Application of Chemicals in Well Casing and Cement- Generic Scenario for Estimating Occupational Exposures and Environmental Releases -Draft-

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Generic Scenario: Application of Chemicals in Well Casing and Cementing

Background

Each year, approximately 300 companies in the United States drill and complete several thousand wells for oil or gas production (Calvert and Smith, 1990). Many different types of chemicals may be used during well casing and cementing processes to improve the strength and cohesiveness of the cement. Chemicals may be used as a component of the spacer fluid or chemical wash, or may be used as an additive to the cement. Cement additives are classified by the following categories: accelerators; light weight; heavy weight; retarders; lost circulation; filtration control additives; friction reducers; and specialty materials.

Spacer fluids are pumped into the wellbore after placement of the well casing in order to remove drilling fluid and prevent contact of the drilling mud with the cement slurry (Borchardt, 1989). A chemical wash generally is used to wash the borehole and remove any residual caked mud. Efficient removal of the drilling mud promotes bonding of the cement slurry to rock surfaces. Polymers are often added to the spacer fluid in order to increase fluid viscosity. Surfactants may be added to improve removal of the drilling mud from formation surfaces and to aid in making the casing and the rock surfaces water-wet, which promotes bonding with the cement slurry. A typical spacer fluid composition may include:

- emulsifier composed of slaked lime, oleyl amide, oleic acid , and red oil (15 to 40 lb per barrel)
- dispersant composed of fatty acid amide and sulfonated lignin mixture (0.5 to 10 lb per barrel)
- a weighting material in 50/50 water/oil emulsion (0.25 to 10 lb per barrel).

A chemical wash typically may be composed of an ethylene/vinyl acetate copolymer (12 to 20 wt%), an alkyl aromatic hydrocarbon resin (8 to 12 wt%), an anticoagulant (2 to 10 wt%), and a reaction product of triethanolamine with fatty acids (20 to 35 wt%).

Cement Additives and Their Uses

Most wells are cemented with Portland cement or with Portland cement plus additives to enhance the cementing process. Specific additives that may be used and the purpose for their use are discussed in the following paragraphs.

Additives may be used to accelerate the cement set time. A faster set time shortens the thickening time and increases the early strength. Typical additives include calcium chloride (2 to 4 wt%), sodium chloride (1.5 to 5 wt%), and sodium silicate (1 to 7.5 wt%).

Reduced-density cements often are preferred when cementing a high-pressure gas formation, because the gas can penetrate the cement before it sets, resulting in a weaker final product. Additives that prevent penetration include bentonite, fly ash, silicates, perlite, gilsonite, diatomaceous earth, and oil emulsions. When used, concentrations of these compounds may range from 0.5 wt% up to 40 wt%.

Additives may be used to increase the density of the cement in order to restrain pressure or to improve mud displacement. Typical additives include sand (5 to 25 wt%), barite (10 to 108 wt%), ilmenite (5 to 100 wt%), hematite (4 to 104 wt%), and salt (5 to 16 wt%).

Other additives reduce the set time to ensure that the cement will be distributed appropriately before setting occurs. Lignosulfates and lignosulfate derivatives (4 to 5 wt%) are used extensively as set time retarders. Calcium-sodium lignosulfate or calcium lignosulfate often is used at approximately 0.1 to 1.0 wt%. The lignosulfate derivatives also may be used to improve salt tolerance. Zinc salt with alkylaryl sulfonic acid salt has been used at 0.5 to 1 wt% of dry cement and carboxymethyl hydroxyethyl cellulose at 0.1 to 1.5 wt% to retard setting.

Corrosion resistance in cement becomes more important in wells used for injection of supercritical carbon dioxide for enhanced oil recovery. In general, corrosion-resistant additives include high levels of fly ash (up to 40 wt%) and certain epoxy resins.

Carbon black may be used at 0.1 to 5% by weight of dry cement to increase the compressive strength of cement. Carbon black is used primarily for high-temperature operations.

Additives may be used for filtration control or as friction reducers. Chemicals typically used include the following: cellulose (0.5 to 1.5 wt%); organic polymers (0.5 to 1.25 wt%); carboxymethyl hydroxyethyl cellulose (0.3 to 1.0 wt%); latex (1.0 gallon per 100 lb dry cement); calcium lignosulfonate (0.5 to 1.5 pounds per sack); and sodium chloride (1 to 16 pounds per sack).

