Final Technical Report

Demonstration Project for Arsenic Removal from Drinking Water at Keystone, South Dakota

Submitted to

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Introduction

This demonstration project extended ongoing research into the commercialization of a limestone-based media to remove arsenic from drinking water. Previous research results have demonstrated effective arsenic removal at small scales and under controlled conditions. This project was designed to provide the opportunity to scale up the arsenic removal process and apply it to a field setting. For the field study, a city well in Keystone, South Dakota, was used as the demonstration site. Keystone City Well #4 was drilled in 2003. After extensive pumping of the well, arsenic concentrations leveled out at about 86 parts per billion (ppb), above both the current maximum contaminant level (MCL) of 50 ppb for drinking water and the future MCL of 10 ppb (to be applied in 2006).

The specific objectives of this demonstration project were to:

1. Characterize the water quality of Keystone Well #4 by completing a full-suite analysis of water quality parameters to quantify potential influences of water quality (i.e. competitive ions and their concentrations) on arsenic removal.
2. Conduct laboratory trials with water collected from Keystone Well #4 using both batch experiments and prototype filter cartridges (column experiments) to test the limestone-based material under aerated natural water conditions.
3. Conduct field trials with prototype filter cartridges to confirm laboratory results and to test the limestone-based material with well water derived directly from the well (i.e. non-aerated water).
4. Conduct a scale-up field test on Keystone Well #4 and examine the efficiency of the process under real-world conditions through investigation of engineering constraints.

Background

Arsenic in the aquatic environment has very complex chemistry that is dependent on a number of factors, including pH and redox potential. The speciation of arsenic governs its availability, accumulation, and toxicity to organisms as well as its mobility in the environment. This is particularly important for arsenic, whose arsenite form (As(III)) is much more toxic than arsenate (As(V)). The solubility of these species depends on a number of factors including pH, ions present, and adsorbing surfaces.

Under certain conditions, the solubility and adsorption of arsenic is controlled by the presence of iron, manganese, and their respective oxides (Driehaus et al., 1995). Surface adsorption of arsenic to iron hydroxide and clay minerals has been extensively characterized (Goldberg, 1986; Grossl et al., 1997; Jing et al., 2003; Manning and Goldberg, 1997; McNeill and Edwards, 1997; Pierce and Moore, 1982; Raven et al., 1998). Under oxidizing conditions, Fe (III)-arsenate compounds are stable. Under reducing conditions, Fe (III) is converted to Fe (II) and arsenate to arsenite, significantly increasing the solubility of arsenic.

Even though knowledge of speciation is essential in predicting the environmental impacts of arsenic, the speciation of arsenic in the environment and its transformations with time are poorly understood (Mariner et al., 1996; Edwards et al., 1998; Manning and Martens, 1997; Hug et al., 2001). Arsenic (V) is the form that is more readily precipitated with or adsorbed onto metal oxides.

Prasad (1994) compiled an overview of arsenic adsorption research onto geologic materials, although limestone was not included in this review. Zachara et al. (1993) summarized research looking at metal cation/anion adsorption on calcium carbonate, although arsenic adsorption was not discussed. Research has been completed examining arsenic adsorption by limestone and calcite (Bothe and Brown, 1999; Bothe and Brown, 2002; Cheng et al, 1999; Golonev and Egizaryan, 1994; Maeda et al., 1992, Ohki et al, 1996; Ongley et al., 2001; and Wang and Reardon, 2001). However, only several articles (Maeda et al., 1992; Ohki et al., 1996; Ongley et al., 2001) have examined the use of limestone specifically as an adsorption medium for arsenic in drinking water. Ongley et al. (2001) used untreated crushed limestone, whereas both Maeda et al. (1992) and Ohki et al. (1996) treated crushed and sieved limestone grains with chemicals to enhance arsenic removal.

The influence of natural aquifer material on arsenic transport, speciation, and retention continues to be a subject of investigation. Mariner et al. (1996) examined the effects of high pH on arsenic mobility in a sandy aquifer in the state of Washington. It was determined that high pH ground water from caustic brine industrial waste greatly enhanced arsenic mobility, but mixing with sea water caused precipitation of a number of minerals and reduced permeability along the shoreline. Carillo and Drever (1998) found that significant levels of iron oxides present in natural aquifer material caused some retention of arsenic in a heavily mined area.

The current technologies most commonly considered for reduction or removal of arsenic in drinking water are iron-based media, activated alumina, coagulation-filtration (Han et al., 2003), and ion exchange (Clifford et al., 2003; Kim et al., 2003). These technologies have been shown to reduce arsenic to 2 to 5 ppb. They are more effective when arsenic is in the form of As(V). If As(III) is present, it must be oxidized to As(V), necessitating pretreatment and adding to the overall treatment cost. Coagulation-filtration is most efficient at mid-range pH, and the efficiency of the process depends on the type of coagulant, residence time, and dosage range (Scott et al., 1995). Additionally, disposal of sludge is a cost factor. Such a treatment method is not an appropriate choice for small, rural systems such as the City of Keystone, South Dakota, because of the high cost, need for specialized operators, and difficulties in maintaining optimum operating conditions. The efficiency of ion exchange treatment is affected by competition with sulfate, selenium, fluoride, nitrate, and total dissolved solids. Although this technology is considered appropriate for small ground water systems (less than 10,000 users), it is still too costly for water supply systems in rural areas.

Previous Research Using Limestone-Based Material

Previous research completed by HydroTech Engineering, LLC, during a Phase I EPA Small Business Innovation Research (SBIR) grant demonstrated arsenic removal of greater than 95% by limestone. This limestone-based arsenic removal technology is being developed with a combination of local, state, and federal funding. Other funding sources have included grants from the South Dakota Department of Environment and Natural Resources, the United States Geological Survey, the South Dakota Water Resources Institute, the West Dakota Water Development District, the Kentucky Science and Engineering Foundation, and a University of South Dakota Partnerships for Innovations Grant (with funding provided by the National Science Foundation).

