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Generic Scenario: Application of Chemicals in Enhanced Oil Recovery Steam Stimulation, Steam Flooding, and Polymer/Surfactant Flooding

Background

The petroleum industry has adopted the use of enhanced oil recovery as a way of extending the life of current oil reserves. Enhanced oil recovery research began in the 1920's during the first petroleum shortage in the United States. The first methods that were developed employed waterflooding; however, even at that time chemicals often were used in conjunction with water. Today, polymer/surfactant flooding is one of the most efficient and expensive methods of enhanced oil recovery. However, steam stimulation and flooding also show promise and are more economical than polymer/surfactant flooding. In 1991 alone, 93 new chemicals were being marketed for enhanced oil recovery processes (Petroleum Engineer International, 1991).

Enhanced oil recovery currently accounts for 10% of domestically produced oil (Moritis, 1992) with approximately 761,000 barrels per day produced. Polymer/surfactant flooding accounts for only 0.3% of the total production, whereas steam stimulation and flooding account for 64% of the total enhanced oil recovery production. Overall, 117 active enhanced oil recovery sites (i.e. areas where recovery wells are in use) in the United States utilize steam stimulation and 26 active sites utilize some form of polymer flooding. No known active sites utilized surfactant flooding exclusively as of April, 1992 (Moritis, 1992). Use of steam for enhanced oil recovery increased between 1980 and 1986; however, since 1986, the number of active sites using steam stimulation for enhanced oil recovery has leveled off (Moritis, 1992). The use of polymer/surfactant flooding has been decreasing since 1984, possibly due to the expense involved with that particular process (Moritis, 1992).

Production Process

In general, two factors affect the amount of oil recovery possible: the oil displacement efficiency and the volumetric sweep efficiency. The oil displacement efficiency is related to the ability of an injected fluid to displace the oil it contacts in the reservoir. The volumetric sweep efficiency is defined as the relative amount of reservoir invaded by the injected fluid. In general, chemicals are used in enhanced oil recovery either to improve the oil displacement efficiency or to improve the volumetric sweep efficiency (Borchardt, 1989).

High-permeability streaks or layers known as *thief zones*, or natural or induced rock fractures can channel the injected fluid through a small portion of the reservoir resulting in a low-volumetric sweep efficiency. Four types of chemicals are used to seal the thief zones and fractures in order to direct the injected fluid to other areas of the reservoir:

- crosslinked polymers (1,000 to 5,000 ppm polyacrylamides or xanthan gums)
- reactive monomers (2 to 5 wt% acrylamides)
- lignosulfates (2 to 3 wt%)
- surfactants through precipitation.

Crosslinked polymers are the most commonly used compounds with partially hydrolyzed polyacrylamides and some xanthan gums. They usually are injected at concentrations of 1000 to 5000 ppm and crosslinked in situ. The most commonly used crosslinkers are Al(III) as aluminum citrate and sodium aluminate and Cr(III) compounds, although organic compounds such as glyoxal and formaldehyde have been used. Chromium compounds are often injected as Cr(VI), then oxidized in situ to Cr(III).

Steam stimulation and flooding are used to reduce the viscosity of the oil, making it easier to extract the oil from the reservoir because of the increased mobility of the oil. The two methods differ in that steam stimulation involves steam injection followed by a waiting period before pumping begins, whereas steam flooding involves continuous steam injection. Surfactants and/or polymers often are used in conjunction with steam to control the

mobility of the steam or to plug thief zones. For example, gravity override is the migration of steam to the upper portion of the formation and is caused by low steam density. This results in channeling of the steam through the upper portion of the reservoir and a low-volumetric sweep efficiency. Surfactants are used in conjunction with steam to control gravity override and thus increase the volumetric sweep efficiency.

Chemicals Used

Polymers, such as polyacrylamides and xanthan gums, and surfactants are also used to control mobility. Concentrations of these polymers as low as 100 ppm may be used to achieve the desired results. These concentrations are much lower than when the polymer is used to seal thief zones; therefore, the purpose for using the polymer must be known. Surfactants also require lower concentrations when used to control mobility, with concentrations as low as 0.1 wt% being effective.

Surfactants can be classified generally as anionic and nonionic. Anionic surfactants typically contain linear alkylbenzene sulfonates (ABS), alpha olefinsulfonates (AOS), and occasionally lignosulfonates (never a primary constituent). Nonionic surfactants include alcohol ethoxylates and alkyl phenol ethoxylates. Alkyl sulfates and ethoxylated alcohol sulfates often are used as cosurfactants.