Production Process

Well-cementing operations typically are performed by special crews, separate from the drilling crew, although the drilling crew may assist with the work. In a typical operation (Figure 1), the cementing crew mixes the dry cement with water and any additives using a jet mixing hopper. The jet mixing hopper is an enclosed system, with the cement poured directly from trucks into a storage silo. The dry cement is then metered into the jet cement mixer to be mixed with the water supply. The cement slurry is then pumped directly from the mixer into the wells. Volumes of cement used per well vary, depending on the size and depth of the well. Some typical values for wells would be 106 m^3 for a 3,000-m-deep well, 170 m^3 for a 4,500-m-deep well, or 230 m^3 for a 6,000-m-deep well. .

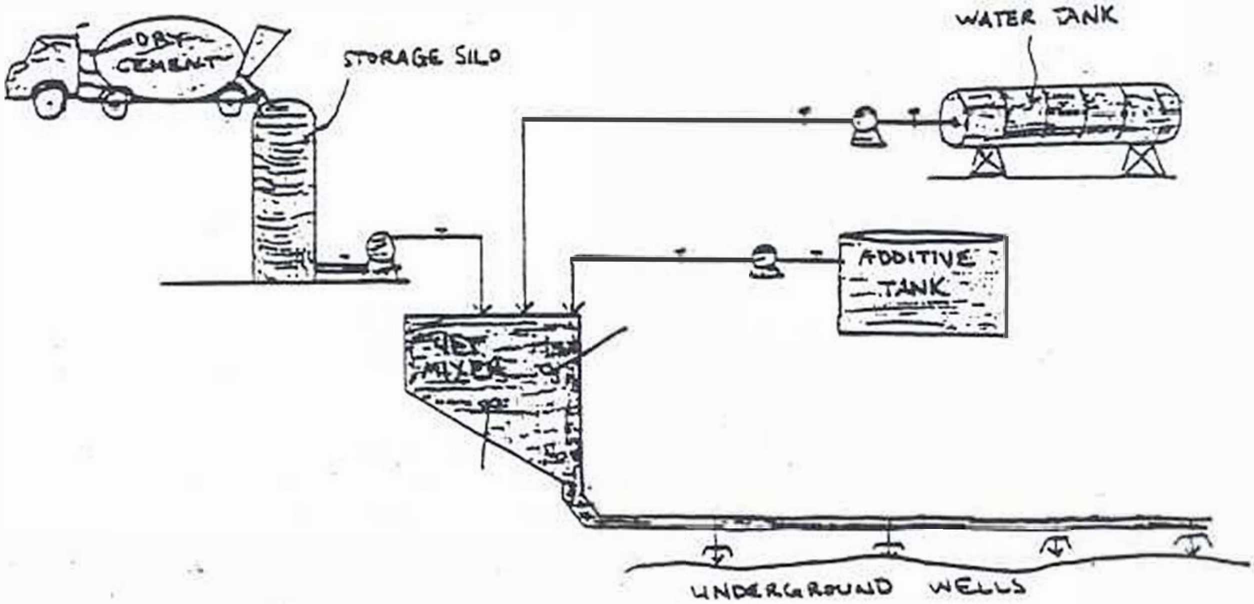

Figure 1. Production process of well-casing and cementing of an oil well.

Spacer fluids and chemical washes are handled and prepared similar to the cement. Quantities of spacer fluids or chemical washers used vary tremendously, depending on the site. However, an average quantity for the spacer fluid may be assumed to be approximately 20 barrels per well, with approximately 15 barrels per well used for the chemical wash.

Depending on the size and depth of the well, a cementing crew may consist of two to four workers plus the drilling crew and various managers. The total number of workers who may have heavy exposure to the cementing chemicals can be estimated at 18 to 27, while approximately 13 people may have light to moderate exposure. Exposure typically is of relatively short duration because the cementing operation may require only 3 to 5 days. The dry or wet cement is handled only a fraction of this time.

Worker exposure during cementing operations typically is via inhalation of cement dust or ocular or dermal exposure to dust or to the finished cement. Much of this exposure is minimized through the use of enclosed systems such as the jet cement mixer described above or through the use of dust masks, gloves, and eyewear.

Small amounts of environmental releases may occur through spills or leakage. In general, spacer fluids and chemical washers recovered from the well are reused in the drilling fluid for development of additional wells.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Assumptions

The assumptions shown 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 for a PMN material that provides specific information for any of these variables may be substituted for the values shown below.