Research has shown that as the particle size is reduced, the efficiency and capacity of arsenic removal are improved dramatically. Estimations of the surface area of limestone particles used in earlier research were on the order of 0.001 m^2/gram of material. This surface area is indicative of a fairly non-porous material. It is estimated that by size reduction through ball-milling, the surface area has been increased to approximately 1 m^2/gram. The reduced particle size with increased surface area per gram of material significantly improved the capacity and efficiency of arsenic adsorption. To maintain high specific surface area, while limiting pressure loss through a packed treatment column, granules of fine limestone powder mixed with additives to improve arsenic removal and an insoluble binder, were manufactured and tested on a bench scale during Phase II research and shown to be effective.

Arsenic removal by limestone is a process that operates effectively over a wide range of pH values. Ten grams of limestone (1-2 mm) were agitated with a 100-ppb arsenic solution at varying initial solution pH values. The results were not dependent on pH between 4 and 10.

Inexpensive disposal of arsenic-enriched material is critical to achieve commercial viability of the limestone-based treatment method. Because the arsenic is strongly bound by the alkaline surface pH of the limestone, it does not significantly leach out under normal waste disposal conditions. This was confirmed by TCLP (Toxicity Characteristic Leaching Procedure) tests. A TCLP test was performed by MidContinent Testing Laboratories in Rapid City, South Dakota. The final arsenic concentration in the extraction fluid was 24 ppb, well within the standards set for disposal in a landfill. Even under high acid conditions, it appears arsenic remained on the limestone surface to a great extent or that calcium arsenate re-precipitated onto the remaining limestone after pH stabilization at about pH 6. This is facilitated by the highly alkaline limestone surface.

Based on TCLP results, the spent waste product is suitable for disposal in municipal landfills. The potential for the waste product to be incorporated into cement as aggregate has also been investigated and preliminary results indicate excellent stability of the product. Because of the ready availability of limestone, its use for arsenic remediation is relatively inexpensive.

The proposed mechanism for the removal of arsenic by limestone is the precipitation/adsorption of calcium arsenate, $Ca_3(AsO_4)_2$, or magnesium arsenate, $Mg_3(AsO_4)_2$, onto the amorphous, rough surface of the limestone. The solubility product of calcium arsenate, $Ca_3(AsO_4)_2$, is 6.8 x 10^{-19}. The solubility product of magnesium arsenate, $Mg_3(AsO_4)_2$, is 2.0 x 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) and the net positive surface charge of limestone. Calcium arsenate crystals and calcium-rich arsenic compounds have been observed with scanning electron microscopy when samples were prepared with approximately 1,000 to 8,000 ppm arsenic concentrations.

For materials on which arsenate crystals were detected, the coverage was approximately 0.12 mg arsenic per gram limestone, with more space clearly available.

Characterization of Limestone Material

Physical characterization of the limestone used in the arsenic removal process is described below. BET surface area analysis, particle size analysis, x-ray diffraction analysis, thin section analysis, and examination by scanning electron microscope were completed. Limestone used in this research was collected at the Pete Lien Quarry in Rapid City, South Dakota, and is from the Minnekahta Limestone rock formation.

BET (Brunauer, Emmett, and Teller) specific surface area analysis was completed to determine the total surface area of the material. Specific surface area was analyzed using the Micromeritics Gemini III 2375 specific surface area analyzer. Table 1 is a summary of the BET specific surface area results for ball-milled limestone and reagent grade magnesium carbonate used in batch experiments. BET results show that ball-milled limestone varies in surface area from about 0.8 to 4.6 m^2/g, depending on the degree to which milling occurred.

Sample Description	**BET Surface Area (m^2/g)**
Ball-milled Minnekahta Limestone, 6/30/04 (Sample ID: BMMNLS-1)	0.7922
Ball-milled Minnekahta Limestone, 7/5/04 (Sample ID: BMMNLS-2)	0.8815
Ball-milled Minnekahta Limestone, 8/9/04 (Sample ID: BMMNLS-6)	4.6806
$MgCO_3$ – Reagent Grade (Source: Fisher)	22.2600

Table 1. BET surface area measurements for ball-milled Minnekahta Limestone and reagent grade magnesium carbonate ($MgCO_3$).

Particle size analysis was completed on Minnekahta Limestone and reagent grade magnesium carbonate using the Microtrac Model S3000 Particle Size Analyzer. This instrument uses the phenomenon of scattered light from laser beams projected through a stream of suspended particles to measure particle size. The amount and direction of light scattered by the suspended particles is measured by an optical detector array and analyzed using Microtrac software. Results are reported as average particle size in microns and are presented in Table 2. Ball-milled Minnekahta Limestone averaged about 6.6 microns in size. Ball-milling of limestone material generally reduced the average particle size by about half of that seen in the limestone that was sieved to less than 0.5 mm.

Material Type	Average Particle Size (microns)
Minnekahta Limestone (ball-milled on 4/14/03)	6.66
Minnekahta Limestone (ball-milled on 4/12/04)	6.55
$MgCO_3$ (reagent grade)	16.34

Table 2. Particle size measurements for Minnekahta Limestone and $MgCO_3$.

X-ray diffraction (XRD) analysis was conducted to determine the mineralogic content of Minnekahta Limestone. Minnekahta Limestone is primarily composed of calcite, with about three percent quartz and smaller amounts of microcline and albite minerals.

Limestone Type and Source	XRD Analysis Results	
Minnekahta Limestone - Rapid City, SD	Calcite – 92.7% +/- 2.1	Microcline – 1.2% +/- 0.8
	Quartz – 2.9% +/- 1.3	Albite – 0.2% +/- 0.2

Table 3. XRD analysis results for Minnekahta Limestone.

Thin-section analysis of Minnekahta Limestone was also performed. The purpose of this analysis was to examine the mineralogic composition of the material. This analysis provided a description of the limestone in terms of purity, grain size, structure, mineralogy, and possible alteration of original material. Thin-section analysis of Minnekahta Limestone (Figure 1) showed grain sizes typically less than 0.05 mm. Bedding was visible in the sample, seen as banding with gradations of high to low iron content. Calcite was the most common component of the material, with either clay minerals or clay-sized particles composing the rest of the sample.