In general, the polymers or surfactants are received in 55-gallon steel drums. The polymers may be provided in a fine powder; in microbeads; or possibly, in liquid form. The solids comprise 88 to 92% active ingredient, with the remainder made up of excess moisture. The liquids typically contain 20 to 30% of the active ingredient, with the remainder made up by the carrier material. Typical carrier materials include processed diesel, purified kerosene, or high-quality mineral oil.

If the product is provided in powder or microbead form, a solution is made based on the manufacturer's recommendation. The powders or microbeads generally are mixed in a continuous- stirred tank reactor at the well site, which typically is enclosed. The solids are introduced into the reactor by means of a device similar to an eductor, which wets the particles prior to releasing them into the reactor. The wetting greatly reduces the quantity of dust that is generated. This solution, which is contained in another storage tank at the well site, is then pumped in with the injection fluid during injection via metering pumps. Figure 1 illustrates this process.

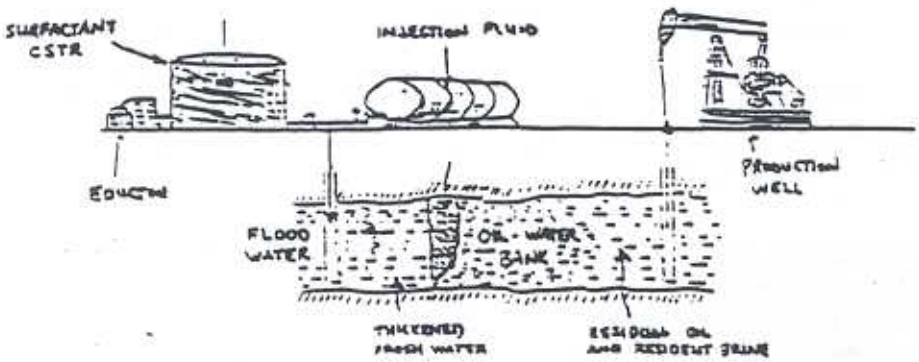

Figure 1. Schematic diagram of surfactant/polymer flooding process

It is difficult to estimate how much polymer or surfactant is required, because the amount used is highly site-specific. However, a successful enhanced oil recovery operation is considered one that recovers 20% as much oil as fluid injected. For example, to produce 4,000 barrels of oil per day at a well-site would require injecting 20,000 barrels of injection fluid per day. If a surfactant is added for mobility control at 0.1 wt%, approximately 20 barrels per day (840 gallons per day) of surfactant would be used.

Application of the Chemicals Used

Application of these chemicals typically is quite simple and involves few people. Worker exposure generally is limited to the time involved with mixing the chemicals for the injection fluids. If the chemicals are received in liquid form, they are injected as received with the injection fluid at concentrations either recommended by the manufacturer or determined from field tests. If the chemicals are received in a solid form, they are first mixed into a solution with water as described above and are then injected with the injection fluid. Generally, up to 5 people mix solutions during several hours per shift. During production, there would be two or three shifts per site, which would mean up to 15 people per site may be exposed. Given that there are approximately 143 sites using steam stimulation, steam flooding, or polymer/surfactant flooding, a maximum of 2,145 people could be exposed on a daily basis in the United States.

Fluid retrieved from the reservoir is sent to a holding tank where it is mixed with oil. There the mixture of the chemicals and the oil is separated so that the oil can be recovered. The water that is generated from the separation process contains the chemicals that initially were injected to start the oil recovery process; however, standard practice is to recycle this fluid back into the reservoir. Recycling of the water/chemical fluid is done continuously during the oil recovery process. The recycling eliminates most of the solid and liquid waste that would be generated by the oil recovery process.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Assumptions

The assumptions in Table 1 represent estimated numbers based on the discussion in the previous section. These assumptions may be used to estimate typical worker exposure for new chemicals using the calculations presented in this section. Any information which is provided in a PMN which provides specific information for any of these variables may be substituted for the values shown below.

Table 1. Assumptions Used to Calculate Exposure Levels

Variable	Value Assumed
Number of shifts	2
Number of sites	143 (max)
Total number of workers	12 workers/site, 250 days/year
Production rate (PR)	5,300 barrels/site/day
Number of hours for transfer/mixing (H_T)	10 hours (5 per shift)
Fuel recovery (FR)	20%
% PMN	0.5%

Environmental Releases

Solid Wastes: The chemicals used in enhanced oil recovery operations are all assumed to be used in injection operations (i.e., fluid recycled back into the process). Some small amount of solid waste may arise from the separation process used to recover oil from the oil-injection fluid mixture retrieved from the oil reservoir. To prevent any stoppage in the recycling lines, the solid waste would be cleared from the line occasionally and packaged as solid waste in 55-gallon drums.

