

Report for 2001SD1541B: Arsenic Remediation of Drinking Water: Phase II

- Other Publications:

- Pogany, Michael, 2001, Natural adsorbate removal of arsenic for improved water quality: Final technical report, Research Experiences for Undergraduates, National Science Foundation Summer Program, South Dakota School of Mines and Technology.
- Davies, Laura, 2001, Pelletization of limestone fines for use as an arsenic adsorption medium: Final technical report, Research Experiences for Undergraduates, National Science Foundation Summer Program, South Dakota School of Mines and Technology.

Report Follows:

INTRODUCTION

This research represents Phase II of an on-going project to investigate removal of arsenic from drinking water. Arsenic is harmful to human health in relatively small amounts. The United States Environmental Protection Agency (EPA) recently announced the lowering of arsenic's maximum contaminant level (MCL) to 10 parts per billion (ppb) by 2006. This reflects the harmful nature of arsenic, especially inorganic arsenic. The lower MCL will affect water suppliers and users in many regions of the United States. Figure 1 shows counties with water supplies that will be affected by the new arsenic MCL; darker areas have higher arsenic concentrations (Focazio et al., 2000).

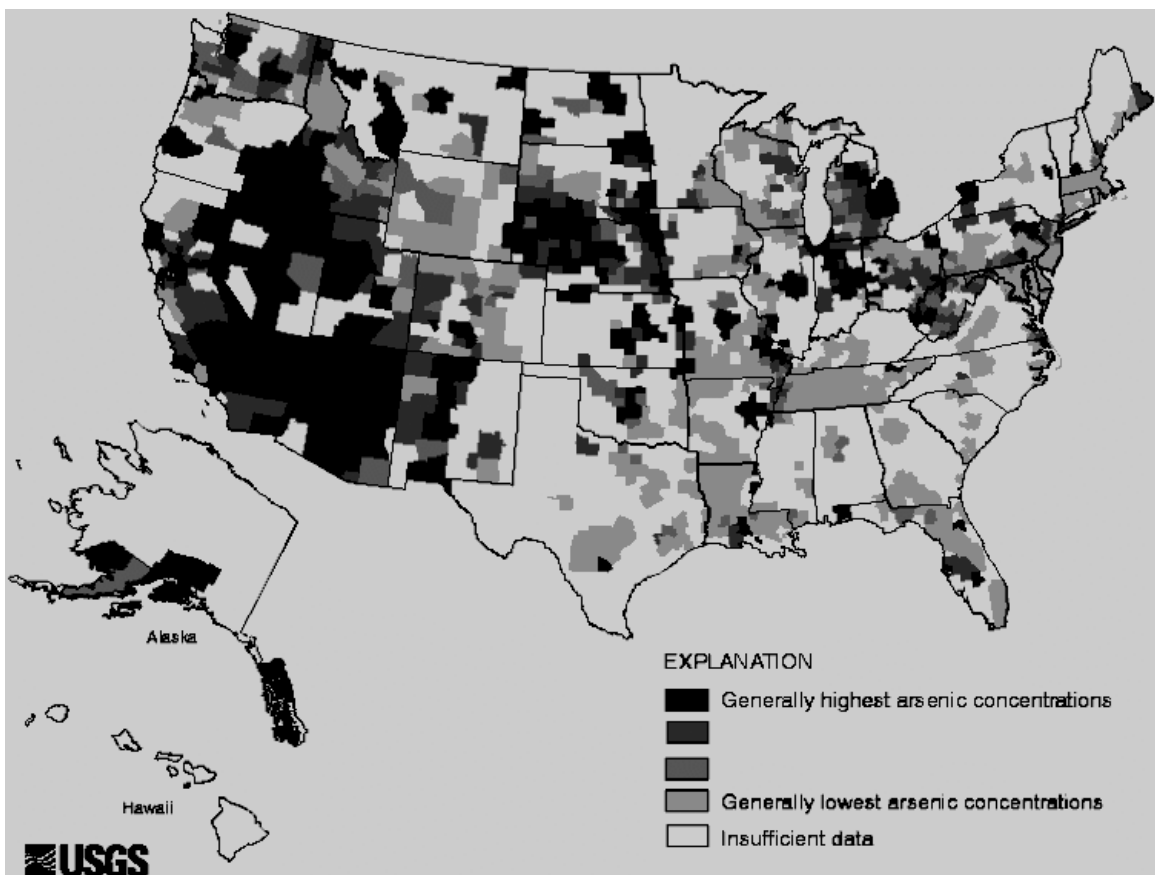


Figure 1. Counties in the U.S. with elevated arsenic concentrations (from Focazio et al., 2000).

