

Report as of FY2006 for 2006SD37B: "Fixed-Bed Adsorption Column Studies and Engineering Scale-Up Design of a Limestone-Based Metals Removal Technology for Small Water Supply Systems"

Publications

- Conference Proceedings:
 - Sorensen, J.L., Davis, A.D., Dixon, D.J., and Hocking, C.M., 2007, Further testing of limestone-based material for arsenic removal from small water systems: Presented at 2007 Western South Dakota Hydrology Conference, April 19, 2007, Rapid City, South Dakota.
 - Davis, A.D., Dixon, D.J., and Sorensen, J.L., 2006, Fixed-bed adsorption column studies and engineering scale-up design of a limestone-based metals removal technology: Eastern South Dakota Water Conference, Brookings, South Dakota, November, 2006.
 - Sorensen, J.L., Davis, A.D., Dixon, D.J., and Webb, C.J., 2006, Development of an agglomeration process to increase the efficiency of limestone-based material for removing metals from drinking water: Presented at 18th Annual South Dakota Ground-Water Quality Conference, March, 2006, Pierre, South Dakota.
 - Sorensen, J.L., Davis, A.D., Dixon, D.J., and Webb, C.J., Controlling factors on arsenic removal from water by limestone-based material: Presented at Western South Dakota Hydrology Conference, April, 2006, Rapid City, South Dakota.
 - Webb, C.J., Campbell, C., Davis, A.D., Dawadi, S., Dixon, D.J., and Sorensen, J.L., 2006, Arsenic remediation of drinking water using limestone-based material: American Chemical Society, Division of Environmental Chemistry, Symposium on Current Status of Research on Arsenic Remediation, 231st National Meeting, March 26-30, Atlanta, Georgia.
- Other Publications:
 - Process and apparatus to reduce the amounts of arsenic in water: Dr. Cathleen J. Webb, Dr. Arden D. Davis, and Dr. David J. Dixon; U.S. Patent Application Serial No. 10/861,586; patent pending. Continuation-in-part filed in 2005.
- Articles in Refereed Scientific Journals:
 - 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.
 - Webb, C.J., Davis, A.D., Dixon, D.J., Sorensen, J.L., Berryman, G., and Williamson, T.E., Arsenic remediation of drinking water using limestone: characterization of limestone and dolomite: Submitted for publication, *Environmental Science and Technology*.
 - Davis, A.D., Webb, C.J., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2006, Arsenic removal from drinking water by limestone-based material: Preprint 06-034, Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, 3 p.

Report Follows

Progress Report

State Water Resources Institute Program (SWRIP) March 2006 to February 2007

Part I.

Title: Fixed-Bed Adsorption Column Studies and Engineering Scale-Up Design of a Limestone-Based Metals Removal Technology for Small Water Supply Systems

Investigators: Dr. Arden D. Davis, S.D. School of Mines and Technology
Dr. David J. Dixon, S.D. School of Mines and Technology

This project quantified and compared the effectiveness of both unprocessed limestone chips and manufactured limestone-based granules to remove arsenic from naturally occurring arsenic-contaminated ground water. Keystone, South Dakota, City Well No. 4 was used as the water source. By running column studies with three columns in series, the researchers extended the amount of adsorbent used to treat the water, in comparison to previous column studies that have used only one column at a time. This extended the length of the mass transfer zone established as the adsorbent media reacts with arsenic in the water. The length of the mass transfer zone is directly affected by contact time with the adsorbent. Longer contact time results in a shorter mass transfer zone and results in more complete utilization of the adsorbent.

A breakthrough curve was plotted for each column in each study. Breakthrough in this study occurred when the arsenic concentration went from undetectable to 10 ppb, the new drinking water standard. Exhaustion of a column, the point at which the media must either be replaced or regenerated, occurred when the influent and effluent concentrations of the metal in question were equal. Empty bed contact time (EBCT) for each column study also was calculated. The EBCT was used to represent the length of time a stream of water was in contact with the adsorbent media. This is related to the system's kinetics.

The principal investigators requested a one-year extension on the project because of unexpected difficulties that delayed column work with Keystone water. Column studies have been completed. Results from the column studies using Keystone well water are being used to design a scaled-up pilot project for future application at Keystone City Well No. 4. Pilot project operating variables include: adsorbent type, column diameter, water flow rate, adsorbent bed depth, weight of adsorbent in column(s), contact time, influent and effluent impurity concentrations (ions present other than arsenic), and desired effluent impurity concentrations. More than one design method will be applied for comparison purposes. In addition, column testing of the limestone-based granules as a treatment method for cadmium removal will help quantify cadmium removal capacity of the adsorbent in a fixed-bed adsorption column.

