a variety of problems if allowed to collect in mine workings. Therefore, means must be developed to collect water and pump it out of the mine. This drainage water is often used directly to make up for water losses in concentration operations.

Underground methods are utilized only when stripping ratios become too high for economical open pit mining. Mining techniques consist of sinking vertical shafts adjacent to the deposit but far enough away to avoid the effects of surface subsidence resulting from mining operations. Construction of shafts, tunnels, underground haulage and development workings, and elaborate pumping facilities usually requires expensive capital investments. Production in terms of iron ore/day is much lower than in the case of open pit production, necessitating the presence of very high grade ores for economic recovery. General techniques utilized in the beneficiation of iron ore are illustrated in Figure III-1. Processes enhance either the chemical or physical characteristics of the crude ore to make more desirable feed for the blast furnace.

Crude ore not requiring further processing may be crushed and screened in order to eliminate handling problems and to increase heat transfer and, hence, rate of reduction in the blast furnace. Blending produces a more uniform product to comply with blast furnace requirements.

Physical concentrating processes such as washing remove unwanted sand, clay, or rock from crushed or screened ore. For those ores not amenable to simple washing operations, other physical methods such as jigging, heavy-media separation, flotation, and magnetic separation are used. Jigging involves stratification of ore and gangue by pulsating water currents. Heavy-media separation employs a water suspension of ferrosilicon in which iron ore particles sink while the majority of gangue (quartz, etc.) floats. Air bubbles attached to ores conditioned with flotation reagents separate out iron ore during the flotation process, while magnetic separation techniques are used where ores containing magnetite are encountered.

At the present time, there are only three iron ore flotation plants in the United States. Figure III-2 illustrates a typical flowsheet used in an iron ore flotation circuit, while Table III-3 lists types and amounts of flotation reagents used per ton of ore processed. Various flotation methods which utilize these reagents are listed in Table III-4. The most commonly adopted flowsheet for the beneficiation of low grade magnetic taconite ores is illustrated in Figure III-3. Low grade ores containing magnetite are very susceptible to concentrating processes, yielding a high quality blast furnace feed. Higher grade ores containing hematite cannot be upgraded much above 55% iron.

Agglomerating processes follow concentration operations and increase the particle size of iron ore and reudces "fines" which normally would be lost in the flue gases. Sintering, pelletizing, briquetting, and nodulizing are all possible operations involved in agglomeration. Sintering involves the mixing of small portions of coke and limestone with the iron ore, followed by combustion. A granular, coarse, porous product is formed. Pelletizing involves the

Figure III-1. BENEFICIATION OF IRON ORES

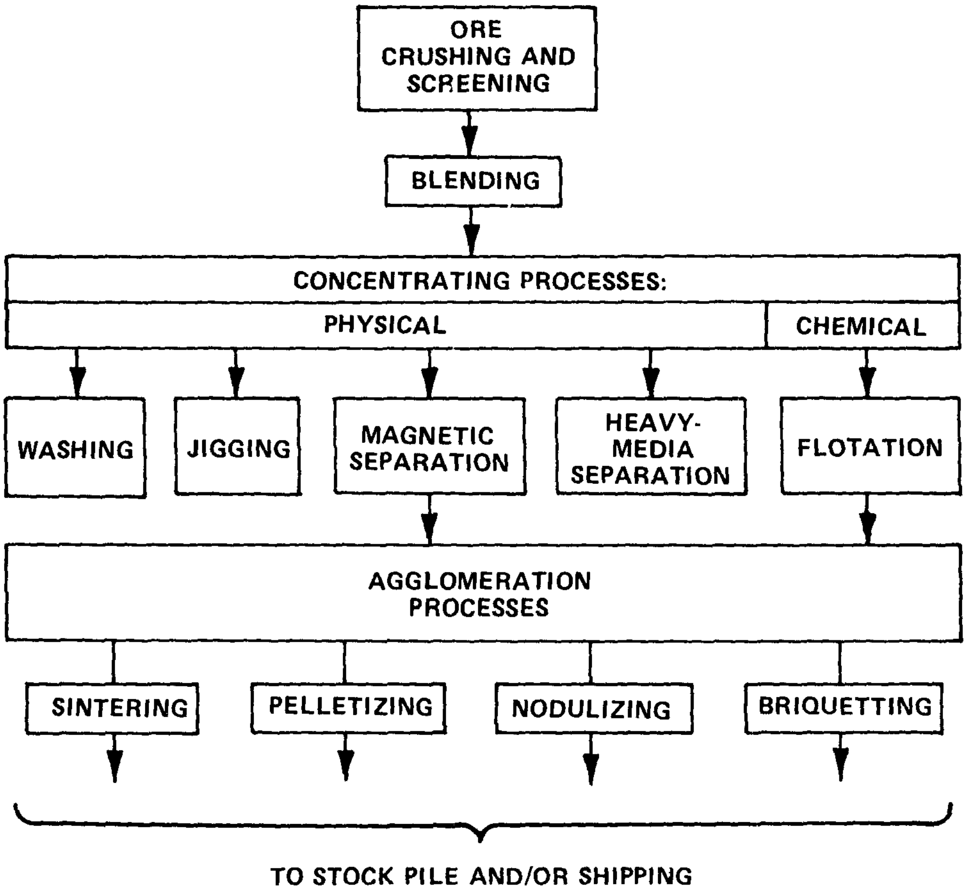


Figure III-2. IRON-ORE FLOTATION-CIRCUIT FLOWSHEET

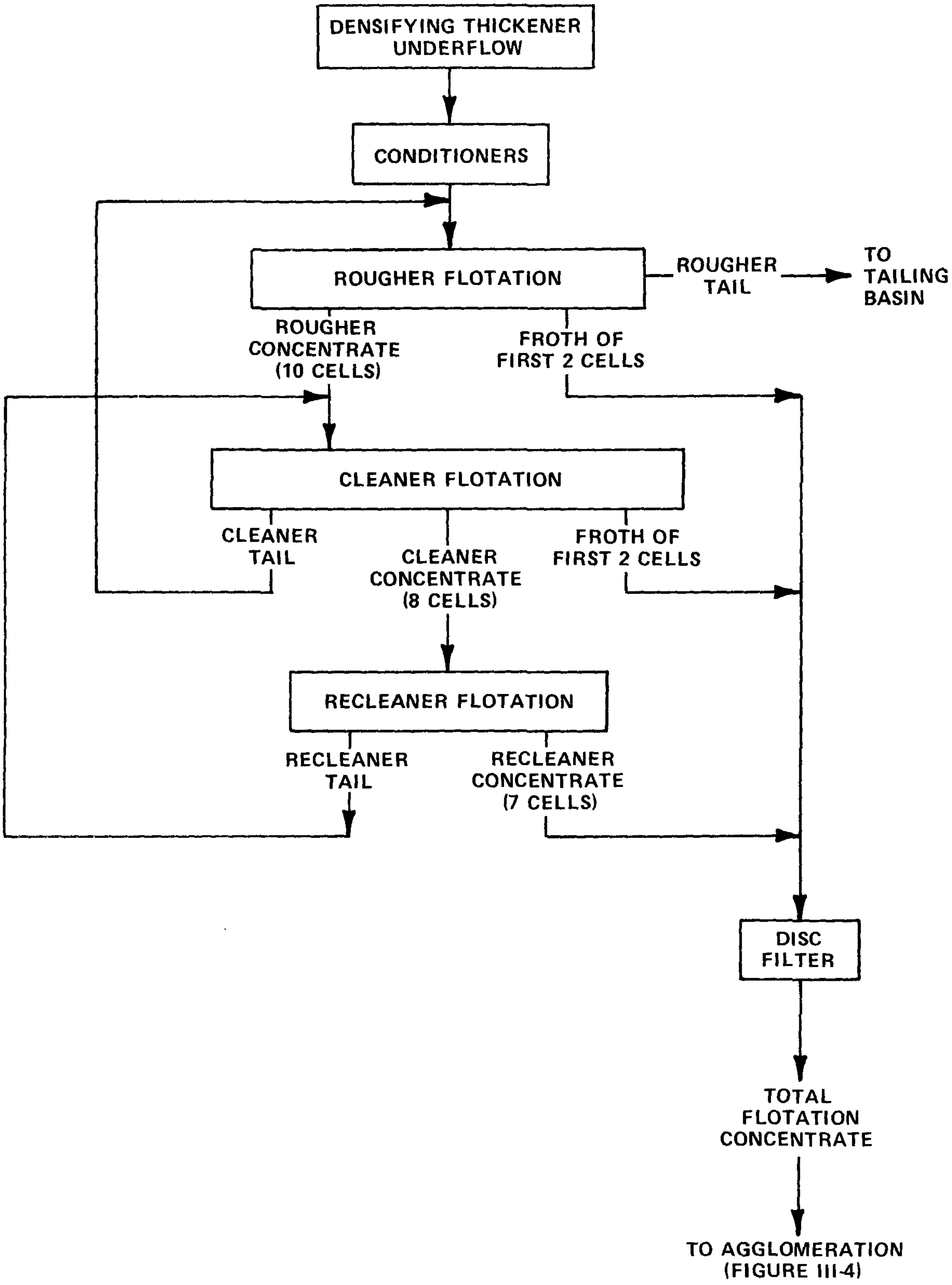


TABLE III-3. REAGENTS USED FOR FLOTATION OF IRON ORES

(Reagent quantities represent approximate maximum usages. Exact chemical composition of reagent may be unknown.)

1. Anionic Flotation of Iron Oxides (from crude ore)

   Petroleum sulfonate: 0.5 kg/metric ton (1 lb/short ton)
   Low-rosin, tall oil fatty acid: 0.25 kg/metric ton (0.5 lb/short ton)
   Sulfuric acid: 1.25 kg/metric ton (2.5 lb/short ton) to pH3
   No. 2 fuel oil: 0.15 kg/metric ton (0.3 lb/short ton)
   Sodium silicate: 0.5 kg/metric ton (1 lb/short ton)

2. Anionic Flotation of Iron Oxides (from crude ore)

   Low-rosin tall oil fatty acid: 0.5 kg/metric ton (1 lb/short ton)

3. Cationic Flotation of Hematite (from crude ore)

   Rosin amine acetate: 0.2 kg/metric ton (0.4 lb/short ton)
   Sulfuric acid: 0.15 kg/metric ton (0.3 lb/short ton)
   Sodium fluoride: 0.15 kg/metric ton (0.3 lb/short ton)
   (Plant also includes phosphate flotation and pyrite flotation steps. Phosphate flotation employs sodium hydroxide, tall oil fatty acid, fuel oil, and sodium silicate. Pyrite flotation employs xanthate collector.)

4. Cationic Flotation of Silica (from crude ore)

   Amine: 0.15 kg/metric ton (0.3 lb/short ton)
   Gum or starch (tapioca fluor): 0.5 kg/metric ton (1 lb/short ton)
   Methylisobutyl carbinol: as required

5. Cationic Flotation of Silica (from magnetite concentrate)

   Amine: 5 g/metric ton (0.01 lb/short ton)
   Methylisobutyl carbinol: as required

TABLE III-4. VARIOUS FLOTATION METHODS AVAILABLE FOR PRODUCTION OF HIGH-GRADE IRON-ORE CONCENTRATE

1. Anionic flotation of specular hematite
2. Upgrading of natural magnetite concentrate by cationic flotation
3. Upgrading of artificial magnetite concentrate by cationic flotation
4. Cationic flotation of crude magnetite
5. Anionic flotation of silica from natural hematite
6. Cationic flotation of silica from non-magnetic iron formation

Figure III-3. MAGNETIC TACONITE BENEFICIATION FLOWSHEET

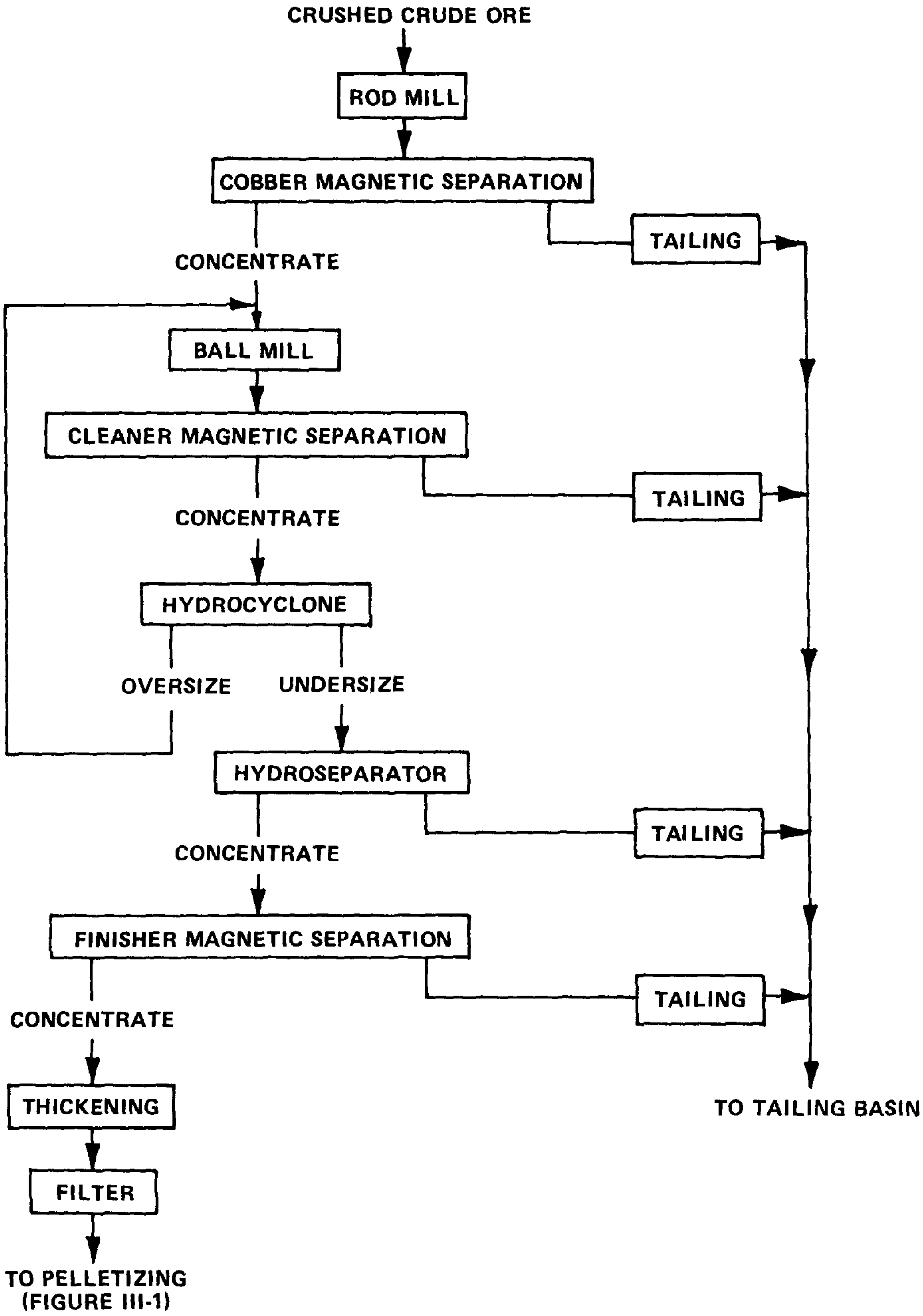
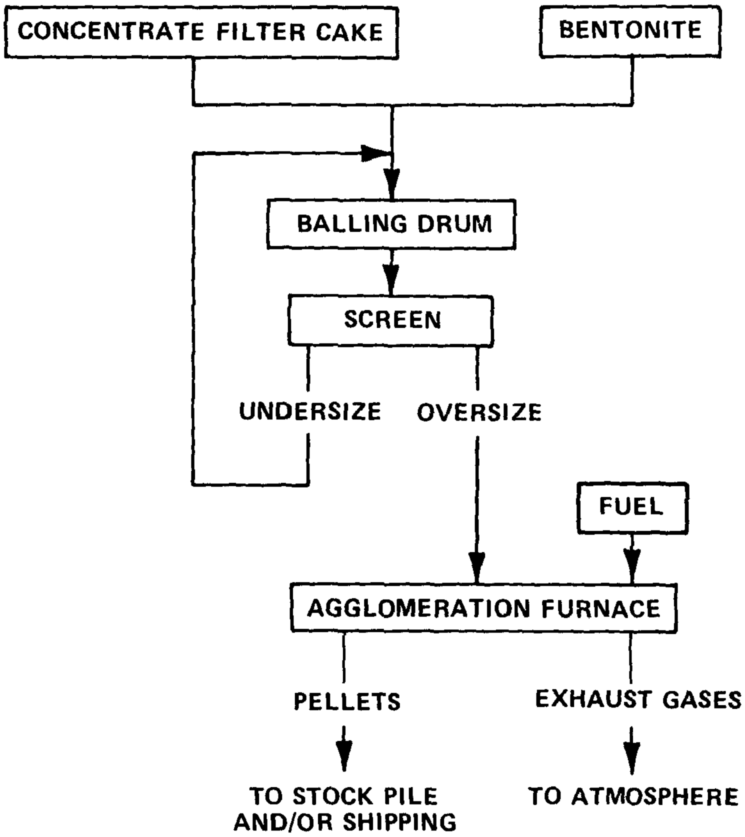


Figure III-4. AGGLOMERATION FLOWSHEET



formation of pellets or balls of iron ore fines, followed by heating. (Figure III-4 illustrates a typical pelletizing operation.) Nodules or lumps are formed when ores are charged into a rotary kiln and heated to incipient fusion temperatures in the nodulizing process. Hot ore briquetting requires no binder, is less sensitive to changes in feed composition, requires little or no grinding and requires less fuel than sintering. Small or large lumps of regular shape are formed.

Copper Ore

The copper ore segment of the ore mining and dressing industry includes facilities mining copper from open pit and underground mines, and those processing the ores and wastes by hydrometallurgical and/or physical-chemical processes. Other operations for processing concentrate and cement copper, and for manufacturing copper products (such as smelting, refining, rolling, and drawing) are classified under other SIC codes and are covered under limitations and guidelines for those industry classifications. However, to present a comprehensive view of the history and statistics of the copper production in the United States, statistics pertaining to finished copper are included with those for ore production and beneficiation.

Evidence of the first mining of copper in North America, in the Upper Peninsula of Michigan, has been found by archeologists. Copper was first produced in the colonies at Simsbury, Connecticut, in 1709. In 1820, a copper ore body was found in Orange County, Vermont. In the early 1840's, ore deposits located in Northern Michigan accounted for extensive copper production in the United States. Other discoveries followed in Montana (1860), Arizona (1880), and Bingham Canyon, Utah (1906). Since 1883, the United States has led copper production in the world. As indicated by the tabulation which follows, seven states presently produce essentially all of the copper mined in the U.S. (See also Figure III-5.)

Arizona	56%
Utah	16%
New Mexico	10%
Montana	7%
Nevada	6%
Michigan	4%
Tennessee	0.8%
	98.8%

Figure III-5. MAJOR COPPER MINING AND MILLING ZONES OF THE U.S.

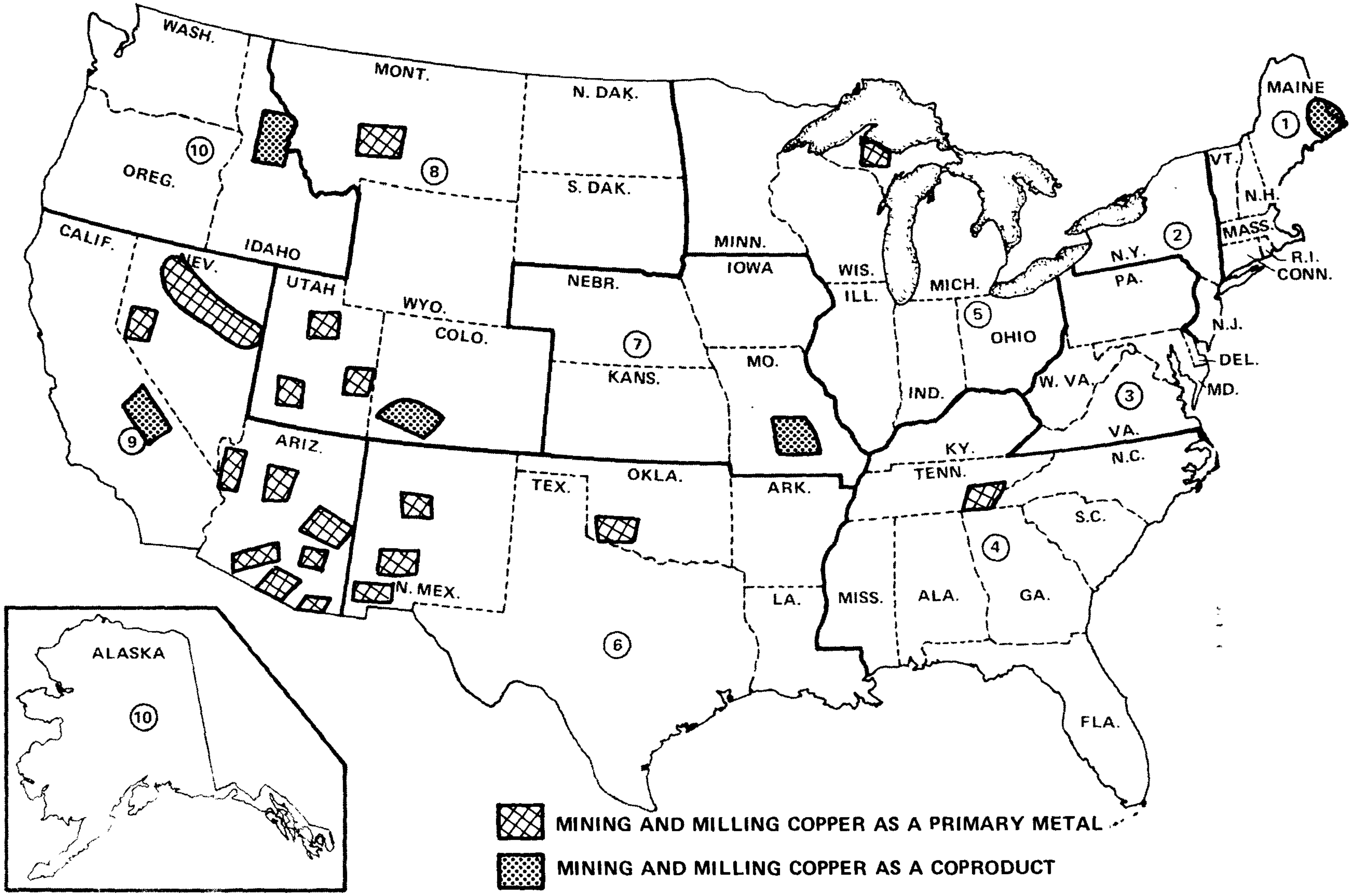


TABLE III-5. TOTAL COPPER-MINE PRODUCTION OF ORE BY YEAR

YEAR	PRODUCTION	
	1000 METRIC TONS	1000 SHORT TONS
1968	154,239	170,054
1969	202,943	223,752
1970	233,760	257,729
1971	220,089	242,656
1972	242,016	266,831
1973	263,088	290,000

SOURCE: REFERENCE 2

TABLE III-6. COPPER-ORE PRODUCTION FROM MINES BY STATE [1972]

STATE	PRODUCTION	
	1000 METRIC TONS	1000 SHORT TONS
ARIZONA	150,394	165,815
UTAH	32,250	35,557
NEW MEXICO	18,077$^+$	19,930$^+$
MONTANA	15,531$^+$	17,126$^+$
NEVADA	12,052$^+$	13,288$^+$
MICHIGAN	7,483	8,250
TENNESSEE	1,598	1,762
ALL OTHER	< 4,631	< 5,106
TOTAL U.S.	242,016	266,831

SOURCE: REFERENCE 2

A series of tables follow which give statistics for the U.S. copper industry. Table III-5 lists total copper mine production of ore by year, and Table III-6 gives copper ore production by state for 1972. The average copper content of domestic ores is given by Table III-7. The average concentration of copper recovered from domestic ores, classified by extraction process, is listed in Table III-8. Copper concentrate production by froth flotation is given in Table III-9, while production of copper concentrate by major producers in 1972 is given as part of Supplement B.

Twenty-five mines account for 95% of the U.S. copper output, with more than 50% of this output produced by three companies at five mines. Approximately 90% of present reserves (77.5 million metric tons, 85.5 million short tons, of copper metal as ore) average 0.86% copper and are contained in five states: Arizona, Montana, Utah, New Mexico, and Michigan. Mining produced 154 million metric tons (170 million short tons) of copper ore and 444 million metric tons (490 million short tons) of waste in 1968.

Open pit mines produce 83% of the total copper output with the remainder of U.S. production from underground operations. Ten percent of mined material is treated by dump (heap) and in-situ leaching producing 229,471 metric tons (253,000 short tons) of copper. Recovery of copper from leach solutions by iron precipitation accounted for 87.5% of the leaching production; recovery of copper by electromining amounted to 12.5%.

Approximately 98% of the copper ore was sent to concentrators for beneficiation by froth flotation, a process at least 60 years old. Copper concentrate ranges from 11% to 38% copper as a result of approximately 83% average recovery from ore.

Secondary or coproduction of other associated metals occurs with copper mining and processing. For instance, in 1971, 41% of U.S. gold production was as base-metal byproducts. Fourteen copper plants in 1971 produced molybdenum as well. From 63.5 million metric tons (70 million short tons) of molybdenum byproduct ore, 18,824 metric tons (20,750 short tons) of byproduct molybdenum were produced.

Processes Employed to Extract Copper from Ore. The mining methods employed by the copper industry are open pit or underground operations. Open pit mining produces step-like benched tiers of mined areas. Underground mining practice is usually by block-caving methods.

TABLE III-7. AVERAGE COPPER CONTENT OF DOMESTIC ORE

YEAR	PERCENT COPPER
1968	0.60
1969	0.60
1970	0.59
1971	0.55
1972	0.55
1973	0.53

SOURCE: REFERENCE 2

TABLE III-8. AVERAGE CONCENTRATION OF COPPER IN DOMESTIC ORES BY PROCESS (1972)

STATE	CONCENTRATION (%)		
	FLOTATION*	DUMP/HEAP LEACH	DIRECT SMELTER FEED
ARIZONA	0.51	0.47	1.94
UTAH	0.58	1.10	–
NEW MEXICO	0.70	–	0.07[†]
MONTANA	0.55	–	4.06
NEVADA	0.54	0.38	0.68
MICHIGAN	0.82	N/A	–
IDAHO	–	–	2.65
TENNESSEE[**]	0.64	N/A	–
COLORADO	–	–	10.24
ALL OTHER	1.35	–	2.30
TOTAL U.S.	0.55	0.47	1.68

[*] INCLUDES FROTH FLOTATION AND LEACH-REDUCTION/FLOTATION
[**] FROM COPPER/ZINC ORE
[†] JUST AS A FLUXING MATERIAL

SOURCE: REFERENCE 2

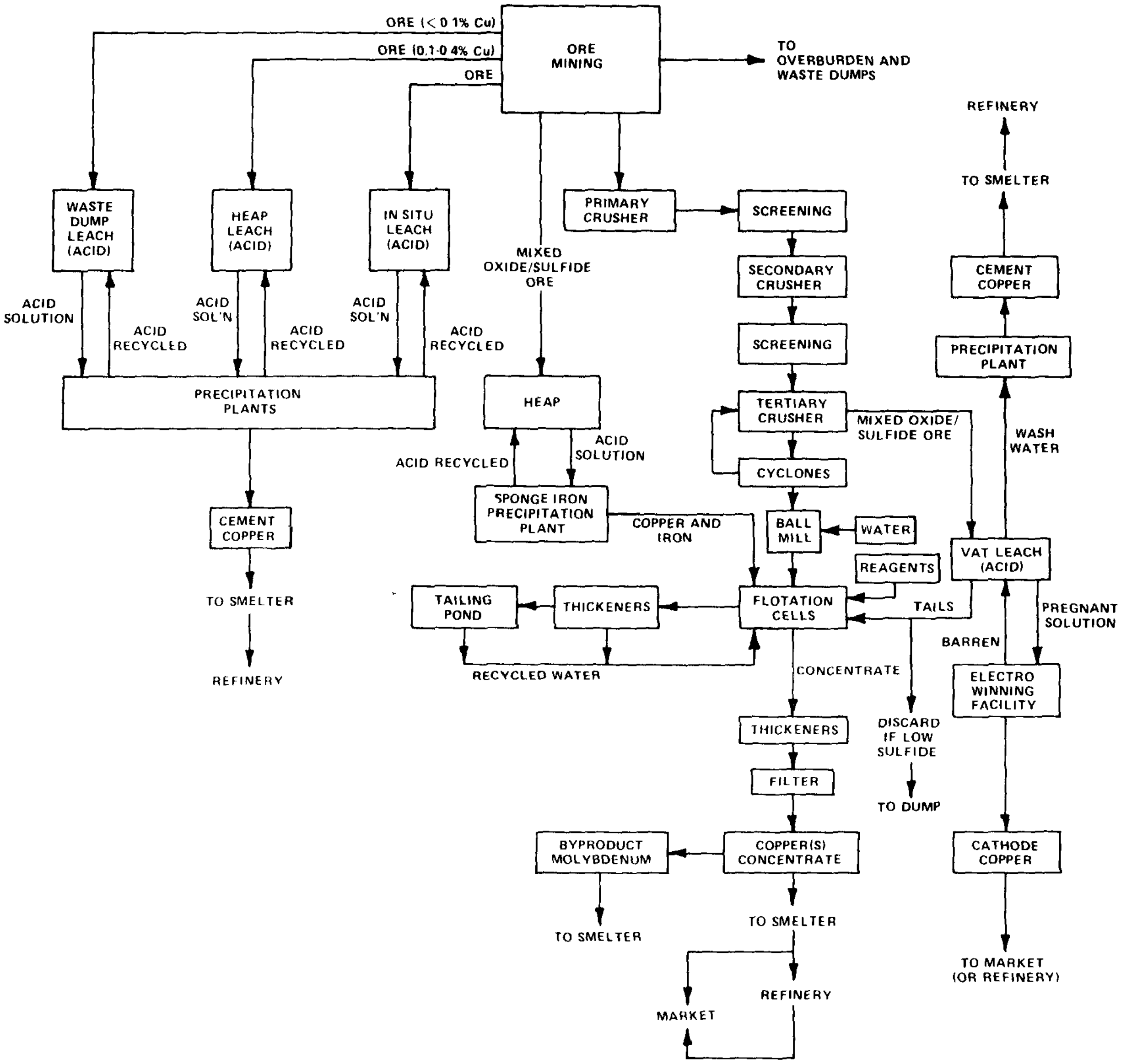
TABLE III-9. COPPER ORE CONCENTRATED IN THE UNITED STATES BY FROTH FLOTATION, INCLUDING LPF PROCESS (1972)

STATE	PRODUCTION	
	1000 METRIC TONS	1000 SHORT TONS
ARIZONA	138,998	153,250
UTAH	31,702	34,952
NEW MEXICO	18,019	19,866
MONTANA	15,508	17,098
NEVADA	12,003	13,234
MICHIGAN	7,483	8,250
TENNESSEE*	1,598	1,762
ALL OTHER	228	251
TOTAL U.S.	225,537	248,663

*FROM COPPER/ZINC ORE

SOURCE: REFERENCE 2

Figure III-6. GENERAL OUTLINE OF METHODS FOR TYPICAL RECOVERY OF COPPER FROM ORE



Processing of copper ores may be hydrometallurgical or physical-chemical separation from the gangue material. A general scheme of methods employed for recovery of copper from ores is given as Figure III-6. Hydrometallurgical processes currently employ sulfuric acid (5-10%) or iron sulfate to dissolve copper from the oxide or mixed oxide-sulfide ores in dumps, heaps, vats or in-situ (Table III-10). Major copper areas employing heap, dump, and in-situ leaching are shown in Figure III-7. The copper is then recovered from solution in a highly pure form by the iron precipitation, electrolytic deposition (electrowinning), or solvent extraction-electrowinning process.

Ore may also be concentrated by froth flotation, a process designed for extraction of copper from sulfide ores. Ore is crushed and ground to a suitable mesh size and is sent through flotation cells. Copper sulfide concentrate is lifted in the froth from the crushed material and collected, thickened, and filtered. The final concentrate, containing 15-30% copper, is sent to the smelter for production of blister copper (98% Cu). The refinery produces pure copper (99.88-99.9% Cu) from the blister copper, which retains impurities such as gold, silver, antimony, lead, arsenic, molybdenum, selenium, tellurium, and iron. These are removed in the refinery.

One combination of the hydrometallurgical and physical-chemical processes, termed LPF (leach-precipitation-flotation) has enabled the copper industry to process oxide and sulfide minerals efficiently. Also, tailings from the vat leaching process, if they contain significant sulfide copper, can be sent to the flotation circuit to float copper sulfide, while the vat leach solution undergoes iron precipitation or electrowinning to recover copper dissolved from oxide ores by acid.

A major factor affecting domestic copper production is the market price of the material. Historically, copper prices have fluctuated but have generally increased over the long term (Table III-11). Smelter production of copper from domestic ores has continuously risen and has increased in excess of a factor of three over the last 68 years (Table III-12).

Lead and Zinc Ores

Lead and zinc mines and mills in the U.S. range in age from over one hundred years to essentially new. The size of these operations ranges from several hundred metric tons of ore per day to complexes capable of moving about six

TABLE III-10. COPPER ORE HEAP OR VAT LEACHED IN THE UNITED STATES (1972)

STATE	PRODUCTION	
	1000 METRIC TONS	1000 SHORT TONS
ARIZONA	11,071	12,228
UTAH	549	605
NEW MEXICO/NEVADA	4,400	4,851
MONTANA	N/A	N/A
TOTAL U.S.	16,039	17,684

SOURCE: REFERENCE 2

Figure III-7. MAJOR COPPER AREAS EMPLOYING ACID LEACHING IN HEAPS, IN DUMPS, OR *IN SITU*

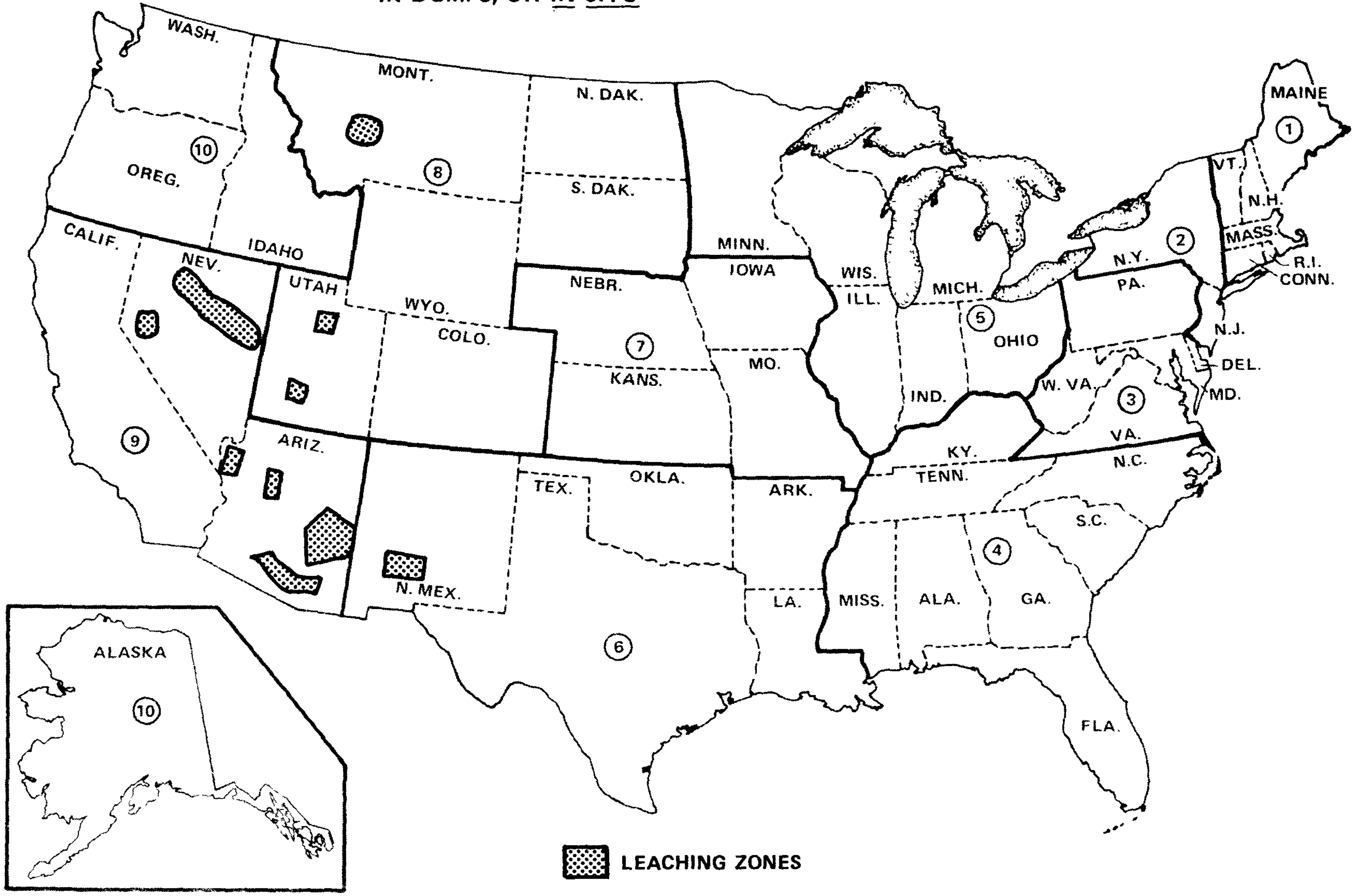


TABLE III-11. AVERAGE PRICE RECEIVED FROM COPPER IN THE UNITED STATES

YEAR	PRICE IN CENTS PER KILOGRAM (CENTS PER POUND)	
	LAKE COPPER*	ELECTROLYTIC COPPER†
1865 - 1874	60.94 (27.70)	-
1907	46.86 (21.30)	-
1910	28.86 (13.12)	-
1915	38.81 (17.64)	-
1917	64.20 (29.18)	-
1920	39.62 (18.01)	-
1925	31.77 (14.44)	-
1930	29.48 (13.40)	-
1932	13.00 (5.91)	-
1935	19.62 (8.92)	-
1940	25.65 (11.66)	-
1945	26.40 (12.00)	-
1950	40.96 - 54.16 (18.62 - 24.62)	42.90 - 53.90 (19.50 - 24.50)
1955	66.00 - 94.60 (30.00 - 43.00)	69.30 - 94.60 (31.50 - 43.00)
1960	66.00 - 72.60 (30.00 - 33.00)	66.00 - (30.00)
1965	74.80 - 83.60 (34.00 - 38.00)	77.00 - 81.40 (35.00 - 37.00)
1970	116.6 - 132.0 (53.00 - 60.00)	116.9 - 132.3 (53.12 - 60.12)
1972	109.7 - 114.7 (49.88 - 52.13)	111.4 - 115.8 (50.63 - 52.63)
1973	110.3 - 159.2 (50.13 - 72.38)	116.9 - 151.1 (53.13 - 68.70)

* COPPER FROM NATIVE COPPER MINES OF LAKE SUPERIOR DISTRICT: MINIMUM 99.90% PURITY, INCLUDING SILVER.

† ELECTROLYTIC COPPER RESULTS FROM ELECTROLYTIC REFINING PROCESSES: MINIMUM 99.90% PURITY, SILVER COUNTED AS COPPER

SOURCE: REFERENCE 3

TABLE III-12. PRODUCTION OF COPPER FROM DOMESTIC ORE BY SMELTERS

YEAR	ANNUAL PRODUCTION	
	METRIC TONS	SHORT TONS
1905	403,064	444,392
1910	489,853	540,080
1915	629,463	694,005
1916	874,280	963,925
1919	583,391	643,210
1921	229,283	252,793
1925	759,554	837,435
1929	908,299	1,001,432
1930	632,356	697,195
1932	246,709	272,005
1935	345,834	381,294
1937	757,038	834,661
1940	824,539	909,084
1943	991,296	1,092,939
1946	543,888	599,656
1950	826,596	911,352
1955	913,631	1,007,311
1960	1,036,563	1,142,848
1965	1,272,345	1,402,806
1970	1,455,973	1,605,262
1971	1,334,029	1,470,815
1972	1,513,710	1,668,920
1973	1,569,110*	1,730,000*

*PRELIMINARY BUREAU OF MINES DATA

SOURCE: REFERENCE 3

thousand metric tons of ore per day. Lead and zinc ores are produced almost exclusively from underground mines. There are some deposits which are amenable to open pit operations; a number of mines during their early opening stages of operation are started as open-pit mines and then developed into underground mines. At present, only one small open-pit mine is in operation, and its useful life is estimated in months. Therefore, for all practical purposes, all mining can be considered to be underground.

In general, the ores are not rich enough in lead and zinc to be smelted directly. Normally, the first step in the conversion of ore into metal is the milling process. In some cases, preliminary gravity separation is practiced prior to the actual recovery of the minerals of value by froth flotation, but, in most cases, only froth flotation is utilized. The general procedure is to initially crush the ore and then grind it, in a closed circuit with classifying equipment, to a size at which the ore minerals are freed from the gangue. Chemical reagents are then added which, in the presence of bubbled air, produce selective flotation and separation of the desired minerals. The flotation milling process can be rather complex depending upon the ore, its state of oxidation, the mineral, parent rock, etc. The recovered minerals are shipped in the form of concentrates for reduction to the respective metals recovered.

The most common lead mineral mined in the U.S. is galena (lead sulfide). This mineral is often associated with zinc, silver, gold, and iron minerals.

The principal zinc ore mineral is zinc sulfide (sphalerite). There are, however, numerous other minerals which contain zinc. The more common include zincite (zinc oxide), willemite (zinc silicate), and franklinite (an iron, zinc, manganese oxide complex). Sphalerite is often found in association with sulfides of iron and lead. Other elements often found in association with sphalerite include copper, gold, silver, and cadmium.

Mine production of lead increased during 1973 and 1974, as illustrated in Table III-13, which has been modified from the Mineral Industry Surveys, U.S. Department of the Interior, Bureau of Mines, Mineral Supply Bulletin (Reference 4).

Missouri was the foremost state with 80.78% of the total United States production, followed by Idaho with 10.24%, Colorado with 4.66%, Utah with 2.28%, and other states with the remaining 2.04%. This same trend continues with the

TABLE III-13. MINE PRODUCTION OF RECOVERABLE LEAD IN THE UNITED STATES

	1973		1973 JAN.-DEC.		1974 (PRELIMINARY) JAN.-JUNE	
STATE	RANK	%	METRIC TONS	SHORT TONS	METRIC TONS	SHORT TONS
Alaska			5	6	---	---
Arizona			692	763	357	394
California			40	44	11	12
Colorado	3	4.66	25,497	28,112	11,317	12,478
Idaho	2	12.24	56,002	61,744	25,667	28,299
Illinois			491	541	122	135
Maine			185	204	98	108
Missouri	1	80.78	441,839	487,143	251,571	277,366
Montana			160	176	51	56
New Mexico			2,318	2,556	1,078	1,189
New York			2,090	2,304	1,331	1,467
Utah	4	2.28	12,456	13,733	5,674	6,256
Virginia			2,392	2,637	1,359	1,499
Washington			2,011	2,217	443	489
Wisconsin			765	844	596	657
Other States			---	---	486	536
	Total		546,943	603,024	300,163	330,941
	Daily average*		1,498	1,652	1,658	1,828

*Based on number of days in month without adjustment for Sundays or holidays.

TABLE III-14. MINE PRODUCTION OF RECOVERABLE ZINC IN THE UNITED STATES (PRELIMINARY)

	1973		1973 JAN.-DEC. TOTALS		1974 JAN. TOTALS	
STATE	RANK	%	METRIC TONS	SHORT TONS	METRIC TONS	SHORT TONS
Arizona			7,638	8,421	600	662
California			16	18	—	—
Colorado	4	11.94	51,533	56,817	3,961	4,367
Idaho	5	9.55	41,216	45,442	3,279	3,615
Illinois			4,823	5,318	224	247
Kentucky			245	270	—	—
Maine	7	4.13	17,843	19,672	1,238	1,365
Missouri	1	17.27	74,576	82,223	6,589	7,265
Montana			379	418	82	90
New Jersey	6	6.94	29,955	33,027	2,361	2,603
New Mexico			11,147	12,290	863	951
New York	2	17.4	73,861	81,435	6,961	7,675
Pennsylvania			17,104	18,858	1,575	1,737
Tennessee	3	13.32	57,474	63,367	7,239	7,981
Utah	9	3.48	15,023	16,564	1,130	1,246
Virginia	8	3.51	15,131	16,682	1,281	1,412
Washington			5,768	6,359	528	582
Wisconsin			7,865	8,672	733	808
	Total		431,599	475,853	38,644	42,606
	Daily average*		1,183	1,304	1,246	1,374

*Based on number of days in month without adjustment for Sundays or holidays.

preliminary figures for 1974 for the period of January through June. Based on this information and the estimated 60-year life for the lead ores in the "Viburnum Trend" of the "New Lead Belt" of southeast Missouri, it is likely that this area will be the predominant lead source for many years to come.

Mine production of zinc during 1973 and preliminary production figures for December and January 1974 and January through May 1974 are presented in Table III-14, which has been modified from the Mineral Industry Surveys, U.S. Department of Interior, Bureau of Mines, Mineral Supply Bulletins.

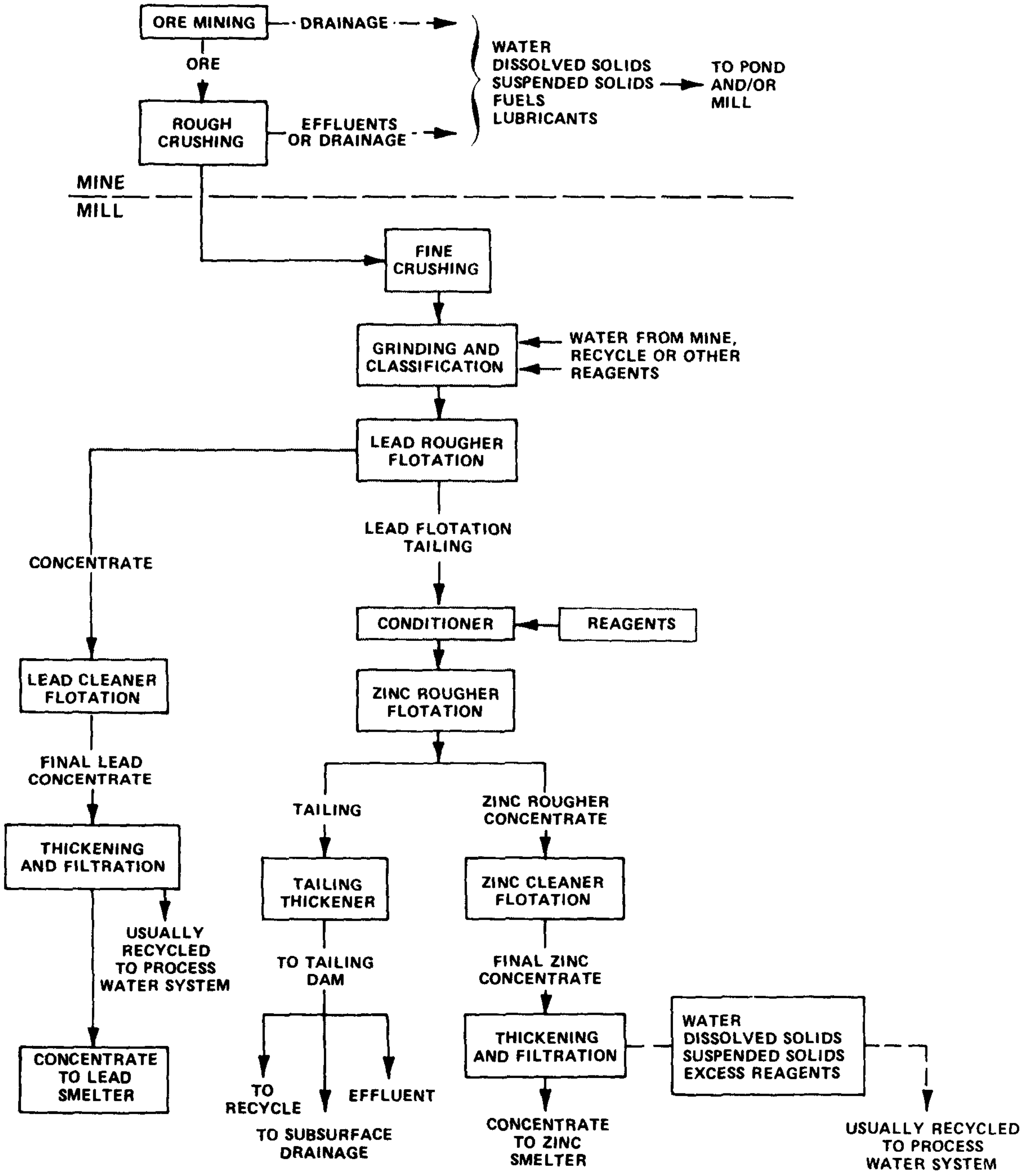
The mine production figures by state for zinc in 1973, however, are misleading, because Tennessee was ranked third due to prolonged strikes, the replacement of some older mine-mills, and the development and construction of new production facilities. Therefore, note that Tennessee led the nation in the production of zinc for 15 consecutive years (until 1973) and should regain the number one ranking back from Missouri (1973), based on the preliminary production figures given for the first half of 1973.

Description of Lead/Zinc Mining and Milling Processes. The recovery of useful lead/zinc minerals involves the removal of ores containing these minerals from the earth (mining) and the subsequent separation of the useful mineral from the gangue material (concentration). A generalized flow sheet for such a mine/mill operation is presented in Figure III-8.

Mine Operations. The mining of lead- and zinc-bearing ores is generally accomplished in underground mines. The mineralcontaining formation is usually fractured utilizing explosives such as ammonium nitrate-fuel oil (AN-FO) or slurry gels, placed in holes drilled in the formation. After blasting, the rock fragments are transported to the mine shaft where they are lifted up the shaft in skips. Primary or rough crushing equipment is often operated underground. The drilling and transportation equipment is, of course, highly mechanized and employs the diesel power. At some locations, the equipment is maintained in underground shops, constructed in mined-out areas of the workings.

Water enters a mine naturally when aquifers are intercepted; in highly fractured and fissured formations, water from the surface may seep into the mine. Minor amounts of water are introduced from the surface by evaporation of cooling water and through water expired by workers. At some locations,

Figure III-8. LEAD/ZINC-ORE MINING AND PROCESSING OPERATIONS



water enters with sand or tailings used in hydraulic backfill operations.

The water is pumped from the mine at a rate necessary to maintain operations in the mine. The amount of water pumped does not bear any necessary relationship to the output of ore or mineral. The amount pumped may vary from thousands of liters per day to 120 to 160 million liters (30 to 40 million gallons) per day. In many cases, there is a substantial seasonal variation in the amount of water which which must be pumped.

The water pumped from a mine may contain fuel, oil, and hydraulic fluid from spills and leaks, and, perhaps, blasting agents and partially oxidized blasting agents. The water, most certainly, will contain dissolved solids and suspended solids generated by the mining operations. The dissolved and suspended solids may consist of lead, zinc, and associated minerals.

Milling Operations. The valuable lead/zinc minerals are recovered from the ore brought from the mine by froth flotation. In some cases, the ore is preconcentrated using mechanical devices based on specific gravity principles. The ore is initially crushed to a size suitable for introduction into fine grinding equipment, such as rod mills and ball mills. These mills run wet and are usually run in circuit with rake or cyclone classifers to recycle to the mill material which is coarser than the level required to liberate the mineral particles. The fineness of grind is dependent on the degree of dissemination of the mineral in the host rock. The ore is ground to a size which provides an economic balance between the additional metal values recovered versus the cost of grinding.

In some cases, the reagents used in the flotation process are added in the mill; in other cases, the fine material from the mill flows to a conditioner (mixing tank), where the reagents are added. The particular reagents utilized are a function of the mineral concentrates to be recovered. The specific choice of reagents at a facility is usually the result of determining empirically which reagents result in an economic optimum of recovered mineral values which reagents result in an economic optimum of recovered mineral values versus reagent costs. In general, lead and zinc as well as copper sulfide flotations are run at elevated pH (8.5 to 11, generally) levels so that frequent pH adjustments with hydrated lime ($CaOH_2$) are common. Other reagents commonly used and their purposes are:

Reagent	Purpose
Methyl Isobutyl-carbinol	Frother
Propylene Glycol Methyl Ether	Frother
Long-Chain Aliphatic Alcohols	Frother
Pine Oil	Frother
Potassium Amyl Xanthate	Collector
Sodium Isopropol Xanthate	Collector
Sodium Ethyl Xanthate	Collector
Dixanthogen	Collector
Isopropyl Ethyl Thionocarbonate	Collectors
Sodium Diethyl-dithiophosphate	Collectors
Zinc Sulfate	Zinc Depressant
Sodium Cyanide	Zinc Depressant
Copper Sulfate	Zinc Activant
Sodium Dichromate	Lead Depressant
Sulfur Dioxide	Lead Depressant
Starch	Lead Depressant
Lime	pH Adjustment

The finely ground ore slurry is introduced into a series of flotation cells, where the slurry is agitated and air is introduced. The minerals which are to be recovered have been rendered hydrophobic (non water accepting) by surface coating with appropriate reagents. Usually, several cells are operated in a countercurrent flow pattern, with the final concentrate being floated off the last cell (cleaner) and the tails taken over the first or rougher cells. In some cases, regrinding is used on the underflow for the cleaner cells to improve recovery.

In many cases, more than one mineral is recovered. In such cases, differential flotation is practiced. The flow shown in Figure III-8 is typical of such a differential flotation process for recovery of lead and zinc sulfides. Chemicals which induce hydrophilic (affinity for water) behavior by surface interaction are added to prevent one of the minerals from floating in the initial separation. The underflow of tailings from this separation is then treated with a chemical which overcomes the depressing effect and allows the flotation of the other mineral.

After the recovery of the desirable minerals, a large volume of tailings or gangue material remains as the underflow from the last rougher cell in the flow scheme. These tails are typically adjusted to a slurry suitable for hydraulic transport to the treatment facility, termed a tailings pond. In some cases, the coarse tailings are separated using a cyclone separator and pumped to the mine for backfilling.

The floated concentrates are dewatered (usually by thickening and filtration), and the final concentrate--which contains some residual water--is eventually shipped to a smelter for metal recovery. The liquid overflow from the concentrate thickeners is typically recycled in the mill.

The tailings from a lead/zinc flotation mill contains the residual solids from the original ore which have been finely ground to allow mineral recovery. The tailings also contains dissolved solids and excess mill reagents. In cases where the mineral content of the ore varies, excess reagents will undoubtedly be present when the ore grade drops suddenly, and lead and zinc will escape with the tails if high-grade ore creates a reagent-starved system. Spills of the chemical used are another source of adverse discharges from a mill.

Gold Ore

The gold ore mining and milling industry is defined for this document as that segment of the industry involved in the mining and/or milling of ore for the primary or byproduct/ coproduct recovery of gold. In the United States, this industry is concentrated in eight states: Alaska, Montana, New Mexico, Arizona, Utah, Colorado, Nevada, and South Dakota. Domestic production of gold for 1972 was 45.1 million grams (1.45 million troy ounces). Of this, approximately 76% come from four producers, while the 25 leading producers accounted for 98% of production. The domestic production of gold has been on a downward trend for the last 20 years, largely as a result of reduction in the average grade of ore being mined, ore depletions at some mines, and a labor strike at the major producer during 1972. However, large increases in the free market price of gold during recent years (approximately $70 in 1972 to nearly $200 in 1974) has stimulated a widespread increase in prospecting and exploration activity. As a result of this, the recovery of gold from low-grade ore may now become economically feasible, and an increase in production might be expected in the near future.

Mining Practices. Gold is mined from two types of deposits: placers and lode or vein deposits. Placer mining consists of excavating gold-bearing gravel and sands. This is currently done primarily by dredging but, in the past, has included hydraulic mining and drift mining of buried placers too deep to strip. Lode deposits are mined by either underground or open-pit methods, the particular method chosen depending on such factors as size and shape of the deposit, ore grade, physical and mineralogical character of the ore and surrounding rock, and depth of the deposit.

Milling Practices. Milling practices for the processing and recovery of gold and gold-containing ores are cyanidation, amalgamation, flotation, and gravity concentration. All these processes have been employed in the beneficiation of ore mined from lode deposits. Placer operations, however, employ only gravity methods, sometimes in conjunction with amalgamation.

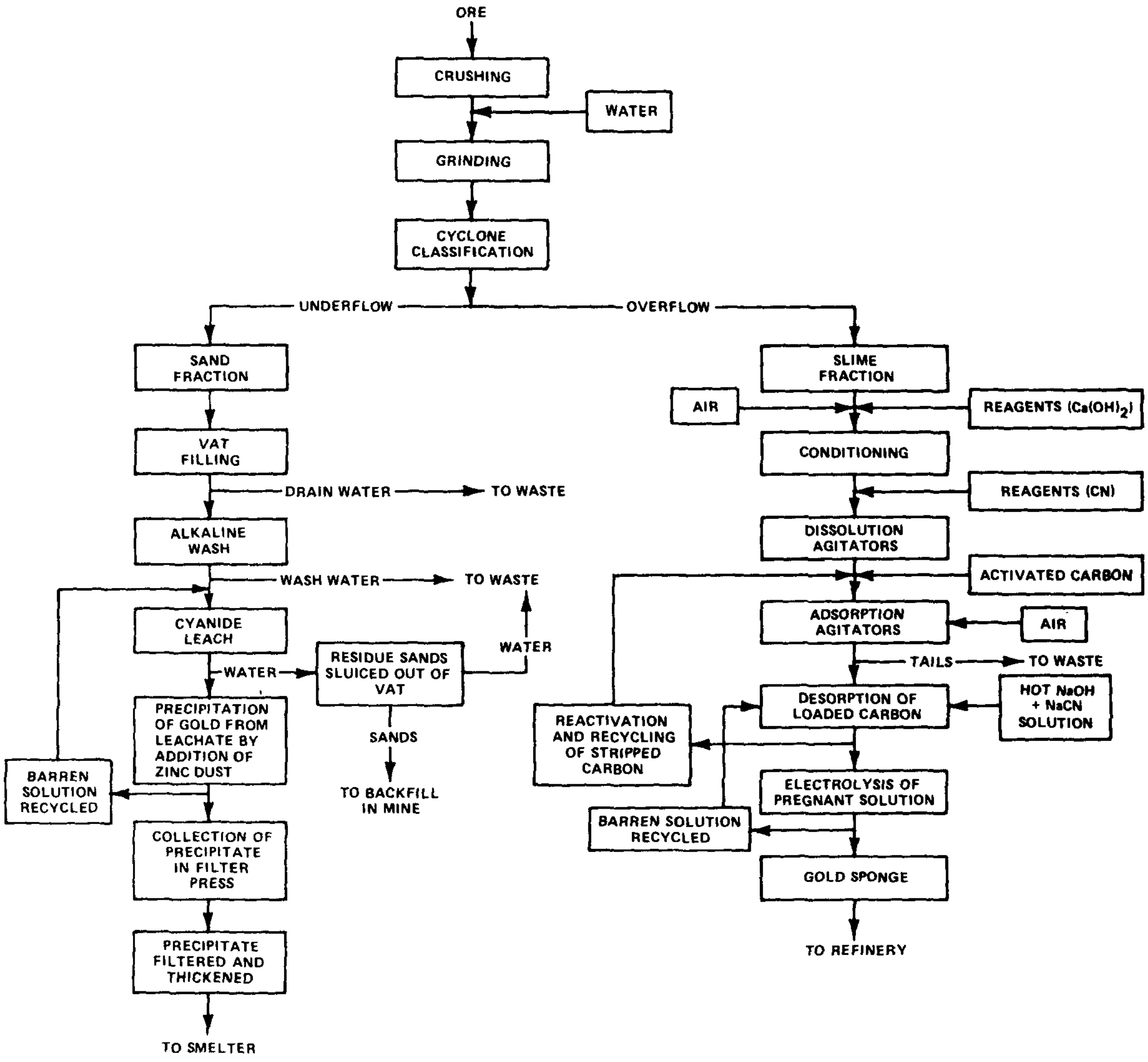
Prior to 1970, amalgamation was the process used to recover nearly 1/4 of the gold produced domestically. Since that time, environmental concerns have caused restricted use of mercury. As a result, the percent of gold produced which was recovered by the amalgamation process dropped from 20.3% in 1970 to 0.3% in 1972. At the same time that the use of amalgamation was decreasing, the use of cyanidation processes was increasing. In 1970, 36.7% of the gold produced domestically was recovered by cyanidation, and this increased to 54.6% in 1972.

Current practice for the amalgamation process (as used by a single mill in Colorado) involves crushing and grinding of the lode ore, gravity separation of the gold-bearing black sands by jigging, and final concentration of the gold by batch amalgamation of the sands in a barrel amalgamator. In the past, amalgamation of lode ore has been performed in either the grinding mill, on plates, or in special amalgamators. Placer gold/silver-bearing gravels are beneficiated by gravity methods, and, in the past, the precious metal-bearing sands generally were batch amalgamated in barrel amalgamators. However, amalgamation in specially designed sluice boxes was also practiced.

There are basically four methods of cyanidation currently being used in the United States: heap leaching, vat leaching, agitation leaching, and the recently developed carbon-in-pulp process. Heap leaching is a process used primarily for the recovery of gold from low-grade ores. This is an inexpensive process and, as a result, has also been used recently to recover gold from old mine waste dumps. Higher grade ores are often crushed, ground, and vat leached or agitated/leached to recover the gold.

In vat leaching, a vat is filled with the ground ore (sands) slurry, water is allowed to drain off, and the sands are leached from the top with cyanide, which solubilizes the gold (Figure III-9). Pregnant cyanide solution is collected from the bottom of the vat and sent to a holding tank. In

Figure III-9. CYANIDATION OF GOLD ORE: VAT LEACHING OF SANDS AND 'CARBON-IN-PULP' PROCESSING OF SLIMES



agitation leaching, the cyanide solution is added to a ground ore pulp in thickeners, and the mixture is agitated until solution of the gold is achieved (Figure III-10). The cyanide solution is collected by decanting from the thickeners.

Cyanidation of slimes generated in the course of wet grinding is currently being done by a recently developed process, carbon-in-pulp (Figure III-9). The slimes are mixed with a cyanide solution in large tanks, and the solubilized gold cyanide is collected by adsorption onto activated charcoal. Gold is stripped from the charcoal using a small volume of hot caustic; an electrowinning process is used for final recovery of the gold in the mill. Bullion is subsequently produced at a refinery.

Gold in the pregnant cyanide solutions from heap, vat, or agitate leaching processes is recovered by precipitation with zinc dust. The precipitate is collected in a filter press and sent to a smelter for the production of bullion.

Recovery of gold by flotation processes is limited, and less than 3% of the gold produced in 1972 was recovered in this manner. This method employs a froth flotation process to float and collect the gold-containing minerals (Figure III-11). The single operation currently using this method further processes the tailings from the flotation circuit by the agitation/cyanidation method to recover the residual gold values.

Silver Ores

The silver ore mining and milling industry is defined for this document as that segment of industry involved in the mining and/or milling of ore for the primary or byproduct/coproduct recovery of silver. Domestic production of silver for 1972 was 1.158 million kilograms (37,232,922 troy ounces). Over 38% of this production came from Idaho, and most of this, from the rich Coeur d'Alene district in the Idaho panhandle. The remaining production was attributable to eleven states: Alaska, Arizona, California, Colorado, Michigan, Missouri, Montana, Nevada, New Mexico, South Dakota, and Utah. The 25 leading producers contributed 85% of this total production, and nine of these operations produced over one million troy ounces each. During the past ten years, the annual production of silver has varied from approximately 1 to 1.4 million kilograms (32 to 45 million troy ounces). Prices have also varied and, during 1972, ranged from a low of 4.41 cents per gram (137.2 cents per troy ounce) to a high of 6.54 cents per gram (203.3 cents

Figure III-10. CYANIDATION OF GOLD ORE: AGITATION/LEACH PROCESS

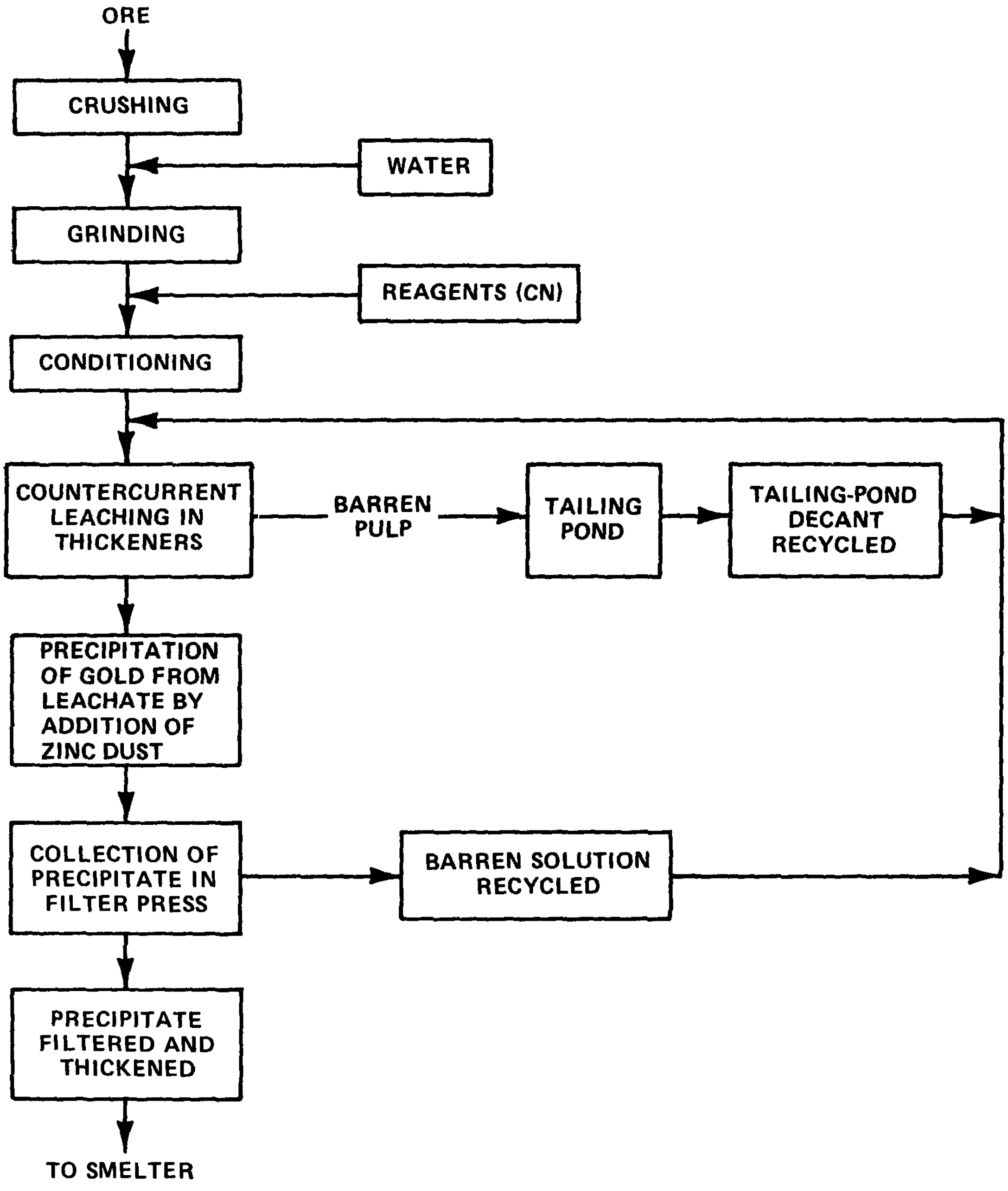
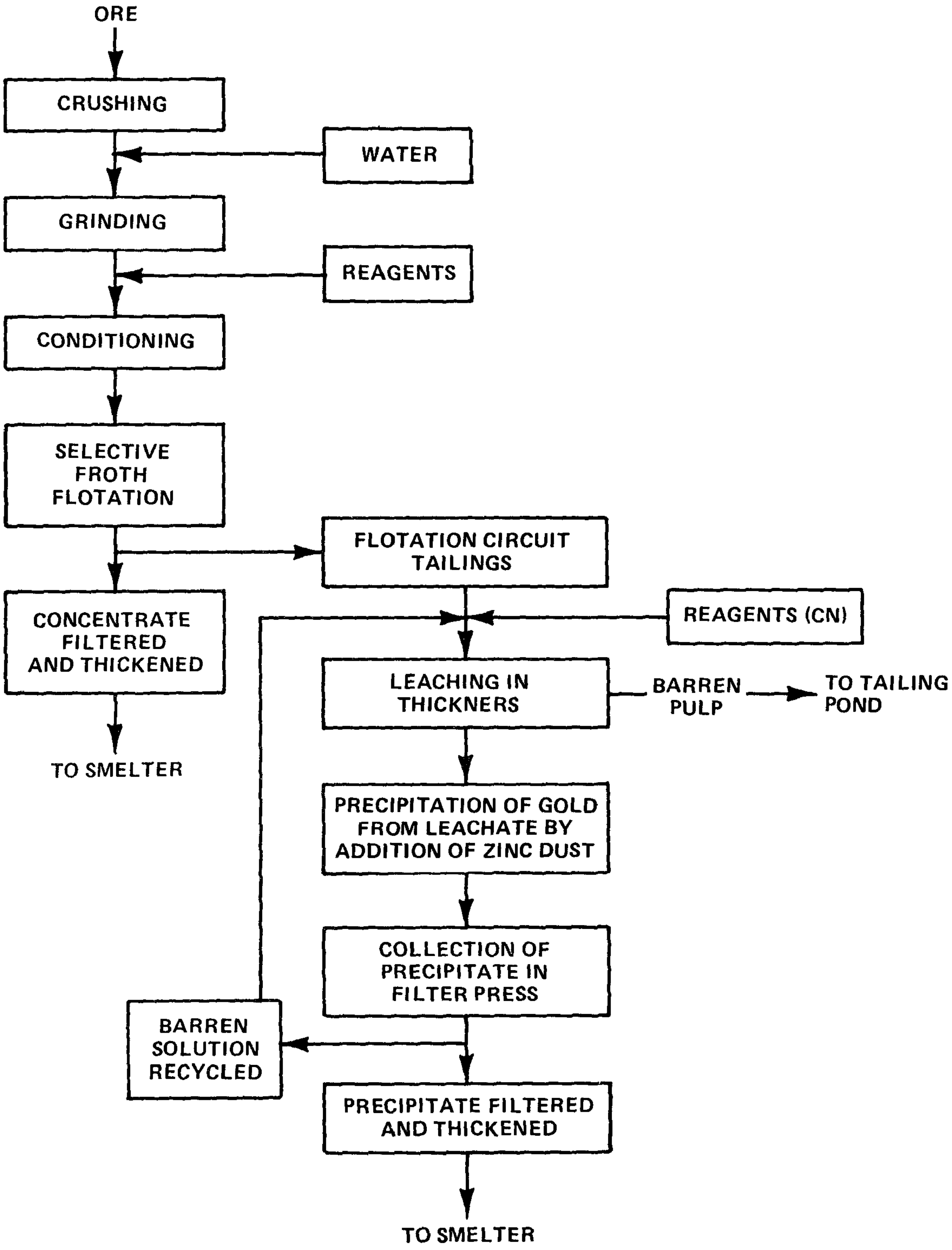


Figure III-11. FLOTATION OF GOLD-CONTAINING MINERALS WITH RECOVERY OF RESIDUAL GOLD VALUES BY CYANIDATION



per troy ounce). Average price for 1972 was 5.39 cents per gram (167.7 cents per troy ounce).

Current domestic production of new silver is derived almost entirely from exploitation of low-grade and complex sulfide ores. About one-fourth of this production is derived from ores wherein silver is the chief value and lead, zinc, and/or copper are valuable byproducts. About three-fourths of this production is from ores in which lead, zinc, and copper constitute the principal values, and silver is a minor but important byproduct. The types, grade, and relative importance of the metal sulfide ores from which domestic silver is produced are listed in Table III-15.

Present extractive metallurgy of silver was developed over a period of more than 100 years. Initially, silver, as the major product, was recovered from rich oxidized ores by relatively crude methods. As the ores became leaner and more complex, an improved extractive technology was developed. Today, silver production is predominantly as a byproduct, and is largely related to the production of lead, zinc, and copper from the processing of sulfide ores by froth flotation and smelting. Free-milling--simple, easily liberated--gold/silver ores, processed by amalgamation and cyanidation, now contribute only 1 percent of the domestic silver produced. Primary sulfide ores, processed by flotation and smelting, account for 99 percent (Table III-16).

Selective froth flotation processing can effectively and efficiently beneficiate almost any type and grade of sulfide ore. This process employs various well-developed reagent combinations and conditions to enable the selective recovery of many different sulfide minerals in separate concentrates of high quality. The reagents commonly used in the process are generally classified as collectors, promotors, modifiers, depressants, activators, and frothing agents. Essentially, these reagents are used in combination to cause the desired sulfide mineral to float and be collected in a froth while the undesired minerals and gangue sink. Practically all the ores presently milled require fine grinding to liberate the sulfide minerals from one another and from the gangue minerals.

A circuit which exemplifies the current practice of froth flotation for the primary recovery of silver from silver and complex ores is shown in Figure III-12. Primary recovery of silver is largely from the mineral tetrahedrite, $(Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$. A tetrahedrite concentrate contains approximately 25 to 32% copper in addition to the 25.72 to

TABLE III-15. DOMESTIC SILVER PRODUCTION FROM DIFFERENT TYPES OF ORES

TYPE	SILVER ORE PRODUCTION		GRADE OF SILVER		DOMESTIC PRODUCTION (%)
	1000 METRIC TONS	1000 SHORT TONS	GRAMS PER METRIC TON	OUNCES PER SHORT TON	
SILVER	405.43	447	679.0	19.8	24
COPPER	187,960.33	207,233	2.06	0.06	32
LEAD/ZINC/ COPPER	35,641.47	39,296	10.29	0.3	28
LEAD	7,929.90	8,743	20.57	0.6	14
ZINC	1,104.73	1,218	3.53	0.1	< 0.5
OTHERS*	1,599.04	1,763	6.86	0.2	1.5

*DERIVED FROM GOLD AND GOLD/SILVER ORE

SOURCE: REFERENCE 2

TABLE III-16. SILVER PRODUCED AT AMALGAMATION AND CYANIDATION MILLS IN THE U.S. AND PERCENTAGE OF SILVER RECOVERABLE FROM ALL SOURCES

YEAR	SILVER BULLION AND PRECIPITATES RECOVERABLE BY			
	AMALGAMATION		CYANIDATION	
	KILOGRAMS	TROY OUNCES	KILOGRAMS	TROY OUNCES
1968	2862.2	92,021	1669.2	53,666
1969	2605.7	83,775	1533.8	49,312
1970	2963.8	95,287	774.2	24.892
1971	30.9	993	3321.4	106,785
1972	77.4	2,490	3110.1	99,992

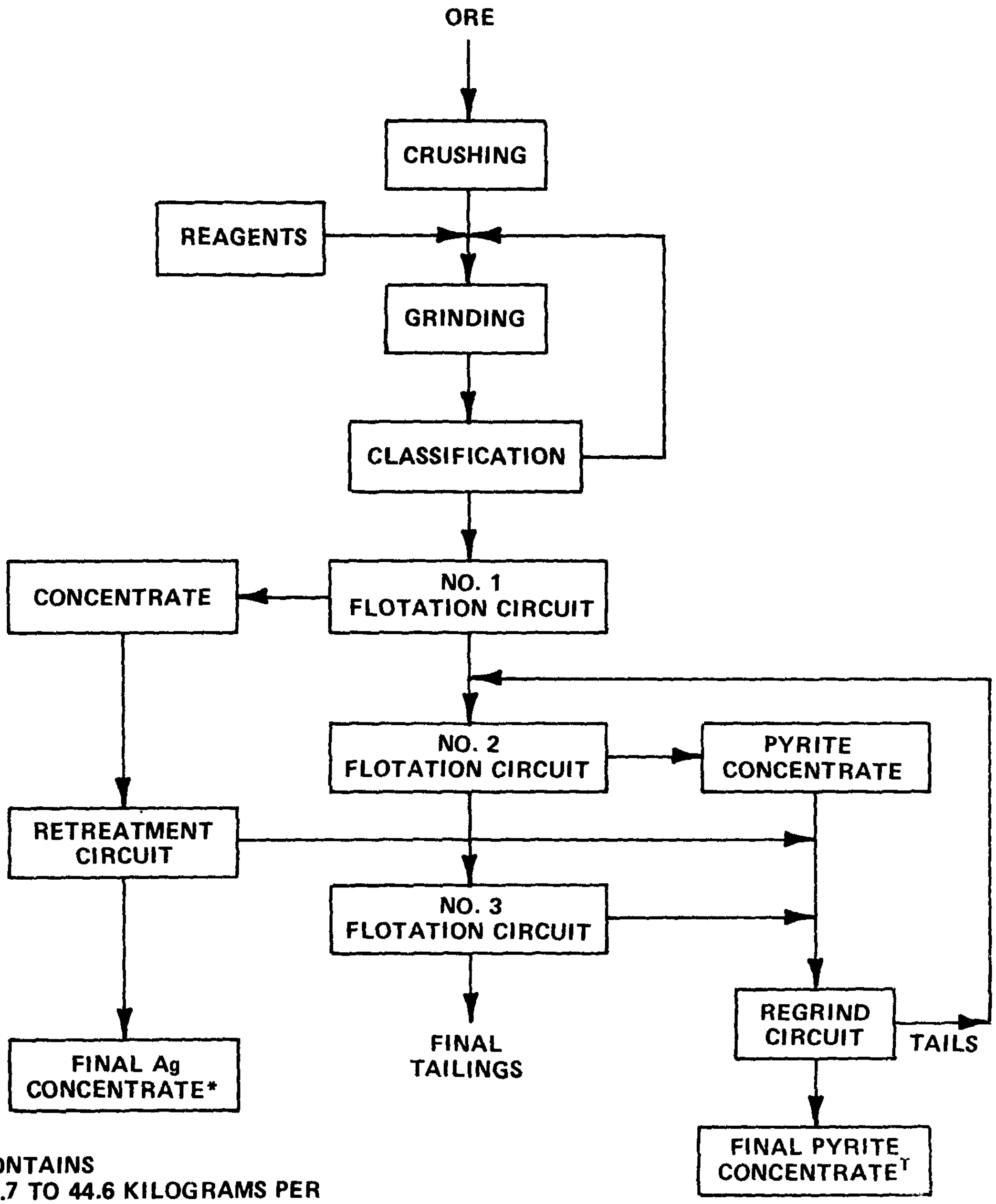
YEAR	SILVER RECOVERABLE FROM ALL SOURCES (%)			
	AMALGAMATION	CYANIDATION	SMELTING*	PLACERS
1968	0.28	0.16	99.55	0.01
1969	0.20	0.11	99.68	0.01
1970	0.21	0.05	99.73	0.01
1971	†	0.26	99.74	†
1972	0.01	0.27	99.72	†

*Crude ores and concentrates

†Less than 1/2 unit

SOURCE: REFERENCE 2

Figure III-12. RECOVERY OF SILVER SULFIDE ORE BY FROTH FLOTATION



*CONTAINS
25.7 TO 44.6 KILOGRAMS PER METRIC TON
(750-1300 OUNCES PER SHORT TON):
25 TO 32% COPPER
0 TO 18% ANTIMONY

†CONTAINS 3.43 KILOGRAMS PER METRIC TON (100 TROY OUNCES PER SHORT TON)

44.58 kilograms per metric ton (750 to 1300 troy ounce per ton) of silver. A low-grade (3.43 kg per metric ton; 100 troy oz per ton) silver/pyrite concentrate is produced at one mill. Antimony may comprise up to 18% of the tetrahedrite concentrate and may or may not be extracted prior to shipment to a smelter.

Various other silver-containing minerals are recovered as byproducts of primary copper, lead, and/or zinc operations. Where this occurs, the usual practice is to ultimately recover the silver from the base-metal flotation concentrates at the smelter or refinery.

Less than 1 percent of the current domestic production of silver is recovered by amalgamation or cyanidation processes. These processes have been described in the discussion of gold ores of this report.

Bauxite

Bauxite mining for the eventual production of metallurgical grade alumina occurs near Bauxite, Arkansas, where two producers mined approximately 1,855,127 metric tons (2,045,344 tons) of ore in 1973. Both operations are associated with bauxite refineries (SIC 2819), where purified alumina (Al_2O_3) is produced. Characteristically, only a portion of the bauxite mined is refined for use in metallurgical smelting, and one operation reports only about 10 percent of its alumina is smelted, while the remainder is destined for use as chemical and refractory grade alumina. A gallium byproduct recovery operation occurs in association with one bauxite mining and refining complex.

The domestic bauxite resource began to be tapped about the turn of the century, and one operation has been mining for about 75 years. However, the aluminum industry began to burgeon during World War II, and, almost overnight the demands for this lightweight metal for aircraft created the large industry of today. Concurrent with the increase in demand for aluminum was the startup of large-scale mining operations by both bauxite producers.

Most bauxite is mined by open-pit methods utilizing draglines, shovels, and haulers. Stripping ratios of as much as 10 feet of overburden to 1 foot of ore are minable, and a 15-to-1 ratio is considered feasible. Pits of 100 feet in depth are common, and 200 feet is considered to be the economic limit for large ore bodies. The pits stand quite well for unconsolidated sands and clays, but some slumping does occur.

Underground mining occurs at one Arkansas facility, and this operation provides the low-silica ore essential to the combination process of refining. Although this type of mining is relatively costly, it is a viable alternative to the purchase of foreign ores at elevated prices. However, one of the operations utilizes imported bauxite for blending of ore grades. Milling of the bauxite ore involves crushing, ore blending, and grinding in preparation for refining. In 1972, less than 10 percent of the bauxite used for primary aluminum production was of domestic origin. With the increasing demand for aluminum, it is expected that the use of imported alumina and aluminum, as well as bauxite, will increase. Therefore, the domestic supply of bauxite is insufficient to meet present needs of the nine domestic refineries. Recent price increases in foreign bauxite supplies aid in assuring the future of domestic bauxite operations, regardless of the limited national reserves.

The search for potential economic sources of aluminum persists, and many pilot projects have been designed to produce aluminum. Currently, the most notable attempt to utilize an alternative source of aluminum is a 9 metric ton (10 ton) per day pilot plant which converts alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, to alumina through a modified Bayer process, preceded by roasting and water leaching. The process yields byproduct sulfuric acid and potassium sulfate as cost credits. Additionally, the processing of alunite creates no significant "red mud" (leach residue). Currently alunite mining is in the exploratory stages, with a commercial scale refinery slated for construction in 1975. Full-scale mining will entail drilling, blasting, and hauling using bench mining techniques. From all indications, alunite may provide an economical new source of aluminum.

Bauxite production in the United States has declined recently from a peak year in 1970, and preliminary production figures for 1974 indicate a continuation of the trend. Production figures in Table III-17 indicate total U.S. production of bauxite, which includes that from mines in Alabama, Georgia, and Arkansas. These mines also produce bauxite for purposes other than metallurgical smelting.

Ferroalloy Ores

The ferroalloy ore mining and milling category embraces the mining and beneficiation of ores of cobalt, chromium, columbium and tantalum, manganese, molybdenum, nickel, and tungsten including crushing, grinding, washing, gravity concentration, flotation, roasting, and leaching. The grouping of

TABLE III-17. PRODUCTION OF BAUXITE IN THE UNITED STATES

YEAR	1000 METRIC TONS*	1000 SHORT TONS*
1964	1626	1793
1965	1680	1852
1966	1825	2012
1967	1680	1852
1968	1692	1865
1969	1872	2064
1970	2115	2332
1971	2020	2227
1972	1930	2128
1973	1908	2104

*Production, given in dry equivalent weight, includes bauxite mined for purposes other than metallurgical smelting these operations is based on the use of a portion of their end product in the production of ferroalloys (e.g., ferromanganese, ferromolybdenum, etc.) and does not reflect any special similarities among the ores or among the processes for their recovery and beneficiation. SIC 1061, although presently including few operations and relatively small total production, covers a wide spectrum of the mining and milling industry as a whole. Sulfide, oxide, silicate, carbonate, and anionic ores all are or have been recovered for the included metals. Open-pit and underground mines are currently worked, and placer deposits have been mined in the past and are included in present reserves. Beneficiation techniques include numerous gravity processes, jigging, tabling, sink-float, Humphreys spirals; flotation, both basic-sulfide and fatty-acid; and a variety of ore leaching techniques. Operations vary widely in scale, from very small mines and mills intermittently worked with total annual volume measured in hundreds of tons, to two of the largest mining and milling operations in the country (Reference 2). Geographically, mines and mills in this category are widely scattered, being found in the southeast, southwest, northwest, north central, and Rocky Mountain regions and operate under a wide variety of climatic and topographic conditions.

Historically, the ferroalloy mining and milling industry has undergone sharp fluctuation in response to the prices of foreign ores, government policies, and production rates of other metals with which some of the ferroalloy metals are recovered as byproducts (for example, tin and copper, Reference 5). Many deposits of ferroalloy metals in the U.S. are of lower grade (or more difficult to concentrate) than foreign ores and so are only marginally recoverable or uneconomic at prevailing prices. Large numbers of mines and mills were worked during World Wars I and II, and during government stockpiling programs after the war, but have since been closed. At present, ferroalloy mining and milling is at a very low level. Increased competition from foreign ores, the depletion of many of the richer deposits, and a shift in government policies from stockpiling materials to selling concentrates from stockpiles have resulted in the closure of most of the mines and mills active in the late 1950's. For some of the metals, there is little likelihood of further mining and milling in the foreseeable future; for others, increased production in the next few years is probable. Production figures for the ferroalloy mining and milling industry since 1945 are summarized in Table III-18.

TABLE III-18. PRODUCTION OF FERROALLOYS BY U.S. MINING AND MILLING INDUSTRY

COMMODITY	ANNUAL PRODUCTION IN METRIC TONS (SHORT TONS)					
	1949*	1953*	1958†	1962†	1968**	1972†
Chromium	394 (433)	53,470 (58,817)	–	0	0	0
Columbium and Tantalum	0.5 (0.5)	6.8 (7.4)	194.7†† (214.2)	–	0	0
Cobalt	237 (261)	572 (629)	2,202 (2,422)	–	550 (605)	0
Manganese	103,835 (114,427)	129,686 (142,914)	–	–	43,557 (48,000)	16,996 (18,730)
Molybdenum	10,222 (11,265)	25,973 (28,622)	18,634 (20,535)	23,250 (25,622)	42,423 (46,750)	46,368 (51,098)
Nickel	0	0	–	–	13,750 (15,150)	15,303 (16,864)
Tungsten (60% WO_3)	1,314 (1,448)	4,207 (4,636)	3,437 (3,788)	7,649 (8,429)	8,908 (9,817)	6,716 (7,401)
Vanadium*	N.A.	N.A.	2,750 (3,030)	4,749 (5,233)	5,580 (6,149)	4,435 (4,887)

*Reference 6

†Reference 3

**Reference 7

††Reference 5

As Table III-18 shows, molybdenum mining and milling constitute the largest and most stable segment of the ferroalloy ore mining and milling industry in the United States. The U.S. produces over 85% of the world's molybdenum supply, with two mines dominating the industry. These two mines are among the 25 largest mining operations in the U.S. Production is expected to increase in the near future with expanded output from existing facilities, and at least one major new operation in Colorado is expected to be in operation soon.

The only commercially important ore of molybdenum is molybdenite, MoS_2. It is mined by both open-pit and underground methods and is universally concentrated by flotation. Commercially exploited ore currently ranges from 0.1 to 0.3 percent molybdenum content (Reference 7). Significant quantities of molybdenite concentrate are recovered as a byproduct in the milling of copper and tungsten ores.

Tungsten ores are mined and milled at many locations in the U.S., but most of the production is from one operation. In 1971, for example, the Bureau of Mines reported 66 active tungsten mines, but total annual production from 59 of them was less than 1000 metric tons (1102 short tons) each and, from five others, less than 10,000 metric tons (11,023 short tons) (Reference 2). These small mines and mills are operated intermittently, so it is quite difficult to locate and contact active plants at any given time. Tungsten production has been strongly influenced by government policies. During stockpiling in 1955, 750 operations produced tungsten ore at $63 per unit in 1970 (unit = 9.07 kg (20 lb) of 70% W concentrate); with the sale of some stockpiled material, only about 50 mines operated with a price of $43 per unit (Reference 7). Projected demand for tungsten will exceed supply before the year 2000 at present prices, and production from currently inactive deposits may be anticipated (Reference 7).

Commercially important ores for tungsten are scheelite ($CaWO_4$) and the wolframite series, wolframite ($(Fe, Mn)WO_4$), ferberite ($FeWO_4$), and huebnerite ($MnWO_4$. Underground mining predominates, and concentration is by a wide variety of techniques. Gravity concentration, by jigging, tabling, or sink float methods, is frequently employed. Because sliming due to the high friability of scheelite ore (most U.S. ore is scheelite) reduces recovery by gravity techniques, fatty-acid flotation may be used to increase recovery. Leaching may also be employed as a major beneficiation step and is frequently practiced to lower the phosphorus content of concentrates. Ore generally contains about 0.6 percent tungsten, and concentrates containing about 70 percent WO_3 are produced. A tungsten concentrate is also produced as a byproduct of molybdenum milling at one operation in a process involving gravity separation, flotation, and magnetic separation.

Manganese and nickel ores are each recovered at only one active operation in the U.S. at this time. The manganese operation is completely dry, having no mine-water discharge and no mill. At the nickel mine, small amounts of conveyor wash water and scrubber water from ore milling are mixed with effluents from an on-site smelter and with seasonal mine-site runoff. Water-quality impact from the mining and milling of these two metals is thus presently minimal. Future production of manganese and nickel, however, may be expected to involve considerable water use.

Manganese is essential to the modern steel industry, both as an alloying agent and as a deoxidizer, and these uses dominate the world manganese industry (Reference 8). Additional uses include material for battery electrodes and agents for impurity removal in glassmaking. Domestic production of manganese ores and concentrates has generally accounted for a very small fraction of U.S. consumption, the majority being supplied from foreign concentrates (Reference 7). A number of significant plants have, however, been operated for manganese recovery using a variety of processing methods, and known ore reserves exist which are economically recoverable.

The U.S. Bureau of Mines divides manganese-bearing ores into three classes (Reference 7):

(1) manganese ores (at least 35 percent manganese content)

(2) ferruginous manganese ore (10 to 35 percent manganese content)

(3) manganiferous iron ore (less than 10 percent manganese content)

The latter two classes are often grouped as manganiferous ores and, in recent years, have accounted for nearly all domestic production. In 1971, for example, only 5 percent of the total production of 43,536 metric tons (48,000 short tons) was in the form of true manganese ores (Reference 7). Future domestic production is likely on a significant scale from manganiferous ores -- particularly, on the Cuyuna Range in Minnesota, where preparations for the resumption of production are currently underway. This area, although currently quiescent, accounted for 85 percent of domestic production in 1971 (Reference 7).

Manganese ores have been processed by a wide variety of techniques, ranging from dry screening to ore leaching. Notable concentrating procedures in the recent past have included sink-float separation, fatty-acid flotation (References 9, 10, 11, 12), and ammonium carbamate leaching (Reference 13). It is most likely that heavy-media separation will be practiced in the immediate future.

Nickel ores are not currently being exploited in the U.S. One nickel lateritic lateritic deposit is currently being mined. Some sulfide nickel ore deposits with commercial possibilities have been found in Alaska (Reference 2). If they are developed, processes entirely different from those in use at the present operation will be employed. Most likely, processing will involve selective flotation with reagent and water usage and pollution problems quite similar to those of Canadian nickel operations (Reference 14).

There are no mines or mills currently active in the U.S. producing ores or concentrates of chromium, cobalt, columbium, and tantalum. Further, no operations could be identified where they are recovered as a significant byproduct, although the metals and their compounds are recovered at a number of domestic smelters and refineries. This production is primarily from foreign ores and concentrates but includes some recovery from domestic concentrates of other metals.

Chromium ore production in the U.S. has occurred only under the impetus of government efforts to stimulate a domestic industry. Production of chromite ore from the Stillwater Complex during World War II, and from 1953 through 1961, involved gravity concentration by tabling, and this mode of operation is likely in the event of future production. Leaching of foreign concentrates, as currently practiced, might provide an alternative method of concentrating chromium values in domestic ores. Domestic production by any means is unlikely, however, for the next several years. Production costs for chromium from domestic ores are estimated to be $110 per metric ton ($100 per short ton), and no shortage is expected in the near future.

Cobalt has been recovered in significant quantities at two locations in the U.S., neither of which is currently active. One of these, in the Blackbird district at Cobalt, Idaho, has some probability of further production in the near future. At these sites, as at essentially all sites around the world, cobalt is a coproduct or byproduct of other metals, and the production rates and world price of these other metals, particularly copper and nickel, exert primary influence on the cobalt market (Reference 5). Known domestic ore from which cobalt might be recovered is a complex copper cobalt sulfide ore which is likely to be processed by selective flotation and roasting and leaching of the cobalt-bearing float product (Reference 5).

Columbium and tantalum concentrates have in the past been produced at as many as six sites in the U.S. (Reference 15), and several potentially workable deposits of the ore minerals pyrochlore and euxenite are known. Economic recovery would require a twofold increase in price for the metals, however, and is considered unlikely before the year 2000 (Reference 5). Production, should it occur, would involve placer mining at one of the known deposits, with the water quality impact and treatment problems peculiar to that activity. Concentration techniques varying widely from fairly simple gravity and hand picking techniques through magnetic and electrostatic separation and flotation have been used in the past. Accurate prediction of the process which would be used in future domestic production is not feasible.

Vanadium. Eighty-six percent of vanadium oxide production has recently been used in the preparation of ferrovanadium. Although a fair share of U.S. vanadium production is derived as a byproduct of the mining of uranium, there are other sources of vanadium ores. The environmental considerations at mine/mill operations not involving radioactive constituents are fundamentally different from those that are important at uranium operations, and it seems appropriate to consider the former operation separately. Vanadium is considered as part of this industry segment: (a) because of the similarity of non-radioactive vanadium recovery operations to the processes used for other ferroalloy metals and (b) because, in particular, hydrometallurgical processes like those used in vanadium recovery are becoming more popular in SIC 1061. These arguments are also presented in the discussion of the SIC 1094 (uranium, vanadium, and radium mining and ore dressing) categories. Other aspects of effluent from uranium/vanadium byproduct operations under Nuclear Regulatory Commission (formerly AEC) license are treated further under that heading.