The cost of current arsenic removal technologies is quite high (Frey et al., 1998). For example, the American Water Works Association (AWWA) has estimated the cost of decreasing the arsenic standard to 10 ppb in South Dakota at \$8.25 million. Generally, larger water systems have the financial resources necessary to meet the expenses and technical demands involved. Smaller suppliers and private well users are likely to be unable or unwilling to implement current arsenic removal methods. Using limestone to precipitate arsenic out of solution could be an inexpensive, viable alternative.

This report, representing Phase II of arsenic removal research, included batch experiments, column experiments, Toxicity Characteristic Leaching Procedure tests, sintering and pelletizing of material, and scanning electron microscopy. In Phase I work, a significant literature review has been conducted on arsenic's uses, history, background exposure, toxicity, and distribution. Experiments investigated the ability of limestone to remove arsenic from a solution of arsenic and deionized water, hereafter referred to as standard solution. Procedures and results are summarized below.

BATCH EXPERIMENTS

The majority of batch experiments performed in this research were conducted by using Minnekahta Limestone from a quarry in Rapid City, South Dakota. Limestone was provided by Pete Lien and Sons, Inc., in coarse rock size (2-4 cm). The limestone then was crushed with a rock crusher and sieved to three uniform particle sizes:

- | | | |
|------------|---------------|---------|
| 1) 8 mesh | >2.362 mm | ~2 mm |
| 2) 16 mesh | 2.362-1.18 mm | ~1-2 mm |
| 3) 35 mesh | 1.18-0.425 mm | ~0.5 mm |

The 0.5 mm fines were the predominant adsorbent used in the batch experiments as well as in the later pelletization process. The smaller particle size increased the allowable surface area per gram of adsorbent (m^2/g).

Batch experiments were conducted according to the methods described in Appendix A. Experiments included different limestone types, different pH pre-adjustment, and introduced interferences from Cl^- and SO_4^{2-} ions.

Comparison Between Different Limestone Samples

Currently, little is known about the chemical kinetics or mechanism responsible for the adsorption of arsenic by limestone. These mechanisms were explored during this phase of the research project. Chemical compositions of different limestone formations could be responsible for improved arsenic removal. Therefore, three different sources of limestone were tested for their respective removal efficiencies at variable mass quantities. The three limestone sources included:

- 1) Minnekahta Limestone from the Pete Lien and Sons quarry at Rapid City, South Dakota. Material was crushed and sieved to 35 mesh $\sim 0.5\text{mm}$ (SEM average particle size $\sim 4\text{-}15\ \mu\text{m}$).
- 2) Minnekahta Limestone from the Pete Lien and Sons quarry. This was waste rock dust from industrial rock crusher ($10\text{-}25\ \mu\text{m}$).
- 3) Pahasapa (Madison) Limestone sample acquired from SDSM&T chemical storage. The sample dates from 1938 and was taken from “a formation near the Rimrock Highway below the old white schoolhouse.” This location is west of Rapid City, South Dakota.

Batch experiments were conducted with 100 ppb arsenic standard solutions with each limestone, varying the amount of adsorbent used. Figure 2 depicts the removal efficiencies of these samples.

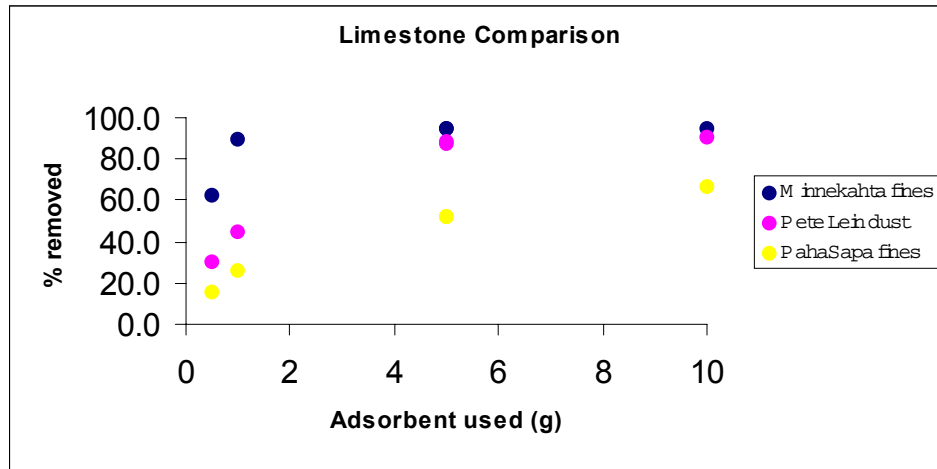


FIGURE 2. Removal efficiencies of various limestone samples.