Benefits of this research include a low-cost treatment technology that will reduce select metals to below drinking water standards. This project will bring installation of a

pilot arsenic treatment technology at the Keystone, South Dakota City Well No. 4 site one step closer to reality.

The objectives of this work were to:

- 1) Determine breakthrough and exhaustion of three columns run in series using crushed limestone of 1-2 mm in size as the treatment media and Keystone city well water as the arsenic source. Empty bed contact time was determined.
- 2) Determine breakthrough and exhaustion of three columns run in series using manufactured limestone-based granules 1-2 mm in size as the treatment media and Keystone city well water as the arsenic source.
- 3) Scale-up the results of column studies in Objectives 1 and 2 using engineering design methods. Design plans are being developed to evaluate the potential for a future onsite field pilot study at Keystone, South Dakota City Well No. 4.
- 4) Determine breakthrough and exhaustion of a column run using manufactured limestone-based granules 1-2 mm in size as the treatment media and an influent cadmium water solution above the drinking water standard of 5 ppb. Results are being used to calculate adsorption capacity of the limestone-based media using a fixed bed treatment method.

Methods and Accomplishments

Tasks achieved during this research were: 1) a review of related published literature was completed, 2) a summary of the properties of arsenic, carbonates, adsorption theory, and agglomeration processes was completed to provide technical background for the research, 3) the properties of other innovative arsenic technologies in comparison to limestone-based arsenic removal were summarized, 4) batch tests were completed for seven manufactured granule formulas using solutions of 100 and 500 ppb initial arsenic concentration, 5) batch tests were completed for the seven granule formulas using Keystone well water, 6) three columns in series were run using 0.5 – 1.0 mm Minnekahta Limestone, 7) a column test of 0.5 – 1.0 mm Minnekahta Limestone and granulated ferric hydroxide was run, and 8) engineering scale-up was begun by using the results from the column test with three columns in series to evaluate the potential for an onsite pilot study at the Keystone well.

Arsenic is a persistent, bio-accumulative toxin. The maximum contaminant level for arsenic, formerly 50 parts per billion (ppb), was lowered to 10 ppb in 2006 because of links to cancer. Lowering of the standard will cause economic pressures for rural communities with high levels of arsenic in their drinking water supplies. Current removal technologies are expensive and their implementation will cause economic pressures for rural communities. The American Water Works Association has estimated the cost of decreasing the arsenic standard to 10 ppb in South Dakota at \$8.25 million, and has estimated a cost of \$550 million per year to meet the new standard nationally (Frost et al., 2002).

Cadmium is a persistent and bio-accumulative toxic metal. Long-term exposure has the potential to cause kidney, liver, bone, and blood damage. The maximum contaminant level for cadmium is set at 5 ppb because of health concerns and links to

cancer. Cadmium in the environment is the result of both natural and anthropogenic sources. Anthropogenic sources are the greater environmental threat, and include industrial activities such as smelting operations, urban and industrial wastes, and fertilizer production and application. About one percent of cadmium ingestion is via drinking water; most cadmium intake is related to the food supply. On average, carbonate rocks contain about 48 ppb cadmium, while shales and igneous rocks contain about 200 ppb cadmium (Hem, 1978)

Materials used for testing arsenic removal (numerous limestone rock types and reagent grade calcium and magnesium carbonates) were characterized by surface area measurements, particle size analysis, and X-ray diffraction analysis (to determine material composition). Research has shown that as the particle size is reduced, the efficiency and capacity of arsenic removal are improved significantly.

The proposed mechanism for the removal of arsenic by limestone is the adsorption/precipitation of hydrated calcium arsenates, $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$, or hydrated magnesium arsenates, $\text{Mg}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$, onto the heterogeneous surface of the limestone. The solubility product of calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, is 6.8×10^{-19} and the solubility product of magnesium arsenate, $\text{Mg}_3(\text{AsO}_4)_2$, is 2.0×10^{-20} . The removal of arsenic, and the subsequent stability of the waste product, is facilitated by the alkaline surface pH of the limestone (pH 9-10). Calcium-rich arsenic compounds have been observed with scanning electron microscopy when samples were prepared with about 1,000 to 8,000 ppm arsenic.

Minnekahta Limestone from the Pete Lien and Sons Quarry in Rapid City, South Dakota, was used as the limestone source for this research. Based on X-ray diffraction analysis, Minnekahta Limestone is composed of about 95 percent calcite, 4 percent quartz, and 1 percent microcline.