Vanadium is chemically similar to columbium (niobium) and tantalum, and ores of these metals may be beneficiated in the same type of process used for vanadium. There is also some similarity to tungsten, molybdenum, and chromium.

Ferroalloy Ore Beneficiation Processes

Ore processing in the ferroalloys industry varies widely, and even ores bearing the same ore mineral may be concentrated by widely differing techniques. There is thus no scheelite recovery process or pyrolusite concentration technique *per se*. On the other hand, the same fundamental processes may be used to concentrate ores of a variety of metals with differences only in details of flow rate, reagent dosage etc., and some functions (such as crushing and grinding ore) that are common to nearly all ore concentration procedures. Fundamental ore beneficiation processes which require water may be grouped into three basic classes:

1. Purely physical separation (most commonly, by gravity)
2. Flotation
3. Ore Leaching

Prior to using any of these processes, ore must, in general, be crushed and ground; in their implementation, accessory techniques such as cycloning, classification, and thickening may be of great importance.

Physical Ore Processing Techniques. Purely physical ore beneficiation relies on physical differences between the ore and accessory mineralization to allow concentration of values. No reagents are used, and pollutants are limited to mill feed components soluble in relatively pure water, as well as to wear products of milling machinery. Physical ore properties often exploited include gravity, magnetic permeability, and conductivity. In addition, friability (or its opposite) may be exploited to allow rejection of gangue on the basis of particle size.

Gravity concentration is effected by a variety of techniques, ranging from the very simple to the highly sophisticated, including jigging, Humphreys spirals, and tabling. Jigging is applicable to fairly coarse ore, ranging in size from 1 mm to 13 mm (approximately 0.04 to 0.50 inch), generally the product of secondary crushing (Reference 5). Ore is fed as a slurry to the jig, where a plunger operating at 150 to 250 cycles per minute provides agitation. The relatively dense ore sinks to the screen, while the lighter gangue is kept suspended by the agitation and is removed with the overflow. Often, a bed of coarser ore or iron shot is used in the jig to aid in separation. Sink-float methods rely on the buoyancy forces in a dense fluid to float the gangue away from denser ore minerals. It is also a coarse ore separation technique generally applicable to particles which are 2 mm to 5 mm (approximately 0.08 to 0.2 inch in diameter) (Reference 5). Most commonly, the separation medium is a suspension of very fine particles of dense materials (ferrosilicon in the heavy media separation, and galena in the Huntington-Heberlein process). Light gangue overflows the separation tank, while ore is withdrawn from the bottom. Both are generally dewatered on screens and washed, the separation medium being reclaimed and returned to the circuit (Reference 16).

Shaking tables and spiral separators are useful for finer particle sizes; generally, ore must be ground before application of these techniques. A shaking table is generally fed at one end and slopes towards the opposite corner. Water flows over a series of riffles or ridges which trap the heavy ore particles and direct them at right angles to the water flow toward the side of the table. The table vibrates, keeping the lighter particles of gangue in suspension, and the particles follow the feed water across the riffles. The separation is never perfect, and the concentrate grades into gangue at the edge of the table through a mixed product called middlings, which is generally collected separately from concentrate and gangue and then retabled. Frequently, several sequential stages of tabling are required to produce a concentrate of the desired grade. Particle size, as well as density, affects the behavior of particles on a shaking table, and the table feed generally must be well classified to ensure both high ore recovery and a good concentration ratio. Humphreys spiral separators are useful for ore ground to between 0.1 mm and 2 mm (approximately 0.004 to 0.08 inch) (Reference 5). They consist of a helical conduit about a vertical axis which is fed at the top with flow down the spiral by gravity. Heavy minerals concentrate at the inner edge and may be drawn off at ports along the length of the spiral; wash water may also be added there to improve separation. The capacity of a single spiral is generally 0.45 to 2.27 metric tons/hour (0.5 to 2.5 short tons/hour) (Reference 17).

Magnetic and electrostatic separation are frequently used for the separation of concentrates of different metals from complex ores -- for example, the separation of cassiterite, columbite, and monazite (Reference 5) or the separation of cassiterite and wolframite (Reference 18). Although they are both most frequently implemented as dry processes, wet-belt magnetic separators are used. Since ore particles are charged to 20,000 to 40,000 volts for electrostatic

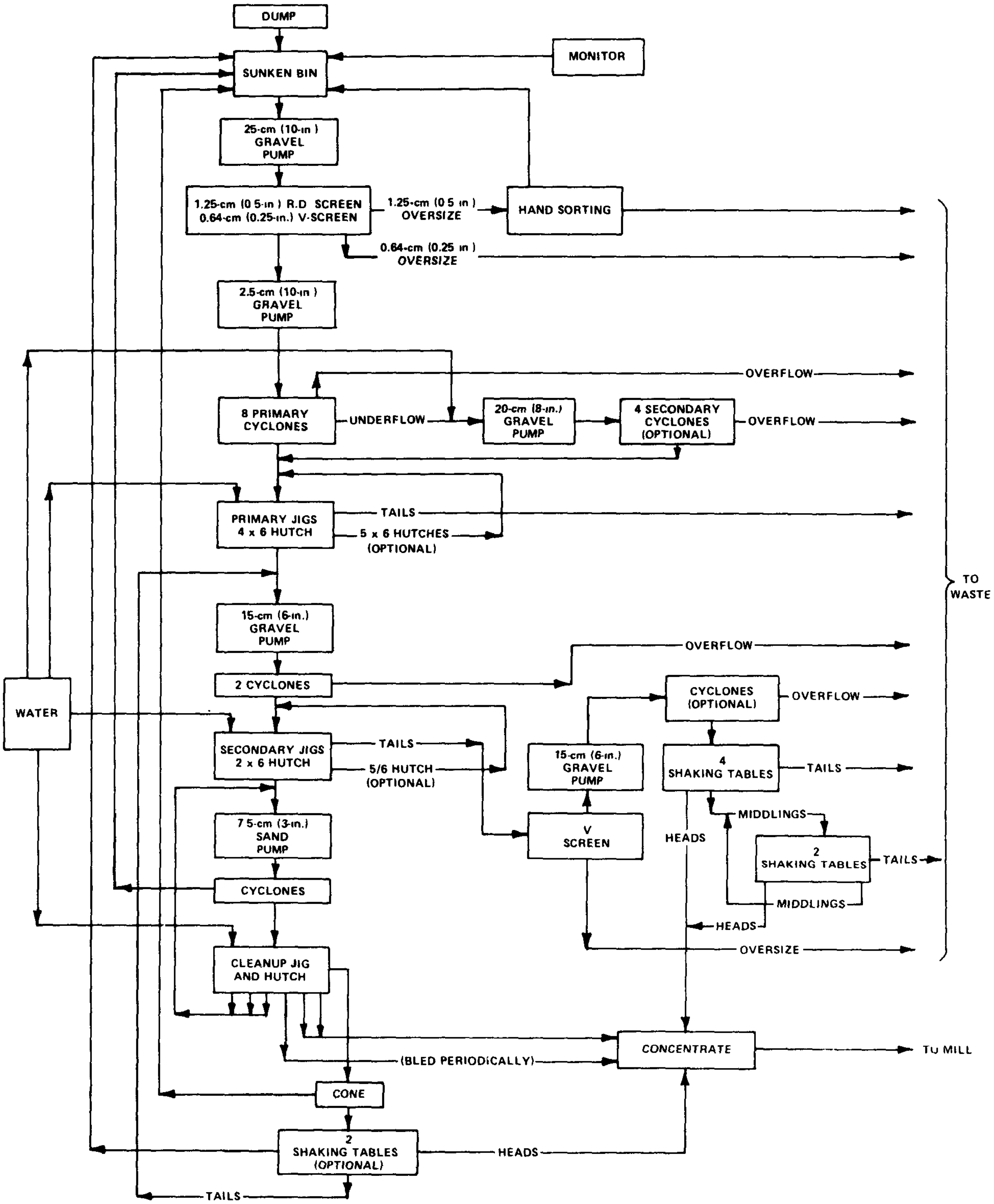
separation, no wet process exists. In magnetic separation, particles of high magnetic permeability are lifted and held to a moving belt by a strong magnetic field, while low permeability particles proceed with the original stream (wet-belt separator) or belt (crossed-belt separator). In electrostatic separation, charged nonconductive particles adhere to a rotating conductive drum, while conductive particles discharge rapidly and fall or are thrown off.

These processes may be combined with each other, and with various grinding mills, classifiers, thickeners, cyclones, etc., in an almost endless variety of mill flow sheets, each particularly suited to the ore for which it has been developed. These flow sheets may become quite complex, involving multiple recirculating loops and a variety of processes as the examples from the columbium and tantalum industry shown in Figures III-13 and III-14 illustrate. It is believed that domestic mills currently employing only physical separation will have fairly simple flow sheets since they are all small processors. Such an operation might be represented by the flow sheet of Figure III-15.

Water use in physical beneficiation plants may vary widely from zero to three or more times the ore milled by weight. However, there are no technical obstacles inherent in the process to total reuse of water (except for the 20 to 30 percent by weight retained by tails) by recycle within the process or from the tailings pond.

Flotation Processes. Flotation concentration has become a mainstay of the ore milling industry. Because it is adaptable to very fine particle sizes (less than 0.01 mm, or 0.0004 inch), it allows high rates of recovery from slimes which are inevitably generated in crushing and grinding and are not generally amenable to physical processing. As a physico-chemical surface phenomenon, it can often be made highly specific, allowing production of high-grade concentrates from very-low-grade ore (e.g., 95+ percent MoS_2 concentrate from 0.3 percent) (Reference 18). Its specificity also allows separation of different ore minerals (e.g., CuS and MoS_2) where desired, and operation with minimum reagent consumption since reagent interaction is typically only with the particular materials to be floated or depressed.

Figure III-13. GRAVITY-PLANT FLOWSHEET FOR NIGERIAN COLUMBITE



SOURCE: REFERENCE 19

Figure III-14. EUXENITE/COLUMBITE BENEFICIATION-PLANT FLOWSHEET

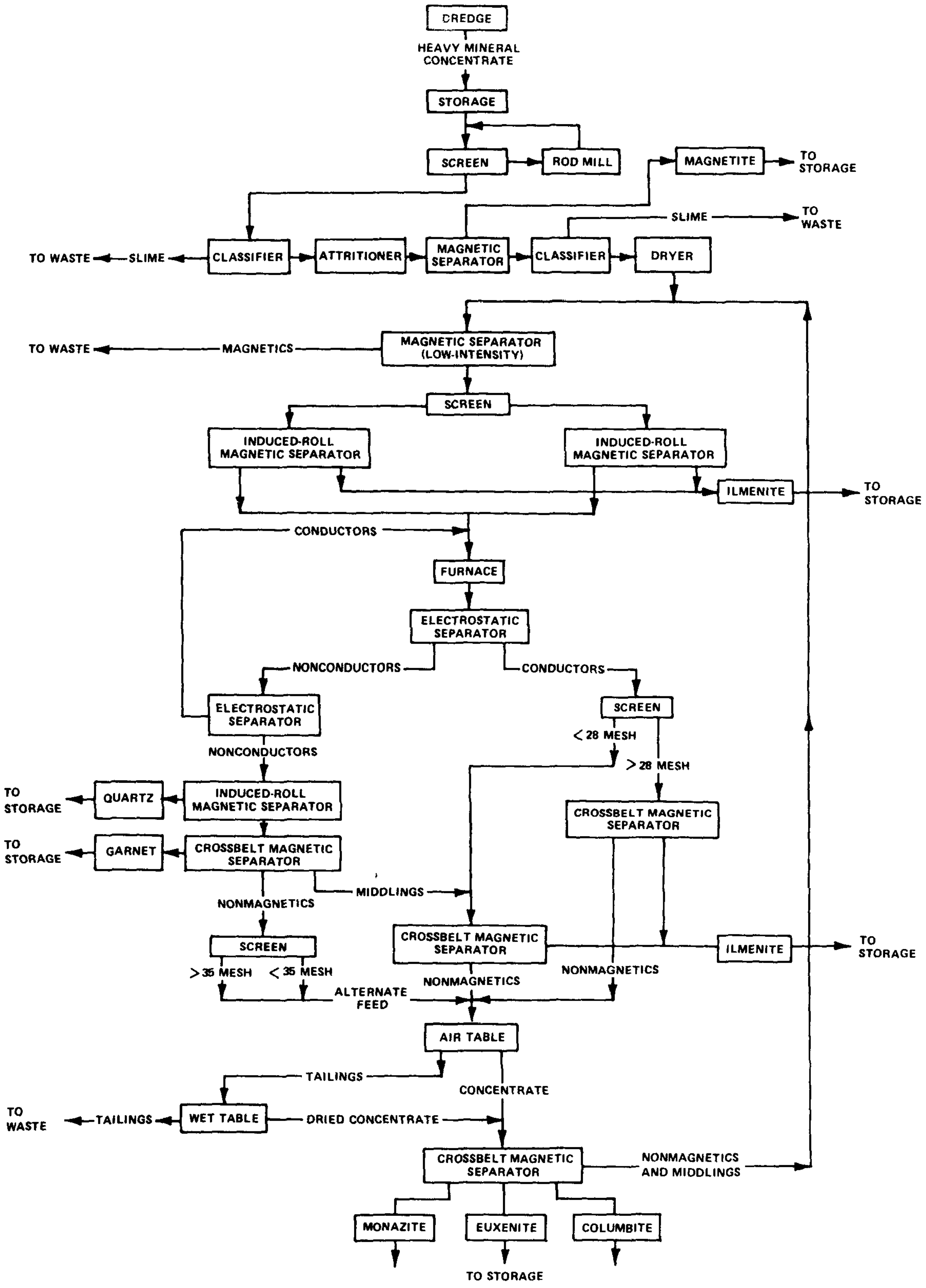
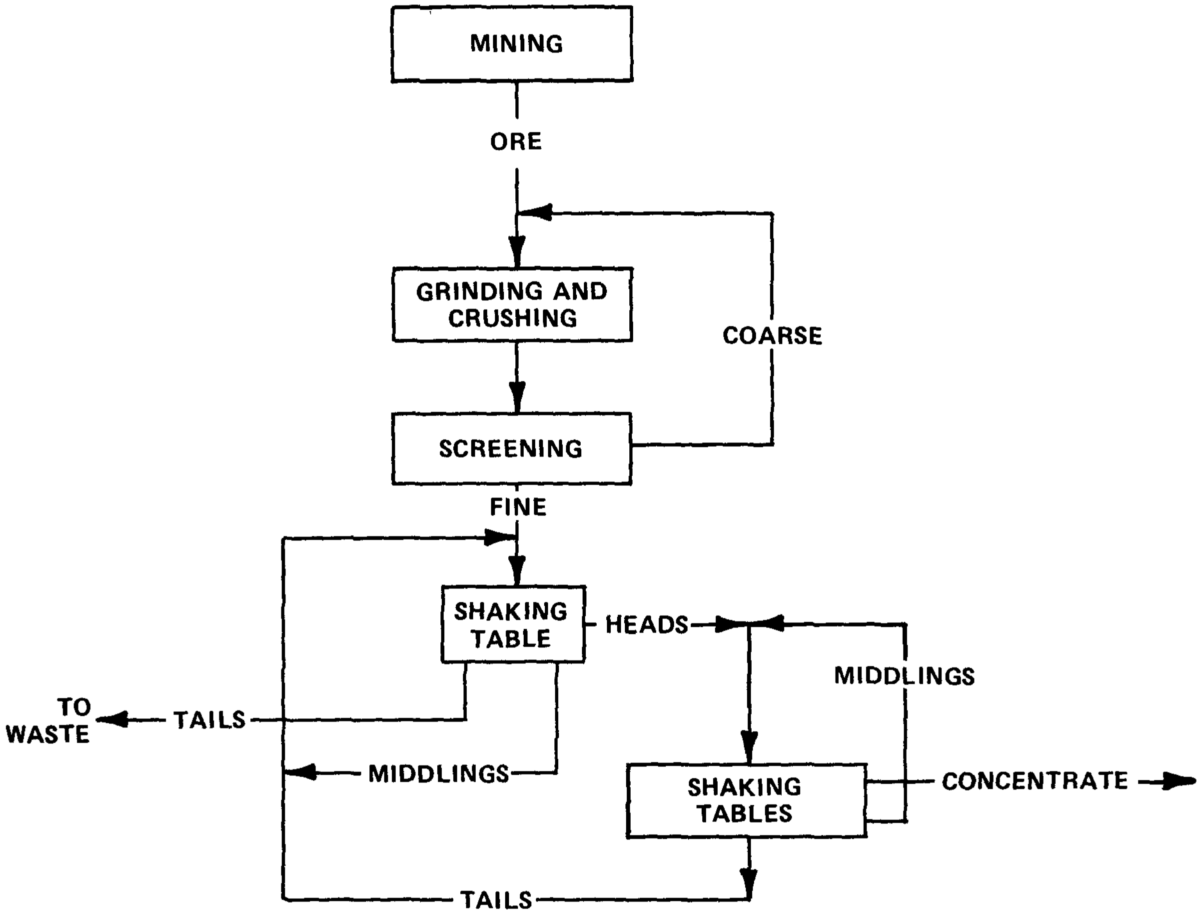


Figure III-15. REPRESENTATIVE FLOW SHEET FOR SIMPLE GRAVITY MILL



Details of the flotation process -- exact suite and dosage of reagents, fineness of grinding, number of regrinds, cleaner-flotation steps etc., -- will differ at each operation where practiced; and may often vary with time at a given mill. The complex system of reagents generally used includes four basic types of compounds: collectors, frothers, activators, and depressants. Frequently, activators are used to allow flotation of ore depressed at an earlier stage of the milling process. In almost all cases, use of each reagent in the mill is low--generally, less than 0.5 kg per metric ton of ore (1.00 lb per short ton)--and the bulk of the reagent adheres to tailings or concentrates. Reagents commonly used and observed dosage rates are shown in Table III-19.

Sulfide minerals are all readily recovered by flotation using similar reagents in small doses, although reagent requirements and ease of flotation do vary through the class. Flotation is generally carried out at an alkaline pH, typically 8.5 for molybdenite (Reference 18). Collectors are most often alkali xanthates with two to five carbon atoms -- for example, sodium ethyl xanthate (C_2H_5O . $NaCS_2$). Frothers are generally organics with a soluble hydroxyl group and a "non-wettable" hydrocarbon (Reference 17). Pine oil ($C_6H_{12}OH$), for example, is widely used. Depressants vary but are widely used to allow separate recovery of metal values from mixed sulfide ores. Sodium cyanide is widely used as a pyrite depressant -- particularly, in molybdenite recovery. Activators useful in sulfide ore flotation may include cuprous sulfide and sodium sulfide.

The major operating plants in the ferroalloy industry recover molybdenite by flotation. Vapor oil is used as the collector, and pine oil is used as a frother. Lime is used to control pH of the mill feed and to maintain an alkaline circuit. In addition, Nokes reagent and sodium cyanide are used to prevent flotation of galena and pyrite with the molybdenite. A generalized, simplified flowsheet for an operation recovering only molybdenite is shown in Figure III-16. Water use in this operation currently amounts to approximately 1.8 tons of water per ton of ore processed, essentially all of which is process water. Reclaimed water from thickeners at the mill site (shown on the flowsheet) amounts to only 10 percent of total use.

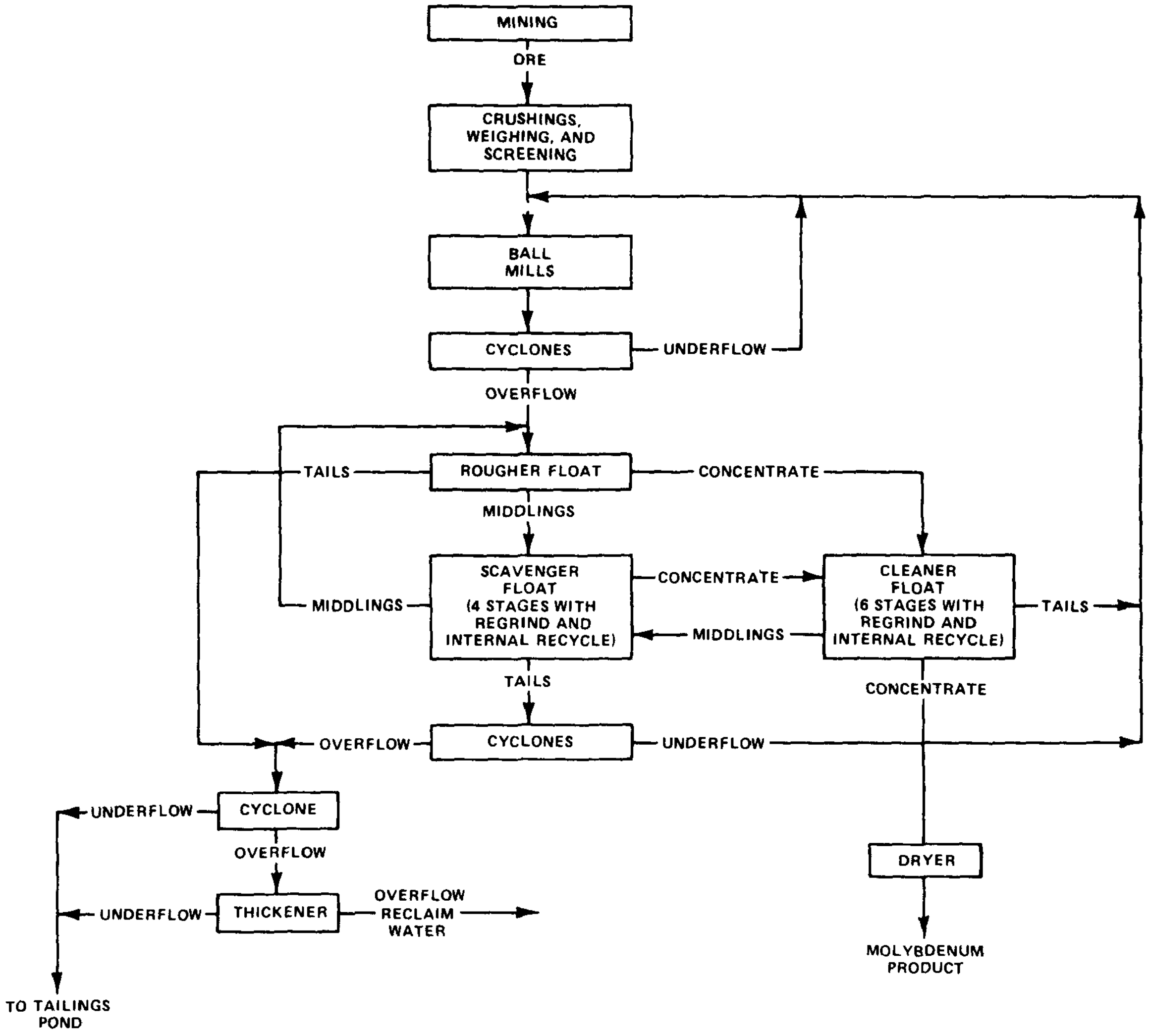
Where byproducts are recovered with molybdenite, a somewhat more complex mill flowsheet results, although the molybdenite recovery circuits themselves remain quite similar. A very simplified flow diagram for such an opera-

TABLE III-19. OBSERVED USAGE OF SOME FLOTATION REAGENTS

REAGENT	OBSERVED USAGE	
	IN KILOGRAMS PER METRIC TON	IN POUNDS PER SHORT TON
SULFIDE FLOTATION		
Vapor oil	0.1 to 0.4	0.2 to 0.8
Pine oil	0.02 to 0.2	0.04 to 0.4
Nokes reagent	0.04	0.08
MIBC (methylisobutyl carbinol)	0.02	0.04
Sodium cyanide	0.005 to 0.02	0.01 to 0.04
Sodium silicate	0.25 to 0.35	0.50 to 0.70
Starch	0.0005	0.001
Butyl alcohol	0.08	0.16
Creosote	0.45	0.90
Miscellaneous xanthates	0.0005 to 0.2	0.001 to 0.4
Commercial frothers	0.002 to 0.2	0.004 to 0.4
OTHER FLOTATION		
Copper sulfate	0.4	0.8
Sodium silicate	0.3 to 3	0.6 to 6
Oleic acid	0.06 to 6.5	0.12 to 13
Sodium oleate	0.05 to 0.2	0.1 to 0.4
Acid dichromate	0.1 to 0.4	0.2 to 0.8
Sodium carbonate	4 to 6	8 to 12
Fuel oil	60 to 95*	120 to 190*
Soap skimmings	20 to 50*	40 to 100*
Sulfur dioxide	6*	12*
Long-chain aliphatic amines	——	——
Alkylaryl sulfonate	——	——
Misc. Tradenamed Products	0.02 to 0.4	0.04 to 0.8

*IN USE AT ONLY ONE KNOWN OPERATION, NOT NOW ACTIVE

Figure III-16. SIMPLIFIED MOLYBDENUM MILL FLOWSHEET



tion is shown in Figure III-17. Pyrite flotation and monazite flotation are accomplished at acid pH (4.5 and 1.5, respectively), somewhat increasing the likelihood of solubilizing heavy metals. Volumes at those points in the circuit are low, however, and neutralization occurs upon combination with the main mill water flows for delivery to the tailing ponds. Water flow for this operation amounts to approximately 2.3 tons per ton of ore processed, nearly all of which is process water in contact with ore. Essentially 100 percent recycle of mill water from the tailing ponds at this mill is prompted by limited water availability as well as by environmental considerations and demonstrates its technical and economic feasibility, even with the complications induced by multiple flotation circuits for byproduct recovery.

Other sulfide ores in the ferroalloy cateogry which may be recovered by flotation are those of cobalt and nickel, although no examples of these practices are currently active in the U.S. It is to be expected that they will be recovered as coproducts or byproducts of other metals by selective flotattion from complex ores in processes involving multiple flotation steps. Some of the most likely reagents to be used in these operations are presented in Table III-20, although the process cannot be accurately predicted at this point. It is expected that, as is generally the case, in sulfide flotation, a small total amount of reagents will be used.

Many minerals in addition to sulfides may be and often are recovered by flotation. Among the ferroalloys, manganese, tungsten, columbium, and tantalum minerals are or have been recovered by flotation. Flotation of these ores involves a very different suite of reagents from sulfide flotation and, in some cases, has required substantially larger reagent dosages. Experience has indicated these flotation processes to be, in general, somewhat more sensitive to feedwater conditions than sulfide floats; consequently, they are less frequently run with recycled water.

In current U.S. operations, scheelite is recovered by flotation using fatty acids as collectors. A typical suite of reagents includes sodium silicate (1.0 kg/metric ton or 2.0 lb/short ton) oleic acid (0.5 kg/metric ton, or 1.0 lb/short ton), and sodium oleate (0.1 to 0.2 kg/metric ton, or 0.2 to 0.4 lb/short ton). In addition, materials such as copper sulfate or acid dichromate may be used in small to moderate amounts as conditioners and gangue depressants. Scheelite flotation circuits may run alkaline or acid, depending primarily on the accessory mineralization in the

Figure III-17. SIMPLIFIED MOLYBDENUM MILL FLOW DIAGRAM

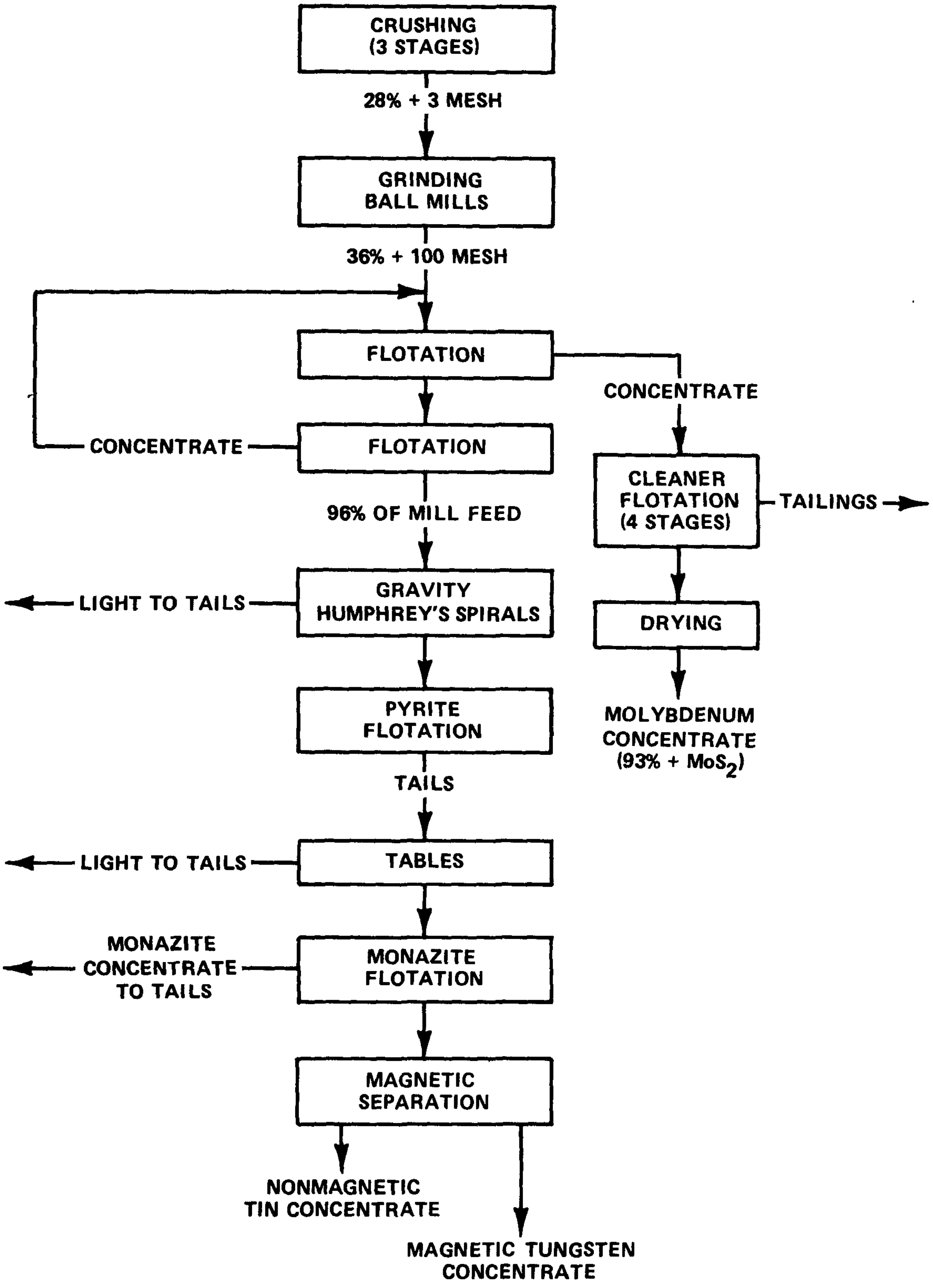


TABLE III-20. PROBABLE REAGENTS USED IN FLOTATION OF NICKEL AND COBALT ORES

- Lime
- Amyl Xanthate
- Isopropyl Xanthate
- Pine Oil
- Methyl Isobutyl Carbinol
- Triethoxybutane
- Dextrin
- Sodium Cyanide
- Copper Sulfate
- Sodium Silicate

ore. Flotation of sulfides which occurs with the scheelite is also common practice. Sulfide float products may be recovered for sale or simply removed as undesirable contaminants for delivery to tails. Frequently, only a portion of the ore (generally, the slimes) is processed by flotation, the coarser material being concentrated by gravity techniques such as tabling. A simplified flow diagram for a small tungsten concentrator illustrating these features is shown in Figure III-18. Note that, in this operation, an acid leach is also performed on a part of the tungsten concentrate. This is common practice in the tungsten industry as a means of reducing phosphorus content in the concentrates. Approximately four tons of water are used per ton of ore processed in this operation.

The basic flotation operations for manganese ores and columbium and tantalum ores are not much different from scheelite flotation; in general, they differ in specific reagents used and, sometimes, in reagent dosage. One past process for a manganese ore, however, bears special mention because of its unusually high reagent usage -- which could, obviously, have a strong effect on effluent character and treatment.

Reagents used include:

Diesel oil	80 kg/metric ton (160 lb/short ton)
Soap skimmings	40 kg/metric ton (80 lb/short ton)
Oronite S (wetting agent)	5 kg/metric ton (10 lb/short ton)
SO_2	5 kg/metric ton (10 lb/short ton)

With the exception of reagent consumption, the plant flow sheet is typical of a straight flotation operation (like that shown in Figure III-16), involving multiple cleaning floats with recycle of tailings.

While the flotation processes are similar, columbium and tantalum flotation plants are likely to possess an unusual degree of complexity due to the complex nature of their ores, which necessitates multiple processes to effectively separate the desired concentrates. This is illustrated in the flowsheet for a Canadian pyrochlore ($NaCaCb_2O_6F$) mill in Figure III-19.

Figure III-18. SIMPLIFIED FLOW DIAGRAM FOR SMALL TUNGSTEN CONCENTRATOR

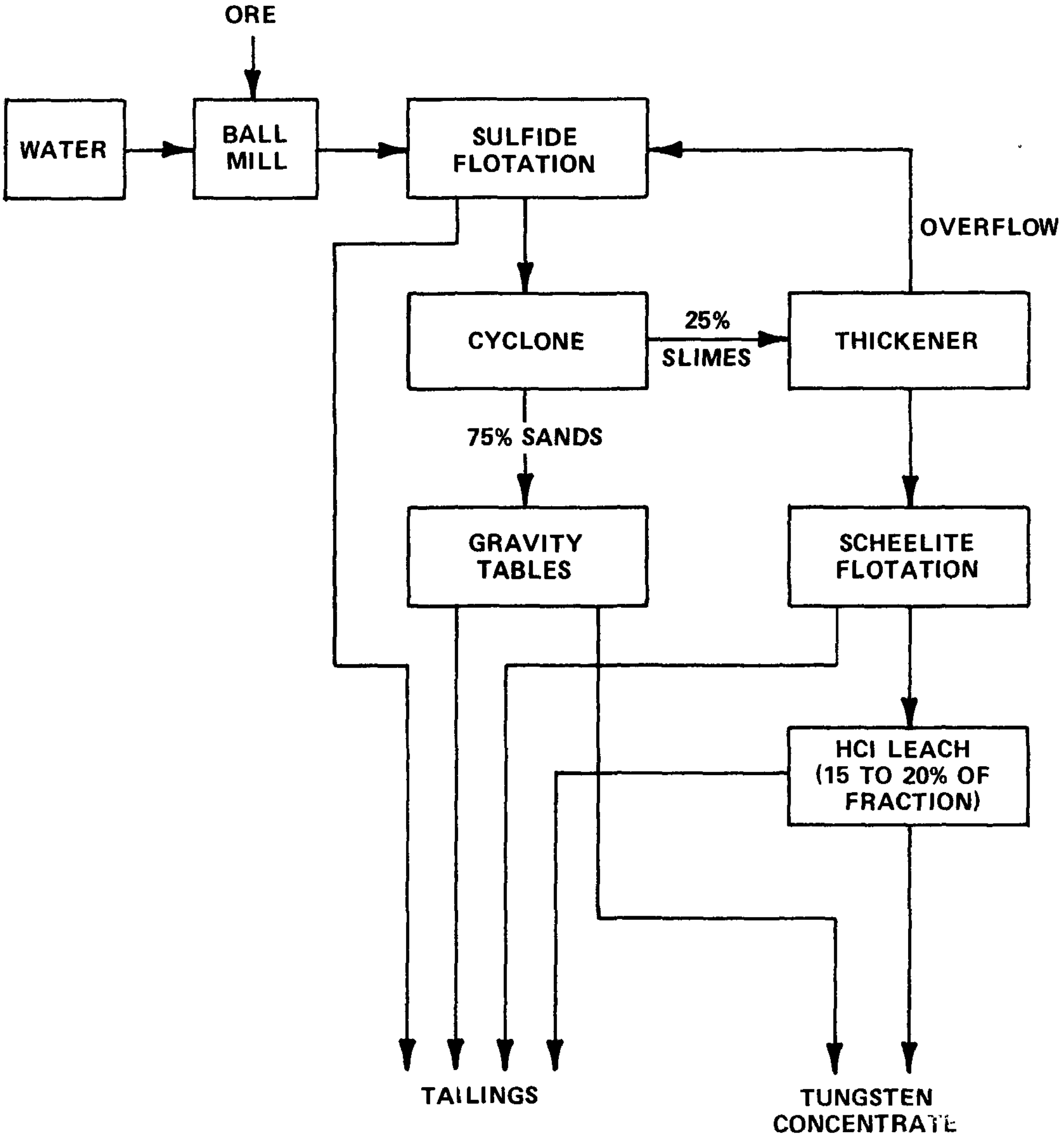
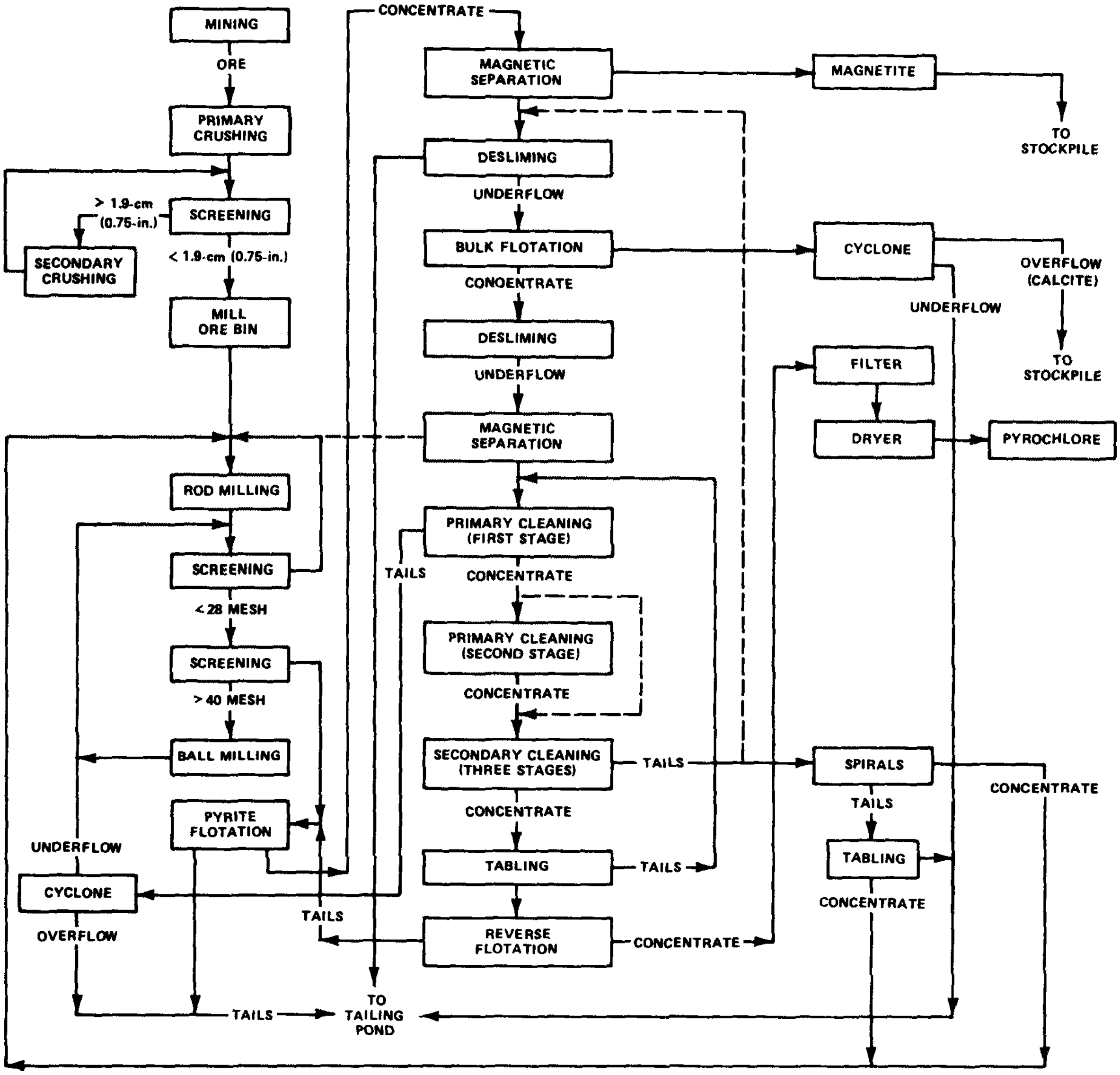


Figure III-19. MILL FLOWSHEET FOR A CANADIAN COLUMBIUM OPERATION



SOURCE: REFERENCE 5

Ore Leaching Processes. While not a predominant practice in the ferroalloys industry, ore leaching has played a part in a number of operations and is likely to increase as segments of the industry process ores of lower grade or which are less easily beneficiated. A number of leaching processes have been developed for manganese ores in the search for methods of exploiting plentiful, low-grade, difficult-toconcentrate domestic ore (that from most of the state of Maine, for example) (Reference 6), and one such process has been commercially employed. As mentioned previously, leaching of concentrates for phosphorus removal is common practice in the tungsten industry, and the largest domestic tungsten producer leaches scheelite concentrates with soda ash and steam to produce a refined ammonium paratungstate product. Leaching is also practiced on chromite concentrates (although not as a part of the domestic mining and milling industry). Vanadium production by leaching nonradioactive ores will also be considered here, because of vanadium's use as a ferroalloy, and because it provides a welldocumented example of ferroalloy beneficiation processes not well-represented in current practice, but likely to assume importance in the future.

Leaching processes for the various ores clearly differ significantly in many details, but all have in common (1) the deliberate solubilization of significant ore components and (2) the use of large amounts of reagents (compared to flotation, for example). These processes share pollution problems not generally encountered elsewhere, such as extremely high levels of dissolved solids and the possibility of establishing density gradients in receiving waters and destroying benthic communities despite apparently adequate dilution.

The processes for the recovery of vanadium in the presence of uranium are discussed in the subsection on uranium. Recovery from phosphate rocks in Idaho, Montana, Wyoming, and Utah -- which contain about 28% P_2O_5, 0.25% V_2O_5, and some Cr, Ni, and Mo -- yields vanadium as a byproduct of phosphate fertilizer production. Ferrophosphate is first prepared by smelting a charge of phosphate rock, silica, coke, and iron ore (if not enough iron is present in the ore). The product separated from the slag typically contains 60 percent iron, 25 percent phosphorus, 3 to 5 percent chromium, and 1 percent nickel. It is pulverized, mixed with soda ash (Na_2CO_3) and salt, and roasted at 750 to 800 degrees Celsius (1382 to 1472 degrees Fahrenheit). Phosphorus, vanadium, and chromium are converted to water-soluble trisodium phosphate, sodium metavanadate, and sodium chromate, while the iron remains in insoluble form and is not extracted in a water leach following the roast.

Phosphate values are removed from the leach in three stages of crystallization (Figure III-20). Vanadium can be recovered as V_2O_5 (redcake) by acidification, and chromium is precipitated as lead chromate. By this process, 85 percent of vanadium, 65 percent of chromium, and 91 percent phosphorus can be extracted.

Another, basically non-radioactive, vanadium ore, with a grade of 1 percent V_2O_5, is found in a vanidiferous, mixed-layer montmorillonite/illite and goethite/montroseite matrix. This ore is opened up by salt roasting, following extrusion of pellets, to yield sodium metavanadate, which is concentrated by solvent extraction. Slightly soluble ammonium vanadate is precipitated from the stripping solution and calcined to yield vanadium pentoxide. A flow chart for this process is shown in Figure III-21.

The Dean Leute ammonium carbamate process has been used commercially for the recovery of high-purity manganese carbonate from low-grade ore on the Cuyuna Range in Minnesota and could be employed again (Reference 13). A flow sheet is shown in Figure III-22.

Mercury Ores

The mercury mining and milling industry is defined for this document as that segment of industry engaged in the mining and/or milling of ore for the primary or byproduct/coproduct recovery of mercury. The principal mineral source of mercury is cinnabar (HgS). The domestic industry has been centered in California, Nevada, and Oregon. Mercury has also been recovered from ore in Arizona, Alaska, Idaho, Texas, and Washington and is recovered as a byproduct from gold ore in Nevada and zinc ore in New York.

Due to low prices and slackened demand, the mercury industry has been in a decline during recent years (Table III-21). During this time, the potential environmental problem and toxic nature of mercury have come under public scrutiny. One result has been the cancellation in March 1972 of all biocidal uses of mercury under the terms of the Federal Insectide, Fungicide, and Rodenticide Act. In addition, registration has been suspended for mercury alkyl compounds and nonalkyl uses on rice seed, in laundry products, and in marine antifouling paint. An immediate effect of this has been a substantial reduction in the demand for mercury for paints and agricultural applications. However, future

Figure III-20. FLOWSHEET OF TRISTAGE CRYSTALLIZATION PROCESS FOR RECOVERY OF VANADIUM, PHOSPHORUS, AND CHROMIUM FROM WESTERN FERROPHOSPHORUS

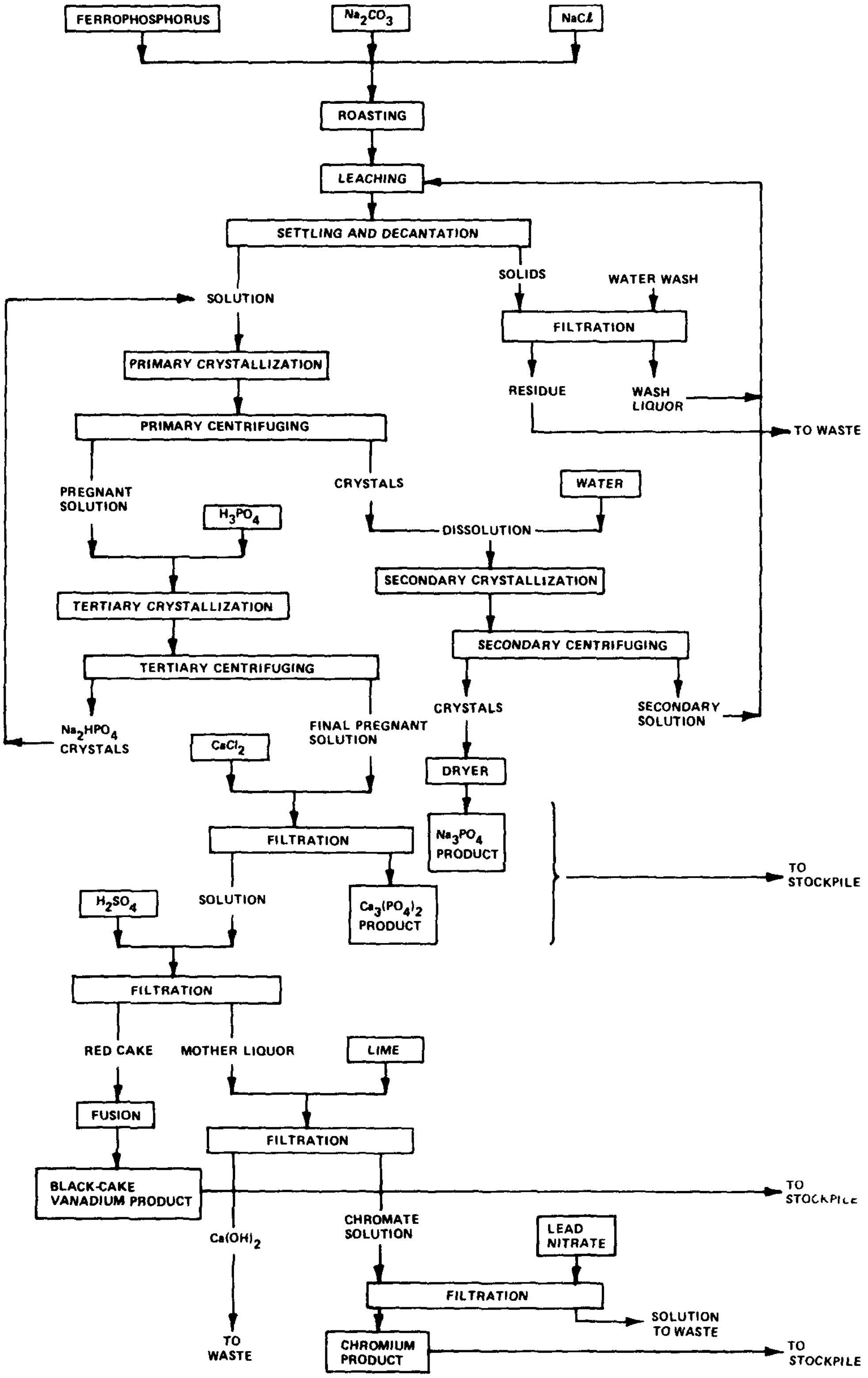


Figure III-21. ARKANSAS VANADIUM PROCESS FLOWSHEET

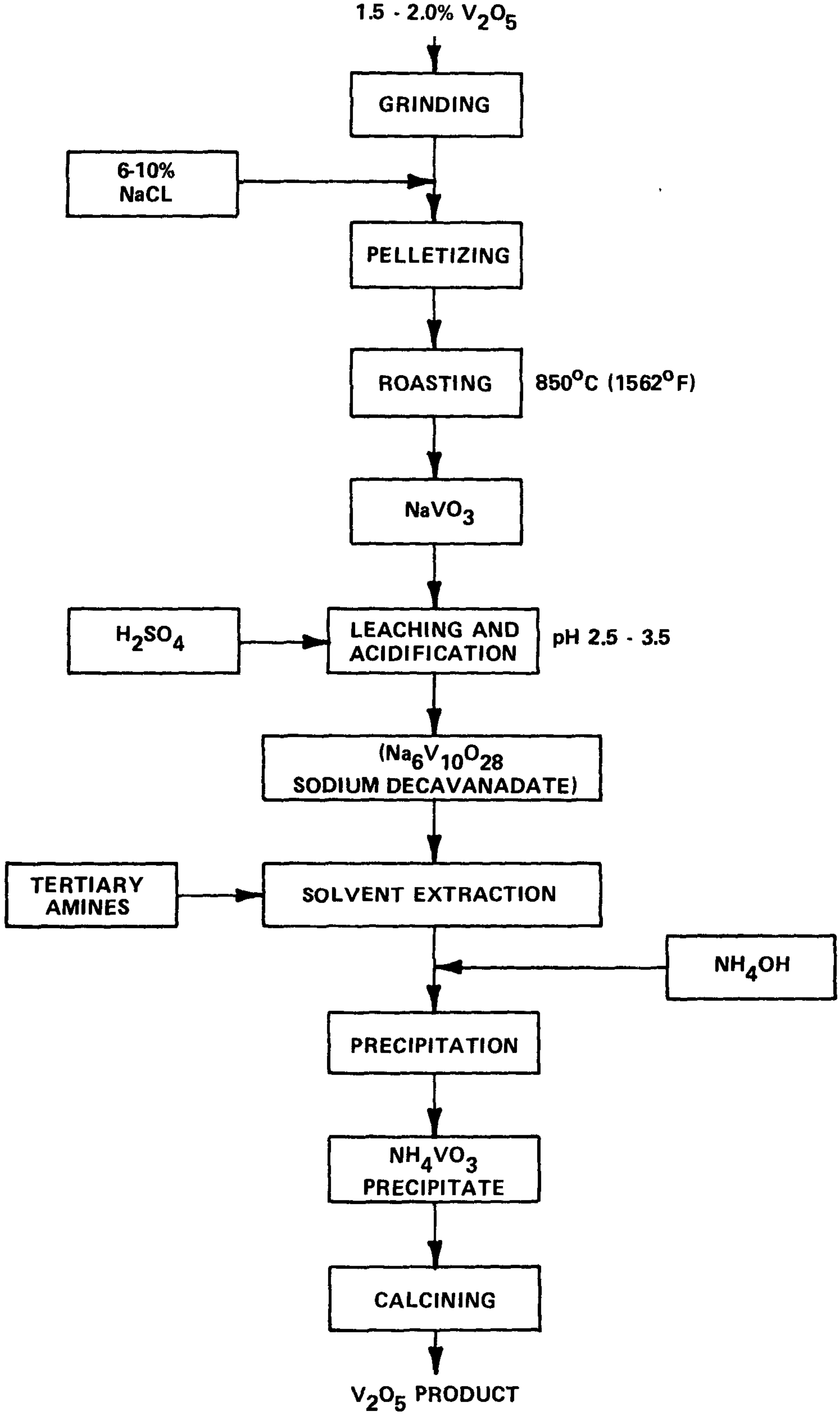


Figure III-22. FLOWSHEET OF DEAN-LEUTE AMMONIUM CARBAMATE PROCESS

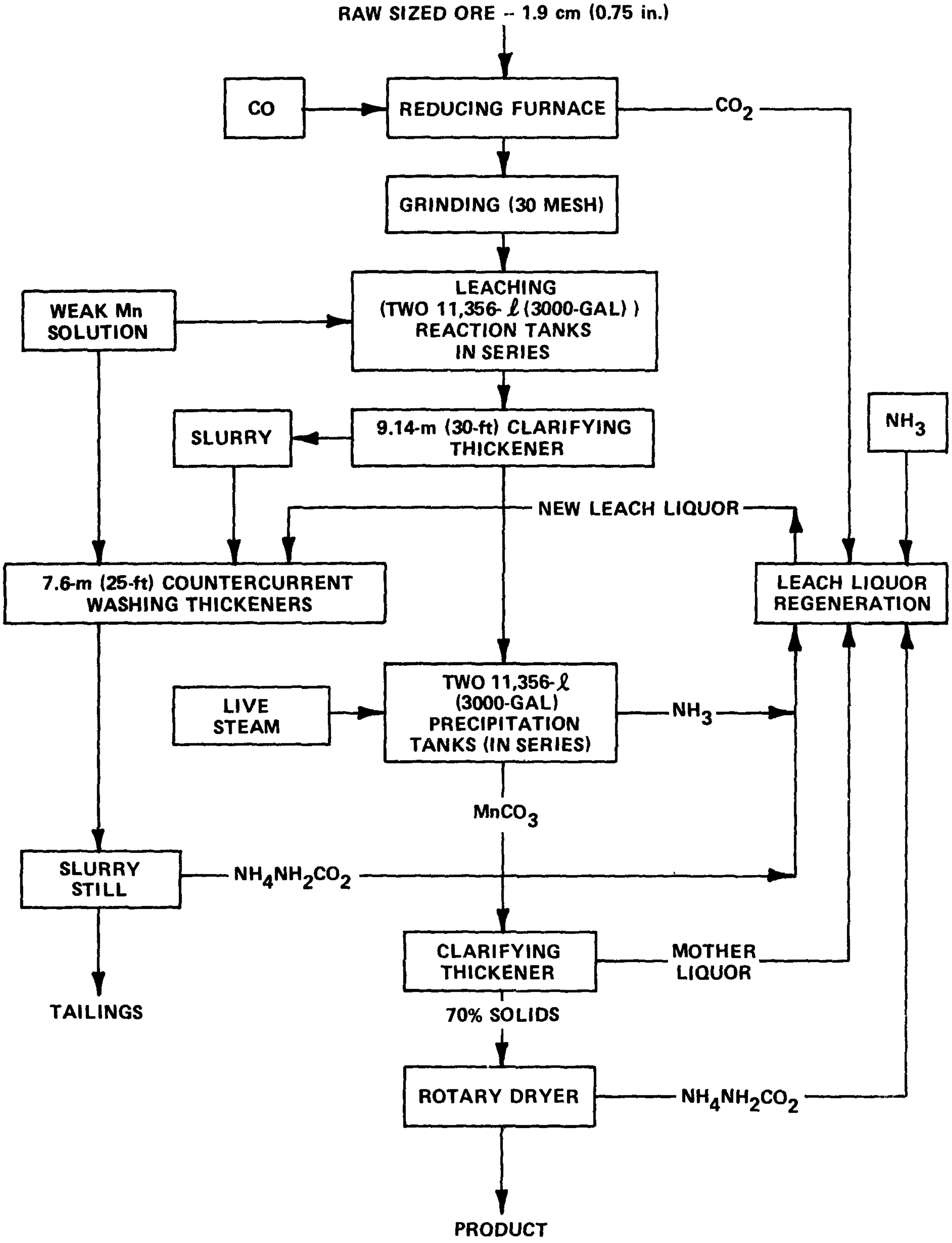


TABLE III-21. DOMESTIC MERCURY PRODUCTION STATISTICS

CATEGORY	YEAR				
	1969	1970	1971	1972	1973
No. of producing mines	109	79	56	21	6
Production in metric tons (flasks)	1,029 (29,640)	948 (27,296)	621 (17,883)	253 (7,286)	
Dollar value (thousands)	$14,969	$11,130	$ 5,229	$1,590	

SOURCE: REFERENCE 2

growth in the consumption of mercury is anticipated for electrical apparatus, instruments, and dental supplies. From consideration of these factors, it is anticipated that demand for mercury in 1985 will remain at the 1972 level. Given such variables as market prices and effects of emission standards promulgated in April 1973, it has been predicted that production of primary mercury will range from a high of 20,000 flasks (695 metric tons, or 765 short tons) to a low of 3,000 flasks (104 metric tons, or 115 short tons) by 1985.

Mercury ore is mined by both open-pit and underground methods. In recent years, underground methods have accounted for about two-thirds of the total mercury production. Ore grade has varied greatly, ranging from 2.25 to 100 kg of mercury per metric ton (5 to 200 pounds of mercury per short ton). The grade of ore currently mined averages 3.25 kg of mercury per metric ton (6.5 pounds of mercury per short ton).

The typical practice of the industry has been to feed the mined mercury ore directly into rotary kilns for recovery of mercury by roasting. This is such an efficient method that extensive beneficiation is precluded. However, with the depletion of high grade ores, concentration of low-grade mercury ores is becoming more important. The ore may be crushed -- and, sometimes, screened -- to provide a feed suitable for furnacing. Gravity concentration is also done in a few cases, but its use is limited since mercury minerals crush more easily and more finely than gangue rock.

Flotation is the most efficient method of beneficiating mercury ores when beneficiation is practiced. An advantage of flotation, especially for low-grade material, is the high ratio of concentration resulting. This permits proportionate reductions in the size and costs of the subsequent mercury extraction installation. Flotation of mercury ore has not been used to date in the United States. However, an operation scheduled to begin in Nevada later in 1975 will concentrate mercury ore by flotation. This concentrate will be furnaced, and annual production of mercury from the operation is expected to reach 20,000 flasks (695 metric tons, or 765 short tons).

Uranium, Radium, and Vanadium Ores

The mining and milling of uranium, vanadium, and radium constitute one industry segment, because uranium and vanadium are sometimes found in the same ore and because radium, resulting from the radioactive decay of uranium, has always been obtained from uranium ores. In the past 20 years, the demand for radium has diminished as radioactive isotopes (e.g., Co 60, Pu 239) with tailored characteristics as sources of radiation have become available. Radium is now treated as a pollutant in the wastes. Uranium is mined primarily for its use in generating energy and isotopes in nuclear reactors. In the U.S., vanadium is primarily generated as a byproduct of uranium mining for use as a ferroalloying metal and, in the form of its oxide, as a catalyst. Vanadium used as a ferroalloy metal has been discussed in the Ferroalloys Section.

The ores of uranium, vanadium, and radium are found both in the oxidized and reduced states. The uranium (IV) oxidation state is easily oxidized and the resulting uranium (VI), or uranyl, compounds are soluble in various bases and acids. In arid regions of the western United States, the ores are found in permeable formations (e.g., sandstones), while uranium deposits in humid regions are normally associated with more impervious rocks. Uranium is often found in association with carbonaceous fossils, i.e., lignite and asphalts. Ores with a grade in excess of a fraction of a percent uranium are rare (80% of the industry operates with ores below 0.2%).

Because it would be uneconomical to transport low-grade uranium ores very far, mines are closely associated with mills that yield a concentrate containing about 90 percent uranium oxide. This concentrate is shipped to plants that produce compounds of natural and isotopically enriched uranium for the nuclear industry. The processes of crushing and grinding, conventionally associated with a mill, are intimately connected with the hydrometallurgical processes that yield the concentrate, and both processes normally share a waste water disposal system. Mine water, when present, is often treated separately and is sometimes used as a source of mill process water. Mine water frequently contains a significant amount of uranium values, and the process of cleaning up mine water not only yields as much as one percent of the product of some mines but is also quite profitable.

The uranium oxide concentrate, whose grade is usually quoted in percent of U_3O_8 (although that oxide figures in the assay, rather than in the product), is generated by one of several hydrometallurgical processes. For purposes of waste water categorization, they may be distinguished as follows:

(1) The ore is leached either in sulfuric acid, or in a hot solution of sodium carbonate and sodium

bicarbonate, depending on the content of acid-wasting limestone in the gangue.

(2) Values in the leachate are usually concentrated by ion exchange (IX) or by solvent extraction (SX). They are then precipitated as the concentrate, yellowcake.

Some vanadium finds are not associated with significant uranium concentrations. Some byproduct concentrate solutions are sold to vanadium mills for purification, and not all uranium mills separate vanadium, which appears to be in adequate supply and could be recovered later from tailings.

<u>Ores</u> <u>and</u> <u>Mining</u>. Consideration of thermonuclear equilibria suggests an initial abundance of uranium in the solar system of 0.14 ppm (parts per million). Since uranium is radioactive, its concentration decreases with time, and its present abundance is estimated as 0.054 ppm. The four longest-lived isotopes are found in the relative abundances shown in Table III-22.

Primary deposits of uranium ore contain uraninite, the U(IV) compound UO_2, and are widely distributed in granites and pegmatites. Pure speciments of this compound, with density ranging to 11, are rare, but its fibrous form, pitchblende, has been exploited in Saxony since the recognition of uranium in 1789.

Secondary, tertiary, and higher-order deposits of uranium ores are formed by transport of slightly water-soluble uranyl (U(VI)) compounds, notably carbonates. Typically, a primary deposit is weathered by oxidized water, forming hydrated oxides of uranium with compositions intermediate between UO_2 and UO_3. The composition U_3O_8 -- i.e., $UO_2 . 2UO_3$ -- is particularly stable. The process occasionally stops at gummite ($UO_2 . H_2O$), an orange or red, waxy mineral, but usually involves further oxidation and reactions with alkaline and alkaline-earth oxides, silicates, and phosphates. The transport leads to the surface uranium ores of arid lands, including carnotite ($K_2(UO_2)_2(VO_4)_2 . 3H_2O$), uranophane ($CaU_2Si_2O_{11} . 7H_2O$), and autunite ($Ca(UO_2)_2(PO_4)_2 . 10\text{-}12H_2O$) and, if reducing conditions are encountered, to the redeposition of U(IV) compounds. Vanadium is seen to follow a similar route. Radium, with a halflife of only 1600 years, is generated from uranium deposits in historical times.

TABLE III-22. ISOTOPIC ABUNDANCE OF URANIUM

ISOTOPE	HALF-LIFE (YEARS)	ABUNDANCE
U 238	4.51×10^9	99.27%
U 235	7.13×10^8	0.72%
U 234	2.48×10^5	0.0057%
U 236	2.39×10^7	Traces Identified (Moon-1972; Earth-1974)

A reducing environment is often provided by decaying biological materials; uranium is found in association with lignite, asphalt, and dinosaur bones. One drift at a mine in New Mexico passes lengthwise through the ribcage of a fossil dinosaur. Since the requisite conditions are often encountered in the sediments of lakes or streams, stratiform uranium deposits are common, constituting 95% of U.S. reserves. Stratiform deposits comprise sandstone, conglomerate, and limestone with uranium values in pores or on the surface of sand grains or as a replacement for fossilized organic tissue. A small fraction of steeply sloping vein deposits, similar to those in Saxony, is found in association with other minerals. Some sedimentary deposits extend over many kilometers with a slight dip with respect to modern grade that makes it profitable to mine a given deposit by open-pit methods at one point and by underground mining at others.

Exploration is conducted initially with airborne and surface radiation sensors that delineate promising regions and is followed by exploratory drilling, on a 60-m (200-ft) grid, and development drilling, on a 15-m (50-ft) grid. Test holes are probed with scintillation counters, and cores are chemically analyzed. Reserves have usually been specified in terms of ore that can yield uranium at $18 per kg (2.2 lb), a price paid by the government for stockpiling. Recent increases in price and the possibility of increased uranium demand due to the current energy situation have resulted in the mining, for storage, of ore below this threshold and may effect an increase in reserves. Currently, reserves are concentrated in New Mexico and Wyoming, as shown in the tabulation below.

DISTRIBUTION OF U.S. URANIUM ORE RESERVES (JAN. 1, 1975)

	U3O8 (Short Tons)	No. of Known Deposits	% of total
New Mexico	137,108	66	69
Wyoming	28,300	14	14
Utah and Colorado	11,400	99	5
Texas	14,400	45	7
Others	8,800	60	5

The number of separate known deposits in the western United States is 284, but half of the reserves lie in 15 deposits. Four of these, in central Wyoming, on the border between Colorado and Utah, in northwestern New Mexico, and on the

Texas gulf coast, dominate the industry. In 1974, New Mexico provided 43 percent and Wyoming 32 percent of uranium production. In 1974, the U. S. production was 7.1 million tons of ore with a U_3O_8 equivalent of 12,600 tons.

In the eastern United States, uranium is found in conjunction with phosphate recovery in Florida, in states throughout the Appalachian Mountains, and in Vermont and New Hampshire granites. The grade of these deposits is currently too low for economic recovery of uranium, which is recovered as a byproduct only in Florida. Vanadium, in ores that do not contain uranium values, is mined in Arkansas and Idaho. The humid environment of current and prospective eastern deposits presents special problems of water management. Ocean water contains 0.002 ppm of uranium, and its recovery with a process akin to ion exchange using titanium compounds as a "resin" has been explored in the United Kingdom. Uranium can be recovered in this fashion at a cost of $150 to $300 per kg (2.2 lb).

Mining practice is conventional. There are 122 underground mines as of 1 January 1974, with a typical depth of 200 m (656 ft). Special precautions for the ventilation of underground mines reduce the exposure of miners to radon, a shortlived, gaseous decay product of radium that could leave deposits of its daughters in miners lungs, Mine water is occasionally recycled through the mine to recover values by leaching and ion exchange.

Because of the small size of pockets of high-grade ore, openpit mines are characterized by extensive development activity. At present, low-grade ore is stockpiled for future use. Stockpiles on polyethylene sheets are heap leached at several locations by percolation of dilute H_2SO_4 through the ore stockpiles. On January 1974, 33 open pit mines were being worked, and 20 other (e.g., heap-leaching) sources were in operation.

Most mines ship ore to the mill by truck. In at least one instance, a short (100-km, or 62-mi.) railroad run is involved. Most mining areas share at least two mill processes, one using acid leaching and the other, for high limestone content, using alkaline leaching.

Milling. Mills range in ore processing capacity from 450 metric tons (495 short tons) per day to 6500 metric tons (7,150 short tons) per day, and 15 to 25 mills have been in operation at any one time during the last 15 years. Mill activities, listed by state, are given in Table III-23 and are tabulated by company in Supplement B.

TABLE III-23. URANIUM MILLING ACTIVITY BY STATE, 1972

STATE	TOTAL MILL HANDLING CAPACITY		NO. OF MILLS
	METRIC TONS PER DAY	SHORT TONS PER DAY	
New Mexico	12,300	13,600	3
Wyoming	8,250	9,100	7
Colorado	4,000	4,400	3
Utah	1,850	2,000	2
Texas	3,400	3,750	3
South Dakota	600	660	1
Washington	450	500	1
TOTAL	30,850	34,010	20

Blending, Crushing, and Roasting. Ore from the mine tends to be quite variable in consistency and grade and may come from mines owned by different companies. Fairly complex procedures have been developed for weighing and radiometric assay of ores, to give credit for values to the proper source and to achieve uniform grade, and for blending to assure uniform consistency. Sometimes, coarse material is separated from fines before being fed to crushers that reduce it to the 5 to 20 mm (0.2 to 0.8 in.) range. This material is added to the fines.

Ore high in vanadium is sometimes roasted with sodium chloride at this stage to convert insoluble heavy-metal vanadates (vanadium complex) and carnotite to more soluble sodium vanadate, which is then extracted with water. Ores high in organics may be roasted to carbonize and oxidize these and prevent clogging of hydrometallurgical processes. Clayey ores attain improved filtering and settling characteristics by roasting at 300 degrees Celsius (572 degrees Fahrenheit).

Grinding. Ore is ground to less than 0.6 mm (28 mesh) (0.024 in.) for acid leaching and to less than .07 mm (200 mesh) for alkaline leaching in rod or ball mills with water (or, preferably, leach) added to obtain a pulp density of about two-thirds solids. Screw classifiers, thickeners, or cyclones are sometimes used to control size or pulp density.

Acid Leach. Ores with a calcium carbonate ($CaCO_3$) content of less than 12 percent are preferentially leached in sulfuric acid, which extracts values quickly (in four hours to a day), and at a lower capital and energy cost than alkaline leach for grinding, heating, and pressurizing. Any tetravalent uranium must be oxidized to the uranyl form by the addition of an oxidizing agent (typically, sodium chlorate or manganese dioxide), which is believed to facilitate the oxidation of U(IV) to U(VI) in conjunction with the reduction of Fe (III) to Fe (II) at a redox (reduction/oxidation) potential of about minus 450 mV. Free-acid concentration is held to between 1 and 100 grams per liter. The larger concentrations are suitable when vanadium is to be extracted. The reactions taking place in acid oxidation and leaching are:

$$2UO_2 + O_2 \longrightarrow 2UO_3$$

$$2UO_3 + 2H_2SO_4 + 5H_2O \longrightarrow 2\,(UO_2SO_4)\cdot 7H_2O$$

Uranyl sulfate (UO_2SO_4) forms a complex, hydrouranyl trisulfuric acid ($H_4UO_2(SO_4)_3$), in the leach, and the anions of this acid are extracted for value.

Alkaline Leach. A solution of sodium carbonate (40 to 50 g per liter) in an oxidizing environment selectively leaches uranium and vandium values from their ores. The values may be precipitated directly from the leach by raising the pH with the addition of sodium hydroxide. The supernatant can be recycled by exposure to carbon dioxide. A controlled amount of sodium bicarbonate (10 to 20 g per liter) is added to the leach to lower pH during leaching to a value that prevents spontaneous precipitation.

This leaching process is slower than acid leaching since other ore components are not attacked and shield the uranium values. Alkaline leach is, therefore, used at elevated temperatures of 80 to 100 degrees Celsius (176 to 212 degrees Fahrenheit) under the hydrostatic pressure at the bottom of a 15 to 20 m (49.2 to 65.6 ft) tall tank, agitated by a central airlift (Figure III-23). In some mills, the leach tanks are pressurized with oxygen to increase the rate of reaction, which takes on the order of one to three days. The alkaline leach process is characterized by the following reactions:

$$2UO_2 + O_2 \text{ ---> } 2UO_3$$

(oxidation)

$$3Na_2(CO_3) + UO_3 + H_2O \text{ ---> } 2NaOH + Na_4(UO_2)(CO_3)_3$$

(leaching)

$$2NaOH + CO_2 \text{ ---> } Na_2CO_3 + H_2O$$

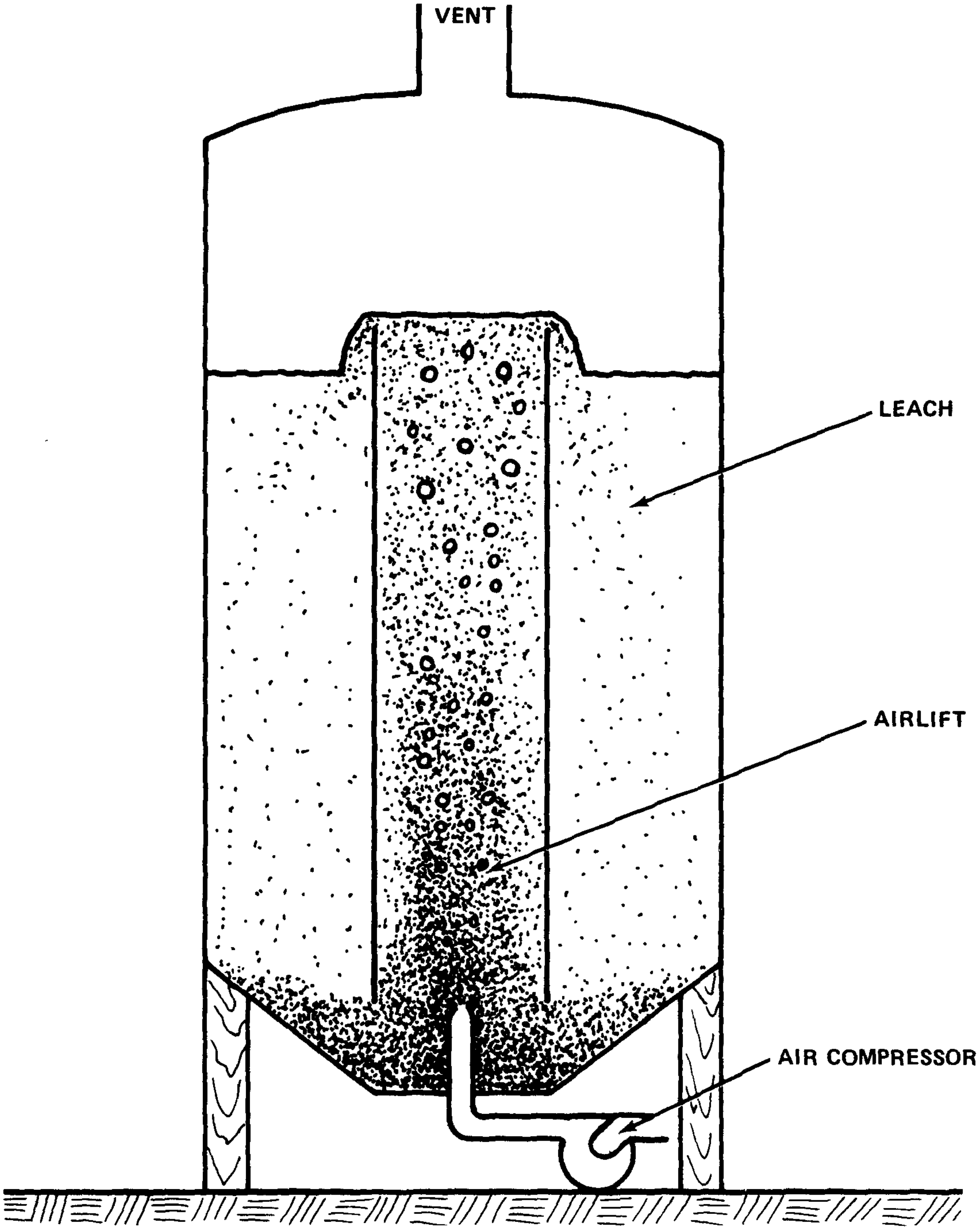
(recarbonization)

$$2Na_4(UO_2)(CO_3)_3 + 6NaOH \text{ ---> } Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$$

(precipitation)

The efficient utilization of water in the alkaline leach circuit has led to the trend of recommending its expanded application in the uranium industry. Alkaline leaching can be applied to a greater variety of ores than in current practice; however, the process, because of its slowness, appears to involve greater capital expenditures per unit production. In addition, the purification of yellow cake, generated in a loop using sodium as the alkali element, consumes an increment of chemicals that tend to appear in stored or discharged waste water but are often ignored. Purification to remove sodium ion is necessary both to meet the specifications of American uranium processors and for

Figure III-23. PACHUCA TANK FOR ALKALINE LEACHING



the preparation of natural uranium dioxide fuel. The latter process will be used to illustrate the problem caused by excess sodium. Sodium diuranate may be considered as a mixture of sodium and uranyl oxides--i.e., $Na_2U_2O_7 = Na_2O + 2UO_3$.

The process of generating UO_2 fuel pellets from yellow-cake feed involves reduction by gaseous ammonia at a temperature of a few hundred degrees C. At this temperature, ammonia thermally decomposes into hydrogen, which reduces the UO_3 component to UO_2 and nitrogen (which acts as an inert gas and reduces the risk of explosion in and around the reducing furnace). With sodium diuranate as a feed, the process results in a mix of UO_2 and Na_2O that is difficult to purify (by water leaching of NaOH) without impairing the ceramic qualities of uranium dioxide. When, in contrast, ammonium diuranate is used as feed, all byproducts are gaseous, and pure UO_2 remains. The structural integrity of this ceramic is immediately adequate for extended use in the popular CANDU (Canadian deuterium-uranium) reactors. Sodium ion, as well as vanadium values, can be removed from raw yellow cake (sodium diuranate) produced by alkaline leaching in two steps. In the first step, the yellow cake is roasted, and some of the sodium ion forms water-soluble sodium vanadate, while organics are carbonized and burned off. The roasted product is water leached, yielding a V_2O_5 concentrate as described below. The remaining sodium diuranate is redissolved in sulfuric acid,

$$Na_2U_2O_7 + 3H_2SO_4 \longrightarrow Na_2SO_4 + 3H_2O + 2(UO_2)SO_4$$

and the uranium values are precipitated with ammonia and filtered, to yield a yellow cake (ammonium diuranate or UO_3) that is low in or free of sodium.

$$UO_2SO_4 + H_2O + 2NH_3 \longrightarrow (NH_4)_2SO_4 + UO_3$$

The reactions leading to this product are interesting for their byproduct--namely, sodium sulfate. The latter, being classed approximately in the same pollutant category as sodium chloride, requires expensive treatment for its removal. Ammonium-ion discharges which might result from an ammonium carbonate leaching circuit that would yield the desired product immediately are viewed with more concern, even though there is a demand for ammonium sulfate to fertilize alkaline southwestern soils. Ammonium sulfate could be generated by neutralizing the wastes of the ammonium loop with sulfuric acid wastes from acid leaching wastes. Opponents of a tested ammonium process argue that nitrites, an intermediate oxidation product of accidentally discharged ammonium ion, present a present health hazard more severe than that from sulfate ion.

Vanadium Recovery. Vanadium, found in carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) as well as in heavy metal vanadates--e.g., vanadinite ($9PbO \cdot 3V_2O_5 \cdot PbCl\_$)--is converted to sodium orthovanadate (Na_3VO_4), which is water-soluble by roasting with sodium chloride or soda ash (Na_2CO_3). After water leaching, ammonium chloride is added, and poorly soluble ammonium vanadates are precipitated:

$$Na_3VO_4 + 3NH_4Cl + H_2O \longrightarrow 3NaOH + NH_4VO_3 + 2NH_4OH$$

(ammonium metavanadate)

$$Na_3VO_4 + 3NH_4Cl \longrightarrow 3NaCl + (NH_4)_3VO_4$$

(ammonium orthovanadate)

The ammonium vanadates are thermally decomposed to yield vanadium pentoxide:

$$2(NH_4)_3VO_4 \longrightarrow 6NH_3 + 3H_2O + V_2O_5$$

A significant fraction (86 to 87%) of V_2O_5 is used in the ferroalloys industry. There, ferrovanadium has been prepared in electric furnaces by the reaction:

$$V_2O_5 + Fe_2O_3 + 8C \longrightarrow 8CO + 2FeV$$

or by aluminothermic reduction (See Glossary) in the presence of scrap iron.

Air pollution problems associated with the salt roasting process have led many operators to a hydrometallurgical process of vanadium recovery that is quite similar to uranium recovery by acid leaching and solvent exchange. The remainder of V_2O_5 production is used in the inorganic chemical industry, and its processing is not within the scope of these guidelines. Since the mining and beneficiation of vanadium ores not containing uranium values present an excellent example of hydrometallurgical processes in the mining and ore dressing of ferroalloy metals (under SIC 1061), it will be explored further under that heading. Because of the chemical similarity of vanadium to columbium, tantalum, and other ferroalloy metals, recovery processes for vanadium are likely to be quite similar to hydrometallurgical processes that will be used in the ferroalloys mining industry when it becomes more active again.

Concentration and Precipitation. To a rough approximation, a metric ton of ore with a grade of about 0.2% is treated with a metric ton (or cubic meter) of leach, and the concentration(s) of uranium and/or vanadium in the pregnant solution are also of the order of 0.2%. If values were directly precipitated from this solution, a significant fraction would remain in solution. Yellow cake is, therefore, recycled and dissolved in pregnant solution to increase precipitation yield. Typically, five times as much yellow cake is recycled as is present in the pregnant solution. Direct precipitation by raising pH is effective only with alkaline leach, which is somewhat selective for uranium and vanadium. If it were applied to the acid leach process, most heavy metals --particularly, iron -- would be precipitated and would severly contaminate the product.

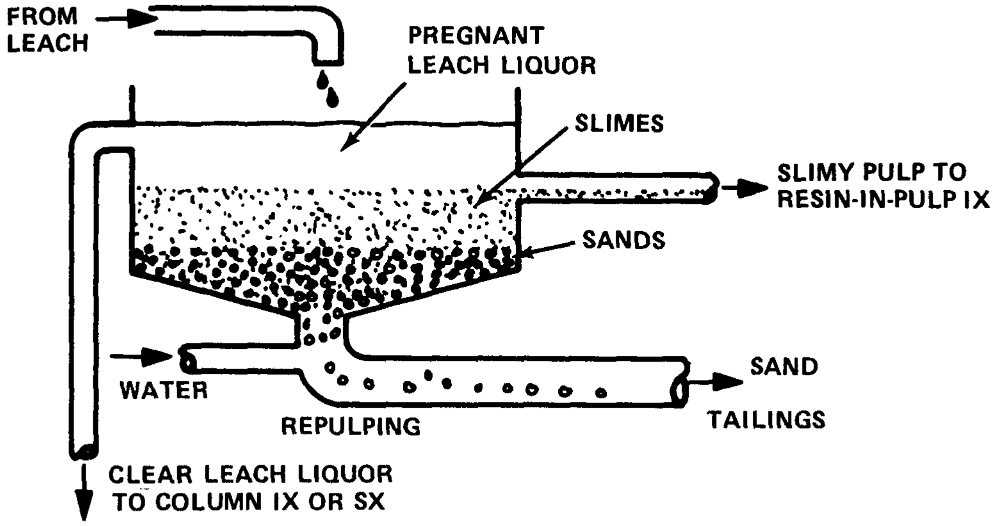
Uranium (or vanadium and molybdenum) in the pregnant leach liquor can be concentrated by a factor of more than five through ion exchange or solvent extraction. Typical concentrations in the eluate of some of these processes are shown in Table III-24.

Precipitation of uranium from the eluates is practical without recycling yellow cake, and the selectivity of these processes under regulated conditions (particulary, pH) improves the purity of the product.

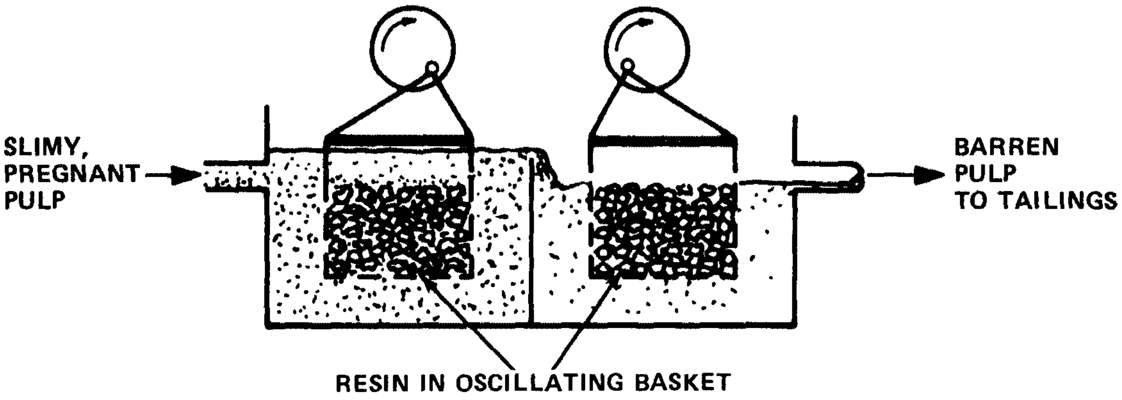
All concentration processes operate best in the absence of suspended solids, and considerable effort is made to reduce the solids content of pregnant leach liquors (Figure III-24a). A somewhat arbitrary distinction is made between quickly settling sands that are not tolerated in any concentration process and slimes that can be accommodated to some extent in the resin-in-pulp process (Figure III-24b, c). Sands are often repulped, by the addition of some waste water stream or another, to facilitate flow to the tailing pond as much as a few kilometers away. Consequently, there is some latitude for the selection of the waste water sent to the tailing pond, and mill operators can take advantage of this fact in selecting environmentally sound waste-disposal procedures.

Ion exchange and solvent extraction (Figure III-24b-e) are based on the same principle: Polar organic molecules tend to exchange a mobile ion in their structure -- typically, Cl^-, NO_3^-, HSO_4^-, CO_3^{--} (anions), or H^+ or Na^+ (cations) -- for an ion with a greater charge or a smaller ionic radius. For example, let R be the remainder of the polar molecule (in the case of a solvent) or polymer (for a resin), and let

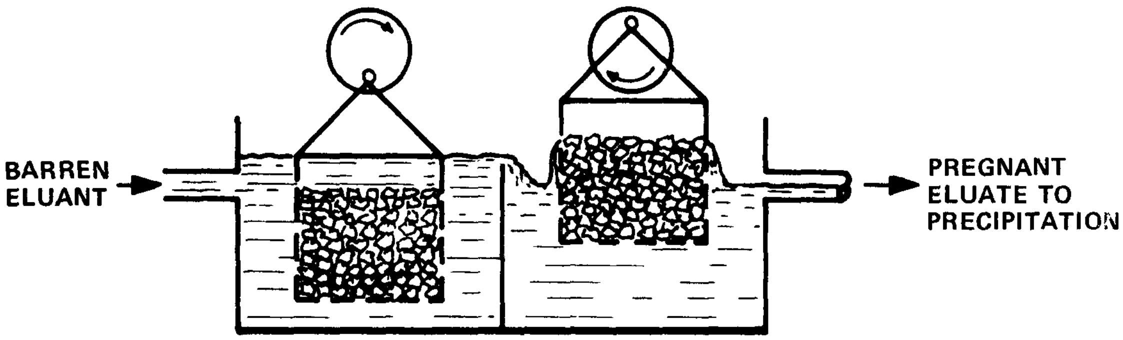
Figure III-24. CONCENTRATION PROCESSES AND TERMINOLOGY (Sheet 1 of 2)



a) LIQUID/SOLID SEPARATION

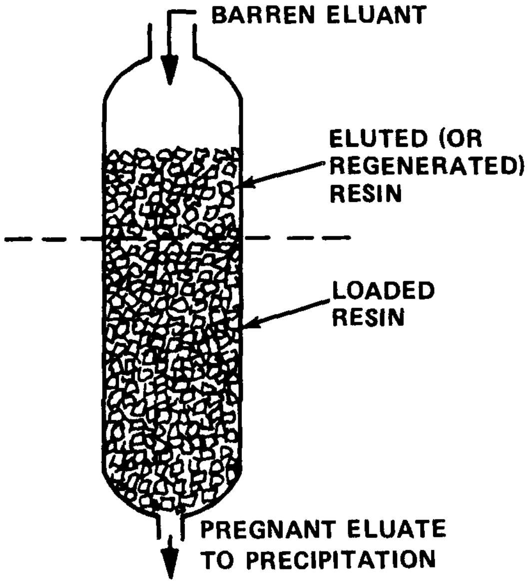


b) RESIN-IN-PULP PROCESS: LOADING

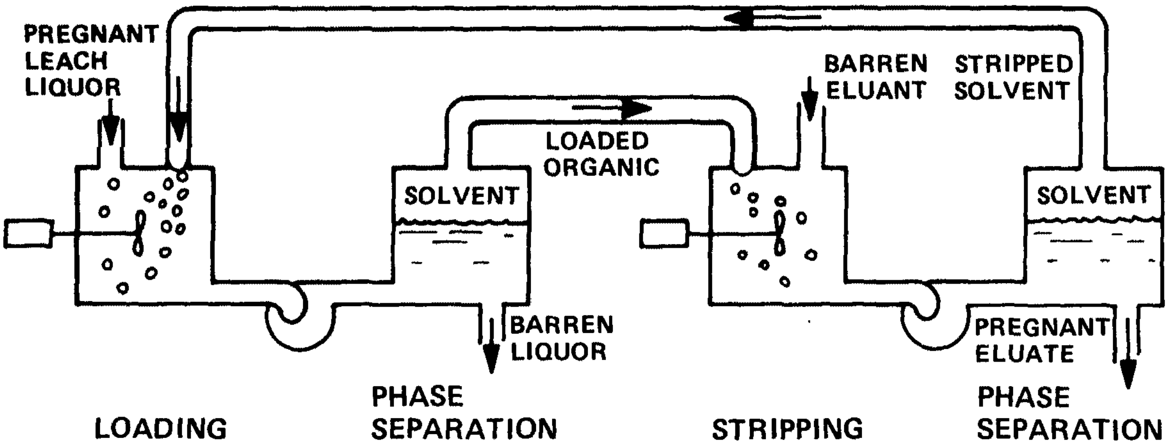


c) RESIN-IN-PULP PROCESS: ELUTING

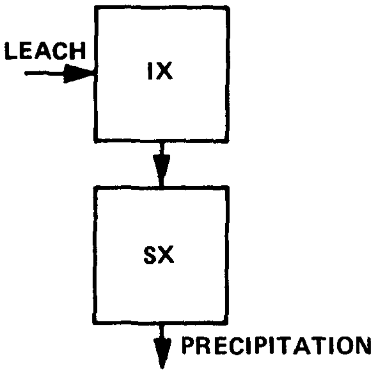
Figure III-24. CONCENTRATION PROCESSES AND TERMINOLOGY (Sheet 2 of 2)



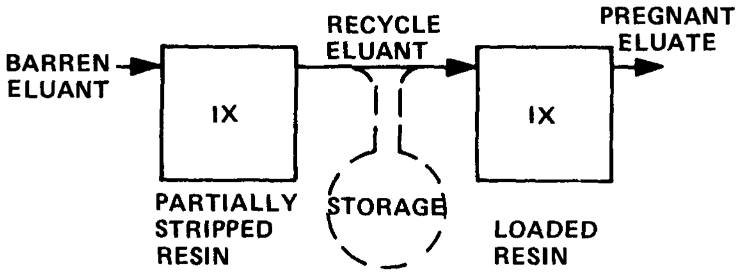
d) FIXED-BED COLUMN ION EXCHANGE/ELUTION



e) SOLVENT EXTRACTION



f) ELUEX PROCESS



g) SPLIT ELUTION

TABLE III-24. URANIUM CONCENTRATION IN IX/SX ELUATES

PROCESS	U_3O_8 CONCENTRATION (%)
Ion exchange	
Resin-in-pulp	0.8 to 1.2
Fixed-bed IX:	
Chloride elution	0.5 to 1.0
Nitrate elution	1.0 to 2.0
Moving-bed IX:	
Nitrate elution	1.9
Solvent extraction	
Alkyl phosphates, HCl eluent	30.0 to 60.0
Amex process	3 to 4
Dapex process	5.0 to 6.5
Split elution minewater treatment	1.2 to 1.6
IX/SX combination	
Eluex process	3.0 to 7.5

brittle, radioactive, and magnetic, permitting concentration by magnetic means. There are some deposits of consolidated monazite sands in Wyoming.

Hydrometallurgical processes are used to separate a thorium and rare-earth concentrate from magnetically and gravity concentrated sands (Figures III-25 and III-26). Either acid or alkaline leach processes may be used, but cationic rather than anionic species predominate in the leach, in contrast with otherwise analogous uranium processes. Thorium precipitates from sulfuric acid solution at a pH below one (Figure III-27), in contrast to rare earths and uranium; this fact, as well as its reduced solubility in dilute monazite sulfate solution, is utilized for thorium concentration. The latter process, when used alone, requires as much as 300 liters (318 qt) of water per kilogram (2.2 lb) of monazite sulfate and is not very economical. When used in conjunction with neutralizing agents as a fine control on pH, it is very effective.

Recycle of leachant should be possible with an alkaline leach process that has been evaluated in pilot-plant scale. The process consumes caustic soda in the formation of trisodium phosphate, which can be separated to some extent by cooling the hot (110 to 137 degrees Celsius) (230 to 279 degrees Fahrenheit) leach to about 60 degrees Celsius (140 degrees Fahrenheit) and filtering. Uranium is precipitated with the phosphate if NaOH concentration is too low during the crystallization step, and NaOH concentration should be raised to more than 10N before cooling. The cyclic cooling and heating of leach to separate phosphate values represents an energy expenditure that must be weighed against the environmental benefits of the process.

The alkaline leach process is unusual in that the leaching action removes the gangue in the solute, as sodium silicate, and leaves the values as rare-earth oxides, thorium, and uranium diuranate in the residue. They are preserved as a slurry or filter cake, which is then dissolved in sulfuric/nitric acid and subjected to fractional precipitation, as in the acid leach process.

The methods for recovering thorium and uranium from monazite sands are almost identical to those used in the acid and alkaline leach processes for recovering uranium from its primary ores. Thorium production in the U.S. is currently not sufficient to characterize exemplary operations. Guidelines developed for the uranium mining and ore dressing industry and other subcategories related to thorium ore may generally apply.

advantage of both the slime resistance of resin-in-pulp ion exchange and the separatory efficiency of solvent exchange (Eluex process). The uranium values are precipitated with a base or a combination of base and hydrogen peroxide. Ammonia is preferred by a plurality of mills because it results in a superior product, as mentioned in the discussion of alkaline leaching. Sodium hydroxide, magnesium hydroxide, or partial neutralization with calcium hydroxide, followed by magnesium hydroxide precipitation, are also used. The product is rinsed with water that is recycled into the process to preserve values, filtered, dried and packed into 200-liter (55-gal) drums. The strength of these drums limits their capacity to 450 kg (1000 lb) of yellow cake, which occupies 28% of the drum volume.

Thorium. Thorium is often combined with the rare earths, with which it is found associated in monazite sands. It is actually an actinide (rather than lanthanide) and chemically, as well as by nuclear structure, is closely allied to uranium. Although it finds some use in the chemical and electronics industry, thorium is primarily of value as a fertile material for the breeding of fissionable reactor fuel. In this process, thorium 232, used in a "blanket" around the core of a nuclear reactor, captures neutrons to form thorium 233, which decays to uranium 233 by the emission of two beta particles with halflives of 22 minutes and 27 days. Uranium 233 is fissile and can be used as a fuel. The cycle is very attractive since it may be operated in thermal-neutron, as well as fast-neutron, reactors. A pseudo-breeding reactor (burning uranium 235 or plutonium 239 in the core and producing uranium 233 in the blanket), with net breeding gain (quantity of fissile material bred/quantity burned) less than one is already in commercial operation.