Removal down to the detection limit of 5 ppb was achieved in the Minnekahta sample at 5.0 g. The removal efficiency therefore was greater than 95%.

Experiments on pH Dependence

In early phases of this work, the pH of the arsenic solution was pre-adjusted to approximately 8.0. This was done primarily to simulate “real-world” ground-water and surface-water pH values. However, pH values of sites with high arsenic concentration are not always within this range. For example, acidic mine drainage (AMD) can have pH values in the ranges of 1 to 5. Therefore, the effectiveness of arsenic removal was explored in the acidic and basic range of pH conditions. A batch experiment was conducted to simulate pH conditions in the range of $4 \leq \text{pH} \leq 10$. Ten grams of limestone (1-2 mm) were agitated with a 100 ppb arsenic solution at varying pH values. Samples

were studied at every 0.5 pH unit for the range $4 \leq \text{pH} \leq 6$ and $8 \leq \text{pH} \leq 10$, and then compared with work from Phase I of this project (Davis and Webb, 2001), in which the pH range varied between 6 and 8. Figure 3 shows the results of pH dependence.

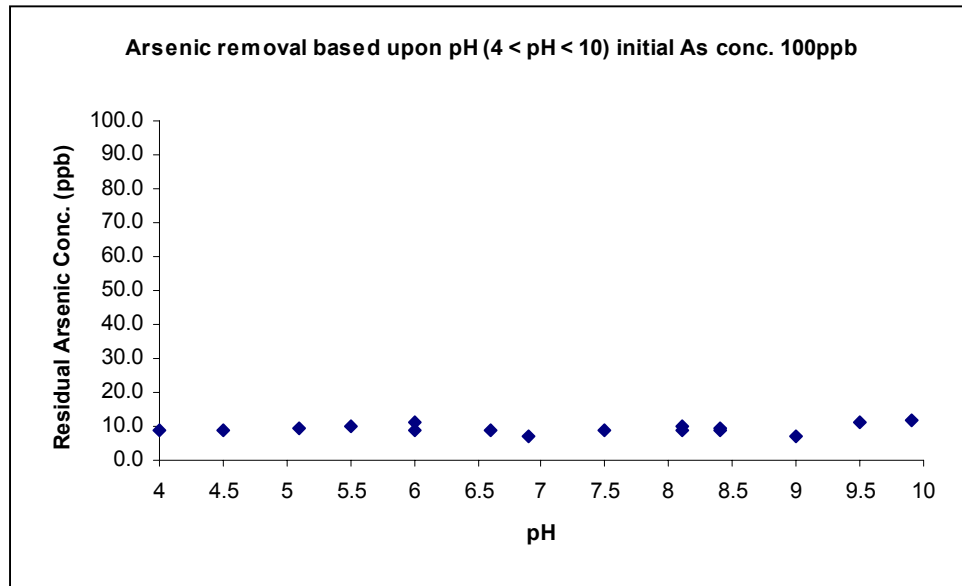


FIGURE 3. Residual arsenic concentration versus initial pH value.

Results indicate that the initial pH of the arsenic solution has very little impact upon the arsenic removal. One possible reason could be that the buffer, created by the carbonate ion present in the limestone, negates the dependence of initial pH upon arsenic removal.

Introduced Interference Study

Field water quality issues such as high total dissolved solids (TDS) and dissolved trace elements are usually absent in the laboratory setting, where all solutions are typically prepared using distilled-deionized water (DI-H₂O), or water that has undergone

some type of reverse osmosis or nanofiltration. All solutions prepared to this point of the research had previously used deionized water.

Concentrations of chlorides and sulfates in ground and surface water can be in the 3 to 30 ppm range or greater, which could interfere with the adsorption process. A batch experiment was conducted to explore these possible interferences and their effects upon arsenic removal. Solutions of 100 ppb arsenic were prepared with interferences as listed below and reagent grade NaCl and NaSO₄ were used for interference solution preparation.

S1	100 ppb As	+	5 ppm Cl ⁻	+	1.0 g Limestone
S2	100 ppb As	+	5 ppm Cl ⁻	+	5.0 g Limestone
S3	100 ppb As	+	10 ppm SO ₄ ²⁻	+	1.0 g Limestone
S4	100 ppb As	+	10 ppm SO ₄ ²⁻	+	5.0 g Limestone

The chloride in the samples was precipitated before analysis by using 0.1M AgNO₃. The addition of AgNO₃ to the samples was to try to precipitate any chlorides before inductively coupled plasma – mass spectrometry (ICP-MS) analysis. Because of problems associated with this method, samples were analyzed by graphite furnace – atomic absorption (GFAA). The samples then were compared to the standard solutions. Results are shown in Table 1, below.

