Report of the

NJDEP

Science Advisory Board

Evaluation of Acrylamide Monomer

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April 26, 2017

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Acrylamide Monomer Working Group

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Background

Gibraltar Rock of Belle Mead (GRBM) has proposed to use polyacrylamide (PAM) in its stone washing process and to stockpile the dewatered material on site for potential use in their Dense Graded Aggregate (DGA) products. A solution containing PAM would be used as a flocculant during GRBM's stone washing and process-water recovery procedures. The PAM solution will be metered and pumped automatically into the stone washing process and water leaving the process will flow into a settling basin. Decanted process water from the basin will be recycled back into the process stream for additional stone washing. Make-up water from GRBM wells may be added to the recycled water to account for evaporative losses or losses of water adhering to the fines during processing. The settling basin was intentionally over-sized so that there would be no discharge from the basin; however, if this proposal is accepted, the GRBM NJPDES permit would be modified to add the basin area as a possible discharge location in the event water does discharge. The fines will be stockpiled onsite; however, the fines will only be stored temporarily as they will be used soon after stockpiling in the DGA products. Any potential runoff from the fines will be directed into a sump/holding area and this storage area will also be regulated through the GRBM NJPDES permit. GRBM anticipates blending 100% of the fines into their existing DGA products to be sold.

Pilot Study

A concern was raised that this process may result in the release of acrylamide monomer (AM), which is present as an impurity in the PAM used at < 500 ppm. Because GRBM proposes to stockpile the treated fines on-site for future re-use, a pilot leaching study was designed by GRBM to evaluate whether AM would leach from the stockpile since AM is very water soluble and toxic and may pose a threat to surface water and groundwater if released from the site. NJDEP requested the SAB's assistance in evaluating the proposed Acrylamide Decay Pilot Study (included in the *Quality Assurance Project Plan for Acrylamide Decay Pilot Study*, prepared by GBRM, revision 3, September 29, 2014 (QAPP revision 3)).

Several recommendations were made by a Working Group of the SAB in October 2014 to improve the Pilot Study and evaluate the AM leachability under worst-case conditions (to conduct the Pilot Study on fines generated immediately after dewatering in cold weather conditions to minimize the degradation of AM). After several conference calls between NJDEP, the Working Group, and GRBM and their consultants, the Working Group recommended various revisions to the QAPP revision 3, particularly to the design of the Pilot Study and proposed testing protocols. Most significantly, column tests were recommended by the Working Group to simulate leaching of the AM through the dewatered material rather than the original plan design, which would not have specifically addresses leachability of AM (the QAPP revision 3 proposed collecting leachate from a drain hole in a platform containing dewatered material: rainwater would be showered onto the stockpile with a watering can).

The QAPP was revised in November 2014 (QAPP revision 4) and again reviewed by the Working Group and the NJDEP Office of Quality Assurance. Additional recommendations for improvement of the study were made to GRBM and are listed below:

1. The dewatered material should be analyzed for AM.
2. There is a concern about freezing of the columns as it has been proposed (in QAPP revision 4) that they be located outdoors. The committee recommends that duplicate columns be located indoors to avoid freezing.
3. The revised QAPP proposes 6" diameter columns. The committee is concerned about potential short-circuiting in the columns, and so recommends that 8" columns be used. The committee also recommends that clear, plastic columns be used to allow for visual observation of any short-circuiting.
4. The committee recommends that, initially, lab tests be conducted to determine AM desorption from the dewatered material. We recommend mixing aliquots of the dewatered material with water, filtering the material, and analyzing the filtrate for AM.
5. It is recommended that someone with experience in laboratory testing of fate-and-transport in soil be added to the investigation team.
6. The committee recommends that the testing laboratory review the sampling plan and sign-off on it.
7. It is recommended that the column tests be run at 4 °C and ambient temperatures.
8. When AM is no longer is detected in the leachate from the columns, the column material should be mixed with water and agitated, and the water should be analyzed for AM.
9. It is recommended that the independent QA officer conduct an audit of the testing to assure that the testing is conducted properly and that the test results will be scientifically acceptable.

The following additional recommendations were shared with the NJDEP Office of Quality Assurance.