Air Emissions: Air emissions of a chemical product used in enhanced oil recovery will depend on whether the product is in powder, microbead, or liquid form.

Powder Formulations: In enhanced oil recovery operations, the powdered chemical products usually are wetted prior to their release into the reactor; hence, the release of powders to the air can be expected to be low. Typically, the handling and mixing of powders in manufacturing applications lead 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 oil recovery operations site, air emissions of PMN material resulting from the use of powdered chemical products can be calculated as:

$$PR * 0.16 \frac{m^3}{barrel} * H_T * \rho_F * \frac{100}{FR} * \frac{(0.1 \text{ through } 1)}{100} * \frac{\% PMN}{100} = ?\, kg/site/day \qquad (1)$$

where PR: Production rate at the oil recovery site (barrels/day)
H_T: Number of hours involved in transfer/mixing operations (hours/day)
FR: Fuel recovery of fluid injected (weight percent)
% PMN: weight percent in injection fluid of the PMN material (active ingredient)
ρ_F: Assumed to be 1080 kg/m^3 density of fuel recovered (constant)

Microbead Formulations: Air emissions from microbead formulations of chemical products used in enhanced oil recovery operations are expected to be negligible unless components of the formulation are volatile. In general, air emissions from a PMN material contained in a microbead formulation can be assumed to be minimal.

Liquid Formulations: In the case of a liquid product, only a portion of the product, typically 20 to 30%, is the active ingredient. The remainder is a carrier material such as diesel, kerosene, or mineral oil. If the PMN material is nonvolatile, releases to the air are expected to be negligible. The majority of the various types of chemicals currently used in enhanced fuel recovery operations are nonvolatile (i.e. a vapor pressure of 10^{-4} torr or lower), including the polyacrylamides, xanthan gums, acrylamides, and lignosulfates. However, several of the surfactants such as alcohol ethoxylates and alkyl phenol ethoxylates, as well as organic in situ crosslinkers such as formaldehyde, are sufficiently volatile to result in air emissions from their use. Releases may arise from chemical storage areas; transfer operations (tank working and breathing losses [CEB, 1991]); fugitive emissions from reactors, valves and compressor seals, and tank cleaning; oil separation/recovery processing; and other secondary processes. Volatile PMN material releases can be estimated either directly from measurements of other compounds in the product mixture or by using U.S. EPA database estimates of air emissions of organic compounds from these operations. In the case of the former approach, the air emissions can be calculated as (CEB, 1991):

$$Q_{org} * \frac{P_{PMN} X_{PMN}}{P_{org} X_{org}} * T = ?\ kg/site/day \qquad (2)$$

where Q_{org}: Estimated emission factor for the organic compound with a vapor pressure P_{org} (kg/second)

P_{PMN}: Vapor pressure of the PMN material
X_{PMN}: Mole fraction of the PMN material in the product mixture
P_{org}: Vapor pressure of the organic compound in the product mixture
X_{org}: Mole fraction of the organic compound in the product mixture
T: Duration that volatile releases are expected to occur (seconds/day)

Water: Releases to water are assumed to be negligible, because most wastewater and liquid wastes generally are recycled and injected back into the reservoir during enhanced oil recovery operations.

Subterranean Releases: The enhanced oil recovery process will result in the release of injection fluid and the PMN material to underground oil reservoirs. The subterranean release of the PMN material can be estimated as:

$$PR * 0.16 \frac{m^3}{barrel} * \rho_F * \frac{100}{FR} * \frac{\%PMN}{100} = ?\,kg/site/day \qquad (3)$$

Disposal Concerns: Drums used to transport the chemical products to the oil recovery site are assumed to be recycled, cleaned to remove contamination, or appropriately landfilled. All liquid and water wastes are assumed to be injected into the oil reservoir. The manufacturer submitting the PMN must address any potential mechanisms by which the PMN material may leave the site.

Worker Exposure

Worker exposure to the PMN material may occur during transfer operations and to a lesser extent from storage, use, and injection fluid recovery/separation operations. Worker exposure is dependent on whether the chemical product containing the PMN material is a powder, microbead, or liquid formulation. Inhalation and dermal exposures to the PMN material from drum transfer operations are assumed to predominate over the exposure potential of the other operations. The use of chemicals in enhanced oil recovery operations at a site is assumed to involve transfers from 55-gallon drums to a reactor or other enclosure at a specific frequency dependent on the oil production rate.