Thorium is about three times as abundant as uranium in rocks, but rich deposits are rare. Typical monazite sand ores contain from 1 to 10 percent thoria (ThO_2). American ores from the North and South Carolinas, Florida, and Idaho contain 1.2 to 7 percent ThO_2, with a typical value of 3.4 percent. Monazite, a phosphate of cerium and lanthanum with some thorium and some uranium and other rare earths, is found in granites and other igneous rocks, where its concentration is not economically extractable. Erosion of such rocks concentrates the monazite sands, which constitute about 0.1 percent of the host rock, in beach and stream deposits. Mining often is combined with the recovery of ilmenite, rutile, gold, zircon, cassiterite, or other materials that concentrate in a similar way. Monazite is

X be the mobile ion. Then, the exchange reaction for the uranyltrisulfate complex is

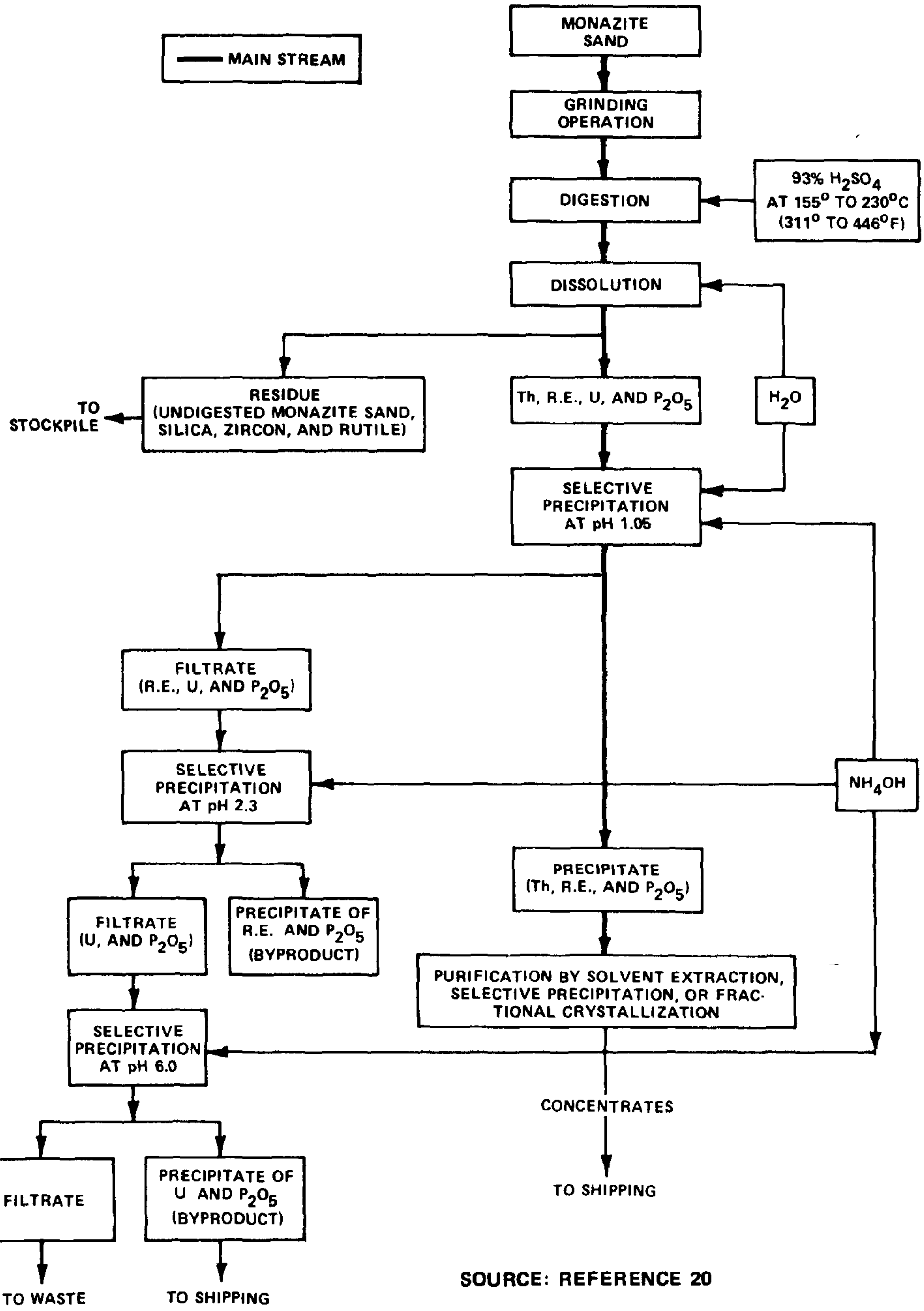
$$4RX + (UO_2(SO_4)_3) \underset{<---}{--->} R_4UO_2(SO_4)_3 + 4X-$$

This reaction proceeds from left to right in the loading process. Typical resins adsorb about ten percent of their mass in uranium and increase by about ten percent in density. In a concentrated solution of the mobile ion -- for example, in N-hydrochloric acid -- the reaction can be reversed and the uranium values are eluted -- in this example, as hydrouranyl trisulfuric acid. In general, the affinity of cation exchange resins for a metallic cation increases with increasing valence (Cr+++ Mg++ Na+) and, because of decreasing ionic radius, with atomic number (92U 42 Mo 23V). The separation of hexavalent 92U cations by IX or SX should prove to be easier than that of any other naturally occurring element.

Uranium, vanadium, and molybdenum -- the latter being a common ore constituent -- almost always appear in aqueous solutions as oxidized ions (uranyl, vanadyl, or molybdate radicals), with uranium and vanadium additionally complexed with anionic radicals to form trisulfates or tricarbonates in the leach. The complexes react anionically, and the affinity of exchange resins and solvents is not simply related to fundamental properties of the heavy metal (uranium, vanadium, or molybdenum), as is the case in cationic exchange reactions. Secondary properties, including pH and redox potential, of the pregnant solutions influence the adsorption of heavy metals. For example, seven times more vanadium than uranium is adsorbed on one resin at pH 9; at pH 11, the ratio is reversed, with 33 times as much uranium as vanadium being captured. These variations in affinity, multiple columns, and control of leaching time with respect to breakthrough (the time when the interface between loaded and regenerated resin, Figure III-24d, arrives at the end of the column) are used to make an IX process specific for the desired product.

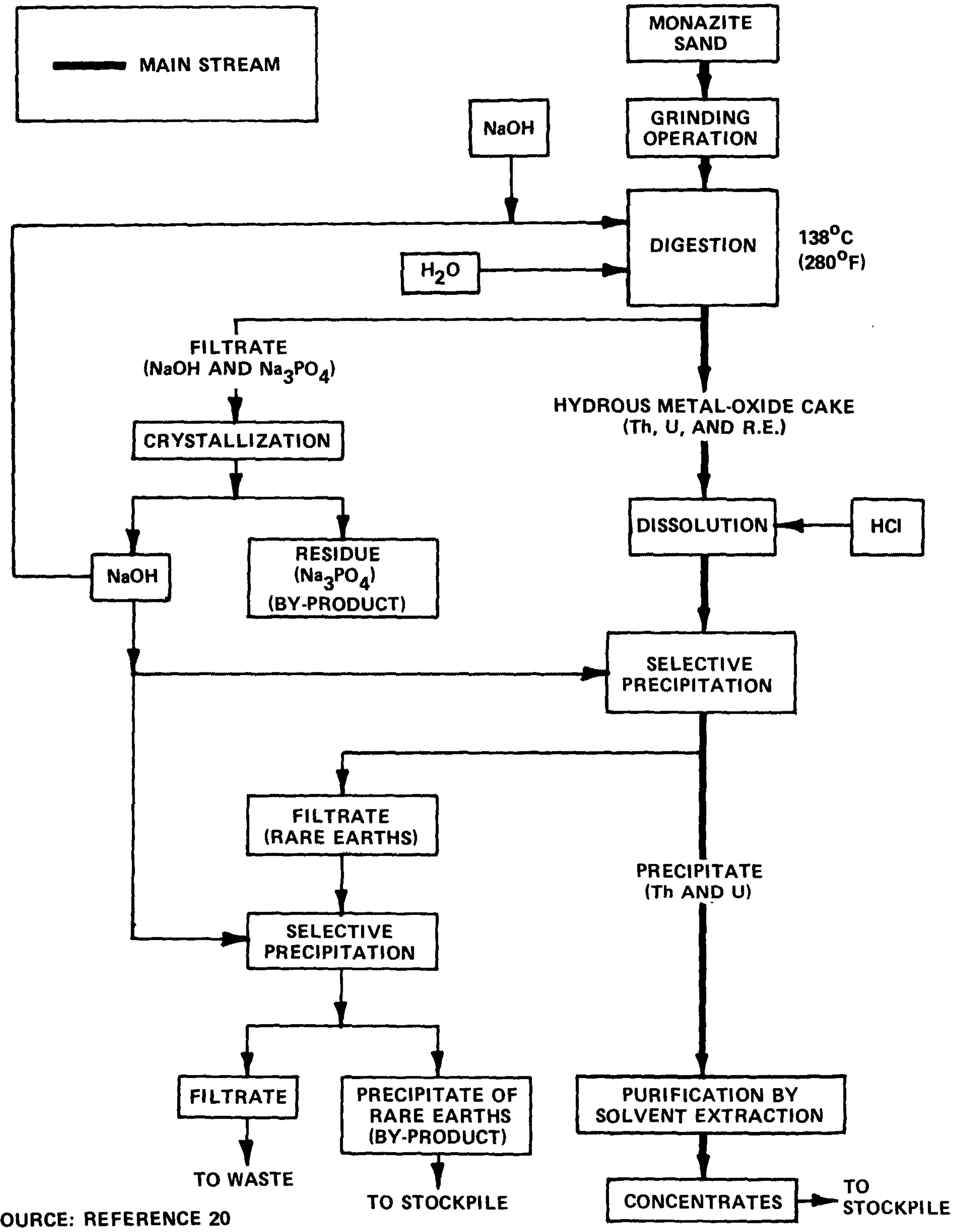
In the case of solvent exchange, the type of polar solvent and its concentration in a typically nonpolar diluent (e.g., kerosene) effect separation of the desired product. The ease with which the solvent is handled (Figure III-24e) permits the construction of multistage co-current and countercurrent SX concentrators that are useful even when each stage effects only partial separation of a value from an interferent. Unfortunately, the solvents are easily polluted by slimes, and complete liquid/solid separation is necessary. IX and SX circuits can be combined to take

Figure III-25. SIMPLIFIED SCHEMATIC DIAGRAM OF SULFURIC ACID DIGESTION OF MONAZITE SAND FOR RECOVERY OF THORIUM, URANIUM, AND RARE EARTHS



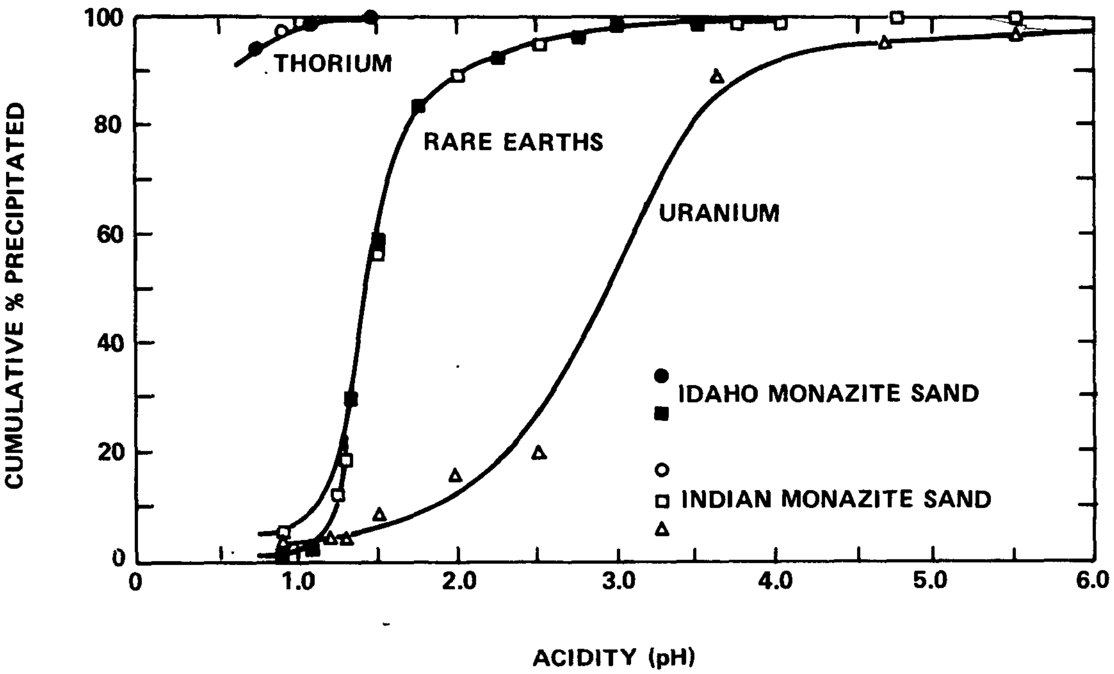
SOURCE: REFERENCE 20

Figure III-26. SIMPLIFIED SCHEMATIC DIAGRAM OF CAUSTIC SODA DIGESTION OF MONAZITE SAND FOR RECOVERY OF THORIUM, URANIUM, AND RARE EARTHS



SOURCE: REFERENCE 20

Figure III-27. EFFECT OF ACIDITY ON PRECIPITATION OF THORIUM, RARE EARTHS AND URANIUM FROM A MONAZITE/SULFURIC ACID SOLUTION OF IDAHO AND INDIAN MONAZITE SANDS



AGITATION TIME: 5 MINUTES
DILUTION RATIO: H_2O: SAND = 45:1 TO 50:1
DIGESTION RATIO: 93% H_2SO_4: SAND = 1.77
NEUTRALIZING AGENT: 3.1% NH_4OH

SOURCE: REFERENCE 20

Radiation parameters of thorium and uranium daughters are somewhat different. The two decay series are compared in Table III-25. The uranium series is dominated by radium, which--with a halflife of 1620 years and chemical characteristics that are distinctly different from those of the actinides and lanthanides--can be separately concentrated in minerals and mining processes. It then forms a noteworthy pollutant entity that is discussed further in Section V. Thorium, by contrast, decays via a series of daughters with short halflives; the longest being Ra228 at 6.7 years.

Industry Flow Charts. Of the sixteen mills operating in 1967 (Table III-26), no two used identical leaching concentration, and precipitation steps. The same was probably true of the 15 mills operating in 1974 (Table III-23, also Supplement B). A general flow chart, to be used in conjunction with Table III-26, is presented in Figure III-28. Detailed flow charts of exemplary mills are presented in Section VII.

Production Data. Recent uranium production data (U.S. Atomic Energy Commission, 1974) show that uranium production has been relatively stable (between 12,600-14,000 ton U_3O_8 per year) since 1968.

Table III-27 shows uranium production for the period 1968 through 1972, expressed in terms of both ore movement and U_3O_8 production and reserves. The reserves are estimated to be recoverable at the traditional AEC stockpiling price of \$18/kg (\$8/lb); with inflation, this price figure should be revised upward. Reserves were seen to be increasing even before this adjustment. They are presumably expanding even faster when measured in terms of the energy to be extracted from uranium. Additional uranium (and its derivative, plutonium) will become available if and when environmental problems of fuel recycling are resolved--particuarly, when breeder reactors become practical. The latter step alone should increase the economic (\$18/kg) reserves, estimated to last for about 20 years, to about 500 years.

Vanadium production, Table III-28, is treated somewhat differently, since vandium is often an unwanted byproduct of uranium mining and is only concentrated (recovered) when needed. Value of the product fluctuates with demand, unlike uranium, as indicated in the table. World production is also shown, to indicate that U.S. production presents a fair fraction of the world supply. The applications of vanadium are illustrated in Table III-29.

TABLE III-25. DECAY SERIES OF THORIUM AND URANIUM

ELEMENT OR NAME	SYMBOL(S)	HALF-LIFE	ENERGY OF RADIATION (MeV)		
			α	β	γ
		Thorium Series			
Thorium	$_{90}\mathrm{Th}^{232}$	1.34×10^{10} years	4.20	–	–
Mesothorium 1	$_{88}\mathrm{Ra}^{228}$ (MsTh_1)	6.7 years	–	0.053	–
Mesothorium 2	$_{89}\mathrm{Ac}^{228}$ (MsTh_2)	6.13 hours	4.5	1.55	–
Radiothorium	$_{90}\mathrm{Th}^{228}$ (RdTh)	1.90 years	5.42	–	γ
Thorium X	$_{88}\mathrm{Ra}^{224}$ (ThX)	3.64 days	5.68	–	–
Thoron	$_{86}\mathrm{Rn}^{220}$ (Tn)	54.5 seconds	6.28	–	–
Thorium A	$_{84}\mathrm{Po}^{216}$ (ThA)	0.158 seconds	6.77	β	–
Thorium B	$_{82}\mathrm{Pb}^{212}$ (ThB)	10.6 hours	–	0.36	–
Thorium C	$_{83}\mathrm{Bi}^{212}$ (ThC)	60.5 min	6.05	2.20	γ
Thorium C′	$_{84}\mathrm{Po}^{212}$ (ThC′)	3×10^{-7} second	8.77	–	–
Thorium C″	$_{81}\mathrm{Tl}^{208}$ (ThC″)	3.1 minutes	–	1.82	2.62
Thorium D	$_{82}\mathrm{Pb}^{208}$ (ThD)	Stable	–	–	–
		Uranium Series			
Uranium	$_{92}\mathrm{U}^{238}$ (UI)	4.55×10^{9} years	4.21	–	–
Thorium	$_{90}\mathrm{Th}^{234}$ (UX_1)	24.1 days	–	0.13	0.09
Protactinium	$_{91}\mathrm{Pa}^{234}$ (UX_2)	1.14 minutes	–	2.32	0.80
Uranium	$_{92}\mathrm{U}^{234}$ (UII)	2.69×10^{5} years	4.75	–	–
Thorium	$_{90}\mathrm{Th}^{230}$ (Io)	8.22×10^{4} years	4.66	–	γ
Radium	$_{88}\mathrm{Ra}^{226}$	1600 years	4.79	–	0.19
Radon	$_{86}\mathrm{Rn}^{222}$	3.825 days	5.49	–	–
Polonium	$_{84}\mathrm{Po}^{218}$ (RaA)	3.05 minutes	5.99	β	–
Lead	$_{82}\mathrm{Pb}^{214}$ (RaB)	26.8 minutes	–	0.65	γ
Bismuth	$_{83}\mathrm{Bi}^{214}$ (RaC)	19.7 minutes	5.50	3.15	1.8
Polonium	$_{84}\mathrm{Po}^{214}$ (RaC′)	1.5×10^{-4} second	7.68	–	–
Thallium	$_{81}\mathrm{Tl}^{210}$ (RaC″)	1.32 minutes	–	1.80	–
Lead	$_{82}\mathrm{Pb}^{210}$ (RaD)	22.2 years	–	0.025	0.047
Bismuth	$_{83}\mathrm{Bi}^{210}$ (RaE)	4.97 days	–	1.17	–
Polonium	$_{84}\mathrm{Po}^{210}$ (RaF)	139 days	5.30	–	γ
Lead	$_{82}\mathrm{Pb}^{206}$ (RaC)	Stable	–	–	–

TABLE III-26. URANIUM MILLING PROCESSES

(a) 1967 Uranium Mills by Process

MILL	LEACH	CONCENTRATION	PRECIPITATION	VANADIUM
American Metal Climax	Acid	SX	H_2O_2	Salt roast
Anaconda	Acid	RIP, IX	Lime/MgO	–
Atlas (Acid)	Acid	SX	Ammonia	SX
Atlas (Alkaline)	Alkaline	RIP, IX	Ammonia	–
Cotter	Alkaline	–	NaOH	–
Federal/American	Acid	RIP, IX & SX	Ammonia	–
Foote Mineral	Acid	SX	MgO	SX
United Nuclear/Homestake	Alkaline	–	NaOH	–
Kerr-McGee	Acid	SX	Ammonia	–
Mines Development	Acid	RIP, IX & SX	Ammonia	$Na_2 CO_3$ roast
Petrotomics	Acid	SX	MgO	–
Susquehanna Western	Acid	SX	NaOH	–
UCC Uravan	Acid	IX	Ammonia	IX
UCC Gas Hills	Acid	RIP, IX	Ammonia	–
Utah Construction & Mining	Acid	IX & SX	Ammonia	–
Western Nuclear	Acid	RIP, IX & SX	Ammonia	–

(b) Process by Number of Operations (1967)

ORE TREATMENT	
Salt Roasting	1
Flotation	2
Pre-leach Density Control	3
LEACHING	
Acid	3
Alkaline	3
2-Stage	4
LIQUID-SOLID SEPARATION	
Countercurrent Decantation	9
Staged Filtration	3
Sand/Slime Separation	7
RESIN ION EXCHANGE (IX)	
Basket Resin In Pulp (Acid)	2
Basket RIP (Alkaline)	1
Continuous RIP	3
Fix Bed IX	1
Moving Bed IX	1
SOLVENT EXTRACTION (SX)	
Amine	7
Alkyl Phosphoric	3
Eluex	4
PRECIPITATION	
Lime/MgO	1
MgO	3
Caustic Soda (NaOH)	3
Ammonia (NH_4OH)	8
Peroxide (H_2O_2)	1
VANADIUM RECOVERY	5

SOURCE: REFERENCE 21

Figure III-28. GENERALIZED FLOW DIAGRAM FOR PRODUCTION OF URANIUM, VANADIUM, AND RADIUM

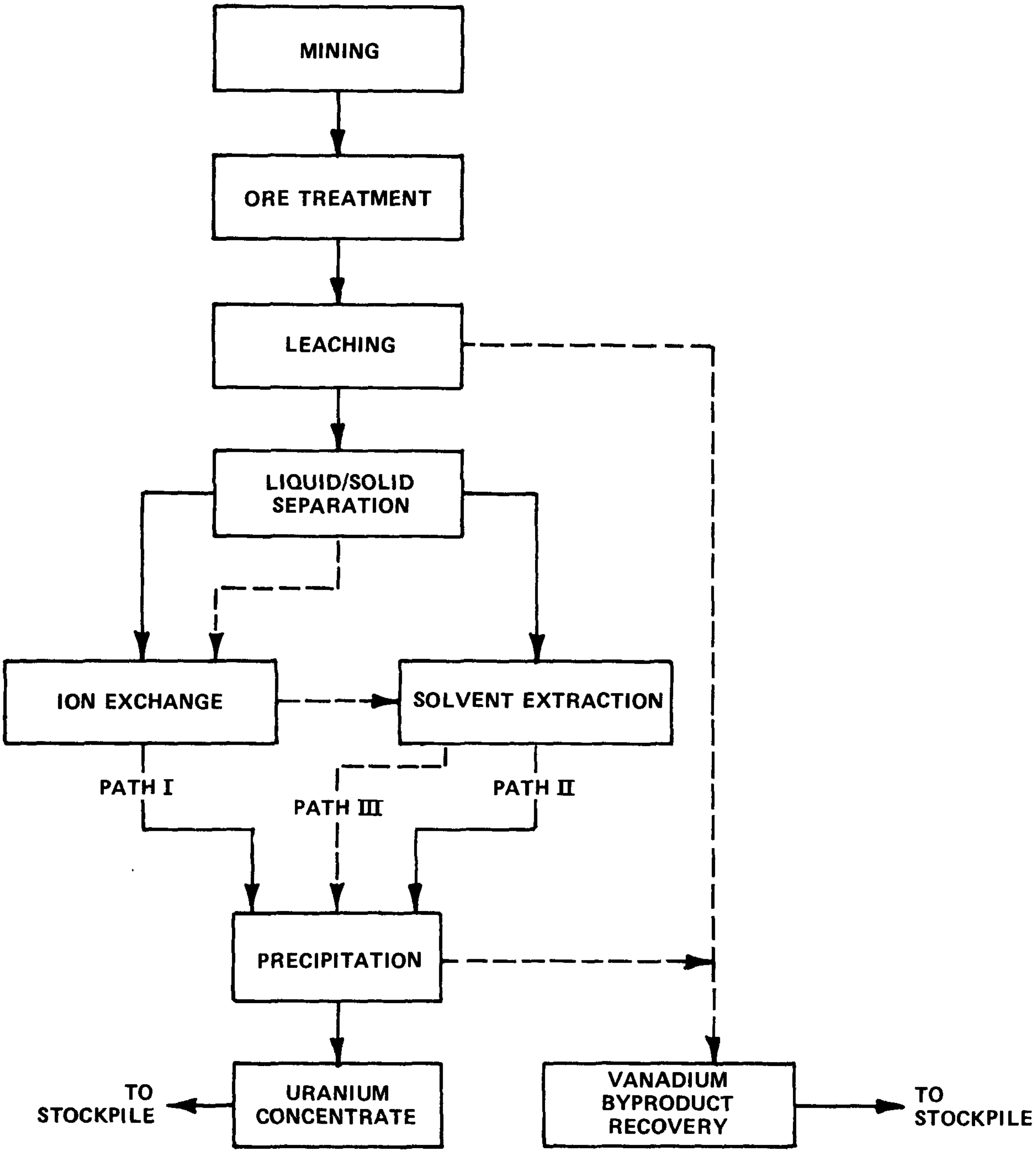


TABLE III-27. URANIUM PRODUCTION

YEAR	ORE MOVEMENT		U_3O_8 PRODUCTION		U_3O_8 RESERVES*	
	1000 METRIC TONS	1000 SHORT TONS	1000 METRIC TONS	1000 SHORT TONS	1000 METRIC TONS	1000 SHORT TONS
1968	5,861	6,461	11.244	12.394	146	161
1969	5,367	5,916	10.554	11.634	185	204
1970	5,749	6,337	11.732	12.932	224	247
1971	5,708	6,292	11.157	12.298	248	273
1972	5,834	6,431	11.727	12.927	248	273
1973	6,152	6,781	12.032	13.263	251	277

*At $18,000 per metric ton ($16,340 per short ton).

TABLE III-28. VANADIUM PRODUCTION

YEAR	U.S. V_2O_5 PRODUCTION			WORLD V_2O_5 PRODUCTION		V_2O_5 VALUE	
	1000 METRIC TONS	1000 SHORT TONS	% OF WORLD	1000 METRIC TONS	1000 SHORT TONS	PER METRIC TON	PER SHORT TON
1968	5,590	6,192	46	12,119	13,359	$3,910	$3,547
1969	5,369	5,918	31	16,892	18,620	$5,190	$4,708
1970	5,085	5,605	27	18,337	20,213	$7,216	$6,546
1971	4,812	5,304	28	16,883	18,610	$7,887	$7,155
1972	4,771	5,259	26	18,135	19,990	$6,941	$6,297

TABLE III-29. VANADIUM USE

CATEGORY	1971			1972		
	METRIC TONS	SHORT TONS	%	METRIC TONS	SHORT TONS	%
Ferrovanadium	3,792	4,180	87	4,084	4,502	86
Vanadium Oxide	130	143	3	172	190	4
Ammonium Metavanadate	32	35	1	43	47	1
Vanadium Metal/alloys	412	454	9	453	499	9

Radium is traded from foreign sources, but not mined, in quantities of about 40 grams (or curies) (1.4 ounce), at a price of about $20,000/gram ($567,000/ounce) each year. The high price is set by the historically determined cost of refining and not by current demand. Reserves of radium in uranium tailings are plentiful at this price. It has been estimated that concentration of radium to prevent its discharge to uranium tailings would approximately double the cost of uranium concentrate (reference 28).

Thorium production in the U.S. during 1968 was 100 metric tons (110 short tons) as was demand, mostly for the chemical and electronic uses. The U.S. imported 210 metric tons (231 short tons) to increase privately held stocks from 560 to 770 metric tons (616 to 847 short tons). The General Services Administration also held a stockpile of 1465 metric tons (1612 short tons) which was intended to contain only 32 metric tons (35 short tons)--i.e., was in surplus by 1433 metric tons (1577 short tons).

Metal Ores, Not Elsewhere Classified

This category includes ores of metals which vary widely in their mode of occurrence, extraction methods, and nature of associated effluents. The discussion of metals ores under this category which follows treats antimony, beryllium, platinum, tin, titanium, rare-earth, and zirconium ores. Thorium ores (monazite) have been previously discussed under the Uranium, Radium, Vanadium category because of the similarity of their extractive methods and radioactivity.

Antimony Ores

The antimony ore mining and milling industry is defined for this document as that segment of industry involved in the mining and/or milling of ore for the primary or byproduct/ coproduct recovery of antimony. In the United States, this industry is concentrated in two states: Idaho and Montana. A small amount of antimony also comes from a mine in Nevada. Table III-30 summarizes the sources and amounts of antimony production for 1968 through 1972. The decrease in domestic production during 1972 indicated in Table III-30 was largely due to a fire which forced the major byproduct producer of antimony to close in May of that year.

Antimony is recovered from antimony ore and as a byproduct from silver and lead concentrates.

Only slightly more than 13 percent of the antimony produced in 1972 was recovered from ore being mined primarily for its

TABLE III-30. PRODUCTION OF ANTIMONY FROM DOMESTIC SOURCES

	ANTIMONY CONCENTRATE		ANTIMONY*		ANTIMONIAL LEAD† (ANTIMONY CONTENT)	
YEAR	METRIC TONS	SHORT TONS	METRIC TONS	SHORT TONS	METRIC TONS	SHORT TONS
1968	4,774	5,263	776	856	1,179	1,300
1969	5,176	5,707	851	938	1,065	1,174
1970	6.060	6.681	1,025	1,130	542	598
1971	4,282	4,721	930	1,025	751	828
1972	1,879	2,072	444	489	468	516

*Includes production from antimony ores and concentrates and byproduct recovery from silver concentrates.

†Byproduct produced at lead refineries in the United States.

antimony content. Nearly all of this production can be attributed to a single operation which is using a froth flotation process to concentrate stibnite (Sb_2S_3) (Figure III-29).

The bulk of domestic production of antimony is recovered as a byproduct of silver mining operations in the Coeur d'Alene district of Idaho. Antimony is present in the silver-containing mineral tetrahedrite and is recovered from tetrahedrite concentrates in an electrolytic antimony extraction plant owned and operated by one of the silver mining companies in the Coeur d'Alene district. Mills are usually penalized for the antimony content in their concentrates. Therefore, the removal of antimony from the tetrahedrite concentrates not only increases their value, but the antimony itself then becomes a marketable item. In 1972, the price for antimony was $1.25 per kilogram ($0.57 per pound).

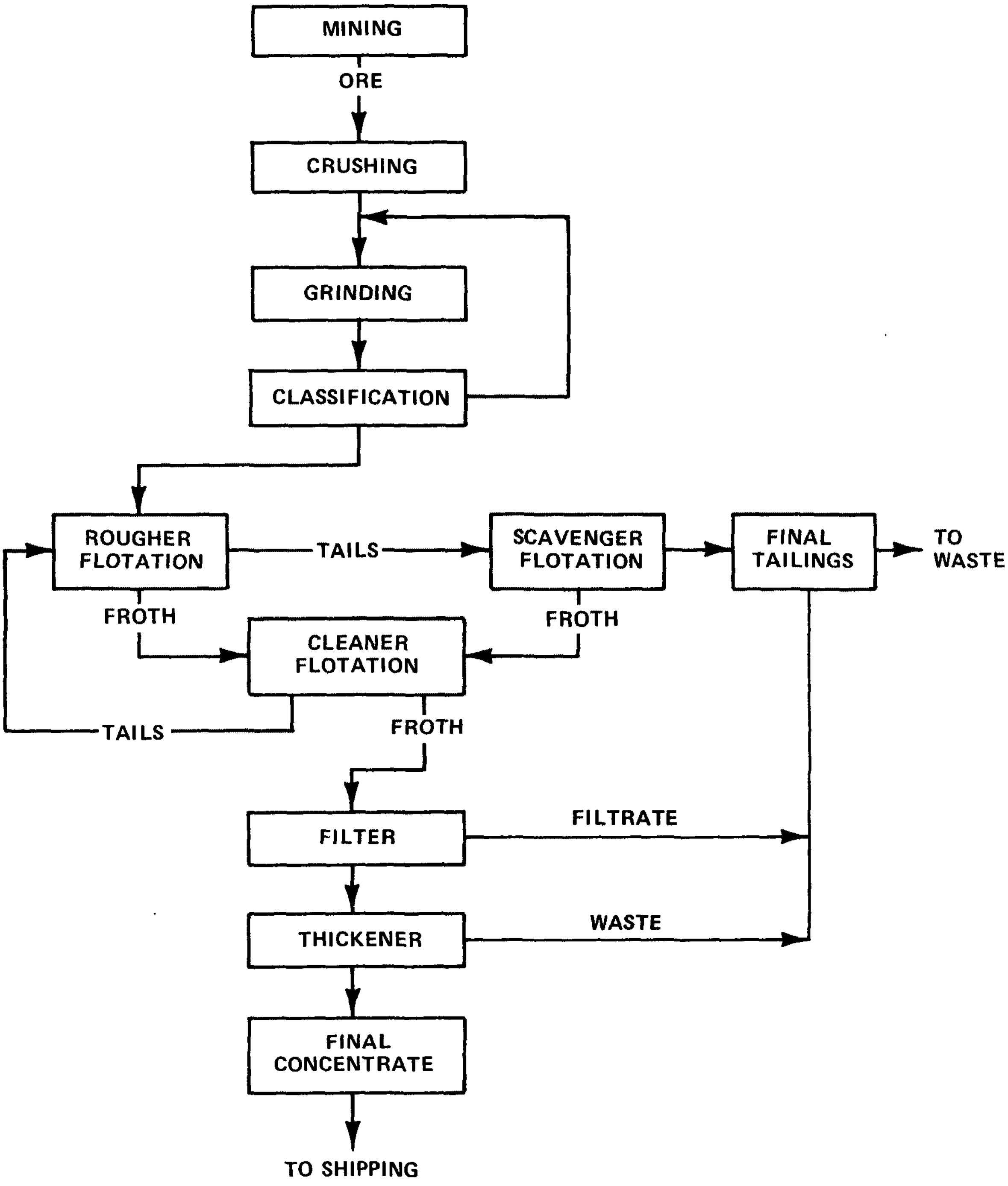
Antimony is also contained in lead concentrates and is ultimately recovered as a byproduct at lead smelters usually as antimonial lead. This source of antimony represents about 30 to 50 percent of domestic production in recent years.

Beryllium Ores

The beryllium ore mining and milling industry is defined for this document as that segment of industry involved in the mining and/or milling of ore for the primary or byproduct/coproduct recovery of beryllium. Domestic beryllium production data are withheld to avoid disclosing individual company confidential data. During 1972, some beryl ($Be_3Al_2(Si_6O_{18})$) was produced in Colorado and South Dakota. The largest domestic source of beryllium ore is a bertrandite ($Be_4Si_2O_7(OH)_2$) mine in the Spor Mountain district of Utah. Domestic beryl prices were negotiated between producers and buyers and were not quoted in the trade press.

Mining and milling techniques for beryl are unsophisticated. Some pegmatite deposits are mined on a small scale--usually, by crude opencut methods. Mining is begun on an outcrop, where the minerals of value can readily be seen, and cuts are made or pits are sunk by drilling and blasting the rock. The blasted rock is hand-cobbed, by which procedure as much barren rock as practicable is broken off with hand hammers to recover the beryl. Beryl and the minerals it is commonly associated with have densities so nearly the same that it is difficult to separate beryl by mechanical means. Consequently, beryl is recovered by hand cobbing.

Figure III-29. BENEFICIATION OF ANTIMONY SULFIDE ORE BY FLOTATION



A sulfuric acid leach process is employed to recover beryllium from the Spor Mountain bertrandrite. This is a proprietary process, however, and further details are withheld. No effluent results from this operation.

Platinum-Group Metal Ores

The platinum-group metal ore mining and milling industry is defined for this document as those operations which are involved in the mining and/or milling of ore for the primary or byproduct/coproduct recovery of platinum, palladium, iridium, osmium, rhodium, and ruthenium. These metals are characterized by their superior resistance to corrosion and oxidation. The industrial applications for platinum and palladium are diverse, and the metals are used in the production of high-octane fuels, catalysts, vitamins and drugs, and electrical components. Domestic production of platinum-group metals is principally as a byproduct of copper smelting, with production also from platinum placers. Table III-31 lists annual U.S. mine production and value for the period 1968 through 1972.

The geologic occurrence of the platinum-group metals as lodes or placers dictates that copper, nickel, gold, silver, and chromium will be either byproducts or coproducts in the recovery of platinum metals, and that platinum will be largely a byproduct. With the exception of occurrences in the Stillwater Complex, Montana, and production as a byproduct of copper smelting, virtually all the known platinum-group minerals in the United States come from placers. Platinum placers consist of unconsolidated alluvial deposts in present or ancient stream valleys, terraces, beaches, deltas, and glaciofluvial outwash. The other domestic source of platinum is as a byproduct of refining copper from porphyry and other copper deposits and from lode and placer gold deposits, although the grade is extremely low.

Platinum-group metals occur in many placers within the United States. Minor amounts have been recovered from gold placers in California, Oregon, Washington, Montana, Idaho, and Alaska, but significant amounts have been produced only from the placers of the Goodnews Bay District, Alaska. Production over the past several years from this district has remained fairly constant, although domestic mine production declined 5 percent in quantity and 7 percent in value in 1972 (Reference 2).

TABLE III-31. DOMESTIC PLATINUM-GROUP MINE PRODUCTION AND VALUE

YEAR	MINE PRODUCTION		VALUE
	KILOGRAMS	TROY OUNCES	
1968	460.1	14,793	$1,500,603
1969	671.4	21,586	$2,094,607
1970	538.6	17,316	$1,429,521
1971	560.8	18,029	$1,359,675
1972	532.2	17,112	$1,267,298

SOURCE: REFERENCE 2

Beneficiation of Ores.

The mining and processing techniques for recovering crude platinum from placers in the U.S. are similar to those used for recovering gold. The bulk of the crude placer platinum is recovered by large-scale bucket-line dredging, but small-scale hand methods are also used in Columbia, Ethiopia, and (probably) the U.S.S.R. A flow diagram for a typical dredging operation is presented as Figure III-30.

In the Republic of South Africa, milling and beneficiation of platinum-bearing nickel ores consist essentially of gravity concentration, flotation, and smelting to produce a high-grade table concentrate called "metallic" for direct chemical refining and a nickel-copper matte for subsequent smelting and refining.

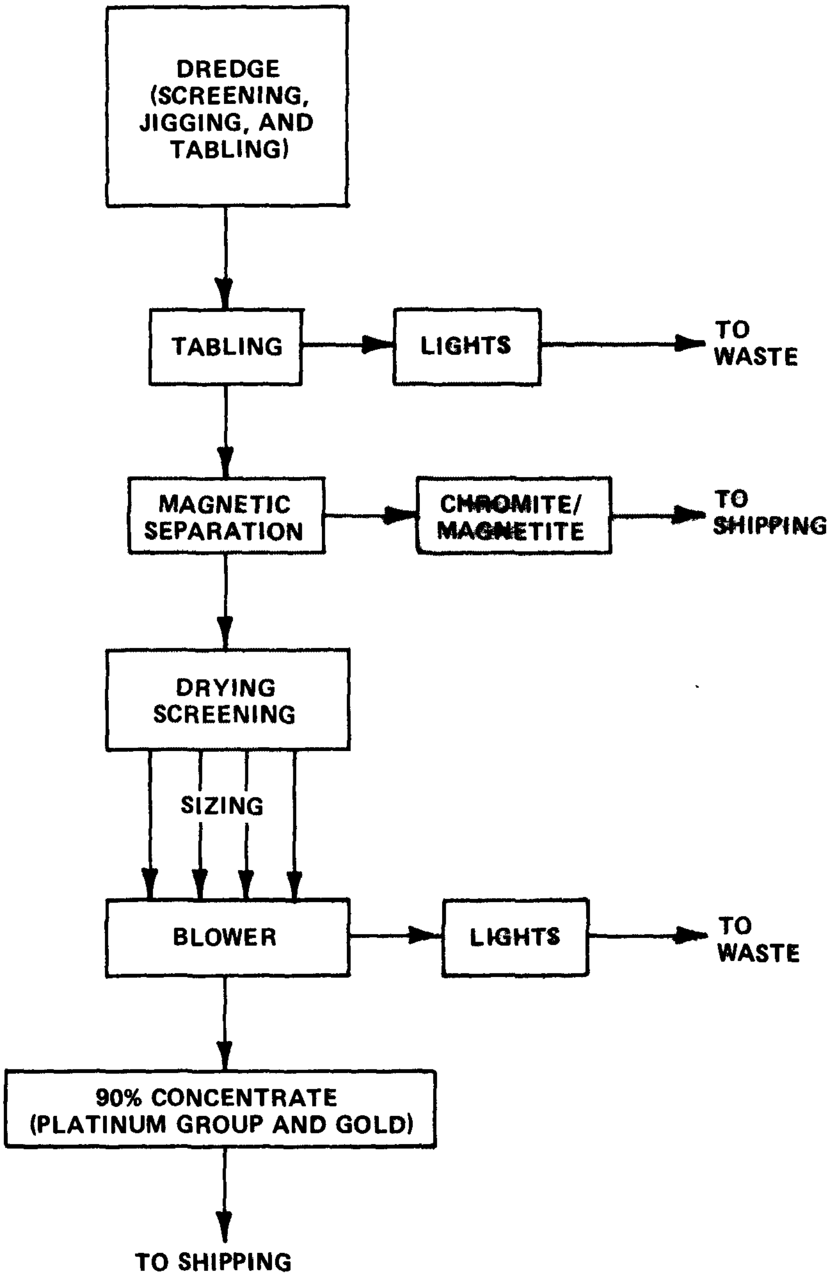
Byproduct platinum-group metals from gold or copper ores are sometimes refined by electrolysis and chemical means. In the Sudbury District of Canada, sulfide ore is processed by magnetic flotation techniques to yield concentrates of copper and nickel sulfides. The nickel flotation concentrate is roasted with a flux and melted into a matte, which is cast into anodes for electrolytic refining, from which the precious metal concentrate is recovered.

In the U.S., the major part of output of platinum is recovered as a byproduct of copper refining in Maryland, New Jersey, Texas, Utah, and Washington. Byproduct platinum-group metals from gold or copper ores are sometimes refined by electrolysis and by chemical means. Metal recovery in refining is over 99 percent.

Rare-Earth Ores

The rare-earth minerals mining and milling industry is defined for this document as that segment of industry engaged in the mining and/or milling of rare-earth minerals for their primary or byproduct/coproduct recovery. The rare-earth elements, sometimes known as the lanthanides, consist of the series of 15 chemically similar elements with atomic numbers 57 through 71. Yttrium, with atomic number 39, is often included in the group, because its properties are similar, and it more often than not occurs in association with the lanthanides. The principal mineral sources of rare-earth metals are bastnaesite ($CeFCO_3$) and monazite $(Ce, La, Th, Y)PO_4$. The bulk of the domestic production of rare-earth metals is from a bastnaesite deposit in Southern California which is also the world's largest known single commercial source of rare-earth

Figure III-30. GRAVITY CONCENTRATION OF PLATINUM-GROUP METALS



elements. In 1972, approximately 10,703 metric tons (11,800 short tons) of rare-earth oxides were obtained in flotation concentrate from 207,239 metric tons (approximately 228,488 short tons) of bastnaesite ore mined and milled (Reference 2). Monazite is domestically recovered as a byproduct of titanium mining and milling operations in Georgia and Florida. A company which recently began a heavy-mineral (principally, titanium) sand operation in Florida is expected to produce over 118 metric tons (130 short tons) of byproduct monazite annually.

At the Southern California operation, bastnaestite is mined by open-pit methods. The ore, containing 7 to 10 percent rare-earth oxides (REO) is upgraded by flotation techniques to a mineral concentrate containing 63 percent REO. Calcite is removed by leaching with 10 percent hydrochloric acid and countercurrent decantation. The bastnaesite is not dissolved by this treatment, and the concentrate is further upgraded to 72 percent REO. Finally, the leached product is usually roasted to remove the carbon dioxide from the carbonate, resulting in a product with over 90 percent REO.

Monzazite is recovered from heavy-mineral sands mined primarily for their titanium content. Beneficiation of monazite is by the wet-gravity, electrostatic, and magnetic techniques discussed in the titanium portion of this document. Monazite, an important source of thorium, is also discussed under SIC 1094 (Uranium, Radium, and Vanadium). Extraction of the thorium is largely by chemical techniques.

Tin Ores

The tin mining and milling industry is defined for this document as that segment of industry engaged in the mining and/or milling of ore for the byproduct/coproduct recovery of tin.

There are presently no known exploitable tin deposits of economic grade or size in the United States. Most of the domestic tin production in 1972, less than 102 metric tons (112 short tons), came from Colorado as a byproduct of molybdenum mining. In addition, some tin concentrate was produced at dredging operations and as a byproduct of placer gold mining operations in Alaska. A small placer operation began production in New Meixco in June 1973. Feasability studies continue for mining and milling facilities for a 4,065-metric-ton-per-day (4,472-short-ton-per-day) open-pit fluorite tin/tungsten/beryllium mine in Alaska's Seward Peninsula which is to open by 1976. Reserves at the prospect area represent at least a 20-year supply. As technological improvements in beneficiation are made and demands for tin increase, large deposits considered only submarginal resources, in which tin in only one of several valuable commodities, are expected to be brought into production.

In general, crude cassiterite concentrate from placer mining is upgraded by washing, tabling,and magnetic or electrostatic separation. Tin ore from lode deposits is concentrated by gravity methods involving screening, classification, jigging, and tabling. The concentrate is usually a lower grade than placer concentrate, owing to associated sulfide minerals. The sulfide minerals are removed by flotation or magnetic separation, with or without magnetic roasting. The majority of tin production in the United States is the result of beneficiation as a byproduct. Cassiterite concentrate recovery takes place after flotation of molybdenum ore by magnetic separation of the dewatered and dried tailings. Despite considerable research, successful flotation of tin ore has never been completely achieved.

Titanium Ores

The titanium ore mining and milling industry is defined for this document as that segment of industry engaged in the mining and/or milling of titanium ore for its primary or byproduct/ coproduct recovery. The principal mineral sources of titanium are ilmenite ($FeTiO_2$) and rutile (TiO_2). The United States is a major source of ilmenite but not of rutile. Since 1972, however, a new operation in Florida has been producing (5,964 metric tons, or 6,575 short tons, in 1974) rutile. About 85 percent of the ilmenite produced in the United States during 1972 came from two mines in New York and Florida. The remainder of the production came from New Jersey, Georgia, and a second operation in Florida. A plant with a planned production of 168,000 metric tons (185,000 short tons) per year opened in New Jersey during 1973. This plant and another which opened during 1972 in Florida are not yet at full production capability but are expected to contribute significantly to the domestic production of titanium in the future. Domestic production data are presented in Table III-32.

Two types of deposits contain titanium minerals of economic importance: rock and sand deposits. The ilmenite from rock deposits and some sand deposits commonly contains 35 to 55 percent TiO_2; however, some sand deposits yield altered ilmenite (leucoxene) containing 60 percent or more TiO_2, as well as rutile containing 90 percent or more TiO_2.

TABLE III-32. PRODUCTION AND MINE SHIPMENTS OF TITANIUM CONCENTRATES FROM DOMESTIC ORES IN THE U.S.

YEAR	PRODUCTION*		SHIPMENTS*	
	METRIC TONS	SHORT TONS	METRIC TONS	SHORT TONS
1968	887,508	978,509	870,827	960,118
1969	884,641	931,247	809,981	893,034
1970	787,235	867,955	835,314	920,964
1971	619,549	683,075	647,244	713,610
1972	618,251	681,644	661,591	729,428

*Includes a mixed product containing rutile, leucoxene, and altered ilmenite.

SOURCE: REFERENCE 2

The method of mining and beneficiating titanium minerals depends upon whether the ore to be mined is a sand or rock deposit. Sand deposits occurring in Florida, Georgia, and New Jersey, contain 1 to 5 percent TiO_2 and are mined with floating suction or bucket-line dredges handling up to 1,088 metric tons (1,200 short tons) of material per hour. The sand is treated by wet gravity methods using spirals, cones, sluices, or jigs to produce a bulk, mixed, heavy-mineral concentrate. As many as five individual marketable minerals are then separated from the bulk concentrate by a combination of dry separation techniques using magnetic and electrostatic (high-tension) separators, sometimes in conjunction with dry and wet gravity concentrating equipment.

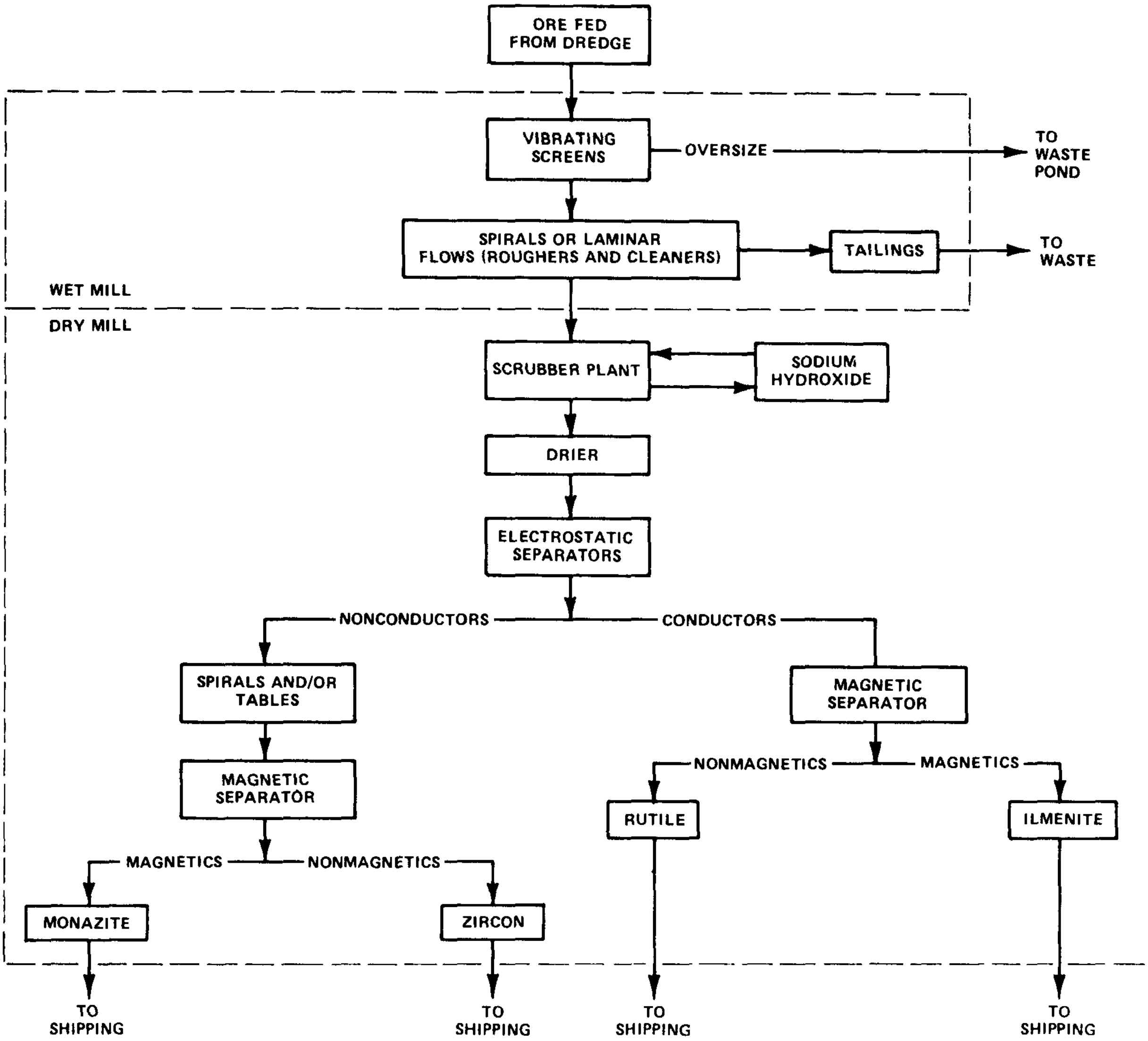
High-tension (HT) electrostatic separators are employed to separate the titanium minerals from the silicate minerals. In this type of separation, the minerals are fed onto a high- speed spinning rotor, and a heavy corona (glow given off by high- voltage charge) discharge is aimed toward the minerals at the point where they would normally leave the rotor. The minerals of relatively poor electrical conductance are pinned to the rotor by the high surface charge they receive on passing through the high- voltage corona. The minerals of relatively high conductivity do not as readily hold this surface charge and so leave the rotor in their normal trajectory. Titanium minerals are the only ones present of relatively high electrical conductivity and are, therefore, thrown off the rotor. The silicates are pinned to the rotor and are removed by a fixed brush.

Titanium minerals undergo final separation in induced-roll magnetic separators to produce three products: ilmenite, leucoxine, and rutile. The separation of these minerals is based on their relative magnetic propertities which, in turn, are based on their relative iron content: ilmenite has 37 to 65 percent iron, leucoxine has 30 to 40 percent iron, and rutile has 4 to 10 percent iron.

Tailings from the HT separators (nonconductors) may contain zircon and monazite (a rare-earth mineral). These heavy minerals are separated from the other nonconductors (silicates) by various wet gravity methods (i.e., spirals or tables). The zircon (nonmagnetic) and monazite (slightly magnetic) are separated from one another in induced-roll magnetic separators.

Beneficiation of titanium minerals from beach-sand deposits is illustrated in Figure III-31.

Figure III-31. BENEFICIATION OF HEAVY-MINERAL BEACH SANDS



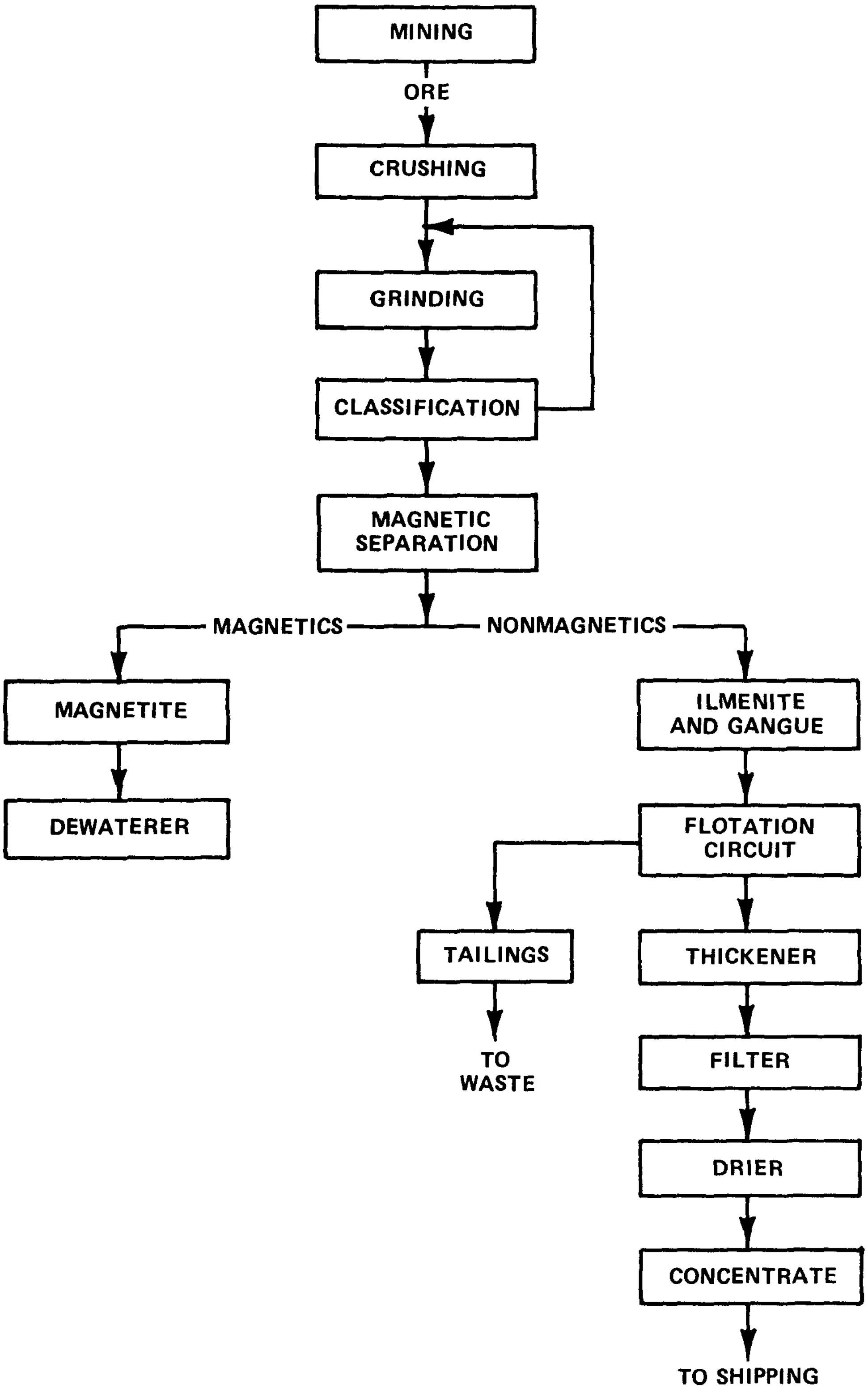
Ilmenite is also currently mined from a rock deposit in New York by conventional open-pit methods. This ilmenite/magnetite ore, averaging 18 percent TiO_2, is crushed and ground to a small particle size. The ilmenite and magnetite fractions are separated in a magnetic separator, the magnetite being more magnetic due to its greater iron content. The ilmenite sands are further upgraded in a flotation circuit. Beneficiation of titanium from a rock deposit is illustrated in Figure III-32.

Zirconium Ore

The zirconium ore mining and milling industry is defined for this document as that segment of industry engaged in the mining and/or milling of zirconium or for its primary or byproduct/coproduct recovery.

The principal mineral source of zirconium is zircon ($ZrSiO_4$), which is recovered as a byproduct in the mining of titanium minerals from ancient beach-sand deposits, which are mined by floating suction or bucket-line dredges. The sand is treated by wet gravity methods to produce a heavy-mineral concentrate. This concentrate contains a number of minerals (zircon, ilmenite, rutile, and monazite) which are separated from one another by a combination of electrostatic and magnetic separation techniques, sometimes used in conjunction with wet gravity methods. (Refer to the titanium section of this document.) Domestic production of zircon is currently from three operations: two in Florida and one in Georgia. The combined zircon capacity of these three plants is estimated to be about 113,400 metric tons (125,000 short tons). The price of zircon in 1972 was $59.50 to $60.50 per metric ton ($54.00 to $55.00 per short ton).

Figure III-32. BENEFICIATION OF ILMENITE MINED FROM A ROCK DEPOSIT



SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

In the development of effluent limitations and recommended standards of performance for new sources in a particular industry, consideration should be given to whether the industry can be treated as a whole in the establishment of uniform and equitable guidelines for the entire industry or whether there are sufficient differences within the industry to justify its division into categories. For the ore mining and dressing industry, which contains nine major ore categories by SIC code (many of which contains more than one metal ore), many factors were considered as possible justification for industry categorization and subcategorization as follows:

(1) Designation as a mine or mill;

(2) Type of mine;

(3) Type of processing (beneficiation, extraction process);

(4) Mineralogy of the ore;

(5) End product (type of product produced);

(6) Climate, rainfall, and location;

(7) Production and size;

(8) Reagent use;

(9) Wastes or treatability of wastes generated;

(10) Water use or water balance;

(11) Treatment technologies employed;

(12) General geologic setting;

(13) Topography;

(14) Facility age;

(15) Land availability.

Because of their frequent use in this document, the definitions of a mine and mill are included here for purposes of recommending subcategorization and effluent limitations guidelines and standards:

Mine

"A mine is an area of land upon which or under which minerals or metal ores are extracted from natural deposits in the earth by any means or methods. A mine includes the total area upon which such activities occur or where such activities disturb the natural land surface. A mine shall also include land affected by such ancillary operations which disturb the natural land surface, and any adjacent land the use of which is incidental to any such activities; all lands affected by the construction of new roads or the improvement or use or existing roads to gain access to the site of such activities and for haulage and excavations, workings, impoundments, dams, ventilation shafts, drainage tunnels, entryways, refuse banks, dumps, stockpiles, overburden piles, spoil banks, culm banks, tailings, holes or depressions, repair areas, storage areas, and other areas upon which are sited structures, facilities, or other property or materials on the surface, resulting from or incident to such activities."

Mill

"A mill is a preparation facility within which the mineral or metal ore is cleaned, concentrated or otherwise processed prior to shipping to the consumer, refiner, smelter or manufacturer. This includes such operations as crushing, grinding, washing, drying, sintering, briquetting, pelletizing, nodulizing, leaching, and/or concentration by gravity separation, magnetic separation, flotation or other means. A mill includes all ancillary operations and structures necessary for the cleaning, concentrating or other processing of the mineral or metal ore such as ore and gangue storage areas, and loading facilities."

Examination of the metal ore categories covered in this document indicates that ores of 23 separate metals (counting the rare earths as a single metal) are represented. Two materials are treated in two places in this document: (1) vanadium ore is considered as a source of ferroalloy metals (SIC 1061) and also in conjunction with uranium/vanadium extraction under NRC licensing surveillance (SIC 1094); and (2) monazite, listed as a SIC 1099 mineral because it is a source of rare-earth elements, also serves as an ore of a radioactive material (thorium) and, therefore, is also treated in SIC 1094.

The discussion that follows is organized into five major areas which illustrate the procedures and final selection of subcategories which have been made as part of these recommendations:

(1) The factors considered in general for all categories. (Rationale for selection or rejection of each as a pertinent criterion for the entire industry is included.)

(2) The factors which determined the subcategorization within each specific ore category.

(3) The procedures which led to the designation of tentative and, then, final subcategories within each SIC code group.

(4) The final recommended subcategories for each ore category.

(5) Important factors and particular problems pertinent to subcategorization in each major category.

FACTORS INFLUENCING SELECTION OF SUBCATEGORIES IN ALL ORE CATEGORIES

The first categorization step was to examine the ore categories and determine the factors influencing subcategorization for the industry as a whole. This examination evolved a list of 15 factors considered important in subcategorization of the industry segments (as tabulated above). The discussion which follows describes the factors considered in general for all categories and subcategories.

Designation as a Mine or Mill

It is often desirable to consider mine water and mill process water separately. There are many mining operations which do not have an associated mill or in which many mines deliver ore to a single mill located some distance away. In many instances, it is advantageous to separate mine water from mill process waste water because of differing water quality, flow rate or treatability. Levels of pollutants in mine waters are generally lower or less complex than those in mill process waste waters. Mine water contact with finely divided ores, (especially oxidized ores) is minimal and mine water is not exposed to the suite of process water reagents often added in milling. Waste water volume reduction from a mine is seldom a viable option whereas the technology is available to eliminate all discharge from many milling operations.

While it is generally more efficient to treat mine waste water and mill waste water separately, there are some situations in which combining the mine waste water and mill process waste water cause a co-precipitation of pollutants with their resultant discharge being of higher quality than either of the individual treated discharges. In some instances, use of the mine waste water as mill process water will also result in an improved quality of discharge because of the interactions of the chemicals added to the process water with the pollutants in the mine water.

Type of Mine

The choice of mining method is determined by the ore grade, size, configuration, depth, and associated overburden of the orebody to be exploited rather than by the chemical characteristics or mineralogy of the deposit. Because the general geology is the determining factor in selection of the mining method, and because no significant differences resulted from application of control and treatment technologies for mine waters from either open pit or underground mines, designation of the type of mine was not selected as a suitable basis for general subcategorization in the industry.

Type of Processing (Beneficiation, Extraction Process)

The processing or beneficiation of ores in the ore mining and dressing industry varies from crude hand methods to gravity separation methods, froth flotation with extensive reagent use, chemical extraction, and hydrometallurgy. Purely physical processing using water provides the minimal pollution potential consistent with recovery of values from an ore. All mills falling in this group are expected to share the same major pollution problem--namely, suspended solids generated either from washing, dredging, crushing, or grinding. The exposure to water of finely divided ore and gangue also leads to solution of some material but, in general, treatment required is relatively simple. The dissolved material will vary with the ore being processed, but treatment is expected to be essentially similar, with resultant effluent levels for important parameters being nearly identical for many subcategories.

The practice of flotation significantly changes the character of mill effluent in several ways. Generally, mill water pH is altered or controlled to increase flotation efficiency. This, together with the fact that ore grind is generally finer than for physical processing, may have the secondary effect of substantially increasing the solubility of ore components. Reagents added to effect the flotation may include major pollutants. Cyanide, for example, is used in several subcategories. Although usage is usually low, its presence in effluent streams has potentially harmful effects. The added reagents may have secondary effects on the waste water as well, such as in the formation of cyanide complexes. The result may be to increase solubility of some metals and decrease treatment effectiveness. Some flotation operations may also differ from physical processors in the extent to which water may be recycled without major process changes or serious recovery losses.

Ore leaching operations differ substantially from physical processing and flotation plants in waste water character and treatment requirements. The use of large quantities (in relation to ore handled) of reagents, and the deliberate solubilization of ore components characterizes these operations. Wide diversity of leaching and chemical extraction processes, therefore, affects the character and quantities of water quality parameters, as well as the treatment and control technologies employed.

To a large extent, mineralogy and extractive processes are inextricable, because mineralogy and mineralogical variations are responsible for the variations in processing technologies. Both factors influence the treatability of wastes and efficiency of removal of pollutants by treatment and control technologies. Therefore, processing methods were a major factor in subcategorizing each major ore category.

Mineralogy of the Ore

The mineralogy and host rock present greatly determine the beneficiation of ores. Ore mineralogy and variations in mineralogy affect the components present in effluent streams and thus the treatability of the wastes and treatment and control technology used. Some metal ores contain byproducts and other associated materials, and some do not. The specific beneficiation process adopted is based upon the mineralogical characteristics of the ore; therefore, the waste characteristics of the mine or mill reflect both the ores mined and the extraction process used. For these reasons, ore mineralogy was determined to be a primary factor affecting subcategorization in all categories.

End Product

The end product shipped is closely allied to the mineralogy of the ores exploited; therefore, mineralogy and processing were found to be more advantageous methods of subcategorization. Two ores, vanadium ores and monazite ores, are the exceptions treated here which were based upon considerations of end product or end use.

Climate, Rainfall, and Location

These factors directly influenced subcategorization consideration because of the wide diversity of yearly climatic variations prevalent in the United States. Mining and associated milling operations cannot locate in areas which have desirable characteristics unlike many other industry segments. Therefore, climate and rainfall variations must be accommodated or designed for. Some mills and mines are located in arid regions of the country, allowing the use of evaporation to aid in reduction of effluent discharge quantity or attainment of zero discharge. Other facilities are located in areas of net positive precipitation and high runoff conditions. Treatment of large volumes of water by evaporation in many areas of the United States cannot be utilized where topographic conditions limit space and provide excess surface drainage water. A climate which provides icing conditions on ponds will also make control of excess water more difficult than in a semi-arid area. Although climate, rainfall, and location were not used as primary subcategorization factors, they were given consideration when determining treatment technology and effluent limitations (i.e., copper ore industries).

Production and Size

The variation of size and production of operations in the industry ranges from small hand cobbing operations to those mining and processing millions of tons of ore per year. The size or production of a facility has little to do with the quality of the water or treatment technology employed, but have considerable influence on the water volume and costs incurred in attainment of a treatment level in specific cases. Mines and mills processing less than 5,000 metric tons (5,512 short tons) of ore per year in the ferroalloys industry (most notably, tungsten) are typically intermittent in operation, have little or no discharge, and are economically marginal. Pollution potential for such operations is relatively low due to the small volume of material handled if deliberate solution of ores is not attempted. Few of the operations are covered by NPDES permits. Accordingly, size or production was used in a limited sense for subcategorization in the ferroalloys categories but was not found to be suitable for the industry as a whole.

Reagent Use

The use of reagents in many segments of the industry, such as different types of froth flotation separation processes, can potentially affect the quality of waste water. However, the types and quantities of reagents used are a function of the mineralogy of the ore and extraction processes employed. Reagent use, therefore, was not a suitable basis for subcategorization of any of the metals ores examined in this program.

Wastes or Treatability of Wastes Generated

The wastes generated as part of mining and beneficiating metals ores are highly dependent upon mineralogy and processes employed. This characteristic was not found to be a basis for general subcategorization, however, it was considered in all subcategories.

Water Use and/or Water Balance

Water use or water balance is highly dependent upon choice of process employed or process requirements, routing of mine waters to a mill treatment system or discharge, and potential for utilization of water for recycle in a process. Processes employed play a determining role in mill water balance and, thus, are a more suitable basis for subcategorization.

Treatment Technologies Employed

Many mining and milling establishments currently use a single type of effluent treatment method today. While treatment procedures do vary within the industry, widespread adoption of these technologies is not prevalent. Since process and mineralogy control treatability of wastes and, therefore, treatment technology employed, treatment technology was not used as a basis for subcategorization.

General Geologic Setting

The general geologic setting determines the type of mine--i.e., underground, surface or open-pit, placer, etc. Significant differences which could be used for subcategorization with respect to geology could not be determined.

Topography

Topographic differences between areas are beyond the control of mine or mill operators and largely place constraints on treatment technologies employed, such as tailing pond location. Topographic variations can cause serious problems with respect to rainfall accumulation and runoff from steep slopes. Topographic differences were not found to be a practical basis on which subcategorization could be based, but topography is known to influence the treatment and control technologies employed and the water flow within the mine/mill complex. While not used for subcategorization, topography has been considered in the determination of effluent limits for each subcategory.

Facility Age

Many mines and mills are currently operating which have operated for the past 100 years. In virtually every operation involving extractive processing, continuous modification of the plant by installation of new or replacement equipment results in minimal differences for use in subcategorization within a metal ore category. Many basic processes for concentrating ores in the industry have not changed considerably (e.g., froth flotation, gravity separation, grinding and crushing), but improvements in reagent use and continuous monitoring and control have resulted in improved recovery or the extraction of values from lower grade ores. New and innovative technologies have resulted in changes of the character of the wastes, but this is not a function of age of the facilities, but rather of extractive metallurgy and process changes. Virtually every facility continuously updates in-plant processing and flow schemes, even though basic processing may remain the same. Age of the facility, therefore, is not a useful factor for subcategorization in the industry.

DISCUSSION OF PRIMARY FACTORS INFLUENCING SUBCATEGORIZATION BY ORE CATEGORY

The purpose of the effluent limitation guidelines can be realized only by categorizing the industry into the minimum number of groups for which separate effluent limitation guidelines and new source performance standards must be developed.

This section outlines and discusses briefly the factors which were used to determine the subcategories within each ore category. A presentation of the procedures leading to the tentative and then final subcategories, together with a listing of the final recommended subcategories, is included. The treatment by ore category also includes a brief discussion, where applicable, of important factors and pertinent problems which affect each category.

Iron Ore

In developing a categorization of the iron ore industry, the following factors were considered to be significant in providing a basis for categorization. These factors include characteristics of individual mines, processing plants, and water uses.

1. Type of Mining
   a. Open-Pit
   b. Underground

2. Type of Processing
   a. Physical
   b. Physical - Chemical

3. Mineralogy of the Ore

4. General Geologic Setting, Topography, and Climate (also Rainfall and Location)

Information for the characterization was developed from published literature, operating company data, and other information sources discussed in Section III.

As a result of the above, the first categorization developed for the iron mining and beneficiation industry was based on whether or not a mine or mill produces an effluent. This initial categorization considered both the mining and milling water circuits separately, as well as a category where mines and mills were in a closed water system. The resulting tentative subcategories which resulted are presented in the listing given below:

I. Mine producing effluent - processing plant with a closed water circuit.

IIa. Mine producing effluent - processing plant producing an effluent - physical processing.

IIb. Mine producing effluent - processing plant producing an effluent - physical and chemical processing.

III. Mine and processing plant with a closed water circuit.

Examination of the preliminary subcategorization and further compilation of information relative to iron mining and processing methods resulted in a classification of the mines and mills into the following order by production:

Open-Pit Mining, Iron Formation, Physical Processing
Open-Pit Mining, Iron Formation, Physical and Chemical Processing
Open-Pit Mining, Natural Ores, Physical Processing
Underground Mining, Iron Formation, Physical Processing
Underground Mining, Iron Formation, Physical and Chemical Processing
Underground Mining, Natural Ores, Physical Processing

In preparation for selection of sites for visitation and sampling, the operations were further classified on the basis of size, relative age, and whether they had closed water systems or produced an effluent from either the mining or processing operation:

Operation A
High tonnage
Open-pit
Iron formation
Physical processing
Older plant (1957)
Mine produces effluent
Processing plant has closed water system

Operation B
Medium tonnage
Open-pit
Iron formation
Physical processing
Medium age plant (1965)
Mine produces effluent
Processing plant has closed water system

Operation C
Medium tonnage
Open-pit
Natural ore
Physical processing
Older plant (1948)
No effluent

Operation D
Low tonnage
Open-pit
Natural ore
Older plant (1953)
Mine produces effluent
Processing plant produces effluent

Physical processing	
Operation E	
High tonnage	Medium age plant (1967)
Open-pit	
Iron formation	Mine produces effluent
Physical processing	Processing plant has closed water system
Operation F	
High tonnage	Medium age plant (1967)
Open-pit	No effluent
Iron formation	
Physical processing	
Operation G	
Low tonnage	Older plant (1959)
Open-pit	Mine produces effluent
Iron formation	Processing plant produces effluent
Physical and chemical processing	
Operation H	
Medium tonnage	Older plant (1956)
Open-pit	Mine produces effluent
Iron formation	Processing plant produces effluent
Physical and chemical processing	
Operation I	
Medium tonnage	Medium age plant (1964)
Open-pit	Mine produces effluent
Iron formation	Processing plant produces effluent
Physical and chemical processing	
Operation J	
Low tonnage	Older plant (1958)
Underground	Mine produces effluent
Iron formation	Processing plant produces effluent
Physical and chemical processing	

The mines visited and sampled had a 1973 production of approximately 43,853,450 metric tons (48,350,000 short tons), or 47.5 percent of the total United States production of iron ore.

One of the initial goals of this study was determination of the validity of the initial categorization. The primary source of the data utilized for this evaluation was information obtained during this study, plant visits, and sampling program. This information was supplemented with data obtained through personal interviews and literature review and with historical effluent quality data from NPDES permit applications and monitoring data supplied by the iron mining and beneficiating industry.

Based on this exhaustive review, the preliminary industrial categorization was substantially altered.

The data review revealed two distinct effluents from the mining and milling of iron. The first (I) coming from the mines and second (II) coming from the mills. It was also determined that all mills in general could not be classed together. This is primarily because a large number of milling operations achieve zero discharge without major upset to presently used concentrating technology.

The milling categorized into three distinct classes based on the type of ore and the type of processing.

Category IIa. Mills using physical separation techniques, exclusive of magnetic separation (washing, jigging, cyclones, spirals, heavy media).

Category IIb. Mills using flotation processes and using the addition of chemical reagents.

Category IIc. Mills using magnetic separation for the benefication of iron formations.

Final Iron-Ore Subcategorization. Based on the types of discharges found from all mills, the first two subcategories can be grouped into a single segment. Mills employing magnetic separation (No chemical separation) have demonstrated that a distinct subcategory can be made because of the type of ore, and the mode of beneficiation.

I. Mines Open-pit or underground, removing natural ores or iron formations.

II. Iron ore mills employing physical and chemical separation and iron ore mills employing only physical separation (not magnetic)

III. Iron ore mills employing magnetic and physical separation

Copper Ores

The copper-ore subcategorization consideration began with the approach that mineralization and ore beneficiating or process method were intimately related to one another. This relationship together with a basic division into mining, milling and hydrometallurgical processing resulted in a preliminary subcategorization scheme based primarily on division into mine or concentrating facility and then further based the method of concentrating or extraction of values from the ore. Examination of water quality data supplied by the industry and other sources indicated that division of mills into further subcategories based upon process resulted in grouping operations with similar water quality characteristics. Other factors such as climate and rainfall presented problems of subcategorization particularly with respect to conditions prevalent in certain areas during approximately two months of the year.

Final Copper-Ore Subcategorization

Based on data collected from existing sources in addition to visits and sampling of copper mines and extraction facilities, the following final subcategories have been established based primarily on designation as a mine or concentrating or chemical extraction facility:

I. Mines - Open-pit or underground, removing sulfide, oxide, mixed sulfide oxide ores, or native copper.
II. Copper mines employing hydrometallurgical processes

III. Copper mills employing the vat-leaching process

IV. Copper mills employing froth flotation

Problems in Subcategorizing the Copper Industry. Copper is produced in many areas of the United States which vary in mineralization, climate, topography, and process-water source. The processes are outlined in Section V. The froth flotation of copper sulfide is adjusted to conditions at each plant and will also vary from day to day with the mill feed.

Excess runoff from rainfall and snow melt do alter the subcategorization, but they can be controlled by enlargement of tailing ponds and construction of diversion ditching. Presently a few mines send the drainage to the mill tailings lagoon or use the water in the leach circuits. A decrease in excess water problems can be realized in many cases if mine water is treated separately from mill process water.

Some industry personnel have indicated concern that dissolved salt buildup may cause problems in the recycling of mill process waters when the makeup water source and/or ore body contain a high content of dissolved salts; however, data has not been provided to support this concern. molybdenum mills in Canada indicate that the mill tailings include a built-in blowdown in the form of water trapped in the interstitial voids of the tailings and the product. This blowdown removes part of the dissolved salts from a recyle operation with the result that the circuits can operate on a zero discharge. Additional treatment of the process water for removal of some of the waste constituents may be necessary for recycle of process water and may produce a zero effluent from many plants where buildup of materials may adversely affect recovery.

Lead and Zinc Ores

As a result of an initial review of the lead/zinc mining and milling industry which considered such factors as mineralogy of ore, type of processing, size and age of facility, wastes and treatability of waste, water balance associated with the facilities, land availability, and topography, a preliminary scheme for subcategorization of the lead/zinc industry was developed. The preliminary analysis disclosed that size and age of a facility should have little to do with the characteristics of the wastes from these operations in that the basic flotation cells have not changed significantly in a decade. The reagents used, even in very old facilities, can be utilized the same as in the newest. These factors, in addition to life of an ore body, and such factors as land availability, topography, and, perhaps, volume of water which must be removed from a mine have little to do with technology of treatment but can have considerable effect on the cost of a treatment technology employed in a specific case.

The preliminary subcategorization scheme utilized was selected to provide subcategorization on basic technological factors where possible. The factors considered in the preliminary scheme were:

I. End Product Recovered:
    (a) Lead/zinc
    (b) Zinc
    (c) Lead
    (c) Others with lead/zinc byproducts

II. Designation as a Mine or Mill:
   (a) Mine
   (b) Mill
   (c) Mine/mill complex

III. Type of Processing:
   (a) Gravity separation (no reagents)
   (b) Flotation

IV. Wastes or Treatability of Wastes Generated:
   (a) Potential for development of conditions with soluble undesirable metals or salts
   (b) No potential for solubilization

V. Water Balance:
   (a) Total recycle possible
   (b) Total recycle not possible

The plant visits and subsequent compilation of data and literature review were aimed at establishing which factors were really significant in determining what effluent quality could be achieved with respect to the tentative subcategorization.

An analysis of the data compiled indicated that subcategorization within the lead/zinc industry could be simplified considerably. No basic differences in treatability were found to be associated with the type of concentrates obtained from a facility.

The proposed subcategorization based on what facility is discharging--that is, a mine or a mill--is justified because effluents from a mine dewatering operation and those from a milling operation, into which various chemicals may be introduced, are different. In the case of a mine discharging only into the water supply of the mill, the only applicable guideline would be that of the mill.

No evidence of current practice of strictly physical concentration by gravity separation was found. The recovery of desirable minerals from known deposits utilizing only such physical separations is likely to be so poor as to result in discharge of significant quantities of heavy-metal sulfide to the tailing retention area. The only ore concentration process currently practiced in the lead/zinc industry is froth flotation. Subcategorization based on milling process is, therefore, not necessary.

The treatability of mine waste water is significantly affected by the occurrence of local geological conditions which cause solubilization of undesirable metals or salts. A common, and well-understood, example is acid mine drainage caused by the oxidation of pyrite (FeS_2) to ferrous sulfate and sulfuric acid. This oxidation requires both moisture and air (oxygen source) to occur. The acid generated then leaches heavy metals from the exposed rock on particle surfaces. Heavy metals may also enter solution as a result of oxidation over a period of time through fissured ore bodies to form more soluble oxides of heavy metals (such as zinc) in mines which do not exhibit acidic mine drainages. Another route which may result in solubilized heavy metals involves the formation of acid and subsequent leaching in very local areas in an ore body. The resultant acid may be neutralized by later contact with limestone or dolomitic limestone, but the pH level attained may not be high enough to cause precipitation of the solubilized metals. The important aspect of all of these situations is that the mine water encountered is much more difficult to treat than those where solubilization conditions do not occur. The treated effluents from mines in this situation often exhibit higher levels of heavy metals in solution than untreated mine waters from mines where solubilization conditions do not occur.

It has been determined that subcategorization on the basis of solubilization potential is not justified, however, the effluent limits recommended have taken into consideration this factor.

The water-balance parameter, of course, does not apply to mine only operations. In the case of milling operations, system design and alteration of process flows can have considerable effect on the water balance of a milling operation. No justification was found for substantiation of subcategorization on this basis.

The final recommended subcategorization for the lead/zinc mining and milling industry is, therefore, condensed to:

I. Lead and/or zinc mines

II. Lead and/or zinc mills

Gold Ores

The most important factors considered in determining whether subcategorization was necessary for the gold ore category were ore mineralogy, general geologic setting, type of processing, wastes and waste treatability, water balance, and final product. Upon intensive background data compilation (as discussed in Section III), mill inspections, and communications with the industry, most of the factors were found to reduce to mineralogy of the ore (and, thus, product) and milling process employed. The initial subcategorization was found to differ little from final subcategorization selection after site visitation and sampling data were obtained.

The most effective means of categorizing the gold industry is based upon relative differences among existing sources of discharge (mine or mill/mine-mill complexes) and on characteristics of the beneficiation process. The rationale for this is based on several considerations:

(1) Apart from milling processing, the characteristic difference between mine effluents and mill/mine-mill effluents is their quantitative and qualitative pollutant loadings. This difference between mines and mills makes necessary the application of differing waste-treatment technologies and/or the segregation of sources for purposes of treatment. A mill effluent normally contains a greater quantity of total solids--up to 40 to 50 percent more than a mine effluent. Much of these solids are suspended solids, and treatment involves removal by settling. This is usually treated in tailing ponds. Where mines occur alone, or where their effluents are treated separately from the mill, these effluents may be treated on a smaller scale by a different technology.

(2) The specific beneficiation process adapted is based on the geology and mineralogy of the ore. The waste characteristics and treatability of the mill effluent are a function of the particular beneficiation process employed. This takes into account the reagents used and the general mineralization of the ore by each particular process as these factors affect differing waste characteristics. The waste characteristics affect treatability; for example, cyanide removal requires different technology than that used for metal removal.

Consideration was also given to the regional availability of water, as this factor is relevant to water conservation and "no discharge" and waste-control feasibility. Since it is common engineering practice to design tailing ponds to accommodate excesses of water, and also since pond design can include systems to divert surface runoff away from the pond, regional availability of water was judged not to be a limiting factor with respect to the feasibility of a no-discharge system.

Final Gold-Ore Subcategorization

On the basis of the rationale developed above and previously discussed in the introductory portion of this section, six subcategories were identified for the gold mining and milling industry:

I. Mine(s) alone.

II. Mill(s) or mine/mill complex(es) using the process of cyanidation for primary or byproduct recovery of gold.

III. Mill(s) or mine/mill complex(es) using process of amalgamation (includes dredging operations, if amalgamation is used).

IV. Mill(s) or mine/mill complex(es) using the process of flotation.

V. Mill(s) or mine/mill complex(es) using gravity separation (includes dredging or hydraulic mining operation).

Silver Ores

The development of subcategorization in the silver industry was essentially identical to that of the gold industry previously discussed. The primary basis for division into subcategories was mineralogy of the ore and type of processing. Since mineralogy and type of extraction processing are intimately related, these factors served, just as in the gold industry, to divide the industry into mine and mill categories, and then further into milling categories based upon type of processing. Also note that, in many places, gold and silver are exploited as coproducts or, together, as byproducts of other base metals (such as copper).

Final Silver-Ore Subcategorization

Based upon the previous rationale developed in the introductory portion of this section (and also discussed in connection with gold ores), tentative subcategorization was developed and then verified by field sampling and site visits. Based upon field confirmation, the tentative subcategories, found to be unchanged, are:

I. Mine(s) alone

II. Mill(s) or mine/mill complex(es) using flotation for primary or byproduct recovery of silver.

III. Mill(s) or mine/mill complex(es) using cyanidation for primary or byproduct recovery of silver.

IV. Mill(s) using amalgamation process for primary or byproduct recovery of silver.

V. Mill(s) using gravity separation process for primary or byproduct recovery of silver.

Bauxite Ores

In the bauxite mining industry, most criteria for subcategorization bear directly or indirectly upon two basic factors: (1) nature of raw mine drainage, which is a function of the mineralogy and general geological setting related to percolating waters; and (2) treatability of waste generated, based upon the quality of the effluent concentrations. Initially, general factors, such as end products, type of processing, climate, rainfall, and location, proved to be of minor importance as criteria for subcategorization. The two existing bauxite mining operations are located adjacent to one another in Arkansas and share similar rainfall and evaporation rates, 122 cm (48 in.) and 109 cm (43 in.). Both operations produce bauxite, though slightly different in grade, which is milled by a process emitting no waste water.

After the site visits to both operating mines, it was evident that the mining technique is closely associated with the characteristics of the mine drainage, and that mineralization is directly responsible for mining-technique and raw minedrainage characteristics. In addition, an evaluation of removal efficiency for a treatment process common to both members of the industry became the prime consideration in determining attainable treated effluent concentrations.

Final Bauxite-Ore Subcategorization

Based on the results of intensive study, facility inspections, NPDES permit applications, and communication with the industry, it was concluded that the bauxite mining and milling industry should not be subcategorized beyond that presented below.

Bauxite mining and associated milling operations
(essentially grinding and crushing)

Ferroalloy Ores

In development of subcategories for the ferroalloy mining and milling category, the following factors were considered initially: type of process, and product, mineralogy, climate, topography, land availability, size, age, and wastes or treatability of wastes generated.

A tentative subcategorization of the industry was developed after collection and review of initial data, based primarily on end product (e.g., tungsten, molybdenum, manganese, etc.), with further division on the basis of process, in some cases. Further data, particularly chemical data on effluents and more complete process data for past operations, indicated that process was the dominant factor influencing waste-stream character and treatment effectiveness. Examination of the industry additionally showed that size of operation could also be of great importance. Other factors, except as they are reflected in or derived from the above, are not believed to warrant industry subcategorization.

Final Ferroalloy-Ore Subcategorization

It has been determined that the ferroalloy mining and milling category should be divided into five subcategories for the purpose of establishing effluent limitations and new source performance standards:

I. Mines

II. Mines and Mills processing less than 5,000 metric tons (5,512 short tons) per year of ore by methods other than ore leaching.

III. Mills processing more than 5,000 metric tons per year of ore by purely physical methods (e.g., crushing, ore washing, gravity separation, and magnetic and electrostatic separation).

IV. Mills processing more than 5,000 metric tons per year of ore and employing flotation.

V. Mills practicing ore leaching and associated chemical beneficiation techniques.

The subcategory including mills processing less than 5,000 metric tons of ore per year is representative of operations which are typically both intermittent in operation and economically marginal. This subcategory is believed to contain, at present, almost exclusively processors of tungsten ores.

Purely physical processing provides the minimum pollution potential consistent with recovery of values from an ore using water. All mills falling into this subcategory are expected to share the same major pollution problem--namely, suspended solids generated by the need for crushing and grinding. The exposure of finely divided ore (and gangue) to water may also lead to solution of some material, but, in general, pretreatment levels will be low and treatment, relatively simple. The dissolved material will clearly vary with the ore being processed, but treatment is expected to be essentially the same in all cases and to result in similar maximum effluent levels. There are currently no active major water using physical processors in the ferroalloy industry except in the case of nickel, where water use is not really in the process. Information has been drawn heavily, therefore, from past data and related milling operations--particularly, in the iron ore industry. The close relationship between iron ores and manganiferous ores, where such production is likely in the near future, as well as the nature of the data itself, makes this transfer reasonable. These milling processes are fully compatible with recycle of all mill water.

The practice of flotation significantly changes the character of mill effluent in several ways. Generally, mill water pH is altered or controlled to increase flotation efficiency. This, together with the fact that ore grind is generally finer than for physical processing, may have the secondary effect of substantially increasing solubility of ore components. Reagents added to effect the flotation may include major pollutants. Cyanide, for example, is commonly used and, though usage is low, may necessitate treatment. The added reagents may have secondary effects on the effluent as well; the formation of cyanide complexes, for example, may increase solubility of some metals and decrease treatment effectiveness. Some flotation operations may also differ from physical processors in the extent to which water may be recycled without process changes or serious recovery losses.

Ore leaching operations differ substantially from physical processors and flotation plants in effluent character and treatment requirements. The use of large quantities (in relation to ore handled) of reagents, and the deliberate solubilization of ore components, characterizes these operations. The solubilization process is not, in general, entirely specific, and the recovery of desired material is less than 100 percent. Large amounts of dissolved ore may be expected, therefore, to appear in the mill effluent, necessitating extensive treatment prior to discharge. For these operations, even commonly occurring ions (i.e., Na^+, SO_4, etc.) may be present in sufficient quantities to cause major environmental effects, and total dissolved-solid levels can become a real (although somewhat intractable) problem. Wide variations in leaching processes might justify further division of this subcategory (into acid and alkaline leaching, as in the uranium industry, for example), but the limited current activity and data available at this time do not support such a division.

Other Considerations. Climate, topography, and land availability are extremely important factors influencing effluent volume, character, and treatment in the mining and milling industry--particularly, the attainment of zero pollutant discharge by means of discharge elimination. Zero discharge may be attainable, for example, despite a net positive water balance for a region because rainfall input to a tailing impoundment balances part of the process water loss, including evaporative losses in the mill and retention in the tails and product. It is anticipated that, under the impetus of effluent limitations established under PL 92-500, and the resultant pollution control costs, many mills in the defined subcategories will choose the often less expensive option of discharge elimination.

Mercury Ores

The mercury industry in the United States currently is at a reduced level of activity due to depressed market prices. One facility was found to be operating at present, although it is thought that activity will again increase with increasing demand and rising market prices. The decreased use of mercury due to stringent air and water pollution regulations in the industrial sector may be offset in the future by increased demand in dental and other uses. Very little beneficiating of mercury ores is known in the industry. Common practice for most producers (since relatively low production characterizes most operators) is to feed the cinnabar-rich ore directly to a kiln or furnace without beneficiation. Water use in most of the operations is at a minimum, although a rather large (20,000-flask-per-year, or 695-metric-ton-per-year or 765-short-ton-per-year) flotation operation with high water use is expected to be operating in the near future. In the year 1985, the industry could be producing 3,000 to 20,000 flasks (104 to 695 metric tons, or 115 to 765 short tons) per year, depending on market price, technology, and ore grade (U.S. Bureau of Mines projection).

Final Mercury Ore Subcategorization

Since most mercury operations are direct furnacing facilities, the resulting subcategorization represents that fact. Little or no beneficiation is done in the industry, with few exceptions. There are a few operations from which mercury is recovered as a byproduct at a smelter or refinery. A single known flotation operation is expected in the near future and is reflected in the subcategorization scheme below based on processing.

I. Mine(s) alone or mine(s) with crushing and/or grinding prior to furnacing (no additional beneficiation).

II. Mill(s) or mine/mill complex(es) using the process of gravity separation for primary or byproduct recovery of mercury.

III. Mill(s) or mine/mill complex(es) using flotation for primary or byproduct recovery of mercury.

Uranium, Radium, and Vanadium Ores

The factors evaluated in consideration of subcategorization of the uranium, radium, and vanadium mining and ore dressing industry are: end product, type of processing, ore mineralogy, waste characteristics, treatability of waste water, and climate, rainfall, and location. Based upon an intensive literature search, plant inspections, NPDES permits, and communications with the industry, this category is categorized by milling process and mineralogy (and, thus, product). A discussion of each of the primary factors as they affect the uranium/radium/vanadium ore category follows.

The milling processes of this industry involve complex hydrometallurgy. Such point discharges as might occur in milling processes (i.e., the production of concentrate) are expected to contain a variety of pollutants that need to be limited. Mining, for the ores, is expected to lead to a smaller set of contaminants. While mining or milling of ores for uranium or radium produces particularly noxious radioactive pollutants, these are largely absent in an operation recovering vanadium only. On the basis of these considerations, the SIC 1094 industry was tentatively subcategorized into: (1) The mining of uranium/radium ores; (2) The processing of the ores of the first subcategory to yield uranium concentrate and, possibly, vanadium concentrate; (3) The mining of non-radioactive vanadium ores; and (4) The processing of the ores of the third subcategory to yield vanadium concentrate.

A careful distinction will be drawn between the radioactive processes and the vanadium industry by including in the former all operations within SIC 1094 that are licensed by the U.S. Nuclear Regulatory Commission (NRC, formerly AEC, Atomic Energy Commission) or by agreement states. The agreement states, including the uranium producing states of Colorado, Texas, New Mexico and Washington, have been delegated all licensing, record keeping, and inspection responsibilities for radioactive materials regulated by the NRC upon establishing regulations regarding radioactive materials that are compatible with those of the NRC(AEC). The licensing requirements, as set forth in the code of Federal Regulations, Title 10, Parts 20 and 40 constitute present restrictions on the discharge of radionuclides. Uranium mines are regulated by some states for discharge of radioactive materials but this regulation is not based on "agreement state" authority since the NRC does not regulate the uranium mines.

To further emphasize the distinction between the NRC-licensed uranium subcategories and the pure vanadium subcategories, the latter, whose products are used in the inorganic chemical industry and, to a large extent, the ferroalloy smelting industry, are discussed further in connection with ferroalloymetal ore mining and dressing, in another portion of these guidelines. The vanadium subcategories are summarized there as members of the mining and hydrometallurgical process subcategories.

The variety of ores and milling processes discussed in Section III might lead to the generation of as many subcategories based on the major characteristics of the mill process as there are ores and mills. It is possible, however, to group mills into fewer subcategories. This simplification is based on the observations discussed below.

