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Environmental Impacts of Water Treatment Chemicals at Industrial Sand Mines

summary

The silica sand unique to western Wisconsin and southeastern Minnesota is used as a proppant in the hydraulic fracturing process that is fueling the resurgence in domestic energy production. Siting and permitting of these "frac sand" mines tend to be controversial, with opponents focusing on potential negative impacts of increased truck traffic, changing land use, air emissions, and concerns about water quality. This paper explores concerns about potential water quality degradation by the use of the two most common flocculants—or settling agents—at these mines, polyacrylamide and polydimethyldiallyammonium chloride (polyDADMAC). Although other types of flocculants are in use, these chemicals currently appear to make up a majority of our clients' flocculant use.

introduction

Polyacrylamide anionic flocculants are commonly used to enhance settling of solids in the clarifier associated with the wash plant at a silica sand facility.

This compound has been safely used for decades in the United States to treat public drinking water. Polyacrylamide also is widely used in a variety of industries and can be found at food processing facilities, used as blasting agents, used for drilling mud and grout products, and used as a soil-stabilization agent.

Acrylamide is a monomer used in the production of the anionic polyacrylamide flocculant. It is not a breakdown or daughter product of polyacrylamide. A small amount of residual, unreacted acrylamide monomer remains in the polyacrylamide flocculant as an impurity when it is added to the wash process.

PolyDADMAC cationic coagulants are commonly used to enhance the performance of the belt press associated with wash plants. This compound is also widely used in the United States to treat public drinking water. DADMAC is a monomer used in the production of the cationic polyDADMAC coagulant.

These products serve a significant benefit to the operation of a mine site because they reduce the overall footprint of the mine, which would otherwise require extensive settling basins. In some cases, these settling basins can result in additional costs related to water management and berm construction.

Both of these compounds are readily biodegradable and monitoring at frac sand mines in the Midwest indicate that there is no evidence of groundwater contamination associated with either of these compounds. This paper provides additional background on each of these chemicals and a detailed analysis of the fate of these compounds using a kinetic model that includes biodegradation and other chemical processes.

regulatory background

Although no adverse human health effects are associated with the polyacrylamide polymer, adverse human health effects have been linked to an impurity called acrylamide, which is a monomer, or part of the polyacrylamide molecule used in the production of the anionic polyacrylamide flocculant. A very small amount of the monomer molecule is present in the raw chemical feedstock that remains unreacted in the polyacrylamide flocculant when it is mixed in the wash process used in the mine's wet plant.

It is this acrylamide monomer (not polyacrylamide) that is classified by the U.S. Environmental Protection Agency (EPA) as a B2, a probable human carcinogen.[1] There are no negative health effects associated with the actual polyacrylamide flocculant itself; only the acrylamide monomer.

Because of this classification and its common use as a settling agent, or flocculant, at municipal drinking water treatment plants, the EPA has established a National Primary Drinking Water Regulation (NPDWR) for acrylamide. This NPDWR established the de facto limit of 0.5 micrograms per liter (ug/L) for acrylamide through a treatment technology standard. This standard is based on a maximum concentration of acrylamide monomer in commercial polyacrylamide flocculant (500 ppm) and a maximum dosing concentration of flocculants (1.0 ppm) directly to potable water. While the EPA has approved laboratory methods for acrylamide, Barr has found no laboratory able and willing to perform the procedure on process wastewater. Barr has identified at least one laboratory that can measure acrylamide monomer concentrations near these low concentrations (less than 1 ug/L) using a non-EPA approved method.

This paper addresses uses typical of polyacrylamide at mine sites and related processing facilities. However, it is appropriate to note that polyacrylamide can be highly toxic to aquatic life if discharged directly into surface water habitats. Although this type of discharge is not typical of the mine site processing, any potential discharge involving unreacted polyacrylamide entering surface water should be avoided.