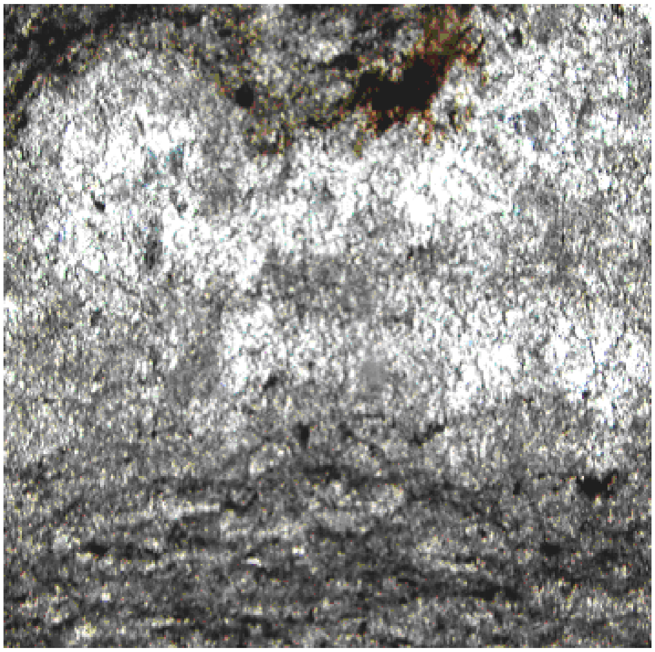

Figure 1. Petrographic image of Minnekahta Limestone (10x; image dimensions 1.5mm x 1.5 mm).

Scanning electron micrograph (SEM) images of Minnekahta Limestone and reagent grade magnesium carbonate were collected to characterize the surfaces of the different adsorption materials used for this research. Figure 2 is an image of the surface of a 1-2 mm sized Minnekahta limestone chip. Figure 3 is an image of the magnesium carbonate used as an additive with limestone to improve arsenic removal efficiency.

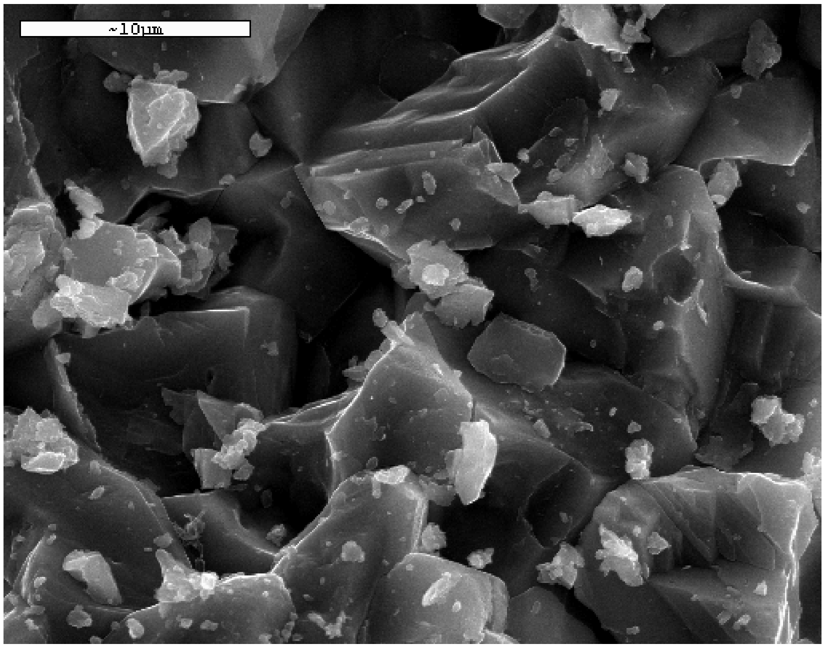

Figure 2. Minnekahta limestone chip (1-2 mm in size) at 3,500x magnification.

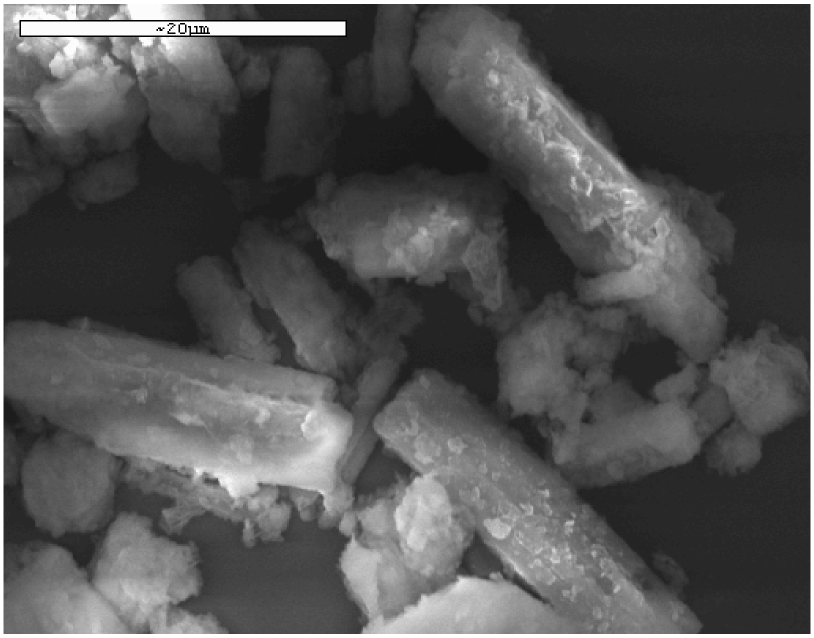

Figure 3. Reagent grade magnesium carbonate at 2,500x magnification.

Batch Experiment Methodology

Batch experiments were conducted using Minnekahta Limestone. Limestone was crushed using a roller crusher and then sieved to various size ranges. Samples of the limestone adsorbent were placed in labeled round-bottomed flasks. Samples were mixed with 100 mL of Keystone Well #4 water (KEY-1 with 52 ppb As). In addition, batch tests included a blank sample of 100 mL deionized water rather than well water. Flasks were secured to a wrist shaker and agitated for 48 hours. After mixing, the samples were filtered with a 0.45 µm filter. The pH and conductivity of the samples were measured. The samples were analyzed by MidContinent Testing in Rapid City, South Dakota for arsenate concentration. Figure 4 shows a typical batch experiment set up.