Water from Keystone Well No. 4 was obtained during spring, 2006, in five-gallon buckets that were sealed and transported to the laboratory at South Dakota School of Mines and Technology for testing. An analysis of a sample of the water is shown in Table 1.

Parameter	KEY-2, Sampled 11/12/04
Physical Properties	
Electrical Conductivity	461 umhos/cm
Hardness	116 mg/L
Total Dissolved Solids	252 mg/L
Total Suspended Solids	<5.00 mg/L
Turbidity	1.5 NTU
pH	8.06
Non-Metallics	
Acidity	<10.0 mg/L
Alkalinity	217 mg/L
Bicarbonate	264 mg/L
Carbonate	0.00 mg/L
Chloride	4.50 mg/L
Sulfate	23.8 mg/L
Metals – Total	
Aluminum	0.043 mg/L
Arsenic	0.053 mg/L
Cadmium	<0.001 mg/L
Chromium	0.001 mg/L
Copper	<0.005 mg/L
Iron	0.043 mg/L
Lead	<0.001 mg/L
Lithium	0.058 mg/L
Manganese	0.047 mg/L
Nickel	0.008 mg/L
Selenium	<0.005 mg/L
Silicon	5.33 mg/L
Strontium	2.69 mg/L
Vanadium	<0.001 mg/L
Zinc	<0.050 mg/L
Metals – Dissolved	
Aluminum	<0.010 mg/L
Arsenic	0.050 mg/L
Cadmium	<0.001 mg/L
Calcium	23.6 mg/L
Chromium	<0.001 mg/L
Copper	<0.005 mg/L
Iron	<0.050 mg/L
Lead	<0.001 mg/L
Lithium	0.058 mg/L
Magnesium	13.8 mg/L
Manganese	0.047 mg/L
Nickel	0.008 mg/L
Selenium	<0.005 mg/L
Silicon	5.21 mg/L
Sodium	62.5 mg/L
Strontium	1.33 mg/L
Vanadium	<0.001 mg/L
Zinc	<0.050 mg/L

Table 1. Water analysis from Keystone City Well No. 4, Keystone, South Dakota.

The columns were constructed of PVC pipe of varying diameters and lengths, depending on the column design. Columns were constructed using plumbing materials available in most hardware stores. PVC pipe was used as the column bed. PVC female adapters were cemented to each end of the length of PVC pipe. Threaded PVC plugs were used to seal each end of the column. A 3/8-inch threaded hole was drilled at the center of each plug and 3/8-inch nylon barb adapters were cemented into each hole. Wire mesh (mesh size 0.175 mm), slip joint washers, and drain strainers were used to hold the packed material in the column bed. Vinyl tubing and shut-off valves were used at the inlet and outlet of the column to control flow through the column. Metal pipe hangers were used to mount the column to a vertically-hanging plywood board attached to a table. Figure 1 shows a typical column set up.

For this research 12 inch by 1.5 inch columns were used. Flow was eight bed volumes per hour (2.9 L/hr or 48 mL/minute). Column effluent samples were collected regularly during a column run. The pH and conductivity of the collected samples were measured and effluent samples were filtered through a 0.45 μm pore size membrane filter. Collected samples were acidified using concentrated nitric acid and analyzed by MidContinent Testing Laboratories in Rapid City, South Dakota for total arsenic concentration.

Influent metals solutions were mixed to varying concentrations, depending on the experiment and the metal being examined. Metals solutions are pH balanced to a pH of 8 ± 2 prior to use. The influent solution was pumped into the column from the bottom up and a constant flow rate out of the column is set using valves at the flow outlet at the top of the column. Samples of effluent were collected regularly and the pH and conductivity of the effluent are measured. Samples were filtered with a 0.45 μm filter and then were analyzed by MidContinent Testing for metals concentrations. Figure 1 shows a typical column set up for two columns. Later experiments used three columns in series.



Figure 1. Photo of column experiments being run.

A column test of 0.5-1.0 mm sized Minnekahta Limestone in three columns in series using Keystone well water was performed for this research. Each column was 1.5 inches in diameter by 12 inches long. The columns were run from the bottom up, with hose connecting each column to the next. All three columns were sampled regularly in unison. An unfiltered water sample from the last column in series was collected after about 2 hours of running the column for comprehensive water quality analysis. A column

test of 0.5-1.0 mm sized Minnekahta Limestone and Granular Ferric Hydroxide (GFH) was also run using Keystone well water. The column was 1.5 inches in diameter by 12 inches long. The column was run from the bottom up. Of the total mass of material added to the column, about 0.5 percent consisted of GFH mixed in with the limestone during packing as thin layers.