Unlike the acrylamide monomer, the DADMAC monomer has not been linked to adverse health effects. DADMAC has no NPDWR and no secondary standards, nor has it been designated by the EPA as a Contaminate of Concern in CCL1 (Contaminate of Concern List 1), CCL2 or CCL3.[2] Furthermore, there are no EPA or MPCA surface water standards for DADMAC, nor has the Minnesota Department of Health or the Wisconsin Department of Natural Resources established health-risk limits. The water

1 EPA. 1994. Chemical Summary for Acrylamide. http://www.epa.gov/chemfact/s_acryla.txt

2 EPA. 2012. Basic Information on CCL and Regulatory Determinations. http://water.epa.gov/scitech/drinkingwater/dws/ccl/basicinformation.cfm

treatment industry has established standards (NSF/ANSI 60) that limit DADMAC monomer in drinking water to 50 ug/L, or 100 times the de facto standard for acrylamide.[3]

Because DADMAC has no known human health concerns associated with it, there is less published data and little risk analysis concerning its fate in the environment.

mining process water

Most industrial sand mines utilize a wash water loop, similar to the one depicted in Figure 1 (below). Water from a reservoir (augmented with makeup water, usually from a groundwater source) is used to slurry raw sand. This slurry is processed by a series of screens, scalpers, and density separators to separate the sand by particle size. Fines are generally returned to the mine pit or stockpiled until used for site reclamation, while sized sand is transported to the dry plant for further processing.

Polyacrylamide anionic flocculants are used to enhance settling of solids in the clarifier, or thickener, associated with the process. The clarifier produces an underflow, which is essentially a thick mud. Some facilities use a belt press to convert this mud into a solid or filter cake, which offers easier disposal. It is common for facilities that use a belt press to use a polydimethyldiallyammonium chloride (polyDADMAC) cationic coagulant to enhance the performance of the belt press.

fate of polyacrylamide

The acrylamide monomer is highly soluble in water, is biodegradable under aerobic and anaerobic conditions, and has poor adsorption to minerals and organic matter.[4] The fate of this residual acrylamide monomer in the environment is discussed later in this document.

Steady-State Kinetic Model of Acrylamide Monomer Concentration in Process Water and Quarry Pit

The acrylamide monomer is highly soluble in water, and has poor adsorption to minerals and organic matter. Thus, the concentration of acrylamide that will exit the clarifier in the underflow slurry will equal the concentra-

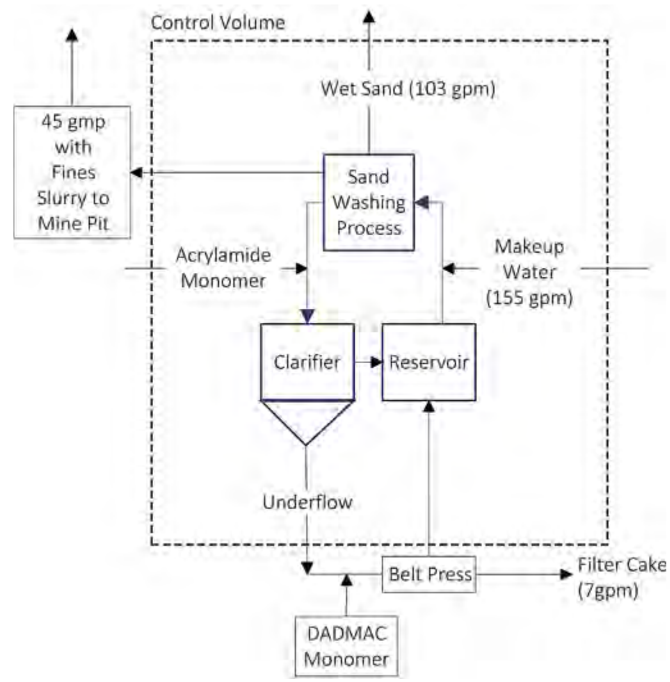

Figure 1. *Control volume used in estimating the steady-state DADMAC monomer concentration in the water leaving the sand wash loop.*

tion of the process water that overflows the clarifier and is recycled in the process.

