Generic Scenario: Water Treatment Disinfectants - Application

Industry Description

Approximately 325 billion gallons of water are used daily in the United States. Depending on its use, most water must be treated, including water used by industry, municipalities, and power-generating utilities. Pollutants in the water that may impede its use or discharge into surface waters are treated by physical, chemical, and biological methods. The market for water treatment chemicals in the United States totaled $2.3 billion in 1988 and was estimated to grow to $3.2 billion by 1993 (Taylor, 1990). This overall market equates roughly to 12.9 billion pounds of water treatment chemicals sold in 1988 (Taylor, 1990). Of the total volume of chemicals used in 1988,

- 54% was used to treat municipal, utility, and institutional water.
- 34% was used to treat industrial water, including that used in manufacturing, processing, and refining.
- 12% was used by residential and commercial markets (Taylor, 1990).

About 59,000 public water treatment plants exist in the United States (AWWA, in press). Among them, 612 systems serve 50,000 people or more, 2400 systems serve 10,000 to 50,000 people, and 56,000 serve fewer than 10,000 people. Assuming 180 gal per capita (Achtermann, 1992), average throughputs can be calculated. In addition to public water treatment plants, a total of 15,438 wastewater treatment plants were in operation in 1986. It is estimated that 17,000 wastewater plants will be in existence by the year 2005 (National Council, 1987). About 70% of the population is served by these facilities along with 160,000 industries and an unknown number of commercial establishments. Of these plants, 32% have flowrates in the range of 0.01 to 10 million gallons per day (MGD), 45% in 0.11 to 1.00 MGD, 19% in 1.01 to 10.00 MGD, and 4% greater than 10.00 MGD (National Council, 1987).

Market

All potable water and wastewater treatment plants employ some type of disinfection process. In 1988, disinfectants accounted for 31.5% ($733 million dollars) of the market value for water treatment chemicals. In 1988, 2186 million pounds of disinfectants were used. It is projected that the annual rate of consumption will grow to 2675 lb by the year 2000 (Taylor, 1990). Table 1 displays the types of disinfectants that are in use and the percent of utilities that use them (WQDDC, 1992).

Chlorine Compounds

Chlorine is the most common type of disinfectant because it is inexpensive and is very effective. However, because it reacts with organic matter in the water to produce suspected carcinogenic trihalomethanes (THM), it is slowly being replaced by other types of disinfectants. Chlorine usually is shipped as a compressed liquid. The manufacturer generally ships the chlorine, in bulk form (tank car or tank truck), to a packager. The packager transfers the chlorine to tank cars or cylinders for shipment to the treatment facility. The type of container used depends on the quantity of material needed as well as the design of the treatment facility. Chlorine gas can be fed to the process by withdrawing the gas from the top of the container. Evaporators are necessary if the chlorine needs to be withdrawn at a high flowrate. In this instance, liquid chlorine is withdrawn from the bottom of the container and passed into the evaporator where it is converted into a gas. After evaporation, the gas passes into a chlorinator where it is converted to a constant pressure stream. The stream is then piped to the point of application (ASCE, 1990).

Sodium hypochlorite occasionally is used at smaller treatment facilities as a replacement for chlorine. It is available only in liquid form containing 12 to 16% available chlorine (ASCE, 1990). The concentrated solution is added to a mix tank along with a certain quantity of dilution water. The tank generally is automated so that a constant level of slurry is maintained. The resulting solution is then decanted or pumped to the point of application.

Table 1. Comparison of Disinfectant Chemicals Utilized by Treatment Facilities

Chemicals Used	Percent of Utilities
Chlorine Gas (Cl_2)	67
Cl_2 + Ammonia	20
Cl_2 + Chlorine Dioxide	3.0
Cl_2 + Hypochlorite	4.5
Cl_2 + Chlorine Dioxide + Ammonia	1.5
Hypochlorite	1.5
Cl_2 + Hypochlorite + Ammonia	0.75
Cl_2 + Chlorine Dioxide + Hypochlorite	0.37
Ozone	0.37
Other	0.75

Ammonia Compounds

Anhydrous ammonia, aqueous ammonia, or ammonium sulfate sometimes is added before, during, or after chlorination to produce chloramines. Chloramines offer the advantages of longer residual life, reduced amount of THM formed, and, in most cases, a milder taste and odor compared to free chlorine residuals. Anhydrous and aqueous ammonia are most commonly used. Anhydrous ammonia usually is received as a compressed liquid by cylinder, tank car, or tank truck. It is applied in a similar fashion to chlorine. Aqueous ammonia is commonly received in concentrations of 33% by weight. It is generally fed through a diaphragm metering pump to the point of application. Ammonium sulfate is either volumetrically or gravimetrically fed to a mixing tank where it is diluted to the desired concentration. It is then pumped to the point of application. It has been recommended that a 1 to 3 ratio of ammonia to chlorine be used (ASCE, 1990).