Also, using the data shown in Table 1 for wells of the three depths, the following equations respectively show the number of wells that will be case cemented, given a production volume of 125,000 kg of PMN material per day.

$$\left(\frac{PV \cdot V_{PMN/barrel}}{\left[V_{well} \cdot (PMN_{SP} \cdot PMN_{CW} \cdot PMN_{C})\right]}\right) = 71.8\ wells/day \qquad (1)$$

$$\left(\frac{PV \cdot V_{PMN/barrel}}{\left[V_{well} \cdot (PMN_{SP} \cdot PMN_{CW} \cdot PMN_{C})\right]}\right) = 44.8\ wells/day \qquad (2)$$

$$\left(\frac{PV \cdot V_{PMN/barrel}}{\left[V_{well} \cdot (PMN_{SP} \cdot PMN_{CW} \cdot PMN_{C})\right]}\right) = 33.1\ wells/day \qquad (3)$$

Therefore, on average 50 wells per day, or 18,250 wells per year, can be case cemented from a given production volume of 125,000 kg of PMN material per day.

Table 1. Assumptions Used to Calculate Worker Exposure Levels

Variable	Assumed Value
Number of workers per work crew	3 workers
Total number of days to cement a well	5 days
Number of hours for transfer/mixing (H_T)	6 hours
Volume of PMN material per barrel	15 to 33 barrels per well
Barrels of spacer fluid/chemical wash	7.0 m^3
PMN_{SP}	3 kg per barrel
PMN_{CW}	100 kg per barrel
PMN_C	12 kg per barrel
Volume per well (depth 3,000 m)	106 m^3
Volume per well (depth 4,500 m)	170 m^3
Volume per well (depth 6,000 m)	230 m^3
Well effluent volume	400 m^3

Environmental Releases

Solid Wastes: Potential solid wastes from well casing and cementing operations could include the drilling and caked mud (mixed with drilling fluid) removed from the well by the spacer fluid and chemical wash. In addition, solid wastes could arise from excess or unused cement from well- cementing operations. The slurry of mud, drilling fluid, spacer fluid, and chemical wash resulting from well casing operations generally is reused in drilling other wells. PMN material would be present in this slurry as a result of mixing the spacer fluid or chemical wash with the mud in the well. Release of PMN material as a solid waste could then occur by injection into the ground at another drilling site, or if there is another solid waste disposal process in practice at the site, the drilling and caked mud could be removed by that method. The amount of PMN material generated in the slurry at a well site can be estimated roughly as follows:

$$\left(\frac{SF \cdot PMN_{SP}}{\left[V_{well} \cdot 6.29\,\frac{barrels}{m^3}\right] + SF}\right) \cdot V_{effluent} = ?\ kg/well/day \tag{4}$$

$$\left(\frac{CW \cdot PMN_{CW}}{\left[V_{well} \cdot 6.29\,\frac{barrels}{m^3}\right] + CW}\right) \cdot V_{effluent} = ?\ kg/well/day \tag{5}$$

where: SF: barrels of spacer fluid used at the well site
PMN_{SP}: kg of PMN material per barrel of spacer fluid
V_{well}: volume of the well (m^3)
$V_{effluent}$: volume of mud and fluid slurry removed from the well (barrels)
CW: barrels of chemical wash used at the well site
PMN_{CW}: kg of PMN material per barrel of chemical wash

This approach assumes that the PMN material introduced into the well with the spacer fluid or chemical wash becomes completely mixed in the volume of mud/fluid in the well.

Air Emissions: Emissions of PMN material due to well casing and cementing operations could potentially arise from: (1) transfer operations during addition of PMN material to spacer fluid, chemical wash, and cement; or (2) volatilization/resuspension of PMN material during and after use. A review of the types of PMN materials used in typical well cementing operations suggests a low probability of volatilization due to the low vapor pressures of the typical materials. Mixing of PMN materials used in preparing the cement mixture is commonly done in an enclosed jet mixing hopper, hence minimizing the potential for air emissions of PMN materials from this route. Air emissions of PMN materials from well-cementing operations therefore are likely to be small.

Water: Releases to water are assumed to be minimal. The water-based slurry of mud, drilling fluid, chemical wash, and spacer fluid generally is recycled by injection into another well site. If the slurry from casing and cementing operations is not reinjected or otherwise treated but is disposed of as wastewater, the amount of PMN material released can be calculated using the equations developed above for solid waste. Double-counting of PMN releases as both solid wastes and wastewater must be avoided.