The water-phase concentrations of acrylamide monomer within each water reservoir at a typical wash plant facility (see Figure 1) can be characterized by the following mass balance equation:

Accumulation = Incoming - Outgoing - Biodegradation

Incoming

The incoming rate of acrylamide monomer is directly related to the feed rate of the polyacrylamide flocculant added to the clarifier (see Figure 1). The Wisconsin DNR, as part of the Nonmetallic Mining Operations General Permit, requires permitted facilities to record on a monthly basis all water treatment additives and to report this amount annually. The concentration of the acrylamide monomer in polyacrylamide flocculants is limited to 500 ppm.

Biodegradation

Acrylamide monomer is biodegradable. Biodegradation rates vary with the availability of oxygen, temperature, concentration of acrylamide monomer, concentration of capable microorganisms, and whether the capable

3 www.nsf.org/newsroom_pdf/NSFFactSheetPolyelectrolytes.pdf

4 EPA. 1994. Chemical Summary for Acrylamide. http://www.epa.gov/chemfact/s_acryla.txt

microbial community had previous exposure to acrylamide monomer. For soil microbial communities not previously exposed to acrylamide, higher initial acrylamide concentrations correspond to slower initial degradation kinetics[5]. One of the slower reported acrylamide biodegradation rates was for a previously unexposed soil sample subjected to a high initial acrylamide loading (999 mg acrylamide/kg soil), a low temperature (10°C), and aerobic conditions. The corresponding apparent first-order rate constant was 0.0027 hr^{-1} [6].

With prior exposure and acclimation to acrylamide, aerobic microbial communities can biode grade acrylamide at much faster rates. Apparent first-order rate constants can approach 0.125 hr^{-1}. [7 8]

analysis of kinetic model

The system of reservoirs provided in Figure 1 was evaluated using three apparent first-order biodegradation rate constants: K = 0.0 hr^{-1} (no biodegradation), K = 0.0027 ( ) hr^{-1} (slow biodegradation), and K = 0.125 hr^{-1} (rapid biodegradation). The estimated steady-state reservoir concentrations (clarifier, fresh water tank, and quarry pit) associated with the three K values are provided in Table 1. With no biodegradation, the estimated steady-state acrylamide concentrations were between 10 and 12 µg/L. With biodegradation, the estimated steady-state acrylamide concentrations ranged from 0.001 to 1.5 µg/L. This compares to the de facto standard of 0.5 ug/L for potable drinking water.

5 Lande S. S., Bosch S. J., and Howard P. H. 1979. Degradation and leaching of acrylamide in soil. Journal of Environmental Quality 8(1): 133-137.

6 Abdelmagid H. M. and Tabatabai M. A. 1982. Decomposition of acrylamide in soils. Journal of Environmental Quality 11(4): 701-704.

7 Arimitu H., Ikebukuro H. and Seto I. 1975. The biological degradability of acrylamide monomer. Journal of the Japan Water Works Association 487: 31-39. Cited in WHO. 2011. Acrylamide in Drinking Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality. World Health Organization, Geneva, Switz. http://www.who.int/water_sanitation_health/dwq/chemicals/acrylamide.pdf

8 U.S. EPA. 1994. Chemical Summary for Acrylamide. Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, EPA 749-F-94-005a. http://www.epa.gov/chemfact/s_acryla.txt

Table 1. Estimated steady-state acrylamide monomer concentrations

	Reservoir Concentration of Acrylamide (ug/L)		
K Value (hr^{-1})	Clarifier	Fresh Water Tank	Quarry Pit
0	11.7	11.5	10.3
0.0027	1.45	1.29	0.13
0.125	0.54	0.41	0.0010

Fate of acrylamide monomer in soil and groundwater

The acrylamide monomer exits the clarifier/ sand wash loop through wet sand and reject material produced by the sand washing process. Virtually all of the polyacrylamide flocculants introduced to the clarifier are expected to adhere to soil particles and exit the clarifier in the underflow, and are ultimately disposed with filter cake (or alternatively in clarifier mud ponds.)