Raw waste waters from mills using acid leaching remain acid at the process discharge (not to be confused with a point discharge), retain various heavy metals, and are generally not suitable for recycling without additional and specialized treatment. Those from the alkaline leach process are normally recycled in part, since the leach process is somewhat selective for uranium and vanadium, and other metals remain in the solid tailings. At one time, it was expected that mills using solvent exchange would have a radically different rawwaste character due to the discharge of organic compounds. The fact that mills not using solvent exchange often process ore that is rich in organics make this distinction less important. As a result, a distinction must be made between mills using acid leaching (or both acid and alkaline leaching) of ore and mills using alkaline leaching of ore only.

While other differences between ores and processes, in addition to those mentioned above, can have an effect on waste water characteristics, they are not believed to justify further subcategorization. For example, there are some uranium/radium ores that contain molybdenum and others that do not. Effluent limitations which may restrict molybdenum content must be applied at all times and should not be restricted to those operations which happen to run on ore containing molybdenum. The two subcategories (acid and alkaline) retained reflect not only differences in waste water characteristics but also (a) differences in the volume of waste water that must be stored and managed in a zero-effluent condition and (b) differences in the ultimate disposition of wastes upon shutdown of an operation.

Climatic conditions (such as rainfall versus evaporation factors for a region), although subject to questions of measurement, have an important influence on the existence of present-day point discharges and, thus, have been considered relative to present and future exploitation of uranium reserves in the United States. All exploitable uranium reserves presently economical to develop are found in arid climates. Therefore, no point discharges are needed to manage the raw waste water from most current mining and ore dressing operations in the uranium industry. In addition, other milling operations that now discharge waste water plan to terminate their discharges within a year or two.

Ore characteristics were considered and, within a subcategory, cause short-term effect on waste water characteristics that does not justify further subcategorization. Waste characteristics were, as described above, considered extensively, and it was found difficult to distinguish whether the acid/alkaline leach distinction is based on process, mineralogy, waste characteristics, or treatability of waste water, since all are interrelated. Vanadium operations which are not extracting radioactive ore or covered under government licensing regulations (NRC or agreement states), are subcategorized in the ferroalloys section.

Final Subcategorization of Uranium, Radium, and Vanadium Category

The uranium, radium, and vanadium segment of the mining and ore dressing industry considered here has been separated into the following subcategories for the purpose of establishing effluent guidelines and standards. These subcategories are defined as:

I. Mines which extract (but do not concentrate) ores of uranium, radium, or vanadium.

II. Mills which process uranium, radium, or vanadium ores to yield uranium concentrate and, possibly, vanadium concentrate by either acid or combined acid-and-alkaline leaching.

III. Mills which process uranium, radium, or vanadium ores to yield concentrates by alkaline leaching only.

Metal Ores, Not Elsewhere Classified

This group of metal ores was considered on a metal-by-metal basis because of the wide diversity of mineralogies, processes of extraction, etc. Most of the metal ores in this group do not have high production figures and represent relatively few operations. For this entire group, ore mineralogies and type of process formed the basis of subcategorization. The metals ores examined under this category are ores of antimony, beryllium, platinum, tin, titanium, rare earths (including monazite), and zirconium.

Antimony Ores

Mining and milling of ore for primary recovery of antimony is paracticed at one location in the United States. Although antimony is often found as a byproduct of lead extraction, producers are often penalized for antimony content at a smelter.

Final Antimony-Ore Subcategorization

The antimony ore mining and dressing industry has been separated into two subcategories for the purpose of establishing effluent guidelines and standards. These subcategories are defined as:

I. Mine(s) alone operating for the extraction of ores to obtain primary or byproduct antimony ores.

II. Mill(s) or mine/mill complex(es) using a flotation process for the primary or byproduct recovery of antimony ore.

Beryllium Ores

Beryllium mining and milling in the United States are represented by one operating facility. Therefore, subcategorization consists simply of division into mines and mills:

I. Mine(s) operated for the extraction of ores of beryllium.

II. Mill(s) or mine/mill complex(es) using solvent extraction (sulfuric-acid leach).

Platinum Ores

As discussed previously, most production of platinum in the United States is as byproduct recovery of platinum at a smelter or refinery from base- or other precious-metal concentrates. A single operating location mines and beneficiates ore by use of dredging, followed by gravity separation methods. A single category, thus, is listed for platinum ores:

I. Mine/mill complex(es) obtaining platinum concentrates by dredging, followed by gravity separation and beneficiation.

Rare-Earth Ores

Rare-earth ores currently are obtained from two types of mineralogies: bastnaesite and monazite. Monazite is an ore both of thorium and of rare-earth elements, such as cerium. The subcategorization which follows is based primarily upon division into mines and mills, as well as on the type of processing employed for extraction of the rare- earth elements.

I. Mine(s) operated for the extraction of primary or byproduct ores of rare-earth elements.

II. Mill(s) or mine/mill complex(es) using flotation process and/or leaching of the flotation concentrate for the primary or byproduct recovery of rare-earth minerals.

III. Mill(s) or mine/mill complex(es) operated in conjunction with dredging or hydraulic mining methods; wet gravity methods are used in conjunction with electrostatic and/or magnetic methods for the recovery and concentration of rare-earth minerals (usually, monazite).

Tin Ores

Some tin concentrate was produced at dredging operations in Alaska and placer operations in New Mexico. A single operating facility currently produces tin as a byproduct of molybdenum mining and beneficiation. Other placer deposits of tin may be discovered and could be exploited. Therefore, a single subcategory for mining and one subcategory for milling are listed:

I. Mine(s) operating for the primary or byproduct recovery of tin ores.

II. Mill(s) or mine/mill complex(es) using gravity methods.

Titanium Ores

Titanium ores exploited in the United States occur in two modes and mineralogical associations: as placer or heavy sand deposits of rutile, ilmenite, and leucoxene, and as a titaniferous magnetite in a hard-rock deposit. The titanium ore industry, therefore, is subcategorized as:

I. Mine(s) obtaining titanium ore by lode mining alone.

II. Mill(s) or mine/mill complex(es) using electrostatic and/or magnetic methods in conjunction with gravity and/or flotation methods for primary or byproduct recovery of titanium minerals.

III. Mill(s) or mine/mill complex(es) in conjunction with dredge mining operation; wet gravity methods used in conjunction with electrostatic and/or magnetic methods for the primary or byproduct recovery of titanium minerals.

Zirconium Ores

Zirconium is obtained from the mineral zircon in conjunction with dredging operations. No additional subcategorization is required.

I. Mill(s) or mine/mill complex(es) operated in conjunction with dredging operations. Wet gravity methods are used in conjunction with electrostatic and/or magnetic methods for the primary or byproduct recovery of zirconium minerals.

SUMMARY OF RECOMMENDED SUBCATEGORIZATION

Based upon the preceding discussion and choice of final subcategories, a summary of categories and subcategories recommended for the ore mining and dressing industry is presented here in Table IV-1. The discussions in the following sections, including the recommended effluent limitations in sections IX, X, and XI, will address the categories and subcategories presented in Table IV 1.

FINAL SUBCATEGORIZATION

After an analysis of available treatment technologies and the effluent quality that could be achieved by the application of the available treatment technologies, and the fact that many metals occur in conjunction with other metals, it was determined that the final subcategories previously discussed could be combined into seven subcategories based on the product or products. The seven subcategories can then be further divided into 22 subdivisions for which separate limitations will be set, based on considerations of type of process and waste water characteristics and treatability. The other factors recognized as causing differences in the wastes discharged do not significantly effect the treatability of the wastes within a subcategory. Table IV-2 shows the final subcategorization and the components of each subcategory as they will be presented in the regulations derived from the development document.

TABLE IV-1. SUMMARY OF INDUSTRY SUBCATEGORIZATION RECOMMENDED

CATEGORY		SUBCATEGORIES	
IRON ORES		MINES	
		MILLS	Physical and Chemical Separation, Physical Separation Only
			Magnetic and Physical Separation
COPPER ORES		MINES	Open-Pit, Underground, Stripping
			Hydrometallurgical (Leaching)
		MILLS	Vat Leaching
			Flotation Process
LEAD AND ZINC ORES		MINES	
		MILLS	
GOLD ORES		MINES	
		MILLS	Cyanidation Process
			Amalgamation Process
			Flotation Process
			Gravity Separation
			Byproduct of Base-Metal Operation
SILVER ORES		MINES	
		MILLS	Flotation Process
			Cyanidation Process
			Amalgamation Process
			Gravity Separation
			Byproduct of Base-Metal Operation
BAUXITE ORE		MINES	
FERROALLOY ORES		MINES	
		MILLS	< 5,000 metric tons (5,512 short tons)/year
			> 5,000 metric tons/year by Physical Processes
			> 5,000 metric tons/year by Flotation
			Leaching
MERCURY ORES		MINES	
		MILLS	Gravity Separation
			Flotation Process
			Byproduct of Base/Precious-Metal Operation
URANIUM, RADIUM, & VANADIUM ORES		MINES	
		MILLS	Acid or Acid/Alkaline Leaching
			Alkaline Leaching
METAL ORES, NOT ELSEWHERE CLASSIFIED	ANTIMONY ORES	MINES	
		MILLS	Flotation Process
			Byproduct of Base/Precious-Metal Operation
	BERYLLIUM ORES	MINES	
		MILLS	
	PLATINUM ORES	MINES OR MINE/MILLS	
	RARE EARTH ORES	MINES	
		MILLS	Flotation or Leaching
			Dredging or Hydraulic Methods
	TIN ORES	MINES	
		MILLS	
	TITANIUM ORES	MINES	
		MILLS	Electrostatic/Magnetic and Gravity/Flotation Processes
			Physical Processes with Dredge Mining
	ZIRCONIUM ORES	MILLS OR MINE/MILLS	

TABLE IV-2. FINAL RECOMMENDED INDUSTRY SUBCATEGORIES

SUBCATEGORY	SUBDIVISION	
Iron Ores	Mines	Physical and Chemical Separation Physical Separation Only
	Mills	Magnetic and Physical Separation
Base and Precious Metals	Mines (Open Pit, Underground, Stripping)	Copper Lead and zinc Gold Silver
	Mines	Hydrometallurgical (Leaching) (Copper)
	Mills	Vat Leaching (Copper)
	Mills	Flotation Process (Copper) Flotation Process (Silver) Flotation Process (Lead and zinc) Flotation Process (Gold)
	Mills	Cyanidation Process (Gold) *Cyanidation Process (Silver)*
	Mills	Amalgamation Process (Gold) Amalgamation Process (Silver)
	Mine or Mine/Mills	Gravity Separation (Gold) Gravity Separation (Silver) Gravity Separation (Platinum) Gravity Separation (Tin)
Bauxite Ore	Mines	
Ferroalloy Ores	Mines	>5,000 metric tons
	Mills & Mines	<5,000 metric tons (5,512 short tons/year
	Mills	>5,000 metric tons/year by Physical Processes
	Mills	*>5,000 metric tons/year by Flotation*
	Mills	Leaching
Mercury Ores	Mines	
	Mills	Gravity Separation Flotation Process
Uranium, Radium, & Vanadium Ores	Mines	
	Mills	Acid or Acid/Alkaline Leaching Alkaline Leaching
Antimony Ores	Mines	
	Mills	Flotation Process
Beryllium Ores	Mines	
	Mills	
Rare-Earth Ores	Mines	
	Mills	
Titanium Ores	Mines	
	Mills	Electrostatic/Magnetic and Gravity/ *Flotation Processes*
	Mills or Mine/Mills	Physical Processes with Dredge Mining Zirconium Ores Dredging or Hydraulic Methods (Monazite)

SECTION V

WASTE CHARACTERIZATION

INTRODUCTION

This section discusses the specific water uses in the ore mining and dressing industry, as well as the amounts of process waste materials contained in these waters. The process wastes are characterized as raw waste loads emanating from specific processes used in the extraction of materials involved in this study and are specified in terms of kilograms per metric ton (and as pounds per short ton) of product produced in ore processed. The specific water uses and amounts are given in terms of cubic meters (and gallons) or liters per metric ton (and gallons per short ton) of concentrate produced or ore mined. Many mining operations are characterized by high water inflow and low production, or by production rates that bear little relationship to mine water effluent due to infiltration or precipitation. Where this occurs, waste characteristics are expressed in units of concentration (mg/l = ppm). The discussion of the necessity for reporting the data in this fashion in some instances is discussed below under the heading "Mine Water."

The introductory portions of this section briefly discuss the principal water uses found in all categories and subcategories in the industry. A discussion of each mining and milling subcategory, with the waste characteristics and loads identified for each, concludes this section.

Because of widely varying waste water characteristics, it was necessary to accumulate data from the widest possible base. Effluent data presented for each industry category were derived from historical effluent data supplied by the industry and various regulatory and research bodies, and from current data for effluent samples collected and analyzed during this study. The waste water sampling program conducted during this study had two purposes. First, it was designed to confirm and supplement the existing data. In general, only limited characterization of raw wastes has been previously undertaken by industry. Second, the scope of the water-quality analysis was expanded to include not only previously monitored parameters, but also waste parameters which could be present in mine drainage or mill effluents.

Mine Water

The waste water situation evident in the mining segment of the ore mining and dressing industry is unlike that encountered in most other industries. Usually, most industries (such as the milling segment of this industry) utilize water in the specific processes they employ. This water frequently becomes contaminated during the process and must be treated prior to discharge. In the mining segment, process water is not normally utilized in the actual mining of ores and is present only in placer operations operating by gravity methods, in hydraulic mining, and in dust control. Water is a natural feature that interferes with mining activities. It enters mines by ground-water infiltration and surface runoff and comes into contact with materials in the host rock, ore, and overburden. The mine water then requires treatment depending on its quality before it can be safely discharged into the surface drainage network. Generally, mining operations control surface runoff through the use of diversion ditching, and grading to prevent, as much as possible, excess water from entering the working area. The quantity of water from an ore mine thus is unrelated, or only indirectly related, to production quantities. Therefore, raw waste loadings are expressed in terms of concentration rather than units of production in the ore categories discussed in Section IV.

In addition to handling and treating often massive volumes of mine drainage during active mining operations, metal ore mine operators are faced with the same problems during startup, idle periods, and shutdown. Water handling problems are generally minor during initial startup of a new underground mining operation. These problems may increase as the mine is expanded and developed and may continue after all mining operations have ceased. The long-term drainage from tailing disposal also presents long-term potential problems. Surface mines, on the other hand, are somewhat more predictable and less permanent in their production of mine drainage period. Water handling within a surface mine is fairly uniform throughout the life of the mine. It is highly dependent upon precipitation patterns and precautionary methods employed, such as the use of diversion ditches, burial of toxic materials, and concurrent regrading and revegetation.

Because mine drainage does not necessarily cease with mine closure, a decision must be made as to the point at which a mine operator has fulfilled his obligations and responsibilities for a particular mine site. This point will be further discussed in Section VII, "Control and Treatment Technology."

SPECIFIC WATER USES IN ALL CATEGORIES

Water is used in the ore mining and dressing industry for ten principal uses falling under three major categories. The principal water uses are:

(1) Noncontact cooling water

(2) Process water - wash water
- transport water
- scrubber water
- process and product consumed water

(3) Miscellaneous water -
- dust control
- domestic/sanitary uses
- washing and cleaning
- drilling fluids

Noncontact cooling water is defined as that cooling water which does not come into direct contact with any raw material, intermediate product, byproduct, or product used in or resulting from the process.

Process water is defined as that water which, during the beneficiation process, comes into direct contact with any raw material, intermediate product, byproduct, or product used in or resulting from the process.

Noncontact Cooling Water

The largest use of noncontact cooling water in the ore mining and dressing industry is for the cooling of equipment, such as crusher bearings, pumps, and air compressors.

Wash Water

Wash water comes into direct contact with either the raw material, reactants, or products. An example of this type of water usage is ore washing to remove fines. Waste effluents can arise from these washing sources because the resultant solution or suspension may contain dissolved salts, metals, or suspended solids.

Transport Water

Water is widely used in the ore mining and dressing industry to transport ore to and between various process steps. Water is often used to move crude ore from mine to mill, to move ore from crushers to grinding mills, and to transport tailings to final retention ponds.

Scrubber Water

Wet scrubbers are often used for air pollution control--primarily, in association with grinding mills, crushers, and screens.

Process and Product Consumed Water

Process water is primarily used in the ore mining and dressing industry in wet screening, gravity separation processes (tabling, jigging), heavy-media separation, flotation unit processes (as carrier water), and leaching solutions; it is also used as mining water for dredging and hydraulic mining. Mine water is often pumped from a mine and discharged, but, at many operations, mine water is used as part of processing water at a nearby mill. Water is consumed by being trapped in the intersitual voids of the product and tailings and by evaporation.

Miscellaneous Water

These water uses include dust control (primarily at crushers), truck and vehicle washing, drilling fluids, floor washing and cleanup, and domestic and sanitary uses. The resultant streams are either not contaminated or only slightly contaminated with wastes. The general practice is to discharge such streams without treatment or through leaching fields or septic systems. Often, these streams are combined with process water prior to treatment or discharged directly to tailing ponds. Water used at crushers for dust control is usually of low volume and is either evaporated or adsorbed on the ore.

PROCESS WASTE CHARACTERISTICS BY ORE CATEGORY

Iron Ore

The quality and quantity of water discharged from open-pit and underground iron mining operations and beneficiation facilities vary from operation to operation. In general, the quality of the water in mines is highly dependent on the deposit mined and the substrata through which the water flows prior to entry into the mine.

Sources of Waste. The main sources of waste in iron mining and ore processing are:

(1) Waste water from the mine itself. This may consist of ground water which seeps into the mine, underground aquifers intersected by the mine, or precipitation and runoff which enter from the surface.

(2) Process water, including spillage from thickeners, lubricants, and flotation agents.

(3) Water used in the transport of tailings, slurries, etc., which, because of the volume or impurities involved, cannot be reused in processing or transport without additional treatment.

In most cases, the last category constitutes the greatest amount of waste.

Waste Loads and Variability. Waste loads from mines and processing operations are often quite different, and there is variability on a day-to-day and seasonal basis, both within an operation and between operations. At times, mine water is used as process feed water, and variability in its quality is reflected in the process water discharge.

Nature of Iron Mining Wastes. Mine water can generally be classified as a "clear water," even though it may contain large amounts of suspended solids. The water may, however, contain significant quantities of dissolved materials. If the substrata are high in soluble material (such as iron, manganese, chloride, sulfate, or carbonate), the water will most likely be high in these components. Because rain water and ground water are usually slightly acidic, there will be a tendency to dissolve metals unless carbonates or other buffers are present.

Some turbidity may result from fine rock particles, generated in blasting, crushing, loading, and hauling. This "rock flour" will depend on the methods used in a particular mine and on the nature of the ore.

Nitrogen-based blasting agents have been implicated as a source of nitrogen in mine water. The occurrence of this element (as ammonia, nitrite, or nitrate) would be expected to be highly variable and its concentration a function of both the residual blasting material and the volume of dilution water present.

These effluents in the iron mining operations are generally unrelated to production quantities from the operation. Therefore, waste loadings are expressed in concentration rather than units of production. Constituents which may be present in the mine water are:

(1) Suspended solids resulting from blasting, crushing, and transporting ore; finely pulverized minerals may be a constituent of these suspended solids.

(2) Oils and greases resulting from spills and leakages from material handling equipment.

(3) Natural hardness and alkalinity associated with the host rock or overburden.

(4) Natural levels of salts and nutrients in the intrusive water.

(5) Residual quantities of unburned or partially burned explosives.

Processing Wastes. The processing of ore from the mine may result in the presence of a number of waste materials in the waste water. Some of these are derived from the ore itself, and others are added during processing. Still others are not intentionally added but are inadvertent and inherent contributions.

Dissolved and suspended solids are contributed by the ore to water used in transport and processing. Included in this are metals. The nature and quantity of these are dependent on the nature of the water, the ore, and the length of contact.

During processing, various flotation agents, acids, clays, and other substances may be added and thereby become constituents of waste water. Oil and grease from machinery and equipment may also contaminate the water.

Inadvertent additions include metals (such as zinc) from buildings and machinery, runoff from the plant area and from stockpiles which may contain dissolved and suspended solids, and spills of various substances.

Sanitary sewage from employees and domestic sewage from washrooms, lunchrooms, and other areas is usually disposed of separately from process and transport wastes through municipal or drainfield systems. Even when not, it would be expected to constitute a minor part of the load.

The principal characteristics of the waste stream from the mill operations are:

(1) Loadings of 10 to 50 percent solids (tailings).

(2) Unseparated minerals associated with the tailings.

(3) Fine particles of minerals (particularly, if the thickener overflow is not recirculated).

(4) Excess flotation reagents which are not associated with the iron concentrate.

(5) Any spills of reagents which occur in the mill.

One aspect of mill waste which has been poorly characterized from an environmental-effect standpoint is the excess of flotation reagents. Unfortunately, it is very difficult to detect analytically the presence of these reagents--particularly, the organics. COD, TOC, and surfactant tests may give some indication of the presence of organic reagents, but no definitive information is related by these parameters.

The substances present in mine-water discharges are given in Table V-1; those present in process-water discharges are given in Table V-2. These values are historically representative of what is present before and after discharge to the receiving water. When mine water is used as processing water, its characteristics often cannot be separated from those of the processing water.

As part of this study, a number of mining and beneficiation operations were visited and sampled. The results of the sample analyses show certain potential problem areas with respect to the discharge of pollutants. Summaries of the major chemical parameters in raw wastes from mine and mill water, measured as part of site visits, are given in Tables V-3 and V-4. The basic waste characteristics, on the average, are very similar for both mines and mills. Elevated concentrations of particular parameters tend to associate with a particular mining area or ore body. For example, the dissolved iron and manganese tend to be much higher in Michigan ores than in ores from the mining areas of the Mesabi Range in Minnesota.

In the beneficiation of iron-containing minerals, as much as 27.2 cubic meters of water per metric ton (7,300 gallons per long ton) and as little as 3.4 cubic meters of water per metric ton (900 gallons per long ton) of concentrate may be

TABLE V-1. HISTORICAL CONSTITUENTS OF IRON-MINE DISCHARGES

PARAMETER	CONCENTRATION (mg/ℓ)							
	BEFORE TREATMENT				AFTER TREATMENT			
	MIN	MAX	AVG	NO.	MIN	MAX	AVG	NO.
TSS	1.000	5,000.0	371.51	19	1.000	30.0	10.693	27
TDS	140.0	1,880.0	436.18	17	100.0	1,090.0	390.10	20
COD	0.200	36.0	6.470	10	0.026	42.0	12.116	14
pH	5.00*	8.40*	7.45*	18	6.800*	8.500*	7.652*	21
Oil and Grease	1.800	9.000	4.511	9	0.400	20.400	4.313	16
Al	0.003	0.350	0.066	7	0.007	0.350	0.131	9
Ca	0.003	256.0	85.39	3	0.002	0.158	0.045	4
Cr	0.001	0.010	0.007	9	0.010	0.010	0.010	6
Cu	0.001	1.000	0.167	12	0.005	0.370	0.120	10
Fe	0.060	178.0	13.3	14	0.008	2.100	0.446	11
Pb	0.001	0.100	0.018	9	0.008	0.100	0.023	8
Mg	0.020	118.0	39.35	3	0.008	0.029	0.017	3
Hg	0.002	2.000	1.001	2	-	-	-	-
Ni	0.003	0.100	0.024	6	0.010	0.075	0.023	5
Na	0.023	15.0	7.511	2	-	-	-	-
Mn	0.001	18.0	2.462	14	0.001	6.900	1.720	11
Zn	0.001	8.0	1.869	9	0.010	0.340	0.185	5
Chloride	1.000	120.0	27.143	14	0.900	180.00	33.225	20
Cyanide	0.010	0.02	0.013	4	0.005	0.020	0.011	4

*Value in pH units

TABLE V-2. HISTORICAL CONSTITUENTS OF WASTEWATER FROM IRON-ORE PROCESSING

PARAMETER	CONCENTRATION (mg/ℓ)							
	BEFORE TREATMENT				AFTER TREATMENT			
	MIN	MAX	AVG	NO.	MIN	MAX	AVG	NO.
TSS	1.20	9,999.0	1,894.8	11	0.400	200.0	25.133	15
TDS	0.500	356.0	207.1	10	0.300	1,090.0	393.27	16
COD	0.200	36.0	16.986	7	0.200	90.0	19.518	12
pH	5.000*	8.300*	7.187*	12	6.000*	8.300*	7.259*	16
Oil and Grease	0.030	40.400	14.229	8	0.100	90.0	12.0	13
Al	0.030	5.000	0.994	6	0.009	0.270	0.107	8
Ca	55.0	250.0	120.0	3	82.0	181.0	131.5	2
Cu	-	-	-	-	0.010	0.450	0.230	2
Fe	0.200	10.0	2.568	9	0.050	1.610	0.453	10
Pb	0.100	5.0	3.367	3	0.045	0.250	0.111	4
Ni	0.010	0.050	0.023	3	0.010	0.200	0.087	3
Mn	0.007	20.0	2.772	9	0.016	2.100	0.529	10
Zn	0.006	10.0	3.013	5	0.010	0.115	0.056	4
Chloride	1.000	110.0	22.145	11	0.350	180.0	42.875	15
Cyanide					0.008	0.020	0.013	4

*Value in pH units

TABLE V-3. CHEMICAL COMPOSITIONS OF SAMPLED MINE WATERS

PARAMETER	CONCENTRATION (mg/ℓ) in WASTEWATER FROM MINE												
	Mine 1101	MINE 1106	MINE 1102	1105 - Discharge 1	1105 - Pit Discharge 1	1105 - Pit Discharge 2	1105 - Discharge 2	MINE 1107	1108 - Pre-Mine Drainage	1108 - Mine Drainage	MINE 1109	MINE 1110	Average (All Discharges)
pH	7 3*	7.2*	7.5*	7.2*	7.4*	7.4*	7.6*	8.4*	7 1*	7.2*	8.3*	7.9*	7.54*
Alkalinity	204	–	–	176	–	–	211	218	37.4	118	181	66.0	151
COD	27 4	48 2	9.2	4.5	1.0	18.3	22.8	18	4.5	9.0	27.5	<10	16.7
TSS	2	2	5	30	<1	21	20	6	10	2	12	48	13.25
TDS	455	505	609	246	281	169	271	1,302	118	440	308	1,290	499.5
Conductivity	440†	400†	700†	310†	320†	215†	340†	1,950†	110†	550†	342†	1,125†	566.8†
Total Fe	0.04	<0 02	<0.02	<0 02	<0.02	<0.02	0.18	4.50	2.80	1.30	0.30	1.10	0.86
Dissolved Fe	<0 02	<0 02	<0 02	<0.02	<0.02	<0.02	<0.02	<0.02	<0 02	0.04	0.02	0.08	0.027
Mn	0.21	<0 02	0 40	<0.02	<0.02	0.059	<0.02	3.20	0.025	0.054	0.65	<0.02	0.39
Sulfate	85	175	215	45	28	21	26	152	11.2	33.2	36.7	780	134

*Valuein pH units

†Value in micromhos/cm

TABLE V-4. CHEMICAL COMPOSITIONS OF SAMPLED MILL WATERS

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER FROM MILL							
	1102	1103	1105	1107	1108	1109	1110	
	Tailing-Pond Influent	Tailing-Pond Influent	Tailing-Pond Influent	Tailing-Pond Influent	Tailing-Pond Influent	Tailing-Pond Influent	Tailing-Pond Influent and Minewater	Average (All Mills)
pH	–	7.5*	8.2*	7.6*	7.3*	9.5*	9.00*	8.2*
Alkalinity	–	–	–	–	–	238	13.4	125.7
COD	9.3	<1.0	9.2	22.5	13.5	13.5	11.9	11.5
TSS**	30	12	50	15	12	55	22	28
TDS	533	198	287	712	230	360	2,360	669
Conductance	–	350†	375†	–	130†	262†	1,900†	603†
Total Fe	210.0	90.0	1180.0	0.70	8.20	0.04	< 0.62	212.8
Dissolved Fe	< 0.02	0.06	0.10	< 0.02	0.16	0.04	< 0.02	0.06
Mn	330.0	37.50	320.0	67.0	7.50	16.0	0.032	111.1
Sulfate	175	40	55	236	19.5	20.7	475	146

*Value in pH units

†Value in micromhos

**Expressed in %

used. The average amount of water per metric ton of ore produced is approximately 11.8 cubic meters (3,200 gallons per long ton). Most processing water in beneficiation operations is recycled to some extent. The amount of recycle is dependent on the type of processing and the amount of water that is included in the overall recycle system in the mill.

Mills that employ flotation techniques currently discharge a percentage of their water to keep the concentration of soluble salts from increasing to excessive levels. Soluble salts--especially, those of the multivalent ions--are deleterious to the flotation process, causing excessive reagent use and loss of recoverable iron. Even these operations currently recycle at least 80 percent of their water.

Mills using physical methods of separation (magnetic, washing, jigging, heavy media, spirals, and cyclones) can and do recycle greater than 80 percent of their water. The amount of water discharged from these operations is solely dependent on how much water drains and accumulates into their impoundment systems.

Typical mining operations take the water that accumulates in the mine and pump it either to discharge or to a tailing basin, where a portion is recycled in the processing operation. Mine water is generally settled to remove suspended matter prior to discharge or before use in plant processes. A typical flow scheme for the treatment of mine water is given in Figure V-1.

Process operations generally recycle high percentages of their water. Water in the plant process is used to wash and transport the ore through grinding processes. After separation of the concentrate, the tailings are discharged to a tailing pond, where the coarse and fine waste rock particles settle (Figure V-2). Clarified water is returned to be used in further processing, and a portion is discharged to receiving waters.

Plants or mines that have zero discharge have not been discussed in this section because they discharge no waste materials. It should be pointed out, however, that every plant operation loses water to some degree and has to make up this water loss to maintain a water balance. The main sources of water loss are losses to within the concentrated product, evaporation and percolation of water through

Figure V-1. FLOW SCHEME FOR TREATMENT OF MINE WATER

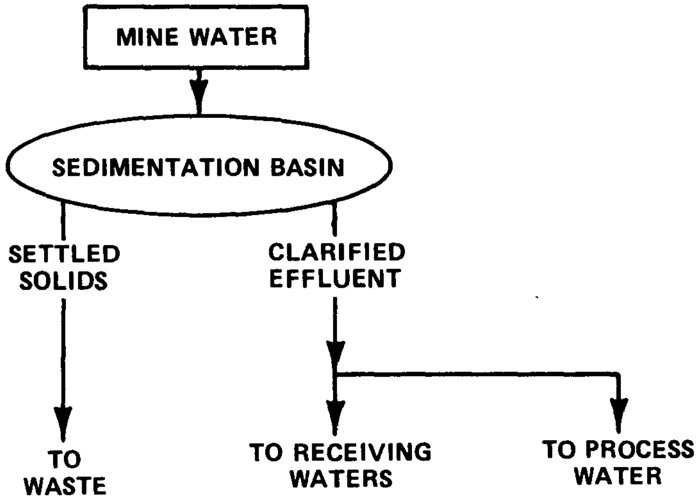
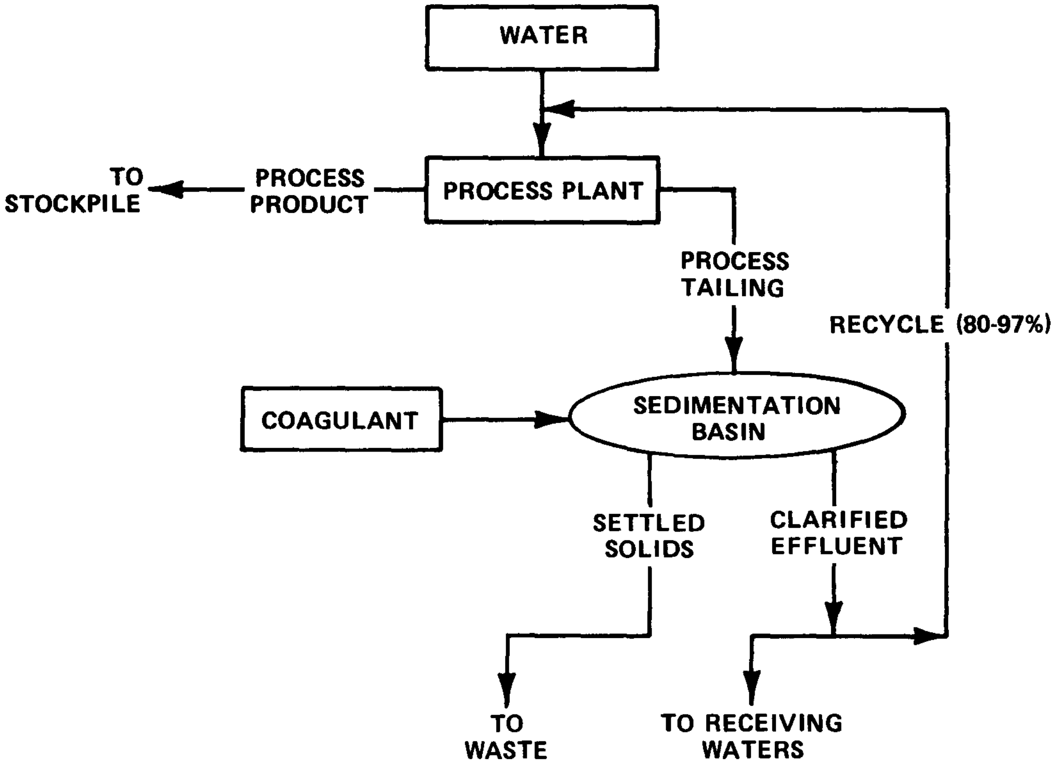


Figure V-2. WATER FLOW SCHEME IN A TYPICAL MILLING OPERATION



impoundment structures, loss of water to the tailings, and evaporation or water loss during processing.

Process Descriptions

The following subsections discuss particular processing operations to demonstrate how water is utilized during different ore processing, the water flow within each system, and the waste loads generated.

Mine and Mill 1105. Mine and mill 1105 is a typical taconite operation. Open-pit mines associated with the operation produce an effluent, and the mill operates with a closed water system.

Crude magnetic taconite is mined, mainly from the lower cherty member of the Minnesota Biwabik formation, by conventional open-pit methods and then milled to produce a fine magnetite. The fine magnetite from the mill is agglomerated in a grate-kiln system to produce approximately 2.64 million metric tons (2.6 million long tons) of oxide pellets annually for blast-furnace feed.

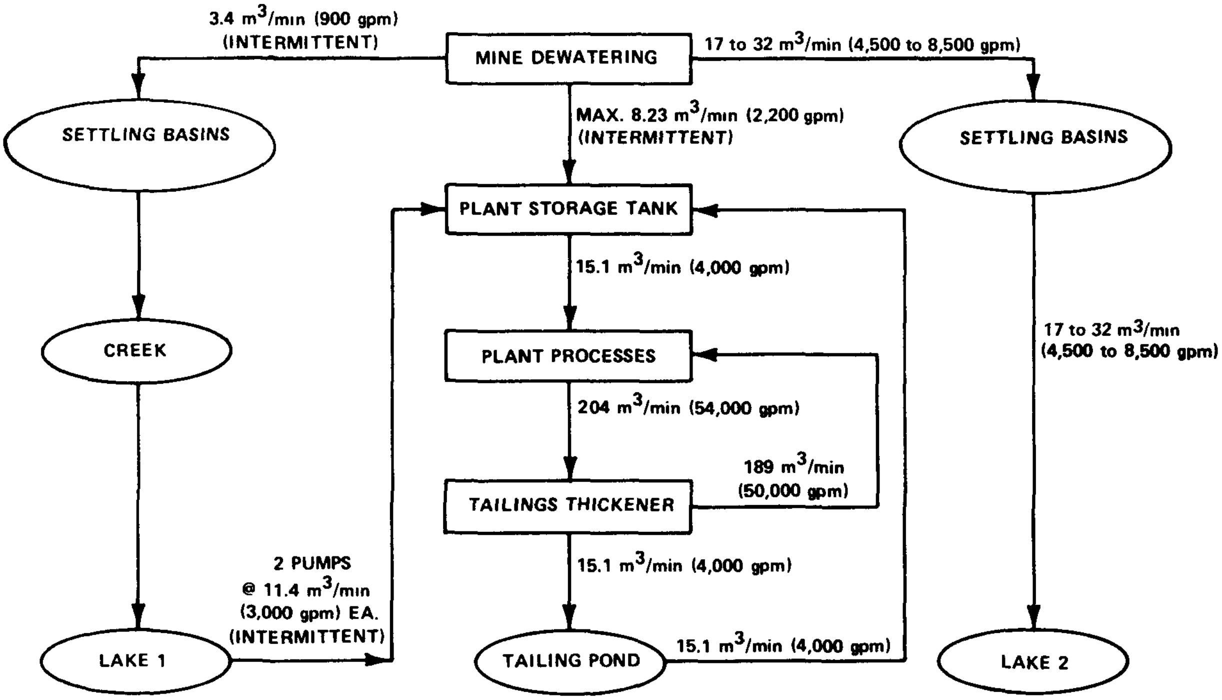
The mine, mill, and pelletizing plant are located on a large site controlled by the operating company, with 8094 hectares (20,000 acres) utilized at present. An initial tailing pond of 405 hectares (1000 acres) has been filled. A second 1,619hectare (4,000-acre) pond is now being used.

An open system is used in mine dewatering. A sketch of the system with flow rates is shown in Figure V-3. Settling basins are used to contain the water before it is discharged to two lakes.

The mill water system is a closed loop. Plant processes use 204 cubic meters per minute (78 mgd), with 189 cubic meters per minute (72 mgd) returned from the 91.4-meter (300-foot) diameter tailing thickener overflow and 15.1 cubic meters per minute (5.7 mgd) returned from the tailing pond or basin. The tailing thickener receives waste or tailings in a slurry from the concentrate pellet plant. A nontoxic, anionic polyacrylamide flocculant is added to the thickener to assist in settling out solids. Tailing thickener underflow is pumped to the tailing basin.

Rotary drilling machines are used in the mine to prepare blast holes for the ammonium nitrate-fuel oil (ANFO) and metallized slurry blasting agents. Electric shovels are used to load the broken ore into 100-ton-capacity diesel/electric trucks for haulage to the primary crusher.

Figure V-3. WATER BALANCE FOR MINE/MILL 1105 (SEPTEMBER 1974)



The 1.52-meter (60-inch) primary crusher is housed in the pit and reduces the ore to a size of less than 0.15 meter (6 inches). From the crusher, coarse ore is conveyed to a storage building.

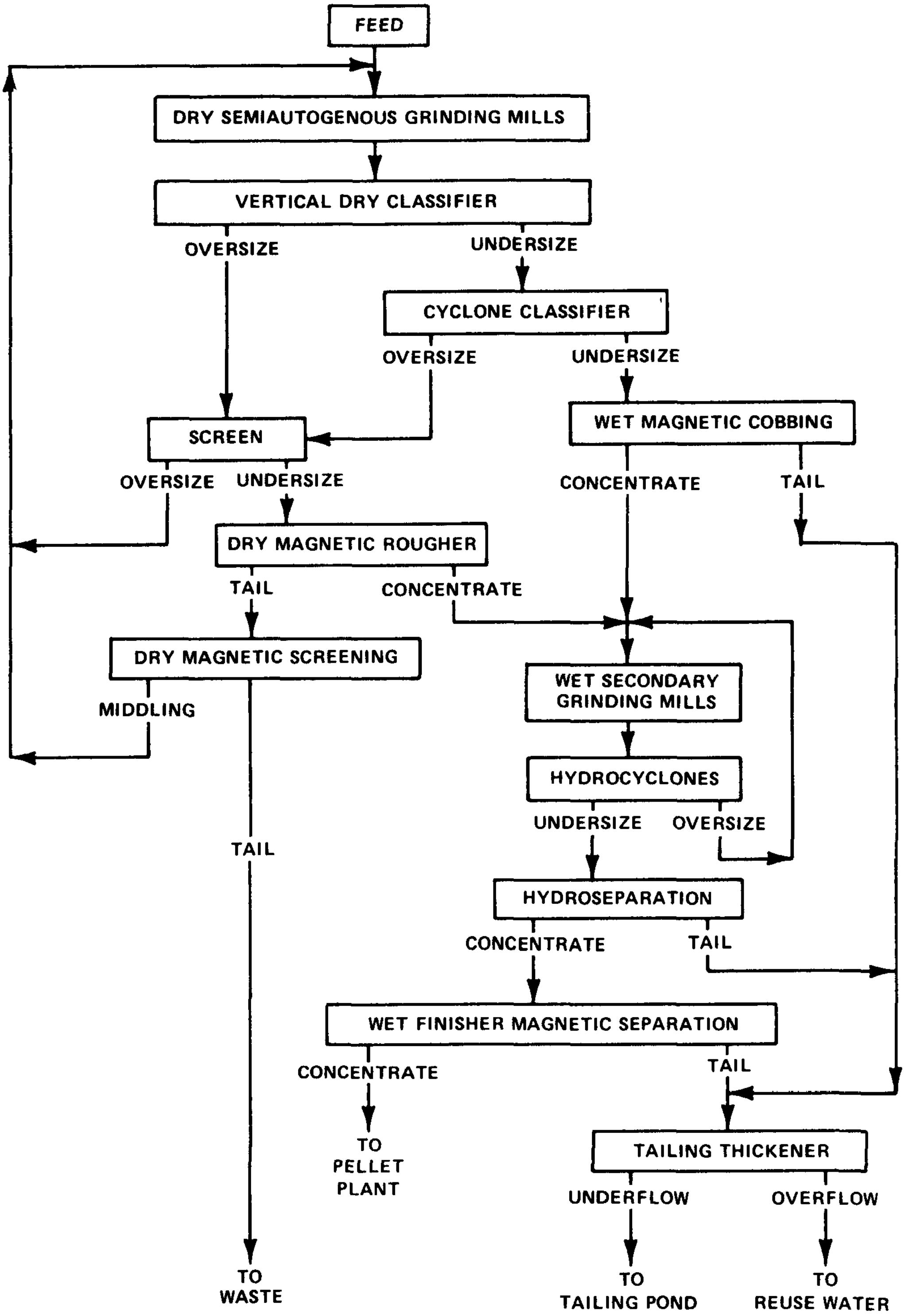
Figure V-4 is a flowsheet showing the physical processing used in the mill. Coarse ore assaying 22 percent magnetic iron is reclaimed from the storage building and ground to 14-mesh size in the primary, air-swept dry grinding system. Broken ore is removed from the mill by a heated air stream and is air classified and screened. The coarse fraction goes to a vertical classifier, and the fine fraction goes to two cyclone classifiers. From the cyclone classifiers, the fine product goes to a wet cobber to recover the magnetics for the secondary grinding circuit. Coarse product of the air classifiers is screened, and the oversize is returned to the primary mill for further grinding. Undersize from the classifiers is separated magnetically to produce a dry cobber concentrate, a dry tailing, and a weakly magnetic material which is recycled for further grinding and concentration. About 37 percent of the crude weight is rejected in the primary circuit.

Dust collected in sweeping the dry mill is pulped with water and fed to a double-drum wet magnetic separator to produce a final tailing and a wet concentrate for grinding in the secondary mills.

Ball mills are used in the secondary wet grinding section to reduce the size of the dry cobber and wet dust concentrates. Slurry from the ball mills is sized in wet cyclones. Oversize from the cyclones is returned to the ball mill. Undersize ore from the cyclones is pumped to hydroseparators. A rising current of water is used in the hydroseparator to overflow a fine silica tailing. Hydroseparator underflow is sent to finisher magnetic separators. The finisher separators upgrade the hydroseparator underflow and produce a fine tailing or discard. Finisher magnetic concentrate can be further upgraded, if necessary, by fine screening and regrinding and then reconcentrating the screen-oversize material.

The final concentrate is thickened and dewatered to about 10 percent moisture prior to the formation of 'green balls' from this material. A bentonite binder is blended with the concentrate before balling in drums. The balling drums are in closed circuit with screens to return undersize material to the drum and to control the green ball size.

Figure V-4. CONCENTRATOR FLOWSHEET FOR MILL 1105



Fines are again removed from the green balls on a roller feeder before they enter a traveling grate. These fines are recirculated to a balling drum or to the pellet plant feed.

Green balls are dried in an updraft and downdraft section of the grate. Dried balls then pass through a preheat section on the grate. The magnetite begins to oxidize, and the balls strengthen while passing through the preheat section.

Balls go directly from the grate to a kiln, where they are baked at 1315 degrees Celsius (2400 degrees Fahrenheit) before they are discharged to a cooler, where oxidation of the pellets is completed and pellet temperature is reduced. The finished pellets contain 67 percent iron and 5 percent silica and are transported for lake shipment to the steel industry.

Mine and Mill 1104. This mine/mill complex is a typical natural ore (one not requiring fine grinding for concentration) operation, with the mine and mill both producing effluents. Physical processes are used in the mill to remove waste material from the iron. The plant processes a hematite/limonite/goethite ore and was placed in operation at the start of the 1962 shipping season. The operation is seasonal for 175 days per year, from the last week in April to about the middle of October.

Mine water from one of the two active pits is pumped to an abandoned mine (settling basin) and overflows to a river at a maximum rate of 7,086 cubic meters per day (1,872,000 gpd) and at an average rate of 5,826 cubic meters per day (1,539,000 gpd) per day at Discharge No 1. Mill process water, mine drainage from the other pit, and fine tailings from the mill are pumped to a 105-hectare (260-acre) tailing basin. Process water is recycled from the basin at a rate of 45 cubic meters (12,000 gallons) per minute. Excess water from the tailing basin is siphoned to a lake intermittently at an average rate of 3,717 cubic meters (981,900 gallons) per day at Discharge No. 2. Table V-5 is a compilation of the chemical characteristics and waste loads present in mine water (Discharge No. 1--concentration only) and combined mine and mill process effluent.

Mining is carried out by conventional open-pit methods. Ammonium nitrate explosives are used in blasting. Shovels load the ore into trucks for transport to the plant.

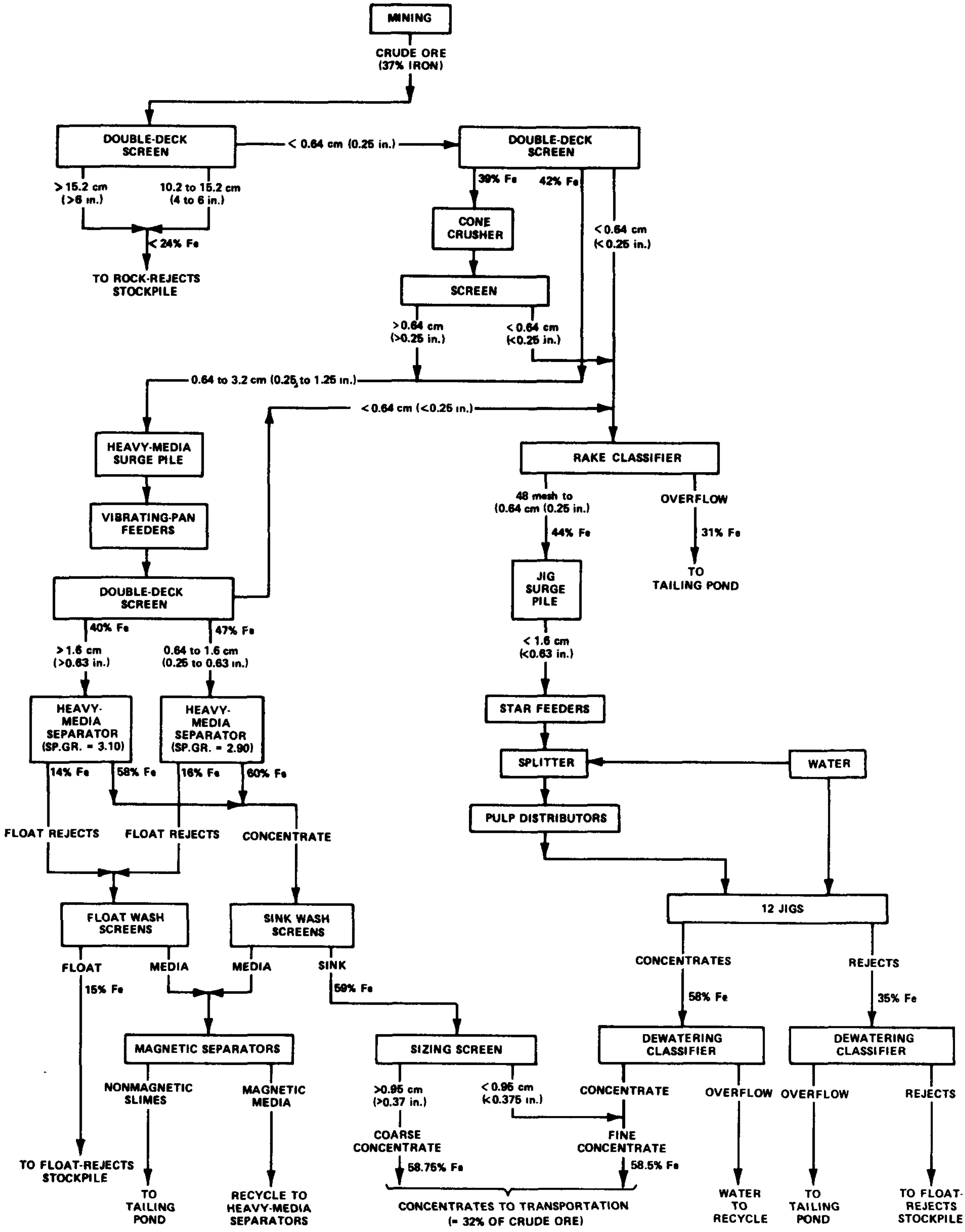
At the mill, the ore, averaging 37 percent iron, is fed to a preparation section for screening, crushing, and scrubbing. A plant flowsheet is shown in Figure V-5.

TABLE V-5. CHEMICAL ANALYSIS OF DISCHARGE 1 (MINE WATER) AND DISCHARGE 2 (MINE AND MILL WATER) AT MINE/MILL 1104, INCLUDING WASTE LOADING FOR DISCHARGE 2

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER		RAW WASTE LOAD	
	DISCHARGE 1	DISCHARGE 2	g/metric ton	lb/short ton
pH	6.7*	7.3*	–	–
TSS	6	6	3.8	0.0074
TDS	263	210	132	0.26
Total Fe	<0.02	<0.02	<0.013	<0.00003
Dissolved Fe	<0.02	<0.02	<0.013	<0.00003
Mn	<0.02	<0.02	<0.013	<0.00003

*Value in pH units

Figure V-5. FLOWSHEET FOR MILL 1104 (HEAVY-MEDIA PLANT)



Reversible conveyors permit rock coarser than 10.2 centimeters (4 inches) from the first stage of screening to be removed as a reject and stockpiled or processed further depending on the quality of the oversize material. Plant feed is processed in a crusher/screen circuit to produce fractions which are 3.2 cm by 0.64 cm (1.25 inches by 0.25 inch) and less than 0.64 cm (0.25 inch). The material which is 3.2 cm by 0.64 cm (1.25 inches by 0.25 inch) goes to a heavymedia surge pile. The fraction which is less than 0.64 cm (0.25 inch) after classification to remove tailings which are less than 48 mesh is sent to a jig surge pile.

Material from the heavy-media surge pile is split into fractions which are 3.2 cm by 1.6 cm (1.25 inches x 0.63 inch) and 1.6 cm x 0.64 cm (0.63 inch by 0.25 inch). Both fractions go to identical sink/float treatment in a ferrosilicon suspension. Float rejects or tailings from the heavy suspension treatment are trucked to a stockpile. Concentrates go directly to a railroad loading pocket. The ferrosilicon medium is recovered by magnetic separation. The magnetic medium is recycled to the process. Nonmagnetic slimes go to the tailing pond. The material which is less than 0.64 cm (0.25 inch) but greater than 48 mesh goes from the surge pile to jigs, where pulsating water is used to separate the concentrate and tailing. Concentrates are dewatered before shipment, and water from this operation is recycled in the plant. Jig tailings are sent to a dewatering classifier. Sands from the classifier are trucked to a reject pile. Overflow from the classifier is pumped to the tailing basin.

Concentrates produced in the plant are shipped by rail and boat to the lower Great Lakes. The 58-percent-iron heavy-media concentrate serves as blast-furnace feed. The 58-percentiron jig concentrate is later sintered at the steel plant before entering the blast furnace.

Mine and Mill 1108. This mine/mill complex is located in Northern Michigan. The ore body consists of hematite (major economic material), magnetite, martite, quartz, jasper, iron silicates, and minor secondary carbonates. All of the constituents appear in the tailing deposit. The concentration plant processes approximately 21,000 metric tons (20,700 long tons) per day of low-grade hematite at 35.5 percent iron to produce approximately 9,850 metric tons (9,700 long tons) per day of concentrated ore at 65.5 percent iron. The remaining 11,200 metric tons (12,346 short tons), at approximately 10 percent total iron, are discharged to the tailing basin.

Mine water is currently pumped from the actively mined pit and discharged directly. The chemical constituents of the discharged water are given in Table V-6.

Water in the concentration process is utilized at a rate of 114 cubic meters (30,000 gallons) per minute. Ore is first ground to a fine state (80 percent less than 325 mesh) and the slime materials removed by wet cycloning. A simplified flow scheme is included in Figure V-6. Subsequently, the concentrated ore is floated using tall oil - fatty acid. The flotation underflows are discharged to a tailing stream, which is discharged directly to a 385-hectare (950-acre) tailing basin. Approximately 80 percent of the water from the tailing pond is returned to the concentrating plant as reuse water (untreated). The remaining 20 percent is discharged, after treatment, to a local creek. This discharged waste water is first treated with alum, then with a long-chain polymer to promote flocculation. It then passes to a 8.5-hectare (21-acre) pond, where the flocculated particles settle. The concentration of chemical parameters and the waste loading in this discharge are given in Table V-7.

<u>Copper Ore</u>

Frequently, discharged wastes encountered in the copper ore mining and dressing industry include waste streams from mining, leaching, and milling processes. These waste streams are often combined for use as process water or treated together for discharge. Other wastes encountered in this segment are discharge wastes from copper smelting and refining facilities, treated sewage effluent, storm drains, and filter backwash. The uses of water in copper mining and milling are summarized below.

I. Mining:
    a. Cooling
    b. Dust control
    c. Truck washing
    d. Sanitary facilities
    e. Drilling

II. Hydrometallurgical processes associated with mining: Dump, heap, and *in situ* leaching solutions.

III. Milling Processes:
    a. Vat leach
        1. crusher dust control

TABLE V-6. CHEMICAL CHARACTERISTICS OF DISCHARGE WATER FROM MINE 1108

PARAMETER	CONCENTRATION (mg/ℓ)
pH	7.2*
Alkalinity	118
COD	9.0
TSS	2
TDS	440
Total Fe	1.3
Dissolved Fe	0.04
Mn	0.054
Sulfate	33.2

*Value in pH units

Figure V-6. SIMPLIFIED CONCENTRATION FLOWSHEET FOR MINE/MILL 1108

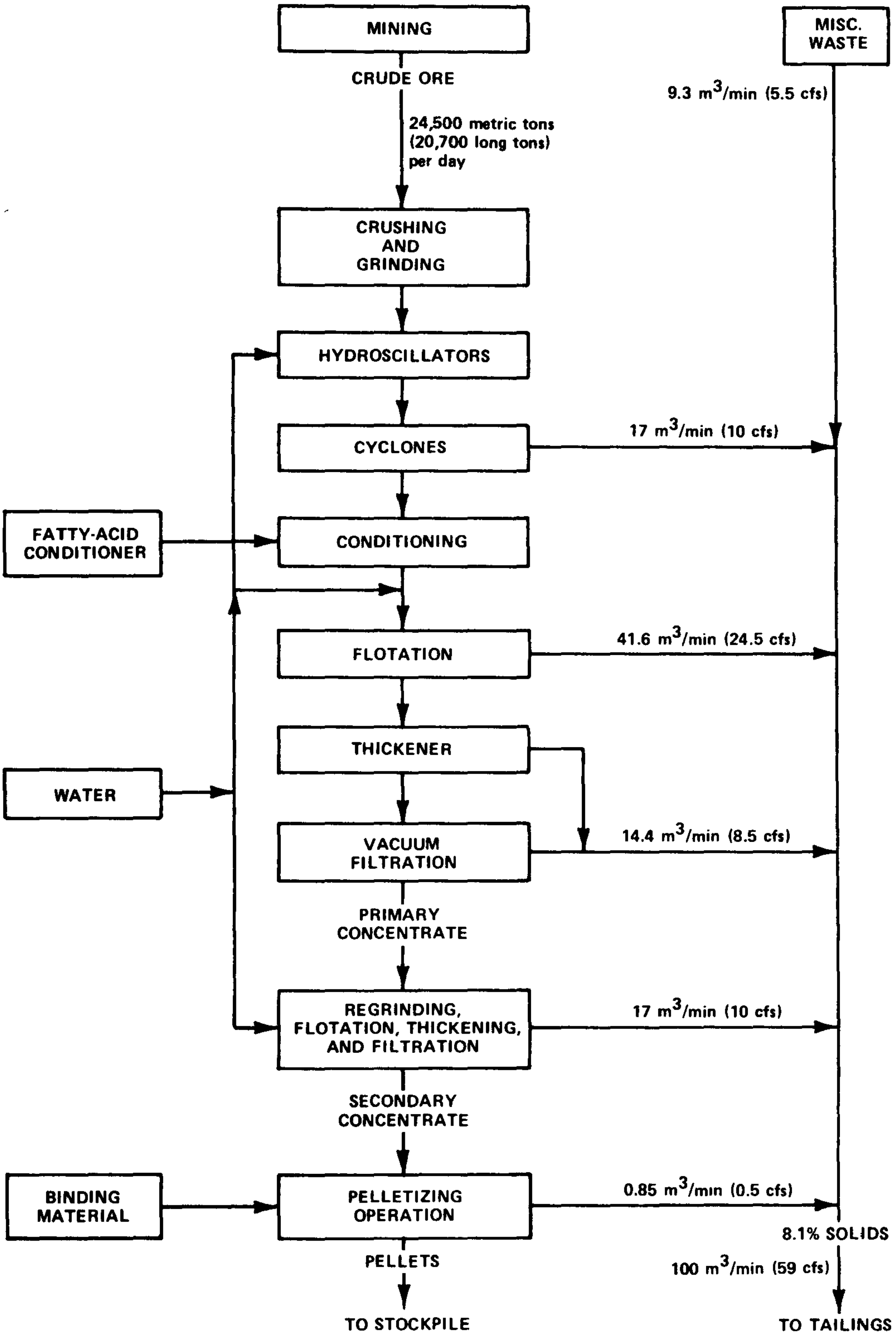


TABLE V-7. CHARACTERISTICS OF MILL 1108 DISCHARGE WATER

PARAMETER	PROGRAM SAMPLE		10-MONTH AVERAGES			
	CONCENTRATION (mg/ℓ) IN WASTE WATER	WASTE LOAD in g/metric ton (lb/short ton) PRODUCT	AVERAGE CONCENTRATION (mg/ℓ)	WASTE LOAD in g/metric ton (lb/short ton) PRODUCT	HIGH CONCENTRATION (mg/ℓ)	LOW CONCENTRATION (mg/ℓ)
pH	7.1*	–	7.0*	–	7.9*	6.5*
Alkalinity	62.0	213 (0.42)	–	–	–	–
COD	22.5	77.4 (0.15)	–	–	–	–
TSS	10	3.4 (0.007)	8.6	20.7 (0.040)	53	1
TDS	160	550 (1.08)	–	–	–	–
Total Fe	2.05	7.05 (0.013)	–	–	–	–
Dissolved Fe	0.93	3.2 (0.006)	0.76	1.83 (0.0036)	3.60	0.01
Mn	0.05	0.17 (0.0003)	0.66	1.59 (0.0031)	5.80	0.01
Sulfate	5	17.2 (0.034)	–	–	–	–

*Value in pH units

        2. Vat leach solution
        3. Wash solutions
    b. Flotation
        1. Crusher dust control
        2. Carrier water for flotation

Copper Ore Mining. Most of the domestic copper is mined in low-grade ore bodies in the western United States. All mining and milling activities adjust to the type of copper mineralization which is encountered. The principal minerals exploited may be grouped as oxides or sulfides and are listed in Table V-8. Porphyry copper deposits account for 90 percent of the domestic copper ore production and are mined by either blockcaving or open-pit methods. The choice of method is determined by the size, configuration, and depth of the ore body.

Open-pit (undercut) mining accounted for 83 percent of the copper produced in the United States in 1968. The mining sequence includes drilling, blasting, loading, and transportation. Primary drilling involves sinking vertical or near-vertical blast holes behind the face of an unbroken bank. Secondary drilling is required to break boulders too large for shovels to handle, or to blast unbroken points of rock that project above the digging grade in the shovel pit. Ore and overburden are loaded by revolving power shovels and hauled by large trucks (75 to 175 ton capacity) or by train. Ore and waste may be moved by tractor-drawn scrapers or belt conveyors. Some mines have primary crushers installed in the pit which send crushed and semi-sorted material by conveyor to the mill.

In 1968, 445 million metric tons (490 million short tons) of waste material were discarded (mostly from open-pit operations) after production of 154 million metric tons (170 million short tons) of copper ore. The cutoff grade of ore, which designates it as waste, is usually less than 0.4 percent copper. However, oxide mineralization of 0.1 to 0.4 percent copper in waste is separated and placed in special dump areas for leaching of copper by means of sulfuric acid.

Underground mining methods provided 17 percent of the U.S. copper in 1968. Deep deposits have been mined by either caving or supported stopes. Caving methods include block caving and sublevel caving. For supported stope mining, installation of systematic ground supports is a necessary part of the mining cycle. In underground mining, solid waste may be left behind. More than 60 percent of the material produced is discarded as too low in copper content

TABLE V-8. PRINCIPAL COPPER MINERALS USED IN THE UNITED STATES

MINERAL	COMPOSITION	OCCURRENCE*
	SULFIDES	
Chalcocite	Cu_2S	SW, NW, NC,**
Chalcopyrite	$CuFeS_2$	SW, NW, **
Bornite	Cu_5FeS_4	NW, SW
Covellite	CuS	NW, SW
Enargite	Cu_3AsS_4	NW
	OXIDES	
Chrysocolla	$CuSiO_3 \cdot H_2O$	SW**
Malachite	$Cu_2(OH)_2 \cdot CO_3$	SW, NW**
Azurite	$Cu_3(OH)_2 \cdot (CO_3)_2$	SW, NW**
Cuprite	Cu_2O	SW
Tenorite	CuO	SW
	NATIVE ELEMENTS	
Copper	Cu	NC, SW**

*SW = Southwest U.S.
NW = Northwest U.S.
NC = Northcentral U.S.

**Major minerals

or as oxide ore, which does not concentrate economically by flotation.

Water Sources and Usage. In the mining of copper ores, water collected from the mines may originate from subsurface drainage or infiltration from surface runoff, or from water pumped to the mine when its own resources are insufficient. A minimal amount of water in mining is needed for cooling, drilling, dust control, truck washing, and/or sanitary facilities (Figure V-7). For safety, excess mine water not consumed by evaporation must be pumped from the mines. Table V-9 lists the amount of mine water pumped from selected mines and the ultimate fate of this waste water at surveyed mines. Open-pit mines pumped 0 to 0.27 cubic meter per metric ton (0 to 64.7 gallons per short ton) of ore produced, while underground mines pumped 0.008 to 3.636 cubic meters per metric ton (1.91 to 871 gallons per short ton) of ore produced.

Solid wastes produced are summarized in Table V-10 as metric tons (or short tons) of waste (actually, overburden and wastes) per metric ton (short ton) of ore produced. Underground operations rarely have waste. Those mines which do produce wastes yield relatively small amounts in comparison to open-pit mining operations.

Air quality control within open-pit mines consists of spraying water on roads for dust control. Underground mines may employ scrubbers, which produce a sludge of particulates. The sludge is commonly evaporated or settled in holding ponds.

Waste Water Characterization. The volume of mine water pumped from mines was previously summarized in Table V-9. The chemical characteristics of these waters are summarized in Table V-11, which includes the flow per day, concentration of constituents, and raw-waste load per day.

A portion of the copper industry (less than 5 percent) must contend with acid mine water produced by the percolation of natural water through copper sulfide mineralization associated with deposits of pyrite (FeS_2). This results in acid water containing high concentrations of iron sulfate. Acid iron sulfate oxidizes metal sulfides to release unusually high concentrations of trace elements in the mine water. The pH of mine water most often is in the range of 4.0 to 8.5. In the southwestern U.S., mine water is obtained from underground shafts, either in use or abandoned on the property. This source of water is valuable and is used for other copper-producing processes. In contrast,

Figure V-7. WASTEWATER FLOWSHEET FOR PLANT 2120-B PIT

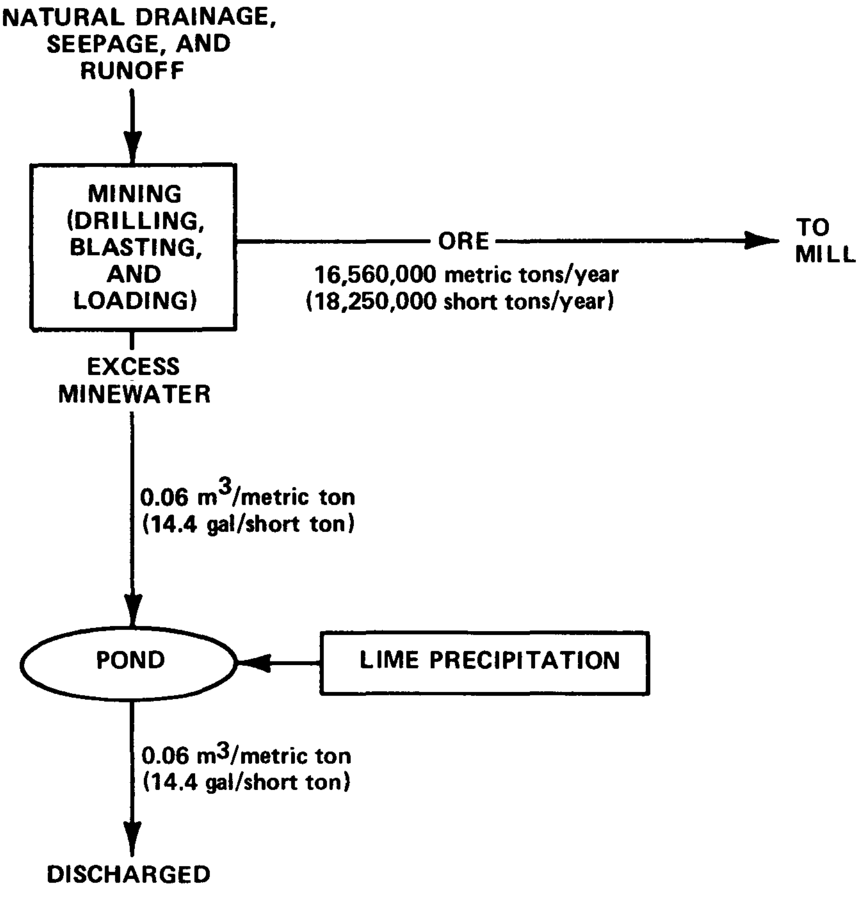


TABLE V-9. MINE-WATER PRODUCTION FROM SELECTED MAJOR COPPER-PRODUCING MINES AND FATE(S) OF EFFLUENT

MINE	TYPE*	MINE-WATER PRODUCTION m^3/metric ton ore produced	MINE-WATER PRODUCTION gal/short ton ore produced	EFFLUENT FATE(S)
2101	OP	0.270	64.7	Reuse in Dump Leach
2102	UG	0.008	1.85	Reuse in Mill and Leach
2103	OP	N.E.	N.E.	Mine above Water Table
2104	OP	0.086	20.6	Reuse in Dump Leach
2107	UG	N/A	N/A	Reuse in Mill
2108	OP	N.E.	N.E.	Evaporation and Seepage in Mine
2109	OP	N.E.	N.E.	Evaporation and Seepage in Mine
2110	OP	N.E.	N.E.	Evaporation and Seepage in Mine
2111	OP	N.E.	N.E.	Evaporation and Seepage in Mine
2113	OP	0.015	3.5	Reuse in Mill
2114	OP	40.5 (avg)†	9,715.0(avg)†	Discharged
2115	UG	1.769	424.0	Reuse in Mill
2116	OP	0.030	7.1	Reuse in Leaching
2117	UG	0.886	212.3	Discharged
2118	OP	0.014	3.4	Reuse in Dump Leach
2119	UG	0.654	156.7	Reuse in Mill
2120	UG,OP	0.486	116.4	Discharged
2121	UG	0.170	40.85	Discharged
2122	OP	0.034	8.1	Reuse in Dump Leach
2123	OP	0.075	18.0	Reuse in Mill
2124	OP	N.E.	N.E.	Evaporation and Seepage in Mine

* OP = open pit; UG = underground.

† 0 to 81.1 m^3/metric ton (0 to 19,432 gal/short ton) ore produced; variable due to seasonal rainfall and open-pit operations; average calculated assuming six dry (0) and six wet (81.1-m^3/19,432-gal) months.

N/A = not available

N.E. = no effluent

TABLE V-10. SUMMARY OF SOLID WASTES PRODUCED BY PLANTS SURVEYED

MILL MILL	HAULED WASTE (1973)		MILL ORE (1973)		RATIO (WASTE/ORE)
	metric tons	short tons	metric tons	short tons	
2101	34,765,038*	38,321,250*	7,198,015	7,934,320	4.83
2102	19,534,193*	21,532,400*	7,967,575	8,782,600	2.45
2103	51,903,633	57,213,000	13,977,230	15,407,000	3.71
2104	20,075,681*	22,129,279*	7,349,938	8,101,784	2.73
2107	0 (UG)	0 (UG)	N/A	N/A	–
2108	11,400,238*	12,566,400*	3,562,574	3,927,000	3.20
2109	24,222,246	26,700,000	1,567,460	1,727,800	15.45
2110	104,328	115,000	3,712,262	4,092,000	0.03
2111	8,545,824	9,420,000	1,480,550	1,632,000	5.77
2112	45,360 (UG)	50,000 (UG)	635,040	700,000	0.07
2113	17,938,604	19,773,594	9,383,475	10,343,337	1.91
2114	10,886,400†	12,000,000†	130,386	143,723	83.5†
2115	18,144 (UG)	20,000 (UG)	471,375	519,593	0.04
2116	32,257,310*	35,557,000*	11,465,193	12,638,000	2.81
2117	0 (UG)	0 (UG)	1,211,680	1,335,626	–
2118	33,623,553*	37,063,000*	16,656,192	18,360,000	2.02
2119	82,737 (UG)	91,200 (UG)	19,935,266	21,974,500	0.004
2120	33,112,800*	36,500,000*	23,342,256	25,730,000	1.42
2121	0 (UG)	0 (UG)	8,059,688	8,884,136	–
2122	88,452,000*	97,500,000*	34,745,760	38,300,000	2.55
2123	10,886,400 *	12,000,000*	1,970,438	2,172,000	5.53
2124	15,339,844	16,909,000	7,912,598	8,722,000	1.94

* All or a portion leached

† Stripping operation

N/A = Not available

UG = Underground

TABLE V-11. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES (Sheet 1 of 4)

PARAMETER	MINE 2119			MINE 2120-K		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	42,013.5m^3/day	752 m^3/1000 metric tons	180,332 gal/1000 short tons	27,524.5m^3/day	15,173 m^3/1000 metric tons	3,635,997 gal/1000 short tons
pH	9.64*	9.64*	9.64*	3.49*	3.49*	3.49*
TDS	544	418.5	837.0	4,590	69,630.3	139,260.6
TSS	8	6.2	12.4	4	60.7	121.4
Oil and Grease	1	0.77	1.54	< 1.0	< 15.17	< 30.34
TOC	5	3.85	7.70	31	7.13	14.26
COD	<10	< 7.69	<15.38	20	303.4	606.8
B	0.2	0.154	0.308	0.10	1.52	3.04
Cu	0.5	0.385	0.770	92.0	1,395.6	2,791.2
Co	< 0.05	< 0.038	< 0.076	0.32	4.85	9.7
Se	< 0.003	< 0.002	< 0.004	N/A	N/A	N/A
Te	< 0.50	< 0.385	< 0.770	< 0.02	< 3.03	< 6.06
As	< 0.07	< 0.054	< 0.108	< 0.07	< 1.06	< 2.12
Zn	< 0.05	< 0.038	< 0.076	172.0	2,609.2	5,218.4
Sb	< 0.2	< 0.154	< 0.308	< 0.5	< 7.59	< 15.17
Fe	3.80	2.923	5.846	2,000.0	30,340	60,680
Mn	< 0.05	< 0.0385	< 0.0770	100	1,517	3,034
Cd	< 0.05	< 0.0385	< 0.0770	0.33	5.01	10.02
Ni	< 0.10	< 0.077	< 0.154	0.24	3.64	7.28
Mo	< 0.2	< 0.154	< 0.308	< 0.5	< 7.59	< 15.17
Sr	0.13	0.10	0.20	1.35	20.48	40.96
Hg	0.0008	0.00062	0.00124	0.0784	1.19	2.38
Pb	< 0.05	< 0.038	< 0.076	< 0.1	< 1.52	< 3.04

*Value in pH units

TABLE V-11. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES (Sheet 2 of 4)

PARAMETER	MINE 2120-B			MINE 2120-CE		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	2,725.2m^3/day	60.08 m^3/1000 metric tons	14,400 gal/1000 short tons	272.52m^3/day	17.685 m^3/1000 metric tons	4,239 gal/1000 short tons
pH	6.1*	6.1*	6.1*	4.7*	4.7*	4.7*
TDS	2,152	129.3	258.6	454	8.03	16.06
TSS	40	2.4	4.8	34	0.60	1.2
Oil and Grease	< 1.0	< 0.060	< 0.12	17.0	0.30	0.6
TOC	3.2	0.192	0.384	2.3	0.041	0.082
COD	< 10	< 0.601	< 1.202	< 10	< 0.177	< 0.354
B	0.04	0.002	0.004	0.01	0.0002	0.0004
Cu	5.30	0.318	0.636	6.2	0.11	0.22
Co	0.1	0.006	0.012	0.06	0.0011	0.0022
Se	0.007	0.0004	0.0008	0.042	0.00074	0.00148
Te	< 0.2	< 0.012	< 0.024	< 0.2	< 0.0035	< 0.007
As	< 0.07	< 0.004	< 0.008	< 0.07	< 0.0012	< 0.0024
Zn	31.25	1.88	3.76	6.17	0.109	0.218
Sb	< 0.5	< 0.03	< 0.06	< 0.5	< 0.009	< 0.018
Fe	6.00	0.361	0.722	8.6	0.152	0.304
Mn	26.5	1.592	3.184	1.42	0.025	0.05
Cd	1.3	0.781	1.562	0.034	0.0006	0.0012
Ni	0.13	0.008	0.016	< 0.05	< 0.0009	< 0.0018
Mo	< 0.5	< 0.03	< 0.06	< 0.5	< 0.009	< 0.018
Sr	1.55	0.093	0.186	0.09	0.002	0.004
Hg	0.0005	0.00003	0.00006	0.0005	0.000009	0.000018
Pb	< 0.1	< 0.006	< 0.012	< 0.1	< 0.002	< 0.004

*Value in pH units

TABLE V-11. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES (Sheet 3 of 4)

PARAMETER	MINE 2121			MINE 2122		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	3,815.3m^3/day	17.28 m^3/1000 metric tons	4,141 gal/1000 short tons	3,274m^3/day	34 m^3/1000 metric tons	8,053 gal/1000 short tons
pH	7.37*	7.37*	7.37*	7.61*	7.61*	7.61*
TDS	29,250	5,053.9	10,107.8	2,288	78.69	157.38
TSS	69	11.9	23.8	2	0.069	0.138
Oil and Grease	< 1.0	< 0.173	< 0.346	3	0.103	0.206
TOC	< 4.5	< 0.778	< 1.556	21	0.722	1.444
COD	819	141.5	283	38.9	1.34	2.68
B	2.19	0.378	0.756	0.11	0.004	0.008
Cu	0.87	0.150	0.3	1.90	0.065	0.130
Co	< 0.04	< 0.007	< 0.014	1.90	0.065	0.130
Se	< 0.077	< 0.013	< 0.026	< 0.003	< 0.0001	< 0.0002
Te	0.60	0.104	0.208	0.2	0.007	0.014
As	< 0.07	< 0.012	< 0.024	< 0.07	< 0.002	< 0.004
Zn	2.8	0.484	0.968	1.33	0.046	0.092
Sb	< 0.5	< 0.086	< 0.172	< 0.2	< 0.007	< 0.014
Fe	< 0.1	< 0.017	< 0.034	9.5	0.327	0.654
Mn	2.22	0.384	0.768	0.83	0.029	0.058
Cd	< 0.02	< 0.003	< 0.006	< 0.05	< 0.002	< 0.004
Ni	< 0.05	< 0.009	< 0.018	0.13	0.004	0.008
Mo	< 0.5	< 0.086	< 0.172	< 0.2	< 0.007	< 0.014
Sr	119	20.6	41.2	0.83	0.029	0.058
Hg	< 0.0001	< 0.00002	< 0.00004	< 0.0001	< 0.000003	< 0.000006
Pb	< 0.1	< 0.017	< 0.034	< 0.5	< 0.017	< 0.034

*Value in pH units

TABLE V-11. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES (Sheet 4 of 4)

PARAMETER	MINE 2123		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT ORE MINED	
		kg/1000 metric tons	lb/1000 short tons
Flow	409m^3/day	75 m^3/1000 metric tons	18,000 gal/1000 short tons
pH	6.96*	6.96*	6.96*
TDS	1,350	101	202
TSS	2	0.2	0.4
Oil and Grease	7	0.5	1.0
TOC	10	0.75	1.5
COD	4	0.3	0.6
B	0.07	0.005	0.01
Cu	1.05	0.08	0.16
Co	< 0.06	< 0.005	< 0.01
Se	0.096	0.007	0.014
Te	< 0.2	< 0.02	< 0.04
As	< 0.01	< 0.0008	< 0.0016
Zn	0.1	0.008	0.016
Sb	< 0.5	< 0.04	< 0.08
Fe	< 0.1	< 0.008	< 0.016
Mn	0.9	0.07	0.14
Cd	< 0.03	< 0.002	< 0.004
Ni	< 0.05	< 0.004	< 0.008
Mo	< 0.2	< 0.02	< 0.04
Sr	0.8	0.06	0.12
Hg	< 0.0001	< 0.000008	< 0.000016
Pb	< 0.5	< 0.04	< 0.08

*Values in pH units

mine water in Utah, Montana, Colorado, Idaho, Oklahoma, Michigan, Maine, and Tennessee--especially, in underground mines--is often unwanted excess, which must be disposed of if reuse in other processes (such as leaching and flotation) is not possible.

The primary chemical characteristics of mine waters are: (1) occasional presence of pH of 2.0 to 9.5; (2) high dissolved solids; (3) oils and greases; and (4) dissolved metals. Often, mine water is characterized by high sulfate content, which may be the result of sulfide-ore oxidation or of gypsum deposits. Mine water--particularly, acid mine water--may cause the dissolution of metals such as aluminum, cadmium, copper, iron, nickel, zinc, and cobalt. Selenium, lead, strontium, titanium, and manganese appear to be indicators of local mineralogy and are not solubilized additionally by acid mine water.

Handling of Mine Water. As shown in Table V-9, mine waters are pumped to leach and mill operations as a water source for those processes whenever possible. However, four of the plants surveyed discharge all of their mine water to surface waters. Half of these treat the water first by lime precipitation and settling.

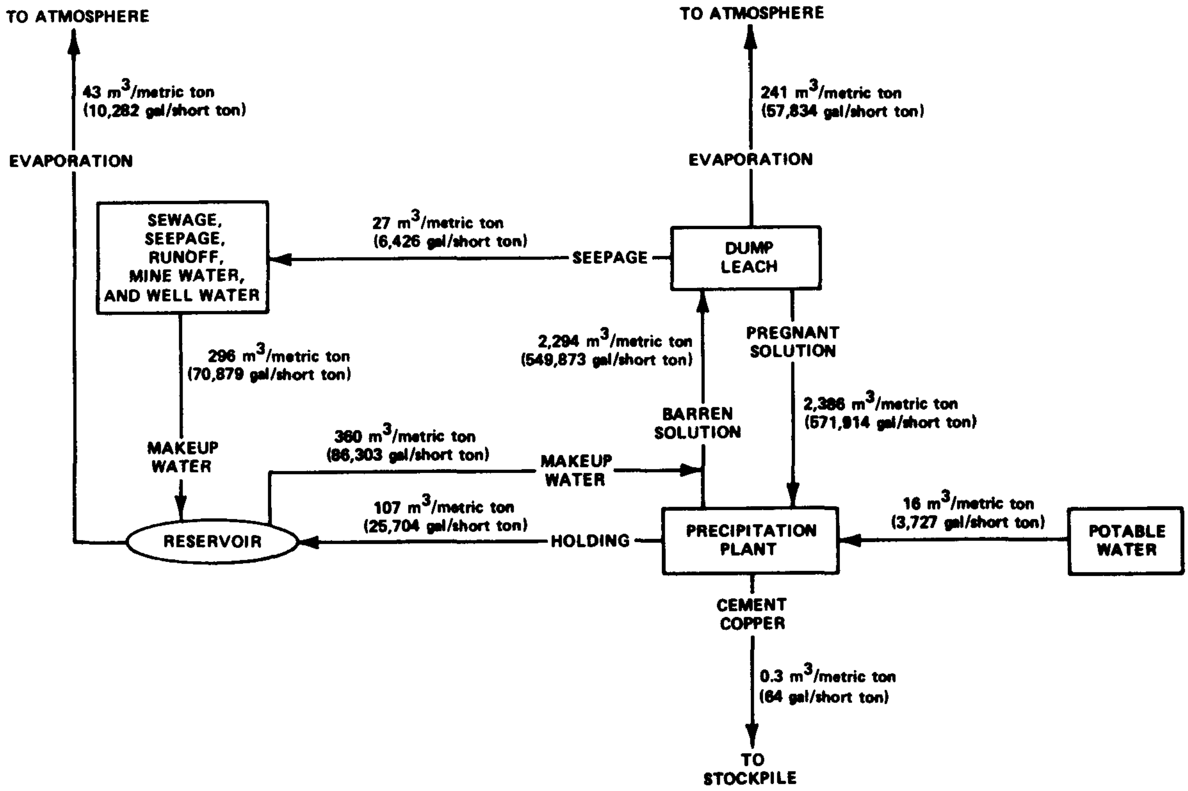
Process Description-Hydrometallurgical Extraction Processes (Mining)

The use of acid leaching processes on low-grade oxide ores and wastes produces a significant amount of cement copper each year. All leaching is performed west of the Rocky Mountains. Figure V-8 is a flow diagram of the process of acid leaching.

Leaching of oxide mineralization with dilute sulfuric acid or acid ferric sulfate may be applied to four situations of ore. Dump leaching extracts copper from low-grade (0.1 to 0.4 percent Cu) waste material derived from open-pit mining. The cycle of dissolution of oxide mineralization covers many years.

Most leach dumps are deposited upon existing topography. The location of the dumps is selected to assure impermeable surfaces and to utilize the natural slope of ridges and valleys for the recovery and collection of pregnant liquors. In some cases, dumps have been placed on specially prepared surfaces. The leach material is generally less than 0.61 meter (2 feet) in diameter, with many finer particles. However, it may include large boulders. Billions of tons of

Figure V-8. FLOWSHEET OF HYDROMETALLURGICAL PROCESSES USED IN ACID LEACHING AT MINE 2122



material are placed in dumps that are shaped as truncated cones.

The leach solution is recycled from the precipitation or other recovery operation, along with makeup water and sulfuric acid additions (to pH 1.5 to 3.0). It is pumped to the top of dumps and delivered by sprays, flooding, or vertical pipes. Factors such as climate, surface area, dump height, mineralogy, scale of operation, and size of leach material affect the choice of delivery method. Figure V-9 summarizes the reactions by which copper minerals are dissolved in leaching.

Heap leaching of wastes approaching a better grade ore is usually done on specially prepared surfaces. The time cycle is measured in months. Copper is dissolved from porous oxide ore. Very little differentiates heap from dump leaching. In the strictest sense, the pad is better prepared, the volume of material is less, the concentration of acid is greater, acid is not regenerated due to the absence of pyrite in the ore, and the ore is of better copper grade in heap leaching, compared to dump leaching.

In-situ leaching techniques are used to recover copper from shattered or broken ore bodies in place on the surface or in old underground workings. Oxide and sulfide ores of copper may be recovered over a period of years. The principle is the same as in dump or heap leaching. Usually, abandoned underground ore bodies previously mined by block-caving methods are leached although, in at least one case, an ore body on the surface of a mountain was leached after shattering the rock by blasting. In underground workings, leach solution is delivered by sprays, or other means, to the upper areas of the mine and allowed to seep slowly to the lower levels, from which the solution is pumped to the precipitation plant at the surface. The leaching of surface ore bodies is similar to a heap or dump leach.

Recovery of Copper From Leach Solutions. Copper dissolved in leach solutions may be recovered by iron precipitation, electrowinning, or solvent extraction (liquid ion exchange). Hydrogen reduction has been employed experimentally.

Copper is often recovered by iron precipitation as cement copper. Burned and shredded scrap cans are most often used as the source of iron, although other iron scrap and sponge iron may also be used. In 1968, 12 percent of the domestic mine copper production was in the form of cement copper recovered by iron precipitation. Examples of iron launders and cone precipitators are shown in Figures V-10 and V-11.

Figure V-9. REACTIONS BY WHICH COPPER MINERALS ARE DISSOLVED IN DUMP, HEAP, OR IN-SITU LEACHING

AZURITE

$$Cu_3(OH)_2 \cdot (CO_3)_2 + 3H_2SO_4 \rightleftharpoons 3CuSO_4 + 2CO_2 + 4H_2O$$

MALACHITE

$$Cu_2(OH)_2 \cdot CO_3 + 2H_2SO_4 \rightleftharpoons 2CuSO_4 + CO_2 + 3H_2O$$

CHRYSOCOLLA

$$CuSiO_3 \cdot 2H_2O + H_2SO_4 \rightleftharpoons CuSO_4 + SiO_2 + 3H_2O$$

CUPRITE

$$Cu_2O + H_2SO_4 \rightleftharpoons CuSO_4 + Cu + H_2O$$

$$Cu_2O + H_2SO_4 + Fe_2(SO_4)_3 \rightleftharpoons 2CuSO_4 + H_2O + 2FeSO_4$$

NATIVE COPPER

$$Cu + Fe_2(SO_4)_3 \rightleftharpoons CuSO_4 + 2FeSO_4$$

TENORITE

$$CuO + H_2SO_4 \rightleftharpoons CuSO_4 + H_2O$$

$$3CuO + Fe_2(SO_4)_3 + 3H_2O \rightleftharpoons 3\ CuSO_4 + 2Fe(OH)_3$$

$$4CuO + 4FeSO_4 + 6H_2O + O_2 \rightleftharpoons 4CuSO_4 + 4Fe(OH)_3$$

CHALCOCITE

$$Cu_2S + Fe_2(SO_4)_3 \rightleftharpoons CuS + CuSO_4 + 2FeSO_4$$

$$Cu_2S + 2Fe_2(SO_4)_3 \rightleftharpoons 2CuSO_4 + 4FeSO_4 + S$$

COVELLITE

$$CuS + Fe_2(SO_4)_3 \rightleftharpoons CuSO_4 + 2FeSO_4 + S$$

Chalcopyrite will slowly dissolve in acid ferric sulfate solutions and also will oxidize according to:

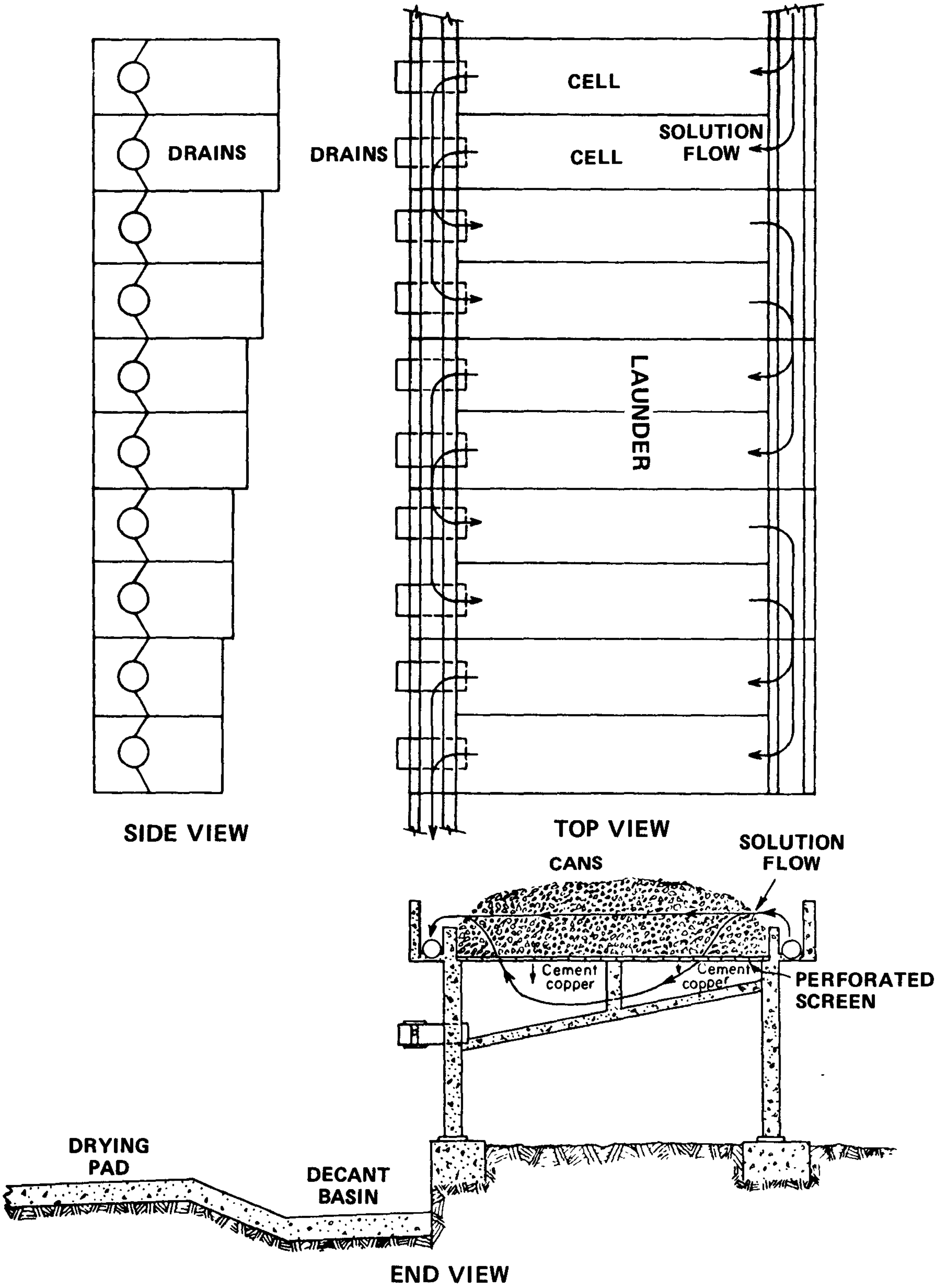
$$CuFeS_2 + 2O_2 \rightleftharpoons CuS + FeSO_4;$$

$$CuS + 2O_2 \rightleftharpoons CuSO_4.$$

Pyrite oxidizes according to:

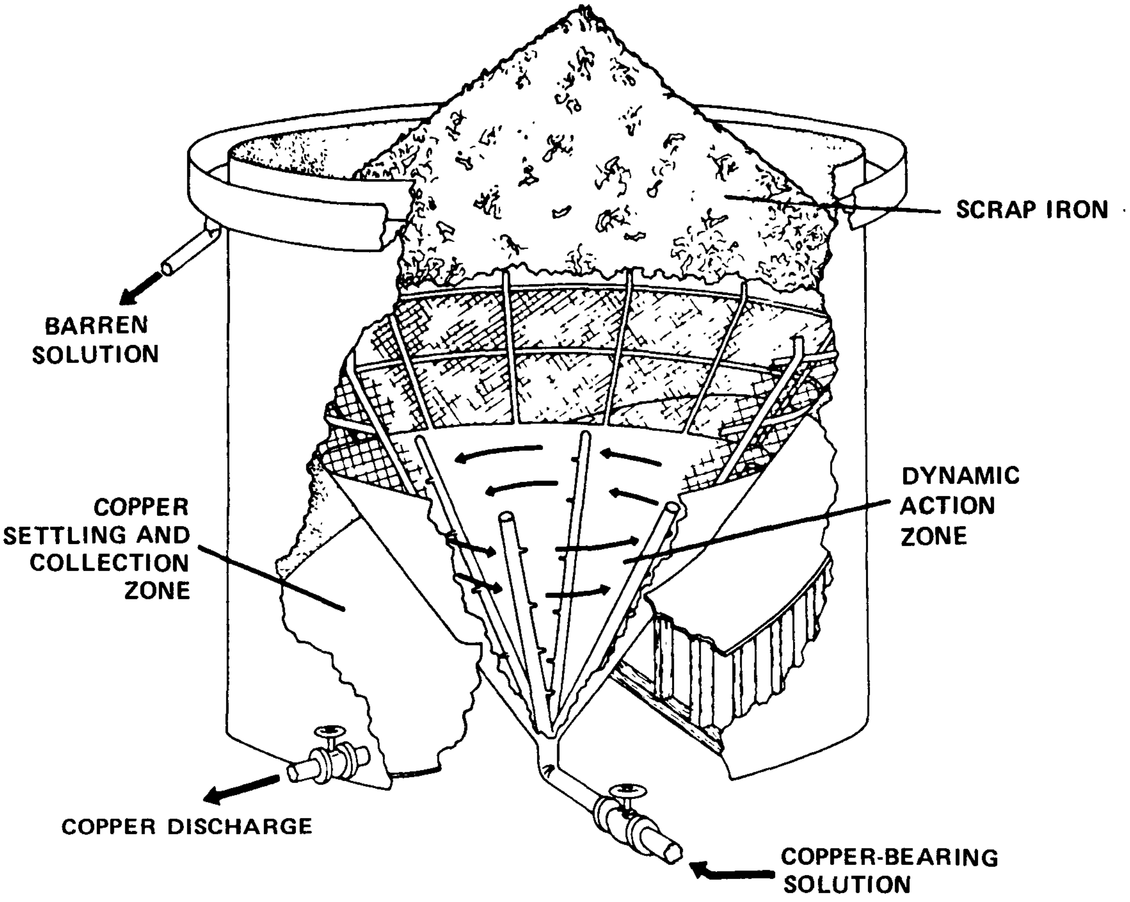
$$2FeS_2 + 2H_2O + 7O_2 \rightleftharpoons 2FeSO_4 + 2H_2SO_4.$$

Figure V-10. TYPICAL DESIGN OF GRAVITY LAUNDER/PRECIPITATION PLANT



SOURCE: REFERENCE 23

Figure V-11. CUTAWAY DIAGRAM OF CONE PRECIPITATOR



SOURCE: REFERENCE 23

The pregnant copper solution (0.5 to 2.2 g/l) is passed over shredded or burned iron scrap and precipitates copper by replacement according to the reaction:

$$CuSO_4 + Fe \rightleftarrows Cu + FeSO_4$$

Scrap iron of other forms and sponge iron may be employed.