Disposal Concerns: Drums used to transport the chemical products to the oil well site are assumed to be recycled, cleaned to remove contamination, or appropriately landfilled. All liquid and water wastes are assumed to be reinjected into a different well, unless another method of disposing the solid waste exists at the site. The manufacturer submitting the PMN must address any other 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 from use and disposal of the spacer fluid, chemical wash, and cement. The potential routes of exposure are expected to be through inhalation of dusts and vapors for powders and volatile PMNs, respectively, as well as dermal and ocular exposure to PMNs in process dusts and liquids.

Inhalation: Inhalation exposure to workers is due to cement dust in the air, or from inhalation of the fumes of spacer fluid and/or chemical wash. A typical work crew (i.e., 3 workers) works on approximately 75 wells per year. Therefore, given a production volume of 125,000 kg of PMN material per day, which is used to cement 18,250 wells per year, the total number of workers exposed per year can be found by the following equations:

$$\frac{N_{wells/year}}{N_{wells/work\ crew}} = 250\ \textit{work crews required/year} \tag{6}$$

$$N_{work\ crews\ required/year} * N_{workers/work\ crew} = 750\ \textit{workers exposed/year} \tag{7}$$

Cement Dust Exposure: Inhalation exposure of workers to PMN contained in cement mixture dusts can result during preparation of the mixture. Assume that the powders can be classified as an inert or nuisance dust [overall OSHA Permissible Exposure Level (PEL) = 15 mg/m^3; OSHA PEL for the respirable powder fraction = 5 mg/m^3]. If the cement dusts 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 cement dusts will be lower than that estimated. Inhalation exposure of a worker during an operating day to powder-based PMN material in cement dusts is:

$$5 \frac{mg}{m^3} * \frac{kg}{10^6 mg} * IR * H_C * \frac{\% PMN_C}{100} = ? kg/well/day \tag{8}$$

where: IR: Inhalation rate assumed to be 1.25 m^3/hr (CEB, 1991)
H_C: 1 to 2 hours per day during which the dry cement mixture is prepared
PMN_C: weight % of PMN material in cement

Spacer Fluid and Chemical Wash Exposure: Inhalation of PMN contained in spacer fluid and chemical wash could result from the transfer operations required to prepare and handle the fluids. Inhalation of 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. Non-volatile PMN materials are assumed to result in minimal inhalation exposure to PMN materials from transfer operations. For a volatile PMN material, the following relation can be used to estimate the concentration of PMN material resulting from transfer operations for the worst-case scenario involving transfer operations from 55-gal drums (CEB, 1991):
where: C_{PMN}: Concentration of PMN in the atmosphere (mg/m^3)
P: Vapor pressure at ambient temperature (10^{-4} torr or greater)

$$C_{PMN} = 95 P * \frac{MW}{MV} \tag{9}$$

MW: Molecular weight
MV: Molar volume = 24.5 L/mole @ 25°C, 1 atm

For a given number of transfer operations per day and a certain number of hours per day that each worker is involved in the transfer operations, the inhalation exposure to the volatile liquid PMN material is:

$$C_{PMN} * \frac{kg}{10^6 mg} * IR * FT * H_T = ? kg/well/day \tag{10}$$

where: FT: Frequency of transfers per day (transfers/day)
H_T: Number of hours per day for a transfer operation (1 to 2 hours per transfer)

Dermal Exposure: Dermal exposure can arise from cement dusts present during the addition of the PMN material to the dry cement, as well as from transferring and handling the spacer fluid and chemical wash. 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.

Cement Dusts: Using estimates of the typical dermal exposure from these types of operations (CEB, 1991), the dermal exposure to PMN material is:

$$(1{,}300 \textit{ through } 3{,}900) \frac{mg}{m^3} * \frac{kg}{10^6 mg} * FT * H_T * \frac{\% PMN_C}{100} = ? kg/well/day \tag{11}$$

This 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. In the case of microbead product formulations, the dermal exposure can be expected to be lower than the above estimates.

Spacer Fluid and Chemical Wash Liquids: 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:

$$(1{,}300 \textit{ through } 3{,}900)\ \frac{mg}{m^3} \cdot \frac{kg}{10^6 mg} \cdot FT \cdot H_U \cdot \frac{\% PMN^*}{100} = ?\, kg/well/day \qquad (12)$$

where: H_U: Number of hours per day for unloading of drums (hours/day)
PMN^* = weight % of PMN material in the spacer fluid and chemical wash liquids

Note that these estimates for dermal exposure are worst-case estimates. Actual dermal exposures would be lower if protective equipment such as gloves and eyewear were worn by the workers.

References

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