On-Site Production of Disinfectants

Both chlorine dioxide and ozone are manufactured on site. The production of chlorine dioxide involves reacting the raw materials, generally chlorine solution and sodium chlorite, in a ceramic glass-packed column. The chlorine dioxide mixes with water and is transferred to a diffuser. Due to its instability in water, chlorine dioxide is produced prior to the point of application (ASCE, 1990).

Ozone is produced in an ozone generator. An oxygen-containing feed gas (under pressure) is passed through two discharging electrodes. The resulting ozone is piped into a gas diffuser. The ozone then enters the contactor where it diffuses through the water. Figure 1 illustrates a typical contacting system (adapted from Rice et al., 1986). Contactors can be used in series to accommodate large quantities of water. Various methods exist for eliminating the off-gas emitted from the contactors. These include reinjection, heating to cause autodecomposition, chemical reduction, and dilution (ASCE, 1990).

Disinfectant Interactions

For most treatment applications, it is necessary to maintain a residual concentration of the PMN disinfectant in the water. The purpose of the residual is to maintain a presence of the disinfectant to prevent the growth of

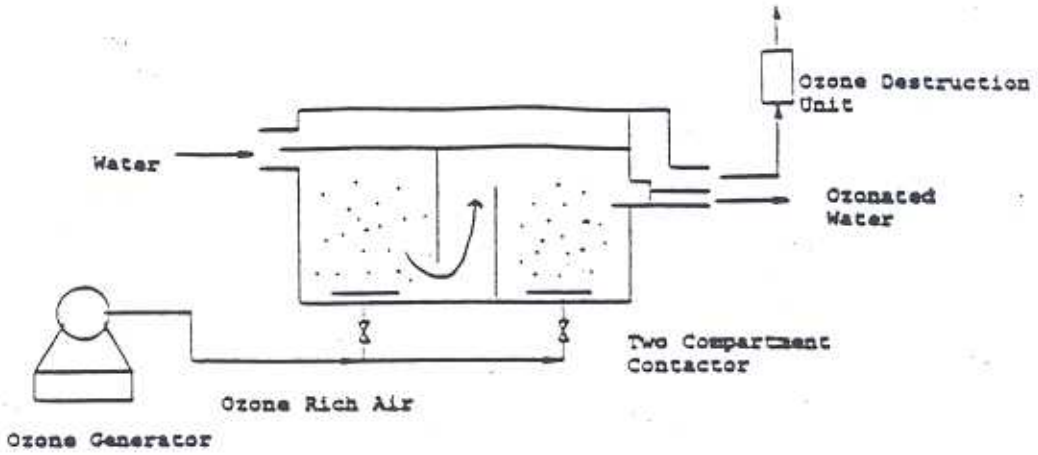

Figure 1. Two-Compartment Ozone Contacting System

algae, bacteria, and viruses up to the point of consumer use. Chlorine, chlorine dioxide, and sodium hypochlorite produce free residuals in the water. However, ammonia compounds and ozone do not. These chemicals must be used in conjunction with other disinfectants to provide the desired residual. The ammonia compounds are used in conjunction with chlorine gas to produce combined residuals. Combined residuals are useful for destroying various algae and bacteria aftergrowth as well as for maintaining a stable residual to the point of consumer use (ASCE, 1990). Ozone generally is used in conjunction with chlorination. Ozone may be used for the initial disinfection, followed by a chlorine treatment to provide the desired residual. If a PMN chemical produces a stable residual, it may be possible to use it alone for disinfection. However, it is more likely that the PMN chemical will not provide the residuals necessary, and therefore, will need to be used in conjunction with other disinfectants.

Chemical Dosage

Table 2 illustrates typical dosage rates for various disinfectants (Keifer et al., 1983). The dosage rate is the amount of disinfectant that is placed into the treatment process. The dosage rate varies depending on the biological demand of the water. Note that, for both solids and liquids, 1 ppm is equivalent to 8.34 lb per 1,000,000 gallons of water.