Gravity iron launders employ gravity to allow solutions to trickle over and through iron scrap. Spray water washes remove copper frequently from the can surfaces. Occasionally, solution is introduced from below and flows upward through the iron to produce a coarser, but highly pure, cement copper. (See Figure V-10.)

Cone precipitators may be employed for copper recovery. Solution is injected, through nozzles at the bottom of the cone, into the shredded iron scrap. This injection, under pressure, both precipitates copper rapidly and removes it from the iron surface by the turbulent action. (See Figure V-11.)

Precipitated copper is recovered by draining and scooping out the solids. Recovery from pregnant solution may be 60 percent. The resulting cement copper is 85 to 99 percent pure and is sent to the smelter for further purification.

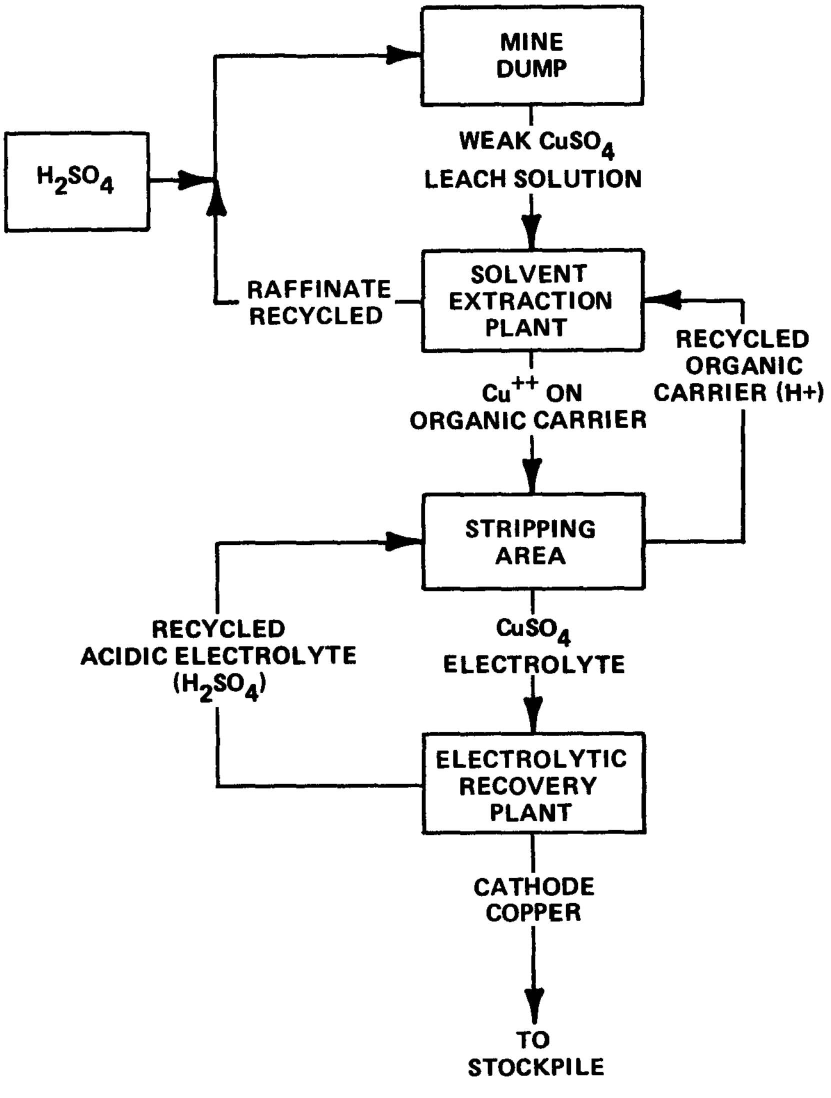
The barren solution from a precipitation plant is recycled from a holding pond to the top of the ore body, after sulfuric acid and makeup water are added, if necessary.

Leach solutions containing greater than 25 to 30 grams per liter of copper are usually sent to electrowinning facilities. The cathode copper produced is highly pure and does not require smelting.

Solvent extraction of copper from acid leach solutions by organic reagents is rapidly becoming an important method of recovery. When pregnant liquors contain less than 30 grams of copper per liter, the process is most applicable. (See Figure V-12.)

In solvent extraction, a reagent with high affinity for copper and iron in weak acid solutions, and with low affinity for other ions, is carried in an organic medium. It is placed in intimate contact with copper leach solutions, where H+ ions are exchanged for Cu(++) ions. This regenerates the acid, which is recycled to the dump. The organic medium, together with copper, is sent to stripping cell, where acidic copper sulfate solutio

Figure V-12. DIAGRAM OF SOLVENT EXTRACTION PROCESS FOR RECOVERY OF COPPER BY LEACHING OF ORE AND WASTE



exchange H+ ion for Cu(++). This regenerates the organic/H+ media and passes copper to the electrolytic cells, where impurity-free copper (99.98 to 99.99 percent Cu) is electrolytically deposited on cathodes (electrowinning). Typically, 3.18 kg (7 lb) of acid is used per 0.454 kg (1 lb) of copper produced.

Acid Leach Solution Characterization. Water sources for heap, dump, and in situ leaching are often mine water, wells, springs, or reservoirs. All acid water is recycled. Makeup water needs result only from evaporation and seepage; therefore, the water consumption depends largely on climate. Table V-12 lists the amount of water utilized for various operations.

The buildup of iron salts in leach solutions is the worst problem encountered in leaching operations. The pH must be maintained below 2.4 to prevent the formation of iron salts, which can precipitate in pipelines, on the dump surface, or within the dump, causing uneven distribution of solution. This may also be controlled by the use of settling or holding ponds, where the iron salts may precipitate before recycling.

Table V-13 lists the chemical characteristics of barren leach solutions at selected plants. This solution is always recycled and is almost always totally contained.

Other metals, such as iron, cadmium, nickel, manganese, zinc, and cobalt, are often found in high concentrations in leach solutions. Total and dissolved solids often build up so that a bleed is necessary. A small amount of solution may be sent to a holding or evaporation pond to accomplish the control of dissolved solids.

Handling and Treatment of Water. No discharge of pollutants usually occurs from leaching operations, except for a bleed, which may be evaporated in a small, nearby lagoon.

Process Description - Mill Processing

Vat Leaching. Vat leaching techniques require crushing and grinding of high-grade oxide ore (greater than 0.4 percent Cu). (See Figure V-13.) The crushed ore, either dry or as a slurry, is placed in lead-lined tanks, where it is leached with sulfuric acid for approximately four days. This method is applicable to nonporous oxide ores and is employed for better recovery of copper in shorter time periods.

TABLE V-12. 1973 WATER USAGE IN DUMP, HEAP, AND IN-SITU LEACHING OPERATIONS

MILL	WATER USAGE (1973)	
	m^3/metric ton precipitate produced	gallons/short ton precipitate produced
2101	4,848.6	1,162,131
2103	1,600.0*	383,490*
2104	1,335.1†	320,000†
2107	967.8*	231,967*
2108	1,096.5	262,800
2110	1,308.7	313,683
2116	N/A	N/A
2118	1,185.3	284,108
2120	4,264.0	1,022,000
2122	1,973.6	473,040
2123	922.2	221,026
2124	746.3	178,876
2125	626.0	150,048

*Estimated from 1972 copper-in-precipitate production and assuming precipitates are 85% copper (Source: Copper - A Position Survey, 1973, Reference 24)

† Production taken from NPDES permit application

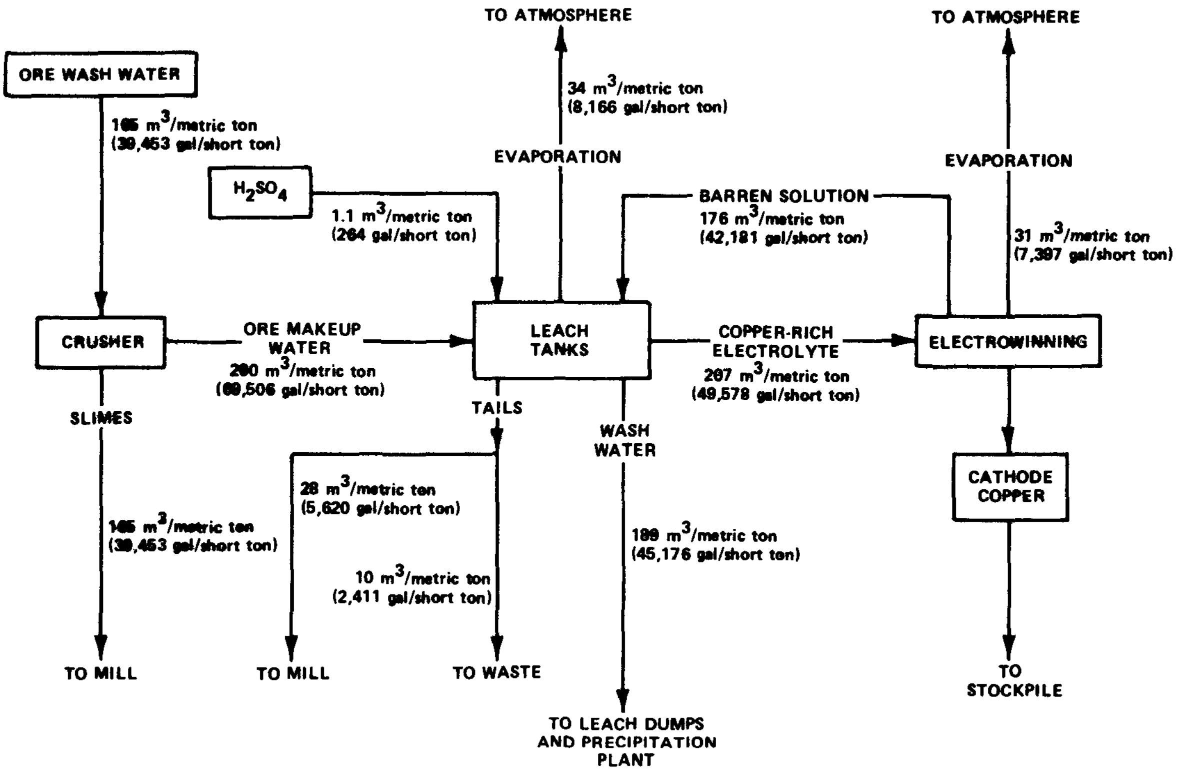
N/A = Production not available; only flow available

TABLE V-13. CHEMICAL CHARACTERISTICS OF BARREN HEAP, DUMP, OR IN-SITU ACID LEACH SOLUTIONS (RECYCLED: NO WASTE LOAD)

PARAMETER	CONCENTRATION (mg/ℓ) IN LEACH SOLUTION FROM MINE					
	2120	2124	2123	2122	2125	2104
pH	3.56*	2.82*	3.56*	2.49*	4.24*	3.39*
TS	28,148	47,764	44,368	83,226	29,494	-
TSS	14	186	162	34	218	-
COD	515.8	1,172	80	385.1	440.0	-
TOC	1.3	28.0	27.5	46.0	11.0	-
Oil and Grease	< 1.0	6.0	2.0	5.0	< 1.0	-
S	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
As	< 0.07	0.23	0.07	< 0.01	< 0.07	0.04 to 0.60
B	0.11	0.31	< 0.01	0.08	0.03	-
Cd	7.74	0.092	5.55	4.50	0.20	0.56
Cu	36.0	145.0	97.0	72.0	7.00	52.25
Fe	2,880.0	6,300.0	650.0	3,500.0	3,688.0	-
Pb	0.1	< 0.1	0.1	1.14	< 0.1	0.68
Mn	260.0	94.0	123.5	190.0	149.4	-
Hg	0.0009	0.0012	0.0010	0.0003	0.0007	0.0003
Ni	2.40	7.20	5.68	31.1	6.90	-
Tl	< 1.0	< 0.1	< 0.1	< 0.1	< 0.1	-
Se	< 0.003	< 0.040	0.030	< 0.003	< 0.020	0.13
Ag	< 0.1	< 0.1	< 0.1	0.038	< 0.1	-
Te	1.0	1.0	1.8	2.5	1.1	-
Zn	940.0	28.5	33.0	74.5	21.0	-
Sb	< 0.5	< 0.5	< 0.5	< 2.0	< 0.5	-
Au	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	-
Co	3.30	3.80	7.3	72.0	13.70	-
Mo	-	0.75	1.33	0.35	0.5	-
Sn	-	-	-	2.40	-	-
Cyanide	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-

*Value in pH units

Figure V-13. VAT LEACH FLOW DIAGRAM (MILL 2124)



The pregnant copper solution, as drawn off the tanks, contains very high concentrations of copper, as well as some other metals. The copper may be recovered by iron precipitation or by electrowinning.

Water is utilized in the crusher for dust control, as leach solution, and as wash water. The wash water is low in copper content and must go to iron precipitation for copper recovery. Table V-14 summarizes water usage at vat leach plants. The vat ores are washed and discarded in a dump. If the sulfide concentration is significant, these ores may be floated in the concentrator to recover CuS.

Vat Leach Water Characterization. Table V-15 summarizes the chemical characteristics of vat leach solutions. These solutions are recycled directly. Makeup water is usually required when there are evaporative losses from the tanks and recovery plants.

Of the three vat leach facilities surveyed, one recycles directly. Another employs holding (evaporative) ponds for dissolved-iron control. Still another reuses all the leach solution in a smelter process and requires new process water. Therefore, no discharge results.

Variation Within the Vat Leach Process. Ores which are crushed prior to the vat leach process may be washed in a spiral classifier for control of particulates (slimes) undesirable for vat leaching. These slimes may be floated in a section of the concentrator to recover copper sulfide and then leached in a thickener for recovery of oxide copper. The waste tails (slimes) are deposited in special evaporating ponds. The leach solution undergoes iron precipitation to recover cement copper, and the barren solution is sent to the evaporation pond as well. These wastes are characterized in Table V-16. No effluent results, as the wastes are evaporated to dryness in the special impoundment.

The process has application when mined ores contain significant amounts of both oxide and sulfide copper.

Process Description - Froth Flotation

Approximately 98% of ore received at the mill is beneficiated by froth flotation at the concentrator. The process includes crushing, grinding, classification, flotation, thickening, and filtration. (See Figure V-14.)

Typically, coarse ore is delivered to the mill for two- or three-stage reduction by truck, rail or conveyor and is then

TABLE V-14. WATER USAGE IN VAT LEACHING PROCESS AS A FUNCTION OF AMOUNT OF PRODUCT (PRECIPITATE OR CATHODE COPPER) PRODUCED

MILL	WATER USAGE (1973)		METHOD OF RECOVERY
	m^3/metric ton product	gallons/short ton product	
2102	133.7	32,040	Solvent Extraction/Iron Precipitation*
2116	52.4	12,568 †	Electrowinning**
2124	206.85	49,578	Electrowinning**

* Product is cement copper or copper precipitate

† No 1973 data were received through surveys. 1972 data from Reference 24 were used to calculate a value which may be a low estimate of water use.

**Product is cathode copper

TABLE V-15. CHEMICAL CHARACTERISTICS OF VAT-LEACH BARREN ACID SOLUTION (RECYCLED: NO WASTE LOAD, MILL 2124)

PARAMETER	CONCENTRATION (mg/ℓ)
pH	1.1*
TDS	169,000
TSS	515
COD	331
TOC	96
Oil and Grease	1.0
Al	1,540.0
Cd	0.42
Pb	2.0
Cr	17.0
Cu	27,800
Fe	4,800.0
Mn	47.3
Ni	1.70
V	2.50
Tl	< 0.03
Se	< 0.003
Ag	0.17
Zn	11.5
Co	51.0
Mo	2.0
Cyanide	< 0.01

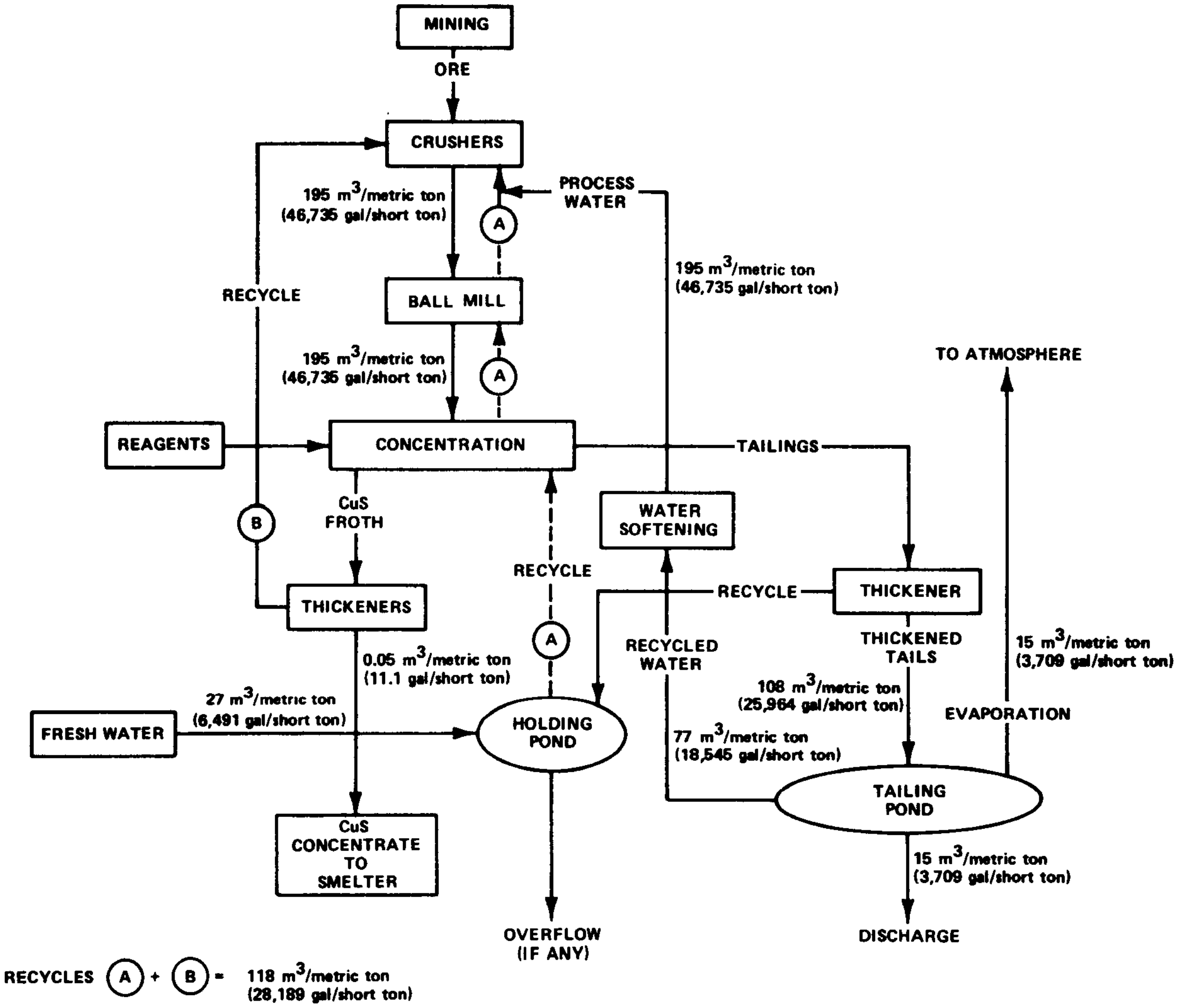
*Value in pH units

TABLE V-16. MISCELLANEOUS WASTES FROM SPECIAL HANDLING OF ORE WASH SLIMES IN MINE 2124 (NO EFFLUENT)

PARAMETER	CONCENTRATION (mg/ℓ)	
	SLIME LEACH-THICKENER UNDERFLOW	SLIME PRECIPITATION-PLANT BARREN SOLUTION
pH	2.4*	1.8*
TDS	19,600	23,000
TSS	292,000	277
COD	515	226
TOC	21	8
Oil and Grease	4.0	1.0
Al	320.0	305.0
Cd	0.27	0.40
Cu	4,800	4,800
Fe	5,500	4,500
Pb	0.22	0.59
Mn	2.7	3.0
Hg	0.0026	0.0560
Ni	1.5	1.75
Se	< 0.003	< 0.003
Ag	0.057	0.054
Ti	3.8	4.2
Zn	8.9	35.0
Co	1.0	1.0
Mo	0.5	3.75
Cyanide	< 0.01	< 0.01

*Value in pH units

Figure V-14. FLOW DIAGRAM FOR FLOTATION OF COPPER (MILL 2120)



fed to a vibrating grizzly feeder, which passes its oversize material to a jaw crusher. The ore then travels by conveyor to a screen for further removal of fines ahead of the next reduction stage. Screen oversize material is crushed by a cone crusher. When ore mineralogy is chalcopyrite, or contains pyrite, an electromagnet is inserted before secondary crushing to remove tramp iron. Crushing to about 65 mesh is required for flotation of porphyry copper.

The crushed material is fed to the mill for further reduction in a ball mill and/or rod mill. A spiral classifier or screen passes properly sized pulp to the flotation cells. Ahead of the flotation cells, conditioners are employed to properly mix flotation reagents into the pulp. (See Figure V-15.)

Reagents employed for this process might include, for instance:

Reagent type	Example of Reagent	lb/short ton mill feed	kg/metric ton mill feed
pH control	lime	10.0	5.0
collector	Xanthate	0.01	0.005
collector	Minerec compounds	0.03	0.015
frother	MIBC	0.02	0.04

The specific types of reagents employed and amounts needed vary considerably from plant to plant, although one may classify them, as in Table V-17, as precipitating agents, pH regulators, dispersants, depressants, activators, collectors, and frothers.

Rougher-cell concentrate is cleaned in cleaner flotation cells. The overflow is thickened, filtered, and sent to the smelter. Tailings (sands) from the cleaner cells are returned to the mill for regrinding. Tailings from the rougher cells are sent to the tailing pond for settling of solids. Scavenger cells, in the last cells of the rougher unit, return their concentrate (overflow) to one of the first rougher cells.

In flotation, copper sulfide minerals are recovered in the froth overflow. The underflow retains the sands and slimes (tailings). The final, thickened and filtered concentrate contains 15 to 35 percent copper (typically, 25 to 30 percent) as copper sulfide. Copper recoveries average 83 percent, so a significant portion of the copper is discarded

Figure V-15. ADDITION OF FLOTATION AGENTS TO MODIFY MINERAL SURFACE

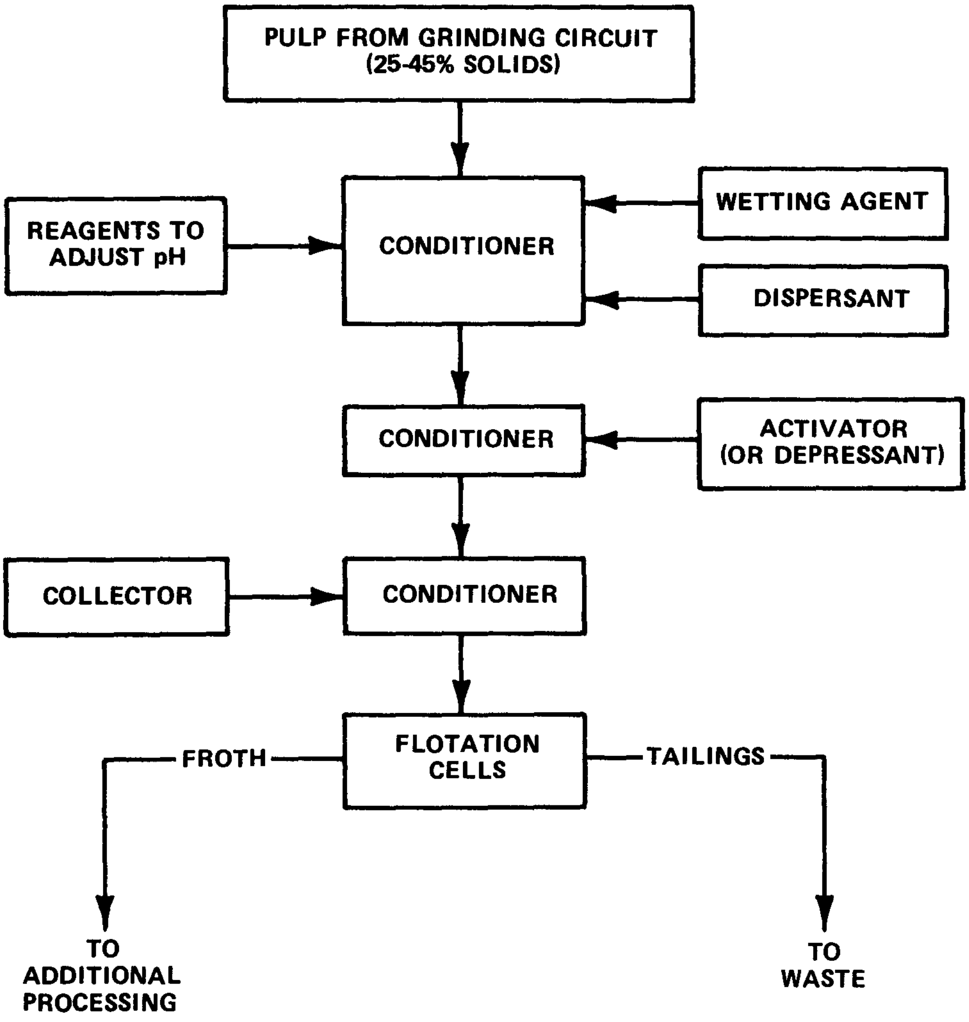


TABLE V-17. EXAMPLES OF CHEMICAL AGENTS WHICH MAY BE EMPLOYED IN COPPER FLOTATION

MINERAL	PRECIPITATION AGENT	pH REGULATION	DISPERSANT	DEPRESSANT	ACTIVATOR	COLLECTOR	FROTHER
Bornite	—	Lime	Sodium silicate	Sodium cyanide	—	Xanthate Aerofloats	Pine oil
Chalcocite	—	Lime	Sodium silicate	Sodium cyanide	—	Xanthate Aerofloats	Pine oil
Chalcopyrite	—	Lime	Sodium silicate	Sodium cyanide	—	Xanthate Aerofloats	Pine oil
Native Copper	—	Lime	Sodium silicate	Sodium cyanide	—	Xanthate Aerofloats	Pine oil
Azurite	Sodium monosulfide	Sodium carbonate	Sodium silicate	Quebracho	Polysulfide	Xanthate Aerofloats, Fatty acids and salts	Pine oil, Vapor oil, Cresylic acid
Cuprite	Sodium monosulfide	Sodium carbonate	Sodium silicate	Quebracho	Polysulfide	Fatty acids and salts, Xanthates	Pine oil, Vapor oil, Cresylic acid
Malachite	Sodium monosulfide	Sodium carbonate	Sodium silicate	Tannic acid	Polysulfide	Fatty acids and salts, Xanthates	Pine oil, Vapor oil, Cresylic acid

Source: Reference 25

to tailing ponds. Tailings contains 15 to 50 percent solids (typically, 30 percent) and 0.05 to 0.3 percent copper.

Selective or differential flotation is practiced in copper concentrators, which (for example) may separate molybdenum from copper concentrate, copper sulfide from pyrite, and copper sulfide from copper/lead/zinc ore. Silver may be floated from copper flotation feed; gold and silver may be leached by cyanide from the copper concentrate, with precipitation by zinc dust.

Water Usage in Flotation. The major usage of water in the flotation process is as carrier water for the pulp. The carrier water added in the crushing circuit also serves as contact cooling water. Sometimes, water sprays are used to control dust in the crusher. Process water for flotation comes from mine-water excess, surface and well water, recycled tailing thickener, and lagoon water. The majority of the copper industry recycles and reuses as much water as is available because the industries are located in an arid climate (i.e., Arizona, New Mexico, and Nevada). There are plants in areas of higher rainfall and less evaporation which have reached 70, 95, and 100 percent recycle (or zero discharge) and are researching process changes and treatment technology in order to attain zero discharge of all mill water. Three major copper mills discharge all process water from the tailings lagoon at this time.

Table V-18 outlines the amount of water used in flotation per ton of concentrate produced.

Noncontact cooling water in the crushers, if not entirely in a closed circuit, may be reused in the flotation circuit and either settled in holding ponds prior to recycle or evaporated. The use of noncontact cooling water in crushing appears to be rare, since pulp carrier water serves as contact cooling water.

Waste Characterization. The chemical characteristics of tailing-pond (settled) decant water are summarized in Table V-19. Residual flotation agents or their degradation products may be harmful to aquatic biota, although their constituents and toxicity have not been fully determined. Their presence (if any), however, does not appear to hamper the recycling of tailing decant water to the mill process. Water is characterized by 1 to 4 grams per liter of dissolved solids and by the presence of alkalinity, sulfate, surfactant, and fluoride. Dissolved metals in decant water are usually low, except for calcium (from lime employed in flotation process), magnesium, potassium, selenium, sodium,

TABLE V-18. WATER USAGE IN FROTH FLOTATION OF COPPER

MILL	WATER USAGE (1973)	
	m^3/metric ton concentrate produced	gal/short ton concentrate produced
2101	95.8	22,967
2102	188.7	45,233
2103	77.6	18,610
2104	474.3	113,674
2106	36.0	8,625
2108	141.9	34,009
2109	N.P.	N.P.
2111	280.4*	67,201*
2112	78.6	18,847
2113	68.3	16,377
2114	85.5	20,503
2115	366.7	87,888
2116	51.8	12,417
2117	145.0	34,763
2118	112.0	26,846
2119	161.6	38,738
2120	234.7	56,257
2121	149.4	35,801
2122	160.9	38,570
2123	370.9	88,905
2124	110.3	26,440

*Concentrate production estimated from known copper content and assuming concentrate contains 20.43% copper, as in 1972

N.P. = No (1973) production

SOURCE: Reference 24

TABLE V-19. RAW MILL WASTE LOADS PRIOR TO SETTLING IN TAILING PONDS (Sheet 1 of 4)

PARAMETER	MILL 2119			MILL 2120		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	213,996 m^3/day (56,530,000 gal/day)	168 m^3/metric ton	40,280 gal/short ton	105,990 m^3/day (28,000,000 gal/day)	109.2 m^3/metric ton	261,890 gal/short ton
pH	9.12*	9.12*	9.12*	11.00*	11.09*	11.00*
SES†	30%	–	–	35%	–	–
TDS	1,422	239,032	478,063	2,652	289,602	579,384
TSS	4	672	1,345	< 2	< 218	< 437
Oil and Grease	< 1.0	< 168.1	< 336.2	3.0	327.7	655.4
SiO_2	–	–	–	–	–	–
Al	< 1.0	< 168.1	< 336.2	–	–	–
As	< 0.07	< 11.77	< 23.53	–	–	–
Cd	< 0.05	< 8.40	< 16.81	< 0.02	< 2.18	< 4.37
Cu	0.28	47.07	94.13	0.77	84.11	168.22
Fe	0.95	159.69	319.38	5.20	568.02	1,136.05
Pb	< 0.5	< 84	168.1	< 0.1	< 10.9	< 21.8
Mn	< 0.05	< 8.4	< 16.81	0.07	7.65	15.29
Hg	0.0004	0.0672	0.1346	0.0008	0.0874	0.1748
Ni	< 0.1	< 16.8	< 33.6	< 0.05	< 5.46	< 10.92
Se	< 0.003	< 0.504	< 1.008	–	–	–
Ag	< 0.1	< 16.8	< 33.6	< 0.1	< 10.9	< 21.8
Sr	0.83	139.52	279.04	–	–	–
Zn	< 0.05	< 8.40	< 16.81	0.1	10.92	21.85
Sb	< 0.2	< 33.6	< 67.2	< 0.5	< 54.6	< 109.2
Co	< 0.05	< 8.40	< 16.81	< 0.04	< 4.37	< 8.74
Au	< 0.05	< 8.40	< 16.81	< 0.05	< 5.46	< 10.92
Mo	< 0.2	< 33.6	< 67.2	–	–	–
Phosphate	–	–	–	–	–	–
Cyanide	< 0.01	< 1.68	< 3.36	< 0.01	< 1.09	< 2.18
Operating days/year	357			360		
Annual Production of Concentrate	464,420 metric tons (500,904 short tons)			349,272 metric tons (385,000 short tons)		

*Value in pH units

†Settleable solids

TABLE V-19. RAW MILL WASTE LOADS PRIOR TO SETTLING IN TAILING PONDS (Sheet 2 of 4)

PARAMETER	MILL 2121 (Slime Tails)			MILL 2121 (sands)		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	64,954 m^3/day (17,161,000 gal/day)	104.7 m^3/metric ton	25,097 gal/short ton	32,825 m^3/day (8,672,400 gal/day)	52.9 m^3/metric ton	12,683 gal/short ton
pH	9.3[*]	9.3[*]	9.3[*]	9.28[*]	9.28[*]	9.28[*]
SES[†]	30%	–	–	10%	–	–
TDS	438	45,863	91,725	310	16,404	32,808
TSS	202	21,151	42,302	6	317	635
Oil and Grease	1.0	104.7	209.4	< 1	< 52.9	< 105.8
SiO_2	4.75	49,737	99,474	–	–	–
Al	5.9	617.8	1,236	900	47,624	95,248
As	< 0.07	< 7.33	< 14.66	< 0.07	< 3.70	< 7.41
Cd	< 0.02	< 2.09	< 4.19	0.03	1.59	3.17
Cu	3.50	366.48	732.96	46	2,434.1	4,868.2
Fe	10.05	1,052.23	2,104.65	1,216	64,345.3	128,690.7
Pb	0.22	23.04	46.07	0.40	21.17	42.33
Mn	0.25	26.18	52.35	48	2,539.9	5,079.9
Hg	0.0098	1.0261	2.0523	0.0001	0.0053	0.0106
Ni	< 0.05	< 5.24	< 10.47	1.72	91.01	182.03
Se	0.022	2.304	4.607	< 0.003	< 0.159	< 0.317
Ag	< 0.1	< 10.5	< 20.9	< 0.1	< 5.3	< 10.6
Sr	0.07	7.33	14.66	0.06	3 17	6.35
Zn	0.9	94.24	188.48	8.50	449.78	899.56
Sb	< 0.5	< 52.4	< 104.7	< 0.5	< 26 5	< 52.9
Co	< 0.04	< 4.19	< 8.38	1.1	58.21	116.41
Au	< 0.05	< 5 24	< 10.47	< 0 05	< 2.65	< 5 29
Mo	< 0.5	< 52.4	< 104.7	< 0.5	< 26.5	< 52.9
Phosphate	0.24	25.13	50.26	–	–	–
Cyanide	< 0.01	< 1 05	< 2.09	< 0.01	< 0.53	< 1 06
Operating days/year	360			360		
Annual Production of Concentrate	223,318 metric tons (246,162 short tons)			223,318 metric tons (246,162 short tons)		

[*] Value in pH units

[†] Settleable solids

TABLE V-19. RAW MILL WASTE LOADS PRIOR TO SETTLING IN TAILING PONDS (Sheet 3 of 4)

PARAMETER	MILL 2122			MILL 2123		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT		CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
Flow	278,084 m^3/day (73,470,000 gal/day)	134 m^3/metric ton	32,079 gal/short ton	11,446 m^3/day (3,024,000 gal/day)	371 m^3/metric ton	88,905 gal/short ton
pH	8.54*	8.54*	8.54*	13.00*	13.00*	13.00*
SES[†]	15%	–	–	30%	–	–
TDS	4,276	573,188	1,146,376	2,494	925,136	1,850,272
TSS	24	3,217	6,434	20	7,419	14,838
Oil and Grease	3	402.1	804.3	10	3,709	7,418.9
SiO_2	12.25	1,675.60	3,351 19	27	10,015.5	20,031
Al	<1	< 134	< 268.1	1	370.9	741.9
As	< 0.07	< 9.38	< 18.77	< 0.07	< 25.97	< 51.93
Cd	< 0.05	< 6.7	< 13.4	< 0.03	< 11.13	< 22.26
Cu	0.08	10.72	21.45	0.77	285.63	571.25
Fe	< 0.1	< 13.4	< 26.8	0.15	55.64	111.28
Pb	2.79	373.99	747.99	< 0.1	< 37.09	< 74.19
Mn	0.047	6.3	12.6	< 0.06	< 22.26	< 44.51
Hg	0.0002	0.0268	0.0536	0.0019	0.7048	1.4096
Ni	< 0.1	< 13 4	< 26.8	< 0.05	< 18.55	< 37.09
Se	0.022	2.949	5.898	0.07	25.966	51.932
Ag	< 0.1	< 13.4	< 26.8	< 0.1	< 37.09	< 74.19
Sr	1.81	242.63	485.25	2.26	838.33	1,676.67
Zn	< 0.05	< 6.7	< 13.4	< 0.05	< 18.55	< 37.09
Sb	< 1.0	< 134	< 268.1	< 0.5	< 185.5	< 370.9
Co	0.08	10.72	21.45	< 0.06	< 22.26	< 44.51
Au	< 0.05	< 6 7	< 13.4	< 0.05	< 18.55	< 37.09
Mo	< 0.2	< 26.8	< 53.6	< 0.5	< 185.5	< 370.9
Phosphate	0.15	20.11	40 21	20.2	7,493.1	14,986.2
Cyanide	< 0.01	< 1.34	< 2.68	0.01	3.71	7.42
Operating days/year	357			362		
Annual Production of Concentrate	740,602 metric tons (817,636 short tons)			11,170 metric tons (12,313 short tons)		

*Value in pH units

[†] Settleable solids

TABLE V-19. RAW MILL WASTE LOADS PRIOR TO SETTLING IN TAILING PONDS (Sheet 4 of 4)

PARAMETER	MILL 2124		
	CONCENTRATION (mg/ℓ)	RAW WASTE LOAD PER UNIT PRODUCT	
		kg/1000 metric tons	lb/1000 short tons
Flow	19,322 m^3/day (5,104,800 gal/day)	100.8 m^3/metric ton	24,170 gal/short ton
pH	10.05*	10.05*	10.05*
SES†	50%	–	–
TDS	2,846	286,995	573,989
TSS	6	605	1,210
Oil and Grease	1	100.8	201.7
SiO_2	46.75	4,714.34	9,428.67
Al	< 0.5	< 50.4	< 100.8
As	< 0.07	< 7.06	< 14.12
Cd	0.05	5.04	10.08
Cu	912.5	92,017.8	184,035.6
Fe	1,982	199,867 7	399,735.5
Pb	0.35	35.29	70.59
Mn	31	3,126 1	6,252.2
Hg	0.0006	0.0605	0.1210
Ni	2.8	282.36	564.71
Se	< 0.003	< 0.303	< 0.605
Ag	< 0.1	< 10.08	< 20.17
Sr	1.2	121.01	242.02
Zn	5.6	564.71	1,129.42
Sb	< 0.5	< 50.4	< 100.8
Co	1.68	169.41	338.83
Au	< 0.05	< 5.04	< 10.08
Mo	29.29	2,953.65	5,907.29
Phosphate	20.8	2,097.5	4,195.0
Cyanide	< 0.01	< 1.01	< 2.02
Operating days/year	362		
Annual Production of Concentrate	69,362 metric tons (76,457 short tons)		

*Value in pH units

†Settleable solids

and strontium--which do not respond to precipitation with lime. On occasion, cyanide, phenol, iron, lead, mercury, titanium, and cobalt are detectable in the decant. However, in these cases, the water is either recycled fully or partially discharged.

Handling or Treatment of Decanted Water From Mill Tailing Ponds. The majority of the industry recycles all mill process water from the thickeners and the tailing pond due to the need for water in the areas of major copper-ore production. Of the balance of the industry, which includes approximately six major copper producing facilities and an undetermined number of operations producing copper as a byproduct, at least half (50 percent) are currently working toward attaining recycle of mill process water. Also, of the six, three have sophisticated lime and settling treatment, or are installing it, to protect the quality of the discharge.

Three of the copper mills surveyed , all of which discharge water from the tailing pond, are compared in Table V-20 as to the quality of, and the amount of loading in, the discharged decant water. In the calculations made to present these data, no allowance was made for incoming process water.

As discussed previously, noncontact cooling water, if present, remains either in a closed system or joins the carrier water to the flotation cells.

Sewage from the mill is either handled in a treatment plant or, in one case, is sent to an acid leach holding reservoir. Overflow from the treatment plants is either discharged or sent to the tailing pond.

Variations in Flotation Process. Flotation tailings may be separated at the concentrator into slimes and sands. The sands usually are transferred directly to the tailing pond. However, in one case, the slimes (fines) are leached in a thickener prior to rejoining the thickener underflow with the sand tails. Sand and slimes are then sent to the tailing pond. Thickener overflow is sent to a precipitation plant for recovery of oxide copper (Figure V-16). This variation is employed when mined ores contain a mixture of sulfide and oxide copper.

TABLE V-20. WASTEWATER CONSTITUENTS AND WASTE LOADS RESULTING FROM DISCHARGE OF MILL PROCESS WATERS

PARAMETER	MILL 2120*			MILL 2121†			MINE 2122		
	CONCENTRATION	WASTE LOAD		CONCENTRATION	WASTE LOAD		CONCENTRATION	WASTE LOAD	
	(mg/ℓ) IN WASTEWATER	kg/1000 metric tons	lb/1000 short tons	(mg/ℓ) in WASTEWATER	kg/1000 metric tons	lb/1000 short tons	(mg/ℓ) IN WASTEWATER	kg/1000 metric tons	lb/1000 short tons
FLOW	15,140**	18,628††	42,229***	101,937**	236.6††	56,716***	62,789**	30,897††	7,243,078***
pH	9.6†††	9.6†††	9.6†††	8.4†††	8.4†††	8.4†††	8.39†††	8.39†††	8.39†††
TDS	3,328	61,994	123,988	1,142	190,269	380,538	2,912	88,001	176,002
TSS	8	149	298	6	1,000	2,000	16	484	968
Oil and Grease	15.0	279	558.0	4.0	666	1,332	4.0	120.9	241.8
As	< 0.07	< 1.304	< 1.608	< 0.07	< 11.66	< 23.32	< 0.01	< 0.302	< 0.604
B	< 0.01	< 0.186	< 0.372	0.95	158.3	316.6	0.16	4.84	9.68
Cd	< 0.005	< 0.093	< 0.186	< 0.02	< 3.33	< 6.66	< 0.005	< 0.15	< 0.30
Cu	0.06	1.12	2.24	0.26	43.32	86.64	0.12	3.63	7.26
Fe	< 0.10	< 1.863	< 3.726	< 0.1	< 16.66	< 33.32	0.93	28.105	56.21
Pb	< 0.1	< 1.863	< 3.726	< 0.1	< 16.66	33.32	2.0	60.44	120.88
Mn	0.03	0.56	1.12	0.04	6.66	13 32	0.06	1.81	3.62
Hg	0.0011	0.02	0.04	< 0.0001	< 0.017	< 0.034	< 0.0001	< 0.003	< 0.006
Ni	< 0.05	< 0.93	< 1.86	< 0.05	< 8.33	< 16.66	< 0.10	< 3.02	< 6.04
Se	0.043	0.801	1.602	0.015	2.50	5.0	0.030	0.91	1.82
Sr	2.40	44.71	89.42	3.4	566.5	1,133 0	0.98	29.62	59.24
Zn	< 0.05	< 0.931	< 1.862	< 0.05	< 8.33	< 16.66	< 0.05	< 1.51	< 3.02
Co	< 0.04	< 0.745	< 1.490	< 0.04	< 6.66	< 13.32	0.12	3.63	7.26
Cyanide	< 0.01	< 0.186	< 0.372	< 0.01	< 1.67	< 3.34	< 0.01	< 0.302	< 0.604
CONTROL	70% RECYCLE			NONE			35% RECYCLE		
TREATMENT	LIMING AND SETTLING			LIMING AND SETTLING			NONE		

*Influenced by acid mine water and leach solution

†Influenced by mine water and smelter wastes

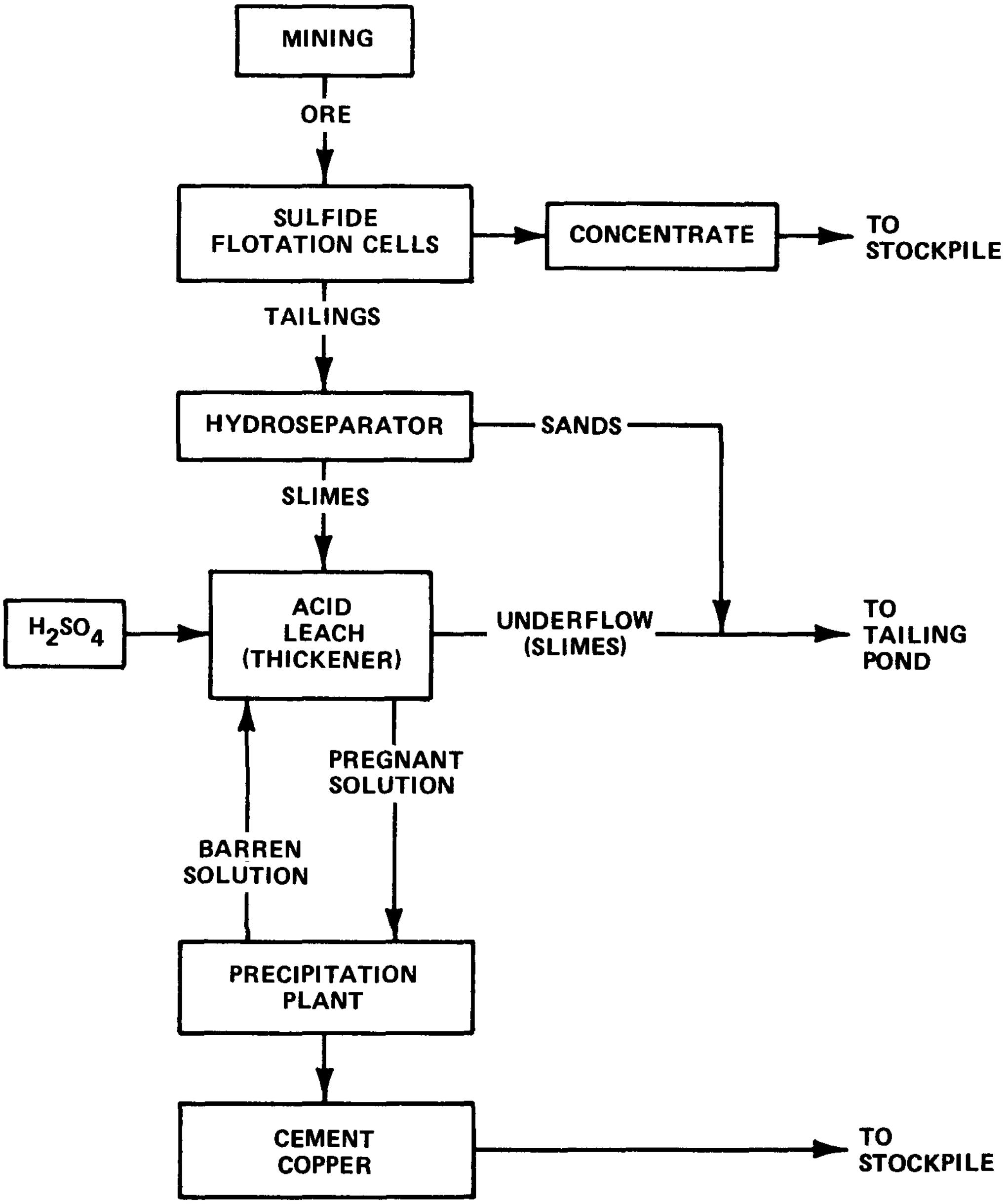
**In m^3/day

††In m^3/1000 metric tons

***In gal/1000 short tons

†††Value in pH units

Figure V-16. FLOWSHEET FOR MISCELLANEOUS HANDLING OF FLOTATION TAILS (MILL 2124)



Variations in Mill Processes

Dual Process. Ores which contain mixed sulfide and oxide mineralization in equal ratios (greater than 0.4 percent copper sulfides or oxides) may be treated with vat leaching, as well as with froth flotation, in a dual process (Figure V-17).

Ore is crushed and placed in vats for leaching with sulfuric acid, as described under "vat leaching." The leachate is sent to iron precipitation or electrowinning plants for recovery of copper. The residue, or tails, remaining in the vats contains nonleachable copper sulfides and is treated by froth flotation to recover the copper, as described under "Froth Flotation."

Water usage and tailing-water quality are similar to the processes of vat leaching and froth flotation. No discrete discharge differences result from this variation compared to vat leaching and froth flotation.

Leach/Precipitation/Flotation (LPF) Process. Mixed sulfide and oxide mineralization may also be handled by the leach/precipitation/flotation process. Crushing may be in two or three stages (Figure V-18). Both rod and ball mills may be employed to produce a pulp of less than 65 mesh and 25 percent solids. The pulp flows to acid-proof leach agitators. Sulfuric acid (to a pH of 1.5 or 2.0) is added to the feed. The leaching cycle continues for approximately 45 minutes. The acid pulp then is fed to precipitation cells, where burned and shredded cans or finely divided sponge iron (less than 35 mesh) may be used to precipitate copper by means of an oxidation/reduction reaction, which increases the pH of the pulp to 3.5 to 4.0:

$$CuSO_4 + \underset{\text{(excess)}}{Fe} \longrightarrow Cu + FeSO_4$$

Copper precipitates as a sponge, and the entire copper sponge, together with pulp-sponge iron feed, is carried to flotation cells. Flotation recovers both sponge copper and copper sulfide in the froth by means of the proper conditioning reagents, such as Minerec A as a collector and pine oil as a frother. Flotation is accomplished at a pH of 4.0 to 6.0 ($\pm$0.5). The concentrate is thickened and filtered before it is shipped to the smelter. Copper recovery may be as high as 91 percent. An example of reagent consumption for this process is:

Figure V-17. DUAL PROCESSING OF ORE (MILL 2124)

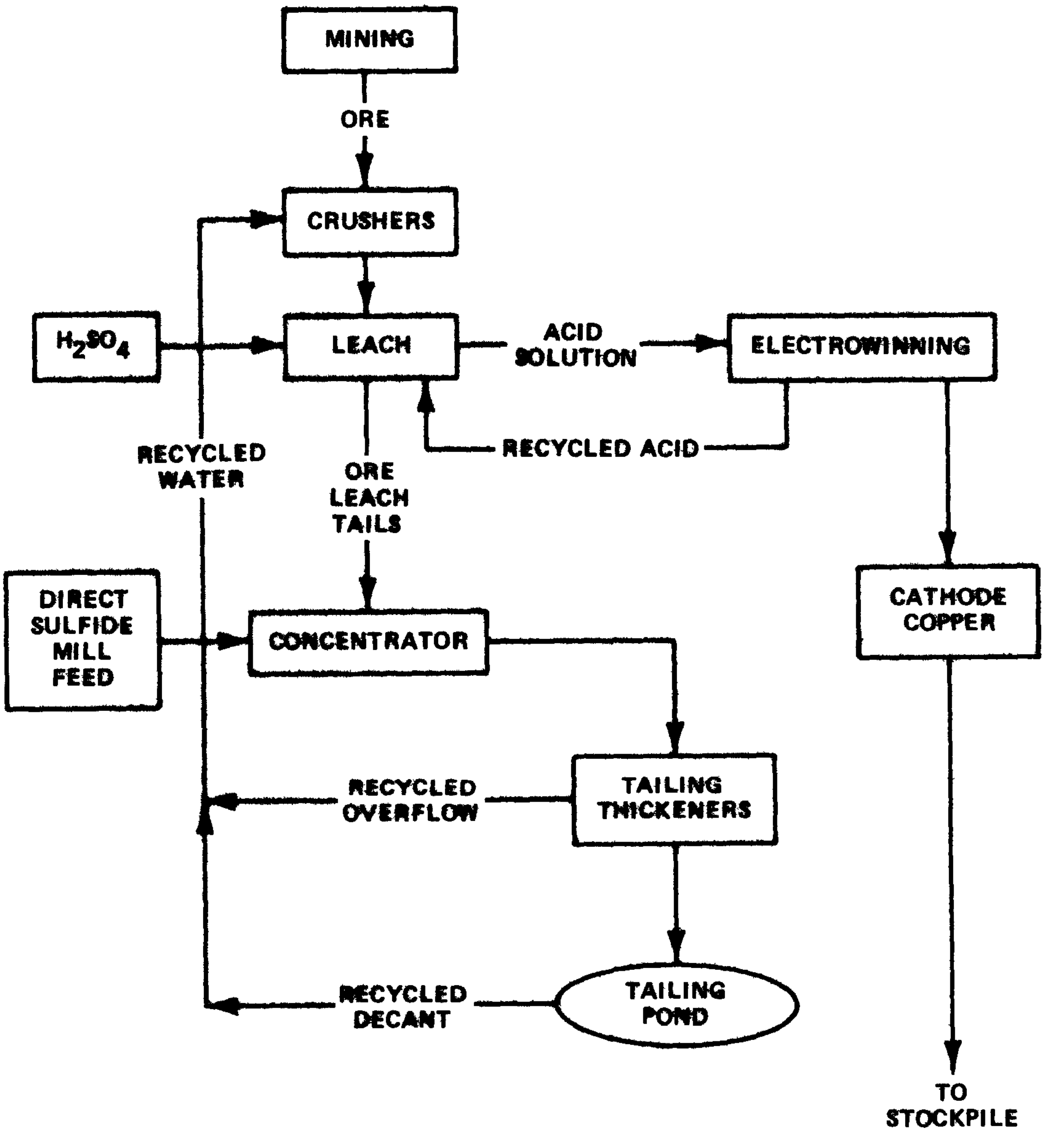
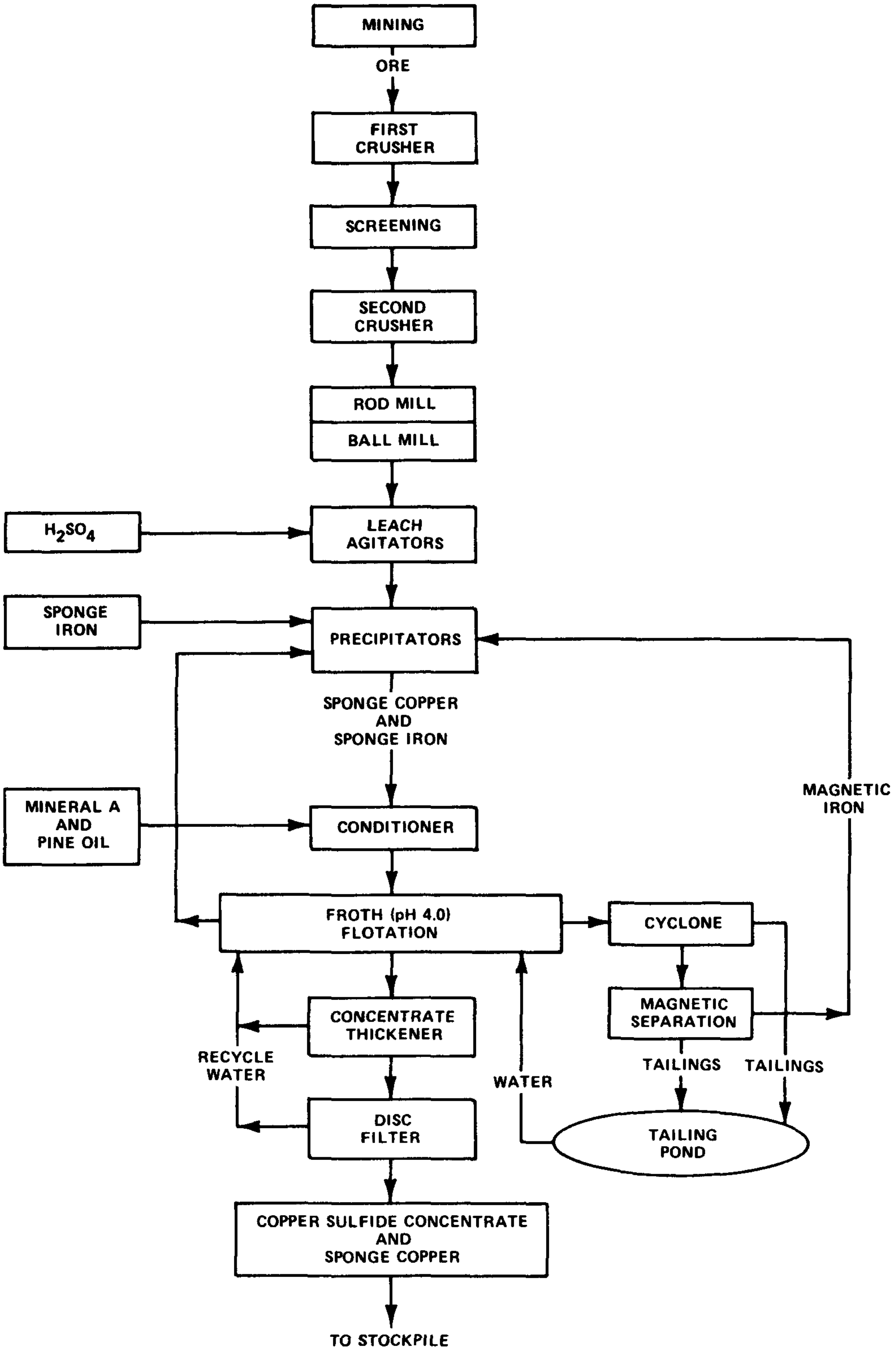


Figure V-18. LEACH/PRECIPITATION/FLOTATION PROCESS



Reagent type	kg/metric ton of mill feed	lb/short ton of mill feed
Sulfuric acid	12.5	25
Sponge iron	18	36
Minerec A	0.09	0.18
Pine oil	0.04	0.08

Lead and Zinc Ores

The chemical characteristics of raw mine drainage are determined by the ore mineralization and by the local and regional geology encountered. Pumping rates for required mine dewatering in the lead and zinc ore mining industry are known to range from hundreds of cubic meters per day to as much as 200,000 cubic meters per day (52 million gallons per day).

The chemical characteristic of raw waste water from the milling operation appear to be considerably less variable from facility to facility than mine waste water. The volume of mill discharge varies from as little as 1000 cubic meters per day (264,200 gallons per day) to as much as 16,000 cubic meters per day (4 million gallons per day). When expressed as the amount of water utilized per unit of ore processed, quantities varying from 330 cubic meters per metric ton per day (79,070 gal/short ton/day) to 1,100 cubic meters per metric ton per day (263,566 gal/short ton/day) are encountered. The sources and characteristics of wastes in each recommended subcategory are discussed below.

Sources of Wastes - Mine Water (No Solubilization Potential).

The main sources of mine water are:

(1) Ground-water infiltration.

(2) Water pumped into the mine for machines and drinking.

(3) Water resulting from hydraulic backfill operations.

(4) Surface-water infiltration.

The geologic conditions which prevail in the mines in this subcategory consist of limestone or dolomitic limestone with little or no fracturing present. Pyrite may be present, but the limestone is so prevalent that, even if acid is formed, it is almost certainly neutralized *in situ* before any metals are solubilized. Therefore, the extent of heavy metals in solution is minimal. The principal contaminants of such mine waters are:

(1) Suspended solids resulting from the blasting, crushing, and transporting of the ore. (Finely pulverized minerals may be constituents of these suspended solids.)

(2) Oils and greases resulting from spills and leakages from material-handling equipment utilized (and, often, maintained) underground.

(3) Hardness and alkalinity associated with the host rock and ore.

(4) Natural nutrient level of the subterranean water.

(5) Dissolved salts not present in surface water.

(6) Small quantities of unburned or partially burned explosive substances.

A simplified diagram illustrating mining operations and mine waste water flow for a mining operation exhibiting no solubilization potential is shown in Figure V-19. Typically, mine water may be treated and discharged or used in a nearby mill as flotation-process water.

The range of chemical constituents measured for three mines sampled as part of this program is given in Table V-21. The data, although limited to 4-hour composite samples obtained during three site visits, generally confirm other data with a narrower range of parameters. Generally, raw mine water from this class of mine is of good quality, and any problem parameters appear to be readily remedied by the current treatment practice of sedimentation-pond systems.

Sources of Wastes - Mine Water (Solubilization Potential)

The sources of water from mines with solubilization potential are the same as those for mines with no solubilization potential. The key difference in this situation is the local geologic conditions that prevail at the mine. These conditions lead to either gross or localized solubilization caused by acid generation or solubilization of oxidized minerals. The resultant waste water pumped from the mine contains the same waste parameters as that from the preceding subcategory but also contains substantial soluble metals. Table V-22 shows the

Figure V-19. WATER FLOW DIAGRAM FOR MINE 3105

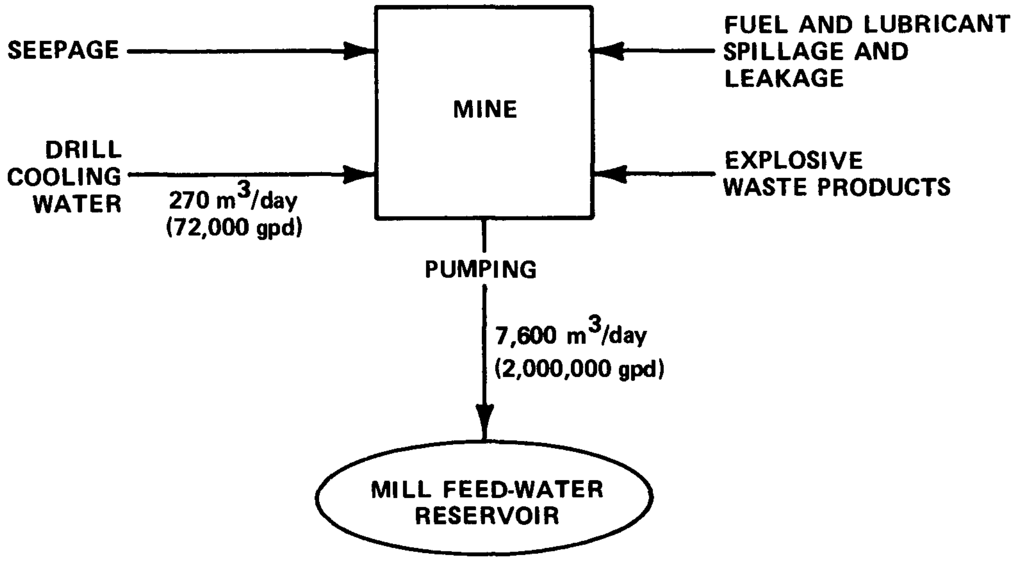


TABLE V-21. RANGE OF CHEMICAL CHARACTERISTICS OF SAMPLED RAW MINE WATER FROM LEAD/ZINC MINES 3102, 3103, AND 3104 SHOWING LOW SOLUBILIZATION

PARAMETER	CONCENTRATION (mg/ℓ)
pH	7.4 to 8.1*
Alkalinity	180 to 196
Hardness	200 to 330
TSS	2 to 138
TDS	326 to 510
COD	< 10 to 631
TOC	< 1 to 4
Oil and Grease	3 to 29
P	0.03 to 0.15
NH_3	<0.05 to 1.0
Hg	<0.0001 to 0.0001
Pb	< 0.2 to 4.9 †
Zn	0.03 to 0.69
Cu	<0.02
Cd	<0.002 to 0.015
Cr	<0.02
Mn	<0.02 to 0.06
Fe	<0.02 to 0.90
Sulfate	37 to 63
Chloride	3 to 57
Fluoride	0.3 to 1.2

* Value in pH units

† Data may reflect influence of acid stabilization on sediment

TABLE V-22. RANGE OF CHEMICAL CHARACTERISTICS OF RAW MINE WATERS FROM FOUR OPERATIONS INDICATING HIGH SOLUBILIZATION POTENTIAL)

PARAMETER	CONCENTRATION (mg/ℓ) IN RAW MINE WATER
pH	3.0 to 8.0*
Alkalinity	14.6 to 167
Hardness	178 to 967
TSS	< 2 to 58
TDS	260 to 1,722
COD	15.9 to 95.3
TOC	1 to 11
Oil and Grease	0 to 3
P	0.020 to 0.075
NH_3	< 0.05 to 4.0
Hg	0.0001 to 0.0013 < 0.0001 to 0.0001
Pb	0.1 to 0.3
Zn	1.38 to 38.0
Cu	< 0.02 to 0.04
Cd	0.016 to 0.055
Cr	0.17 to 0.42
Mn	< 0.02 to 57.2
Fe	0.12 to 2.5
Sulfate	48 to 775
Chloride	< 0.01 to 220
Fluoride	0.06 to 0.80

*Value in pH units

range of chemical constituents from four mines exhibiting solubilization potential.

The following reactions are the basic chemical reactions that describe an acid mine-drainage situation:

Reaction 1--Oxidation of Sulfide to Sulfate

When natural sulfuritic material in the form of a sulfide (and, usually, in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapor) as the limiting condition:

(A) Assuming that the process takes place in a dry environment, an equal amount of sulfur dioxide will be generated with the formation of (watersoluble) ferrous sulfate:

$$FeS_2 + 3O_2 \longrightarrow FeSO_4 + SO_2$$

(B) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapor), the direct formation of sulfuric acid and ferrous sulfate, in equal parts, results:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

In most mining environments in this subcategory (underground, as well as in the tailing area), reaction (B) is favored.

Reaction 2--Oxidation of Iron (Ferrous to Ferric)

Ferrous sulfate, in the presence of quantities of sulfuric acid and oxygen, oxidizes to the ferric state to form (water-soluble) ferric sulfate:

$$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

Here, water is not limiting since it is not a requirement for the reaction but, rather, is a product of the reaction. Most evidence seems to indicate that bacteria (*Thiobacillus ferrobacillus*, *Thiobacillus sulfooxidans*) are involved in the above reaction and, at least, are responsible for accelerating the oxidation of ferrous iron to the ferric state.

Reaction 3--Precipitation of Iron

The ferric iron associated with the sulfate ion commonly combines with the hydroxyl ion of water to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and precipitates:

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4$$

Note that the ferric ion can, and does, enter into an oxidation/ reduction reaction with iron sulfide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulfuritic materials (iron sulfides, etc.) to the sulfate form, thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \longrightarrow 3FeSO_4 + 2S$$

$$S + 3O + H_2O \longrightarrow H_2SO_4$$

The fact that very little "free" sulfuric acid is found in mine waste drainage is probably due to the reactions between other soluble mineral species and sulfuric acid.

In some ore bodies, such reactions--and subsequent solubilization of metals--may occur in local regions in which little or no limestone or dolomite is available for neutralization before the harmful solubilization occurs. Once a metal such as copper, lead, or zinc is in solution, the subsequent mixing and neutralization of that water may not precipitate the appropriate hydroxide unless a rather high pH is obtained. Even if some of the metal is precipitated, the particles may be less than 0.45 micrometer (0.000018 inch) in size and, thus, appear as soluble metals under current analytical practice.

Conditions compatible with solubilization of certain metals-particularly, zinc--are associated with heavily fissured ore bodies. Although the minerals being recovered are sulfides, fissuring of the ore body allows the slight oxidation of the ore to oxides, which are more soluble then the parent minerals.

When conditions exist which provide a potential for solubilization, the mine water resulting is of a quality which requires treatment beyond conventional sedimentation. The best current practice suggests that the treated mine water is likely to be of a quality inferior to raw discharge from mines where the potential for such solubilization does not exist.

A flow diagram illustrating flows encountered in a mine of the type described in this subcategory is shown as Figure V-

20. The characteristics of mine waters from this subcategory are illustrated by Table V-22, which amplifies the above observations.

These data suggest that particular problems are encountered in achieving zinc and cadmium levels approaching the levels of raw mine water from the class of mines with no solubilization potential.

Process Description - Mill Flows and Waste Loading

The raw waste water from a lead/zinc flotation mill consists principally of the water utilized in the flotation circuit itself, along with any housecleaning water used. The waste streams consist of the tailing streams (usually, the underflow of the zinc rougher flotation cell), the overflow from the concentrate thickeners, and the filtrate from concentrate dewatering. The water separated from the concentrates is often recycled in the mill but may be pumped with the tails to the tailing pond, where primary separation of solids occurs. Usually, surface drainage from the area of the mill is also collected and sent to the tailing-pond system for treatment.

The principal characteristics of the waste stream from mill operations are:

(1) Solid loadings of 25 to 50 percent (tailings).
(2) Unseparated minerals associated with the tails.
(3) Fine particles of minerals--particularly, if the thickener overflow is not recirculated.
(4) Excess flotation reagents which are not associated with the mineral concentrates.
(5) Any spills of reagents which occur in the mill.

Figure V-21 illustrates the sources, flow rates, and fates of water used for the flotation process in beneficiation of lead and zinc ores.

One aspect of mill waste which has been relatively poorly characterized from an environmental-effect standpoint is the excess flotation reagents. Unfortunately, it is very difficult to analytically detect the presence of these reagents--particularly, those which are organic. The TOC and MBAS surfactant parameters may give some indication of the presence of the organic reagents, but no definitive information is implied by these parameters.

The raw and treated waste characteristics of four mills visited during this program are presented in Table V-23.

Figure V-20. WATER FLOW DIAGRAM FOR MINE 3104

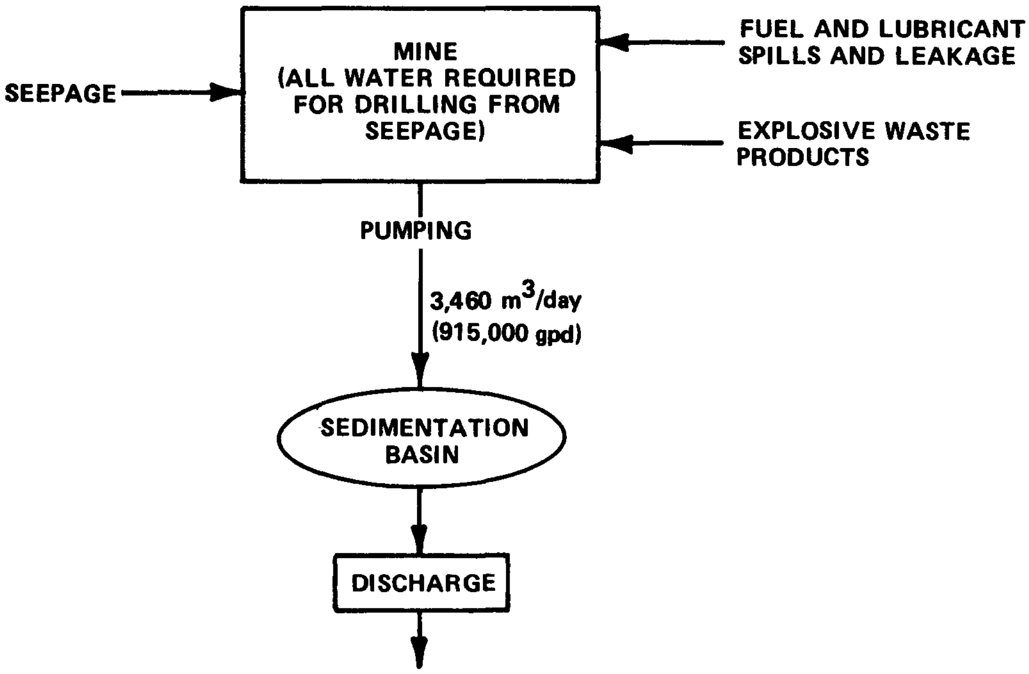
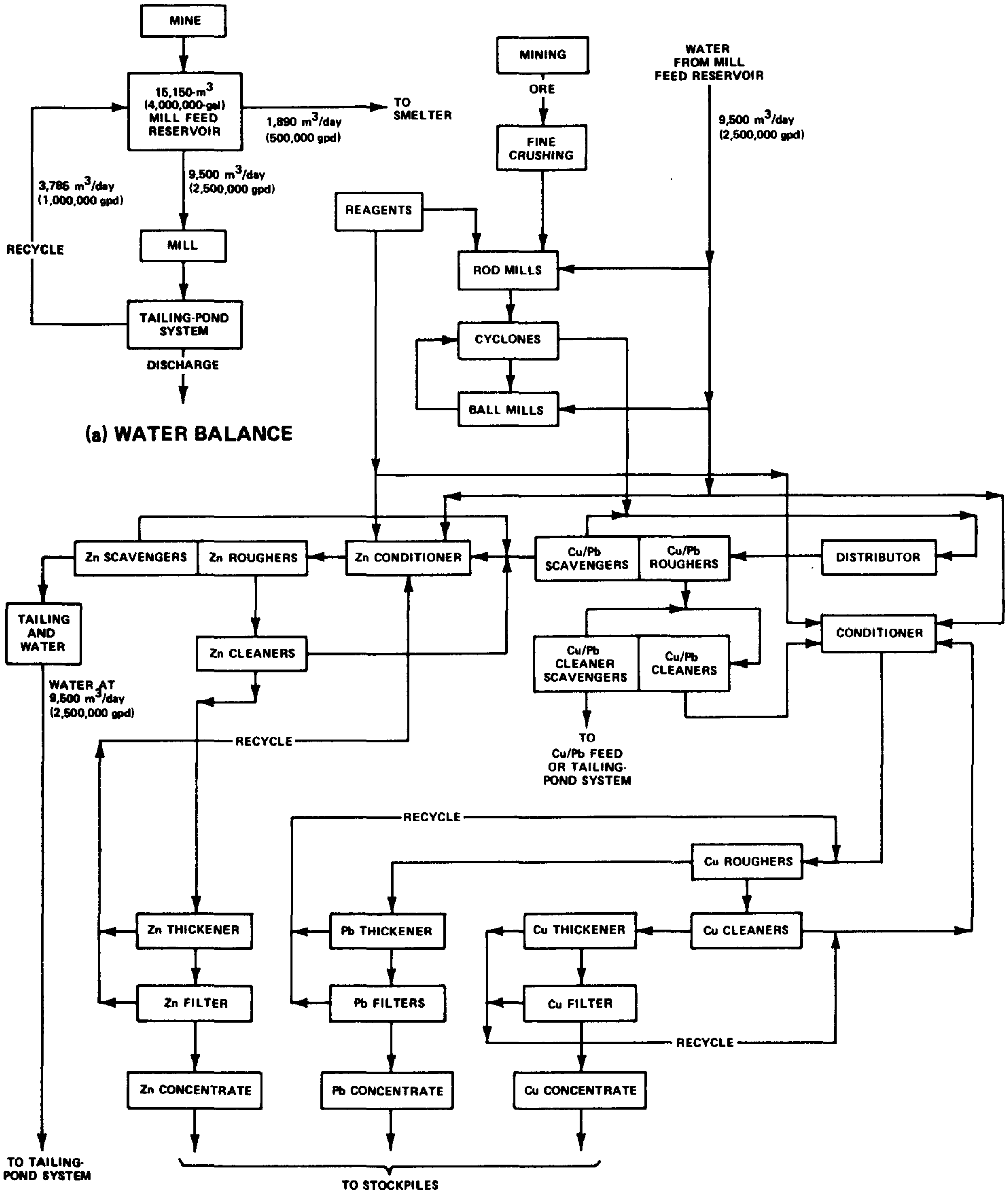


Figure V-21. FLOW DIAGRAM FOR MILL 3103



(a) WATER BALANCE

(b) MILL PROCESS

TABLE V-23. RANGES OF CONSTITUENTS OF WASTEWATERS AND RAW WASTE LOADS FOR MILLS 3102, 3103, 3104, 3105, AND 3106

PARAMETER	RANGE OF CONCENTRATION (mg/ℓ) IN WASTEWATER		RANGE OF RAW WASTE LOAD							
			per unit ore milled				per unit concentrate produced			
			kg/1000 metric tons		lb/1000 short tons		kg/1000 metric tons		lb/1000 short tons	
	lower limit	upper limit	lower limit	upper limit	lower limit	upper limit	lower limit	upper limit	lower limit	upper limit
pH	7.9*	8 8*	–	–	–	–	–	–	–	–
Alkalinity	26	609	410	1,600	820	3,200	1,450	10,200	2,900	20,400
Hardness	310	1,760	460	4,700	920	9,400	2,290	32,500	4,580	65,000
TSS	< 2	108	7	285	14	570	30	2,000	60	4,000
TDS	670	2,834	940	8,500	1,840	17,000	4,800	50,900	9,600	101,800
COD	71.4	1,535	6	4,800	12	9,600	30	50,000	60	100,000
TOC	11	35	6 35	130	13	260	30	580	60	1,160
Oil and Grease	0	8	5	21	10	42	30	130	60	260
MBAS Surfactants	0 18	3.7	0 236	13	0 47	26	2 05	60 7	5 70	121 4
P	0 042	0 150	0 108	0 876	0 21	1 75	0 54	2 54	1.08	5 08
Ammonia	< 0 05	14	0 064	26.4	0 125	52 8	0 32	185	0 64	370
Hg	< 0 0001	0 1	< 0 00013	0 0026	< 0.00026	0 0052	< 0 00168	0 130	< 0 00336	0.260
Pb	< 0 1	1 9	< 0 127	6 9	< 0.25	13 8	< 0 900	32 2	< 1 8	64 4
Zn	0 12	0 46	0 089	17 2	0 19	34 4	0 62	86 0	1 24	172
Cu	< 0 02	0 36	< 0 026	0 158	< 0 052	0 316	< 0 18	1 96	< 0 36	3 92
Cd	0 005	0.011	0 008	0 018	0 016	0 036	< 0 18	8 85	< 0 36	17 7
Cr	< 0 02	0 67	< 0 026	1 77	< 0.052	3 44	< 0 18	1 36	< 0 36	2 72
Mn	< 0 02	0 08	< 0 026	0 290	< 0 052	0 580	< 0 45	10 0	< 0.90	20
Fe	0 05	0 53	0 064	1 16	0 000129	2 32	0 012	0 198	< 0.024	0 396
Cyanide	< 0 01	0 03	< 0 013	0 109	< 0 026	0 218	0.091	0 509	0 182	1 18
Sulfate	295	1 825	130	4,800	260	9,600	1,260	33,700	2,520	67,400
Chloride	21	395	20	870	40	1,740	210	4,070	420	8,140
Fluoride	0 13	0 26	0 370	0 944	0 74	1 88	2 03	5 45	4.06	10.9

*Value in pH units

Information for a mill using total recycle and one at which mill wastes are mixed with metal refining wastes in the tailing pond are not included in this summary. Feed water for the mills is usually drawn from available mine waters; however, one mill uses water from a nearby lake. These data illustrate the wide variations caused by the ore mineralogy, grinding practices, and reagents utilized in the industry.

Gold Ores

Water flow and the sources, nature, and quantity of the wastes dissolved in the water during the processes of gold-ore mining and beneficiation are described in this section.

Water Uses

The major use of water in this industry is in beneficiation processes, where it is required for the operating conditions of the individual process. Water is normally introduced at the grinding stage of lode ores (shown in the process diagrams of Section III) to produce a slurry which is amenable to pumping, sluicing, or classification into sand and slime fractions for further processing. In slurry form, the ground ore is most amenable to beneficiation by the technology currently used to process the predominantly low-grade and sulfide gold ores--i.e., cyanidation and flotation. The gravity separation process commonly used to beneficiate placer gravels also requires water as a medium for separation of the fine and heavy particles.

Other uses of water in gold mills include washing of floors and machinery and domestic applications. Wash water is normally combined with the process waste effluent but constitutes only a small fraction of the total effluent. Some fresh water is also required for pump sealing. A large quantity of water is required in the vat leach process to wash the leached sands and residual cyanide from the vats. Because the sands must be slurried for pumping twice, the vat leach process requires approximately twice the quantity of water necessary for the milling of gold ore by any of the other leaching processes.

With the exception of hydraulic mining and dredgind water is not normally directly used in mining operations but, rather, is discharged as an indirect result of a mining operation. Cooling is required in some underground mines, and water is used to this end in air conditioning systems. This water does not come into direct contact with the materials or the mine and is normally discharged separately from the mine effluent.

Water flows of four gold mining and milling operations visited during this study are presented in Figure V-22.

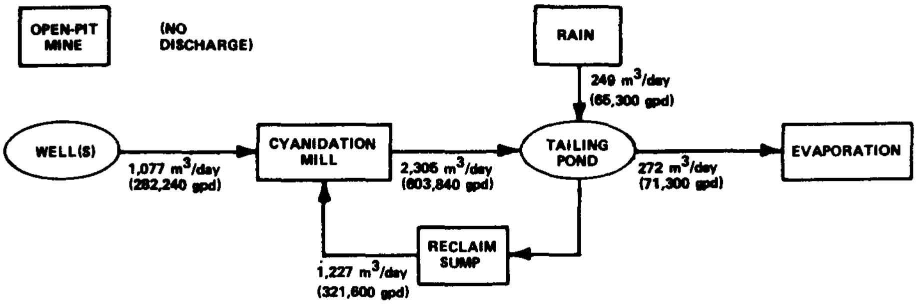
Sources of Wastes

There are two basic sources of effluents containing pollutants: (1) mines and (2) beneficiation processes. Mines may be either open-pit or underground operations. In the case of an open pit, the source of the pit discharge, if any, is precipitation, runoff, and ground-water infiltration into the pit. Ground-water infiltration is the primary source of water in underground mines. However, in some cases, sands removed from mill tailings are used to backfill stopes. These sands may initially contain 30 to 60 percent moisture, and this water may constitute a major portion of the mine effluent. The particular waste constituents present in a mine or mill discharge are a function of the mineralogy and geology of the ore body and the particular milling process employed. The rate and extent to which the minerals in an ore body become solubilized are normally increased by a mining operation, due to the exposure of sulfide minerals and their subsequent oxidization to sulfuric acid. At acid pH, the potential for solubilization of most heavy metals is greatly increased. Not all mine discharges are acid, however; in those cases where they are alkaline, soluble arsenic, selenium, and/or molybdenum may present problems.

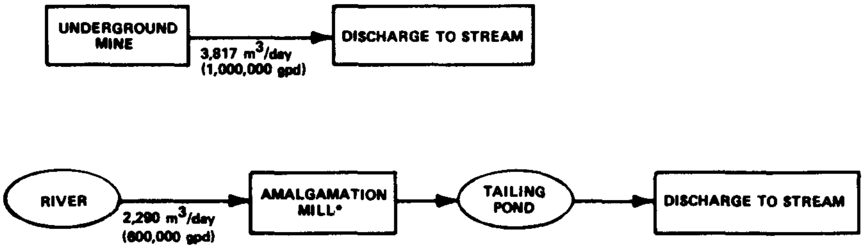
Waste water from a placer operation is primarily water that was used in a gravity separation process. Where a placer does not occur in a stream, water is used to fill a pond on which a barge is floated. The process water is generally discharged into either this pond or an on-shore settling pond. Effluents of the settling pond usually are combined with the dredge-pond discharge, and this constitutes the final discharge. The principal waste water constituents from placer operations are high suspended solids.

Waste water emanating from mills consists almost entirely of process water. High suspended-solid loadings are the most characteristic waste constituent of a mill waste stream. This is primarily due to the necessity for fine grinding of the ore to make it amenable to a particular beneficiation process. In addition, the increased surface area of the ground ore enhances the possibility for solubilization of the ore minerals and gangue. Although the total dissolved-solid loading may not be extremely high, the dissolved heavy-metal concentration may be relatively high as a result of the highly mineralized ore being processed. These heavy metals, the suspended solids, and process reagents present

Figure V-22. WATER FLOW IN FOUR SELECTED GOLD MINING AND MILLING OPERATIONS

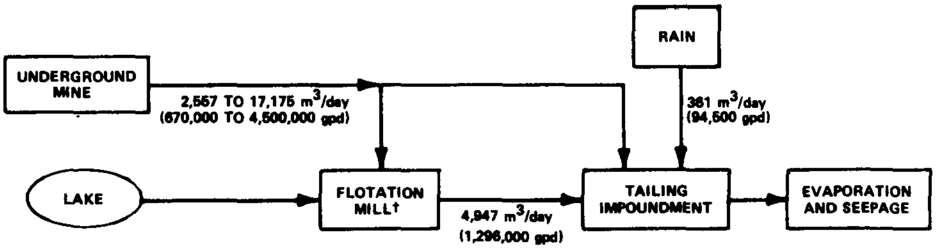


(a) MINE/MILL 4101



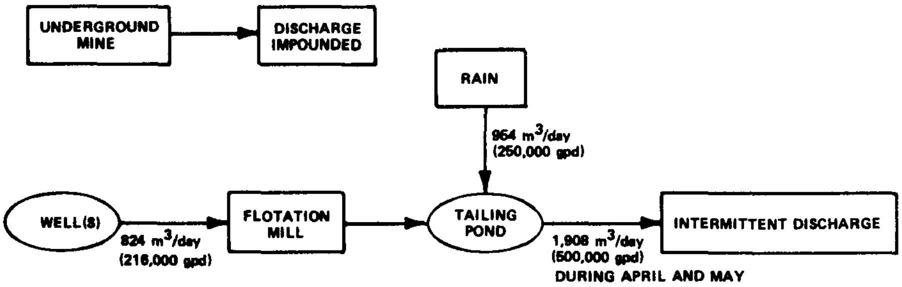
*AMALGAMATION OF GRAVITY-SEPARATED SANDS; FINES AND GOLD-EXTRACTED SANDS ARE FLOATED FOR RECOVERY OF BASE METALS.

(b) MINE/MILL 4102



†GOLD VALUES PRESENT IN BASE-METAL CONCENTRATES, RECOVERED AT SMELTER OR REFINERY.

(c) MINE/MILL 4103



(d) MINE/MILL 4104

are the principal waste constituents of a mill waste stream. Depending on the process conditions, the waste stream may also have a high or low pH. The pH is of concern, not only because of its potential toxicity, but also because of the resulting effect on the solubility of the waste constituents.

Process Description - Mining

Gold is mined from two types of deposits: placers and lode (vein) deposits. Placer mining consists of excavating gold-bearing gravel and sands. This is currently done primarily by dredging but, in the past, has included hydraulic and drift mining of buried placers too deep to strip. Lode deposits are mined either by either underground (mines 4102, 4104, and 4105) or open-pit (mine 4101) methods, the particular method chosen depending on such factors as size and shape of the deposit, ore grade, physical and mineralogical character of the ore and surrounding rock, and depth of the deposit.

The chemical composition of raw mine effluent measured at two of the mines visited is listed in Table V-24. Although incomplete chemical data for mine 4102 are listed, considerable variability was observed with respect to several key components (TS, TDS, SO_4^{--}, Fe, Mn, and Zn).

Process Descriptions - Milling

The gold milling processes requiring water usage with subsequent waste loading of this water, as discussed previously, are:

(1) cyanidation,

(2) amalgamation, and

(3) flotation.

There are four variations of the cyanidation process currently being practiced in the U.S.:

(1) agitation-leaching,

(2) vat leaching,

(3) carbon-in-pulp, and

(4) heap leaching.

TABLE V-24. CHEMICAL COMPOSITION OF RAW MINE WATER FROM MINES 4105 AND 4102

PARAMETER	CONCENTRATION (mg/ℓ)	
	MINE 4105	MINE 4102**
pH		6.15*
Alkalinity	275	-
Color	34†	-
Turbidity (JTU)	2.40	-
TOS	1,190	535
TDS	1,176	530
TSS	14	5
Hardness	733	-
COD	35.01	27
TOC	12.0	-
Oil and Grease	1	<0.1
MBAS Surfactants	0.095	-
Al	<0.2	0.143
As	0.03	0.084
Be	<0.002	-
Ba	<0.5	-
B	0.18	-
Cd	<0.02	0.025
Ca	87.0	-
Cr	<0.02	-
Cu	<0.02	0.056
Total Fe	1.2	25.11
Pb	<0.1	0.82

PARAMETER	CONCENTRATION (mg/ℓ)	
	MINE 4105	MINE 4102**
Mg	80.0	-
Mn	0.14	11.93
Hg	<0.0001	-
Ni	0.10	0.06
Tl	<0.05	-
V	<0.2	-
K	44.0	-
Ag	<0.02	-
Na	80.0	-
Sr	0.78	-
Te	0.10	-
Ti	<0.5	-
Zn	<0.01	7.31
Sb	<1	-
Mo	<0.2	-
Sulfate	618.75	1,192
Nitrate	5.05	-
Phosphate	<0.05	-
Cyanide	<0.01	<0.01
Phenol	<0.01	-
Chloride	1.8	3
Fluoride	2.05	-

*Value in pH units

†Value in cobalt units

** Industry data

TOS = Total Solids

In general, the cyanidation process involves solubilization of gold with cyanide solution, followed by precipitation of gold from solution with zinc dust. (See Figure III-9.)

The agitation-leach process employed by mill 4401 requires water to slurry the ground ore. Cyanide solution is added to this pulp in tanks, and this mixture is agitated to maintain maximum contact of the cyanide with the ore. Pregnant solution is separated from the leached pulp in thickeners, and gold is precipitated from this solution with zinc dust. (See Figure III-10.)

The vat leaching process is employed by mill 4105. In this process, vats are filled with ground ore slurry, and the water is allowed to drain off. Cyanide solution is then sprayed into the vats, and gold is solubilized by cyanide percolating through the sands. Pregnant solution is collected at the bottom of the vats, and gold is precipitated with zinc dust.

The carbon-in-pulp process is also used by mill 4105. This process was designed to recover gold from slimes generated in the ore grinding circuit. Water is added to the ore to produce a slurry in the grinding circuit which is subsequently cycloned. Cyclone underflows (sands) are treated by vat leaching, while cyclone overflow is treated by the carbon in-pulp process. In this process, the slimes are mixed with cyanide solution in large tanks, and contact is maintained by agitation of the mixture (much the same as for agitation leach). This mixture is then caused to batch flow through a series of vats, where the solubilized gold is collected by adsorption onto activated charcoal, which is held in screens and moved through the series of vats countercurrent to the flow of the slime mixtures. Gold is stripped from this charcoal using a small volume of hot caustic. An electrowinning process is used to recover the gold from this solution. (See Figure III-9.)

Heap leaching has had only limited application in recent years. This inexpensive process has been used primarily to recover gold from low-grade ores. As the price of gold has risen dramatically since 1970, the principal use of heap leaching during this time has been in the recovery of gold from old mine waste dumps. This process essentially consists of percolating cyanide solution down through piled-up waste rock. The leachate is usually collected by gravity in a sump; in some cases, use is made of a specially constructed pad to support the rock and collect the leachate.

Amalgamation can be done in a number of ways. The process employed by mill 4102 is termed "barrel amalgamation." This essentially consists of adding mercury to gold-containing sands in a barrel. The barrel is then rotated to facilitate maximum contact of mercury with the ore. The amalgam is collected by gravity, and the gold and mercury are separated by pressing in a hand-operated press.

Water is used by mill 4104 to slurry ground ore, making it amenable to a flotation process. The slurried ore is transported to conditioner tanks, where specific reagents are added; essentially, this causes gold-containing minerals to float and be collected in a froth, while other minerals sink and are discarded. This separation is achieved in flotation cells in which the mixture is agitated to achieve the frothing. The froth is collected off the top of the slurry and is further upgraded by filtering and thickening. Tailings from the flotation process of mill 4104 are further processed by the cyanidation/agitation-leach process to recover residual gold values.

In addition to suspended solids and dissolved metals, reagents used in the mill beneficiation process also add to the pollutant loading of the waste stream. The particular reagents used are a function of the process employed to concentrate the ore. In the gold milling industry, cyanide and mercury, clearly, are the most prominent reagents of the cyanidation and amalgamation processes. These reagents are also of primary concern due to their potential toxicities. Table V-25 indicates the quantity of each of these reagents consumed per ton of ore milled. The bulk of these reagents which are used in the process are present in the waste stream.

Because there is a potential solubilization of the ore minerals present, heavy metals from these minerals may exist in the mill waste stream. Table V-26 lists the minerals most commonly associated with gold ore. Since settleable solids and most of the suspended solids are collected and retained in tailing ponds, the dissolved and dispersed heavy metals present in the final discharge are of ultimate concern. Depending upon the extent to which they occur in the ore body, particular heavy metals may be present in a mill waste stream in the range of from below detectable limits to 3 to 4 mg/l. Calcium, sodium, potassium, and magnesium are found at concentrations of less than 100 mg/l to over 1000 mg/l.

High levels of soluble metals usually result from the leaching processes, and this is well-illustrated by the

TABLE V-25. PROCESS REAGENT USE AT VARIOUS MILLS BENEFICIATING GOLD ORE

MILL	MILL PROCESS	REAGENT CONSUMPTION			
		CYANIDATION		AMALGAMATION	
		kg/metric ton ore milled	lb/short ton ore milled	kg/metric ton ore milled	lb/short ton ore milled
4105	Cyanidation/Leach	0.13	0.26	–	–
4105	Cyanidation/Char-in-pulp	0.58	1.16	–	–
4101	Cyanidation/Agitation Leach	0.18	0.35	–	–
4102	Amalgamation	–	–	0.001	0.002

TABLE V-26. MINERALS COMMONLY ASSOCIATED WITH GOLD ORE

MINERAL	COMPOSITION
Arsenopyrite	Fe As S
Pyrite	Fe S
Chalcopyrite	Cu Fe S
Galena	Pb S
Sphalerite	Zn S
Greenockite	Cd S
Cinnabar	Hg S
Pentlandite	$(Fe, Ni)_9 S_8$
Calverite	$Au Te_2$
Sylvanite	$(Au, Ag) Te_2$
Native Gold	Au
Selenium	Se *

*Accompanies sulfur in sulfide minerals

cyanide leach process in the gold industry. Table V-27 summarizes the chemical composition and raw waste loads resulting from four gold milling operations. The processes represented include amalgamation, cyanidation/agitation-leach, cyanidation/vat leach, and the cyanidation/"carbon-in-pulp" process.

Silver Ores

Water flow and the sources, nature, and quantity of the wastes dissolved in the water during the processes of silver-ore mining and beneficiation are described in this section. Coproduct recovery of silver with gold is common, and similar methods of extraction are employed.

Water Uses

The major use of water in the silver-ore milling industry is in the beneficiation process, where it is required for the operating conditions of the process. It is normally introduced at the ore grinding stage of lode ores (see process diagrams, Section III) to produce a slurry which is amenable to pumping, sluicing, or classification for sizing and feed into the concentration process. In slurry form, the ground ore is most amenable to beneficiation by the technology currently used to process the predominantly low-grade sulfide silver ores--i.e., froth flotation. A small amount of silver is recovered from placer gravels by gravity methods, which also require water as a medium for separation of the fine and heavy particles.

