

Water Soluble Polymers and Industrial Sand Mining

What are polymers?

Polymers are chemical compounds or mixtures of compounds that cause very fine particles to quickly cluster into a lesser number of much larger particles. Polymers are made up of constituent monomers. Some polymers are water soluble; some are not.

How do polymers work?

Polymers are composed of long molecular chains that adsorb (stick) quickly and strongly onto the surfaces of adjacent particles through a combination of processes known as electrostatic and hydrogen bonding. Joined together by this polymer "tentacle," these now less-mobile particles are ultimately drawn together to form a much larger particle. This process is the same regardless of the industry in which the polymer is used. Water soluble polymers of the type used in industrial sand mining operations include coagulants and flocculants, which are primarily used to separate materials suspended in water or other aqueous media.

Why are polymers used in the industrial sand mining industry?

Polymers are used in the industry because the sand is washed with water. The washing process makes the industrial sand clean and ready for use. The source of most industrial sand mined in Wisconsin is sandstone, which is 95% to 99% sand and 1% to 5% very fine particles (silt and clay). Users of industrial sand require a clean grain of sand, without any fines or impurities. After mining, sand is rinsed or "washed" using water to remove the silt and clay particles.

When the sand is washed, the fine particles become suspended in the wash water. Polymers are used to clarify or clean the particles out of the wash water. By accelerating the settling of fine particles, the polymers shorten the period of time to clarify the water for reuse in industrial sand processing. Polymer use greatly reduces the need for new makeup water for sand washing that would come from a well or other source. Using polymers also reduces or eliminates the amount of land area that might otherwise be needed for settling ponds, which are another means of clarifying the wash water.

Is the use of polymers unique to industrial sand mining?

No. The same water soluble polymers used in industrial sand mining are used in a variety of other applications, including sewage treatment, municipal drinking water treatment, construction aggregates wash water, and to settle dredge flow sediment during waterway remediation. Acrylamide-based polymers are used to condition bare soil on farm land and construction sites to control erosion and for the manufacturing of many products such as plastics, grouts, cosmetics, paper, and diapers.

What polymers are typically used to wash sand?

The two common polymers used in industrial sand operations are water soluble polymers:

- 1. Poly-DADMAC polymer -- a water solution of a cationic (positively-charged) polymer (poly-diallyldimethylamonium chloride).
- 2. PAM polymer -- an anionic (negatively-charged) co-polymer (polyacrylamide/acrylate).

How much of these polymers are used in the sand washing process?

The two commonly used polymers are poly-DADMAC and PAM. The monomer in the poly-DADMAC polymer is called the DADMAC monomer; the monomer in the PAM polymer is called the acrylamide monomer, and is often referred to simply as acrylamide. These monomers are present in very low concentrations in each polymer.

Industrial sand mining operations that use the poly-DADMAC polymer typically add about 15 parts per million (ppm) to the wash water. The poly-DADMAC polymer averages about 20% poly-DADMAC. The poly-DADMAC portion of the polymer contains less than 0.1% of the DADMAC monomer. That calculates to a DADMAC monomer concentration in the wash water of approximately 3 parts per billion (ppb).

Industrial sand mining operations that use the PAM polymer typically add about 6 to 7 ppm to the wash water. The PAM polymer is an emulsion with an average of about 30% PAM polymer. The acrylamide monomer is present at concentrations less than 0.05% of the PAM polymer portion of the emulsion. That calculates to an acrylamide monomer concentration in the wash water of approximately 1 ppb.

How does Wisconsin Department of Natural Resources (WDNR) regulate polymer use at industrial sand operations?

WDNR regulations protect surface water and groundwater by regulating stormwater and surface water discharges, well drilling, and the application of materials to the land surface with the potential to impact groundwater. Any stormwater or surface water discharge of industrial sand wash water is regulated by WDNR under Ch. NR 216. WDNR approves the application of products containing polymers for sediment control purposes under DNR Conservation Practice Standard 1051 to protect surface waters. WDNR has not established specific groundwater standards for polymers under Ch. NR 140; however, if the wash water is held in a pond, WDNR reports that "[s]ealed ponds will have very little potential for groundwater impacts. Unsealed ponds will likely seal themselves with the fines that are removed from the frac sand."[1]

Does polymer use at industrial sand operations pose a risk to public health?

No. For comparative purposes, it is worth noting that municipal drinking water treatment facilities add polymer directly to the drinking water; industrial sand operations add polymer to the sand wash water, which is part of the industrial sand process and not a source of drinking water. These polymers are also approved by the National Sanitation Foundation (NSF) and American National Standards Institute (ANSI) NSF/ANSI Standard 60 for treatment of drinking water.

The maximum allowable DADMAC monomer concentration in drinking water established by NSF/ANSI (at the request of the United States Environmental Protection Agency (US EPA)) is 50 ppb [2]. By comparison, approximately 3 ppb DADMAC monomer is present in the wash water used in industrial sand mining operations.

Concerns about potential adverse health effects from polymers have focused on acrylamide because it is a possible human carcinogen and a neurotoxin (damages the nervous system). Acrylamide is the monomer present in a very low concentration in PAM polymers. US EPA regulates acrylamide in drinking water using a treatment technique requirement because there is not a standardized analytical method for its measurement in drinking water. US EPA's Phase II Rule limits the allowable residual acrylamide to 0.05% when the polymer is added directly into raw drinking water supplies at 1 ppm. Due to this regulation, acrylamide concentrations in drinking water are not expected to exceed 0.5 ppb. US EPA considers this level low enough to be "safe" accounting for any uncertainty in the data relating acrylamide to cancer and neurotoxic effects. [3]

Environmental fate studies by US EPA report that acrylamide degrades rapidly in the environment – in a matter of a few days in both soil and water. Depending on whether the soil is aerobic or anaerobic, the estimated half-lives range from 22 to 36 hours. Degradation in river water occurred within 2 to 12 days, depending on the availability of microorganisms that utilize the acrylamide. Fish tissue samples showed no appreciable bioconcentration. [4,5]

The maximum allowable acrylamide monomer concentration in drinking water established by NSF/ANSI is 0.5 ppb [2]. By comparison, at typical industrial sand operations the concentration of the acrylamide monomer in the wash water is 1.0 ppb. This wash water is in the clarifiers and settling ponds that are part of the industrial sand production process – which are not sources of drinking water. If the wash water with less than 1 ppb acrylamide were to leave the industrial sand operation -- either through seepage from settling ponds to ground water (unlikely, since the ponds will become sealed as noted above by the WDNR) or discharge to surface water streams or rivers -- it is very unlikely that the acrylamide monomer would be detected because it would degrade and be diluted before it reached any drinking water source.

References

- [1] WDNR Silica Sand Mining in Wisconsin, January 2012, p. 28 accessed at: <u>http://dnr.wi.gov/topic/Mines/documents/SilicaSandMiningFinal.pdf</u>
- [2] The National Sanitation Foundation and American National Standards Institute, Standard 60: Drinking Water Treatment Chemicals Health Effects
- [3] EPA Water: Basic Information about Regulated Drinking Water Contaminants, accessed at <u>http://water.epa.gov/drink/contaminants/basicinformation/acrylamide.cfm</u>
- [4] EPA Technical Fact Sheet on: Acrylamide (Part of a larger publication: National Primary Drinking Water Regulations)
- [5] EPA 749-F-94-005a, Chemical Summary for Acrylamide, Office of Pollution Prevention and Toxics, EPA (1994) available at <u>http://www.epa.gov/chemfact/s_acryla.txt</u>

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