Report as of FY2009 for 2008SD130B: "Thermal Stability of Limestone Waste for Recycling after Arsenic Removal from Drinking Water"

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 Report

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

Thermal Stability of Limestone Waste for Recycling after Arsenic Removal from Drinking Water

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Introduction

Limestone-based material has demonstrated the ability to remove arsenic and other metals from drinking water. The technology offers the potential for low-cost disposal of waste product after arsenic removal, either in an ordinary landfill or by recycling during the manufacture of cement. Research by the principal investigators has shown that the waste product from the limestone-based technology 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 reuse or recycle the waste material in the manufacturing of cement would add a significant economic benefit, further reducing overall costs. Other methods of arsenic removal, such as iron-based material, suffer from the disadvantage of higher disposal costs because of the potential for leaching of arsenic from the waste product.

Project Information

This project investigated recycling of waste product during the manufacturing of cement, and focused on thermal stability tests. The tests will 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 the material in batch tests. The adsorbed mass of arsenic was determined. The limestone waste material then was removed for thermal stability testing and leaching potential. The proposed work could give limestone-based technology a distinct advantage for use in small rural water systems.

Objectives

The objectives of this work are to:

1) Determine arsenic adsorption in batch tests using limestone-based material as the treatment media.
2) Remove the waste material and conduct analysis for thermal stability.
3) Analyze thermal stability test results, and determine the suitable for reuse or recycling of the waste material during the manufacturing of cement.

The research presented in this proposal will focus on improving the economic advantages of disposal of limestone-based material by reuse or recycling, e.g., in a kiln feed during the manufacturing of cement, which could significantly broaden potential applications of limestone-based arsenic removal methods. Overall goals include application as a pilot study at a wellhead with naturally occurring arsenic contamination, and commercial viability of the technology.

The thermal stability tests in this work are designed to determine the stability of the waste material and the potential mobility of contaminants in wastes. Infiltrating water and other liquids that come into contact with the waste can 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. Testing is needed for thermal stability of limestone waste, however, if it is to be used in the manufacture of cement. The proposed research will help demonstrate the viability of this approach.

Methods

The research presented in this proposal will focus on improving the economic advantages of disposal of limestone-based material by reuse or recycling, e.g., in a kiln feed during the manufacturing of cement, which could significantly broaden potential applications of limestone-based arsenic removal methods. Overall goals include application as a pilot study at a wellhead with naturally occurring arsenic contamination, and commercial viability of the technology.

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In laboratory tests, arsenic-contaminated water was combined with limestone-based material in batch tests. The adsorbed mass of arsenic was determined. The waste material then was removed and tested for thermal stability to determine its potential for reuse or recycling during the manufacture of cement. The proposed work could give limestone-based technology a distinct advantage for use in small rural water systems.

Laboratory facilities at South Dakota School of Mines and Technology were used in the work.

Principal Findings and Significance

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 (Table 1). The prepared solutions were introduced into the bottles, which were shaken several times a day.

Table 1. Batch testing set-up.

Components	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5	Bottle 6	Bottle 7	Bottle 8
Amount of Limestone[gm]	1000	1000	1000	1000	500.3	500.2	500.2	500
Concentration of Solution[mg/L]	7.1	7.23	0.713	0.76	7.1	7.23	0.713	0.76
Volume of Solution[ml]	640	640	640	640	350	350	350	350
Volume of Bottle[ml]	1000	1000	1000	1000	500	500	500	500

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. Results are shown in Table 2. The percentage mass of arsenic removal ranged from 64% to 93%. The mass of arsenic removed, in tests under varying conditions, ranged from 0.24 mg to 3.8 mg (Table 2).

Table 2. Results of arsenic-removal tests.

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

The waste material then was removed and tested for thermal stability to determine its potential for reuse or recycling during the manufacture of cement. Heating was done in increments of 100^{o} C, up to 1000^{o} C. Results are shown in Table 3, below.

Table 3. Results of thermal stability testing.

Temperature (^{o} C)	As (ppm)
Room temp.	< 10
200^{o}	< 10
300^{o}	< 10
400^{o}	< 10
500^{o}	< 10
600^{o}	< 10
700^{o}	< 10
800^{o}	< 10
900^{o}	< 10
1000^{o}	< 10

As shown in Table 3, the limestone waste product with adsorbed arsenic appeared to be thermally stable during testing. The arsenic concentrations were less than 10 parts per million at all temperatures up to 1000^{o} C. Therefore, this testing indicates that the limestone waste shows promise for reuse or recycling during the manufacture of cement.

Information Transfer Program

Results of this research were presented at two conferences, the Eastern South Dakota Water Conference, and the Western South Dakota Hydrology Conference.

Student Support

A graduate student, Hailemelekot Betemariam, was supported by this research during spring semester, 2009, while working toward his M.S. degree in Geology and Geological Engineering at South Dakota School of Mines and Technology.

Awards and Achievements

Hailemelekot Betemariam presented the results of his work in the student speaker contest at the annual meeting of the South Dakota Association of Environmental Professionals, in March of 2010 at Pierre, South Dakota. Mr. Betemariam was awarded second place in the contest. It is expected that the results of this work will be incorporated in a Master of Science thesis or a Ph.D. dissertation.

A patent application for the limestone-based arsenic removal process has been filed (SDSM 1036037). The application number is 11/284,440. In May, 2010, South Dakota School of Mines and Technology received a Notice of Allowance from the U.S.

Patent and Trademark Office, stating that the application has been examined is allowed for issuance as a patent.

Related Publications

Davis, A.D., Webb, C.J., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2007, Arsenic removal from drinking water by limestone-based material: Mining Engineering, v. 59, no. 2, p. 71-74.

Chintalapati, P.K., Davis, A.D., Hansen, M.R., Sorensen, J.L., and Dixon, D.J., 2009, Encapsulation of limestone waste in concrete after arsenic removal from drinking water: Environmental Earth Sciences, v. 59, no. 1, p. 185-190.