Other miscellaneous uses of water in silver mills are for washing floors and machinery and for domestic purposes. Wash water is normally combined with the process waste effluent but constitutes only a small fraction of the total effluent. Some fresh water is also required for pump seals.

With the exception of hydralic mining and dredging, water is not normally directly used in mining operations; rather, it is usually discharged where it collects as an indirect result of a mining operation. Cooling is required in some underground mines for the air conditioning systems. This water does not come into direct contact with the mine and is normally discharged separately from the mine effluent.

Water flows of some silver mining and milling operations visited during this program are presented in Figure V-23.

TABLE V-27. WASTE CHARACTERISTICS AND RAW WASTE LOADS AT FOUR GOLD MILLING OPERATIONS (Sheet 1 of 2)

MINE/MILL	TSS			TDS		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	495,000	61,695,315,000 (123,390,630)	2,871,000 (5,742,000)	462	19,942,000 (39,884,000)	930 (1,860)
4101 (Agitation Leach)	545,000	11,541,465,000 (23,082,930,000)	436,000 (872,000)	4,536	96,060,000 (192,120,000)	3,600 (7,200)
4105 (Vat Leach)	–	– –	– –	–	– –	– –
4105 (Carbon-in-Pulp)	485,000	4.7×10^{11} 9.4×10^{11}	4,171,000 (8,342,000)	886	859,900,000 (1,719,800,000)	7,600 (15,200)

MINE/MILL	TOC			COD		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	34.3	4,275,000 (8,550,000)	199 (398)	11 42	1,423,000 (2,847 000)	66 (132)
4101 (Agitation Leach)	50 0	1,059,000 (2,118,000)	40 (80)	43	911,000 (1,822,000)	34 (68)
4105 (Vat Leach)	–	– –	– –	–	– –	– –
4105 (Carbon-in-Pulp)	97.0	94,100,000 (188,200,000)	830 (1,660)	178 94	173,700,000 (347,400,000)	1,540 (3,080)

MINE/MILL	Cu			As		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	0.03	3,740 (7,480)	0.2 (0.4)	<0.07	< 8,700 (<17,400)	< 0.4 (<0.8)
4101 (Agitation Leach)	0.17	3,600 (7,200)	0 1 (0 2)	0 05	106 (212)	0.04 (0.08)
4105 (Vat Leach)	–	– –	– –	3.5	1,510,000 (3,020,000)	14 (28)
4105 (Carbon-in-Pulp)	2.0	1,941,000 (3,882,000)	17 (34)	–	– –	– –

MINE/MILL	Fe			Zn		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	1.5	187,000 (374,000)	8.7 (17.4)	1.3	162,000 (324,000)	7.5 (15.1)
4101 (Agitation Leach)	<0.5	<10,600 (<21,200)	<0.4 (<0.8)	3.1	65,600 (131,200)	2.5 (5)
4105 (Vat Leach)	–	– –	– –	–	– –	– –
4105 (Carbon-in-Pulp)	77.0	74,700,000 (149,400,000)	660 (1,320)	0.22	213,000 (426,000)	2 (4)

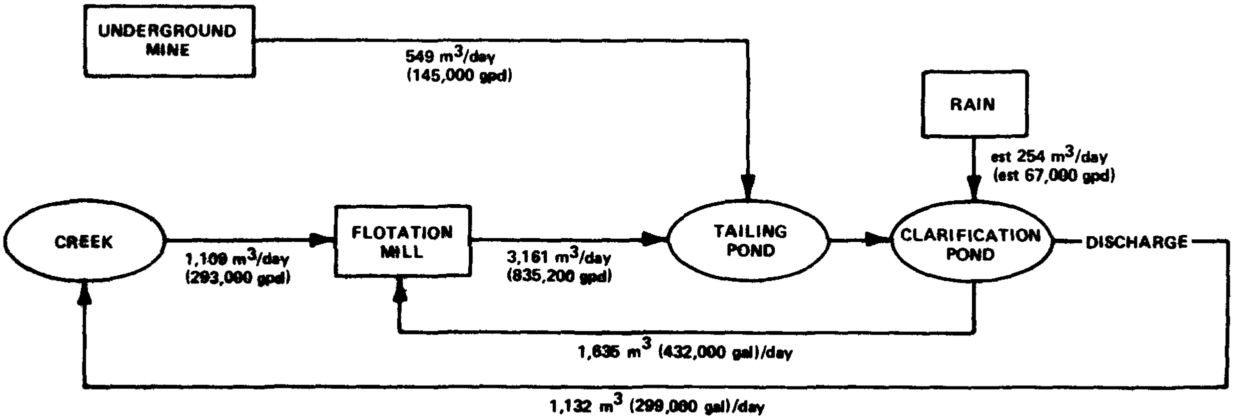
TABLE V-27. WASTE CHARACTERISTICS AND RAW WASTE LOADS AT FOUR GOLD MILLING OPERATIONS (Sheet 2 of 2)

MINE/MILL	Pb			Cd		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	<0.1	<12,500 (<25,000)	< 0.6 (<1.2)	< 0.02	< 2,500 (<5,000)	< 0.1 (< 0.2)
4101 (Agitation Leach)	<0.1	<2,100 (<4,200)	<0.08 (<0.16)	0.10	2,100 (4,200)	0.08 (0.16)
4105 (Vat Leach)	–	– –	– –	<0.01	< 4,300 (<8,600)	<0.04 (<0.08)
4105 (Carbon-in-Pulp)	<0.1	< 97,000 (<194,000)	<0.9 (<1.8)	< 0.02	<19,400 (<38,800)	<0.17 (<0.34)

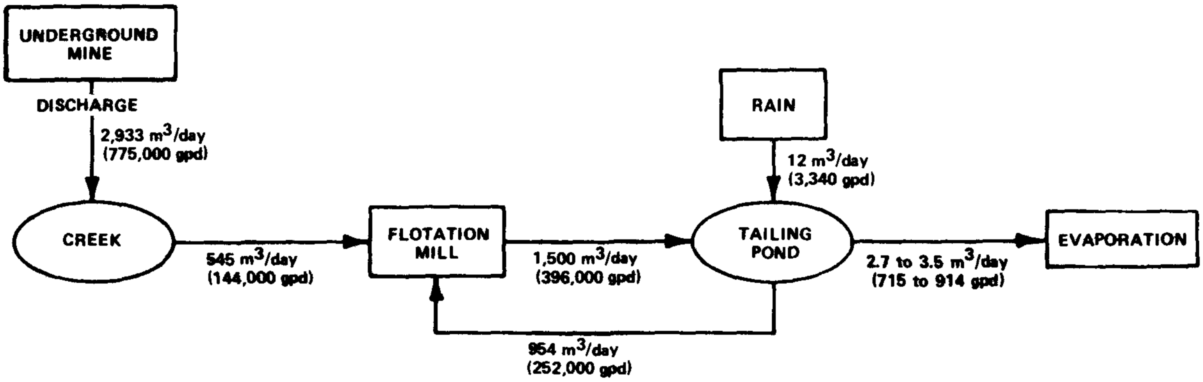
MINE/MILL	Hg			CYANIDE		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	0.0011	137 (274)	0.0064 (0.0128)	<0.01	<1,250 (<2,500)	<0.06 (<0.12)
4101 (Agitation Leach)	–	– –	– –	5.06	107,000 (214,000)	4 (8)
4105 (Vat Leach)	0.004	1,700 (3,400)	0.016 (0.032)	–	– –	– –
4105 (Carbon-in-Pulp)	0.0042	4,070 (8,140)	0.036 (0.072)	0.06	58,000 (116,000)	0.52 (1.04)

MINE/MILL	SULFIDE		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4102 (Amalgamation)	<0.5	< 62,000 (<124,000)	< 2.9 (<5.8)
4101 (Agitation Leach)	<0.5	< 10,600 (<21,200)	< 0.4 (<0.8)
4105 (Vat Leach)	0.2	86,000 (172,000)	0.8 (1.6)
4105 (Carbon-in-Pulp)	1.7	1,650,000 (3,300,000)	15 (30)

Figure V-23. WATER FLOW IN SILVER MINES AND MILLS



(a) MINE/MILL 4401



(b) MINE/MILL 4402

Sources of Wastes

There are two basic sources of effluents: mines and the beneficiation process. Mines may be either open-pit or underground operations. In the case of an open pit, the source of the pit discharge, if any, is precipitation, runoff and ground-water infiltration into the pit. Ground-water infiltration is the primary source of water in underground mines. However, in some cases, sands removed from mill tailings are used to backfill stopes. These sands may initially contain 30 to 60 percent moisture, and this water may constitute a major portion of the mine effluent.

The particular waste constituents present in a mine or mill discharge are a function of the mineralogy and geology of the ore body and the particular milling process employed. The rate and extent to which the minerals in an ore body become solubilized are normally increased by a mining operation, due to the exposure of sulfide minerals and their subsequent oxidization to sulfuric acid. At acid pH, the potential for solubilization of most heavy metals is greatly increased. Not all mine discharges are acid, however; in those cases where they are alkaline, soluble arsenic, selenium, and/or molybdenum may present problems in the silver-ore mining and dressing industry.

Very minor production of silver is obtained from placer deposits as a byproduct of gold recovery. Waste water from placer operations is primarily the water which was used in the gravity separation processing of the ore and/or hydraulic mining of a deposit. The process water is generally discharged into either a barge pond or an onshore settling pond. The effluent of the settling pond usually is combined with the barge pond discharge, and this comprises the final discharge. The principal waste water constituent from any placer operations, whether silver, gold, or other materials, is high loadings of suspended solids.

Waste water emanating from silver mills consists almost entirely of process water. High suspended-solid loadings are the most characteristic waste constituent of silver-mill waste streams. This is caused by fine grinding of the ore, making it amenable to a particular beneficiation process. In addition, the increased surface area of the ground ore enhances the possibility for solubilization of the ore minerals and gangue. Although the total dissolved-solid loading may not be extremely high, the dissolved heavy-metal concentration may be relatively high as a result of the mineralization of the ore being processed. These heavy metals, the suspended solids, and process reagents present are the principal waste constituents of a mill waste stream. In addition, depending on the process conditions, the waste stream may also have a high or low pH. The primary method of ore beneficiation in the silver-ore milling industry is flotation. As a result, mill waste streams can be expected to contain process reagents.

Process Description - Mining

As discussed previously, very little water use is encountered in silver-ore mining, with the exception of dredging for recovery of silver from gold mining operations. As a result of sampling and site visits to mining operations in the silver mining industry, the waste constituents of raw silver-mine water were determined and are presented here in Table V-28. Suspended-solid concentrations are low, while dissolved-solid concentrations constitute the measured total-solid load. Chlorides and sulfates are the principal dissolved-solid constituents observed. Heavy-metal concentrations observed are not notable, with the exception of total iron and total manganese.

Process Description - Milling

Milling processes of silver ore which require water and result in the waste loads present in mill water are:

(1) flotation,

(2) cyanidation, and

(3) amalgamation.

The selective froth flotation process can effectively and efficiently beneficiate almost any type and grade of sulfide ore. This process is employed by mills 4401 and 4403 to concentrate the silver-containing sulfide mineral tetrahedrite and by mill 4402 to concentrate free silver and the silver sulfide mineral argentite. In this flotation process, water is added in the ore grinding circuit to produce a slurry for transporting the ore through the flotation circuit. This slurry first flows through tanks (conditioners), where various reagents are added to essentially cause the desired mineral to be more amenable to flotation and the undesired minerals and gangue to be less amenable. These reagents are generally classified as collectors, depressants, and activators, according to their effect on the ore minerals and gangue. Also, pH modifers are added as needed to control the conditions of the reaction. Following conditioning, frothing agents are added, and the slurry is transported into the flotation cells, where it is mixed and agitated by aerators at the

TABLE V-28. RAW WASTE CHARACTERISTICS OF SILVER MINING OPERATIONS

PARAMETER	CONCENTRATION (mg/ℓ)	
	MINE 4401	MINE 4403
pH	8.0*	-
Acidity	10.2	4.2
Alkalinity	85.0	76.2
Color	47†	<5†
Turbidity (JTU)	2.0	2.2
TOS	504	622
TDS	504	622
TSS	<2	<2
Hardness	240.8	424.8
COD	11.9	19.8
TOC	17	16
Oil and Grease	4	2
MBAS Surfactants	0.085	0.030
Al	<0.2	<0.2
As	<0.07	<0.07
Be	<0.002	<0.002
Ba	<0.6	<0.5
B	0.11	0.09
Cd	<0.02	<0.02
Ca	46.0	44.5
Cr	<0.1	<0.1
Cu	<0.02	<0.02
Total Fe	0.33	2.05
Pb	<0.1	0.18
Mg	27.5	32.0

PARAMETER	CONCENTRATION (mg/ℓ)	
	MINE 4401	MINE 4403
Mn	0.43	6.3
Hg	0.0020	0.0004
Ni	0.09	0.06
Tl	<0.1	<0.1
V	<0.2	<0.2
K	8.0	14.5
Se	0.126	0.068
Ag	<0.02	<0.02
Na	7.0	12.0
Sr	0.15	0.21
Te	<0.3	<0.3
Ti	<0.5	<0.5
Zn	<0.02	0.03
Sb	<0.2	<0.2
Mo	<0.2	<0.2
Chloride	4.2	1.15
Sulfate	175	338
Nitrate	2.45	0.10
Phosphate	0.3	0.25
Cyanide	<0.01	<0.01
Phenol	<0.01	<0.01
Fluoride	0.26	0.21
Kjeldahl N	<0.2	-
Sulfide	<0.5	<0.5
SiO_2	9.75	13.0

*Value in pH units

†Value in cobalt units

TOS = Total Solids

bottom of the cells. The collector and activating agents cause the desired mineral to adhere to the rising air bubbles and collect in the froth, while the undesired minerals or gangue are either not collected or are caused to sink by depressing agents. The froth containing the silver mineral(s) is collected by skimming from the top of the flotation cells and is further upgraded by filtering and thickening (Flow sheets-Section III).

Recovery of silver is also accomplished by cyanidation at mill 4105. This process has been discussed in the part of Section V covering gold ores.

Currently, amalgamation is rarely used for the recovery of silver because most of the ores containing easily liberated silver have been depleted. The amalgamation process is discussed in Sections III and V under gold-ore beneficiation methods.

Quantity of Wastes

Discharge of water seldom exists from open-pit mines. However, most underground mines must discharge water, and the average volume of this water from the crossection of mines visited ranges from less than 199 cubic meters per day (50,000 gallons per day) to more than 13,248 cubic meters per day (3.5 million gallons per day). Where mine discharges occur, the particular metals present and the extent of their dissolution depend on the particular geology and mineralogy of the ore body and on the oxidation potential and pH prevailing within the mine. Concentrations of metals in mine effluents are, therefore, quite variable, and a particular metal may range from below the limit of detectability upwards to 2 ppm. Calcium, sodium, potassium, and magnesium may be present in quantities of less than 5 ppm to about 50 ppm for each metal. However, the heavy metals are of primary concern, due to their toxic effects. Minerals known to be found in association with silver in nature are listed in Table V-29.

For the facilities visited, the volumes of the waste streams discharging from mills processing silver ore range from 1,499 to 3,161 cubic meters per day (396,000 to 835,200 gallons per day). These waste streams carry solids loads of 272 to 1,542 metric tons per day (300 to 1,700 short tons per day) from a mill, depending on the mill. Where underground mines are present, the coarser solids may be removed and used for backfilling stopes in the mine. While the coarser material is easily settled, the very fine particles of ground ore (slimes) are normally suspended to some extent in the waste water and often present removal problems. The quantity of suspended solids present in a particular waste stream is a function of the ore type and mill process because these factors determine how finely ground the ore is.

Heavy metals present in the minerals listed in Table V-29 may also be present in dissolved or dispersed colloidal form in the mill waste stream. Since the settlable solids, and most suspended solids, are collected and retained in tailing ponds, the dissolved and dispersed heavy metals present in the final discharge are of concern. Depending on the extent to which they occur in the ore body, particular heavy metals may be present in a mill waste stream in the range of from below detectable limits to 2 to 3 ppm. Calcium, sodium, potassium, and magnesium normally are found at concentrations of 10 to 250 ppm each. In addition to the suspended solids and dissolved metals, reagents used in the mill beneficiation process also add to the pollutant loading of the waste stream. The particular reagents used are a function of the process employed to concentrate the ore. In the silver milling industry, the various flotation reagents (frothers, collectors, pH modifiers, activating agents, and depressants) are the most prominent reagents of the flotation process. Table V-30 indicates the quantity of these reagents consumed per ton of ore milled. A portion of these reagents which are consumed in the process is present in the waste stream. Note that a large number of compounds fall under the more general categories of frothers, collectors, etc. At any one mill, the particular combination of reagents used is normally chosen on the basis of research conducted to determine the conditions under which recovery is optimized. While flotation processes are generally similar, they differ specifically with regard to the particular reagent combinations. This is attributable, in part, to the highly variable mineralization of the ore bodies exploited. Waste characterizations and raw waste loadings for mill effluents employing flotation and cyanidation in four mills are presented in Table V-31. These characterizations and loadings are based upon analysis of raw waste samples collected during site visits.

Bauxite Ores

Water handling and quantity of waste water flow within surface bauxite mines are largely dependent upon precipitation patterns and local topography. Topographic conditions are often modified by precautionary measures, such as diversion ditching, disposal of undesirable materials, regrading, and revegetation. In contrast,

TABLE V-29. MAJOR MINERALS FOUND ASSOCIATED WITH SILVER ORES

MINERAL	COMPOSITION
Tetrahedrite	$(Cu, Fe, Ag)_{12} Sb_4 S_{13}$
Tennantite	$(Cu, Fe, Ag)_{12} As_4 S_{13}$
Galena	$Pb S$
Sphalerite	$Zn S$
Chalcopyrite	$Cu Fe S_2$
Pyrite	$Fe S$
Naumannite	$Ag_2 S$
Greenockite/ Xanthochroite	$Cd S$
Garnierite	$(Mg, Ni) O \cdot Si O_2 \cdot x H_2O$
Pentlandite	$(Fe, Ni)_9 S_8$
Native Bismuth	Bi
Argenite	$Ag_2 S$
Stephanite	$Ag_5 Sb S_4$
Stibnite	$Sb_2 S_3$

TABLE V-30. FLOTATION REAGENTS USED BY THREE MILLS TO BENEFICIATE SILVER-CONTAINING MINERAL TETRAHEDRITE (MILLS 4401 AND 4403) AND NATIVE SILVER AND ARGENTITE (MILL 4402)

REAGENT	PURPOSE	CONSUMPTION g/metric ton ore milled	CONSUMPTION lb/short ton ore milled
	MILL 4401		
M.I.B.C. (Methylisobutylcarbinol)	Frother	0.00498	0.00000995
D-52	Frother	0.00746	0.0000149
Z-200 (Isopropl ethylthiocarbamate)	Collector	0.00187	0.00000373
Lime (Calcium oxide)	pH Modifier and Depressant	0.109	0.000219
Sodium cyanide	Depressant	0.00498	0.00000995
	MILL 4402		
Cresylic acid	Frother	2.83	0.00566
Mineral oil	Frother	6.9	0.0138
Dowfroth 250 (Polypropylene glycol methyl ethers)	Frother	0.545	0.00109
Aerofroth 71 (Mixture of 6/9-carbon alcohols)	Frother	10	0.02
Aerofloat 242 (Essentially Aryl dithiophosphoric acid)	Collector	90	0.18
Aero Promoter 404 (Mixture of Sulfhydryl type compounds)	Collector	1.82	0.00363
Z-6 (Potassium amyl xanthate)	Collector	70	0.13
Sulfuric acid	pH Modifier	250	0.49
Soda ash (Sodium carbonate)	pH Modifier	1,260	2.51
Caustic soda (Sodium hydroxide)	pH Modifier	3.03	0.00605
Hydrated lime (Calcium hydroxide)	pH Modifier	320	0.64
	MILL 4403		
Cresylic acid	Frother	1.25	0.0025
Hardwood tar oils	Frother	1.25	0.0025
M.I.B.C.	Frother	3.75	0.0075
Aerofloat 242	Collector	7.51	0.015
Aerofloat 31 (Essentially Aryl dithiophosphoric acid)	Collector	5.00	0.01
Xanthate Z-11 (Sodium ethyl xanthate)	Collector	2.50	0.005
Aero S-3477	Collector	25	0.05
Zinc sulfate	Depressant	150	0.3
Sodium sulfite	Depressant	200	0.4

TABLE V-31. WASTE CHARACTERISTICS AND RAW WASTE LOADS AT MILLS 4401, 4402, 4403, AND 4105 (Sheet 1 of 2)

MILL	TSS			TDS		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	550,000	99,000,000 (198,000,000)	2,475,000 (4,950,000)	470	84,600 (169,200)	2,110 (4,220)
4403	203,000	33,901,000 (62,802,000)	1,543,000 (3,086,000)	584	97,500 (195,000)	4,440 (8,880)
4402	90,000	9,720,000 (19,440,000)	990,000 (1,980,000)	960	104,000 (208,000)	10,600 (21,200)
4105 (Company Data only)	–	– –	– –	–	– –	– –

MILL	TOC			COD		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	22.0	4,000 (8,000)	100 (200)	59.5	10,700 (21,400)	270 (540)
4403	24.0	4,000 (8,000)	180 (360)	15.9	2,700 (5,400)	120 (240)
4402	29.0	3,130 (6,260)	320 (640)	22.7	2,450 (4,900)	250 (500)
4105 (Company Data only)	–	– –	– –	–	– –	– –

MILL	Cu			Zn		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	0.25	45 (90)	1 (2)	0.02	3.6 (7.2)	0.09 (0.18)
4403	0.03	5 (10)	0.23 (0.46)	0.17	28 (56)	1.3 (2.6)
4402	0.22	24 (48)	2.4 (4.8)	0.37	40 (80)	4.1 (8.2)
4105 (Company Data only)	–	– –	– –	–	– –	– –

MILL	Pb			As		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	< 0.1	< 18 (< 36)	< 0.45 (< 0.90)	< 0.07	< 13 (< 26)	< 0.3 (< 0.6)
4403	< 0.1	< 17 (< 34)	< 0.8 (< 1.6)	< 0.07	< 12 (< 24)	< 0.5 (< 1.0)
4402	0.56	60 (120)	6.2 (12.4)	0.07	8 (16)	0.8 (1.6)
4105 (Company Data only)	–	– –	– –	3.50	2,265,000 (4,530,000)	21 (42)

TABLE V-31. WASTE CHARACTERISTICS AND RAW WASTE LOADS AT MILLS 4401, 4402, 4403, AND 4105 (Sheet 2 of 2)

MILL	Hg			Cd		
	CONCENTRATION (mg/ℓ)	WASTE LOAD		CONCENTRATION (mg/ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	0.0024	0.4 (0.8)	0.01 (0.02)	<0.02	<3.6 (<7.2)	<0.09 (<0.18)
4403	0.0008	0.13 (0.26)	0.5 (1.0)	<0.02	<3.3 (<6.6)	<0.15 (<0.30)
4402	0.1490	16 (32)	1.6 (3.2)	<0.02	<2.2 (<4.4)	<0.2 (<0.4)
4105 (Company Data only)	0.004	259 (518)	0.024 (0.048)	<0.01	<6,500 (<13,000)	<0.06 (<0.12)

MILL	Te			Se		
	CONCENTRATION (mg/ℓ)	WASTE LOAD		CONCENTRATION (mg/ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	<0.3	<54 (<108)	<1.3 (<2.6)	0.154	28 (56)	0.7 (1.4)
4403	<0.3	<50 (<100)	<2.3 (<4.6)	0.144	24 (48)	1.1 (2.2)
4402	<0.3	<32 (<64)	<3.3 (<6.6)	–	– –	– –
4105 (Company Data only)	–	– –	– –	–	– –	– –

MILL	Ag			Ni		
	CONCENTRATION (mg/ℓ)	WASTE LOAD		CONCENTRATION (mg/ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb, 1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	<0.02	<3.6 (<7.2)	<0.09 (<0.18)	0.14	250 (500)	0.63 (1.26)
4403	<0.02	<3 (<6)	<0.15 (<0.30)	0.05	8 (16)	0.4 (0.8)
4402	<0.02	<2 (<4)	<0.2 (<0.4)	0.10	11 (22)	1 (2)
4105 (Company Data only)	–	– –	– –	0.10	64,700 (129,400)	0.6 (1.2)

MILL	Mo			Sb		
	CONCENTRATION (mg/ℓ)	WASTE LOAD		CONCENTRATION (mg/ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
4401	<0.2	<36 (<72)	<0.9 (<1.8)	1.85	333 (666)	8.3 (16.6)
4403	<0.2	<30 (<60)	<4 (<8)	<0.2	<30 (<60)	<4 (<8)
4402	0.54	58 (116)	6 (12)	<0.2	<22 (<44)	<2 (<4)
4105 (Company Data only)	<0.05	<32,400 (<64,800)	<0.3 (<0.6)	– –	– –	– –

underground mine infiltration occurs as a result of controlled drainage of the unconsolidated sands in the overburden. These sands are under considerable water pressure, and catastrophic collapses of sand and water may occur if effective drainage is not undertaken. Gradual drainage accumulates in the mines and is pumped out periodically for treatment and discharge. As in other mining categories, dewatering is an economic, practical, and safe-practice necessity.

Beneficiation of bauxite ores is not currently practiced beyond size reduction, crushing and grinding. No water use, other than dust suppression, results.

Mining Technique and Sources of Waste water

Open-Pit Mining. The sequence of operations that occurs in a typical open-pit mining operation is that the mine site is cleared of trees, brush, and overburden and then stripped to expose the ore. Timber values are often obtained from areas undergoing site preparation.

Depending upon the consolidation of the overburden, the material may be vertically drilled from the surface, and explosive charges--generally, ammonium nitrate--are placed for blasting. This sufficiently fractures the overburden material to permit its removal by earthmoving equipment, such as draglines, shovels, and scrapers. Removal of this overburden takes the greatest amount of time and frequently requires the largest equipment.

Following removal of the overburden material, the bauxite is drilled, blasted, and loaded into haulage trucks for transport to the vicinity of the refinery. Extracted overburden or spoils are often placed in abandoned pits or other convenient locations, where some attempts have been made at revegetation.

Regardless of the method of mining, water use at the two existing operations is generally limited to dust suppression. Water removal is required because drainage is a hindrance to mining. As such, mine dewatering and handling are a required part of the mining plan at all bauxite mines.

The bauxite mining industry presently discharges about 57,000 cubic meters (15 million gallons) of mine drainage daily at two locations. The open-pit mining technique is largely responsible for accumulation of this water. Underground mining accounts for only a fraction of a percent of the total. In association with the open-pit approach to bauxite mining, water drainage and accumulation occur during the processes of mine site preparation and during active mining.

For the open-pit mine represented in Figure V-24, rainfall and ground water intercepted by the terrain undergoing site preparation are diverted to outlying sumps for transfer to a main collection sump. Diversion ditching and drainage ditches segregate most surface water, depending upon whether it has contacted lignite-containing material. Contaminated water is directed to the treatment plant, while fresh water is diverted to other areas. At other mines, drainage occurring during site preparation and mining is not treated, and segregation of polluted and unpolluted waters may or may not be practiced.

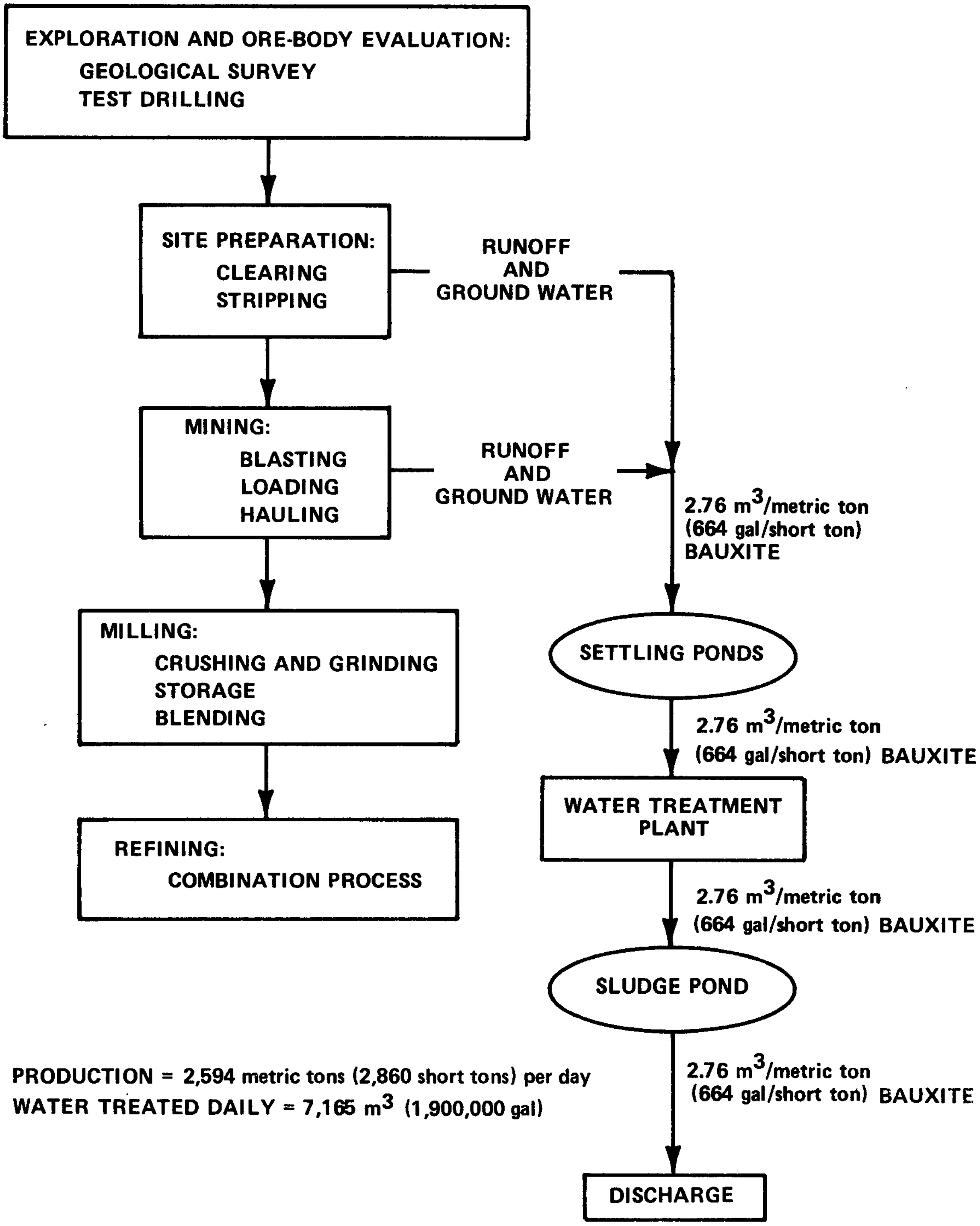
Water from the main collection sump is pumped to a series of settling ponds, where removal of coarse suspended material occurs. These ponds also aid in regulation of flow to the treatment plant. A small sludge pond receives treated wastewater for final settling before discharge.

Bauxite mining operations characteristically utilize several pits simultaneously and may practice site preparation concurrent with mining. Since both bauxite producers have large land holdings (approximately 4,050 hectares or 10,000 acres), mines and site-preparation activities may be located in remote areas, where the economics of piping raw mine drainage to a central treatment plant are unfeasible. For larger quantities of mine drainage in remote areas, separate treatment plants appear necessary. Portable and semiportable treatment plants appear feasible for treating smaller accumulations of wastewater at times when pumping of mine water for discharge is required.

Underground Mining. Underground mining occurs where low-silica bauxite is located deep enough under the land surface so that economical removal of overburden is not feasible. The underground operations have been historically notable for relatively high recovery of bauxite under adverse conditions of unconsolidated water-bearing overburden and unstable clay floors. Controlled caving, timbered stope walls, and efficient drainage systems--both on the surface and underground--have minimized the problems and have resulted in efficient ore recovery.

Initially, shafts are sunk to provide access to the bauxite deposits, and drifts are driven into the sections to be

Figure V-24. PROCESS AND WASTEWATER FLOW DIAGRAM FOR OPEN-PIT BAUXITE MINE 5101



PRODUCTION = 2,594 metric tons (2,860 short tons) per day
WATER TREATED DAILY = 7,165 m^3 (1,900,000 gal)

mined. A room-and-pillar technique is then used to support the mine roof and prevent surface subsidence above the workings. Configurations of rooms and pillars are designed to consider roof conditions, equipment utilized, haulage gradients, and other physical factors.

Ore is removed from the deposits by means of a "continuous miner," a ripping-type machine which cuts bauxite directly from the ore face and loads it into shuttle cars behind the machine. Initial development of the room leaves much bauxite in pillars, and it has been the practice to remove the pillars and induce caving along a retreating caveline. However, resultant roof collapse and fracturing can greatly increase overburden permeability, facilitating mine-water infiltration and subsequently increasing mine drainage problems. Recent charges in mining technique have resulted in a cessation of induced caving, but drainage still occurs in the mines.

Raw mine drainage accumulates slowly in the underground mines and is a result of controlled drainage. The mine water is pumped to the surface at regular intervals for treatment, with subsequent settling and discharge. Excessive water in the underground mine can lead to wetting of clays located in drift floors and in resultant upheaval of the floor.

The most influential factor which determines mine-water drainage characteristics is mineralization of the substrata through which the drainage percolates. Underground mines receive drainage which has migrated through strata of unconsolidated sands and clays, whereas open-pit drainage is exposed to sulfide-bearing minerals in the soil. As shown in this section, open-pit and underground mine drainages differ qualitatively and quantitatively; but, as a factor affecting raw mine-drainage characteristics, mineralization does not constitute a sufficient basis for subcategorization.

Study of NPDES permit applications and analysis of samples secured during mine visitations revealed that the bauxite mining industry generates two distinct classes of raw mine drainage: (1) Acid or ferruginous, and (2) alkaline--determined principally by the substrata through which the drainage flows. Acid or ferruginous raw mine drainage is defined as untreated drainage exhibiting a pH of less than 6 or a total iron content of more than 10 mg/liter. Raw mine drainage is defined as alkaline when the untreated drainage has a pH of more than 6 or a total iron content of less than 10 mg/liter.

The class of raw mine drainage corresponds closely with mining technique, and open-pit drainage is characteristically acid. Acid mine water is produced by oxidation of pyrite contained in lignite present in the soil overburden of the area.

Acid mine drainage with pH generally in the range of 2 to 4 is produced in the presence of abundant water. The sulfuric acid and ferric sulfate formed dissolve other minerals, including those containing aluminum, calcium, manganese, and zinc.

In areas undisturbed by mining operations, these reactions occur because the circulating ground water contains some dissolved oxygen, but the reaction rate is rather slow. Mining activity which disturbs the surface of the ground creates conditions for a greatly accelerated rate of sulfide mineral dissolution.

Alkaline mine water, characteristic of underground mines, may migrate through the lignitic clays located in strata overlying the mines before collecting in the mines, but pH is generally around 7.5. Data evaluation reveals that underground mine drainage differs significantly from open-pit mine drainage (acid), as shown in Tables V-32, V-33, and V-34.

Though these mine drainages differ with respect to mining technique, all mine drainages sampled proved to be amenable to efficient removal of selected pollutant parameters by liming and settling, as exhibited in Section VII. Attainable treated-effluent concentrations are directly related to treatment efficiency, and these two interrelated factors do not justify establishment of subcategories.

Due to acid conditions and general disruption of soils caused by stripping of overburden for open-pit mines, natural revegetation proceeds extremely slowly. The lack of vegetative cover aids in accelerating the weathering of the unconsolidated overburden and compounds the acid mine-water situation. Extensive furrowed faces of exposed silt and sandy clays are evidence of the erosion which infuses the mine water with particulate matter. Fortunately, this material settles rapidly, either in outlying pits or in pretreatment settling basins, and presents no nuisance to properly treated discharges.

TABLE V-32. CONCENTRATIONS OF SELECTED CONSTITUENTS IN ACID RAW MINE DRAINAGE FROM OPEN-PIT MINE 5101

PARAMETER	CONCENTRATION (mg/ℓ)		
	THIS STUDY	INDUSTRY DATA	NPDES PERMIT APPLICATION
pH	2.8*	3.4*,**	3.5*
Specific Conductance	1,000†	–	1,903†
Acidity	397	250	–
Alkalinity	0	0	40
TDS	560	617	1,290
TSS	< 2	2	10
Total Fe	7.2	15.4**	7.0
Total Mn	3.5	59.6**	4.2
Al	23.8	5.9**	38
Zn	0.82	25.3**	1.0
Ni	0.3	0.31	0.37
Sulfate	500	490	700
Fluoride	0.29	0.048	1.4

*Value in pH units †Value in micromhos **Averages of five samples

TABLE V-33. CONCENTRATIONS OF SELECTED CONSTITUENTS IN ACID RAW MINE DRAINAGE FROM OPEN-PIT MINE 5102

PARAMETER	CONCENTRATION (mg/ℓ)		
	THIS STUDY	INDUSTRY DATA**	NPDES PERMIT APPLICATION
pH	3.2*	2.8*	3.0*
Specific Conductance	1,580†	2,652†	2,000†
Acidity	782.0	533	–
Alkalinity	0	–	0
TDS	1,154	–	96
TSS	< 2	416	1,280
Total Fe	64.0	62.2	20.6
Total Mn	7.7	–	9.0
Al	88.0	44.6	51.0
Zn	0.36	–	0.8
Ni	0.063	–	0.01
Sr	0.1	–	–
Sulfate	887.5	726	226
Fluoride	0.59	–	0.26

*Value in pH units †Value in micromhos **Averages of eight or more grab samples taken in 1974

TABLE V-34. CONCENTRATIONS OF SELECTED CONSTITUENTS IN ALKALINE RAW MINE DRAINAGE FROM UNDERGROUND MINE 5101

PARAMETER	CONCENTRATION (mg/ℓ)		
	THIS STUDY	INDUSTRY DATA	NPDES PERMIT APPLICATION
pH	7.2*	7.6*	7.8*
Specific Conductance	1,260†		3,281†
Alkalinity	280	222	150
TDS	780	862	550
TSS	<2	26	300
Total Fe	1.4	2.3	5.0
Total Mn	0.88	0.87	5.0
Al	0.8	< 0.05	2.0
Zn	< 0.02	< 0.01	1.6
Ni	< 0.02	< 0.01	0.01
Sr	1.82		
Sulfate	228.8	246	50
Fluoride	1.25	0.07	2.5

*Value in pH units

†Value in micromhos

Raw Waste Loading

As discussed earlier in this Section, effluents from bauxite mining operations are unrelated, or only indirectly related, to production quantities and exhibit broad variation from mine to mine. Loadings have been calculated for open-pit mine 5101 and underground mine 5101, as shown in Tables V-35 and V-36.

Potential Uses of Mine Water. Since both domestic bauxite mines are intimately associated with refineries, the plausibility of utilizing a percentage of mine water in the refinery arises. Though the bauxite refining process intrinsically has a substantial negative water balance, water is supplied from rainfall on the brown-mud lake or from fresh-water impoundments. More importantly, the brown-mud-lake water posseses a high pH (approximately 10) and remains amenable to recycling in the caustic leach process.

To minimize the effects of dissolved salts in the refining circuit, evaporators are sometimes used to remove impurities from spent liquor. However, mine water contains many dissolved constituents (particularly, sulfate) in large quantities, the effects of which are detrimental or undetermined at this time. The exacting requirements of purified alumina, and the specific process nature of the refinery, largely preclude the introduction of new intake constituents via alternative water sources (treated or untreated mine water) at this time.

Ferroalloy Ores

Waste characterization for the ferroalloy-ore mining and milling industry has, of necessity, been based primarily on presently active operations. Since these comprise a somewhat limited set, many types of operations which may or will be active in the future were not available for detailed waste characterization. Sites visited in the ferroalloy segment are organized by category and product in Table V-37. Since some sites produce multiple products, and/or employ multiple beneficiation processes, they are represented by more than one entry in the table. Where possible, segregated as well as combined waste streams were sampled at such operations. Table V-37 also shows types of operations considered likely in the U.S. in the future (marked with x's), as well as those which represent likely recovery processes for ores not expected to be worked soon (marked with o's). Characteristics of wastes from the latter two groups of operations have been determined, where possible, from historical data; probable ore constituents and process characteristics; and examination of waste streams expected

TABLE V-35. WASTEWATER AND RAW WASTE LOAD FOR OPEN-PIT MINE 5101

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD	
		kg/metric ton	lb/short ton
TDS	560 to 1290	1.55 to 3.56	3.10 to 7.12
TSS	< 2 to 42	< 0.006 to 0.12	< 0.012 to 0.24
Total Fe	7.0 to 129.1	0.02 to 0.36	0.04 to 0.72
Total Mn	2.83 to 9.75	0.008 to 0.027	0.016 to 0.054
Al	2.76 to 52.3	0.008 to 0.14	0.016 to 0.28
Zn	0.82 to 1.19	0.002 to 0.003	0.004 to 0.006
Ni	0.3 to 0.37	0.0008 to 0.001	0.0016 to 0.002
Sulfate	490 to 700	1.35 to 1.93	2.70 to 3.86
Fluoride	0.048 to 1.4	0.0001 to 0.004	0.0002 to 0.008

Daily flow of wastewater = 7,165 m^3 (1,900,000 gal)
Daily mine production = 2,594 metric tons (2,860 short tons)

TABLE V-36. WASTEWATER AND RAW WASTE LOAD FOR UNDERGROUND MINE 5101

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD	
		kg/metric ton	lb/short ton
TDS	550 to 862	0.12 to 0.18	0.24 to 0.36
TSS	< 2 to 300	< 0.0004 to 0.06	< 0.0008 to 0.12
Total Fe	1.4 to 5.0	0.0003 to 0.001	0.0006 to 0.002
Total Mn	0.87 to 5.0	0.0002 to 0.001	0.0004 to 0.002
Al	< 0.05 to 2.0	< 0.00001 to 0.0004	< 0.00002 to 0.0008
Zn	< 0.01 to 1.6	< 0.000002 to 0.0003	< 0.000004 to 0.0006
Ni	< 0.01 to 0.01	< 0.000002 to 0.000002	< 0.000004 to 0.000004
Sulfate	50 to 246	0.01 to 0.05	0.02 to 0.10
Fluoride	0.07 to 2.5	0.00001 to 0.0005	0.00002 to 0.0010

Daily flow of wastewater = 83 m^3 (22,000 gal)
Daily mine production = 390 metric tons (430 short tons)

TABLE V-37. TYPES OF OPERATIONS VISITED AND ANTICIPATED– FERROALLOY-ORE MINING AND DRESSING INDUSTRY

METAL ORE MINED/MILLED	MINE	MILL			
		Category 1 (< 5,000 metric tons [5,512 short tons] per year)	Category 2 (Physical Concentration)	Category 3 (Flotation)	Category 4 (Leaching)
Chromium	O		O		O
Cobalt	X			X	
Columbium and Tantalum	X		X	X	X
Manganese	X		X	X	X
Molybdenum	V(3)			V(3)	
Nickel	V(1)*		V	X	
Tungsten	V(2)	X	V	V	V
Vanadium	V(1)				V

( ) indicates number of operations visited

* seasonal mine discharge, not flowing during visit

X likely in the future; currently, not operating

O most likely process, if ever operated in the U.S.

V types of operations visited

to be similar (for example, gravity processors of iron ore as indicators for gravity manganiferous ore operations).

Treatment of the individual process descriptions by ore category, as adhered to previously in this report, is not used here. Instead, because of the wide diversity of ores encountered, the general character of mine and mill effluents is discussed, followed by process descriptions and raw waste characteristics of several representative operations.

General Waste Characteristics

Ferroalloy mining and milling waste water streams are generally characterized by:

(1) High suspended-solid loads

(2) High volume

(3) Low concentrations of most dissolved pollutants.

The large amounts of material to be handled per unit of metal recovered, the necessity to grind ore to small particle sizes to liberate values, and the general application of wet separation and transport techniques result in the generation of large volumes of effluent water bearing high concentrations of finely divided rock, which must be removed prior to discharge. In addition, the waste stream is generally contaminated to some extent by a number of dissolved substances, derived from the ore processed or from reagent additions in the mill. Total concentrations of dissolved solids vary but, except where leaching is practiced, rarely exceed 2,500 mg/l, with Ca^{++}, Na^{+}, K^{+}, Mg^{++}, CO_3^{--}, and SO_4 accounting for nearly all dissolved materials. Heavy metals and other notably toxic materials rarely exceed 10 mg/l in the untreated waste stream.

The volume of effluent from both mines and mills may be strongly influenced by factors of topography and climate and is frequently subject to seasonal fluctuations. In mines, the water flow depends on the flow in natural aquifers intercepted and may be highly variable. Water other than process water enters the mill effluent stream primarily by way of the tailing ponds (and/or settling ponds), which are almost universally employed. These water contributions result from direct precipitation on the pond, from runoff from surrounding areas or even from seepage. and are only partially amenable to elimination or control.

A number of operations or practices common to many milling operations in this category involve the use of contact process water and contribute to the waste-stream pollutant load. These include ore washing, grinding, cycloning and classification, ore and tail transport as a slurry, and the use of wet dust-control methods (such as scrubbers). In terms of pollutants contributed to the effluent stream, all of these processes are essentially the same. Contact of water with finely divided ore, gangue, or concentrates results in the suspension of solids in the waste stream, and in the solution of some ore constituents in the water. In general, total levels of dissolved material resulting from these processes are quite low, but specific substances (especially, some heavy metals) may dissolve to a sufficient degree to require treatment. These processes may also result in the presence of oil and grease from machinery in the waste water stream. Good housekeeping and maintenance practice should prevent this contribution from becoming significant.

Ore roasting may be practiced as a part of some processing schemes to alter physical or chemical properties of the ore. In current practice, it is used to change magnetic properties in iron-ore processing in the U.S. and in the past was used to alter magnetic/electrostatic behavior of columbium and tantalum ores. Roasting is also used in processing vanadium ores to render vanadium values soluble. Although a dry process, roasting generally entails the use of scrubbers for air pollution control. Dissolved fumes and ore components rendered soluble by roasting which are captured in the scrubber thus become part of the waste stream. This scrubber water may constitute an appreciable fraction of the total plant effluent and may contribute significantly to the total pollutant load. One mill surveyed contributes 0.8 ton of contaminated scrubber bleed water per ton of ore processed.

Effluents from some ferroalloy mining and milling operations are complicated by other operations performed on-site. Thus, smelting and refining at one site, and chemical purification at another, contribute significantly to the waste water generated at two current ferroalloy-ore processing plants. Since waste streams are not segregated, and the other processes involve wastes of somewhat different character then those normally associated with ore mining and beneficiation, such operations may pose special problems in effluent limitation development.

An additional component of the mill waste stream at some sites which is not related to the milling process is sewage.

The use of the mill tailing basin as a treatment location for domestic wastes can result in unusually high levels of a number of pollutants in the effluent stream, including NH_3, COD, BOD, and TOC. At other sites, effluent from separate domestic waste-treatment facilities may be combined with mine or mill effluents, raising levels of NH_3, BOD, TOC, or residual chlorine.

Sources of Wastes - Mine Effluents

Factors affecting pollution levels in mine water flows include:

(1) Contact with broken rock and dust within the mine, resulting in suspended-solid and dissolved-ore constituents.

(2) Oxidation of reduced (especially, sulfide) ores, producing acid and increased soluble material.

(3) Blasting decomposition products, resulting in NH_3, NO_3, and COD loads in the effluent.

(4) Machinery operation, resulting in oil and grease.

(5) Percolation of water through strata above the mine, which may contribute dissolved materials not found in the ore.

As discussed previously, variable (and, sometimes, very high) flow rates are characteristic of mine discharges and can strongly influence the economics of treatment. Data for mine flows sampled in the development of these guidelines are presented in Table V-38. Observed mine flows in the industry range from zero to approximately 36 cubic meters (9,510 gallons) per minute. Generally, total levels of dissolved solids are not great, ranging from 10 to 1400 ppm in untreated mine waters. Total levels of some metals, however, can be appreciable, as the data below, show for some maximum observed levels (in mg/l).

Al	9.4	Mo	0.5
Cu	3.8	Pb	0.19
Fe	17	Zn	0.47
Mn	5.5		

TABLE V-38. CHEMICAL CHARACTERISTICS OF RAW MINE WATER IN FERROALLOY INDUSTRY

MINE	PRODUCT	FLOW (m^3/min (gpm))	pH	CONCENTRATION (mg/ℓ)										
				Oil and Grease	Nitrate	Fluoride	As	Cd	Cu	Mn	Mo	Pb	V	Zn
6102	Mo, W	2.65 (700)	4.5	14	-	44.5	<0.01	0.07	3.8	5.3	0.5	0.0[illegible]	<0.5	7.0
6103	Mo	6.43 (1,700)	7.0	1.0	0.15	4.5	<0.01	<0.01	0.06	5.5	<0.1	0.19	<0.5	0.47
6104	W, Mo	34.06 (9,000)	6.5	2.0	0.12	0.52	<0.07	<0.01	<0.02	0.21	<0.1	0.14	<0.5	0.05
6107	V	11.35 (3,000)	7.3	-	-	-	<0.07	<0.005	<0.02	6.8	<0.1	-	-	0.09

In addition, oil and grease levels as high as 14 mg/l, and COD values up to 91 mg/l, were observed. Since simple settling treatment greatly reduces most of the above metal values, it is concluded that most of metals present were contributed in the form of suspended solids. There is no apparent correlation between waste content or flow volume and production for mine effluents.

Sources of Wastes - Mill Effluents

Physical Processing Mill Effluents. In general, mills practicing purely physical ore beneficiation yield a minimal set of pollutants. Separation in jigs, tables, spirals, etc., contributes to pollution in the same fashion as the general practices of grinding and transport--that is, through contact of ore and water. Suspended solids are the dominant waste constituent, although, as in mine wastes, some dissolved metals (particularly, those with high toxicity) may require treatment. Roasting may be practiced in some future operations to alter magnetic properties of ores. As discussed previously, this could change the effluent somewhat, by increasing solubility of some ore components, and by introducing water from scrubbers used for dust and fume control on roasting ovens. Since solubilization is generally undesirable in such operations, the very high total dissolved solid values observed at mill 6107 are not anticipated elsewhere.

No sites in the ferroalloy category actually practicing purely physical beneficiation of ore using water were visited and sampled in developing these guidelines, since none could be identified. A mine/mill/smelter complex recovering nickel (mill 6106) which was visited, however, produces an effluent which is felt to be somewhat representative, since water contacts ore in belt washing--and gangue in slag granulation-operations at that site. Raw waste data for that operation illustrate the generally low level of dissolved materials in effluents from these operations. In general, these effluents pose no major treatment problems and are generally suitable for recycle to the process after minimal treatment to remove suspended solids.

Flotation Mill Effluents. The practice of flotation adds a wide variety of process reagents, including acids and bases, toxicants (such as cyanide), oils and greases, surfactants, and complex organics (including amines and xanthates). In addition to finer grinding of ore than for physical separation, and modified pH, the presence of reagents may increase the degree of solution of ore components.

Flotation reagents pose particular problems in effluent limitation and treatment. Many are complex organics used in small quantities, whose fates and effects when released to the environment are uncertain. Even their analysis is not simple (References 26 and 27). Historically, effluent data are widely available only for cyanide among the many flotation reagents employed. Similarly, in the guideline-development effort, analyses were not performed for each of the specific reagents used at the various flotation mills visited. The presence of flotation reagents in appreciable quantities may be detected in elevated values for COD, oil and grease, or surfactants, as analytical data on mill effluents indicate. The limitation of reagents individually appears unfeasible, since the exact suite of reagents and dosages is nearly unique to each operation and highly variable over time.

Current practice in the ferroalloy milling industry includes flotation of sulfide ores of molybdenum, and flotation of scheelite (tungsten ore). The ores floated are generally somewhat complex, containing pyrite and minor amounts of lead and copper sulfides. Reagents used in the sulfide flotation circuits and reflected in effluents include xanthates, light oils, and cyanide (as a depressant). Since the flotation is performed at basic pH, solution of most metals is at a low level. Molybdenum is an exception in that it is soluble as the molybdate anion in basic solution and appears in significant quantities in effluents from several operations. Tungsten ore flotation involves the use of a quite different set of reagents--notably, oleic acid and tall oil soaps--and may be performed at acid pH. At one major plant, both sulfide flotation for molybdenum recovery and scheelite flotation are practiced, resulting in the appearance of both sets of reagents in the effluent. Visit sites included plants recovering both molybdenum (6101, 6102, and 6103) and tungsten (6104 and 6105) by flotation. Although flotation would almost certainly be used in such cases, no currently active processors of sulfide ores of nickel or cobalt could be identified in the U.S.

Ore Leaching. In many ways, ore leaching operations maximize the pollution potential from ore beneficiation. Reagents are used in large quantities and are frequently not recovered. Extremes of pH are created in the process stream and generally appear in the mill effluent. Techniques for dissolving the material to be recovered are generally not specific, and other dissolved materials are rejected to the waste stream to preserve product purity. The solution of significant fractions of feed ore, and the use of large quantities of reagents, results in extremely high total-dissolved-solids concentrations. Because of reagent costs, and the benefits of increased concentration in the precipitation or extraction of values from solution, the amount of water used per ton of ore processed by leaching is generally lower than that for physical benefication or flotation. One ton of water per ton of ore is a representative value.

Effluents for several mills in the ferroalloy industry which employ leaching were characterized in this study. Visit sites included a vanadium mill (mill 6107) (properly classed in SIC 1094, but treated here because of lack of radioactives, end use of product, and applicability of general process to other ferroalloy ores) which practices leaching as the primary technique for recovering values from ores, as well as two tungsten mills which employ leaching in the process, though not as the primary beneficiation procedure. One operation (mill 6105) leaches a small amount of concentrate to reduce lime and phosphorus content, and the other (mill 6104) leaches scheelite flotation concentrates as part of a chemical refining procedure. Data for samples from leaching plants in the uranium and copper industries may also be examined for comparison.

Process Description and Raw-Waste Characterization For Specific Mines and Mills Visited

Mine/Mill 6101

At mine/mill 6101, molybdenum ore of approximately 0.2 percent grade is mined by open-pit methods and is concentrated by flotation to yield a 90 percent molybdenite concentrate. The mine and mill are located in mountainous terrain, along a river gorge. The mill is adjacent to and below the mine, the elevation of which ranges from 2,550 meters (8,400 ft) to 3,000 meters (10,000 ft) above MSL (mean sea level). The local climate is dry, with annual precipitation amounting to 28 cm (11 in.) and annual evaporation of 107 cm (42 in.).

Approximately 22,000 cubic meters (6 million gallons) of water per day are used in processing 14,500 metric tons (16,000 short tons) of ore. Reclamation of 10 percent of the water at the mill site, evaporation, and retention in tails reduce the daily discharge of water to 16,000 cubic meters (4.3 million gallons). Process water is drawn from wells on the property and from the nearby river. No mine water is produced.

Ore processing consists of crushing, grinding, and multiple stages of froth flotation, followed by dewatering and drying of concentrates. The complete process is illustrated in the simplified flowsheet of Figure V-25. There are no recoverable byproducts in the ore. Reagent use is summarized in Table V-39.

Recovery of molybdenite averages 78 to 80 percent but varies somewhat, depending on the ore fed to the mill. Recoveries on ore which has been stockpiled are somewhat lower than those achieved on fresh ore. This is, apparently, due to partial oxidation of the molybdenite to (soluble) molybdenum oxide and ferrimolybdite, which are not amenable to flotation. Processing of these oxidized ores is also accompanied by an increase in the dissolved molybdenum content of the plant discharge. The final concentrate produced averages 90 percent MoS_2.

As the flowsheet shows, only one waste stream is produced. Data for this stream, as sampled at the mill prior to any treatment, are summarized in Table V-40.

High COD levels apparently result from the flotation reagents used and provide some indication of their presence. The low cyanide level found reflects significant decreases in cyanide dosage over earlier operating modes and indicates almost complete consumption of applied cyanide. Metal analyses were performed in acidified samples containing the solid tailings. High values may be largely attributed to metals which were solubilized from the unacidified waste stream.

Mine/Mill 6102

Mill 6102 also recovers molybdenite by flotation, but mill processing is complicated by the additional recovery of by-product concentrates. Water use in processing approximately 39,000 metric tons (43,000 short tons) of ore per day amounts to 90,000 cubic meters (25 million gallons) per day. Nearly complete recycle of process water results in the daily use of only 1,700 cubic meters (450,000 gallons) of makeup water. Discharge from the mill tailing basin occurs only during spring snow-melt runoff, when it averages as much as 140,000 cubic meters (38.5 million gallons) per day.

Mining is both underground and open-pit, with underground operations which began approximately 67 years ago, and the first open-pit production in 1973. Recovery of molybdenite is by flotation in five stages, yielding a final molybdenite concentrate containing more than 93 percent MoS_2. Tungsten

Figure V-25. MILL 6601 FLOWSHEET

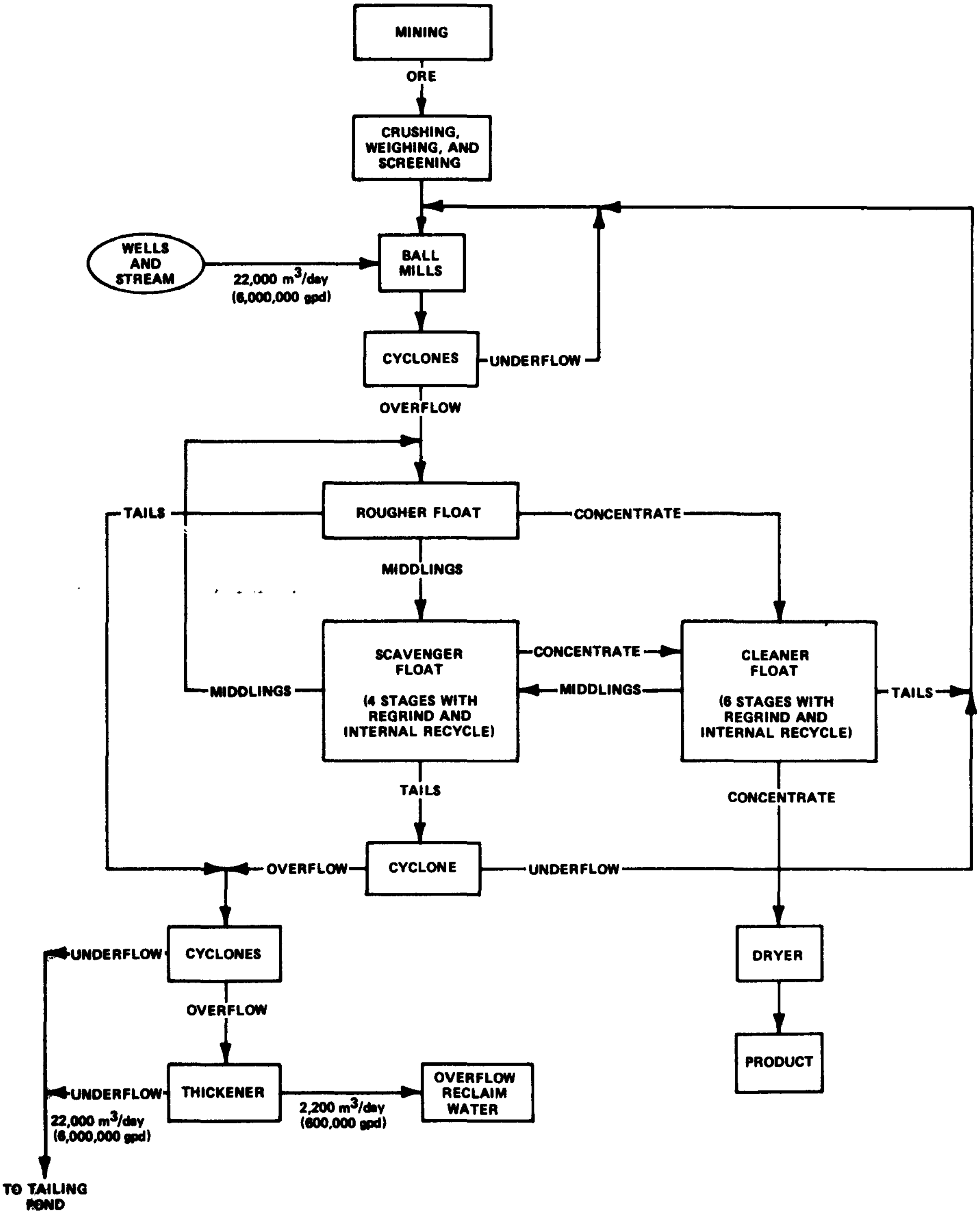


TABLE V-39. REAGENT USE IN MOLYBDENUM MILL 6101

REAGENT	DOSAGE	
	g/metric ton ore	lb/short ton ore
Lime	0.075	0.15
Vapor Oil	0.09	0.18
Pine Oil	0.015	0.03
Hypo (Sodium Thiosulfate) ($Na_2 S_2O_3 \cdot 5H_2O$)	0.035	0.07
Phosphorus Pentasulfide ($P_2 S_5$)	0.005	0.01
MIBC (methyl-isobutyl carbinol)	0.02	0.04
Sodium Cyanide (Na CN)	0.015	0.03

TABLE V-40. RAW WASTE CHARACTERIZATION AND RAW WASTE LOAD FOR MILL 6601

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore milled		per unit concentrate produced	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	500,000	14,000,000	32,000,000	995	1,990	610,000	1,200,000
TDS	2,598	42,000	92,000	3.0	6.0	1,830	3,670
Oil and Grease	2.0	32	70	0.0023	0.0046	1.4	2.8
COD	135	2,200	4,800	0.16	0.32	96	190
As	0.01	0.16	0.35	0.000012	0.000023	0.0070	0.014
Cd	0.74	12	26	0.00086	0.0017	0.52	1.0
Cu	51	820	1,800	0.059	0.11	36	72
Mn	56.5	900	2,000	0.064	0.13	39	79
Mo	5.3	85	190	0.0061	0.012	3.7	7.4
Pb	9.8	160	350	0.011	0.023	7.0	14.0
Zn	76.9	1,200	2,600	0.086	0.17	52.4	105
Fe	1,305	21,000	46,000	1.5	3.0	915	1,830
Total Cyanide	0.02	0.32	0.70	0.000023	0.000046	0.014	0.028
Fluoride	6.2	99	220	0.0071	0.014	4.3	8.7

and tin concentrates are produced by gravity and magnetic separation, with additional flotation steps used to remove pyrite and monazite. Recovered pyrite is sold as possible (currently, about 20 percent of production), with the balance delivered to tails. The monazite float product also reports to the tailing pond, since recovery of monazite is not profitable for this operation at this time.

The mill operation is located on the continental divide at over 3,353 meters (11,000 feet) above MSL. The local terrain is mountainous. Climate and topography have a major impact on water-management and tailing-disposal practices, with a heavy snow-melt runoff and the presence of major drainages above tailing-pond areas posing problems.

Mill Description. Figure V-26 presents a greatly simplified diagram of the flow of ore through the mill. Following crushing and grinding, roughing and scavenging flotation are used to extract molybdenite from the ore. Nearly 97 percent of the incoming material--currently, about 39,000 metric tons (43,000 short tons) per day--is thereby rejected and sent directly to the byproduct recovery plant. The flotation concentrate, averaging about 10 percent MoS_2, is fed to four stages of further flotation. Reagents used in the primary flotation step are summarized in Table V-41. Most are added as the ore is fed to the ball mills for grinding.

Cleaner flotation in four stages and three regrinds yield a final product averaging greater than 93 percent MoS_2 content. Reagent use in the cleaner grinding and flotation circuit is summarized in Table V-42.

Tailings from the rougher flotation are pumped to the byproducts plant, where heavy fractions are concentrated in Humphreys spirals. Pyrite is removed from the concentrate by flotation at pH 4.5, and the flotation tailings are then tabled to further concentrate the heavy fractions. The pH of the table concentrate is then adjusted to 1.5 and its temperature raised to 70 degrees Celsius (158 degrees Fahrenheit), and monazite is removed by flotation. The tailings from this flotation step are dewatered, dried, and fed to magnetic separators, which yield separate tin (cassiterite) and tungsten (wolframite) concentrates. Reagent use in the flotation of pyrite and monazite is summarized in Table V-43.

Effluent samples were taken at three points in mill 6102 due to the complexity of the process. A combined tailing sample was taken representative of the total plant effluent, and,

Figure V-26. SIMPLIFIED MILL FLOW DIAGRAM FOR MILL 6102

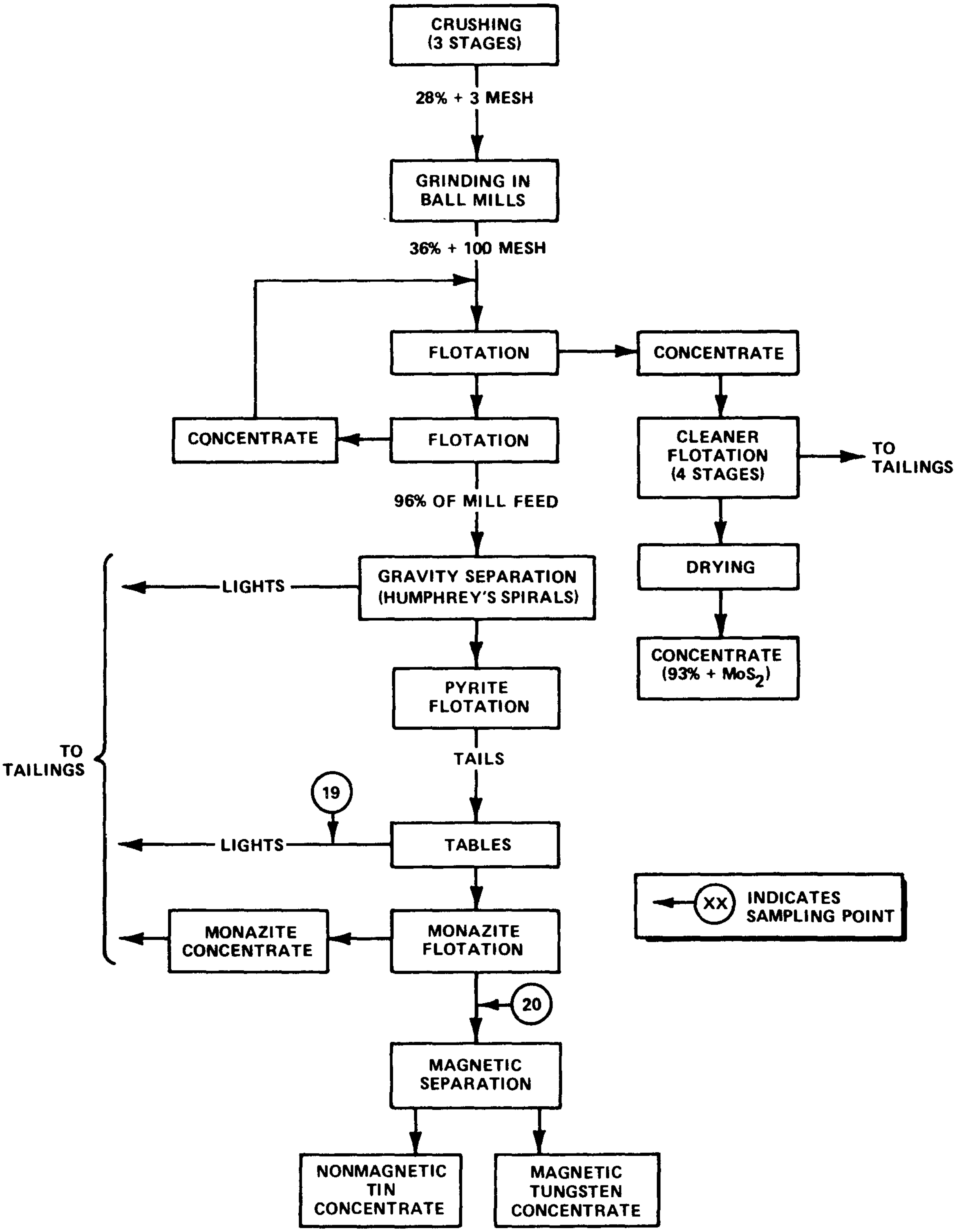


TABLE V-41. REAGENT USE FOR ROUGHER AND SCAVENGER FLOTATION AT MILL 6102

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
Pine oil	Frother	0.18	0.35
Vapor oil	Collector	0.34	0.67
Syntex	Surfactant and Frother	0.017	0.034
Lime (Calcium oxide)	Adjustment of pH to 8.0	0.15	0.30
Sodium silicate	Slime Dispersant	0.25	0.50
Nokes reagent	Lead Depressant	0.015	0.03

TABLE V-42. REAGENT USE FOR CLEANER FLOTATION AT MILL 6102

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
Vapor oil	Collector	0.45	0.90
Sodium cyanide	Pyrite and Chalcopyrite Depressant	0.13	0.25
Nokes reagent	Lead Depressant	0.45	0.90
Dowfroth 250	Frother	0.015	0.03
Valco 1801	Flocculant	0.003	0.006

TABLE V-43. REAGENT USE AT BYPRODUCT PLANT OF MILL 6102
(Based on total byproduct plant feed)

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
PYRITE FLOTATION			
Sulfuric acid	pH Regulation	0.018	0.036
Z-3 Xanthate	Collector	0.0005	0.001
Dowfroth 250	Frother	0.0005	0.001
MONAZITE FLOTATION			
ARMAC C	Collector	0.0005	0.001
Starch	WO_2 Depressant	0.0005	0.001
Sulfuric acid	pH Regulation	0.0005	0.001

TABLE V-44. MILL 6102 EFFLUENT CHEMICAL CHARACTERISTICS (COMBINED-TAILINGS SAMPLE)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore processed		per unit total concentrate produced	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	150,000			998	1996		
TDS	2,254	200,000	440,000	4.7	9.3	2,700	5,400
Oil and Grease	4	360	790	0.0080	0.016	4.6	9.2
COD	23.8	2,100	4,600	0.049	0.098	28	56
As	< 0.1	< 9	< 20	<0.0002	<0.0004	<0.1	< 0.2
Cd	0.19	17	37	0.00040	0.00080	0.23	0.46
Cu	21.0	1,890	4,200	0.047	0.088	25	50
Mn	50	4,500	9,900	0.10	0.21	58	120
Mo	17.5	1,600	3,500	0.037	0.074	21	43
Pb	2.1	190	418	0.0044	0.0088	2.5	5.0
Zn	25.0	2,250	4,950	0.052	0.10	30	60
Fe	1,500	135,000	300,000	3.1	6.3	1,800	3,600
Fluoride	11.7	1,100	2,400	0.026	0.052	15	30
Total Cyanide	0.45	41	90	0.00095	0.0019	0.55	1.1

in addition, effluents were sampled from two points in the process (marked 19 and 20 on the flowsheet, Figure V-26). Although flows at these points are very small compared to the total process flow, they were considered important because of the acid conditions prevailing in monazite flotation. Concentrations and total loadings in the mill effluent, and concentrations in the effluents from pyrite flotation and monazite flotation, are presented in Tables V-44 and V-45.

Considerably heavier use of cyanide than at mill 6101 (almost ten times the dosage per ton of ore) is reflected in significantly higher levels in the untreated mill waste. Total metal contents are again elevated by leaching solid particles in the tailing stream. The increase in solution of most heavy metals as increasingly acid conditions prevail in processing is evident in the data from the monazite and pyrite flotation effluents.

Mine water is produced in the underground mine at mill 6102 at an average rate of 4,000 metric tons per day (700 gpm). Its characteristics are summarized, along with those of other mine waters, in Table V-38. At mill 6102, all mine water is added to the mill tailing pond and then to the process circuit.

Mine 6103

Mine 6103 is an underground molybdenum mine which is under development. Ore from the mine will be processed in a mill at a site approximately 16 kilometers (10 miles) from the mine portal. The mill operation will produce no effluent, all of the process water being recycled. Mine water flow presently averages 9,800 cubic meters per day (1,700 gpm). Its quality prior to treatment has been summarized in Table V-38.

Mine/Mill 6104

This complex operation combines mining, beneficiation, and chemical processing to produce a pure ammonium paratungstate product as well as molybdenum and copper concentrates. A total of 10,000 cubic meters (2.9 million gallons) of water are used each day in processing 2,200 metric tons (2,425 short tons) of ore. The bulk of this water is derived from the 47,000 cubic meters (13 million gallons) of water pumped from the mine each day.

The mill process is illustrated in Figures V-27 and V-28, which also show water flow rates. After crushing and

TABLE V-45. CHEMICAL CHARACTERISTICS OF ACID-FLOTATION STEP

PARAMETER	CONCENTRATION (mg/ℓ) AT INDICATED POINTS OF FIGURE V-26	
	PYRITE FLOAT (19)	MONAZITE FLOAT (20)
pH	4.5*	1.5
Cd	0.01	0.042
Cu	0.2	0.5
Fe	4.2	490
Mn	4.0	53.3
Mo	3.0	4.0
Pb	0.3	1.34

*Value in pH units

Figure V-27. INTERNAL WATER FLOW FOR MILL 6104 THROUGH MOLYBDENUM SEPARATION

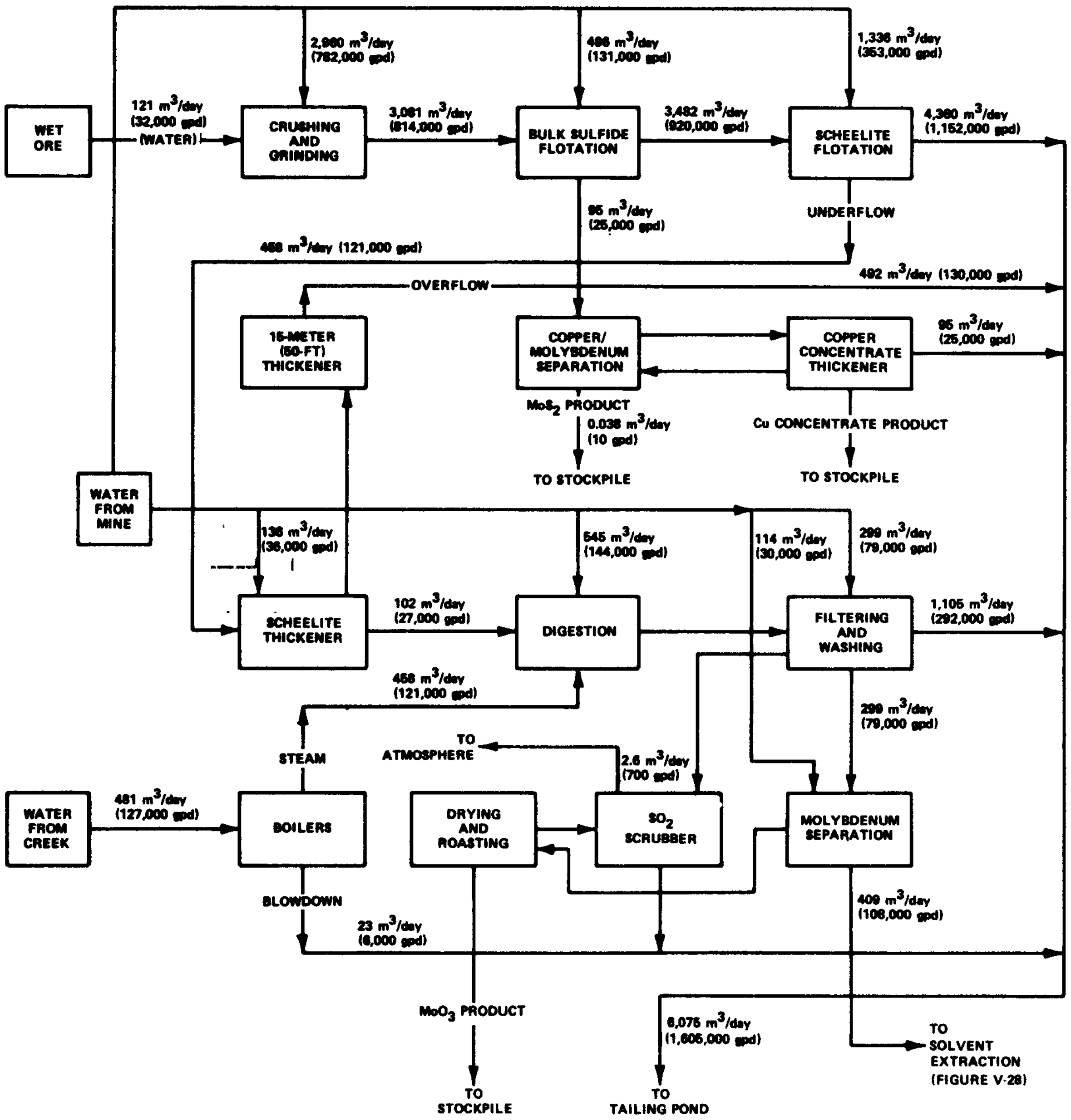
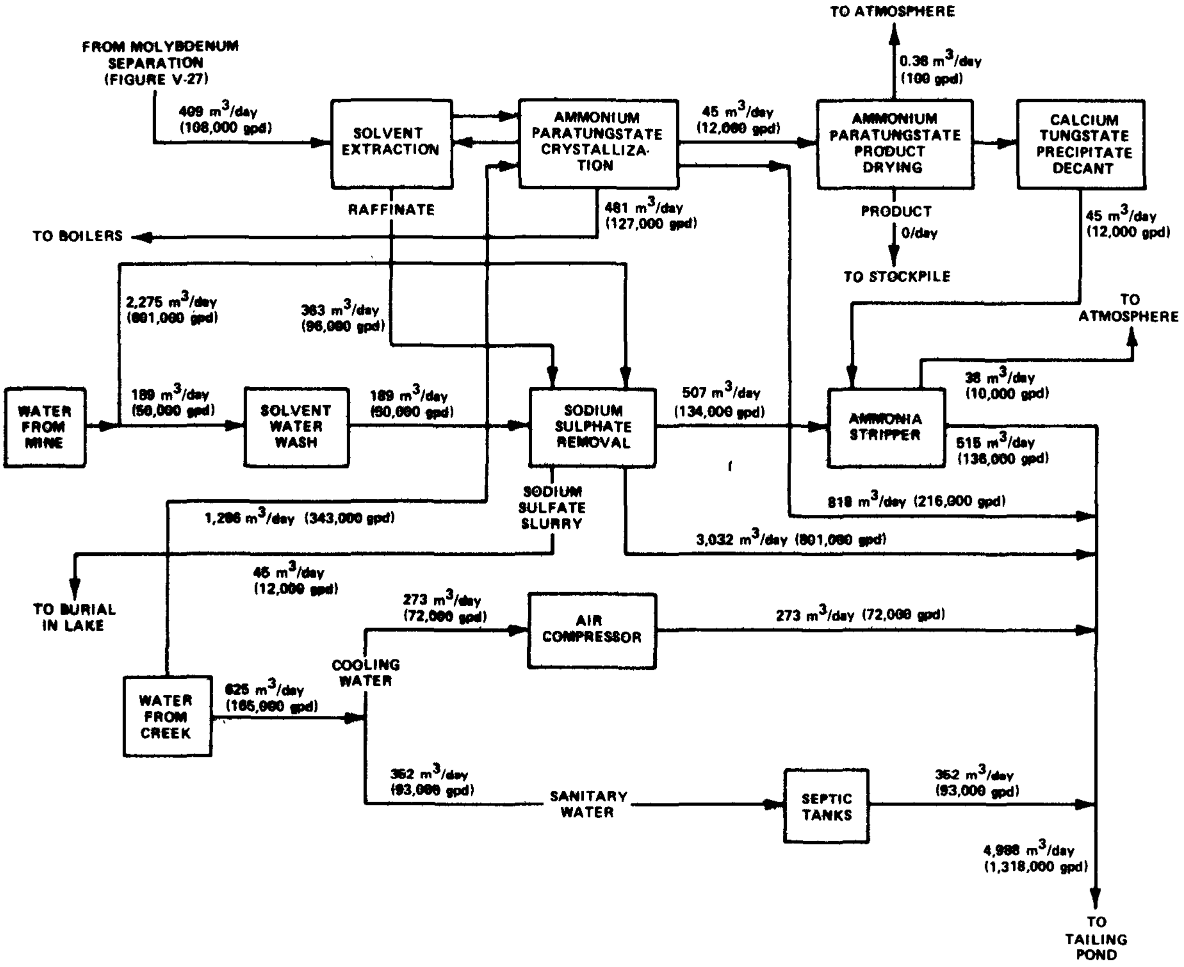


Figure V-28. INTERNAL WATER FLOW FOR MILL 6104 FOLLOWING MOLYBDENUM SEPARATION



grinding, sulfides of copper and molybdenum are floated from the ore, employing xanthate collectors and soda ash for pH modification. This flotation product is separated into copper and molybdenum concentrates in a subsequent flotation using sodium bisulfide to depress the copper. Tailings from the sulfide flotation are refloated using tall oil soap to recover a scheelite concentrate, which is reground and mixed with purchased concentrates from other sites. The scheelite is digested and filtered, and the solution is treated for molybdenum removal. Following solvent extraction and concentration, ammonium paratungstate is crystallized out of solution and dried.

Effluent streams from parts of the operation specifically concerned with beneficiation were sampled and analyzed, along with the combined discharge to tails for the complete mill. Mine water was also sampled, and analyses have been reported in Table V-38. Data for a composite effluent from beneficiation operations, several individual beneficiation effluents, and the combined plant discharge are presented in Tables V-46, V-47, V-48, V-49, and V-50.

The combined-tails discharge characteristics are not truly representative of raw waste from the leaching and chemical processing parts of the operation, since advanced treatments (including distillation and air stripping) are performed on parts of the waste stream prior to discharge to tails. Total dissolved solids and ammonia (not determined for the sample taken), in particular, are greatly reduced by these treatments.

Mine/Mill 6105

Mill 6105, a considerably smaller operation than mine/mill 6104, also recovers scheelite. As shown in the mill flowsheet of Figure III-18, a combination of sulfide flotation, scheelite flotation, wet gravity separation, and leaching is employed to produce a 65 percent tungsten concentrate from 0.7 percent mill feed. A total of 52 metric tons (57 short tons) per day of water drawn from a well on site are used in processing 46 metric tons (51 short tons) of ore. Mill tailings are combined prior to discharge, providing neutralization of acid-leach residues by the high lime content of the ore. Analytical data for a sample of the combined mill effluent are presented in Table V-51.

The mine at this site intercepts an aquifer producing mine water, which must be intermittently pumped out (for approximately hour every 12 hours). Total effluent volume is less

TABLE V-46. COMPOSITE WASTE CHARACTERISTICS FOR BENEFICIATION AT MILL 6104 (SAMPLES 6, 8, 9, AND 11)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore processed		per unit total concentrate produced	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
pH	10*	–	–	–	–	–	–
COD	238	1,100	2,400	0.50	1.0	8.1	16
Oil and Grease	11.4	55	120	0.025	0.050	0.41	0.81
As	< 0.07	< 0.34	< 0.75	< 0.0002	<0.0003	<0.003	<0.007
Cd	0.04	0.19	0.42	0.000086	0.00017	0.0014	0.0028
Cu	4.9	24	53	0.011	0.022	0.18	0.36
Mn	22.5	110	240	0.050	0.10	0.81	1.6
Mo	19.0	91	200	0.041	0.083	0.67	1.3
Pb	0.22	1.1	2.4	0.00050	0.0010	0.0081	0.016
Zn	6.3	30	66	0.014	0.027	0.23	0.46
Fluoride	4.8	23	51	0.010	0.021	0.16	0.32
Cyanide	0.2	0.96	2.1	0.00044	0.00088	0.0072	0.014

*Value in pH units

TABLE V-47. WASTE CHARACTERISTICS FROM COPPER-THICKENER OVERFLOW FOR MILL 6104 (SAMPLE 5)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD per unit ore milled	
		kg/day	lb/day	kg/metric ton	lb/short ton
pH	11*	–	–	–	–
Cd	0.26	0.024	0.053	0.000011	0.000022
Cu	<0.02	<0.002	<0.004	<0.0000009	<0.000002
Mn	1.0	0.091	0.20	0.000041	0.000082
Mo	1.2	0.11	0.24	0.000050	0.00010
Pb	0.07	0.0064	0.014	0.0000029	0.0000058
Fe	26.0	2.4	5.3	0.0011	0.0022

*Value in pH units

TABLE V-48. SCHEELITE-FLOTATION TAILING WASTE CHARACTERISTICS AND LOADING FOR MILL 6104 (SAMPLE 7)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD per unit ore milled	
		kg/day	lb/day	kg/metric ton	lb/short ton
pH	10*	–	–	–	–
Cd	0.32	1.3	2.9	0.00059	0.0012
Cu	1.42	5.9	13	0.0027	0.0054
Mn	41	170	370	0.077	0.15
Mo	1.3	5.5	12	0.0025	0.0050
Pb	0.22	.92	2.0	0.00042	0.00084
Zn	11.2	47	100	0.021	0.043
Fe	0.43	1.8	4.0	0.00082	0.0016

*Value in pH units

TABLE V-49. 50-FOOT-THICKENER OVERFLOW FOR MILL 6104 (SAMPLE 10)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD per unit ore milled	
		kg/day	lb/day	kg/metric ton	lb/short ton
pH	9*	–	–	–	–
Cd	< 0.01	< 0.005	< 0.01	< 0.000002	< 0.000005
Cu	0.31	0.15	0.33	0.000068	0.00014
Mn	1.3	0.61	1.3	0.00028	0.00055
Mo	21.0	9.9	22	0.0045	0.0090
Pb	0.04	0.019	0.042	0.0000086	0.000017
Zn	0.16	0.075	0.17	0.000034	0.000068
Fe	7.7	3.6	7.9	0.0016	0.0033

*Value in pH units

TABLE V-50. WASTE CHARACTERISTICS OF COMBINED-TAILING DISCHARGE FOR MILL 6104 (SAMPLES 15, 16, AND 17)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore processed		per unit concentrate produced	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TDS	2290	22,900	50,000	10.4	21	170	340
Oil and Grease	14.7	147	320	0.067	0.13	1.1	2.2
COD	174	1,740	3,800	0.79	1.6	13	26
As	< 0.07	< 0.7	< 1.5	< 0.0003	< 0.0006	< 0.005	< 0.01
Cd	0.03	0.30	0.66	0.00014	0.00027	0.0023	0.0046
Cr	0.03	0.30	0.66	0.00014	0.00027	0.0023	0.0046
Cu	0.52	5.2	11	0.0024	0.0047	0.039	0.078
Mn	50	500	1,100	0.23	0.45	3.7	7.4
Mo	2.2	22	480	0.010	0.020	0.16	0.32
Pb	< 0.02	< 0.2	< 0.4	< 0.00009	< 0.0002	< 0.0015	< 0.003
V	< 0.5	< 5.0	< 11	< 0.002	< 0.005	< 0.03	< 0.07
Total Cyanide	< 0.01	< 0.1	< 0.2	< 0.00005	< 0.00009	< 0.0008	< 0.002

TABLE V-51. WASTE CHARACTERISTICS AND RAW WASTE LOAD AT MILL 6105 (SAMPLE 19)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore processed		per unit total concentrate produced	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TDS	1232	64	140	1.4	2.8	130	250
Oil and Grease	1	0.052	0.11	0.0011	0.0022	0.10	0.20
COD	39.7	2.1	4.6	0.046	0.092	4.2	8.4
NH_3	1.4	0.073	0.16	0.0015	0.0030	0.14	0.28
As	< 0.07	< 0.004	< 0.01	< 0.0001	< 0.0002	< 0.009	< 0.02
Cd	< 0.01	< 0.0005	< 0.001	< 0.00001	< 0.00002	< 0.0009	< 0.002
Cr	0.02	0.0010	0.0022	0.000022	0.000045	0.002	0.010
Cu	0.52	0.027	0.059	0.00058	0.0012	0.053	0.11
Mn	0.19	0.0099	0.022	0.00022	0.00043	0.020	0.040
Mo	0.5	0.026	0.057	0.00057	0.0011	0.052	0.10
Pb	0.02	0.0010	0.0022	0.000022	0.000045	0.0020	0.010
V	< 0.5	< 0.03	< 0.07	< 0.0007	< 0.001	< 0.06	< 0.13
Zn	< 0.02	< 0.001	< 0.002	< 0.00002	< 0.00004	< 0.002	< 0.004
Fe	0.44	0.023	0.051	0.00050	0.0010	0.045	0.091
Fluoride	6.9	0.36	0.79	0.0078	0.016	0.71	1.4
Total Cyanide	< 0.01	< 0.0005	< 0.001	< 0.00001	< 0.00002	< 0.0009	< 0.002

TABLE V-52. CHEMICAL COMPOSITION OF WASTEWATER, TOTAL WASTE, AND RAW WASTE LOADING FROM MILLING AND SMELTER EFFLUENT FOR MILL 6106

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
		kg/day	lb/day	per unit ore milled		per unit concentrate produced	
				kg/1000 metric tons	lb/1000 short tons	kg/1000 metric tons	lb/1000 short tons
pH	8.6*	–	–	–	–	–	–
TSS	226.9	3,600	7,900	790	1,600	43,000	86,000
TDS	212	3,300	7,300	730	1,500	39,000	79,000
Oil and grease	3.4	54	120	12	24	640	1,300
As	< 0.07	< 1	< 2	< 0.2	< 0.4	< 10	< 20
Cd	< 0.005	< 0.08	< 0.2	< 0.02	< 0.04	< 1	< 2
Cu	< 0.03	< 0.5	< 1	< 0.1	< 0.2	< 6	< 10
Mn	0.53	8.3	18	1.8	3.7	99	200
Mo	0.5	7.9	17	1.7	3.5	94	190
Pb	< 0.1	< 2	< 4	< 0.4	< 0.9	< 20	< 50
Zn	0.05	0.79	1.7	0.17	0.35	9.4	19
Fe	24	380	840	84	170	4,500	9,000
Ni	0.4	6.3	13.9	1.4	2.8	75	150

*Value in pH units.

than 4 cubic meters (1,000 gallons) per day. Samples of this effluent were not obtained because of inactivity during the site visit. It is expected to be essentially the same as the mill water-source well, which drains the same aquifer and which *was* sampled.

Mine/Mill 6106

Ferronickel is produced at this site by direct smelting of a silicate ore (garnierite) from an open-pit mine. Water use is limited and is primarily involved in smelting, where it is used for cooling and for slag granulation. Beneficiation of the ore involves drying, screening, roasting, and calcining but requires water for belt washing and for use in wet scrubbers. Flow from all uses combined amounts to approximately 28 cubic meters (7,700 gallons) per day. This combined waste stream was sampled, and its analysis is shown in Table V-52.

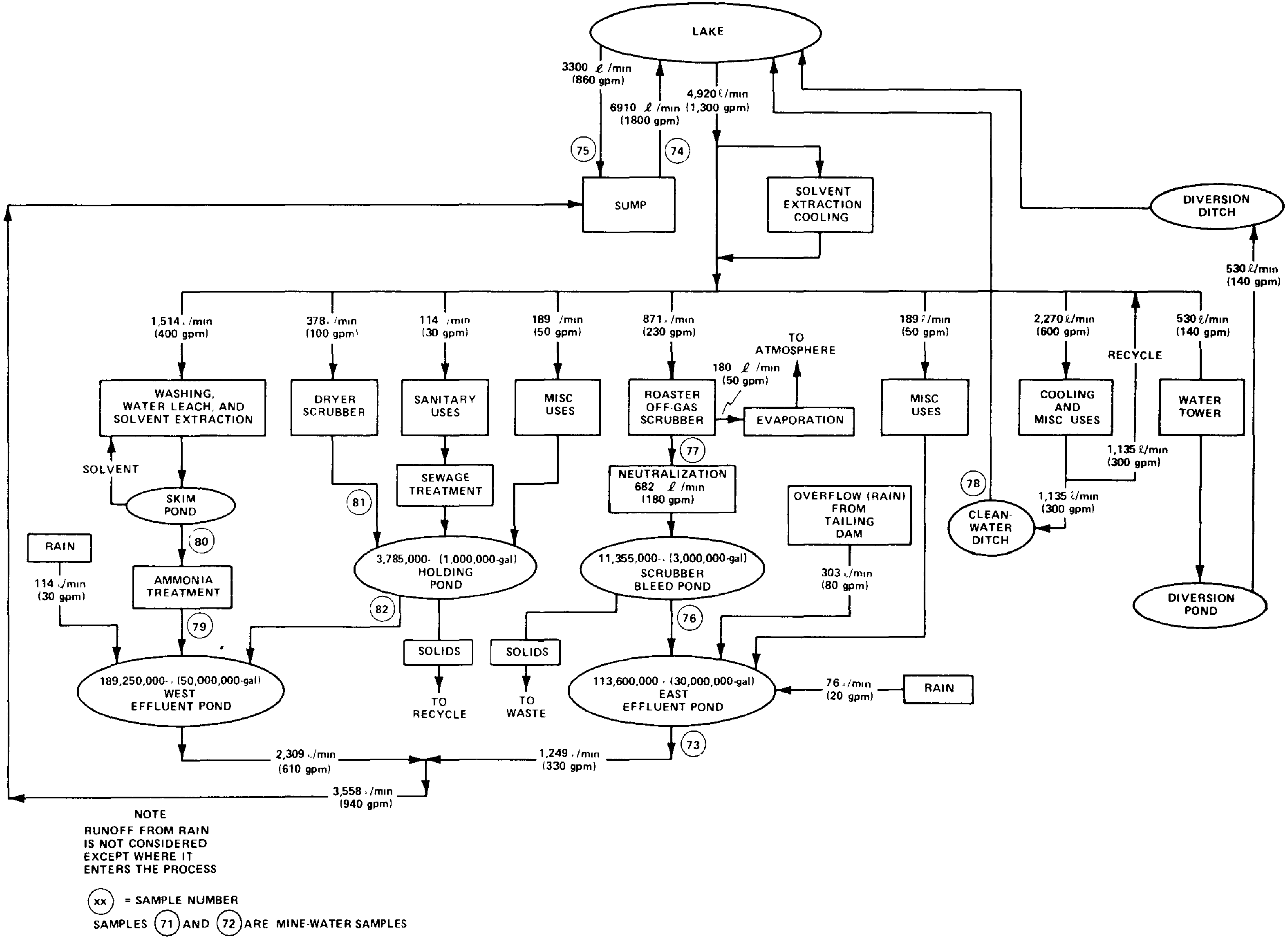
Mine water during wet-weather runoff through a creek bed to an impoundment used for mill water treatment results in discharges as large as 21,000 cubic meters (576,000 gallons) per day from the impoundment. Since the mine was dry during the site visit, no samples of this flow were obtained. Company-furnished data for the impoundment water quality, however, reflect the impact of mine-site runoff.