After testing, limestone particles were examined. Scanning electron micrograph (SEM) images of the surfaces of limestone granules were taken to visually characterize the granule surfaces. Figure 2 shows the surface of a limestone particle. X-ray fluorescence indicated that these crystals are composed of calcium carbonate. This type of crystallization was not observed on all the particles and was not widespread.

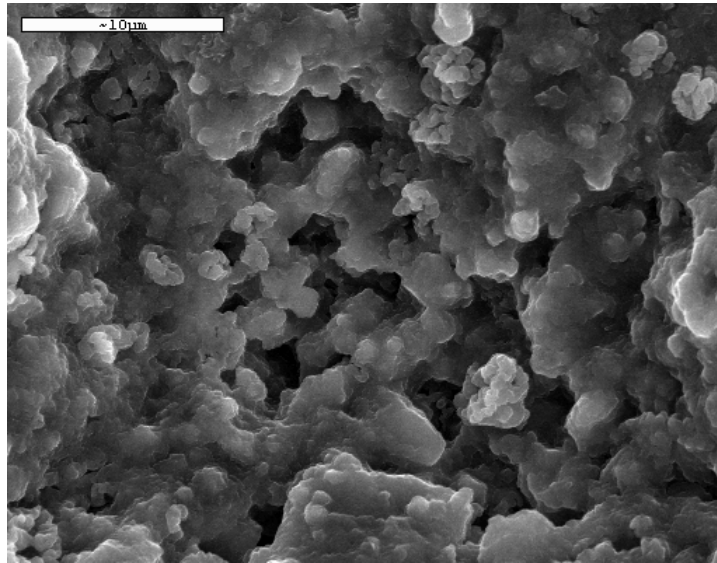
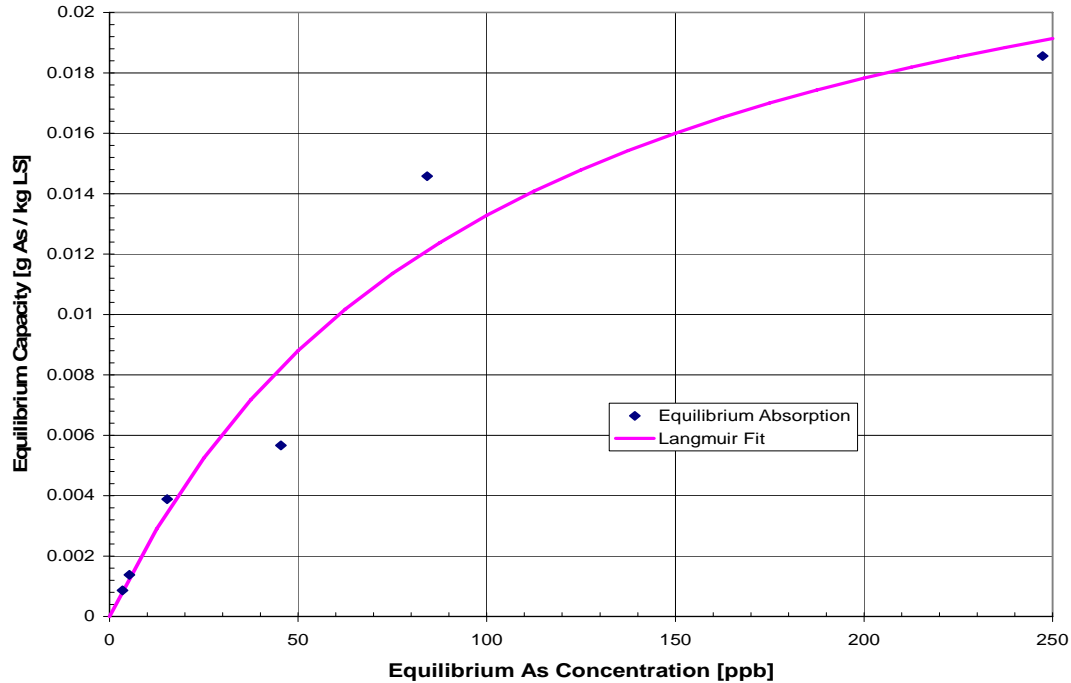


Figure 2. Limestone granule with 10 percent Portland cement binder, taken at 3,500x magnification.

Results of arsenic removal with Minnekahta Limestone showed that the Langmuir isotherm appears to fit the trend of equilibrium adsorption (Figure 3).



Arsenic (V) Adsorption on Minnekahata Limestone (< 0.5 mm) at ~25 °C.