Table 2. Typical Disinfectant Concentrations for Water Treatment

Disinfectant	Typical Dosage
Chloramine	1-10 ppm
Chlorine	1-10 ppm
Chlorine Dioxide	0.2-2.0 mg/L
Ozone	1-1.5 ppm
Sodium Hypochlorite	1-10 ppm

Worker Exposure

Estimates of treatment facility staff requirements can be made for each type of facility. Water treatment facilities, operating 24 hours a day and treating fewer than 10 MGD, will have an average of 9 staff members, 4 of whom would be operators. A plant operating in the range of 20 to 50 MGD will have an average staff of 40 people, 14 of whom would be operators (Montgomery, 1985). The number of staff in a wastewater treatment plant can be assumed to be 2 people for every 1 MGD of wastewater treated. This number assumes that the treatment facilities utilize secondary as well as primary treatment (White, 1991). Worker exposure is most likely to occur during handling of the chemicals. At small facilities, exposure will be from opening the drums and bags containing the chemicals and feeding the chemicals into the process. At large facilities, workers will be exposed primarily during manipulation of the transfer lines between storage tanks and the treatment process (Keifer et al., 1983).

Waste Generation, Environmental Releases, and Exposure-Level Calculations

PMN materials may be used to disinfect water as either additives or substitutes to current disinfecting agents. The PMN materials may be in the form of gases, liquids, or solids (powders, granules, etc.).

Variables

- %PMN: weight percent of PMN material in the disinfectant.
  Table 3 lists the percent PMN for disinfectants commonly used (Keifer et al., 1983).
- D: amount of disinfectant used at the water treatment plant (kg/site/day).
  See Table 2 for typical dosages.
- F: average throughput (MGD) for treatment facility.
  Refer to previous discussion for typical values.
- S: solubility of PMN (mg/L)

Table 3. %PMN for Commonly Used Disinfectants

Chemical Name	Form	%PMN
Ammonia	Gas	99-100% NH_3
Calcium Hypochlorite	Dry	65% available Cl_2
Chlorine	Gas	99.8% available Cl_2
Ozone	Gas	1-2% O_3
Sodium Hypochlorite	Liquid	12-15% available Cl_2

Environmental Releases (total kg/site/day)

Solid Wastes: The PMN material will react with organic matter present to produce chlorinated and oxygenated compounds. Any unreacted material will remain dissolved in the water as a residual or it may volatilize. As a result, there will be no PMN material released as a solid waste.

Air Emissions: Air emissions of the PMN material used in water disinfection will depend on whether the product is initially in a solid, liquid, or gaseous form.

Release to the air of powders can be expected to occur, particularly at smaller facilities that use manual loading of product addition hoppers. At larger facilities, airtight storage facilities and automated feed systems may reduce the releases to the air of PMN powders and disinfectants. Typically, the handling and mixing of powders in manufacturing applications leads to air emissions on the order of 0.1 to 1 wt% of bulk powder usage (U.S. EPA, 1985). Assuming the absence of particulate emission controls at the typical disinfectant plant, air emissions of powder-based PMN material can be estimated as:

$$D * (0.1-1)\%/100 * \%PMN/100 = kg/site/day \quad (1)$$

Improved estimates of the air emissions of powder-based PMN materials can be obtained through measurements of the bulk powder concentrations in the air or by comparisons with analogous powder product concentrations in similar operations.

Air emissions from bead (in contrast to powder) formulations of chemical products used in water disinfection are expected to be negligible, unless components of the formulation are volatile. In general, air emissions of a PMN material contained in a bead formulation can be assumed to be minimal.

If the PMN disinfectant additive or substitute is a gas or liquid, air releases may occur either from leaks in the gas transport system (valves, flanges, etc.) or from the disinfected water itself during treatment or transport. In these situations, air emissions will depend on the solubility, volatility, and reactivity of the chemical. If a worst case scenario is assumed, then the air emissions of the PMN material will be:

$$(\%\ PMN/100 * D\ [kg/day] / F\ [MGD]) - (S\ [mg/L] * 3.785\ [kg/MG/mg/L]) = kg/10^6\ gal \quad (2)$$

As a worst-case scenario, Equation 2 assumes that the PMN in excess of the solubility is released into the air. However, in actual practice, much of the PMN may be consumed through reaction with matter present in the water.

Water: The PMN material added to water will either react out, volatilize, or solubilize remaining as a residual. Residual concentrations of currently used disinfectants are strictly regulated by local authorities. Generally, a 0.2- to 0.3-ppm free chlorine residual in the effluent is sufficient for satisfactory disinfection.

Worker Exposure

Worker exposure to the PMN disinfectant additive or substitute is most likely to occur from handling and transfer operations at the water treatment facility. In addition, exposure of workers to gas-phase PMNs released to the air during treatment operations also is possible. The potential routes of exposure are through inhalation of gaseous PMNs, powders of solid PMNs, and vapors of volatile PMNs, as well as from dermal exposure to PMNs during transfer and handling of solid or liquid PMN materials. Refer to previous discussion for typical numbers,

Inhalation (mg/day): Assuming that water treatment/disinfection operations are medium-duty work in terms of the level of physical activity required, an inhalation rate of 1.25 m^3/hr will be assumed (CEB, 1991).