Mine/Mill 6107

At this operation, vanadium pentoxide, V_2O_5, is produced from an open-pit mine by a complex hydrometallurgical process involving roasting, leaching, solvent extraction, and precipitation. The process is illustrated in Figure III-21 and also in Figure V-29 (which shows system water flows). In the mill, a total of 7,600 cubic meters (1.9 million gallons) of water are used in processing 1,140 metric tons (1,250 short tons) of ore, including scrubber and cooling wastes and domestic use.

Ore from the mine is ground, mixed with salt, and pelletized. Following roasting at 850 degrees Celsius (1562 degrees Fahrenheit) to convert the vanadium values to soluble sodium vanadate, the ore is leached and the solutions acidified to a pH of 2.5 to 3.5. The resulting sodium decavanadate ($Na_6V_{10}O_{28}$) is concentrated by solvent extraction, and ammonia is added to precipitate ammonium vanadate, which is dried and calcined to yield a V_2O_5 product.

Figure V-29. WATER USE AND WASTE SOURCES FOR VANADIUM MILL 6107



The most significant effluent streams are from leaching and solvent extraction, from wet scrubbers on roasters, and from ore dryers. Together, these sources account for nearly 70 percent of the effluent stream, and essentially all of its pollutant content. Analyses for these waste streams are summarized in Tables V-53, V-54, and V-55. Effluents from the solvent-extraction and leaching processes are currently segregated from the roaster/scrubber effluent, although they are both discharged at the same point, to avoid the generation of voluminous calcium sulfate precipitates from the extremely high sulfate level in the SX stream and the high calcium level in the scrubber bleed. Both of these waste streams exhibit extremely high dissolved-solid concentrations (over 20,000 mg/l) and are diluted approximately 10:1 immediately prior to discharge.

Mercury Ores

Water flow and the sources, nature, and quantity of the wastes dissolved in the water during the processes of mercury-ore mining and beneficiation are described in this section.

Water Uses

Historically, water has had only limited use in the mercury-ore milling industry. This is primarily because little, if any, beneficiation of mercury ore is accomplished prior to roasting the ore for recovery of mercury. In the past, mercury ore was typically only crushed and/or ground to provide a properly sized kiln or furnace feed. However, because high-grade ores are nearly depleted at present, lower-grade ores are being mined, and beneficiation is becoming more important as a result of the need for a more concentrated furnace or kiln feed.

Currently in the United States, one small operation (mine/mill 9201) is using gravity methods to concentrate mercury ore. In addition, a large operation (mill 9202), due to open during 1975, will employ a flotation process to concentrate mercury ore. In both of these processes, water is a primary material and is required for the process operating conditions. Water is the medium in which the fine and heavy particles are separated by gravity methods. In the flotation process, water is introduced at the ore grinding stage to produce a slurry which is amenable to pumping, sluicing, and/or classification for sizing and feed into the concentration process.

TABLE V-53. WASTE CHARACTERIZATION AND RAW WASTE LOAD FOR MILL 6107 LEACH AND SOLVENT-EXTRACTION EFFLUENT (SAMPLE 80)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD	
		kg/day	lb/day	per unit ore milled	
				kg/metric ton	lb/short ton
pH	3.5*	–	–	–	–
TDS	39,350	83,000	180,000	73	146
Oil and grease	94	200	440	0.18	0.35
COD	475	1,000	2,200	0.88	1.76
NH_3	0.16	0.34	0.75	0.0003	0.0006
As	0.35	0.74	1.6	0.00065	0.0013
Cd	0.037	0.078	0.17	0.000068	0.00014
Cr	1.15	2.4	5.3	0.0021	0.0042
Cu	0.15	0.32	0.7	0.00028	0.00056
Mn	54	110	240	0.096	0.19
Mo	< 0.1	< 0.2	< 0.4	< 0.0002	< 0.0004
Pb	< 0.05	< 0.1	< 0.2	< 0.0001	< 0.0002
V	31	65	140	0.057	0.11
Zn	0.52	1.1	2.4	0.00096	0.0019
Fe	0.26	0.55	1.2	0.0005	0.001
Ca	206	430	950	0.38	0.75
Chloride	7,900	17,000	37,000	15	30
Fluoride	4.6	9.7	21	0.0085	0.017
Sulfate	26,000	55,000	120,000	48	96

*Value in pH units

TABLE V-54. WASTE CHARACTERISTICS AND WASTE LOAD FOR DRYER SCRUBBER BLEED AT MILL 6107 (SAMPLE 81)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD per unit ore milled	
		kg/day	lb/day	kg/metric ton	lb/short ton
pH	7.8*	–	–	–	–
TSS	–	–	–	–	–
TDS	7,624	4,000	8,800	3.5	7.0
Oil and Grease	15	7.8	17	0.007	0.014
COD	58.4	30.4	67	0.027	0.054
Ammonia	2	1.0	2.2	0.0009	0.0018
As	< 0.07	< 0.035	< 0.07	<0.00003	< 0.00006
Cd	< 0.005	< 0.0025	< 0.005	<0.000002	< 0.000004
Cr	0.25	0.13	0.29	0.00011	0.00023
Cu	0.06	0.03	0.07	0.00003	0.00006
Mn	4	2.1	4.6	0.0018	0.0037
Mo	< 0.1	< 0.05	< 0.1	<0.00004	<0.00009
Pb	< 0.05	< 0.025	< 0.05	<0.00002	<0.00004
V	29	15	33	0.013	0.026
Zn	0.33	0.17	0.37	0.00015	0.00030
Fe	27	14	31	0.012	0.025
Ca	118	61	130	0.054	0.11
Chloride	4,220	2,200	4,800	1.9	3.9
Fluoride	1.35	0.70	1.5	0.0006	0.0012
Sulfate	255	133	290	0.12	0.23

*Value in pH units

TABLE V-55. WASTE CHARACTERISTICS AND LOADING FOR SALT-ROAST SCRUBBER BLEED AT MILL 6107 (SAMPLE 77)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD per unit ore milled	
		kg/day	lb/day	kg/metric ton	lb/short ton
pH	2.3*	–	–	–	–
TSS	2,000	1,900	4,100	1.6	3.3
TDS	80,768	76,000	160,000	67	130
Oil and Grease	5	4.7	10	0.0041	0.0085
COD	1,844	1,700	3,800	1.5	3.1
Ammonia	0.04	0.039	0.086	0.000031	0.000063
As	0.08	0.075	0.15	0.000063	0.00013
Cd	< 0.005	< 0.005	< 0.01	< 0.000004	< 0.000008
Cr	0.9	0.86	1.9	0.00075	0.0015
Cu	< 0.03	< 0.03	< 0.07	< 0.00003	< 0.00006
Mn	5.5	5.2	12	0.0045	0.0094
Mo	–	–	–	–	–
Pb	< 0.05	< 0.05	< 0.1	< 0.00004	< 0.00008
V	–	–	–	–	–
Zn	< 0.003	< 0.003	< 0.007	< 0.000003	< 0.000006
Chloride	59,500	51,000	110,000	45	89
Fluoride	7.5	7.0	16	0.0062	0.012
Sulfate	780	740	1,600	0.64	1.3

*Value in pH units

Water is not used in mercury mining operations and is discharged, where it collects, only as an indirect result of a mining operation. This water normally results from groundwater infiltration but may also include some precipitation and runoff.

Water flows of the flotation mill and the operation employing gravity beneficiation methods are presented in Figure V-30.

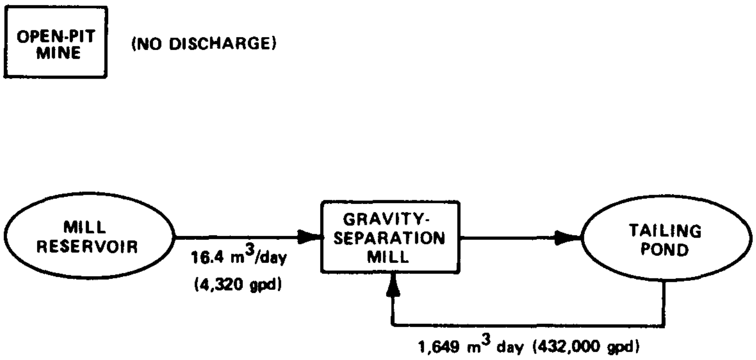
Sources of Wastes

There are two basic sources of effluents: those from mines and the beneficiation process. Mines may be either open-pit or underground operations. In the case of an open pit, the source of the pit discharge, if any, is precipitation, runoff and ground-water infiltration into the pit. Groundwater infiltration is the primary source of water in underground mines. However, in some cases, sands removed from mill tailings are used to backfill stopes. These sands may initially contain 30 to 60 percent moisture, and this water may constitute a major portion of the mine effluent.

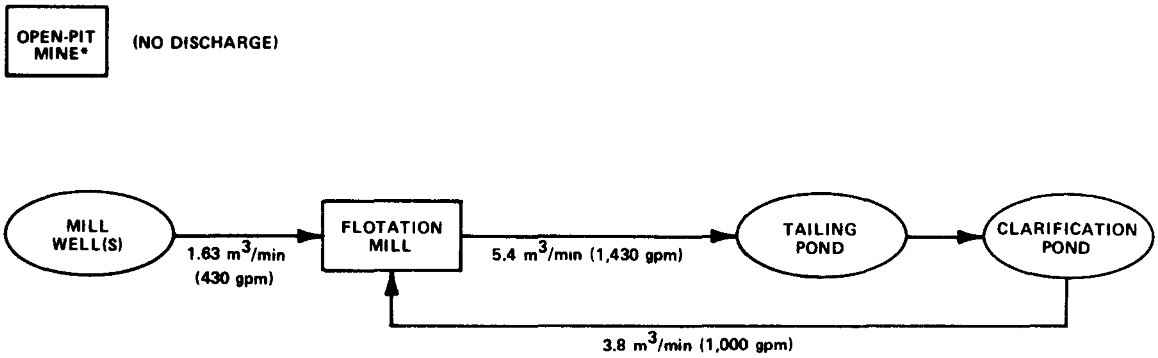
The particular waste constituents present in a mine or mill discharge are a function of the mineralogy and geology of the ore body and the particular milling process employed, if any. The rate and extent to which the minerals in an ore body become solubilized are normally increased by a mining operation, due to the exposure of sulfide minerals and their subsequent oxidization to sulfuric acid. At acid pH, the potential for solubilization of most heavy metals is greatly increased.

Waste water emanating from mercury mills consists almost entirely of process water. High suspended-solid loadings are the most characteristic waste constituent of a mercury mill waste stream. This is primarily due to the necessity for fine grinding of the ore to make it amenable to a particular beneficiation process. In addition, the increased surface area of the ground ore enhances the possibility for solubilization of the ore minerals and gangue. Although the total dissolved-solid loading may not be extremely high, the dissolved heavy-metal concentration may be relatively high as a result of the highly mineralized ore being processed. These heavy metals, the suspended solids, and process reagents present are the principal waste constituents of a mill waste stream. In addition, depending on the process conditions, the waste stream may also have a high or low pH. The pH is of concern, not only because of its potential

Figure V-30. WATER FLOW IN MERCURY MILLS 9101 AND 9102



(a) MINE/MILL 9201



*DUE TO BEGIN OPERATION IN 1975.

(b) MINE/MILL 9202

(NO DISCHARGE. WATER NOT USED. BENEFICIATION LIMITED TO CRUSHING AND/OR GRINDING TO PROVIDE FURNACE FEED.)

(c) OTHER MERCURY OPERATIONS

toxicity, but also because of its effect on the solubility of the waste constituents.

Quantities of Wastes

The few mercury operations still active in late 1974 were, for the most part, obtaining their ore from open-pit mines. In the past, however, more than 2/3 of the domestic production was from ore mined from underground mines. No discharge exists from the open-pit mines visited or contacted during this study. Also, no specific information concerning discharges from underground mercury mines was available during the period of this study. However, it is expected that, where discharges occur from these underground mines, the particular metals present and the extent of their dissolution depend on the particular geology and mineralogy of the ore body and on the oxidation potential and pH prevailing within the mine.

Silica and carbonate minerals are the common introduced gangue minerals in mercury deposits, but pyrite and marcasite may be abundant in deposits formed in iron-bearing rocks. Stibnite is rare but is more common than orpiment. Other metals, such as gold, silver, or base metals, are generally present in only trace amounts.

Process Description - Mercury Mining

Mercury ore is mined by both surface and underground methods. Prior to 1972, underground mining accounted for about 60 percent of the ore and 70 percent of the mercury production in the U.S. Currently, with market prices of mercury falling, only a couple of the lower-cost open-pit operations remain active.

The mode of occurrence of the mercury deposit determines the method of mining; yet, with either type, the small irregular deposits preclude the large-scale operations characteristic of U.S. mining.

Process Description - Mercury Milling

Processes for the milling of mercury which require water and result in the waste loading of this water are:

(1) Gravity methods of separation

(2) Flotation

One mercury operation (mill 9201) visited employs gravity separation methods of beneficiation; the volume of the waste stream emanating from this mill is approximately 1,679 cubic meters (440,000 gallons) per day. In addition, another new plant (mill 9202) due to begin production during early 1975 was contacted. This mill will use a flotation process and expects to discharge 5.5 cubic meters (1,430 gallons) of water per minute. These waste streams function to carry large quantities of solids out of the mill. While the coarser material is easily settled out, the very fine particles of ground ore (slimes) are normally suspended to some extent in the waste water and often present removal problems. The quantity of suspended solids present in a particular waste stream is a function of the ore type and mill process, as these factors determine how finely ground the ore will be.

In addition to suspended solids, solubilized and dispersed colloidal or adsorbed heavy metals may be present in the waste stream. Metals most likely to be present at relatively high levels are mercury; antimony; and, possibly, arsenic, zinc, cadmium, and nickel. The levels at which these metals are present depend on the extent to which they occur in the particular ore body. Calcium, sodium, potassium, and magnesium normally are found at concentrations of 10 to 200 parts per million.

In the past, little beneficiation of mercury ores was accomplished and typically was limited to crushing and/or grinding. In a few cases, gravity methods were used to concentrate the ore. These practices require no process reagents. However, the operation (mill 9202) due to open during 1975 will use a flotation process, which will require the use of flotation reagents. These reagents add to the waste loading of the mill effluent as they are consumed in the process. The reagents which are expected to be used at this mill are listed in Table V-56.

Mill 9201 currently beneficiates mercury ore by gravity methods. The ore is first crushed, washed, and screened to provide a feed suitable for gravity separation. The ore is concentrated by tabling, which essentially involves washing the crushed ore slurry across a vibrating table which has ridges and furrows formed in parallel on its surface. As the ore slurry is washed across this surface, the heavy ore minerals collect in the furrows, while the fines are carried across the ridges and discarded. The vibrating action causes the heavy minerals to travel along the furrows to the end of the table, where they are collected.

TABLE V-56. EXPECTED REAGENT USE AT MERCURY-ORE FLOTATION MILL 9202

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
Dowfroth 250 (Polypropylene glycol methyl ethers)	Frother	0.15	0.30
Z-11 (Sodium isopropyl xanthate)	Collector	0.13	0.25
Lime (Calcium oxide)	Depressing Agent	0.05	0.10
Sodium silicate	Depressing Agent	0.10	0.20

Sometime during the spring or early summer of 1975, mill 9202 is to begin operation for the concentration of mercury sulfide ore by a froth flotation process.

Waste characteristics of mill effluents of the operation visited and of a pilot-plant operation using the flotation process are presented in Table V-57.

Uranium, Radium, and Vanadium Ores

Water use; flow; and the sources, nature, and quantity of wastes during the processes of uranium, radium, and vanadium ore mining and beneficiation are described in this section. For vanadium-ore mining and beneficiation, only those operations beneficiating ores containing source material (i.e., uranium and thorium) subject to NRC licensing, are considered here.

Water Use. Uranium ores often are found in arid climates, and water is conserved as an expensive asset in refining or milling uranium, vanadium, and radium ores. Some mines yield an adequate water supply for the associated mill, and a wateruse pattern as shown in part (a) of Figure V-31 can be employed. Here, all or part of the mine water is used in the mill and then rejected to an impoundment, from which it is removed by evaporation and, possibly, seepage. Mine water--or at least, that portion not needed in the mill--is treated to remove values and/or pollutants. Sometimes the treated water is reintroduced to the mine for in-situ leaching of values. Waste water from the impoundment is recycled to the mill when conditions warrant, and additional recycle loops (not shown in the figure) may be attached to the mill itself.

When mines are dry or too far from the mill to permit economical utilization of their effluents, the mill derives water from wells or, rarely, from a stream (part (b) of Figure V-31). In these instances, any mine water discharge may be treated to remove uranium values and/or pollutants, and these are then shipped to the mill (part (c) of Figure V-31).

There are completely dry underground mines and open-pit mines that lose more water by evaporation than they gain by infiltration from aquifers. All known mills in this industry segment use a hydrometallurgical process.

The quantity of water used in milling is variable and depends upon the process used and the degree of recycle. From these considerations, the effluent quantities are also

TABLE V-57. WASTE CHARACTERISTICS AND RAW WASTE LOADINGS AT MILLS 9201 AND 9202

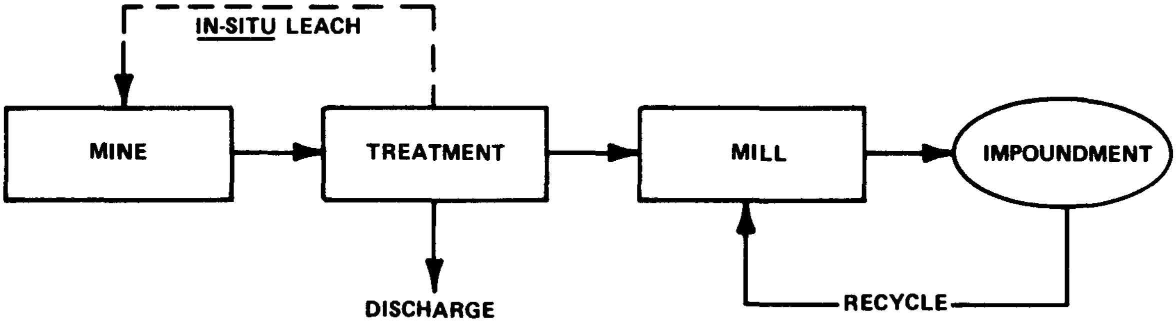
MILL	pH in pH units	Hg			Fe		
		CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
			in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
9201	6.5	–	– –	– –	< 0.5	< 6,900 (<13,800)	< 0.05 (<0.10)
9202 (Pilot Operation)	–	0.0072	11 (22)	0.094 (0.188)	0.05	80 (160)	65 (130)

MILL	Sb			As		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
9201	< 0.5	< 6,900 (<13,800)	< 0.05 (<0.10)	0.02	270 (540)	0.002 (0.004)
9202 (Pilot Operation)	0.03	50 (100)	0.4 (0.8)	0.38	600 (1,200)	5 (10)

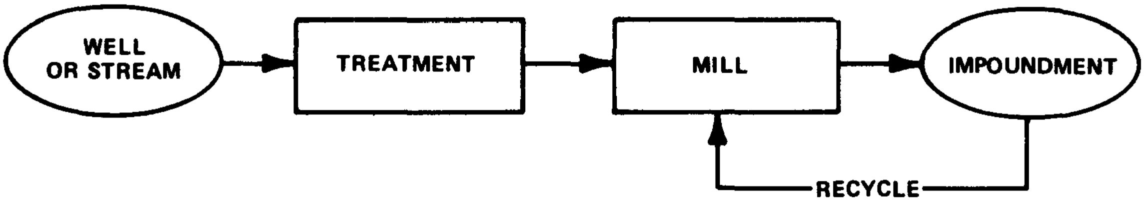
MILL	Te			Mn		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
9201	< 0.08	< 1,100 (<2,200)	< 0.008 (<0.016)	50.0	688,000 (1,376,000)	5 (10)
9202 (Pilot Operation)	–	– –	– –	0.06	79 (158)	0.65 (1.30)

MINE	Zn			SULFIDE		
	CONCENTRATION (mg/ ℓ)	WASTE LOAD		CONCENTRATION (mg/ ℓ)	WASTE LOAD	
		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled		in kg/1000 metric tons (lb/1000 short tons) of concentrate produced	in kg/1000 metric tons (lb/1000 short tons) of ore milled
9201	0.14	1,930 (3,860)	0.014 (0.028)	< 0.5	< 6,900 (<13,800)	< 0.05 (< 0.10)
9202 (Pilot Operation)	–	– –	– –	–	– –	– –

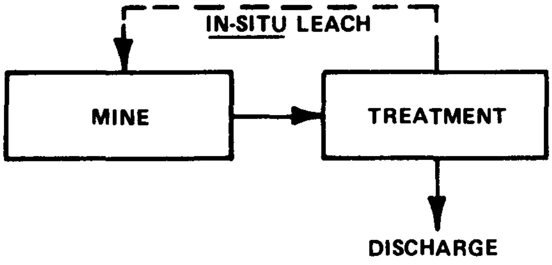
Figure V-31. TYPICAL WATER-USE PATTERNS



(a) WET MINE/MILL COMPLEX



(b) SEPARATED MILL



(c) SEPARATED WET MINE

variable. Acid leach mills generally produce between 1.5 and 2.5 tons of liquid per ton of ore; alkaline leach mills from 0.3 to 0.8 tons of liquid per ton of ore.

Waste Constituents

Radioactive Waste Constituents. Radium is one of the most potentially hazardous radionuelites. The chemistry of radium is similar to that of calcium, barium and strontium. The Environmental Protection Agency has proposed interim drinking water standards for radium -226 and radium -228 at 5pci/l (picocuries per liter) total for both radionuclides.

Radium, with a half-life of 1,620 years, is generated by the radioactive decay of uranium, which has the very long half-life of 4.51 billion years. In uranium ores that are in place for billions of years, an equilibrium may be established between the rate of decay of uranium into radium and the rate of decay of radium into its daughters. Once this equilibrium is established, the ratio of uranium to radium equals the ratio of the half-lives--i.e., 2.7 million. An equilibrated ore with a typical grade of 0.22 percent uranium would contain 0.82 microgram of radium per kilogram. Geological redeposition reduces the amount of radium in the ore. Because milling processes preferentially dissolve uranium and leave radium in solid tailings, actual concentrations of radium in tailing-pond solutions are approximately 17 to 81,000 picograms per liter. These concentrations are often quoted in curies (Ci)--i.e., 17 to 81,000 picocuries per liter (pCi/l)--since the radioactive source strength of a quantity of radium in curies is essentially equal to its content of radium by weight in grams. (Source strength unit for radionuclides has been defined as that quantity of radioactive material that decays at a rate of 37 billion (3.7 x 10 exp 10) disintegrations per second). In an acid leach ciruit, about 50% of the thorium and .4 to 6.7% of the radium are dissolved.

Thorium. There are other radioactive species that result from the decay of uranium. Thorium-230, with a half life of 80,000 years, along with lead 210 and polonium-210, with half lives of 222 years and 139 days, respectively, are considered along with radium-226. Thorium is observed in tailings pond solutions in concentrations from about 10 to 477,000 pCi/liter. A maximum concentration for thorium-230 of 2,000 pCi/liter and for radium-226 of 30 pCi/liter has been recommended by 10 CFR 20 for release to unrestricted areas. Generally, it has assumed that methods for control of radium-226 provide adequate control over thorium and the other radionuclides of interest.

Chemical and Physical Waste Constituents. Chemical contaminants of milling waste waters derive from compounds introduced in milling operations or are dissolved from ore in leaching. The common physical pollutants--primarily, suspended solids-figure prominently in discharges from wet mines, and in the management of deep-well disposal and recycle systems. One ton of ore containing 4 lb of U_3O_8 has about 515 mCi of activity from each member of the decay chain, with a total combined alpha and beta activity of about 7,200 mCi. About 85% of the total activity ends up in the mill waste, and about 15% is in the uranium product. With no parent remaining, the thorium-234 and protactium-234 decay out of the mill wastes so that, after a year, the wastes contain about 70% of the activity originally present in the ore.

Additional pollutants (particularly, metals) are expected to appear in the waste streams of specific plants that might be using unusual ores. Certain compounds, particularly organics, are expected to undergo changes and are not identifiable individually but would appear in waste-stream analysis under class headings (e.g., as TOC, oils and greases, or surfactants). In one specific example, it has been observed that oils and greases that are known to enter alkaline leach processes disappear and are replaced by approximately equivalent quantities of surfactants--presumably, by saponification (the process involved in soap manufacture). Table V-58 shows waste constituents expected from mills based upon the process, chemical consumption, and the ore mineralogies which are commonly encountered. These substances are shown in three groups: those expected from acid leach processes, those expected from alkaline leach processes, and metals expected to be leached from the ore during milling processes. Table V-59 shows two groups of constituents (among the sets of parameters which were analyzed both in background waters and waste streams): (1) Constituents that were found to exceed background by factors from three to ten; and (2) Constituents that were found to exceed background by a factor of more than ten. Comparison of Tables V-58 and V-59 illustrates that more, rather than fewer, pollutants are observed to be "added" by the operation than are predicted from process chemistry and ore characteristics. Observed pollutant increases in conjunction with toxicant lists were, therefore, used to select the parameters on which field sampling programs were to concentrate. (See also Section VI.) Table V-59 also illustrates some specific differences among the subcategories of SIC 1094 that are further explored in the following discussion.

TABLE V-58. WASTE CONSTITUENTS EXPECTED

ACID LEACH PROCESS
ACID-LEACH CIRCUIT:
Sulfuric acid
Sodium chlorate
LIQUID/SOLID-SEPARATION CIRCUIT:
Polyacrylamides
Guar gums
Animal glues
ION-EXCHANGE CIRCUIT:
Strong base anionic resins
Sodium chloride
Sulfuric acid
Sodium bicarbonate
Ammonium nitrate
SOLVENT-EXTRACTION CIRCUIT:
Tertiary amines (usually, alamine-336)
Alkyl phosphoric acid (usually, EHPA)
Isodecanol
Tributyl phosphate
Kerosene
Sodium carbonate
Ammonium sulfate
Sodium chloride
Ammonia gas
Hydrochloric acid
PRECIPITATION CIRCUIT:
Ammonia gas
Magnesium oxide
Hydrogen peroxide

ALKALINE LEACH PROCESS
ALKALINE-LEACH CIRCUIT:
Sodium carbonate
Sodium bicarbonate
ION-EXCHANGE CIRCUIT:
Strong base anionic resins
Sodium chloride
Sulfuric acid
Sodium bicarbonate
Ammonium nitrate
PRECIPITATION CIRCUIT:
Ammonia gas
Magnesium oxide
Hydrogen peroxide

METALS LEACHED FROM ORE BY MILLING PROCESSES
Magnesium
Copper
Manganese
Barium
Chromium
Molybdenum
Selenium
Lead
Arsenic
Vanadium
Iron
Cobalt
Nickel

SOURCE: Reference 28

TABLE V-59. CHEMICAL AND PHYSICAL WASTE CONSTITUENTS OBSERVED IN REPRESENTATIVE OPERATIONS

MINE/ CATEGORY	CONSTITUENTS THAT EXCEED BACKGROUND* BY FACTORS BETWEEN THREE AND TEN	CONSTITUENTS THAT EXCEED BACKGROUND* BY A FACTOR OF MORE THAN TEN
9401/ ALKALINE	Color, Cyanide, Nitrogen as Ammonia, Phosphate, Total Solids, Sulfate, Surfactants Pb	Alkalinity, COD, Fluoride, Nitrate As, Mo, V
9402/ ACID	Acidity, COD, Color, Dissolved Solids, Phosphate, Total Solids Ag, B, Ba, Hg, Zn	Ammonia, Chloride, Sulfate Al, As, Be, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Pb, V
9403/ ALKALINE	Color, Dissolved Solids, Fluoride, Sulfate, Total Solids, Turbidity	Chloride, COD, Nitrate, Surfactants, Suspended Solids, TOC As, Mo, Na, Ti, V
9404 ACID	Chloride, Color, Dissolved Solids, Total Solids, Turbidity Ag, Hg, K, Mg, Na	Acidity, Ammonia, Sulfate, Suspended Solids Al, As, Cr, Fe, Mn, Ni, Pb, Ti, V, Zn
9405/ ACID	Color, Conductivity, Fecal Coliform, Hardness, Phosphate, Suspended Solids, Total Solids, Turbidity Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mo, Ni, Pb, Sb, Se, Zn	Chloride, COD, Dissolved Solids, Kjeldahl Nitrogen, Nitrate, Volatile Solids Co, K, Mn, Na
9406/ MINE	Ammonia, Chloride, Hardness, Nitrate, Nitrite, Oil and Grease, Organic Nitrogen, Sulfate, Total Solids, Turbidity As, B, Be, Ca, Mg, Na	(None among the analyzed items)

*"Background" is defined in text.

Constituents Introduced in Acid Leaching. Acid leaching (discussed in Section III) dissolves numerous ore constituents, approximately five percent of the ore, that appear in the process stream; upon successful extraction of uranium and vanadium values, these ore constituents are rejected to tailing solutions. In plants using a sulfuric-acid leach, calcium, magnesium, and iron form sulfates directly. Phosphates, molybdates, vanadates, sulfides, various oxides, and fluorides are converted to sulfates with the liberation of phosphoric acid, molybdic acid, hydrogen sulfide, and other products. The presence of a given reaction product depends on the type of ore that is being used; since this is variable, pollutant parameters must be selected from an inclusive list. The major pollutant in an acid leach operation is likely to be the sulfuric acid itself, since a free acid concentration of one to one hundred grams of acid per liter is maintained in the leach.

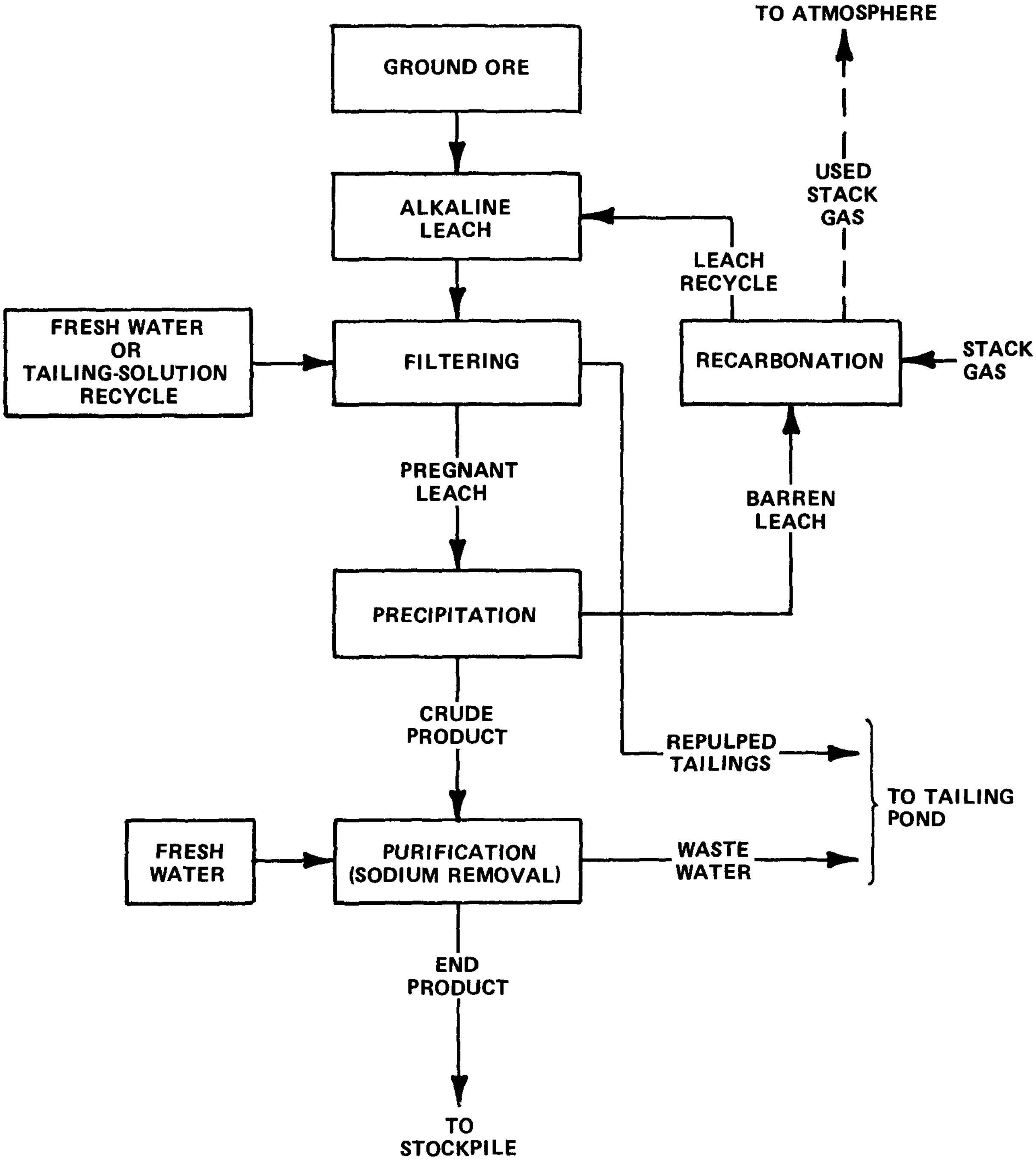
Excess free acid remaining in the leach liquors and in solvent extraction raffinates (nonsoluble portions) can be recycled to advantage. In some operations, this acid is used to condition incoming ores by reaction with acid-consuming gangue. Although this step aids in controlling pH of raw wastes, it does not reduce the amount of sulfates therein.

Oxidants are added to the acid leach liquor following initial contact with ore and after reducing gases, such as hydrogen and H_2S, have been driven from the slurry. They act in conjunction with an iron content of about 0.5 g/l to assure that uranium is in the U(VI) valence state. Sodium chlorate ($NaClO_3$) and manganese dioxide (MnO_2) serve this purpose in quantities of 1 to 4 g/l. The species of a pollutant in the effluent will normally be one of the more oxidized forms-e.g., ferric rather than ferrous iron.

Constituents Introduced in Alkaline Leaching. Alkaline leaching is less likely to solubilize compounds of iron and the light metals and has no effect on the common carbonates of the gangue. Sulfates and sulfides, in the oxidizing conditions required for conversion of U(IV) to U(VI), consume sodium carbonate and, together with the sulfate ion generated in the common method of sodium removal, pollute waste waters.

The waste water of an alkaline leach mill is largely derived from two secondary processes (Figure V-32): tailing repulping, and purification (or sodium removal). The leach itself is recycled via the recarbonation loop. The wastes discarded to tailings often contain organic compounds

Figure V-32. ALKALINE-LEACH WATER FLOW



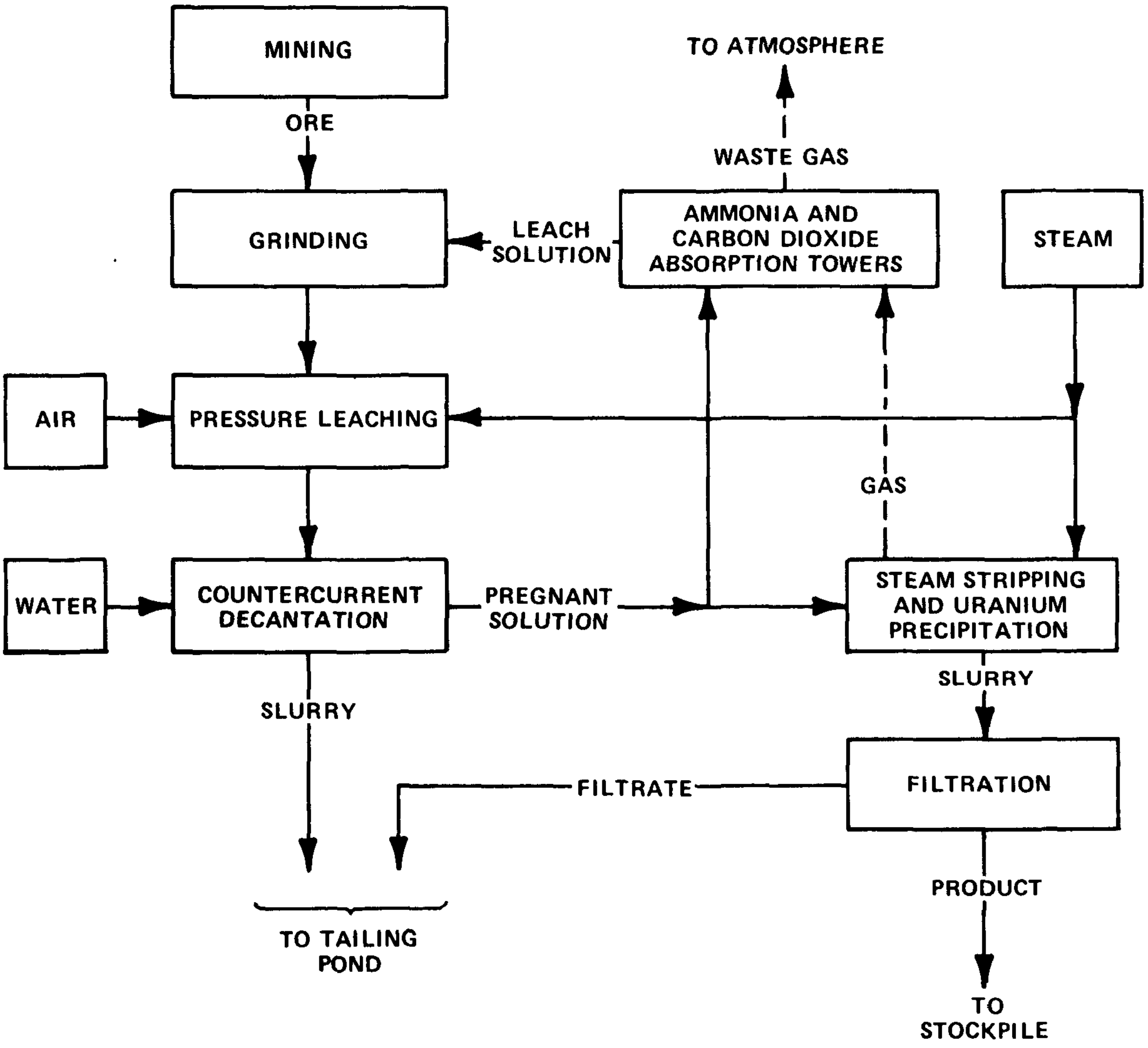
derived from the ores. Oxidizing agents are used in leaching, but air and oxygen gas under pressure have been found to serve as well as more expensive oxidants and to reduce pollutant problems. The concentrations used in alkaline leach are only of academic interest because of recycling. Sodium carbonate concentration varies from 40 to 50 g/l; sodium bicarbonate concentration, from 10 to 20 g/l.

An ammonium carbonate process that leads directly to a sodiumfree uranium trioxide product has been investigated. It is more selective for uranium than the sodium carbonate process, but vanadium, while not being recovered, interferes with uranium recovery. The process does not require bicarbonate and could produce ammonium sulfate, as a byproduct (Section III). A flow chart of an ammonium carbonate process is shown in Figure V-33.

Constituents Introduced in Concentration Processes. Ion-exchange (IX) resins are ground into small particles that appear among suspended solids in raw waste streams. Solvents are not completely recovered in the phase-separation step of solvent-exchange (SX) concentration. The extent of the contributions of each of these pollutants is difficult to judge by observation of the waste stream, since there are no specific analysis procedures for these contaminants. Some prediction of the concentration is possible from the observable loss of (IX) resin and SX solvents. Only a small fraction of IX resin is actually lost by the time it is replaced because of breakage; in one typical operation, the loss amounts to about 100 kg (220 lb) per day at a plant that has an inventory of about 500 metric tons (551 short tons) of resin, and handles 3,000 metric tons (3,307 short tons) per day of ore and about as much water. The raw waste concentration of IX resin can thus be estimated as about 30 ppm. Standard tests for water quality would measure this as a contribution to total organic carbon (TOC) which is also due to other sources (for example, organic ore constituents). Most of this contribution is in suspended solids; this is illustrated by the fact that TOC is only about 6 mg/l in the supernatant of the raw waste stream discussed above.

Solvents are lost at a rate of up to 1/2000 of the water usage in the SX circuit. This ratio is set by the solubilities of utilized solvents, which range from 5 to 25 mg/l, and by the fact that inadequate slime separation can lead to additional loss to tailing solids. TOC of the raw waste supernatant at mills using SX was found to be 20 to 24 mg/l. It is, again, impossible to determine what part of this

Figure V-33. AMMONIUM CARBONATE LEACHING PROCESS



measurement should be ascribed to SX solvents--particularly, in view of highly carbonaceous ores.

The most objectionable constituents present in mill effluents may be the very small amounts (usually, less than 6 ppm) of the tertiary amines or alkyl phosphates employed in solvent extraction. In some cases, these compounds have been found to be toxic to fish. An analytic procedure for the entire class of these materials and their decay products is not available, and they must be identified in specific instances.

Difficulties in distinguishing among solvents, ion-exchange resins, carbonaceous ore constituents, and their degradation products made it impossible to discriminate between the wastes of mills using SX or IX processes. Since some of the solvents have structures with potential for toxic effects in their degradation products, it would be desirable to trace their fates as well as those of ion-exchange resins. Future research in this field could lead to better characterization and improved treatment of wastewater.

Process Descriptions, Water Use, and Waste Characteristics for Uranium, Radium, and Vanadium Ore Mining and Milling

Four mine/mill complexes in the licensed segment of the SIC 1094 category were visited to collect data on the utilization of water and the characteristics of raw and treated wastes. Water use in the mines and mills is listed in Table V-60, and treatment systems employed are listed in Table V-61.

The consumption of water is seen to vary from 0.75 to 4.3 cubic meters per metric ton (180 to 1,000 gal per short ton) of ore capacity, with an average of 1.35 cubic meters per metric ton (323 gal per short ton). Two of the operations (9401 and 9404) derive their water supply from wells, and one (9403) obtains its water from a stream, in the manner shown in Figure V-34c. The fourth operation (9402) utilizes mine water. Where mine water is available, at least some of it is treated by ion exchange to recover uranium values. Water use in representative operations is illustrated in Figure V-34, and the water-flow configurations of these operations are illustrated in Figures V-35, V-36, V-37, and V-38. While an attempt was made to obtain a water balance in each case, there are some uncertainties. In Figure V-35, for example, the loss from tailings by evaporation is probably not quite equal to the raw waste input from the plant, and expansion of the tailing-pond area may be necessary. Similarly, it proved difficult to account for

TABLE V-60. WATER USE AND FLOWS AT MINE/MILLS 9401, 9402, 9403, AND 9404

WATER CATEGORY	WATER USED							
	MINE/MILL 9401		MINE/MILL 9402		MINE/MILL 9403		MINE/MILL 9404	
	m^3/day	gpd	m^3/day	gpd	m^3/day	gpd	m^3/day	gpd
MINE PORTION								
Water Supply	8,339	2,203,000	11,552	3,052,000	N/A	N/A	est 1,530	est 404,200
Discharge	3,339	882,100	4,325	1,143,000	N/A	N/A	0	0
Supplied to Mill	0	0	5,307	1,402,000	N/A	N/A	0	0
Recycled to Mill	5,000	1,321,000	0	0	N/A	N/A	0	0
Loss (Evaporation, etc.)	est 0	est 0	1,920	507,200	N/A	N/A	est 1,530	est 404,200
MILL PORTION								
Makeup Water	2,700	713,300	5,307	1,402,000	6,060	1,601,000	5,300	1,400,000
Water in Circuit	3,200	845,400	8,900	2,351,000	6,580	1,738,000	5,300	1,400,000
Discharge	0	0	0	0	5,400	1,427,000	0	0
Evaporation and Seepage	2,700	713,300	5,307	1,402,000	660	174,400	5,300	1,400,000

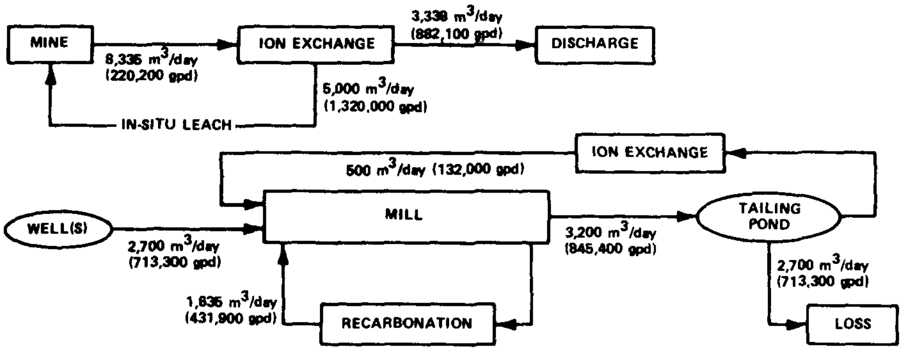
N/A = Not available

TABLE V-61. WATER TREATMENT INVOLVED IN U/Ra/V OPERATIONS

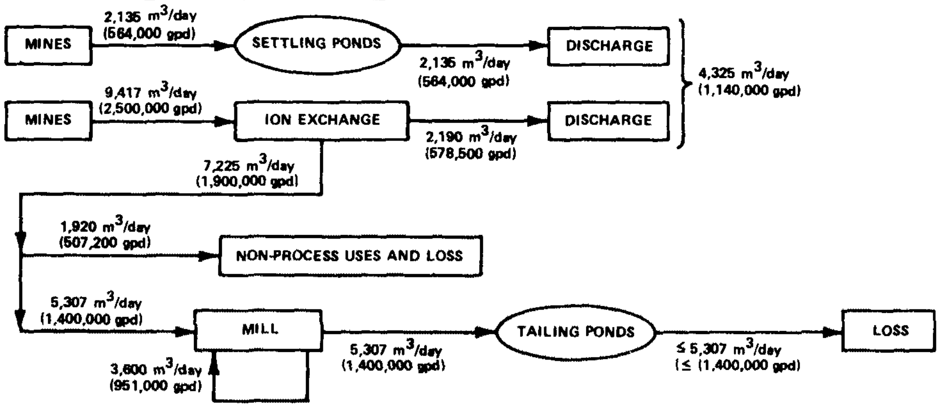
FEATURE	PARAMETER	MINE/MILL			
		9401	9402	9403	9404
MINE PORTION					
Settling Basin	Area in hectares (acres)	0.3 (0.74)	0.7 (1.7)	N/A	N/A
	Retention Time in hours	est 20	est 80	N/A	N/A
Evaporating Pond	Area in hectares (acres)	N/A	N/A	N/A	2 (4.9)
Ion-Exchange Plant	U_3O_8 Concentration in mg/l	25	2 to 12	N/A	N/A
	U_3O_8 Removal in %	96	98	N/A	N/A
MILL PORTION					
Tailing Pond(s)	Area in hectares (acres)	21 (51.8)	100 (247)	24 (59.3)	107 (264)
	Number series-connected	1	5	3	1
Ion-Exchange Plant	Daily Water Use in metric tons (short tons)	490 (540)	N/A	N/A	N/A
Recarbonizer	Daily Water Use in metric tons (short tons)	1,635(1,802)	N/A	520(573)	N/A
Deep Well	*Capacity in metric tons (short tons) water per day*	0	0	0	1,635(1,802)
Utilization of	Sand/Slime Separators	Yes			Yes
	Decant Facilities	Yes	Yes		Yes
	Filters				Yes
	Coprecipitation			Yes	
TOTAL OPERATION					
Ore Handling	Capacity in metric tons (short tons) per day	3,200(3,527)	6,400(7,055)	1,400(1,543)	2,700(2,976)

N/A = Not available

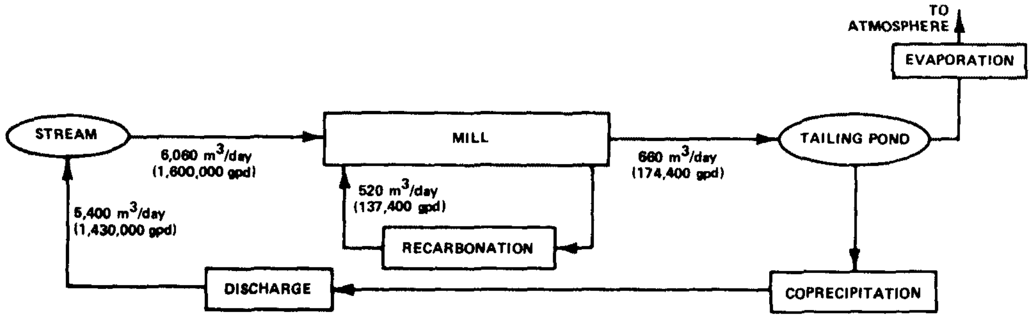
Figure V-34. WATER FLOW IN MILLS 9401, 9402, 9403, AND 9404



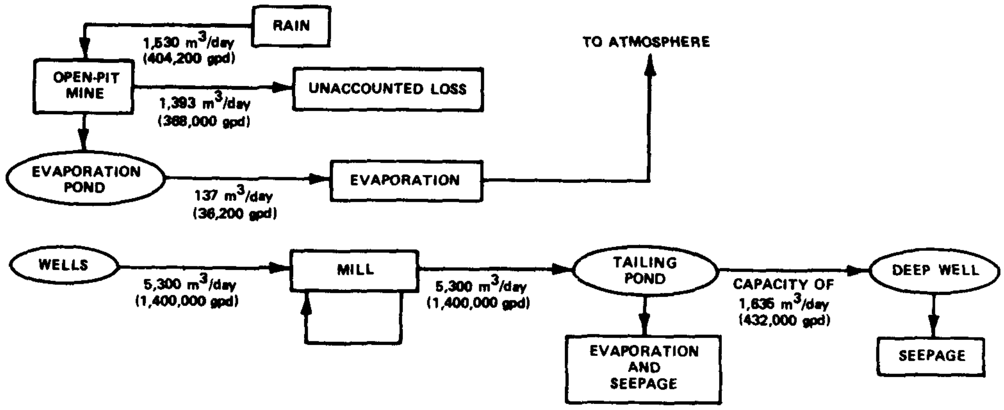
(a) MILL 9401



(b) MILL 9402



(c) MILL 9403



(d) MILL 9404

Figure V-35. FLOWCHART OF MILL 9401

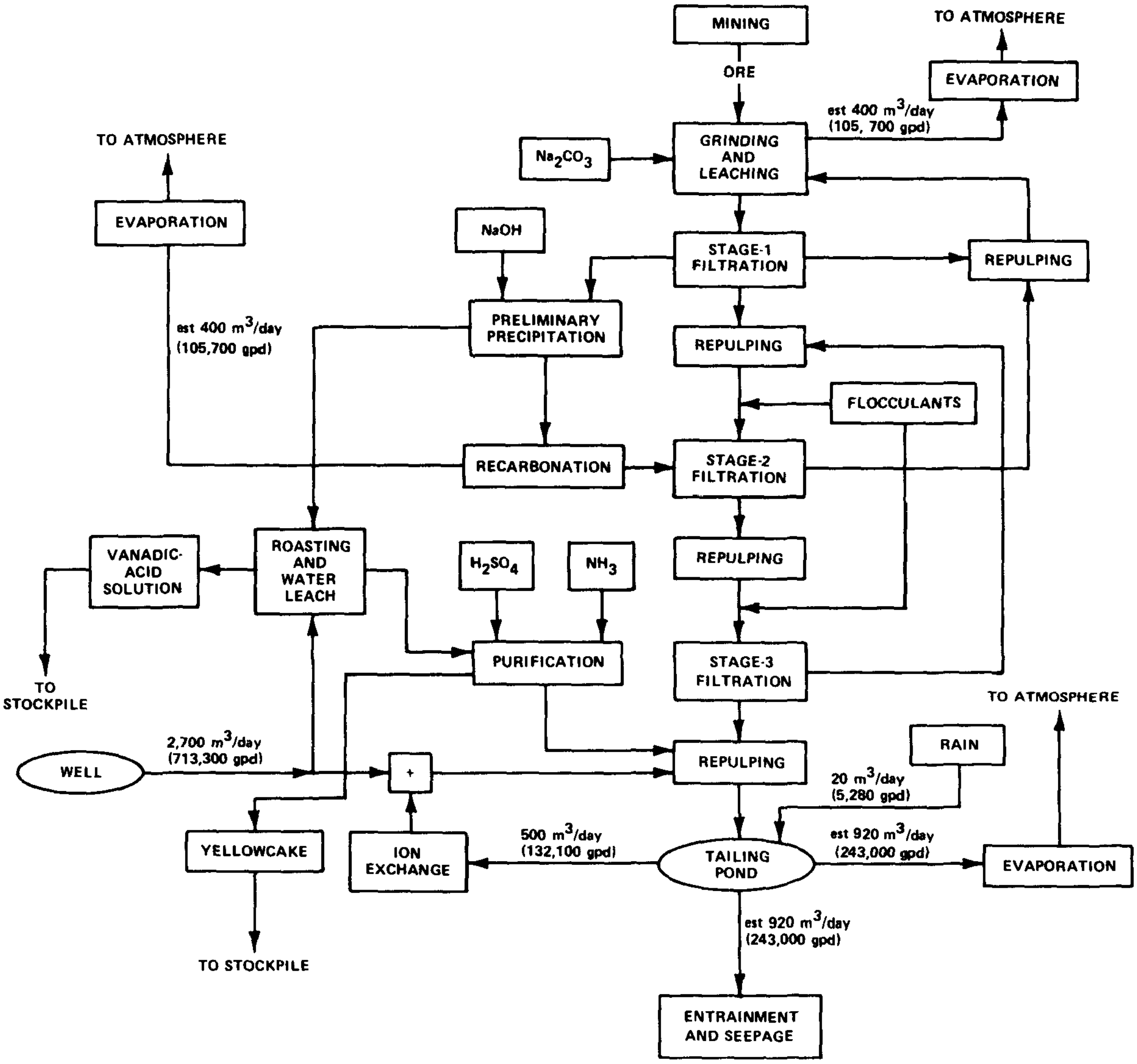


Figure V-36. FLOW CHART FOR MILL 9402

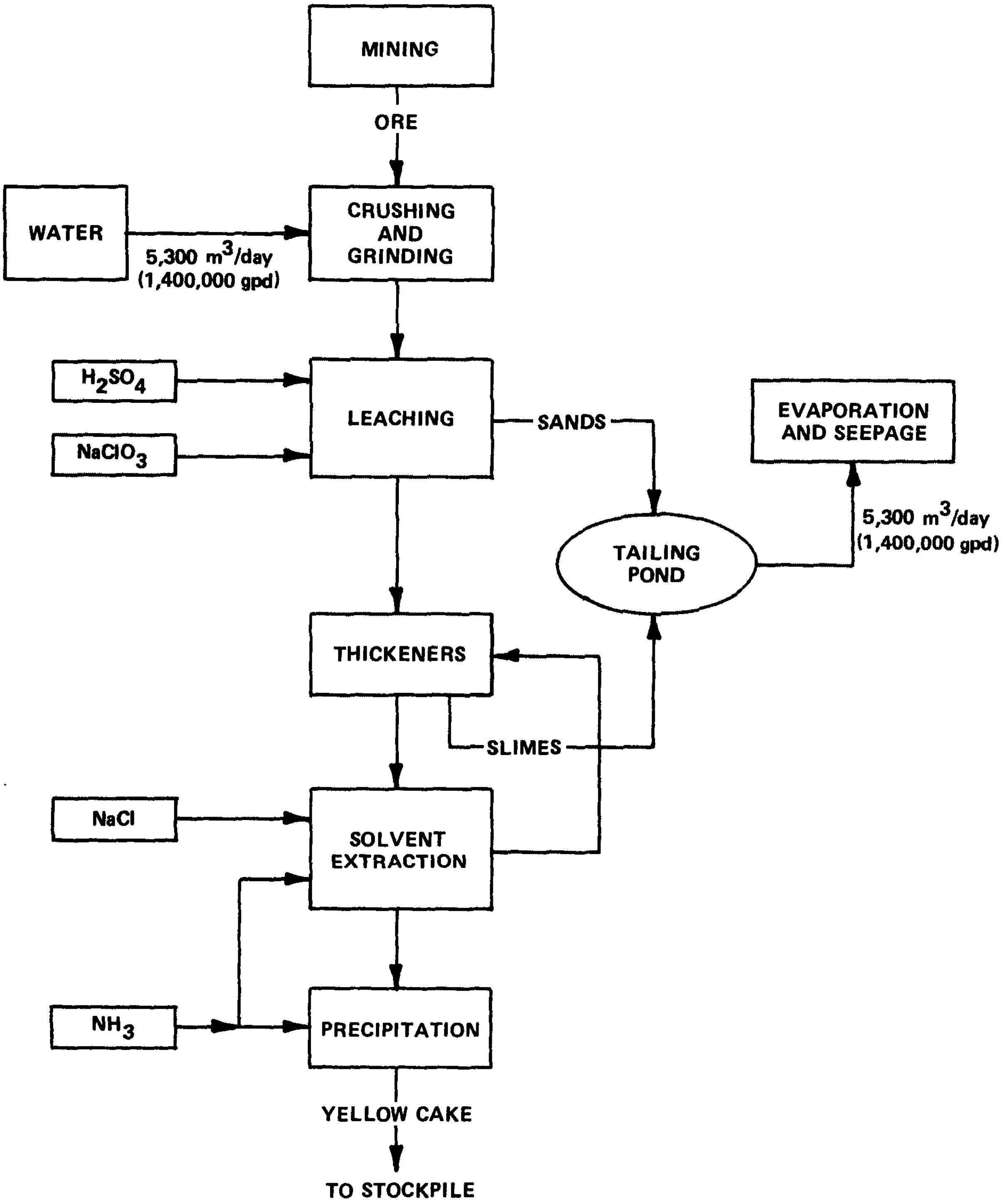


Figure V-37. FLOW CHART OF MILL 9403

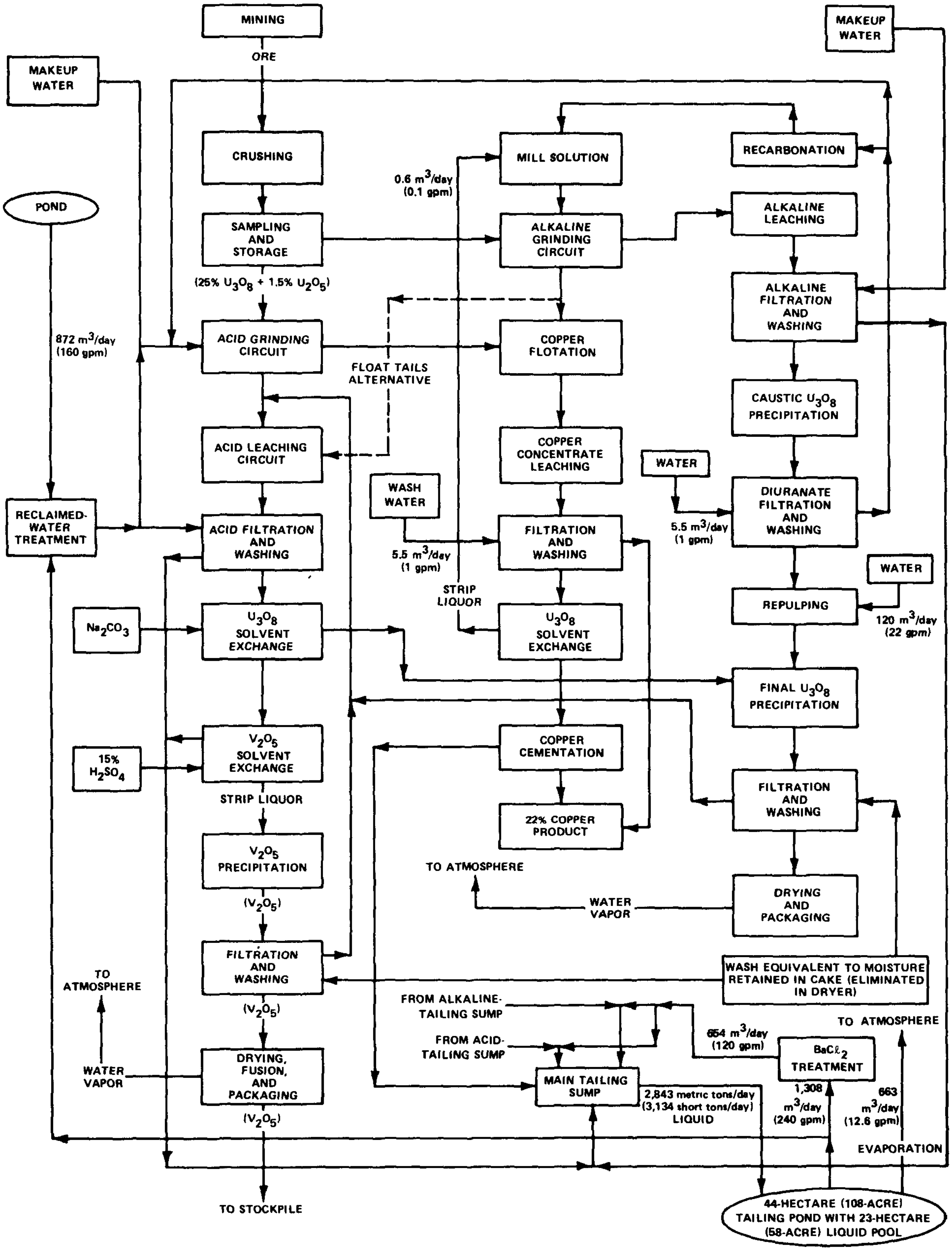
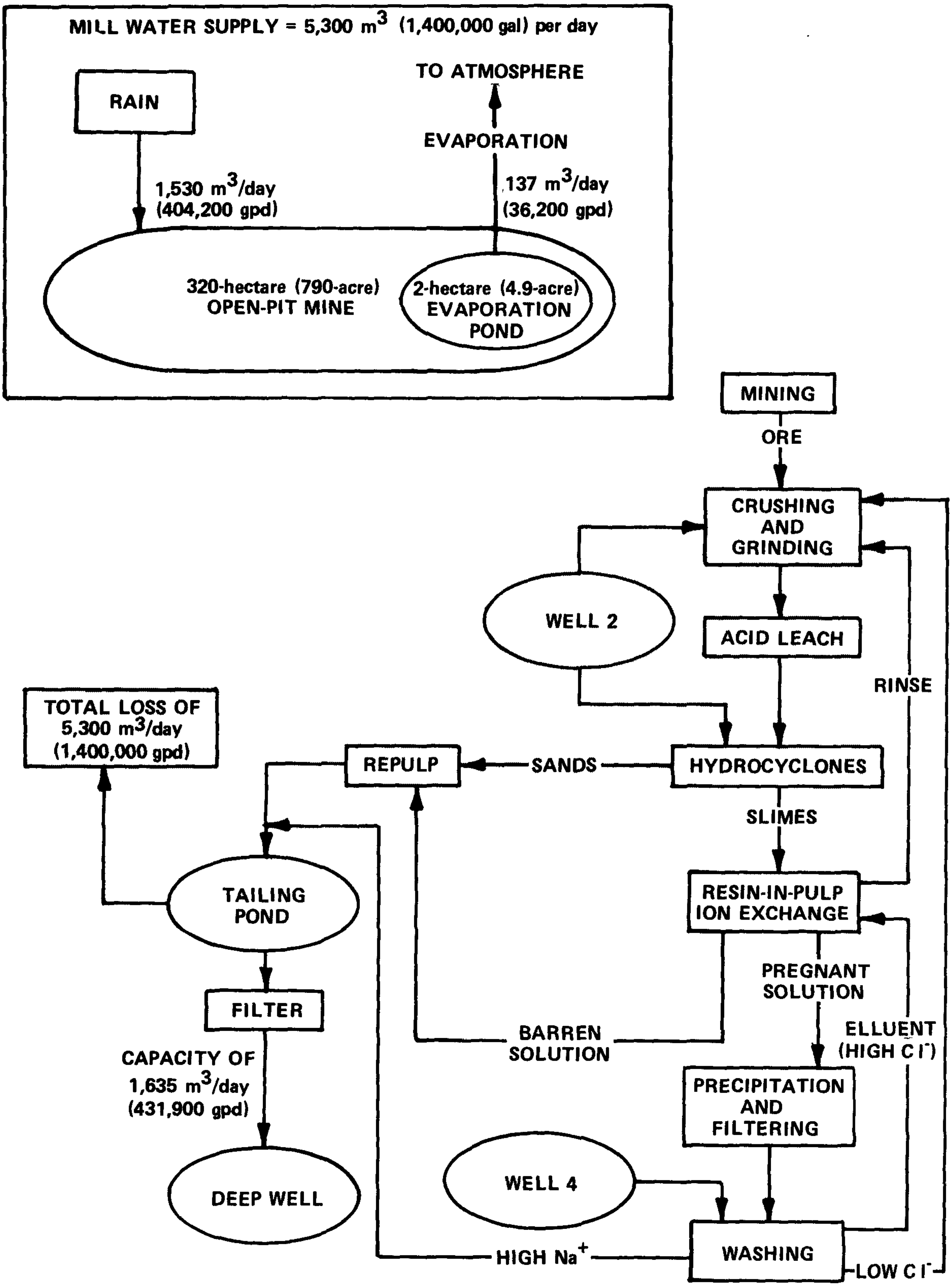


Figure V-38. FLOW CHART OF MILL 9404



the rain water entering the open pit mine of the operation in Figure V-38. If and when it rains into this mine, some water evaporates immediately from the surface, while the rest runs into a central depression or seeps into underground aquifiers. The first and last effects in combination are clearly dominant; less than ten percent of the calculable water input is seen to evaporate from the central depression (Figure V-38).

Waste Characteristics Resulting From Mining and Milling Operations. Two of the operations visited use alkaline leaching, and two use acid leaching, for extraction of uranium values. Only one operation discharges from the mill, while two others discharge from mines. Among the five NRC-licensed subcategories listed in Section IV, only mills employing a combination process of acid-and-alkaline leaching are not represented by the plants visited. An operation representing this subcategory was not visited because its processes were changed recently. During the visits to these mills, industry plans that change water use by factors of up to ten, and which will take place within a year, were presented. The data on raw wastes presented in the following discussion are based mostly on analyses of samples obtained during site visits.

The data obtained are organized into several broad waste categories:

1. Radioactive nuclides.

2. Organics, including TOC, oil and grease, surfactants, and phenol.

3. Inorganic anions, including sulfide, cyanide, fluoride, chloride, sulfate, nitrate, and phosphate.

4. Light metals, relatively nontoxic, including sodium, potassium, calcium, magnesium, aluminum, titanium, beryllum, and the ammonium cation (NH_4+).

5. Heavy metals, some of which are toxic, including silver, aluminum, arsenic, barium, boron, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, selenium, strontium, tellurium, titanium, thallium, uranium, vanadium, and zinc.

This class is further subdivided into the metals forming primarily cationic species and those forming anionic species in the conditions characteristic of raw SIC 1094 wastes (in particular, chromium, molybdenum, uranium, and vanadium).

6. Other pollutants (general characteristics), includding acidity, alkalinity, COD, solids, color, odor, turbidity and hardness.

Radioactive Nuclides. Decay products of uranium include isotopes of uranium, thorium, proactinium, radium, radon, actinium, polonium, bismuth, and lead. These decay products respond to mining and milling processes in accordance with the chemistries of the various elements and, with the exception of the bulk of uranium isotopes, appear in the wastes. Approximately ninety percent or more of the radium 226 remains with solid tailings and sediment in mine-water settling basins. Concentrations of raw waste of radium and uranium observed here should not be released to the environment. The amounts that have been observed under this program are shown in Table V-62, where it is seen that alkaline mills are highest, mines are second highest, and acid mills are lowest in the radium content of wastes. The high levels encountered at mines are partially explainable by buildup in the recycle accompanying ion-exchange recovery of uranium. Recycle also explains the high radium loads found at alkaline mills. The low concentrations observed at acid mills are partially due to the low solubility of radium sulfate (formed by reaction with sulfuric acid leach) and to the lack of recycle, but concentrations-shown in parentheses--for an evaporation pond-- indicate that such impoundments may become a pollution hazard to ground-water supplies.

Organics. Organics derived from carbonaceous ores and from chemicals added in processing are measured as TOC and, occasionally, are distinguishable as oils or greases, surfactants, or phenol. The small amounts of organics that are observed are reviewed in Table V-63.

Inorganic Anions. These may be distinguished into two classes: (1) Sulfides, cyanides, and fluorides, for which technically and economically feasible treatments (e.g., oxidation and lime precipitation) are readily available; and (2) Chlorides, sulfates, nitrates, and phosphates, which are present in fairly large concentrations in mill wastes and cannot be removed economically. Distillation and reverse osmosis, while technically feasible, raise the cost of recovered water and requires a large energy expenditure. Impoundment, in effect, results in distillation in regions like the southwestern states. Other anions are grouped together in conjunction with the light-metal cations as

TABLE V-62. RADIONUCLIDES IN RAW WASTEWATERS FROM URANIUM/RADIUM/VANADIUM MINES AND MILLS

RADIONUCLIDE and units of measurement	CONCENTRATION		
	MINES	ACID MILLS	ALKALINE MILLS
RADIUM 226 in picocuries/ℓ	200 to 3,200	200 to 700 (4,100)*	100 to 19,000
THORIUM in mg/ℓ	<0.1	(1.1)*	N/A
URANIUM in mg/ℓ	4 to 25	30 to 40	4 to 45

*Parentheses denote values measured in wastewater concentrated by evaporation

N/A = Not available

TABLE V-63. ORGANIC CONSTITUENTS IN U/Ra/V RAW WASTE WATER

PARAMETER	CONCENTRATION (mg/ℓ)		
	MINES	ACID MILLS	ALKALINE MILLS
Total Organic Carbon (TOC)	16 to 45	6 to 24	1 to 450
Oil and Grease	3 to 4	1	3
MBAS Surfactants	0.001 to 7	0.5	0.02
Phenol	< 0.2	<0.2	<0.2

total dissolved solids and are found in the levels shown in Table V-64.

Light Metals. The ions of sodium, potassium, and ammonium found in waste waters are subject to inclusion in the category of total dissolved solids. Calcium, titanium, magnesium, and aluminum respond to some treatments (e.g., lime neutralization) and are shown separately. Table V-65 shows concentrations of aluminum, beryllium, calcium, magnesium, and titanium found in waste water effluents of mines and mills covered in this ore category.

Heavy Metals. The leach processes in the uranium/vanadium industry involve highly oxidizing conditions that leave a number of ore metals--specifically, arsenic, chromium, molybdenum, uranium, and vanadium--in their most oxidized states, often as arsenates, chromates, molybdates, uranates and vanadates. These anionic species are, typically, much more soluble than cations of these metals that precipitate as hydroxides or sulfides in response to lime and sulfide precipitation treatments. Most of these anions can be reduced to lower valences by excess sulfide and will then precipitate (actually, coprecipitate with each other) and stay in solid form if buried by sediment. The observed range of concentrations for the anionic heavy metals for mines and mills visited is shown in Table V-66. One or more of the heavy metals is observed in high concentrations in each type of operation.

The cationic heavy metals that had been expected to occur from data on ores and processes include lead, manganese, iron, and copper. Field sampling results added nickel, silver, strontium, and zinc to this list. The observed concentrations of these metals are shown in Table V-67. Cadmium was found in a concentration above the lower detection limit (20 micrograms per liter) at one alkaline mill discharge.

Other Pollutants. Acid leach mills discharge a portion of the acid leach; alkaline leach mills discharge sodium carbonate; and mine water is found to be well buffered with measurable acidity and alkalinity. Chemical oxygen demand is occasionally high, and raw wastes, reslurried only to the extent needed for transport to tailings, carry a high load of total solids. These factors are reflected in the data shown in Table V-68. These measures indicate the need for settling, neutralization, and aeration of the wastes before discharge. Those treatments also effect significant reductions in other pollutants; for example, neutralization depresses heavy metals, and aeration reduces organics.

TABLE V-64. INORGANIC ANIONS IN U/Ra/V RAW WASTEWATER

PARAMETER	CONCENTRATION (mg/l)		
	MINES	ACID MILLS	ALKALINE MILLS
Sulfide	<0.5	< 0.5	< 0.5
Cyanide	< 0.01	< 0.01	< 0.01 to .04
Fluoride	0.45	< 0.01	1.4 to 2.1
Total Dissolved Solids (TDS)	1,400 to 2,000	15,000 to 36,000	5,000 to 13,000

TABLE V-65. LIGHT-METAL CONCENTRATIONS OBSERVED IN U/Ra/V RAW WASTEWATER

PARAMETER	CONCENTRATION (mg/l)		
	MINES	ACID MILLS	ALKALINE MILLS
Aluminum	0.4 to 0.5	700 to 1,600	0.2 to 20
Beryllium	0.01	0.08	0.006 to 0.3
Calcium	90 to 120	220	5 to 3,200
Magnesium	35 to 45	550	10 to 200
Titanium	0.8 to 1.1	7	2 to 15

TABLE V-66. CONCENTRATIONS OF HEAVY METALS FORMING ANIONIC SPECIES IN U/Ra/V RAW WASTEWATER

PARAMETER	CONCENTRATION (mg/ℓ)		
	MINES	ACID MILLS	ALKALINE MILLS
Arsenic	0.01 to 0.03	0.1 to 2.5	0.3 to 1.5
Chromium	< 0.02	2 to 9	< 0.02
Molybdenum	0.5 to 1.2	0.3 to 16	<0.3
Uranium	2 to 25	30 to 180	4 to 50
Vanadium	0.5 to 2.1	120	0.5 to 17

TABLE V-67. CONCENTRATIONS OF HEAVY METALS FORMING CATIONIC SPECIES IN U/Ra/V RAW WASTEWATER

PARAMETER	CONCENTRATION (mg/ℓ)		
	MINES	ACID MILLS	ALKALINE MILLS
Silver	< 0.01	< 0.01	0.1
Copper	< 0.5	0.7 to 3	<0.5 to 1
Iron	0.2 to 15	300	0.9 to 1.6
Manganese	< 0.2 to 0.3	100 to 210	<0.2 to 40
Nickel	< 0.01	1.4	0.5
Lead	0.07 to 0.2	0.8 to 2	<0.5 to 0.7
Zinc	0.02 to 0.03	3	0.4

TABLE V-68. OTHER CONSTITUENTS PRESENT IN RAW WASTEWATER IN U/Ra/V MINES AND MILLS

PARAMETER	CONCENTRATION (mg/ℓ)		
	MINES	ACID MILLS	ALKALINE MILLS
Acidity	2	4,000	0
Alkalinity	200 to 230	0	1,000 to 5,000
Chemical Oxygen Demand (COD)	<10 to 750	30	10
Total Solids	200 to 10,000	300,000 to 500,000	100,000 to 300,000

Waste Loads in Terms of Production. The loads of those pollutants that indicated conditions warranting treatment at the exemplary plants were related to ore production to yield relative waste loads. The data for three subcategories of the SIC 1094 segment are presented in Table V-69 (mines) and Tables V-70, V-71, V-72, and V-73 (mills).

Occasional large ratios between the parameters observed at differing operations are believed to be due to ore quality. The point is illustrated by TOC at mills 9401 and 9403: The operators of mill 9401 had contracted to run an ore belonging to mine 9404 on a toll basis. The ore carried a high carbonaceous material content that caused water at the 9401 mill to turn brown and may have adversely affected the concentration process at mill 9404. Mill 9403, in contrast, was concentrating its own, much cleaner, ore. The ratio of 200:1 in TOC is, therefore, expected.

Metal Ores - Not Elsewhere Classified (SIC 1099)

This section discusses the water uses, sources of wastes, and waste loading characteristics of operations engaging in the mining and milling of ores of antimony, beryllium, platinum-group metals, rare earth-metals, tin, titanium, and zirconium. The approach used in discussion of waste characteristics of these (SIC 1099) metal processes includes a general discussion of water uses and sources of wastes in the entire group, followed by a description of the character and quantity of wastes generated for each individual metal listed above.

Water Uses. The primary use of water in each of these industries is in the beneficiation process, where it is required for the operating conditions of the process. Water is a primary material in the flotation of antimony, titanium, and rare-earth minerals; in the leaching of beryllium ore; in the concentration of titanium, zirconium, and rare-earth minerals (monazite) from beach-sand deposits; and in the extraction of platinum metals from placers by gravity methods. No primary tin ore deposits of any commercial significance are currently being mined in the U.S. However, a small amount of tin is recovered as a byproduct of a molybdenum operation through the use of flotation and magnetic methods.

Water is introduced into flotation processes at the ore grinding stage to produce a slurry which is amenable to pumping, sluicing, or classification for sizing and feed into the flotation circuit. In leaching processes, water is

TABLE V-69. CHEMICAL COMPOSITION OF WASTEWATER AND RAW WASTE LOAD FOR URANIUM MINES 9401 AND 9402

PARAMETER	MINE 9401			MINE 9402		
	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD		CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD	
		kg/day	lb/day		kg/day	lb/day
TSS	–	–	–	299	640	1,400
COD	242	2,300	5,200	600	7,000	15,000
TOC	15.8	150	320	25	290	640
Alkalinity	224.4	2,100	4,600	–	–	–
Ca	93	860	1,900	117	1,300	3,000
Mg	45	420	920	36	410	910
Fe	0.47	4	10	0.23	3	6
Mo	0.5	5	11	0.53	6	13
V	1.0	9	20	<0.5	<6	<13
Ra	3,190*	29,700†	–	2,710*	31,100*	–
Th	–	–	–	<0.1	<1.2	<2.5
U	12.1	113	248	11.6	134	294

*Value in picocuries/ℓ

†Value in picocuries/day

TABLE V-70. CHEMICAL COMPOSITION OF RAW WASTEWATER AND RAW WASTE LOAD FOR MILL 9401 (ALKALINE-MILL SUBCATEGORY)

PARAMETER	CONCENTRATION (mg/) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
		kg/day	lb/day	per unit ore milled		per unit concentrate produced	
				kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	294,000	3,200,000	7,000,000	1,000	2,000	550,000	1,100,000
COD	55.6	150	331	0.047	0.094	26	52
TOC	450	1,215	2,680	0.38	0.76	211	422
Alkalinity	12,200	32,940	72,620	10	21	5,720	11,440
Cu	< 0.5	<1.4	<3	< 0.00042	<0.00084	< 0.23	<0.47
Fe	0.92	2.5	5.5	0.00078	0.0016	0.43	0.86
Mn	< 0.2	<0.54	< 1.2	< 0.00017	<0.00034	< 0.094	< 0.19
Pb	< 0.05	< 0.14	< 0.3	< 0.000042	< 0.000084	< 0.023	< 0.047
As	0.33	0.89	2	0.00028	0.00056	0.15	0.31
Mo	< 0.3	< 0.81	< 1.8	< 0.00025	< 0.00051	<0.14	< 0.28
V	17	46	101	0.014	0.029	8	16
Ra	19,000†	51,300**	-	16††	33***	8,870††	20,100***
U	43.9	118	261	0.041	0.081	22	45
Fluoride	2.1	5.7	13	0.0018	0.0035	0.98	2.0

*On the basis of 1973 production of 94.5% U_3O_8 and 5.5% V_2O_5

†Value in picocuries/ℓ

**Value in microcuries/day

††Value in microcuries/metric ton

***Value in microcuries/short ton

TABLE V-71. CHEMICAL COMPOSITION OF WASTEWATER AND RAW WASTE LOAD FOR MILL 9402 (ACID- OR COMBINED ACID/ALKALINE-MILL SUBCATEGORY)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore milled		per unit concentrate produced[*]	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	525,000	4,100,000	9,000,000	1,000	2,000	450,000	900,000
COD	63.5	337	743	0.082	0.16	37	74
TOC	24.0	127	281	0.031	0.062	14	28
Acidity	35,000	185,700	409,500	45	91	20,400	40,800
Al	1,594	8,460	18,600	2.1	4.1	930	1,860
Cu	2.7	14	32	0.003	0.007	1.6	3.1
Mn	105	557	1,228	0.14	0.27	61	122
Pb	2.1	11	25	0.003	0.005	1.2	2.4
As	2.3	12	27	0.003	0.006	1.3	2.7
Cr	9.0	48	105	0.012	0.023	5.2	10
Mo	16.0	85	187	0.021	0.041	9.3	18.7
V	125	663	1,462	0.16	0.32	73	146
Ra	234[†]	1,240[**]	–	0.30[††]	0.27[***]	136[††]	124[***]
U	31.1	165	364	0.040	0.080	18	36

[*] On the basis of 1973 production of 98.2% U_3O_8 and 1.8% MO_3

[†] Value in picocuries/ℓ

[**] Value in microcuries/day

[††] Value in microcuries/metric ton

[***] Value in microcuries/short ton

TABLE V-72. CHEMICAL COMPOSITION OF WASTEWATER AND RAW WASTE LOAD FOR MILL 9403 (ALKALINE-MILL SUBCATEGORY)

PARAMETER	CONCENTRATION (mg/ ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore milled		per unit concentrate produced*	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	111,000	1,400,000	3,100,000	1,000	2,000	1,050,000	2,100,000
COD	27.8	145	319	0.1	0.2	109	217
TOC	< 1	< 5.2	< 11	< 0.0037	< 0.0074	3.9	7.8
Alkalinity	1,150.6	5,980	13,190	4.3	8.5	4,500	9,000
Ca	3,200	16,640	36,680	12	24	1.3	2.5
Mg	190	990	2,180	0.71	1.4	743	1,486
Ti	0.395	2.1	4.5	0.0015	0.0029	1.5	3.1
Al	18	94	206	0.07	0.13	70	141
Cu	1.1	5.7	13	0.0041	0.0081	4.3	8.6
Fe	1.6	8.3	18	0.0059	0.012	6.3	13
Mn	38	198	436	0.14	0.28	149	297
Ni	0.52	2.7	6	0.0019	0.0039	2.0	4.1
Pb	0.69	3.6	7.9	0.0026	0.0051	2.7	5.4
Zn	< 0.5	< 2.6	< 5.7	< 0.0019	< 0.0037	2	4
As	1.4	7.3	16	0.0052	0.01	5.5	[illegible]
Mo	< 0.3	< 1.6	< 3.4	< 0.0011	< 0.0022	< 1.2	< 2.3
V	< 0.5	< 2.6	< 5.7	< 0.0019	< 0.0037	2	4
Ra	111†	580**	–	0.41††	0.37***	431††	392***
Th	< 0.1	< 0.5	< 1	< 0.0004	< 0.0008	< 0.4	< 0.8
U	3.9	20	45	0.032	0.064	34	68
Fluoride	1.4	7.3	16	0.0052	0.01	5.5	11

*On the basis of 1973 production of 67% U_3O_8 and 33% CuS.

†Value in picocuries/ ℓ

**Value in microcuries/day

††Value in microcuries/metric ton

***Value in microcuries/short ton

TABLE V-73. CHEMICAL COMPOSITION OF WASTEWATER AND RAW WASTE LOAD FOR MILL 9404 (ACID- OR COMBINED ACID/ALKALINE-MILL SUBCATEGORY)

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	TOTAL WASTE		RAW WASTE LOAD			
				per unit ore milled		per unit concentrate produced[*]	
		kg/day	lb/day	kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	350,000	2,700,000	6,000,000	1,000	2,000	530,000	1,060,000
COD	629	3,330	7,350	1.2	2.5	651	1,300
TOC	6.2	33	72	0.012	0.024	6.4	12.8
Acidity	4,040	21,400	47,200	7.9	15.8	418	836
Ca	224	1,190	2,620	0.44	0.88	232	464
Mg	550	2,920	6,430	1.1	2.2	569	1,139
Ti	3	16	35	0.0059	0.012	3.1	6.2
Al	740	3,920	8,650	1.5	2.9	766	1,532
Cu	0.68	3.6	7.9	0.0013	0.0026	0.7	1.4
Fe	325	1,720	3,800	0.64	1.28	336	673
Mn	210	1,110	2,450	0.41	0.82	217	435
Ni	1.38	7 3	16	0.0027	0.0054	1.4	2.9
Pb	0.84	4.5	9.8	0.0016	0.0033	0.9	1.7
Zn	< 0.5	< 2 7	< 5.8	< 0.00098	< 0.002	0.52	1.0
As	0.13	0.69	1.5	0.00026	0.00051	0.13	0.27
Cr	2	11	23	0.0039	0.0079	2.1	4.1
Mo	< 0.3	< 1.6	< 3.5	< 0.00059	< 0.0012	0.31	0.62
V	120	640	1,400	0.24	0.47	124	248
Ra	690[†]	3,660[**]	–	1.35[††]	1.23[***]	718[††]	652[***]
U	174.5	925	2,035	0.38	0.75	180	361

[*] On the basis of 1973 production of 100% U_3O_8.

[†] Value in picocuries/ℓ

[**] Value in microcuries/day

[††] Value in microcuries/metric ton

[***] Value in microcuries/short ton

the solvent extraction medium. Water also serves as the medium for gravity separation of heavy minerals.

In underground mining of antimony ore and in open-pit mining of titanium and beryllium ores, water is not used directly but, rather, is present (if at all) only as an indirect consequence of these mining operations. The mining of sand placer deposits for titanium, zirconium, and rare-earth minerals is done by dredging, in which a pond is required for flotation of the barge. In mining a placer for platinum-group minerals, a barge may be floated either in the stream or on an on-shore pond, depending on the location of the ore.

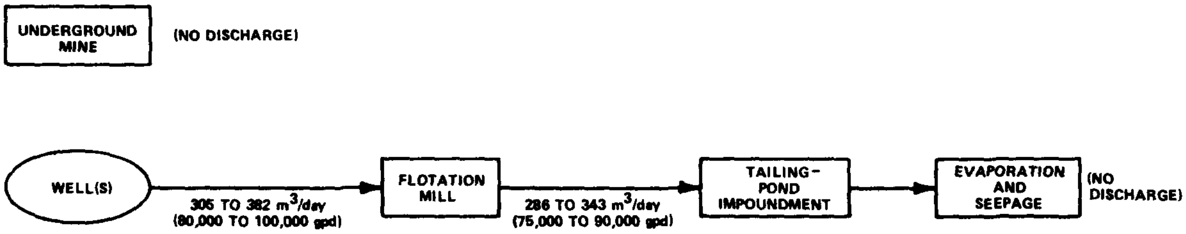
Water flows of the antimony, beryllium, platinum, rare-earth titanium, and zirconium mineral operations visited are presented in Figures V-39, V-40, and V-41.

Sources of Wastes. There are two basic sources of effluents: those from mines or dredging operations and the beneficiation process. Mines may be either open-pit or underground operations. In the case of an open pit, the source of the pit discharge (if any) is precipitation, runoff, and ground-water infiltration into the pit. Only one underground mine was encountered in the SIC 1099 ore mining industry--an antimony mine--and no existing discharges have been reported at this time. Effluents from beach-sand dredging operations orginate as precipitation, runoff, and groundwater infiltration. In addition, effluents result from the fresh water used in wet mill gravity beneficiation of the sands and, subsequently, are usually discharged into dredge ponds.

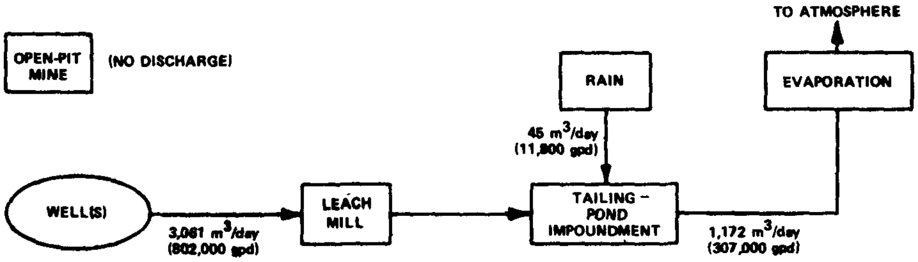
The waste constituents present in a mine or mill discharge are functions of the mineralogy of the ores exploited and of the milling or extraction processes and reagents employed. Acid conditions prevailing at a mine site also affect the waste components by influencing the solubility of many metallic components.

Waste water from a placer or sand mining operation is primarily water that was used in a primary or secondary gravity separation process. Also, where a placer does not occur in a stream, water is often used to fill a pond on which the barge is floated. The process water is generally discharged into either this pond or an on-shore settling pond. Effluents of the settling pond usually are combined with the dredge-pond discharge, and this comprises the final discharge. The principal waste water constituents from these operations are high suspended solid loadings and

Figure V-39. WATER FLOWS AND USAGE FOR MINE/MILLS 9901 (ANTIMONY) AND 9902 (BERYLLIUM)

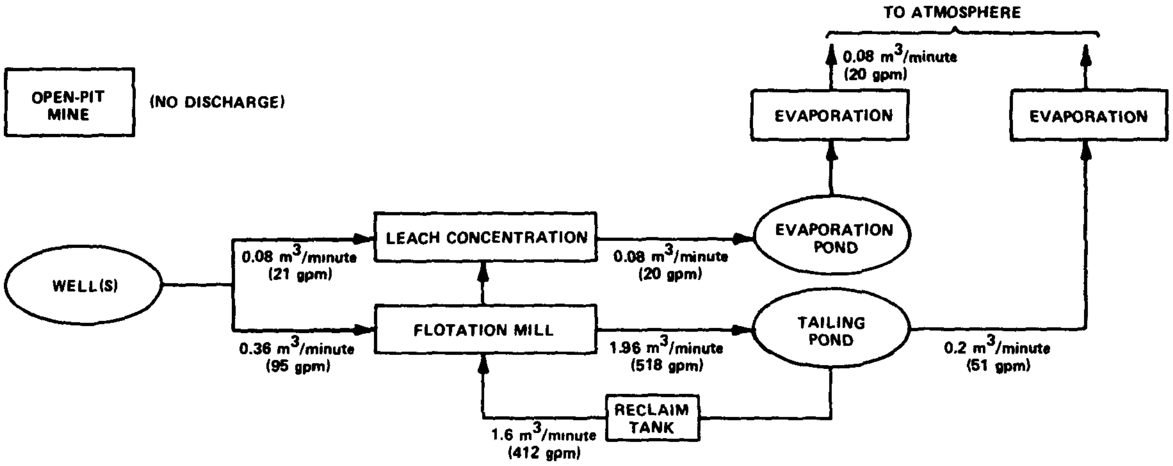


(a) ANTIMONY MINE/MILL 9901



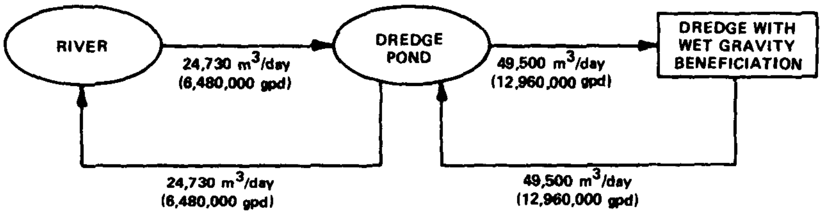
(b) BERYLLIUM MINE/MILL 9902

Figure V-40. WATER FLOWS AND USAGE FOR MINE/MILLS 9903 (RARE EARTHS) AND 9904 (PLATINUM)



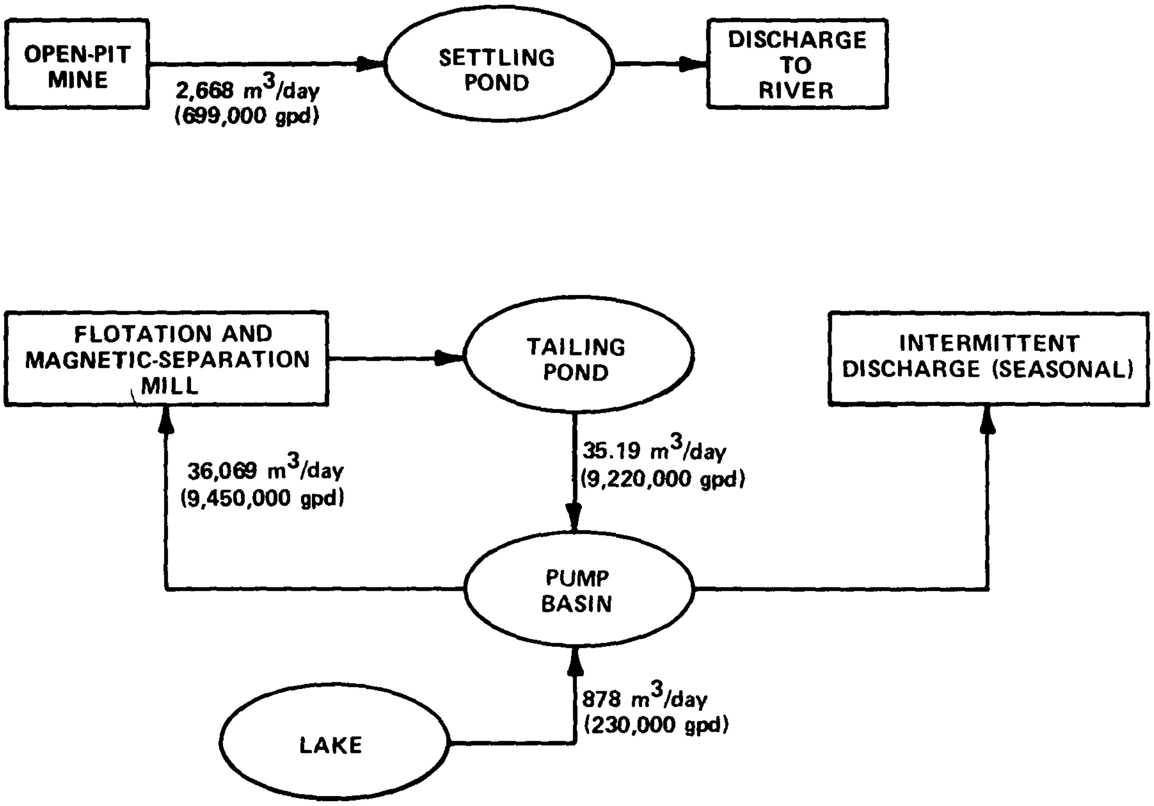
NOTE. FOR BYPRODUCT RECOVERY, SEE PART (b) OF FIGURE V-41 (MINE/MILL 9906)

(a) RARE-EARTH MINE/MILL 9903

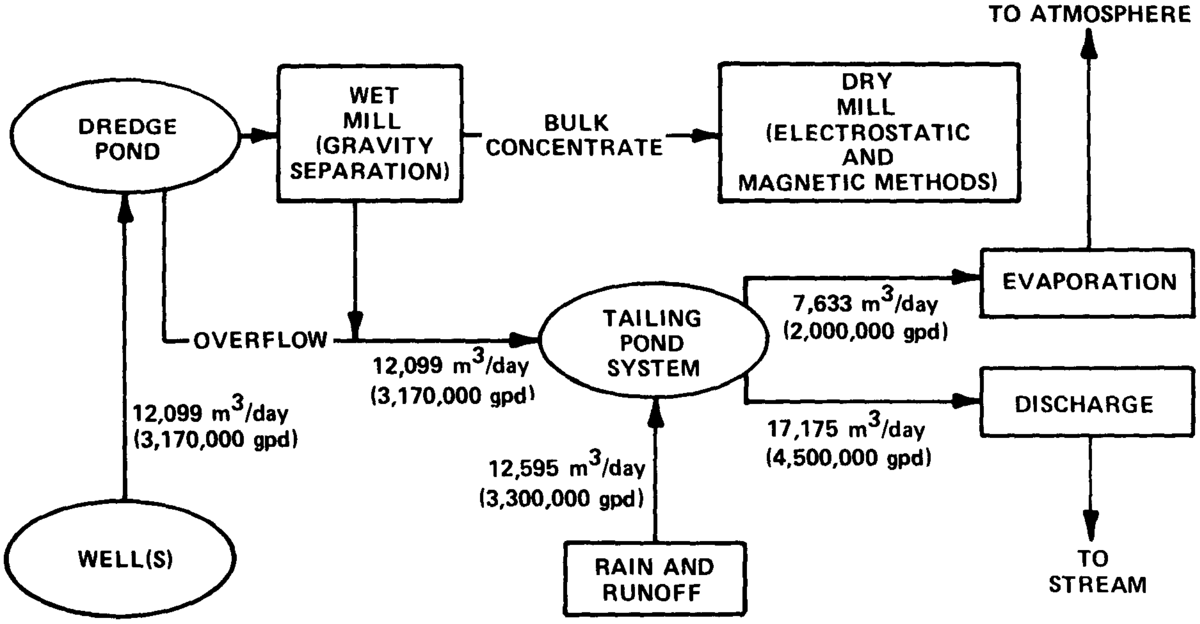


(b) PLATINUM MINE/MILL 9904

Figure V-41. WATER FLOWS AND USAGE FOR TITANIUM MINE/MILLS 9905 AND 9906



(a) TITANIUM MINE/MILL 9905



(b) TITANIUM/ZIRCONIUM/MONAZITE MINE/MILL 9906 coloring due to high concentrations of humic acids and tannic acid from the decay of organic matter incorporated into former beach sands and gravels being mined.

