

# **Report as of FY2010 for 2009SD137B: "Acidic Leaching Tests to Determine Arsenic Mobility from Concrete-Encapsulated Limestone Waste"**

## **Publications**

- Articles in Refereed Scientific Journals:
  - ◆ Davis, A.D., C.J. Webb, D.J. Dixon, J.L. Sorensen, and S. Dawadi, 2007, Arsenic Removal From Drinking Water By Limestone-Based Material: Mining Engineering, Volume 59 (Number 2) pages 71-74.
  - ◆ Chintalapati, P.K., A.D. Davis, M.R. Hansen, J.L. Sorensen, and D.J. Dixon, 2009, Encapsulation Of Limestone Waste In Concrete After Arsenic Removal From Drinking Water, Environmental Earth Sciences, Volume 59, (Number 1)pages 185-190.

## **Report Follows**

## **Final Technical Report**

**South Dakota Water Resources Institute  
U.S. Geological Survey 104b Program**

### **Acidic Leaching Tests to Determine Arsenic Mobility from Concrete-Encapsulated Limestone Waste**

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## **Introduction**

Arsenic contamination of drinking water is a major problem facing many areas of the United States and the world. Limestone-based technology for arsenic removal from water is an innovative and promising method. The technology offers the potential for low-cost disposal of waste product after arsenic removal, either in an ordinary landfill or by encapsulation in concrete. There is a need for an inexpensive remediation technology for the removal of arsenic in drinking water that can be applied to small rural water systems.

Arsenic is a persistent and bioaccumulative toxin. Long-term exposure has the potential to cause heart arrhythmia, nerve damage, vascular damage, bone marrow depression, anemia, and leucopenia, as well as cancer of the lung, liver, skin, and bladder. The maximum contaminant level for arsenic, formerly 50 parts per billion (ppb), was lowered to 10 ppb in 2006 because of links to cancer. In South Dakota, it has been estimated that 15 to 20 water supply systems will not be in compliance with this mandate. Current removal technologies are expensive and their implementation will cause economic pressures for rural communities with high levels of arsenic in their drinking-water supplies.

## **Project Information**

Limestone-based material has previously demonstrated the potential to remove arsenic and other metals from drinking water. Limestone is widely available, with suppliers in South Dakota and other states of the U.S. Earlier research by the principal investigators, using limestone particles and manufactured limestone-based granules as an adsorbent for drinking water treatment, has shown that the efficiency of the arsenic-removal process can be improved by increasing surface area while maintaining flow-through rates needed for adsorption technologies. Research by the authors also has shown that the waste product passes the Toxicity Characteristic Leaching Procedure (TCLP) test. Disposal of arsenic-enriched waste is critical for commercial viability of removal technologies. Low-cost disposal of waste in an ordinary landfill

gives the method an advantage that could help communities meet the new maximum contaminant level for arsenic. The ability to recycle the waste material by encapsulation in concrete or mortar would add a significant economic benefit, reducing overall costs. Other methods of arsenic removal suffer from the disadvantage of higher waste-disposal costs because of the potential for leaching of arsenic from the waste product.

This project investigated acidic leaching of arsenic from limestone waste after encapsulation in concrete or mortar. The work focused on leaching with simulated rainwater and mild sulfuric acidic solutions typical of shale soils that contain minerals such as pyrite. The tests help demonstrate the potential for recycling of the waste material, thereby decreasing overall costs of limestone-based technology. In laboratory tests with limestone-based material, arsenic-contaminated water was combined with limestone material. The waste material then was removed, encapsulated in mortar, and tested for leaching potential under acidic conditions such as rainwater and weak sulfuric acid solutions.

## **Objectives**

The objectives of this work were to:

- 1) Determine adsorption of arsenic by using limestone-based material as the treatment medium.
- 2) Remove the limestone waste material and combine the product in mortar. Prepare mortar cubes with the material.
- 3) Conduct leaching tests with simulated rainwater and mild sulfuric acid solutions, and analyze the leachate for arsenic concentrations.

When arsenic is removed from water by limestone-based material, the process is believed to be either adsorption or the precipitation of hydrated calcium arsenate. Hydrated calcium arsenate has an extremely low solubility as compared to limestone. The proposed research could help answer a critical research question: when arsenic is removed from water by limestone, is the arsenic merely adsorbed on the surface of the limestone, where it could be released after dissolution of the limestone, or is it bound as a low-solubility calcium arsenate and thus unavailable for release even if the limestone base dissolved?

The research presented in this report focused on improving the economic advantages of disposal of limestone-based material by recycling the waste product in concrete. Overall goals include application as a pilot study at a wellhead with naturally occurring arsenic contamination, and commercial viability of the technology. Two of the principal investigators have extensive experience with arsenic removal by limestone, and the third investigator is a recognized expert in the fields of cement and concrete.