Gaseous PMN additive/substitute: Inhalation exposure to gaseous PMN concentrations in the workplace arising due to leakage of PMN from the transfer system or due to release from the treated water can be estimated as:

$$C_g(mg/m^3) * 1.25\ m^3/hr * H/100 = ??\ mg/day \quad (3)$$

where C_g is the typical or average concentration of the gaseous PMN in the air in the facility, and H is the number of hours per day that a worker is exposed to the workplace air containing the gaseous PMN.

Liquid PMNs: Inhalation of liquid PMNs could result from the transfer operations required to prepare and handle the fluids. Inhalation exposure to a liquid PMN will depend on whether the PMN material is sufficiently volatile to be present in the air as a result of transfer and handling operations.

Nonvolatile PMN materials are assumed to result in minimal inhalation exposure to PMN materials during transfer operations.

For a volatile PMN material with a vapor pressure at ambient temperature of P (torr or mmHg), molecular weight (MW), the following relation can be used to estimate the concentration of PMN material resulting from transfer operations (CEB, 1991):

$$C_{PMN}(mg/m^3) = 95\ P * MW/MV, \text{ where } MV = 24.5\ L/mole\ (25°C,\ 1\ atm) \quad (4)$$

for the worst-case scenario involving transfer operations from 55-gal drums.

If there are FT number of transfer operations per day (number/day), and H_t is the number of hours per day that each worker is involved in each of these transfer operations, then the inhalation exposure to the volatile liquid PMN material is:

$$C_{PMN}\ (mg/m^3) * 1.25\ m^3/hr * FT\ (transfers/day) * H_t\ (hours/transfer) = ??\ mg/day \quad (5)$$

Solid PMNs: Air concentrations of powder-based PMNs can be expected in the workplace due to transfer and handling operations. If the disinfectant dust can be classified as an inert or nuisance dust [overall Occupational Safety and Health Administration (OSHA) Permissible Exposure Level (PEL) = 15 mg/m^3; OSHA PEL for the respirable powder fraction = 5 mg/m^3], and H is the number of hours that a worker is exposed to the dust atmosphere (typically 8 hours), the inhalation exposure of a worker during an operating day to powder-based PMN material is:

$$15\ mg/m^3 * 1.25\ m^3/hr * H * \%PMN / 100 = ??\ mg/day \quad (6)$$

This calculation assumes a worst-case scenario and, therefore, uses the PEL of 15 mg/m^3. Also, this calculation assumes that the disinfectant and the PMN material are inert and can be classified as nuisance dusts. In some cases, however, this assumption may not be applicable. Also, if the components of the disinfectant are mixed in an enclosed volume, such as a jet mixer, and the workers are protected by dust masks or respirators, the actual inhalation exposure to PMN in the dusts will be lower than that estimated above.

Dermal Exposure (mg/day): Dermal exposure can result from the dusts arising during the handling of solid (powder) PMN material in preparing the disinfectant, as well as from the transfer and handling of liquid or powder PMN materials. In each of these cases, dermal exposure can be expected to arise from either intermittent or routine contact with the chemical product containing the PMN material. Dermal exposure from airborne dusts likely will be small compared to the dermal exposure from handling and transfer operations.

Assuming that the unloading of drums containing the liquid PMN or of bags/containers containing PMN powders, flakes, or granules occurs with a frequency, FT (number/day), and using estimates of the typical dermal exposure from these types of routine contact operations (CEB, 1991, Table 4-13), the dermal exposure to PMN material is:

$$(6{,}500–18{,}200)\ mg/day * \%PMN/100 = ??\ mg/day \text{ for powder PMN} \quad (7)$$

and $$(1{,}300–3{,}900)\ mg/day * \%PMN/100 = ??\ mg/day \text{ for liquid PMN} \quad (8)$$

where %PMN is the weight percent of solid or liquid PMN material in the disinfectant being prepared. Note that these estimates for dermal exposure are worst-case estimates and the actual dermal exposures would be lower if protective equipment such as gloves, eyewear, etc. were worn by the workers.

Disposal Concerns

The containers used to transport the PMN materials to the facility are assumed to be recycled, cleaned to remove contamination, and appropriately landfilled or incinerated. Solid wastes containing the PMN material, such as sludge, are assumed to be disposed of using appropriate mechanisms.

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