Figure 3. Langmuir isotherm fitted to arsenic-removal data from experiments.

Experiments with cadmium solutions in the range of parts per billion removed all cadmium in solution. Solution concentrations were increased to part per million levels in order to reach effluent cadmium concentrations greater than 10 ppb. Because cadmium removal was greater than 99 percent, an adsorption isotherm could not be developed.

Adsorption capacities showed that cadmium uptake increased dramatically for increasing cadmium concentrations. In Figure 4, initial cadmium concentration values (5, 20, and 50 ppm) are plotted versus adsorption capacity. At an initial concentration of 5 ppm, adsorption capacity is 4.4 $\mu\text{mol/g}$ while at an initial concentration of 50 ppm, adsorption capacity increases to 44.4 $\mu\text{mol/g}$. The data presented in Figure 4 fit the trend line well (R^2 value > 0.9) and it follows that this figure could be useful in predicting limestone cadmium capacities for experiments under similar conditions at other cadmium concentrations in the range of about 0 to 60 ppm. From these results it is clear that the capacity for limestone to remove cadmium is much greater than the capacity for arsenic removal.

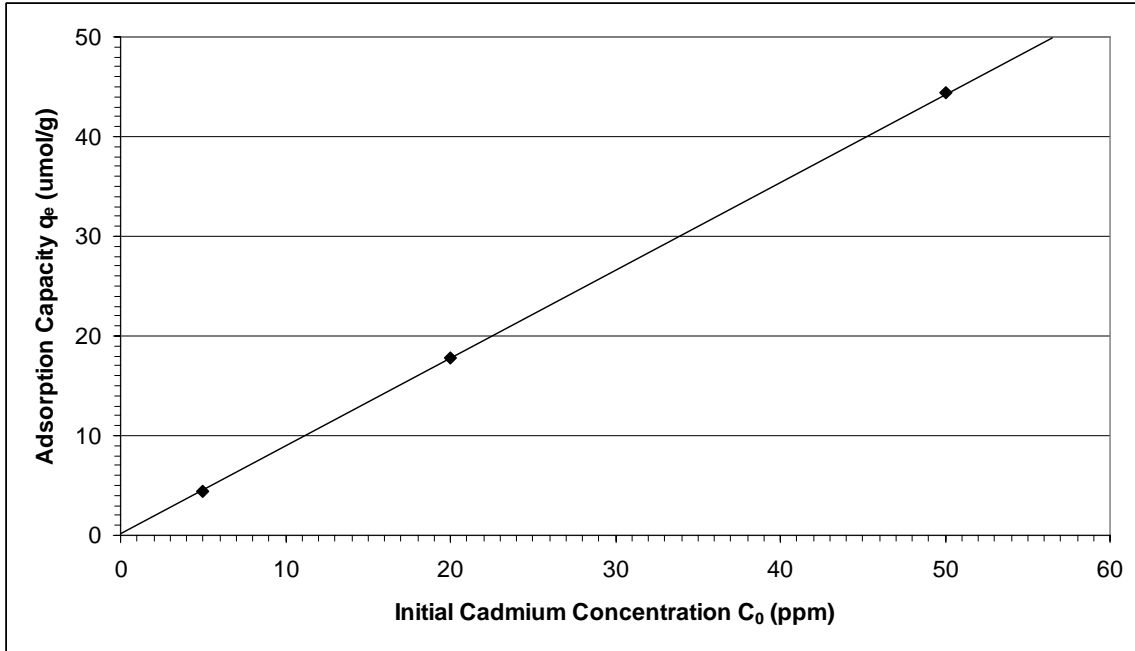


Figure 4. Cadmium adsorption capacity of limestone for initial cadmium concentrations of 5, 20, and 50 ppm. Initial pH 8.0 ± 0.2 pH units, room temperature.

Results of other ongoing work will be presented after completion of the research during the project extension. This will include results of other column experiments and engineering scale-up studies for Keystone City Well No. 4 (shown below on Figure 5).



Figure 5. Keystone City Well No. 4.

Part II.

Information Transfer Program: A field demonstration project was set up for arsenic removal using ground water at a well in Keystone, South Dakota. Well water was used on-site, and water samples also were transported to a laboratory at South Dakota School of Mines and Technology for arsenic-removal tests.

Publications and presentations from the work are listed below.

Student Support: A Ph.D. student, Jenifer L. Sorensen, was funded as a graduate research assistant. Ms. Sorensen defended her Ph.D. dissertation during spring semester, 2006. Her dissertation was based in part on this research work. This research also supported a Master of Science student, Crystal M. Hocking, as a graduate research assistant.