Because acrylamide readily breaks down in soil and water, biodegradation should occur in the sand piles as well as in the soil and groundwater beneath them. In natural aerobic and anaerobic environments, the half-life for the acrylamide monomer can be less than a day.[9] This means more than 90 percent of the original monomer from these sources would be biodegraded in less than three days.

The Department of Land Conservation and Forest Management (DLCFM) in Chippewa County, Wisconsin, has required four permitted mine sites to periodically monitor groundwater for the acrylamide monitor downgradient from where the wash water and flocculated solids are placed into or on the ground surface. As of January 18, 2013 (personal communication, Chippewa County), all samples collected and analyzed for the department have been non-detect for the acrylamide monomer. This represents more than one year of data. One of the sites in Chippewa County, known as the Bloomer Mine, uses a series of wash water trenches to dewater the flocculated fines accumulated during the wash process. (The mine does not utilize a belt press filter.) Acrylamide has not been detected in soil samples collected from the native soil at the base of the trenches providing evidence that biodegradation is occurring even at cooler temperatures found in the subsurface.

9 EPA. 1994. Chemical Summary for Acrylamide. http://www.epa.gov/chemfact/s_acryla.txt

fate of PolyDADMAC

PolyDADMAC cationic coagulants are commonly used to enhance the performance of the belt press associated with wash plants. This compound is also widely used in the United States to treat public drinking water. DADMAC is a monomer used in the production of the cationic polyDADMAC coagulant. A small amount of residual, unreacted DADMAC monomer remains in the polyDADMAC coagulant when it is added to the process. The differences between the DADMAC and acrylamide monomers and the fate of residual DADMAC monomer in the environment are discussed later in this document.

The DADMAC monomer is soluble in water, biodegradable under aerobic conditions, and has poor adsorption to minerals and organic matter.[10] Because of its solubility and its inability to adsorb to solids, the water-phase concentration of the DADMAC monomer in the filtrate produced by the belt press will equal the concentration within the process water that overflows the clarifier and is recycled in the wash loop.

Like acrylamide, the DADMAC monomer is considered readily biodegradable. The acrylamide monomer has a shorter half-life than DADMAC (approximately one day vs. 15 days for DADMAC). Neither monomer is considered bioacculmative. Both monomers are considered to have low environmental toxicity.

Because the DADMAC monomer is readily biodegradable in water, it will achieve a steady-state concentration in the clarifier/ sand wash loop. Due to its higher monomer concentration and longer half-life, it is expected to have a higher steady state concentration than acrylamide. It is important to note that there are no published recommended or regulatory standard for DADMAC. Given the relatively small volume of polyDADMAC used at most facilities (in comparison to polyacrylamide) and the relatively small concentration of DADMAC monomer, the expected steady-state concentration is expected to be relatively low (less than 1 mg/L).

Since DADMAC readily breaks down in soil and water, biodegradation should occur in the sand piles as well as in the soil and groundwater beneath them.

Because DADMAC carries no known human health concerns, there is less published data and little risk analysis concerning its fate in the environment. We have not been able to locate sufficient information on DADMAC to derive steady-state concentrations of the compound as we were for acrylamide. However, given the evidence that it is highly biodegradable, it is assumed that if acrylamide degrades rapidly than the same conditions would result in similar performance from DADMAC monomer.

analytical methods and monitoring requirements

There are no practical, EPA-approved laboratory methods for monitoring of acrylamide or DADMAC. The EPA, through a treatment technology standard, limits the amount of anionic polyacrylamide used at water treatment plants by limiting the amount of the monomer in flocculants to less than 500 parts per million (ppm) acrylamide, used at a concentration of 1.0 ppm or less. This gives a de facto safe drinking water limit of 0.5 ug/L. The EPA has established no treatment standards for DADMAC. NSF 60 has established an allowable concentration in drinking water of 50 ug/L, or 100 times higher than the de facto standard for acrylamide.