Figure 4. Photo of a batch experiment on the wrist shaker.

Column Experiment Methodology

Column experiments were conducted using Minnekahta Limestone. Material with a limestone particle size range of 0.2-0.5 mm was used, and a column with manufactured limestone-based granules was also run. The columns were constructed of PVC pipe with 1.5 inch diameter and a length of 12 inches. Influent arsenic solution was the arsenic concentration in water sample KEY-2 (50 ppb dissolved arsenic), Influent was pumped into the column from the bottom up at a constant flow rate. Samples of effluent were collected regularly. The pH and conductivity of the effluent were measured, the effluent was filtered using a 0.45 um filter, and samples were analyzed by MidContinent Testing for arsenate concentration. Figure 5 shows a typical column set up.

Figure 5. Photo of column experiments being run.

Kinetic Study

A kinetic study of arsenic removal over time was completed. A batch solution of one liter of 97 ppb arsenic was mixed with 10 grams of ball-milled Minnekahta Limestone and mixed using a magnetic stirrer. Figure 6 shows the results of sampling from 5 to 90 minutes after initial mixing. The batch test was run longer (up to 24 hours) but the results were invalid as the action of mixing using the magnetic stirrer increased the solution temperature of the mix and desorption of arsenic was observed. This test will be run again using a different method of stirring to eliminate the effects of temperature changes.

The results of this batch test indicate that the amount of arsenic in solution decreases quickly within the first few minutes of the test, and that by 30 minutes of mixing greater than 90 percent of the arsenic is removed.

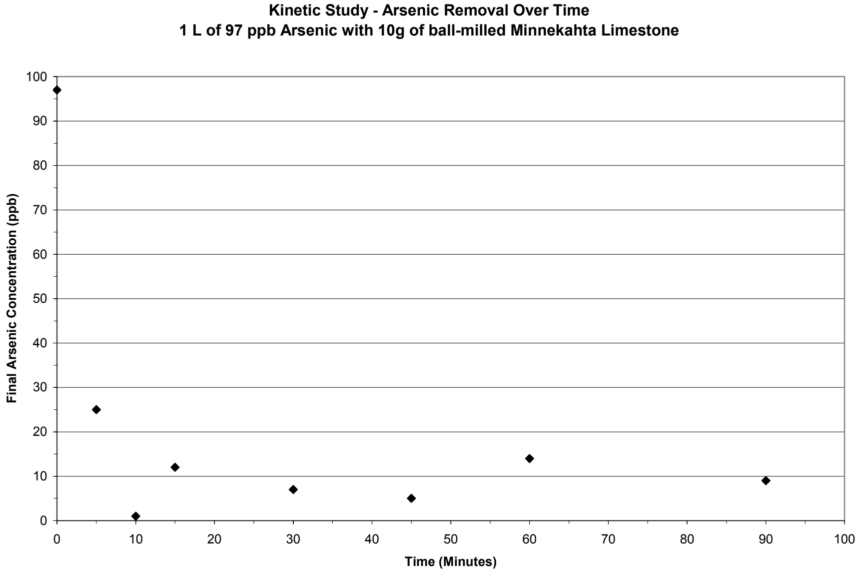

Figure 6. Batch test showing results of arsenic removal over time.

Field Site Work – Keystone, South Dakota

On April 26, 2004, HydroTech Engineering, LLC, presented at the City of Keystone's monthly City Council meeting. The purpose of the meeting was to acquaint the council members with HydroTech Engineering, LLC, and the limestone-based arsenic removal technology. Additional discussions were held on the use of one of the new city wells (Keystone Well #4) for a field testing project. The new city well has been idle since being drilled and tested in 2003 because of higher than allowed naturally occurring arsenic concentrations.

In order to utilize Keystone Well #4, electricity had to be provided to the well. In July 2004, substantial site improvements were made by the private landowner at the well site to prepare for installation of power connections to the pump, which had been left inside the well. Electricity to Keystone Well #4 was installed in September 2004. Figures 7 and 8 are photos of the well site on November 16, 2004. As seen in the site photos, a shed was installed on the site also, for field laboratory use. The wellhead has been plumbed into the shed.

A well dewatering permit was submitted to the South Dakota Department of Environment and Natural Resources and approved in September 2004 in order to discharge water from the well and limestone-treated water. This permit was active through December 2004 and a new permit has been submitted for 2005. Each time the well is pumped, a report is recorded for the permit and these reports are sent monthly to the South Dakota Department of Environment and Natural Resources.

Figure 7. Shed and power installation at Keystone Well #4.

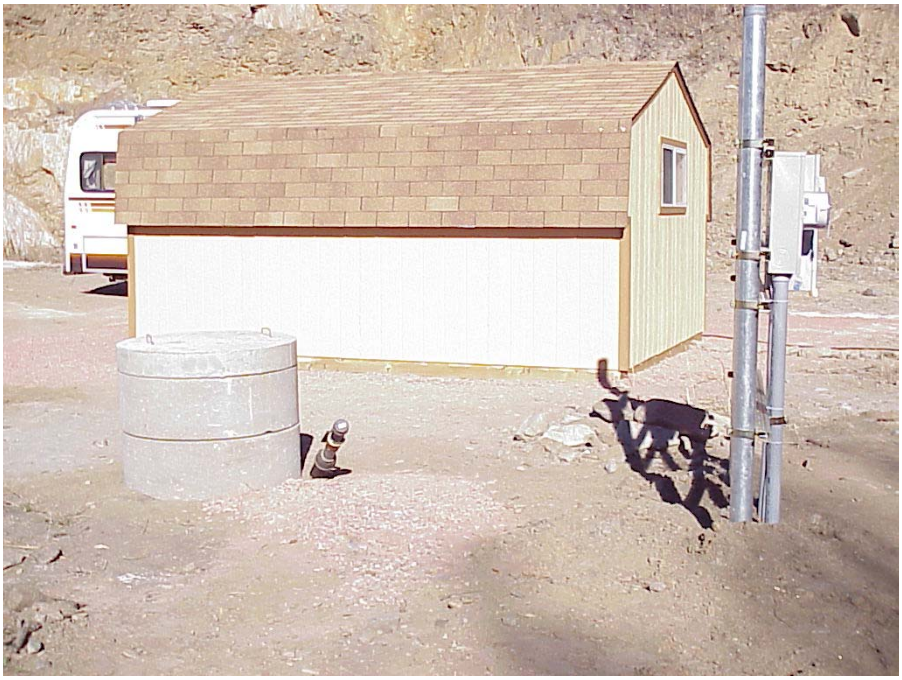

Figure 8. Wellhead of Keystone Well #4. Plumbing into the shed has been completed.