- Section 8.0 (Quality Objectives and Criteria for Measurement Data) needed to be revised to properly address measure of quality
    - Precision needs to not only address LCS/LCSD and MS/MSD precision (RPD $\leq$ 30%), but should also address Replicate precision across multiple columns (using %RSD instead of RPD) or within lab precision (sample/sample duplicate)
    - Accuracy (bias) needs to address recovery of spikes (MS/MSD, LCS, LCSD, and lab surrogates) and acceptance of blanks (effect of blanks with AM contamination on sample data, etc.)
    - Representativeness needs to address whether the pilot test is actually representative of the real-world pile. Precision between columns and comparison of leaching results to total PAM/AM should be discussed to determine whether the leaching experiments worked and were representative of the site conditions. Section 8.3c indicates analysis of PAM dissolved in deionized water, this QC sample should be described in Section 7.0.
    - Comparability needs to address comparability of results to real-life samples
    - Completeness should not be defined as when the test is done only but should also address expectation of the amount of valid data versus amount of data planned
    - Sensitivity section correctly indicates that the DL must be supported by the lowest concentration calibration standard; however, this section contains incorrect

reference to ALS Instrument Calibration accuracy and precision measures, which should be moved to other sections. The most important aspect of sensitivity is to ensure that non-detects are accurate at or below the DL.

- Detection Limit expectations for AM analysis in solid material should be defined.

A revised Pilot Study Plan was received from GRBM addressing most, if not all of the Working Group suggestions. We understand there were several further revisions to the QAPP before the final version was accepted by the Department.

Results

GRBM provided NJDEP with an *Acrylamide Decay Pilot Study*, Summary Report, July 18, 2016 and provided additional clarifications of the report through various e-mail communications with NJDEP. The Pilot Study was conducted in February 2016 with the leaching columns kept just above freezing temperatures as a worst-case scenario (i.e., it is less likely that AM would undergo microbial degradation from the dewatered material prior to completion of the leaching experiments). The dewatered material was prepared after filter-press treatment of fines that were treated with PAM. The PAM solution was added to the Pilot Study fines in the same ratios as proposed for the actual GRBM process. The dewatered material was tested (as requested in Working Group recommendation 1 above) and found to contain AM at a concentration of 150 µg/Kg (ppb) prior to being packed in the columns for the leaching experiments. The flocculation-dewatering process and column leaching experiments were designed to mimic the full scale operation. Six 8" diameter x 10" long columns were packed with the fines and natural rain water was allowed to leach through the columns. Samples of leachate were analyzed from all columns on days 2, 5, and 7 (one column did not have usable results for days 5 & 7 since an obvious fissure developed in the fine packing, short-circuiting the leaching). The results of the Pilot Study indicated: leaching through the fines was very slow; AM was detected at low levels in all leachates (all at < 0.1 µg/L); and the amount of AM leached from the fines decreased over time. For all leachates, the concentrations measured were all below 0.5 µg/L (USEPA limit for the amount of AM that can be applied during treatment of drinking water and is a de facto Maximum Concentration Level (MCL) for AM) as well as below 0.2 µg/L (NJ Groundwater Quality Standard for AM). The lab complied with all of the Working Group recommendations except they did not perform the preliminary AM desorption experiment from the dewatered fines and did not analyze the material in the columns at the conclusion of the experiments for the presence of AM (Working Group recommendations 4 and 8 above, respectively).

Literature

In addition to reviewing the results of the Pilot Study, the Working Group conducted a literature review of work conducted to evaluate the fate and decay of AM in the environment. The Working Group also obtained information from working quarries and mines in New Jersey and Minnesota regarding their experiences.

Brown et al (1980) reported that acrylamide monomer degrades rapidly in "natural and polluted environments" under both aerobic and anaerobic conditions.

Lande et al (1979) indicated the half-life of AM at ambient temperature (22°C) ranged from 18 to 45 hours for 25 ppm acrylamide in soil and that this half-life varies with changes in storage conditions (e.g., changes in storage temperature, acrylamide concentration).

Smith and Oehme (1991) point out that AM is poorly adsorbed to soil, and may be highly mobile in "deep rock aquifers." They also say that bioconcentration and accumulation in the food chain is unlikely and that it can be readily biodegraded by microorganisms after a lag period of days, weeks, or months. It is weakly adsorbed and is thus difficult to remove by water treatment.

Lentz et al (2008) reported on a US Department of Agriculture – Agricultural Research Service study regarding the use of PAM for erosion control in furrow irrigation. This study evaluated AM leaching losses from a corn field treated with PAM using continuous extraction-walled percolation samplers buried to a depth of about 4 feet and located 100 and 500 feet from the inflow source along a 590-ft-long corn field. The corn field was furrow irrigated with PAM at a rate of 10 mg/L. Percolation water and furrow inflows were monitored for AM. "Furrow inflows exhibited average AM levels of 5.5 µg/L, while AM levels in the percolation samples never exceeded the minimum detection limit and 0.5 µg/L". The study concluded "the risk that ground water beneath these water soluble PAM-treated furrow irrigated soils will be contaminated with AMD appears minimal".