Waste water emanating from mills processing lode ores consists almost entirely of process water. High suspended-solid loadings are the most characteristic waste constituent of a mill waste stream. This is primarily due to the necessity for fine grinding of the ore to make it amenable to a particular beneficiation process. In addition, the increased surface area of the ground ore enhances the possibility for solubilization of the ore minerals and gangue. Although the total dissolved solid loading may not be extremely high, the dissolved heavy metal concentration may be relatively high as a result of the highly mineralized ore being processed. These heavy metals, the suspended solids, and process reagents present are the principal waste constituents of a mill waste stream. In addition, depending on the process conditions, the waste stream may also have a high or low pH. The pH is of concern, not only because of its potential toxicity, but also because of its effect on the solubility of the waste constituents.

Waste water emanating from a beach-sand dredging pond consists of water in excess of that needed to maintain the pond at the proper level. This water also originates as wet mill effluent and, as a result, contains suspended solids. However, the primary waste constituents from these milling operations are the humic and tannic acids which are indigenous to the ore body and which result in coloring of the water.

Description of Character and Quantity of Wastes

The quantity of wastes resulting from mining and milling activities is discussed below individually for each of the SIC 1099 metals.

Antimony

Process Description - Antimony Mining. Currently, only one mine exists which is operated solely for the recovery of antimony ore (mine 9901). This ore is mined from an underground mine by drifting (following the vein).

As indicated in Figure V-39, no discharge currently exists from the mine.

Process Description - Antimony Milling. Only one mill is operating for the recovery of antimony ore as the primary product. This mill (9901) employs the froth flotation process to concentrate the antimony sulfide mineral, stibnite (Figure III-28). The particular flotation reagents used by this mill are listed in Table V-74. Water in this operation is added between the crushing and grinding stages at the rate of 305 to 382 cubic meters (80,000 to 100,000 gallons) per day. There is no discharge, but flow to an impoundment totals 286 to 343 cubic meters (75,000 to 90,000 gallons) per day.

Quantities of Wastes. Waste constituents originate from two sources: solubilization and dispersion of ore constituents and consumption of the milling reagents.

In metal mining and milling effluents, heavy-metal constituents are of primary concern, due to their potentially toxic nature. Metallic minerals known to occur with antimony in the commercially valuable ore body of mine 9901 are:

Stibnite	(Sb_2S_3)
Pyrite	(FeS_2)
Arsenopyrite	($FeAsS$)
Sphalerite	(ZnS)
Argentite	(Ag_2S)
Cinnabar	(HgS)
Galena	(PbS)

The metals in these minerals are the ones which would be expected to occur at highest concentrations in the waste stream, and results of raw-waste analysis support this conclusion (Table V-75). The raw-waste characterization presented in Table V-75 is based upon the analysis of samples collected during the mill visit. As would be expected on the basis of the mineralization of the ore body, the metals present at relatively high concentrations in the raw waste are antimony (64.0 mg/l), zinc (4.35 mg/l), and iron (18.8 mg/l). Arsenic is not as high as was expected but is about an order of magnitude greater than mean background levels reported in surface waters of the Pacific Northwest Basin. Waste loadings for important constituents of waste waters from mill 9901 are listed in Table V-76.

Beryllium

Process Description - Beryllium Mining. Beryllium ore is mined on a large scale at only one domestic operation. At mine 9902, bertrandite ($H_2Be_4Si_2O_9$) is recovered by open-pit methods. A small amount of beryl is also mined in the U.S.

TABLE V-74. REAGENT USE AT ANTIMONY-ORE FLOTATION MILL 9901

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
Dowfroth 250 (Polypropylene glycol methyl ethers)	Frother	0.4	0.8
Aerofloat 242 (Essentially Aryl dithiophosphoric acids)	Collector	0.1	0.2
Lead nitrate	Activating Agent	0.5	1.0

TABLE V-75. CHEMICAL COMPOSITION OF RAW WASTEWATER DISCHARGED FROM ANTIMONY FLOTATION MILL 9901

PARAMETER	CONCENTRATION (mg/ℓ)
pH	8.3*
Acidity	8.5
Alkalinity	11.0
Color	113†
Turbidity (JTU)	170
TSS	149
TDS	68
Hardness	40
Chloride	1.5
COD	43
TOC	7.8
Al	6.2
As	0.23
Be	< 0.002
Ba	< 0.3
B	< 0.01
Cd	0.103
Ca	0.57
Cr	0.04
Cu	0.12
Total Fe	18.8
Pb	0.13
Mg	1.93
Total Mn	0.40
Hg	0.0038
Ni	0.10
Tl	< 0.05
V	< 0.2
K	3.5
Se	0.036
Ag	< 0.02
Na	2.0
Sr	0.11
Te	< 0.2
Ti	< 0.5
Zn	4.35
Sb	64.0
Mo	< 0.2
Oil and Grease	< 1
MBAS Surfactants	1.9
Cyanide	< 0.01
Phenol	0.022
Fluoride	< 0.1
Total Kjeldahl N	1.3
Sulfide	0.5
Sulfate	16.5
Nitrate	2.55
Phosphate	0.05

*Value in pH units

†Value in cobalt units

TABLE V-76. MAJOR WASTE CONSTITUENTS AND RAW WASTE LOAD AT ANTIMONY MILL 9901

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD			
		per unit concentrate produced		per unit ore milled	
		kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
pH	8.3*	–	–	–	–
TSS	997	74.78	149.56	7.48	14.96
COD	43	3.22	6.44	0.0322	0.0644
TOC	7.8	0.585	1.170	0.059	0.118
Fe	18.8	1.41	2.82	0.141	0.282
Pb	0.13	0.0097	0.0194	0.00097	0.00194
Sb	64.0	4.8	9.6	0.48	0.96
Zn	4.35	0.366	0.652	0.033	0.066
Cu	0.12	0.009	0.018	0.0009	0.0018
Mn	0.40	0.03	0.06	0.003	0.006
Mo	< 0.2	< 0.015	<0.030	< 0.0015	< 0.0030

*Value in pH units

by crude open-cut and hand-picking methods. As indicated in Figure V-39, no discharge currently exists at mine 9902.

Process Description - Beryllium Milling. Currently, only one domestic beryllium operation uses water in a beneficiation process. This operation is identified as mill 9902 and employs a proprietary acid leach process to concentrate beryllium oxide from the ore.

Quantities of Wastes. As indicated in Figure V-31, approximately 3,061 cubic meters (802,000 gallons) per day of wastewater are discharged from mill 9902. Waste constituents originate from two sources: solubilization and dispersion of ore constituents and consumption of milling reagents. However, because this process involves acid leaching, high solubilization is observed in the waste constituents (Table V-22).

The mineralization of the ore body from which bertrandite is obtained is essentially that presented in the tabulation given below for mine 9902 (beryllium).

Quartz	SiO_2
Feldspar	Al silicates with Ca, K, and Na
Fluorite	CaF_2
Carbonates	
Iron Oxide Minerals	
Tourmaline	$(XY_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4)$
where	X = Na, Ca; Y = Al, Fe(+3), Li, Mg

Constituents of these minerals are also expected to be the main constituents in the mill waste, and results of waste analysis support this (Table V-77). As indicated, the waste stream from this leaching process is exceptionally high in dissolved solids (18,380 mg/l), consisting largely of sulfate (10,600 mg/l). Fluoride (45 mg/l) is also present at relatively high concentration, as are aluminum (552 mg/l), beryllium (36 mg/l), and zinc (19 mg/l).

Rare Earths

Process Description - Rare-Earth Metals Mining. The rare-earth mineral monazite (Ce, La, Th, Y)PO_4) is recovered predominantly as a byproduct from sand placers mined by dredging--primarily, for their titanium mineral content. (Refer to information on mill 9906, as described for titanium.) The rare-earth mineral bastnaesite is also currently recovered, as the primary product, by an operation mining the ore from an open-pit mine (mine 9903).

TABLE V-77. CHEMICAL COMPOSITION OF RAW WASTEWATER FROM BERYLLIUM MILL 9902 (NO DISCHARGE FROM TREATMENT)

PARAMETER	CONCENTRATION (mg/ℓ)
Conductivity	17,000*
Color	88†
Turbidity (JTU)	1.3
TDS	18,380
Acidity	3,035
Alkalinity	0
Hardness	4,000
COD	22
TOC	55
Oil and Grease	< 1
MBAS Surfactants	0.76
Al	552
As	0.15
Be	36.0
Ba	< 5.0
B	0.65
Cd	0.047
Ca	43.0
Cr	0.20
Cu	0.07
Total Fe	< 0.5
Pb	< 0.1
Mg	320.0

PARAMETER	CONCENTRATION (mg/ℓ)
Total Mn	49.0
Ni	0.15
Tl	< 0.05
V	< 0.2
K	77.0
Se	0.062
Ag	0.04
Na	270.0
Sr	0.22
Te	< 0.2
Ti	< 0.5
Zn	19.0
Mo	< 0.2
Chloride	170
Fluoride	45
Sulfate	10,600
Nitrate	1.25
Phosphate	0.8
Cyanide	< 0.01
Phenol	< 0.01
Total Kjeldahl N	0.19
Sulfide	< 0.5

*Value in micromhos/cm

†Value in cobalt units

As indicated in Figure V-40, no discharge currently exists at mine 9903.

Process Description - Milling. Monazite is concentrated by the wet gravity and electrostatic and magnetic separation methods, discussed in the titanium segment of this section.

A single mill (9903) is currently beneficiating rare-earth minerals mined from a lode deposit. Bastnaesite is initially concentrated by the froth flotation process (Figure V-42). Flotation of rare-earth minerals requires rigidly controlled conditions and a pH of 8.95, and temperature-controlled reagent addition is critical to the successful flotation of these minerals. Rare-earth oxides (REO) in the mill heads range from 6 to 11 percent and are upgraded in the flotation circuit to a concentrate that averages 57 to 65 percent REO, depending upon the heads. This concentrate is leached with hydrochloric acid to remove calcium and strontium carbonates, increasing the REO content in the leached concentrate by as much as 5 to 10 percent. This concentrate is processed in a solvent extraction plant to produce high-purity europium and yttrium oxides; a cerium hydrate product; a concentrate of lanthanum, praesodymium and neodymium; and a concentrate of samarium and gadolinium (Figure V-43).

In the solvent extraction plant, the flotation concentrate is initially dried and then roasted to remove carbon dioxide and to convert the rare-earths to oxides. These oxides, with the exception of cerium oxide, are converted to soluble chlorides in a hydrochloric-acid leaching circuit. Following leaching, the acid slurry is passed through a countercurrent decantation circuit. The primary thickener overflow containing the chlorides is fed into the europium circuit, while the leached solids from the countercurrent decantation circuit make up the feed for the cerium process.

The leach liquor (primary thickener overflow) is clarified in a carbon filter and adjusted to a pH of 1.0 and a temperature of 60 degrees Celsius (140 degrees Fahrenheit) prior to countercurrent extraction of europium with organic solvent (90 percent kerosene and 10 percent ethyl/hexyl phosphoric acid). The raffinate from the extraction circuit makes up the feed for the lanthanum circuit, which is discussed later.

After loading the organic with europium, the europium is stripped in the solvent extraction strip circuit with $\underline{4N}$ hydrochloric acid. The pregnant strip solution contains

Figure V-42. BENEFICIATION OF BERTRANDITE, MINED FROM A LODE DEPOSIT, BY FLOTATION (MILL 9903)

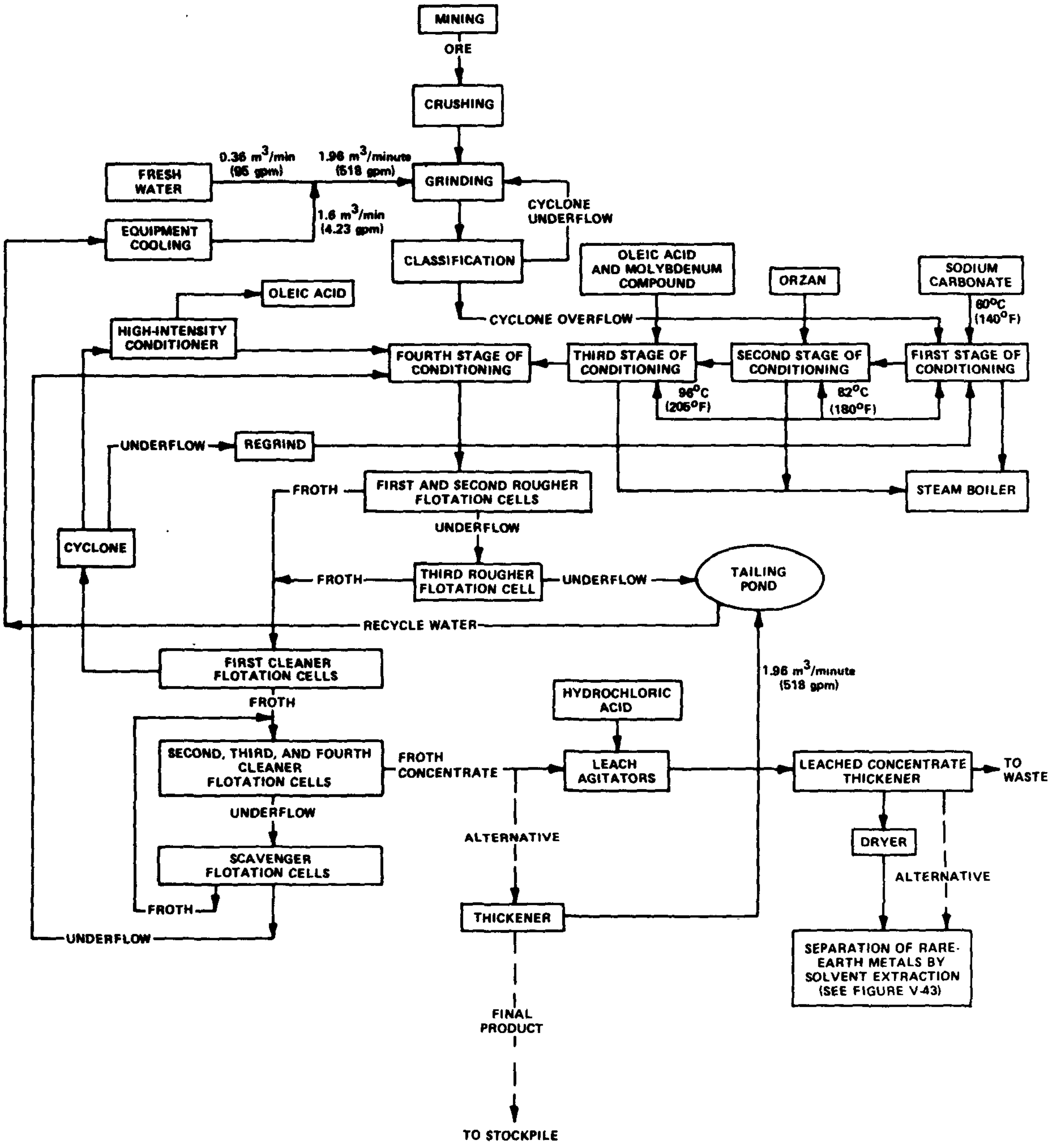
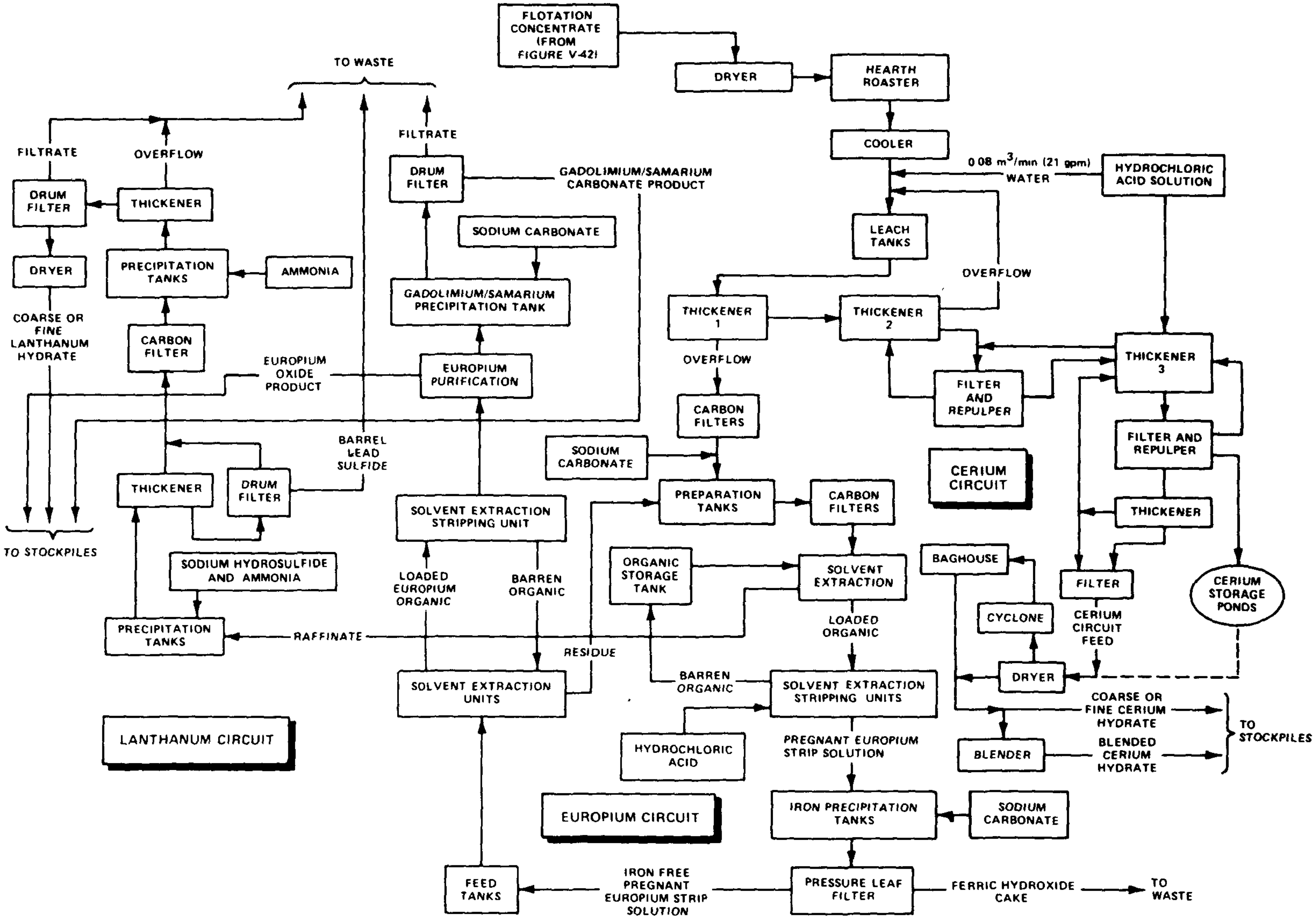


Figure V-43. BENEFICIATION OF RARE-EARTH FLOTATION CONCENTRATE BY SOLVENT EXTRACTION (MILL 9903)



iron, which is removed in precipitation tanks by the addition of soda ash to lower the pH to 3.0 to 3.5. This causes ferric hydroxide to precipitate, and the precipitate is removed in a pressure filter. Following removal of the iron, the europium bearing solution goes through another solvent extraction and stripping circuit, similar to the previous one. The pregnant strip is pumped to a purification circuit, where europium oxide is prepared for the market.

Solutions from the purification circuit are neutralized with sodium carbonate to produce gadolinium and samarium carbonates, which are collected by a drum filter.

Returning to the countercurrent decantation circuit, the solids remaining from leaching are filtered and repulped. The cerium solids are then thickened, filtered, and dried to produce the final concentrate.

As mentioned previously, the raffinate from the first solvent extraction circuit provides the feed for the lanthanum circuit. This raffinate is clarified in a carbon filter, and ammonia is added to precipitate lanthanum hydrate. The precipitate is thickened and filtered to produce the final concentrate.

Quantities of Wastes. As indicated in Figure V-40, raw wastes are discharged at a rate of 1.96 cubic meters (518 gallons) per minute from the flotation circuit and at a rate of 0.08 cubic meter (21 gallons) per minute from the leach/solvent extraction plant. These waste streams are not combined, and both are characterized in Table V-78. These data are based upon the analysis of raw-waste samples collected during the mill visit. Table V-79 presents the results of chemical analyses for the rare-earth metals.

Reagents used in the flotation, leach, and solvent extraction processes of mill 9903 are identified below.

Flotation Circuit

Frother	Methylisobutylcarbinol
Collector	N-80 Oleic Acid
pH Modifier	Sodium Carbonate
Depressants	Orzan, Sodium Silicofluroide
Conditioning Agent	Molybdenum Compound

Leach Circuit

Leaching Agent	Hydrochloric Acid

TABLE V-78. CHEMICAL COMPOSITION OF RAW WASTEWATER FROM RARE-EARTH MILL 9903

PARAMETER	CONCENTRATION (mg/ℓ)	
	FLOTATION	LEACH/ SOLVENT EXTRACTION
pH	9.02*	8.23*
Acidity	-	345
Alkalinity	-	2,125
Color	-	80†
Turbidity (JTU)	-	5.2
TDS	14,476	76,162
TSS	360,000	786
Hardness	-	7,220
COD	-	>1,500
TOC	3,100	47
Oil and Grease	-	< 1
MBAS Surfactants	-	21.2
SiO_2	-	1.25
Al	-	< 0.1
As	-	0.01
Be	-	0.009
B	-	< 0.01
Cd	-	< 0.005
Ca	-	2,910
Cr	0.35	0.04
Cu	-	< 0.03
Total Fe	-	0.03

PARAMETER	CONCENTRATION (mg/ℓ)	
	FLOTATION	LEACH/ SOLVENT EXTRACTION
Pb	-	< 0.05
Mg	-	6.6
Total Mn	0.5	3.0
Ni	-	0.85
Tl	-	< 0.1
V	< 0.3	< 0.3
K	-	94
Se	-	0.015
Ag	-	0.09
Na	-	650
Sr	-	4.5
Te	-	3.36
Ti	-	7.0
Zn	-	< 0.003
Mo	-	< 0.1
Chloride	-	54,000
Fluoride	365	< 0.1
Sulfate	-	2.3
Nitrate	-	1.50
Phosphate	-	0.09
Cyanide	-	< 0.01
Phenol	-	< 0.01

*Value in pH units

†Value in cobalt units

TABLE V-79. RESULTS OF CHEMICAL ANALYSIS FOR RARE-EARTH METALS (MILL 9903–NO DISCHARGE)

PARAMETER	CONCENTRATION (mg/ ℓ)	
	LEACH WASTEWATER	FLOTATION RECLAIM WATER
Y	–	0.014
La	442	1.32
Ce	24	2.75
Pr	6.2	0.27
Nd	9.6	0.51
Sm	0.27	0.041
Eu	< 0.001	< 0.001
Gd	< 0.001	0.006
Th	< 0.001	< 0.001

Solvent-Extraction Circuit

Leaching Agent	Hydrochloric Acid
Precipitants	Sodium Carbonate, Ammonia, Sodium Hydrosulfide
Solvents	Kerosene, Ethyl/Hexyl Phosphoric Acid

In rare-earth metal mining and milling, effluent constituents expected to be present are a function of the mineralogy of the ore and the associated minerals. The principal minerals associated with the ore body of mine 9903 are: bastnaesite ($CeFCO_3$, with La, Nd, Pr, Sm, Gd, and Eu); barite ($BaSO_4$); calcite ($CaCO_3$); and strontianite ($SrCO_3$).

The dissolved-solid content of the leach/solvent-extraction waste stream is extremely high (76,162 mg/l) and is due largely to chlorides (54,000 mg/l). The metals present at highest concentrations are those which would be expected on the basis of known mineralization and use in the process. These are strontium (4.5 mg/l) and barium (less than 10 mg/l). The high concentration of tellurium (3.36 mg/l) is unexplained on the basis of known mineralization, but mineralization is assumed to be the source of this element. Waste characteristics and raw waste loading for the rare-earth flotation and concentrate leaching/solvent extraction processes are given in Table V-80.

Platinum-Group Metals

Process Description - Platinum Mining. Production of platinum group metals is largely as a byproduct of gold and copper refining, and primary ore mining is limited to a single dredging operation (mine 9904), which is recovering platinum-metal alloys and minerals from a placer deposit.

Process Description - Milling. Mill 9904 employs a physical separation process to beneficiate the placer gravels (Figure III-20). The dredged gravels are intially screened, jigged, and tabled to separate the heavy minerals from the nonmineral lights, which are discarded. Chromite and magnetite are separated from the platinum-group metal alloys and minerals by magnetic separation. The final platinum-group metal concentrate is produced from the magnetic-separation product by dry screening and passing the resultant material through a blower to remove the remaining lights.

Quantities of Wastes . Wastes resulting from the mining and milling activities of this operation cannot be considered separately, since the wet mill discharges to the

TABLE V-80. CHEMICAL COMPOSITION AND RAW WASTE LOAD FROM RARE-EARTH MILL 9903

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD †			
		per unit of concentrate		per unit ore milled	
		kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
(a) Flotation Mill					
pH	9.02*	–	–	–	–
TSS	360,000	9,335	18,670	933.5	1,867.0
TOC	3,100	80.4	160.8	8.04	16.08
Cr	0.35	0.009	0.018	0.0009	0.0018
Mn	0.5	0.013	0.026	0.0013	0.0026
V	<0.3	<0.0078	<0.016	<0.0008	<0.0016
Fluoride	365	9.46	18.93	0.95	1.89
(b) Leach/Solvent-Exchange Mill					
pH	8.23*	–	–	–	–
TSS	786	0.833	1.67	–	–
TOC	47	0.047	0.094	–	–
SiO_2	1.25	0.00125	0.00250	–	–
Cr	0.04	0.00004	0.00008	–	–
Mn	3.0	0.003	0.006	–	–
V	<0.3	<0.0003	<0.0006	–	–
Te	3.36	0.003	0.006	–	–
Ni	0.85	0.001	0.002	–	–

* Value in pH units

† Based upon maximum production achievable (part a) or estimated amount of flotation concentrate produced (part b)

dredge pond. No reagents are required in the milling process, and, as a result, the principal waste constituent from this operation is suspended solids (30 mg/l). Table V-81 lists the chemical composition of the waste water and waste loads from mine/mill 9904.

As indicated in Figure V-40, 24,700 cubic meters (6.5 million gallons) per day of water are discharged from the dredge pond to the river. The wet milling process utilizes 49,500 cubic meters (12.96 million gallons) per day.

The principal associated minerals in this placer (mine 9904) are:

Chromite ($FeCr_2O_4$)
Ferroplatinum (Fe, Pt, Ir, Os, Ru, Rh, Pd, Cu, Ni) alloy
Iridium/ruthenium/osmium alloy
Taurite $(Ru, Ir, Os)S_2$
Unnamed mineral (Ir, Rh, Pd)S
Mertieite ($Pt_5(Sb, As)_2$)
Sperrylite ($PtAs_2$)
Gold (Au)

Tin

Tin is recovered in the U.S. as a byproduct of a molybdenum operation. At this mine (6102), the ore is mined by glory-hole methods, in which the sides of an open hole are caved and the broken rock trammed out through a tunnel at the bottom of the hole. No specific waste characteristics and water uses can, therefore, be assigned for this mining milling operation.

Titanium

Process Description - Mining. Titanium minerals are recovered from lode and sand deposits. The single lode deposit being exploited in the U.S. is mined by open-pit methods at mine 9905. Ancient beach-sand placers are mined at several operations by dredging methods. In these operations, a pond is constructed above the ore body, and a dredge is floated on the pond. The dredges currently used normally are equipped with suction head cutters to mine the mineral sands. Wastes from dredge ponds and wet mills are combined; therefore, these operations are discussed under one heading: Dredging Operations.

Quantities of Wastes: Mine 9905. This is the only existing mine from which titanium lode ore is mined. Water is discharged from this open pit at a rate of 2,668 cubic

TABLE V-81. CHEMICAL COMPOSITION AND LOADING FOR PRINCIPAL WASTE CONSTITUENTS RESULTING FROM PLATINUM MINE/MILL 9904 (INDUSTRY DATA)

PARAMETER	CONCENTRATION (mg/ ℓ) WASTEWATER	RAW WASTE LOAD per unit ore milled	
		kg/1000 metric tons	lb/1000 short tons
Alkalinity	83	1.20	2.39
Conductivity	109*	–	–
Hardness	35.6	0.51	1.03
COD	7.6	0.11	0.22
BOD	3.5	0.05	0.10
TS	82	1.18	2.36
TDS	52	0.75	1.50
TSS	30	0.43	0.86
(N) NH_3	0.18	0.003	0.006
Kjeldahl Nitrogen	0.28	0.004	0.008
Al	0.337	0.005	0.010
Cd	< 0.001	< 0.00001	< 0.00002
Cr	< 1.0	< 0.01	< 0.03
Cu	< 1.0	< 0.01	< 0.03
Total Fe	0.166	0.002	0.005
Pb	0.010	0.0001	0.0003
Zn	0.028	0.0004	0.0008
Chloride	11.0	0.16	0.32
Fluoride	0.95	0.01	0.01
Nitrate	4.5	0.06	0.13
Sulfate	5.5	0.08	0.16
Sulfide	1.2	0.02	0.03

*Value in micromhos/cm

TS = Total Solids

TABLE V-82. CHEMICAL COMPOSITION OF RAW WASTEWATER FROM TITANIUM MINE 9905

PARAMETER	CONCENTRATION (mg/ℓ)	PARAMETER	CONCENTRATION (mg/ℓ)
Conductivity	1,000*	Pb	<0.05
Color	11.3†	Mg	26.0
Turbidity (JTU)	0.37	Total Mn	< 0.01
TDS	1,240	Ni	< 0.01
TSS	14	Tl	< 0.1
Acidity	6.4	V	< 0.5
Alkalinity	138.2	K	13.0
Hardness	546.4	Sr	0.129
COD	6.4	Ag	< 0.01
TOC	10.3	Na	140.0
Oil and Grease	3.0	Se	0.75
MBAS Surfactants	0.32	Te	< 0.06
Total Kjeldahl N	2.24	Ti	< 0.2
Al	0.1	Zn	0.007
As	0.1	Mo	< 0.1
Be	0.003	Co	< 0.1
Ba	< 1	Phenol	< 0.01
B	0.01	Chloride	183.5
Cd	< 0.002	Fluoride	3.20
Ca	94.5	Sulfate	270
Cr	< 0.01	Nitrate	15.52
Cu	< 0.03	Phosphate	< 0.05
Total Fe	0.33		

*Value in micromhos/cm

†Value in cobalt units

Figure V-44. BENEFICIATION AND WASTE WATER FLOW OF ILMENITE MINE/MILL 9905 (ROCK DEPOSIT)

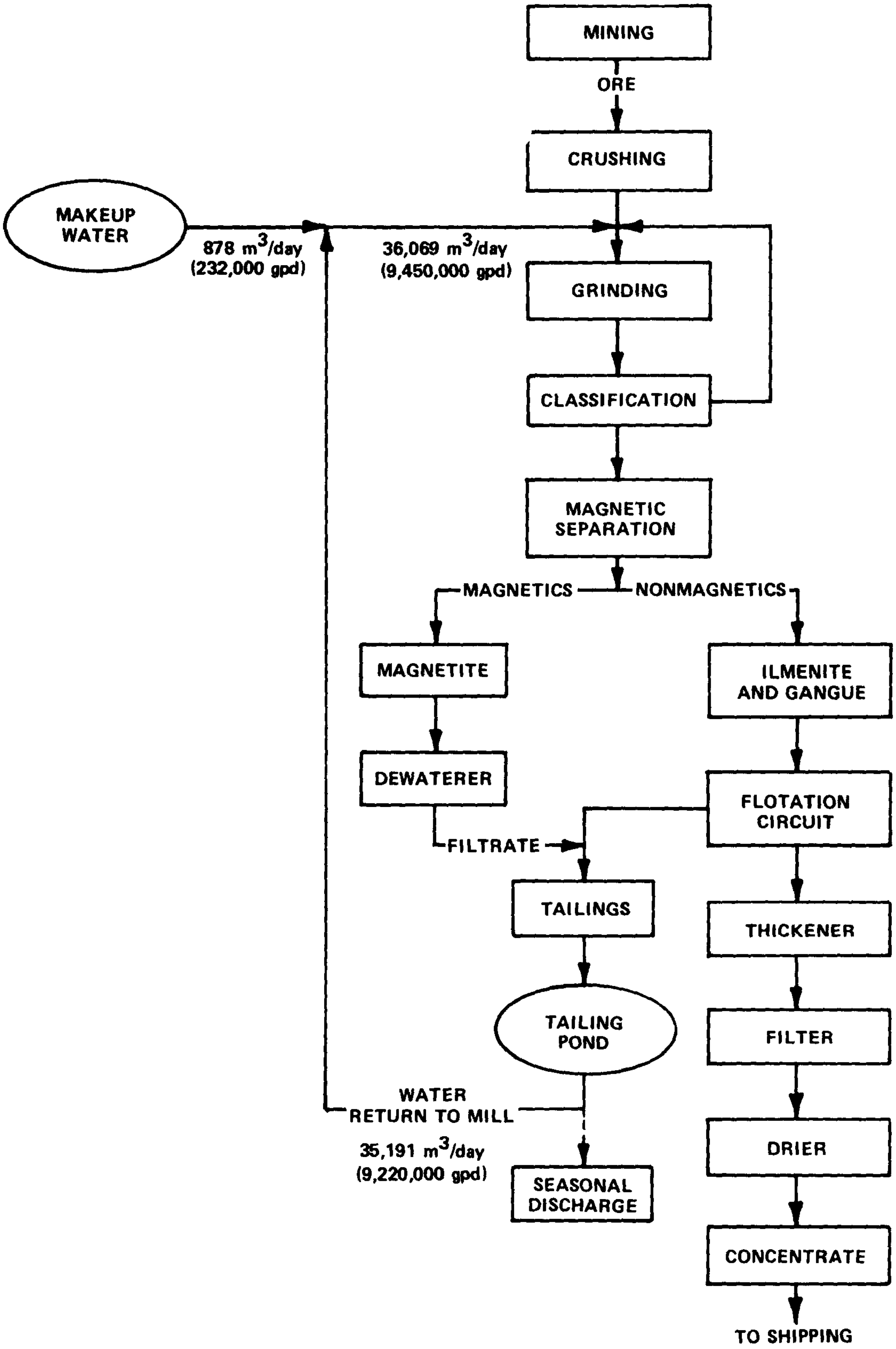


TABLE V-83. CHEMICAL COMPOSITION OF RAW WASTEWATER FROM TITANIUM MILL 9905

PARAMETER	CONCENTRATION (mg/ℓ)	PARAMETER	CONCENTRATION (mg/ℓ)
Conductivity	650*	Pb	< 0.05
Color	18.0†	Mg	187.5
Turbidity (JTU)	2.2	Total Mn	5.9
TDS	518	Ni	1.19
TSS	26,300	Tl	< 0.1
Acidity	6.0	V	2.0
Alkalinity	81.4	K	23.7
Hardness	344.8	Se	0.132
COD	< 1.6	Ag	0.015
TOC	9.0	Na	41
Oil and Grease	2.0	Sr	0.29
MBAS Surfactants	0.04	Te	< 0.06
Total Kjeldahl N	0.65	Ti	2.08
Al	210	Zn	7.6
As	< 0.01	Mo	< 0.1
Be	< 0.002	Co	< 0.1
B	< 0.01	Phenol	< 0.01
Cd	< 0.002	Chloride	19.1
Ca	350	Fluoride	32.5
Cr	0.58	Sulfate	213
Cu	0.43	Nitrate	0.68
Total Fe	500	Phosphate	< 0.05

*Value in micromhos/cm

†Value in cobalt units

TABLE V-84. REAGENT USE IN FLOTATION CIRCUIT OF MILL 9905

REAGENT	PURPOSE	CONSUMPTION	
		kg/metric ton ore milled	lb/short ton ore milled
Tall oil	Frother	1.33	2.66
Fuel oil	Frother	0.90	1.80
Methyl amyl alcohol	Frother	0.008	0.016
Sodium bifluoride	Depressant	0.76	1.52
Sulfuric acid	pH Modifier	1.775	3.55

TABLE V-85. PRINCIPAL MINERALS ASSOCIATED WITH ORE OF MINE 9905

MINERAL	COMPOSITION
Ilmenite	$Fe\,Ti\,O_3$
Magnetite	$Fe_3\,O_4$
Pyroxene	Complex Ferromagnesium Silicate
Feldspar	Aluminum Silicates with Calcium, Sodium, and Potassium

TABLE V-86. MAJOR WASTE CONSTITUENTS AND RAW WASTE LOAD AT MILL 9905

PARAMETER	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD			
		per unit concentrate produced		per unit ore milled	
		kg/metric ton	lb/short ton	kg/metric ton	lb/short ton
TSS	26,300	462.8	925.8	210.4	420.8
TOC	9.0	0.158	0.316	0.072	0.144
Ni	1.19	0.021	0.042	0.01	0.02
Ti	2.08	0.036	0.072	0.017	0.034
Fe	500	8.8	17.6	4.0	8.0
V	2.0	0.035	0.070	0.016	0.032
Cr	0.58	0.010	0.020	0.006	0.01
Mn	5.9	0.103	0.206	0.048	0.096
Se	0.132	0.0002	0.0004	0.001	0.002
Cu	0.43	0.008	0.016	0.0003	0.0006
Zn	7.6	0.133	0.266	0.061	0.122
Fluoride	32.5	0.569	1.14	0.26	0.52

meters (699,000 gallons) per day. The chemical composition of this waste is presented in Table V-82. As these data show, oils and grease (3.0 mg/l), fluorides (3.20 mg/l), total Kjeldahl nitrogen (2.24 mg/l), and nitrates (15.52 mg/l) are present at relatively high concentrations. The oils and greases undoubtably result from the heavy equipment used in the mining operations, and the fluorides are indigenous to the ore body. However, the reason for the high concentrations of nitrogen and nitrates may be explained in part by the use of nitrate-based blasting agents.

Process Description - Titanium Milling: Mill 9905. Ore brought to this mill is beneficiated by a combination of the magnetic-separation and flotation processes (Figure V-44).

The ore is initially crushed and then screened. Both the undersize and the oversize screened ores are magnetically cobbed to remove the nonmagnetic rock, which is discarded. Oversize magnetic rock undergoes further crushing and screening, while undersize material is fed into the grinding circuit. The latter utilizes grinding in rod mills, which are in circuit with "Ty Hukki" classifiers. Final grinding of the undersize material is done in a ball mill.

The magnetite and ilmenite fractions are magnetically separated, with the magnetite further upgraded by additional magnetic processing. The ilmenite sands are then upgraded in a flotation circuit consisting of roughers and three stages of cleaners. The ilmenite concentrate is filtered and dried prior to shipping.

Quantities of Wastes: Mill 9905. Wastes are discharged from this mill at a rate of 35,191 cubic meters (9,220,000 gallons) per day. The results of a chemical analysis of this waste water are presented in Table V-83. These data are based on analysis of raw waste samples collected during the mill visit.

Reagents consumed in the flotation circuit of mill 9905 are identified in Table V-84. The principal associated minerals in the ore body of mine 9905 are listed in Table V-85. These reagents and constituents of the ore body comprise the principal constituents of the waste stream.

As indicated in Table V-84, relatively high levels of iron, titanium, zinc, nickel, vanadium, chromium, and selenium were observed in the wastes of mill 9905. Table V-86 is a compilation of the concentrations of the principal constituents of raw waste water from mill 9905.

Titanium

Dredging Operations: Mill 9906 and 9907. These operations are representative of the operations which recover titanium minerals from beach-sand placers. Operations 9906 and 9907 utilize a dredge, floating on a pond, to feed the sands to a wet mill (Figure V-45). The sands are beneficiated in the wet mill by gravity methods, and the bulk concentrate is sent to a dry mill for separation and upgrading of the heavy minerals. As indicated in Figure V-41, for mill 9906, no discharge exists from the dry mill. Water used in the wet mill is discharged to the dredge pond, which subsequently discharges at a rate of 12,099 cubic meters (3.17 million gallons) per day. Raw waste characterization of the combined wet-mill and dredge-pond discharge is presented in Table V-87. These data are based on analysis of raw waste samples collected during the visits to these operations.

No reagents are used in the beneficiation of the sands, as gravity methods are employed in the wet mill, and magnetic and electrostatic methods are used in the dry mill. Therefore, the principal waste constituents, with the exception of waste lubrication oil from the dredge and wet mill, are influenced primarily by the ore characteristics. The ore bodies of operations 9906 and 9907 contain organic material which, upon disturbance, forms a colloidal slime of high coloring capacity. This organic colloid--primarily, humates and tannic acid--and the wasted oil are the principal waste constituents of the pond discharges. This is reflected in the high carbon oxygen demand (COD) and total organic carbon (TOC) values detected in the waste streams of operations 9906 and 9907 (Table V-87). High levels of phosphate and organic nitrogen are present in these waste streams also. The phosphate and nitrogen are undoubtedly associated with the sediments in the ore body. Raw waste concentrations of principal waste water constituents discharged from the milling operations at mills 9906 and 9907 are given in Table V-88.

Zirconium

Zirconium is recovered as a byproduct of the mining and milling of sand placer deposits, which have been described under Waste Characteristics of Titanium Ores. No operations for zirconium alone are known in the United States. The waste characteristics and water uses accompanying mining and milling to obtain zircon concentrate are, therefore, identical to those of the previously described operations.

Figure V-45. BENEFICIATION OF HEAVY-MINERAL BEACH SANDS (RUTILE, ILMENITE, ZIRCON, AND MONAZITE) AT MILL 9906

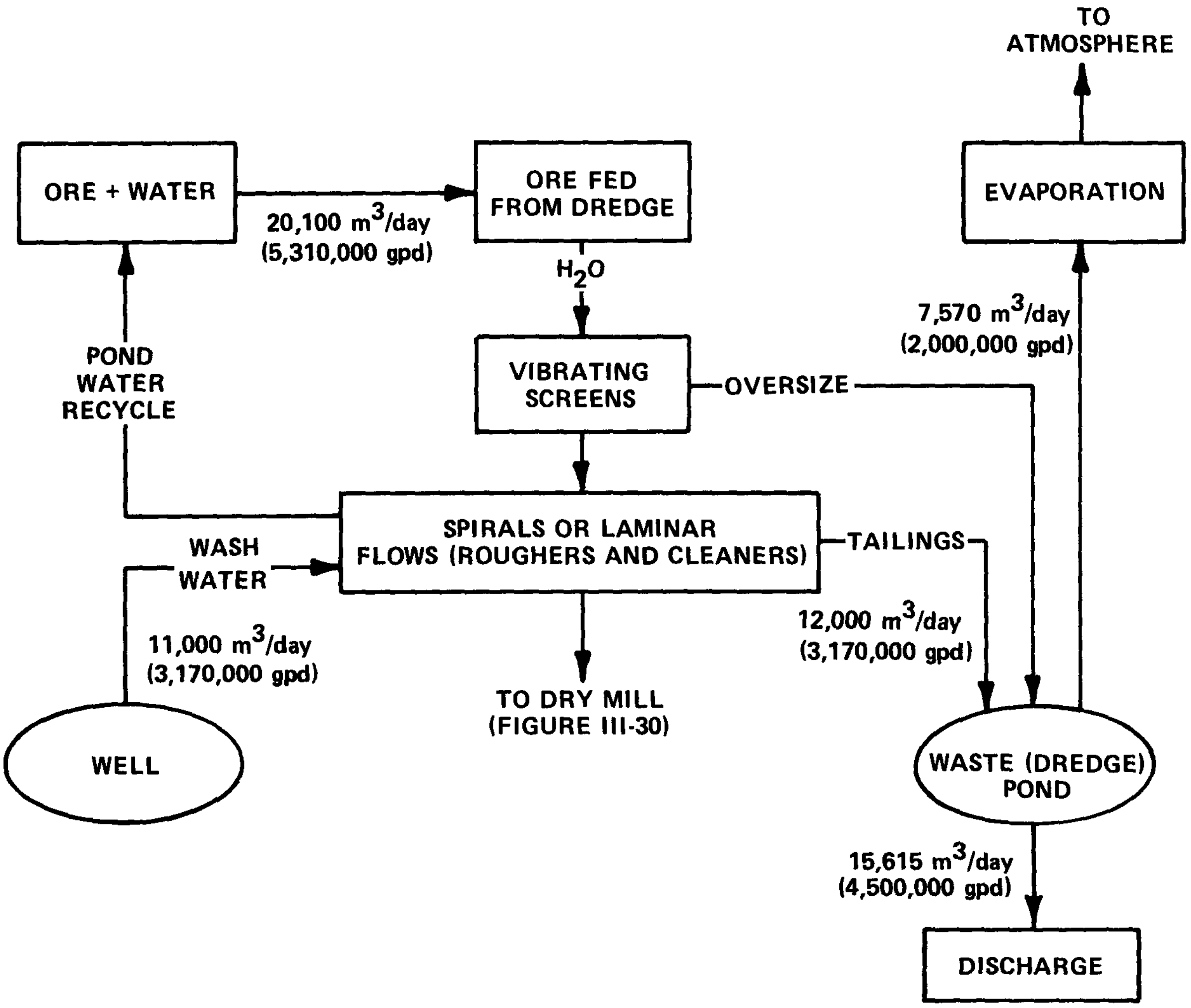


TABLE V-87. CHEMICAL COMPOSITION OF RAW WASTEWATER AT MILLS 9906 AND 9907

PARAMETER	CONCENTRATION (mg/ℓ)	
	MILL 9906	MILL 9907
Conductivity	200*	40*
Color	51,400†	16,240†
Turbidity (JTU)	<0.1	0.54
TDS	1,644	370
TSS	11,000	209
Acidity	47.2	31.4
Alkalinity	47.6	3.4
COD	1,338	362
TOC	972	321
Total Kieldahl N	0.65	0.65
Oil and Grease	400	40.0
MBAS Surfactants	<0.01	<0.01
Al	69.0	15.0
As	0.05	0.03
Be	<0.002	<0.002
Ba	<0.5	<0.5
B	0.10	0.04
Cd	<0.002	<0.002
Ca	0.10	<0.05
Cr	0.03	<0.01
Cu	<0.03	<0.03

PARAMETER	CONCENTRATION (mg/ℓ)	
	MILL 9906	MILL ((07
Total Fe	4.9	0.93
Pb	< 0.05	< 0.05
Mg	1.63	0.66
Total Mn	0.036	0.01
Ni	<0.01	<0.01
Tl	<0.1	<0.1
V	<0.5	<0.5
K	3.5	1.3
Se	< 0.05	< 0.05
Ag	< 0.01	< 0.01
Na	27.0	5.0
Sr	<0.05	<0.05
Te	<0.06	0.15
Ti	<0.2	0.40
Zn	0.014	0.002
Mo	<0.1	<0.1
Co	<0.1	<0.1
Chloride	30.0	15.0
Fluoride	0.03	<0.01
Phosphate	0.35	0.40
Phenol	<0.01	<0.01

*Value in micromhos/cm

†Value in cobalt units

TABLE V-88. RAW WASTE LOADS FOR PRINCIPAL WASTEWATER CONSTITUENTS FROM SAND PLACER MILLS 9906 AND 9907

PARAMETER	MILL 9906			MILL 9907		
	CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD (per unit total concentrate produced)		CONCENTRATION (mg/ℓ) IN WASTEWATER	RAW WASTE LOAD (per unit total concentrate produced)	
		kg/metric ton	lb/short ton		kg/metric ton	lb/short ton
TSS	11,000	330	660	209	5.01	10.02
TOC	972	29.2	58.4	321	7.71	15.42
COD	1,337	40.13	80.26	361.6	8.68	17.36
Oil and Grease	400	12	24	40	0.96	1.92
Ti	< 0.2	< 0.006	< 0.012	0.4	0.01	0.02
Fe	4.9	0.15	0.30	0.93	0.022	0.044
Mn	0.36	0.0011	0.0022	< 0.01	< 0.0024	< 0.0048
Cr	0.03	0.0009	0.0018	< 0.01	< 0.0024	< 0.0048
Phosphate	0.35	0.011	0.022	0.4	0.01	0.02

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

INTRODUCTION

The water-quality investigation which preceded development of recommended effluent guidelines covered a wide range of potential pollutants. After considerable study, a list of tentative control parameters was prepared for each category and subcategory represented in this study. The waste water constituents finally selected as being of pollution significance for the ore mining and dressing industry are based upon (1) those parameters which have been identified as known constituents of the ore-bearing deposits and overburden, (2) chemicals used in processing or extracting the desired metal(s), and (3) parameters which have been identified as present in significant quantities in the untreated waste water from each subcategory of this study. The waste water constituents are further divided into (a) those that have been selected as pollutants of significance (with the rationale for their selection), and (b) those that are not deemed significant (with the rationale for their rejection). This Section is concluded with a summary list of the pollution parameters selected for each category.

GUIDELINE PARAMETER-SELECTION CRITERIA

Selection of parameters for use in developing effluent limitation guidelines was based primarily on the following criteria:

(1) Constituents which are frequently present in mine and mill discharges in concentrations deleterious to human, animal, fish, and aquatic organisms (either directly or indirectly).

(2) The existence of technology for the reduction or removal, at an economically achievable cost, of the pollutants in question.

(3) Research data indicating that excessive concentrations may be capable of disrupting an aquatic ecosystem.

(4) Substances which result in sludge deposits, produce unsightly conditions in streams, or result in undesirable tastes and odors in water supplies.

SIGNIFICANCE AND RATIONALE FOR SELECTION OF POLLUTION PARAMETERS

pH, Acidity, and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis, and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal, and the water is neutral. Lower pH values indicate acidity, while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium, and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH, water tastes "sour." The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul strenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0, and a deviation of 0.1 pH unit from the norm ma result in eye irritation for the swimmer. Appreciab irritation will cause severe pain.

Acid conditions prevalent in the ore mining and dressing industry may result from the oxidation of sulfides in mine waters or discharge from acid-leach milling processes. Alkaline-leach milling processes also contribute waste loading and adversely affect effluent receiving waters.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly, and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes and cause foaming in boilers or encrustation on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems; and power plants. Suspended particles also serve as a transport mechanism for pesticides onto clay particles.

Solids may be suspended in water for a time and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic (and, therefore, decomposable) nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light-scattering and light-absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

High suspended-solid concentrations are contributed as part of the mining process, as well as the crushing, grinding, and other processes commonly used in the milling industry for most milling operations. High suspended-solid concentrations are also characteristic of dredge-mining and gravityseparation operations.

Oil and Grease

Oil and grease exhibit an oxygen demand. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified material ingested by fish may taint the flavor of the fish flesh. Water-soluble components may exert toxic action on fish. Floating oil may reduce the re-aeration of the water surface and, in conjunction with emulsified oil, may interfere with photosynthesis. Water-insoluble components damage the plumage and coats of water animals and fowls. Oil and grease in water can result in the formation of objectionable surface slicks, preventing the full aesthetic enjoyment of the water. Oil spills can damage the surface of boats and can destroy the aesthetic characteristics of beaches and shorelines.

Levels of oil and grease which are toxic to aquatic organisms vary greatly, depending on the type and the species susceptibility. However, it has been reported that crude oil in concentrations as low as 0.3 mg/l is extremely toxic to fresh-water fish. There is evidence that oils may persist and have subtle chronic effects.

This parameter is found in discharges of the ore mining and dressing industry as a result of the contribution from lubricants and spillage of fuels, as well as the usage of reagents in many milling processes.

Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)

The chemical oxygen demand (COD) determination provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. With certain wastes containing toxic substances, this test--or a total organic carbon determination--may be the only method for obtaining the organic load.

Chemical oxygen demand will result in depletion of dissolved oxygen in receiving waters. Dissolved oxygen (DO) is a water-quality constituent that, in appropriate concentrations, is essential, not only to keep organisms living, but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that makes them less competitive and able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish populations through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food efficiency and growth rate, and reduced maximum sustained swimming speed. Fish food organisms are likewise affected adversely in conditions with suppressed DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the total lack of dissolved oxygen due to a high COD can kill all inhabitants of the affected area.

The total organic carbon (TOC) value generally falls below the true concentration of organic contaminants because other constituent elements are excluded. When an empirical relationship can be established between the total organic carbon, the biochemical oxygen demand, and the chemical oxygen demand, the TOC provides a rapid, convenient method of estimating the other parameters that express the degree of organic contamination. Forms of carbon analyzed by this test, among others, are: soluble, nonvolatile organic carbon; insoluble, partially volatile carbon(e.g., oils); and insoluble, particulate carbonaceous materials (e.g., cellulose fibers).

The final usefulness of the two methods is to assess the oxygen-demanding load of organic material on a receiving stream. The widespread use of oil-based compounds, organic acids, or other organic coumpounds in the flotation process, as well as the absence of accurate, reproducible tests which can be routinely performed, points to the use of these tests as indicators of the levels of particular reagent groups which are being discharged.

COD reflects the presence of a variety of materials which may be present in the effluent from ore dressing operations. Many flotation reagents exert a chemical oxygen demand, and the presence of excessive levels of these materials in the effluent stream will be reflected in elevated COD values. Higher COD values are generally observed for flotation effluent streams than for those where flotation is not practiced. In addition, elevated COD values reflect the release of significant quantities of chemicals whose environmental fates and effects are largely unknown.

Cyanide

Cyanides in water derive their toxicity primarily from undissociated hydrogen cyanide (HCN), rather than from the cyanide ion (CN-). HCN dissociates in water into H+ and CN- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10 degrees Celsius (14 degrees Fahrenheit) produces a two- to three-fold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 ppm can have adverse effects. A single dose of about 50 to 60 mg is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as 0.1 part per million can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality--especially, at higher pH values-but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

The presence of cyanide in the effluents of the mining and milling industry is primarily due to the use of cyanide as a depressant in flotation processes and as a leaching reagent-particularly, in the gold and silver ore milling categories.

Ammonia

Ammonia is a common product of the decomposition of organic matter. Dead and decaying animals and plants, along with human and animal body wastes, account for much of the ammonia entering the aquatic ecosystem. Ammonia exists in its nonionized form only at higher pH levels and is the most toxic in this state. The lower the pH, the more ionized ammonia is formed, and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations, including ammonium chloride and other salts.

Nitrates are considered to be among the poisonous ingredients of mineralized waters, with potassium nitrate being more poisonous than sodium nitrate. Excess nitrates cause irritation of the mucous linings of the gastrointestinal tract and the bladder; the symptoms are diarrhea and diuresis, and drinking one liter (1.06 quart) of water containing 500 mg/l of nitrate can cause such symptoms.

Infant methemoglobinemia, a disease characterized by certain specific blood changes, and cyanosis may be caused by high nitrate concentrations in the water used for preparing feeding formulae. While it is still impossible to state precise concentration limits, it has been widely recommended that water containing more than 10 mg/l of nitrate nitrogen (NO_3-N) not be used for infants. Nitrates are also harmful in fermentation processes and can cause disagreeable tastes in beer. In most natural water, the pH range is such that ammonium ions (NH_4^+) predominate. In alkaline waters, however, high concentrations of un-ionized ammonia in undissociated ammonium hydroxide increase the toxicity of ammonia solutions. In streams polluted with sewage, up to one half of the nitrogen in the sewage may be in the form of free ammonia, and sewage may carry up to 35 mg/l of total nitrogen. It has been shown that, at a level of 1.0 mg/l of un-ionized ammonia, the ability of hemoglobin to combine with oxygen is impaired, and fish may suffocate. Evidence indicates that ammonia exerts a considerable toxic effect on all aquatic life within a range of less than 1.0 mg/l to 25 mg/l, depending on the pH and the dissolved oxygen level present. Ammonia can add to the problem of eutrophication by supplying nitrogen through its breakdown products. Some lakes in warmer climates, and others that are aging quickly, are sometimes limited by the nitrogen available. Any increase will speed up the plant growth and the decay process. In leaching operations, ammonia may be used in leaching solutions (as in the 'Dean-Leute' ammonium carbamate process, for precipitation of metal salts, or for pH control. In the ore mining and dressing industry, high levels at selected locations may thus be encountered.

Aluminum

Aluminum is one of the most abundant elements on the face of the earth. It occurs in many rocks and ores, but never as a pure metal. Although some aluminum salts are soluble, aluminum is not likely to occur for long in surface waters because it precipitates and settles or is absorbed as aluminum hydroxide, carbonate, etc. The mean concentration of soluble aluminum is approximately 74 micrograms per liter, with values ranging from 1 to 2,760 micrograms per liter.

Aluminum can be found in all soils, plants, and animal tissues. The human body contains about 50 to 150 mg of aluminum, and aluminum concentrations in fruits and vegetables range up to 37 mg/kg. The total aluminum in the human diet has been estimated at 10 to 100 mg/day; however, very little of the aluminum is absorbed by the alimentary canal. Aluminum is not considered a problem in public water supplies. Note, however, that excessively high doses of aluminum may interfere with phosphorus metabolism. Aluminum present in surface waters can be harmful to aquatic life--particularly, marine aquatic life. Marine organisms tend to concentrate aluminum by a factor of approximately 10,000. Administration of 0.10 mg/l of aluminum nitrate for 1 week proved lethal to sticklebacks. Approximately 5 mg/l of aluminum is lethal to trout when exposed for 5 minutes, but the presence of only 1 mg/l over the same time period produces no harmful effects.

Aluminum is generally a minor constituent of irrigation waters. In addition, most soils are naturally alkaline and, as such, are not subject to the toxic effects of relatively high concentrations of aluminum. Where soils are quite acidic (pH below 5.0), aluminum toxicity to plants becomes very significant. Aluminum presence is primarily observed in waste waters from the bauxite-ore mining industry.

Antimony

Antimony is rarely found pure in nature, its common forms being the sulfide, stibnite (Sb_2S_3) and the oxides cervantite (Sb_2O_4) and valentinite (Sb_2O_3). Any antimony discharged to natural waters has a strong tendency to precipitate and be removed by sedimentation and/or adsorption.

Antimony compounds are toxic to man and are classified as acutely moderate or chronically severe. A dose of 97.2 mg of antimony has reportedly been lethal to an adult. Antimony potassium tartrate, once in use medically to treat certain parasitic diseases, is no longer recommended because of the frequency and severity of toxic reactions, including cardiac disturbances.

Various marine organisms reportedly concentrate antimony to more than 300 times the amount present in the surrounding waters. Few of the salts of antimony have been tested in bioassays; as a result, data on antimony toxicity to aquatic organisms are sketchy. Antimony is commonly found associated with sulfide ores exploited in the silver and lead industry, as well as in operations operated for antimony primary or byproduct recovery.

Arsenic

Arsenic is found to a small extent in nature in the elemental form. It occurs mostly in the form of arsenites of metals or as arsenopyrite ($FeS_2 \cdot FeAs_2$).

Arsenic is normally present in sea water at concentrations of 2 to 3 micrograms per liter and tends to be accumulated by oysters and other shellfish. Concentrations of 100 mg/kg have been reported in certain shellfish. Arsenic is a cumulative poison with long-term chronic effects on both aquatic organisms and mammalian species, and a succession of small doses may add up to a final lethal dose. It is moderately toxic to plants and highly toxic to animals--especially, as arsine (AsH_3).

Arsenic trioxide, which also is exceedingly toxic, was studied in concentrations of 1.96 to 40 mg/l and found to be harmful in that range to fish and other aquatic life. Work by the Washington Department of Fisheries on pink salmon has shown that a level of 5.3 mg/l of As_2O_3 for 8 days is extremely harmful to this species; on mussels, a level of 16 mg/l is lethal in 3 to 16 days.

Severe human poisoning can result from 100-mg concentrations, and 130 mg has proved fatal. Arsenic can accumulate in the body faster than it is excreted and can build to toxic levels, from small amounts taken periodically through lung and intestinal walls from the air, water, and food. Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. Although very low concentrations of arsenates may actually stimulate plant growth, the presence of excessive soluble arsenic in irrigation waters will reduce the yield of crops, the main effect appearing to be the destruction of chlorophyll in the foliage. Plants grown in water containing one mg/l of arsenic trioxides show a blackening of the vascular bundles in the leaves. Beans and cucumbers are very sensitive, while turnips, cereals, and grasses are relatively resistant. Old orchard soils in Washington that contain 4 to 12 mg/kg of arsenic trioxide in the topsoil were found to have become unproductive.

Arsenic is known to be present in many complex metal ores--particularly, the sulfide ores of cobalt, nickel and other ferroalloy ores, antimony, lead, and silver. It may also be solubilized in mining and milling by oxidation of the ore and appear in the effluent stream.

Beryllium

Beryllium is a relatively rare element, found chiefly in the mineral beryl. In the weathering process, beryllium is concentrated in hydrolyzate and, like aluminum, does not go into solution to any appreciable degree. Beryllium is not likely to be found in natural waters in greater than trace amounts because of the relatively insolubility of the oxide and hydroxide at the normal pH range of such waters.

Absorption of beryllium from the alimentary tract is slight, and excretion is fairly rapid. However, as an air pollutant, it is responsible for causing skin and lung diseases of variable severity.

Concentrations of beryllium sulfate complexed with sodium tartrate up to 28.5 mg/l are not toxic to goldfish, minnows, or snails. The 96-hour minimum toxic level of beryllium sulfate for fathead minnows has been found to be 0.2 mg/l in soft water and 11 mg/l in hard water. The corresponding level for beryllium chloride is 0.15 mg/l in soft water and 15 mg/l in hard water.

In nutrient solution, at acid pH values, beryllium is highly toxic to plants. Solutions containing 15 to 20 mg/l of beryllium delay germination and retard the growth of cress and mustard seeds in solution culture. The presence of beryllium in waste waters was detected only in raw-waste effluents from the mining and milling of bertrandite.

Cadmium

Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment, as practiced in the United States, does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 micrograms per day of cadmium.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and (probably) other animals because the metal is not excreted. Cadmium can form organic compounds which may lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms--particularly, mollusks, which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3,000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are, apparently, more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

Cadmium, in general, is less toxic in hard water than in soft water. Even so, the safe levels of cadmium for fathead minnows and bluegills in hard water have been found to be between 0.06 and 0.03 mg/l, and safe levels for coho salmon fry have been reported to be 0.004 to 0.001 mg/l in soft water. Concentrations of 0.0005 mg/l were observed to reduce reproduction of Daphnia magna in one-generation exposure lasting three weeks.

Cadmium is present in minor amounts in the effluents from several ferroalloy-ore and copper mining and milling operations. It is a common constituent in all zinc ores and can be expected to be present in most lead-zinc operations especially those where metals are solubilized.

Chromium

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects--especially, that of hardness. Fish are relatively tolerant of chromium salts, but fish-food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco, and sugar beets have been documented.

Chromium is present at appreciable concentrations in the effluent from mills practicing leaching. It is also present as a minor constituent in many ores, such as those of platinum, ferroalloy metals, lead, and zinc.

Copper

Copper salts occur in natural surface waters only in trace amounts, up to about 0.05 mg/l, so their presence generally is the result of pollution. This is attributable to the corrosive action of the water on copper and brass tubing, to industrial effluents, and--frequently--to the use of copper compounds for the control of undesirable plankton organisms.

Copper is not considered to be a cumulative systemic poison for humans, but it can cause symptoms of gastroenteritis, with nausea and intestinal irritations, at relatively low dosages. The limiting factor in domestic water supplies is taste. Threshold concentrations for taste have been generally reported in the range of 1.0 to 2.0 mg/l of copper, while as much as 5 to 7.5 mg/l makes the water completely unpalatable.

The toxicity of copper to aquatic organisms varies significantly, not only with the species, but also with the physical and chemical characteristics of the water, including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbonate or other insoluble compounds. The sulfates of copper and zinc, and of copper and cadmium, are synergistic in their toxic effect on fish.

Copper concentrations less than 1 mg/l have been reported to be toxic--particularly, in soft water--to many kinds of fish, crustaceans, mollusks, insects, phytoplankton, and zooplankton. Concentrations of copper, for example, are detrimental to some oysters above 0.1 ppm. Oysters cultured in sea water containing 0.13 to 0.5 ppm of copper deposit the metal in their bodies and become unfit as a food substance.

Besides, those used by the copper mining and milling industry, many other ore minerals in the ore mining and dressing industry contain byproduct or minor amounts of copper; therefore, the waste streams from these operations contain copper.

Fluorides

As the most reactive non-metal, fluorine is never found free in nature, but rather occurs as a constituent of fluorite or fluorspar (calcium fluoride) in sedimentary rocks and also as cryolite (sodium aluminum fluoride) in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoridebearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children; for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay--especially, among children.

Chronic fluoride poisoning of livestock has been observed in areas where water contains 10 to 15 mg/l fluoride. Concentrations of 30 to 50 mg/l of fluoride in the total ration of dairy cows are considered the upper safe limit. Fluoride from waters, apparently, does not accumulate in soft tissue to a significant degree, and it is transferred to a very small extent into milk and, to a somewhat greater degree, into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

High fluoride levels in the effluents from mines may result from high levels in intercepted aquifers or from water contact from rock dust and fragments. The use of mine water in milling, as well as extended contact of water with crushed and ground ore, may yield high fluoride levels in mill effluents. Levels may also be elevated by chemical action in leaching operations.

Iron

Iron is one of the most abundant constituents of rocks and soils and, as such, is often found in natural waters. Although many of the ferric and ferrous salts, such as the chlorides, are highly soluble in water, ferrous ions are readily oxidized in natural surface waters to insoluble ferric hydroxides. These precipitates tend to agglomerate, flocculate, and settle or be absorbed in surfaces; hence, the concentration of iron in well-aerated waters is seldom high. Mean concentrations of iron in U.S. waters range from 19 to 173 micrograms per liter, depending on geographic location. When the pH is low, however, appreciable amounts of iron may remain in solution.

Standards for drinking water are not set for health reasons. Indeed, some iron is essential for nutrition, and larger quantities of iron are taken for therapeutic reasons. The drinking-water standards are set for esthetic reasons.

In general, very little iron remains in solution; but, if the water is strongly buffered and a large enough dose is supplied, the addition of a soluble iron salt may lower the pH of the water to a toxic level. In addition, a fish's respiratory channel may become irritated and blocked by depositions of iron hydroxides on the gills. Finally, heavy precipitates of ferric hydroxide may smother fish eggs.

The threshold concentration for lethality to several types of fish has been reported as 0.2 mg/l of iron. Concentrations of 1 to 2 mg/l of iron are indicative of acid pollution and other conditions unfavorable to fish. The upper limit for fish life has been estimated at 50 mg/l. At concentrations of iron above 0.2 mg/l, trouble has been experienced with populations of the iron bacterium Crenothrix.

Iron is very common in natural waters and is derived from common iron minerals in the substrata. The iron may occur in two forms: suspended and dissolved. The iron mining and processing industry inherently increases iron levels present in process or mine waters. The aluminum-ore mining industry also contributes elevated iron levels through mine drainage.

Lead

Lead sulfide and lead oxide are the primary forms of lead found in rocks. Certain lead salts, such as the chloride and the acetate, are highly soluble; however, since the carbonate and hydroxide are insoluble and the sulfide is only slightly soluble, lead is not likely to remain in solution long in natural waters. In the U.S., lead concentrations in surface and ground waters used for domestic supplies average 0.01 mg/l. Some natural waters in proximity to mountain limestone and galena contain as much as 0.4 to 0.8 mg/l of lead in solution.

Lead is highly toxic to human beings and is a cumulative poison. Typical symptoms of advanced lead poisoning are constipation, loss of appetite, anemia, abdominal pain, and gradual paralysis in the muscles. Lead poisoning usually results from the cumulative toxic effects of lead after continuous ingestion over a long period of time, rather than from occasional small doses. The level at which the amount of bodily lead intake exceeds the amount excreted by the body is approximately 0.3 mg/day. A total intake of lead appreciably in excess of 0.6 mg/day may result in the accumulation of a dangerous quantity of lead during a lifetime.

The toxic concentration of lead for aerobic bacteria is reported to be 1.0 mg/l; for flagellates and infusoria, 0.5 mg/l. Inhibition of bacterial decomposition of organic matter occurs at lead concentrations of 0.1 to 0.5 mg/l. Toxic effects of lead on fish include the formation of a coagulated mucus film over the gills--and, eventually, the entire body--which causes the fish to suffocate. Lead toxicity if very dependent on water hardness; in general, lead is much less toxic in hard water. Some data indicate that the median period of survival of rainbow trout in soft water containing dissolved lead is 18 to 24 hours at 1.6 mg/l. The 96-hour minimum toxic level for fathead minnows to lead has been reported as 2.4 mg/l of lead in soft water and 75 mg/l in hard water. Toxic levels for fish can range from 0.1 to 75 mg/l of lead, depending on water hardness, dissolved oxygen concentration, and the type of organism studied. Sticklebacks and minnows have not been visibly harmed when in contact with 0.7 mg/l of lead in soft tap water for 3 weeks. However, the 48-hour minimum toxic level for sticklebacks in water containing 1,000 to 3,000 mg/l of dissolved solids is reported to be 0.34 mg/l of lead. The U.S. Public Health Service Drinking Water Standard specifies a rejection limit of 0.05 ppm (mg/l) for lead.

Elevated concentrations of lead are discharged from lead and zinc mines and mills, as well as from mining and milling operations exploiting other sulfide ores, such as tetrahedrite (for silver and lead); copper ores; ferroalloy ore minerals; or mixed copper, lead, and zinc ores.

Manganese

Pure manganese metal is not naturally found in the earth, but its ores are very common. Similar to iron in its chemical behavior, it occurs in the bivalent and trivalent forms. The nitrates, sulfates, and chlorides are very soluble in water, but the oxides, carbonates, and hydroxides are only sparingly soluble. The background concentration of manganese in most natural waters is less than 20 micrograms per liter.

Manganese is essential for the nutrition of both plants and animals. The toxicological significance of manganese to mammals is considered to be of little consequence, although some cases of manganese poisoning have been reported due to unusually high concentrations. Manganese limits for drinking water have been set for esthetic reasons rather than physiological hazards.

As with most elements, toxicity to aquatic life is dependent on a variety of factors. The lethal concentration of manganese for the stickleback has been given at 40 mg/l. The threshold toxic concentration of manganese for the flatworm Polycelis nigra has been reported to be 700 mg/l when in the form of manganese chloride and 660 mg/l when in the form of manganese nitrate. Trench, carp, and trout tolerate a manganese concentration of 15 mg/l for 7 days; yet, concentrations of manganese above 0.005 mg/l have a toxic effect on some algae.

Manganese in nutrient solutions has been reported to be toxic to many plants, the response being a function of species and nutrient-solution composition. Toxic levels of manganese in solution can vary from 0.5 to 500 mg/l.

On the basis of the literature surveyed, it appears that the concentrations of manganese listed below are deleterious to the stated beneficial uses.

a.	Domestic water supply	0.05 mg/l
b.	Industrial water supply	0.05 mg/l
c.	Irrigation	0.50 mg/l
d.	Stock watering	10.0 mg/l
e.	Fish and aquatic life	1.0 mg/l

Manganese concentrations are found in the effluents of iron-ore, lead, and zinc mining and milling operations and would be expected from any future operations exploiting manganese ores.

Mercury

Elemental mercury occurs as a free metal in certain parts of the world; however, since it is rather inert and insoluble in water, it is not likely to be found in natural waters. Although elemental mercury is insoluble in water, many of the mercuric and mercurous salts, as well as certain organic mercury compounds, are highly soluble in water. Concentrations of mercury in surface waters have usually been found to be much less than 5 micrograms per liter.

The accumulation and retention of mercurial compounds in the nervous system, their effect on developing tissue, and the ease of their transmittal across the placenta make them particularly dangerous to man. Continuous intake of methyl mercury at dosages approaching 0.3 mg Hg per 70 kg (154 lb) of body weight per day will, in time, produce toxic symptoms.

Mercury's cumulative nature also makes it extremely dangerous to aquatic organisms, since they have the ability to absorb significant quantities of mercury directly from the water as well as through the food chain. Methyl mercury is the major toxic form; however, the ability of certain microbes to synthesize methyl mercury from the inorganic forms renders all mercury in waterways potentially dangerous. Fresh-water phytoplankton, macrophytes, and fish are capable of biologically magnifying mercury concentrations from water 1,000 times. A concentration factor of 5,000 from water to pike has been reported, and factors of 10,000 or more have been reported from water to brook trout. The chronic effects of mercury on aquatic organisms are not well-known. The lowest reported levels which have resulted in the death of fish are 0.2 micrograms per liter of mercury, which killed fathead minnows exposed for six weeks. Levels of 0.1 microgram per liter decrease photosynthesis and growth of marine algae and some freshwater phytoplankton.

Mercury has been observed in significant quantities in the waste water in operations associated with sulfide mineralization, including mercury ores, lead and zinc ores, and copper ores, as well as precious-metal operations of gold and silver. It may be liberated in mine waters as well as in effluents of flotation concentration and acid-leaching extraction.

Molybdenum

Molybdenum and its salts are not normally considered serious pollutants, but the metal is biologically active. Although the element occurs in some minerals, it is not widely distributed in nature. The mean level of molybdenum in the U.S. has been reported to be 68 micrograms per liter. The most important water quality aspect of MO is its concentration in plants with irrigation and subsequent possible molybdenosis of ruminants eating the plants.

The 96-hour minimum toxic level of fathead minnows for molybdic anhydride (MoO_3) was found to be 70 mg/l in soft water and 370 mg/l in hard water. The threshold concentration for deleterious effects upon the alga Scenedesmus occurs at 54 mg/l. E. coli and Daphnia tolerate concentrations of 1000 mg/l without perceptible injury. Molybdenum can be concentrated from 8 to 60 times by a variety of marine organisms, including benthic algae, zooplankton, mollusks, crustaceans, and teleosts.

Concentrations of a maximum of 0.05 of the 96-hour minimum toxic level are recommended for protection of the most sensitive species in sea water, while the 24-hour average should not exceed 0.02 of the 96-hour minimum toxic level.

Molybdenum is found in significant quantities in molybdenum mining and in milling of uranium ores, where molybdenum is sometimes recovered as a byproduct.

Nickel

Elemental nickel seldom occurs in nature, but nickel compounds are found in many ores and minerals. As a pure metal, it is not a problem in water pollution because it is not affected by, or soluble in, water. Many nickel salts, however, are highly soluble in water.

Nickel is extremely toxic to citrus plants. It is found in many soils in California, generally in insoluble form, but excessive acidification of such soil may render it soluble, causing severe injury to or the death of plants. Many experiments with plants in solution cultures have shown that nickel at 0.5 to 1.0 mg/l is inhibitory to growth.

Nickel salts can kill fish at very low concentrations. Data for the fathead minnow show death occurring in the range of 5 to 43 mg, depending on the alkalinity of the water.

Nickel is present in coastal and open ocean concentrations in the range of 0.1 to 6.0 micrograms per liter, although the most common values are 2 to 33 micrograms per liter. Marine animals contain up to 400 micrograms per liter, and marine plants contain up to 3,000 micrograms per liter. The lethal limit of nickel to some marine fish has been reported to be as low as 0.8 ppm (mg/l) (800 micrograms per liter). Concentrations of 13.1 mg/l have been reported to cause a 50-percent reduction of photosynthetic activity in the giant kelp (Macrocystis pyrifers) in 96 hours, and a low concentration has been found to kill oyster eggs.

Nickel is found in significant quantities as a constituent of raw waste water in the titanium, rare-earth, mercury, and uranium.

Vanadium

Metallic vanadium does not occur free in nature, but minerals containing vanadium are widespread. Vanadium is found in many soils and occurs in vegetation grown in such soils. Vanadium adversely affects some plants in concentrations as low as 10 mg/l. Vanadium as calcium vanadate can inhibit the growth of chicks and, in combination with selenium, increases mortality in rats. Vanadium appears to inhibit the synthesis of cholesterol and to accelerate its catabolism in rabbits.

Vanadium causes death to occur in fish at low concentrations. The amount needed for lethality depends on the alkalinity of the water and the specific vanadium compound present. The common bluegill can be killed by about 6 mg/l in soft water and 55 mg/l in hard water when the vanadium is expressed as vanadyl sulfate. Other fish are similarly affected.

Limitation and control of vanadium levels appear to be necessary in the effluents from operations employing leaching methods to extract vanadium as a primary product or byproduct. As treated here, it can be expected to be contributed by the ferroalloy industry, where high vanadium levels were observed both in barren solutions from a solvent extraction circuit and in scrubber waters from ore roasting units. High vanadium values are also found associated with uranium operations, where vanadium is also obtained as a byproduct.

Zinc

Occurring abundantly in rocks and ores, zinc is readily refined into a stable pure metal and is used extensively for galvanizing, in alloys, for electrical purposes, in printing plates, for dye manufacture and for dyeing processes, and for many other industrial purposes. Zinc salts are used in paint pigments, cosmetics, pharamaceuticals, dyes, insecticides, and other products too numerous to list herein. Many of these salts (e.g., zinc chloride and zinc sulfate) are highly soluble in water; hence, it is to be expected that zinc might occur in many industrial wastes. On the other hand, some zinc salts (zinc carbonate, zinc oxide, and zinc sulfide) are insoluble in water; consequently, it is to be expected that some zinc will precipitate in and be removed readily from most natural waters.

In zinc-mining areas, zinc has been found in waters in concentrations as high as 50 mg/l; in effluents from metal-plating works and small-arms ammunition plants, it may occur in significant concentrations. In most surface and ground waters, it is present only in trace amounts. There is some evidence that zinc ions are adsorbed strongly and permanently on silt, resulting in inactivation of the zinc.

Concentrations of zinc in excess of 5 mg/l in raw water used for drinking water supplies cause an undesirable taste which persists through conventional treatment. Zinc can have an adverse effect on man and animals at high concentrations. In soft water, concentrations of zinc ranging from 0.01 to 0.1 mg/l have been reported to be lethal to fish. Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills, by damage to the gill epithelium, or possibly by acting as an internal poison. The sensitivity of fish to zinc varies with species, age, and conditions, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of zinc is possible. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so fish relocated from zinc-contaminated water to zinc-free water, after 4 to 6 hours of exposure to zinc, may die 48 hours later. The presence of copper in water may increase the toxicity of zinc to aquatic organisms, but the presence of calcium (hardness) may decrease the relative toxicity.

Observed values for the distribution of zinc in ocean waters very widely. The major concern with zinc compounds in marine water is not one of acute toxicity, but rather of the longterm sublethal effects of the metallic compounds and complexes. From an acute-toxicity point of view, invertebrate marine animals seem to be the most sensitive organisms tested. The growth of the sea urchin, for example, has been retarded by as little as 30 micrograms per liter of zinc.

Zinc sulfate has also been found to be lethal to many plants, and it could impair agricultural uses.

Elevated zinc levels were found at operations for the mining and milling of lead and zinc ores; at copper mines and flotation mills; at gold, silver, titanium, and beryllium operations; and at most ferroalloy-ore mining and milling sites.

Radiation and Radioactivity

Exposure to ionizing radiation at levels substantially above that of general background levels has been identified as harmful to living organisms. Such exposure may cause adverse somatic effects such as cancer and life shortening as well as genetic damage. At environmental levels that may result from releases by industries processing naturally radioactive materials, the existence of such adverse effects has not been definitely confirmed. Nevertheless, it is generally agreed that the prudent public health policy is to assume a non-threshold health effect response to radiation exposure. Furthermore, a linear response curve is generally assumed which enables statistical estimates of risk made from observed effects occurring at higher exposures to be applied at low levels of exposure.

The half-life of the particular radionuclides released to the environment by an industry is extremely important in determining the significance of such releases. Once released to the biosphere, radionuclides with long half-lives can persist for hundreds and thousands of years. This fact coupled with their possible buildup in the environment can lead to their being a source of potential population exposure for many years. Therefore, in order to minimize the potential impact of these radionuclides, they must be excluded from the biosphere as much as possible.

Plants and animals that incorporate radioactivity through the biological cycle can pose a health hazard to man through the food chain. Plants and animals, to be of significance in the cycling of radionuclides in the aquatic environment must assimilate the radionuclide, and retain it. Such processes may lead to bioconcentration of the radioactivity so that the activity per gram of food is greater than the activity per gram of water. Bioconcentration factors as great as several thousand have been observed. Even if an organism is not eaten before it dies, the radionuclides may remain in the biosphere continuing as a potential source of exposure.

Aquatic life may assimilate radionuclides from materials present in the water, sediment, and biota. Humans can assimilate radioactivity through many different pathways. Among them are drinking contaminated water, and eating fish and shellfish that have radionuclides incorporated in them. Where fish or other marine products that may accumulate radioactive materials are used as food by humans, the concentrations of the radionuclides in the water must be restricted to provide assurance that the total intake of radionuclides from all sources will not exceed recommended levels.

Naturally occurring radionuclides, particularly of the uranium-238 and thorium-232 series, can be found in appreciable concentrations in several types of minerals throughout the country. Radium-226, a member of the uranium series, is the radionuclide against which the radiotoxicity of most other bone seeking radionuclides are compared. This is due to the relatively high dose delivered to bones from incorporated radium and the wealth of data on the effects of radium-226 on humans as the result of numerous medical and industrial exposures. However, other radionuclides in the uranium and thorium series may be important, particularly if released into water. These include radium-228, uranium, and lead-210 and its alpha emitting daughter polonium-210. Radium-228, a member of the thorium series, has been designated as a radionuclide for which ingestion should be controlled in proposed drinking water regulations. The isotope lead-210 is of particular interest. Although it is a bone seeker, a small fraction of its daughter polonium-210 is released and distributed to soft tissue, where it concentrates, particularly in the liver and gonads. The levels of radionuclides other than radium-226 and uranium present in process streams and treated effluents are generally not well detailed. Consequently, no other effluent limits are considered at this time. However, because of their potential public health significance, an effluent limitation on radium-228, lead-210 and polonium-210 may be warranted in the future.

Radium-226

Radium-226 is a member of the uranium decay series. It has a half-life of 1620 years. This radionuclide is naturally present in soils throughout the United States in concentrations ranging from 0.15 to 2.8 picocuries per gram. It is also naturally present in ground waters and surface streams in varying concentrations. Radium-226 is present in minerals in the earth's crust. Minerals contain varying concentrations of radium-226 and its decay products depending upon geological methods of deposition and leaching action over the years. If ingested the human body incorporates radium into bone tissue along with calcium. Some plants and animals also concentrate radium so that it can significantly impact the food chain.

As a result of its long half-life, radium-226 which is present in minerals extracted from the earth may persist in the biosphere for many years after its introduction through effluents or wastes. Therefore, because of its radiological consequences, concentrations of this radionuclide need to be restricted to minimize potential exposure to humans.

Flotation Reagents

The toxicity of organic floation agents--particularly, collectors and their decomposition products--is an area of considerable uncertainty, particularly in the complex chemical environment present in a typical flotation-mill discharge. Standard analytical tests for individual organic reagents have not evolved to date. The tests for COD and TOC are the most reliable tests currently available which give indications of the presence of some of the flotation reagents.

Data available on the fates and potential toxicities of many of the reagents indicate that only a broad range of tolerance values is known. Table VI-1 is a list of some of

TABLE VI-I. KNOWN TOXICITY OF SOME COMMON FLOTATION REAGENTS USED IN ORE MINING AND MILLING INDUSTRY

TRADE NAME	CHEMICAL COMPOSITION	FUNCTION	KNOWN TOXIC RANGE (mg/ℓ)	TOXICITY*
Aerofloat 25	Essentially aryl dithiophosphoric acid	Collector/Promoter	-	-
Aerofloat 31	Essentially aryl dithiophosphoric acid	Collector/Promoter	-	-
Aerofloat 238	Sodium di-secondary butyl dithiophosphate	Collector/Promoter	1000 to 10,000	Low
Aerofloat 242	Essentially aryl dithiophosphoric acid	Collector/Promoter	10 to 1000	Moderate
Aerofroth 65	Polyglycol type compound	Frother	1000 to 10,000	Low
Aerofroth 71	Mixture of 6-9 carbon alcohols	Frother	>1000	Low
Aero Promoter 404	Mixture of sulfhydryl type compounds	Collector/Promoter	1 to 100	Moderate
Aero Promoter 3477	Unknown	Collector/Promoter	100 to 1000	Moderate
AROSURF MG-98A	Unknown	Collector/Promoter	-	-
--	Chromium salts (ammonium, potassium, and sodium chromate and ammonium, potassium, and sodium dichromate)	Depressing agent	10 to 1000	Moderate
--	Copper sulfate	Activating agent	0.01 to 1.0	High
--	Cresylic acid	Frother	0.1 to 1.0	High
Dowfroth 250	Polypropylene glycol methyl ethers	Frother	>1000	Low
Dow Z-6	Potassium amyl xanthate	Collector/Promoter	0.1 to 200	Moderate to High
Dow Z-11	Sodium isopropyl xanthate	Collector/Promoter	0.2 to 2.0	High
Dow Z-200	Isopropyl ethylthionocarbamate	Collector/Promoter	10 to 100	Moderate
Jaguar	Based on guar gum	Flocculant	-	-
--	Lime (calcium oxide)	pH modifier and flocculant	10 to 1000	Moderate
M.I.B.C.	Methylisobutylcarbinol	Frother	> 1000	Low
--	Pine oil	Frother	1 to 100	Moderate
--	Potassium ferricyanide	Depressing agent	0.25 to 2.5	Moderate to High
--	Sodium ferrocyanide	Depressing agent	1 to 1000	Moderate
--	Sodium hydroxide	pH modifier	1 to 1000	Moderate
--	Sodium oleate	Frother	1 to 1000	Moderate
--	Sodium silicate	Depressing agent	100 to 1000	Moderate
--	Sodium sulfide	Activating agent	1 to 100	Moderate
--	Sulfuric acid	pH modifier and flocculant	1 to 100	Moderate
Superfloc 16	Polyacrylamide	Flocculant	>1000	Low

*

Toxicity	Tolerance Level
High	<1.0 mg/ℓ
Moderate	1.0 to 1000 mg/ℓ
Low	>1000 mg/ℓ

NOTE: Toxic range is a function of organism tested and water quality, including hardness and pH. Therefore, toxicity data presented in this table are only generally indicative of reagent toxicity. Although the toxicity ranges presented here are based on many different organisms, much of the data are presented in relation to salmon, fathead minnows, sticklebacks, and Daphnia.

the more common flotation reagents and their known toxicities as judged from organism tolerance information.

Asbestos

"Asbestos" is a generic term for a number of fire-resistant hydrated silicates that, when crushed or processed, separate into flexible fibers made up of fibrils noted for their great tensile strength. The asbestos minerals differ in their metallic elemental content, range of fiber diameters, flexibility, hardness, tensile strength, surface properties, and other attributes which may affect their respirability, deposition, retention, translocation, and biologic reactivity.

Asbestos is toxic by inhalation of dust particles, with the tolerance being 5 million particles per cubic foot of air. Prolonged inhalation can cause cancer of the lungs, pleura, and peritoneum. Little is known about the movement of asbestos fibers within the human body, including their potential entry through the gastrointestinal tract. There is evidence that bundles of fibrils may be broken down within the body to individual fibrils. Asbestos has the possibility of being a hazard when waterborne in large concentrations; however, it is insoluble in water.

To date, there is little data on the concentrations of asbestos in ore mining and milling water discharges. Knowledge of the concentrations in water that pose health problems is poorly defined. Currently, this area is being investigated by many researchers concerning themselves with health, movement, and analytical techniques.

Because of public reports concerning the presence of asbestos in waste water from an iron-ore beneficiation operation, a reconaissance analysis for asbestos was performed on samples collected as part of site visits to four discharging iron-ore beneficiation operations. The raw waste water and effluent of tailing ponds at each facility were examined for the presence or absence of asbestos or asbestos-like fibers. The method of analysis used for detection was one based upon published literature and employed scanning electron microscopy.

Fibers were not detected in any of the samples with the exception of the influent to the tailing pond from Mill 1107. Energy-dispersive x-ray analysis indicated, however, that the fiber was not of an asbestos type. Both raw and treated waste waters from mills 1107, 1108, 1109, and 1110 were examined, and no asbestos or asbestos-like minerals were found.

While the results of the survey indicate the absence of asbestos fibers at each of the sites investigated, the presence or absence of asbestos at other locations in the iron-ore mining and beneficiation industry cannot be confirmed. It does not appear possible to recommend effluent levels or treatment technology at this time. It is recommended, however, that a reconaissance evaluation for asbestos be performed at each iron-ore mining and beneficiation operation to determine whether possible asbestos levels of concern are present.

SIGNIFICANCE AND RATIONALE FOR REJECTION OF POLLUTION PARAMETERS

A number of pollution parameters besides those selected and just discussed were considered in each category but were rejected for one or more of these reasons:

(1) Simultaneous reduction is achieved with another parameter which is limited.

(2) Treatment does not "practically" or economically reduce the parameter.

(3) The parameter was not usually observed in quantities sufficient to cause water-quality degradation.

(4) There are insufficient data on water-quality degradation or treatment methods which might be employed.

Because of the great diversity of the ores mined and the processes employed in the ore mining and dressing industry, selections for subcategories of the parameters to be monitored and controlled--as well as those rejected--vary considerably. Parameters listed in this section are parameters which have been rejected for the ore mining and dressing industry as a whole.

Barium and Boron

Barium and boron are not present in quantities sufficient to justify consideration as harmful pollutants.

Calcium, Magnesium, Potassium, Strontium, and Sodium

Although these metals commonly occur in effluents associated with ore mining and dressing activities, they are not present in quantities sufficient to cause water-quality degradation, or there are no practical treatment methods which can be employed on a large scale to control these elements.

Carbonate

There are insufficient data for dissolved carbonate to justify consideration of this ion as a harmful pollutant.

Nitrate and Nitrite

There are insufficient data for dissolved nitrates and nitrites to justify their consideration as harmful pollutants, although nitrogen and nitrate contributions are known to stimulate plant and algal growth. There is no treatment available to practically reduce these ions.

Selenium

The levels of selenium observed in the waste waters from mines and mills are not sufficiently high for selenium to be considered as a harmful pollutant.

Silicates

Silicates may be present in the waste waters from the ore mining and dressing industry, but the levels encountered are not sufficiently high to warrant classification as a harmful pollutant.

Tin

Tin does not exist in sufficient quantities from mines or mills to be considered a harmful pollutant.

Zirconium

There is no information available which indicates that significant levels of zirconium are present in the industry to be classed as harmful.

Total Dissolved Solids

High dissolved-solid concentrations are often caused by acid conditions or by the presence of easily dissolved minerals in the ore. Since economic methods of dissolved-solid reduction do not exist, effluent limitations have not been proposed for this parameter.

SUMMARY OF POLLUTION PARAMETERS SELECTED BY CATEGORY

Because of the wide variations observed with respect to both waste components discharged and loading factors in the different segments of the ore mining and dressing industry, a single, unified list of all parameters selected for the industry as a whole would not be useful. Therefore, Table VI-2 summarizes the parameters chosen for effluent limitation guidelines for each industry metal category.

TABLE VI-2. SUMMARY OF PARAMETERS SELECTED FOR EFFLUENT LIMITATION BY METAL CATEGORY

PARAMETERS	PARAMETERS SELECTED FOR EFFLUENT LIMITATIONS															
										Metal Ores, Not Elsewhere Classified						
	Iron Ore	Copper Ores	Lead and Zinc Ores	Gold Ores	Silver Ores	Bauxite (Al) Ores	Ferroalloy Ores	Mercury Ores	Uranium, Radium, and Vanadium Ores	Antimony Ores	Beryllium Ores	Platinum Ores	Tin Ores	Titanium Ores	Rare-Earth Ores	Zirconium Ores
pH (Acidity/Alkalinity)	●	●	●	●	●	●	●	●	●	●	No separate limitations; zero discharge	●	No separate limitations; tin recovered only as byproduct with molybdenum (ferroalloy ores)	●	No separate limitations; zero discharge	No separate limitations, zirconium recovered only as byproduct with titanium.
Total Suspended Solids (TSS)	●	●	●	●	●	●	●	●	●	●		●		●		
Chemical Oxygen Demand (COD)							●		●					●		
Cyanide		●	●	●	●		●									
Ammonia							●									
Aluminum						●										
Antimony										●						
Arsenic							●		●	●						
Cadmium		●	●	●	●		●		●							
Chromium							●									
Copper		●	●	●	●		●									
Iron	●					●				●				●		
Lead		●	●	●	●		●									
Mercury		●	●	●	●			●								
Molybdenum							●		●							
Nickel								●						●		
Vanadium									●							
Zinc		●	●	●	●	●	●		●	●				●		
Radium									●							
Uranium									●							

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