On October 23, 2004, Keystone City Well #4 was pumped for two hours. Temperature and pH were monitored until they achieved a stable value, indicating effluent water was coming directly from the surrounding aquifer. At the end of the pumping period, water was collected for chemical analysis (sample ID KEY-1) and for use in batch experiments. Flow from the well was about 55.5 gallons per minute. Total water pumped from the well over the two hour period was about 6,658 gallons. This amount is about six times the amount of water stored in the well casing. The water coming out of the well was initially very turbid, but at the end of pumping the well water appeared significantly clearer. This well had not been pumped for over a year. Total arsenic of the KEY-1 water sample was 69 ppb, while dissolved arsenic was 52 ppb.

On November 12, 2004, the Keystone City Well #4 was pumped again, this time for one hour and forty minutes. At the end of the pumping period, water was collected for chemical analysis (sample ID KEY-2) for use in column experiments. Flow from the well was about 60 gallons per minute. Total water pumped from the well over the time period was about 6,000 gallons. A water sample was collected and analysis results for both water samples KEY-1 and KEY-2 are presented in Table 4. Total arsenic of the KEY-2 sample was 53 ppb, while dissolved arsenic was 50 ppb. Arsenite analysis was completed on the KEY-2 sample and was found to be 3 ppb.

A preliminary examination of the water quality analyses completed for the Keystone well water does not provide a clear explanation as to why it requires additional limestone to remove arsenic from the well water sample versus from arsenic spiked de-ionized water. Of the dissolved and total metals measured in the water samples, aluminum appears high in the KEY-1 sample. This could be due to clay from the bedrock being in the water samples (clay/silt fines could be seen in the water). When the well was first pumped by the City of Keystone it was pumped for over a week. Water was pumped for only a total of about 3.5 hours during water collection for this investigation. Although

Parameter	KEY-1, Sampled 10/23/04	KEY-2, Sampled 11/12/04
Physical Properties		
Electrical Conductivity	459 µmhos/cm	461 umhos/cm
Hardness	127 mg/L	116 mg/L
Total Dissolved Solids	278 mg/L	252 mg/L
Total Suspended Solids	14.0 mg/L	<5.00 mg/L
Turbidity	4.6 NTU	1.5 NTU
pH	7.90	8.06
Non-Metallics		
Acidity	<10.0 mg/L	<10.0 mg/L
Alkalinity	215 mg/L	217 mg/L
Bicarbonate	263 mg/L	264 mg/L
Carbonate	0.00 mg/L	0.00 mg/L
Chloride	7.50 mg/L	4.50 mg/L
Sulfate	32.1 mg/L	23.8 mg/L
Metals – Total		
Aluminum	0.517 mg/L	0.043 mg/L
Arsenic	0.069 mg/L	0.053 mg/L
Cadmium	<0.001 mg/L	<0.001 mg/L
Chromium	0.005 mg/L	0.001 mg/L
Copper	<0.005 mg/L	<0.005 mg/L
Iron	0.630 mg/L	0.043 mg/L
Lead	<0.001 mg/L	<0.001 mg/L
Lithium	0.069 mg/L	0.058 mg/L
Manganese	0.049 mg/L	0.047 mg/L
Nickel	0.011 mg/L	0.008 mg/L
Selenium	<0.005 mg/L	<0.005 mg/L
Silicon	6.65 mg/L	5.33 mg/L
Strontium	<1.00 mg/L	2.69 mg/L
Vanadium	<0.005 mg/L	<0.001 mg/L
Zinc	<0.050 mg/L	<0.050 mg/L
Metals – Dissolved		
Aluminum	0.105 mg/L	<0.010 mg/L
Arsenic	0.052 mg/L	0.050 mg/L
Cadmium	<0.001 mg/L	<0.001 mg/L
Calcium	27.3 mg/L	23.6 mg/L
Chromium	<0.001 mg/L	<0.001 mg/L
Copper	<0.005 mg/L	<0.005 mg/L
Iron	<0.050 mg/L	<0.050 mg/L
Lead	<0.001 mg/L	<0.001 mg/L
Lithium	0.058 mg/L	0.058 mg/L
Magnesium	14.4 mg/L	13.8 mg/L
Manganese	0.044 mg/L	0.047 mg/L
Nickel	0.008 mg/L	0.008 mg/L
Selenium	<0.005 mg/L	<0.005 mg/L
Silicon	6.38 mg/L	5.21 mg/L
Sodium	56.0 mg/L	62.5 mg/L
Strontium	<1.00 mg/L	1.33 mg/L
Vanadium	<0.005 mg/L	<0.001 mg/L
Zinc	<0.050 mg/L	<0.050 mg/L

Table 4. Water quality analysis of Keystone City Well #4 (sample IDs KEY-1 and KEY-2). Water sample KEY-1 was collected on October 23, 2004, and water sample KEY-2 was collected on November 12, 2004.

total suspended solids (TSS) are not high for these samples, the water samples sent for analysis could have been collected or analyzed after fines had settled out, skewing the TSS measurements. The clay and silt sized particles in the water could be interfering with the sorption sites on the limestone surface, limiting adsorption.