Barr Engineering Co. (2013) prepared a white paper on the use of PAM in sand mines in western Wisconsin and southeastern Minnesota. They reported on processing facilities, including some using the recycling of process water, that are similar to those proposed at GRBM. The paper indicates that biodegradation of AM occurs rather quickly in soil and water. "In natural aerobic and anaerobic environments, the half-life for AM can be less than a day."…"The Department of Land Conservation and Forest Management (DLCFM) in Chippewa County, Wisconsin, has required four permitted mine sites to periodically monitor groundwater for AM down-gradient from where the wash water and flocculated solids are placed into or on the ground surface." After more than a year of operation, all samples collected and analyzed for the department were non-detect for AM. "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. AM 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." Personal communications with Jim Aiken, Barr Environmental Co., in April 2017 indicated that out of the hundreds of groundwater monitoring wells sampled in Wisconsin and Minnesota as a consequence of the processing of fines using PAM, there was only a single detection of AM in a newly constructed monitoring well in northern Minnesota that was unconfirmed with subsequent sampling of the well (i.e., after well construction, all other samples from this well were non-detect for AM).

In addition to these references, the Working Group contacted the Minnesota Department of Health about working quarries in Minnesota. Although their data are limited, they have one sand and gravel mine

where under a controlled PAM dose rate, AM can be kept below 0.3 µg/L (Minnesota standard), which reduces down to near the MDL (0.017 µg/L) in 1-2 days, and is non-detect (< MDL) after 4 days in the settling pond.

The Belvidere (NJ) Sand and Gravel site uses PAM. They have a NJPDES discharge to groundwater permit. There has been no detection of AM in monitoring wells at this site.

Conclusions and Recommendations

Based on our literature review and since the Pilot Study was done under conditions to minimize degradation of AM, it is expected that the level of AM leached from a real-world stockpile would be negligible. Unfortunately, GRBM did not analyze the material within the leaching columns at the conclusion of the leaching experiments to indicate whether or not AM was still present in the dewatered fines after 7 days of leaching. However, the work of Brown et al (1980) and Lande et al (1979) suggest that under anaerobic conditions, that AM would be degraded within the timeframe of the experiments and would degrade when stockpiled. Additionally, when GRBM will re-use dewatered fines from the stockpile, the time it will take to mix these fines with other material is expected to ensure that AM is not present in blended DGA products. Therefore, while we recognize that the final decision on the beneficial reuse of this material is a DEP decision, based upon the results of this pilot study and other information/literature we reviewed, the beneficial reuse of this material should have no restrictions. However, it is unclear whether run-off from the fines stockpile or from the process-water system could result in AM at levels of environmental concern. Therefore, the SAB recommends that GRBM proceed with their PAM flocculation and fines stockpiling but that effluent from the site, whether from run-off from stockpiles or from process water, be evaluated for AM to ensure that AM is not present at or above 0.2 µg/L (NJ Groundwater Quality Standard for AM). It should be noted that as part of their ACO, GRBM plans to revise their NJPDES permit to add a discharge location from the settling basin to their existing permit, which will be monitored for, among other things, AM levels in the event water is discharged during a rain event or other process water over-flow.

References

Brown, L., M.M. Rhead, K.C.C. Bancroft and N. Allen, (1980) Model Studies of the Degradation of Acrylamide Monomer, *Water Research*, Vol. 14, pp. 775 to 778.

Smith, E.A., F.W. Oehme, (1991) Acrylamide and Polyacrylamide: A Review of Production, Use, Environmental Fate and Neurotoxicity, *Reviews on Environmental Health*, Vol. 9, No. 4. pp. 215 to 228.

Lande, S.S., S.J. Bosch, and P.H. Howard (1979) Degradation and Leaching of Acrylamide in Soil, *Journal of Environmental Quality*, Vol. 8, pp. 133 to 137.

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Barr Engineering Co., (2013), Environmental Impacts of Water Treatment Chemicals at Industrial Sand Mines, White Paper, October 2013.

Quality Assurance Project Plan for Acrylamide Decay Pilot Study, prepared by GBRM, revision 3, September 29, 2014 (QAPP revision 3) and revision 4, October 2014 (QAPP revision 4).

Acrylamide Decay Pilot Study, Summary Report prepared by GRBM, July 18, 2016.

Additional References used in QAPP and Report Review

- Technical Factsheet on: Acrylamide, USEPA, https://www.epa.gov/sites/production/files/2016-09/documents/acrylamide.pdf
- New Jersey Groundwater Standards for Acrylamide, http://www.state.nj.us/dep/wms/bears/Appendix_Table_1.htm
- Contact, MN Department of Health
- Belvidere Sand & Gravel Site, Contact with NJDEP case manager.