ALS-Columbia Laboratory in Kelso, Washington, has developed a practical, non-EPA-approved analysis method for acrylamide. It uses liquid chromatography tandem mass spectrometry (LC-MS/MS) technology and has a minimum detection limit at or below the EPA's limit of 0.5/ug/L.

ATSDR study

In 2008, The U.S. Department of Health and Human Services' Agency for Toxic Substances and Disease Registry (ATSDR) published a Health Consultation regarding potential environmental exposures to acylamide from the on-site disposal of sand fine sludge and wash water from the Belvidere Sand & Gravel (BS&G) site in Warren County, New Jersey. BS&G uses a polyacrylamide flocculant in their closed loop aggregate washing process, similar to those used by the Industrial Sand industry.

Petitioners expressed concern about potential contamination of potable wells by acrylamide and resulting

10 EPA. 2004. Test Plan for DADMAC. http://www.epa.gov/hpv/pubs/summaries/dialdime/c15208tl2.pdf

neurological symptoms reported by area residents. The ATSDR, in conjunction with the New Jersey Department of Health and Senior Services, conducted an extensive study of the site, and concluded "the site poses no public health hazard. Community health concerns (i.e. neurological conditions and cancer) are unlikely to be associated with exposures to site-related acrylamide."[11]

conclusion

Polyacrylamide anionic flocculants and polyDADMAC cationic coagulants are two commonly used water treatment chemicals used at industrial sand mines. Both chemicals contain trace amounts of residual monomers resulting from their manufacture.

The EPA classifies the acrylamide monomer as a probable human carcinogen and has established a de facto National Primary Drinking Water Regulation of 0.5 ug/L for the acrylamide monomer.

There are no federal or state DADMAC concentration limits for either surface water or groundwater, presumably because there are fewer toxicity concerns. Consequently, very little chemical data are available to perform a detailed mass balance and risk evaluation. This leads us to conclude that the compound is unlikely to result in significant environmental effects.

The acrylamide monomer is readily soluble in water, and has poor adsorption to minerals and organic matter. Thus, while the majority of the polyacrylamide flocculant will exit the clarifier with the solids in the underflow, the vast majority of the acrylamide monomer will flow through the clarifier and be recycled. We expect a steady state concentration to form in the clarifier and sand wash loop. This will be the same as the initial concentration of the water contained in the wet sand piles and filter cake. Between biodegradation and dilution, the concentration of acrylamide monomer in the quarry pit will be virtually undetectable, based on the kinetic model.

The acrylamide monomer readily biodegrades in water and soil (acrylic acid and ammonia are break down products). As micro-organisms acclimate, they become more efficient at removing acrylamide from soil and water. At our modeled wet plant, we expect significant biodegradation of acrylamide to occur in the soil beneath the wet sand piles and filter cake so that concentrations of acrylamide reaching groundwater will be insignificant. A monitoring program has been in affect at mines in Chippewa County, Wisconsin, for over a year. To date, the acrylamide monomer has not been detected in any groundwater samples.

Because the DADMAC monomer is readily soluble in water, and has poor adsorption to minerals and organic matter, the majority of the polyDADMAC coagulant will exit the clarifier/ sand wash loop with the filter cake. A relatively small proportion of the coagulant consisting of the DADMAC monomer will enter the clarifier/ sand wash loop and be recycled. We expect a steady state concentration to form in the clarifier and sand wash loop. This will be the same as the initial concentration of the water contained in the wet sand piles and filter cake.

The DADMAC monomer readily biodegrades in water and soil. We expect significant biodegradation of DADMAC to occur in the soil and groundwater beneath the wet sand piles and filter cake.

While no practical EPA-approved analytical method exists for acrylamide, a laboratory has been found that has developed a test method capable of analyzing for acrylamide to the EPA's de facto drinking water standard.

11 www.atsdr.cdc.gov/HAC/pha//BelvidereSandGravelSite/Belvidere_Sand_Gravel_Site%20HC%208-20-2008.pdf