In previous research completed using the interference ions chloride, nitrate, and sulfate, some influence by interference ions on arsenic removal by limestone was observed. For Cl^-, NO_3^-, and SO_4^{2-} as interference ions, each batch test used 1 gram of ball-milled Minnekahta Limestone fines and 100 mL of 100 ppb arsenic solution. Batch tests were performed with increasing amounts of Cl^- (0 ppm, 51 ppm, 205 ppm, 600 ppm, and 1230 ppm) as the interference ion, increasing amounts of NO_3^- (0 ppm, 12 ppm, 46 ppm, 136 ppm, and 255 ppm) as the interference ion, and increasing amounts of SO_4^{2-} (0 ppm, 42.4 ppm, 182 ppm, 537 ppm, and 1120 ppm) as the interference ion. With no interference ion, 1 gram of ball-milled Minnekahta Limestone removed about 82 percent of the arsenic in solution (final concentration 18 ppb). With increasing amounts of Cl^- in solution, final arsenic concentrations in solution increased to about 27 to 43 ppb as compared to the 18 ppb final concentration of limestone not exposed to interference ions. With increasing amounts of NO_3^- in solution, final arsenic concentrations in solution increased to about 35 to 46 ppb. Also, with interference ions present, the standard deviations increased greatly for the final arsenic concentrations. With increasing amounts of SO_4^{2-}in solution, final arsenic concentrations in solution increased to about 18 to 22 ppb, although the final arsenic concentration decreased to about 15 ppb with the addition of 537 ppm SO_4^{2-}. In general, SO_4^{2-} had a very limited influence on the final arsenic concentrations and does not appear to interfere with arsenic removal by limestone.

Batch Experiments

Batch experiments using Keystone City Well #4 were completed to evaluate the effectiveness of using limestone and additives (such as magnesium carbonate) for removing arsenic from a natural water source. Batch tests using 0.1, 0.5, 1.0, and 2.0, 4.0, 6.0, and 8.0. and 10.0 grams of ball-milled Minnekahta Limestone in 100 mL of Keystone well water (sample ID KEY-1) were completed and results are shown in Figure 9. Two grams of limestone removed about 33 percent of the arsenic in solution. In comparison, 1.5 grams of ball-milled limestone removed about 86 percent of the arsenic from a 100 ppb mixed arsenic solution. At 10 grams of limestone, percent arsenic removal was about 64 percent. A water sample from the well (sample ID KEY-2) was analyzed for arsenite and had a concentration of 3 ppb. It does not appear that the reduced arsenic removal from the well water as compared to a mixed arsenic solution is due to arsenite. Further evaluation of the well water analysis profile and batch and column testing will be required to determine the cause of reduced arsenic removal when using natural water.

Batch experiments using Keystone City Well #4 and magnesium carbonate were also completed. Batch tests using 0.1, 0.5, 1.0, and 2.0 grams of reagent grade magnesium carbonate in 100 mL of Keystone well water were completed and results are shown in Figure 10. Two grams of magnesium carbonate removed about 85 percent of the arsenic in solution.

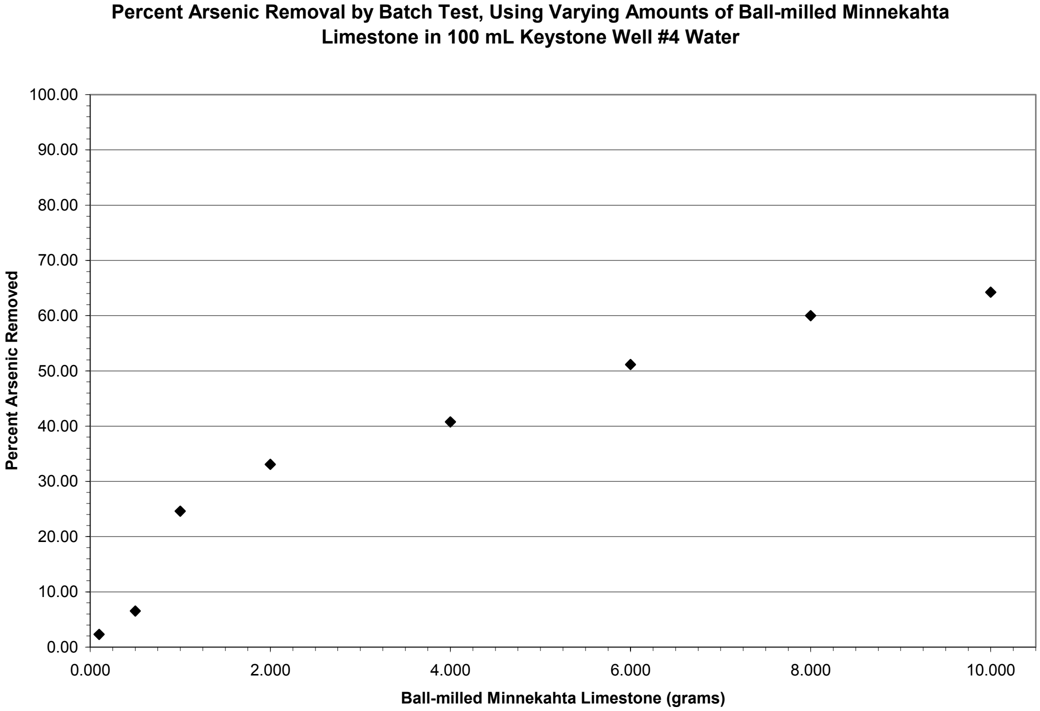

Figure 9. Percent arsenic removal by batch test using varying amounts of ball-milled Minnekahta Limestone in 100 mL of Keystone Well #4 water.