Inhalation

Powder Formulations: Assuming that the powders can be classified as inert or nuisance dust, the overall OSHA Permissible Exposure Level (PEL) is 15 mg/m^3. The OSHA PEL of the respirable portion of the powder is 5 mg/m^3. Inhalation exposure of a worker during an operating day to PMN material in a powder formulation is:

$$5 \frac{mg}{m^3} * \frac{kg}{10^6 mg} * IR * PR * H_T * \frac{\%PMN^*}{100} = ?\,kg/site/day \qquad (4)$$

where IR: Inhalation rate assumed to be 1.25 m^3/hr (CEB, 1991)
H_T: number of hours per day that each worker is involved in drum transfer operations
% PMN*: weight percent of PMN material in the chemical product formulation used

This calculation assumes that the powder and PMN material are inert and can be classified as nuisance dust.

Microbead Formulations: Microbead formulations are assumed to result in negligible airborne PMN material concentrations, so inhalation exposure would be minimal.

Liquid Formulations: Liquid formulations with nonvolatile PMN materials are assumed to result in minimal inhalation exposure to PMN materials from drum transfer operations. For a volatile PMN material with a vapor pressure at ambient temperature with P (torr or mm Hg) and molecular weight (MW), the following relations are used to estimate the concentration of PMN material resulting from transfer operations for the worst-case scenario involving transfer operations from 55-gallon drums (CEB, 1991):

$$C_{PMN} = 95P * \frac{MW}{MV} \tag{5}$$

where C_{PMN}: Concentration of PMN in the atmosphere (mg/m^3)
P: Vapor pressure at ambient temperature (10^{-4} torr or greater)
MW: Molecular weight
MV: Molar volume = 24.5 L/mole @ 25°C, 1 atm

The inhalation exposure to the volatile liquid PMN material is:

$$C_{PMN} * \frac{kg}{10^6 mg} * IR * \left(PR * 0.16\frac{barrels}{m^3}\right) * H_T = ?\ kg/site/day \tag{6}$$

Dermal Exposure: Dermal exposure can arise from the filling/dumping of powders and liquids during drum transfer operations. Dermal exposure can be expected to arise from both intermittent and routine contact with the chemical product containing the PMN material during drum transfer operations.

Powder Formulations: Using estimates of the typical dermal exposure from the filling/dumping of containers of powders (CEB, 1991), the dermal exposure to PMN material is:

$$(6{,}500 - 18{,}200)\ \frac{mg}{m^3} * \frac{kg}{10^6 mg} * H_T * \left(PR * 0.16\frac{barrels}{m^3}\right) * \frac{\%PMN^*}{100} = ?\ kg/site/day \tag{7}$$

The estimate assumes that both hands of the worker routinely come into contact with the powder formulation and that the PMN chemical does not rapidly evaporate or become otherwise transformed.

Microbead Formulations: In the case of microbead product formulations the dermal exposure can be expected to be lower than the estimates for powder formulations.

Liquid Formulations: Using estimates of the typical dermal exposure from routine contact during unloading of drums containing the liquid formulation (CEB, 1991), the dermal exposure to PMN material is:

$$(1{,}300 - 3{,}900)\ \frac{mg}{m^3} * \frac{kg}{10^6 mg} * H_T * \left(PR * 0.16\frac{barrels}{m^3}\right) * \frac{\%\,PMN^*}{100} = ?\,kg/site/day \qquad (8)$$

References

Borchardt, J.K., 1989. "Chemicals Used in Oil-Field Operations," 195th American Chemical Society National Meeting, 3rd Chemical Congress North American, June 5-11, 1988, American Chemical Society Symposium Series N.396, 3-54.

CEB, 1991. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessments*, Volume 1, Contract No. 68-D8-0112, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., February.

Kirk-Othmer Encyclopedia of Chemical Technology, 1983. John Wiley & Sons, Inc., New York, 23:860-861.

Moritis, G., 1992. "EOR Increases 24% Worldwide; Claims 10% of U.S. Production," *Oil and Gas Journal*, April 20, 51-79.

Petroleum Engineer International, 1991. "Chemicals Improve Success of Enhanced Oil Recovery: EOR Chemicals Review," *Petroleum Engineer International*, 63(6):68-71.

U.S. Department of Energy, 1984. *Technical Constraints Limiting Application of Enhanced Oil Recovery Techniques to Petroleum Production in the United States*, DOE/BETC/RI-83/9 (DEB4003910), January.

U.S. Environmental Protection Agency, 1985. *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources*. Research Triangle Park, NC. (AP-42) (emissions estimates for printing ink and soap manufacturing used to provide a range of values for particulate emissions from powder handling and transfer operations)