The leaching tests in this work were designed to determine the stability of the waste material and the potential for mobility of contaminants in wastes. Infiltrating water and acidic liquids that come into contact with the waste could potentially leach toxins from the material. The U.S. Environmental Protection Agency's D List indicates the maximum concentration of

arsenic for toxicity characteristic is five parts per million (ppm). Previous work by the researchers has shown that waste product from limestone-based material, after arsenic removal, is considered benign and suitable for disposal in a landfill. Results from that previous research showed final arsenic concentrations ranging from 8 to 24 parts per billion (ppb). Testing was needed for encapsulated waste in concrete or mortar, however. We see the potential for recycling of the limestone waste product and its adsorbed arsenic in concrete, but testing has been needed to determine long-term stability of the encapsulated waste under mildly acidic conditions typical of weathering. The proposed research helps demonstrate the viability of this approach.

## **Methods**

This project investigated leaching potential and stability of concrete-encapsulated limestone waste product after arsenic removal. The tests help demonstrate the potential for recycling of the waste material, thereby decreasing overall costs of limestone-based technology. In laboratory tests, arsenic-contaminated water was combined with limestone-based material in batch tests. The limestone waste material then was removed, encapsulated in mortar, and tested for leaching under acidic conditions to determine its potential for recycling in concrete. The work could give limestone-based technology a distinct advantage for use in small rural water systems.

A stock As(V) solution was used to prepare influent solutions of water. Four one-liter bottles were filled with 1000 grams of 0.5 to 1 mm sized Minnekahta Limestone, and four 500-mL bottles were filled with 500 grams of 0.5 to 1 mm sized Minnekahta Limestone. The prepared solutions were introduced into the bottles, which were shaken several times a day.

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After batch testing, the solution was drained and samples were analyzed for final arsenic concentrations. From the difference between the initial and final concentrations, the mass of arsenic adsorbed on the limestone was determined.

The waste material then was removed and encapsulated in mortar cubes of 2 in x 2 in x 2 in. After curing, the mortar cubes were broken into pieces of approximately 1 to 2 cm, and placed in acidic solutions ranging from simulated rainwater to weak sulfuric acid. The pH values were 5.6 (simulated rainwater), 4 (prepared with HCl), and 2 (prepared with sulfuric acid). The leachate then was tested for arsenic concentrations.

## **Principal Findings and Significance**

During initial phases of the work, arsenic was removed from prepared solutions of water by limestone. Table 1 (below) shows the mass of arsenic removed during this part of the laboratory work.

Table 1. Arsenic removal by limestone during laboratory testing.

	<b>Bottle 1</b>	<b>Bottle 2</b>	<b>Bottle 3</b>	<b>Bottle 4</b>	<b>Bottle 5</b>	<b>Bottle 6</b>	<b>Bottle 7</b>	<b>Bottle 8</b>
<b>Initial arsenic concentration [mg/L]</b>	7.100	7.230	0.713	0.760	7.100	7.230	0.713	0.760
<b>Initial volume of the solution[L]</b>	0.640	0.640	0.640	0.640	0.350	0.350	0.350	0.350
<b>Initial mass of As in solution[mg]</b>	4.544	4.627	0.456	0.486	2.485	2.531	0.250	0.266
<b>Final arsenic concentration [ml/L]</b>	1.890	3.640	0.038	0.038	4.040	4.380	0.078	0.047
<b>Final volume of the solution[L]</b>	0.375	0.445	0.425	0.420	0.202	0.210	0.180	0.215
<b>Final mass of As in solution[mg]</b>	0.709	1.620	0.016	0.016	0.816	0.920	0.014	0.010
<b>% of the final to the initial concentration</b>	26.620	50.346	5.330	5.000	56.901	60.581	10.940	6.184
<b>Removal [%]</b>	<b>73.380</b>	<b>49.654</b>	<b>94.670</b>	<b>95.000</b>	<b>43.099</b>	<b>39.419</b>	<b>89.060</b>	<b>93.816</b>
<b>Mass of As removed [mg]</b>	<b>3.835</b>	<b>3.007</b>	<b>0.440</b>	<b>0.470</b>	<b>1.669</b>	<b>1.611</b>	<b>0.236</b>	<b>0.256</b>
<b>Percentage mass of the removed As[%]</b>	<b>84.403</b>	<b>64.994</b>	<b>96.461</b>	<b>96.719</b>	<b>67.160</b>	<b>63.651</b>	<b>94.374</b>	<b>96.201</b>

The limestone waste then was used in acidic leaching tests. Samples of leachate were sent to MidContinent Testing Laboratories in Rapid City, South Dakota, for analysis. Results of the leaching tests are shown in Table 2.

Table 2. Results of acidic leaching tests.

<b>Sample</b>	<b>L-1</b>	<b>L-2</b>	<b>L-3 (dup)</b>	<b>L-4</b>	<b>L-5</b>	<b>L-6 (dup)</b>	<b>L-7</b>	<b>L-8</b>
<b>pH</b>	<b>5.6</b>	<b>5.6</b>	<b>5.6</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>2</b>	<b>2</b>
<b>As (mg/L)</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>

As shown in Table 2, the arsenic concentrations in leachate were less than the limit of detection of 0.005 mg/L for all samples. This indicates that measurable leaching did not occur under the acidic conditions used during testing.