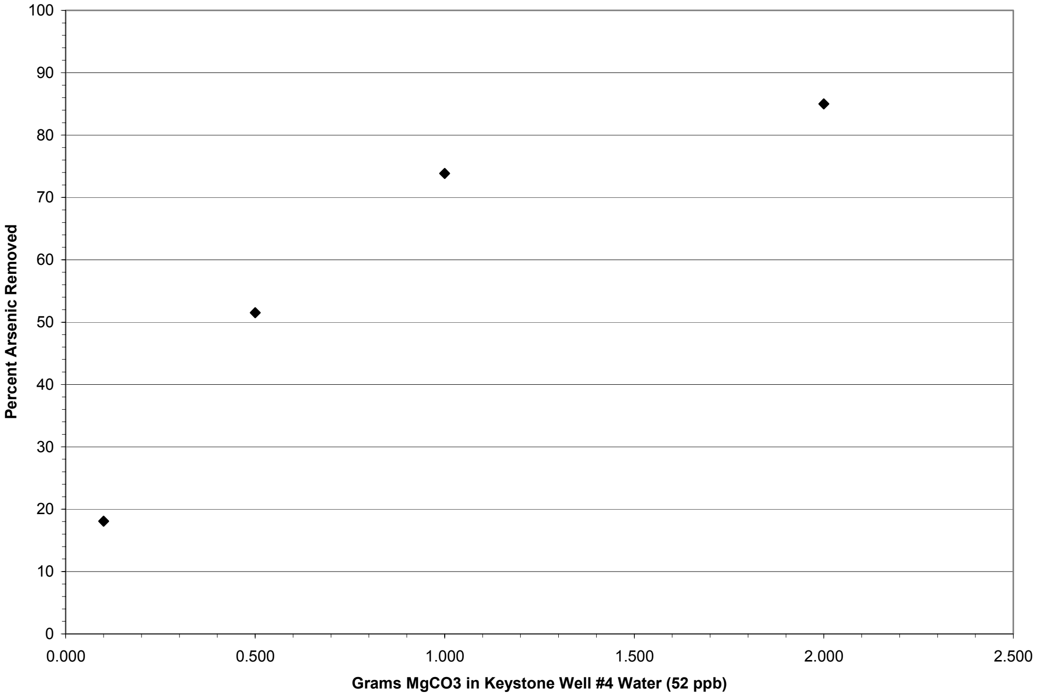

Figure 10. Percent arsenic removal by increasing amounts of magnesium carbonate (0.1-2 grams). Starting solution was 100 mL of well water from Keystone City Well #4.

Column Experiments

Two column studies were completed to examine the efficiency of arsenic removal by crushed limestone and manufactured limestone-based granules from Keystone well water. One column (C-15) was run with 0.2-0.5 mm sieve size Minnekahta Limestone and the other column (C-16) was run with manufactured limestone-based granules (containing Minnekahta Limestone, Portland cement binder, and reagent-grade magnesium carbonate). Both columns were run with water sample KEY-2 (50 ppb dissolved arsenic). Column size for C-15 was 12 inches long by 1.5 inch diameter and column C-16 was 12 inches long by 1 inch diameter.

The purpose of granulation of the limestone material is to increase the limestone surface area relative to the size of the limestone particle. Fine limestone material cannot be used as a filter media in a flow-through column filter system (due to reduced flow-through capacity of the material at grain sizes less than 0.2 mm in diameter). Limestone was granulated in order to maintain high surface area but allow flow through of water. The process of agglomeration was used to form the granules. Agglomeration takes fine materials and forms them into spherical granules. A binder is added to the material mix to bond the individual particles together and to strengthen the granules. Agglomeration significantly increases material surface area without compromising flow through rates. Water is sprayed into the limestone/binder mix and the mixture is tumbled until granules form. The granules are sieved and dried in a curing room. The granules are firm enough to hold their shape in a column and do not disintegrate when exposed to water because the binder used is insoluble. Additives can also be added to the dry mixture in order to enhance arsenic removal efficiency. Limestone agglomeration techniques were derived from the work of McClellan et al. (2002), in which limestone was granulated for purposes of producing an aggregate for incorporation into concrete. Figure 11 is a photo of manufactured limestone granules.

Figure 11. Photo of manufactured granules.

A column of 0.2-0.5 mm sieve size washed Minnekahta Limestone was packed with 587.208 grams of material. Figure 12 is a plot of the measured effluent arsenic concentration during the total run time of 1,620 minutes (27 hours). Breakthrough at 10 ppb occurred prior to the first sampling at 60 minutes. Flow through the column was 2.8 liters per hour (eight bed volumes per hour). About 75.5 liters of water passed through the column by the end of the experiment (column material was exhausted). This corresponds to about 217 bed volumes. Based on 75.5 liters of well water being treated by about 587 grams of limestone, it is estimated that a total of about 0.004 grams of arsenic was treated and that about 0.0065 micrograms of arsenic were treated by each milligram of limestone. This sorption capacity estimate indicates that the limestone under these conditions had a low capacity. In comparison, one study (Chang et al., 2004) estimates that granular ferric hydroxide has a sorption capacity of 2.51 ug/mg and activated alumina has a sorption capacity of 0.56 ug/mg.

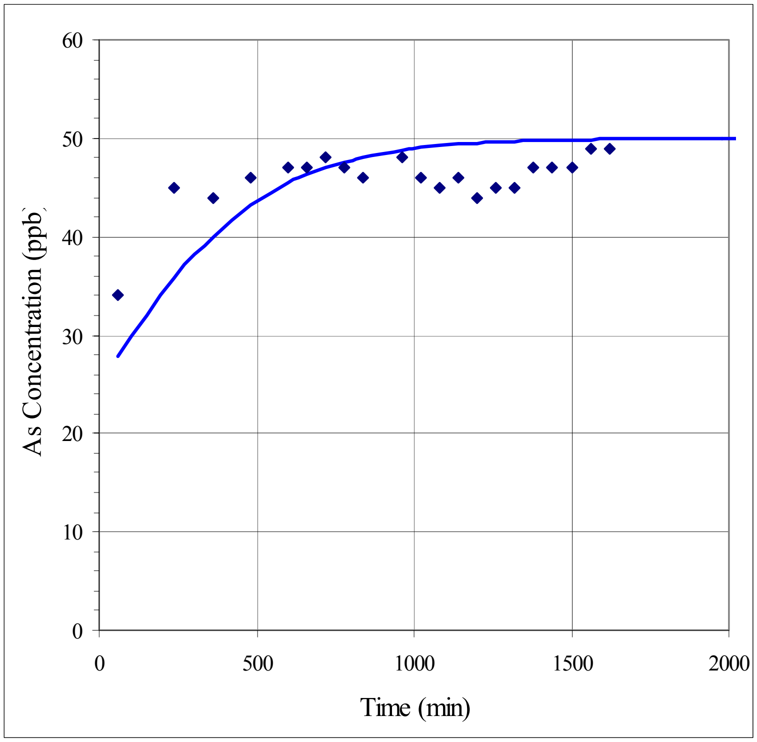

Figure 12. Results of column C-15 study using 12 inch by 1.5 inch diameter column, Minnekahta limestone, sieve size 0.2-0.5 mm, influent arsenic concentration 50 ppb in KEY-2 water sample, and a flow rate of 8 bed volumes/hour (2.8 L/hr).

A column of 1-2 mm diameter manufactured limestone-based granules was packed with 168.681 grams of material. The granules consisted of 87 percent ball-milled Minnekahta Limestone, 10 percent Portland cement binder, and 3 percent reagent grade magnesium carbonate. Figure 13 is a plot of the measured effluent arsenic concentration during the total run time of 1,620 minutes (27 hours). Breakthrough at 10 ppb occurred prior to sampling at 60 minutes. Flow through the column was 1.23 liters per hour (eight bed volumes per hour). About 33 liters of water passed through the column before the experiment was ended (column material was close to exhaustion). This corresponds to about 217 bed volumes. Based on 33 liters of well water being treated by about 168.7 grams of limestone, it is estimated that a total of about 0.0017 grams of arsenic was treated and that about 0.01 micrograms of arsenic were treated by each milligram of limestone. This sorption capacity estimate indicates that the limestone under these conditions had a low capacity, although it is an improvement of 1.5 times over the sorption capacity of the column experiment C-15 that was run with crushed limestone.

Since breakthrough at 10 ppb was not observed in either column, it is suggested that the column flow through rates were too high and the columns should be run again with either larger columns or slower flow through rates.

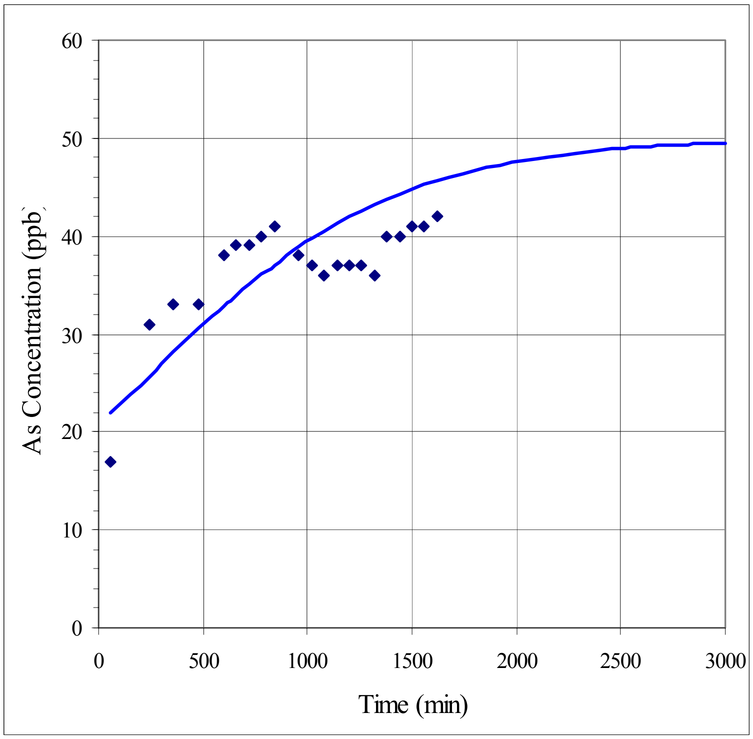

Figure 13. Results of column C-16 study using 12 inch by 1 inch diameter column, manufactured limestone-based granules as the adsorbent, size 1-2 mm, influent arsenic concentration 50 ppb in KEY-2 water sample, and a flow rate of 8 bed volumes/hour (1.23 L/hr).

Conclusions

The Keystone Well #4 water was characterized and a preliminary examination of water quality was completed. Laboratory trials (batch and column experiments) were completed to characterize the removal efficiency of limestone under natural water conditions. Previous research has involved only water spiked with arsenic, or water spiked with arsenic and a second metal, or water spiked with arsenic and one interference ion. It was expected that arsenic removal efficiency would be reduced when limestone was used to treat natural water. However, the reduction in efficiency seen in this research was higher than anticipated. It is suspected that the Keystone well water has many fines in it from its bedrock aquifer source. Extensive pumping of the well to refresh the aquifer water may assist in reducing the amount of clay fines in the water, and thus improve the arsenic removal efficiency seen by limestone treated with Keystone well water.

Batch experiments using Keystone Well #4 water and ball-milled limestone removed about 65 percent of the arsenic in solution when 10 grams of limestone adsorbent was used. In comparison, 1.5 grams of ball-milled limestone removed about 86 percent of the arsenic from a 100 ppb arsenic solution. However, arsenic removal by reagent-grade magnesium carbonate was more effective. Two grams of magnesium carbonate removed 85 percent of the arsenic in the well water. Column experiments using crushed limestone (sieve size 0.2-0.5 mm) and manufactured limestone-based granules were completed and sorption capacities of the two materials were estimated. Manufactured limestone-based granules has a sorption capacity about 1.5 times greater than crushed limestone, although both sorption capacities are low when compared to established technologies such as granular ferric hydroxide and activated alumina.

This research included significant infrastructure improvements at the well site. Electricity was brought onto the site, the well was wired up, dirt work was done to level the site, and a shed was installed onsite as a field laboratory. This work took longer than expected and shortened the time available for field testing. Field trials still need to be conducted that test non-aerated well water (water directly from the well), and a scaled-up field test needs to be completed.

Future Work

Following is a list of activities for future work. This research project has merit and will be continued as resources become available.

1. Pump Keystone well for an extended period of time (at least one week) to clean out silt from the well water. This may be the source of low arsenic removal efficiency by the limestone and is easy to test.
2. After extended pumping, complete preliminary batch tests and compare results to batch tests completed for this research to see if there is an improvement in arsenic removal efficiency.
3. Complete additional column studies to determine breakthrough at 10 ppb and total arsenic removal by the column material.
4. Scale up column size based on column study results and test a larger quantity of crushed limestone, and, if possible, manufactured limestone granules. Testing with granules will require additional manufacture of the granules.
5. Scale up column size again if possible and install on site for field testing at increased flow rates.

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