TABLE 1. Introduced interference results.

Sample #	Gram Quantity	% removal
S1	5ppmCl 1	> 94.8 AgNO3 added
S2	5ppmCl 5	> 94.8 AgNO3 added
S3	10ppmSO4 1	79.0 AgNO3 added
S4	10ppmSO4 5	> 95.0 AgNO3 added
S5	standard with 5ppm Cl (96 ppb)	standard
S6	standard w/10ppm SO4 (100 ppb)	standard
S7	standard with 5ppm Cl (90 ppb)	standard AgNO3 added
S8	standard w/10ppm SO4 (81 ppb)	standard AgNO3 added

Results from this study indicate little or no appreciable effect of introduced species on arsenic removal. The addition of Cl⁻ appeared to slightly enhance the removal of arsenic for sample S1. Typically, the removal of arsenic with one gram of adsorbent is about 80 to 90%, which, as demonstrated here, is below detection limits (> 94.8% or 5 ppb). This experiment could be repeated with the introduction of additional species such as nitrate or phosphate, or using waters high in dissolved species and introduced arsenic.

Alternative Materials Testing

Although the limestone material was effective for arsenic removal, alternative materials also were tested for their adsorptive abilities. The primary motivation for this batch experiment was to find alternative materials that potentially could be used for a pellet binding material or a doping agent to improve removal efficiency. A commercial anion exchange resin also was explored to compare to an equivalent limestone sample. Alternative materials chosen for experimentation are listed below. Table 2 lists results of the batch experiment.

- 1) 5.0 g WyoBen Bentonite 200 mesh (Mills, Wyoming) +100 ppb As
- 2) 5.0 g activated charcoal ~200mesh +100 ppb As
- 3) 5.0 g CaSO₄ (gypsum) anhydrous powder +100 ppb As
- 4) 5.0 g iron [III] oxide powder +100 ppb As
- 5) 5.0 g Dowex® anion exchange resin +100 ppb As

TABLE 2. Alternative materials testing. Initial arsenic concentration 100 ppb.

	Material	Grams	% removal
S1	Bentonite	5	non-filterable no results
S2	Charcoal	5	95.7
S3	CaSO ₄	5	66.3
S4	Fe ₂ O ₃	5	98.4
S5	Dowex	5	68.7

The results above should be viewed with caution. Although the ICP-MS was used for these arsenic determinations, it was later determined through standard solution confirmation that results might have been biased because of chloride interference. A second sample run on GFAA was not possible because sample volumes were not sufficient for determination. Results should be considered with this possible interference in mind.

CONTINUOUS FLOW EXPERIMENT

An adsorption column has been used in earlier phases of this research and will ultimately be explored further. Prior work had focused on gravity feed arsenic removal with vertical columns. Concentrated arsenic solutions were added in numerous volumes in the top of the column, and samples were taken from the bottom. Pore volumes were

recorded and residual arsenic recorded until column breakthrough. Another application of the column concept in this phase of the work used a continuous flow reactor vessel.

The reactor was a cylinder with an input tube directing water into the bottom of the vessel. Limestone (1.0 kg of 1-2 mm Minnekahta fines) was placed in the bottom of the vessel, and a standard arsenic solution was forced up through the rock. In the middle of the vessel was a PVC reservoir (1½” pipe, ~5 in. length) that acted as a “flushing mechanism.” When full, the water was directed out of the reactor through a tube. This tube was connected directly to the arsenic reservoir (1.0 L Nalgene bottle). An exit tube from the arsenic reservoir was connected to a centrifugal pump, which was driven by an ordinary ½” variable-speed drill. The exit or dump tube was connected to the input on the reactor vessel.

The speed control was variable and the flow rate was controlled with a clamp. For this experiment, the flow rate was set at ~1.0 L/min to allow adequate circulation in the system. The setup was run for 24 hours with 3.0 L of 100 ppb arsenic solution, and small aliquots were taken at set time intervals to determine the effectiveness of the method. Figure 4, below, shows the results of the continuous flow reactor.

A unique result was demonstrated in the analysis of the continuous flow reactor. The arsenic in the system has reached a “quasi” equilibrium, or saturation with the limestone adsorbent. It also shows that a majority of arsenic removal in the system occurred within the first few hours. Although not completely successful (with respect to total arsenic removal), the data indicates a process that removes a majority of the arsenic relatively quickly. This is a positive outcome, and applications to a large-scale process should be explored further.

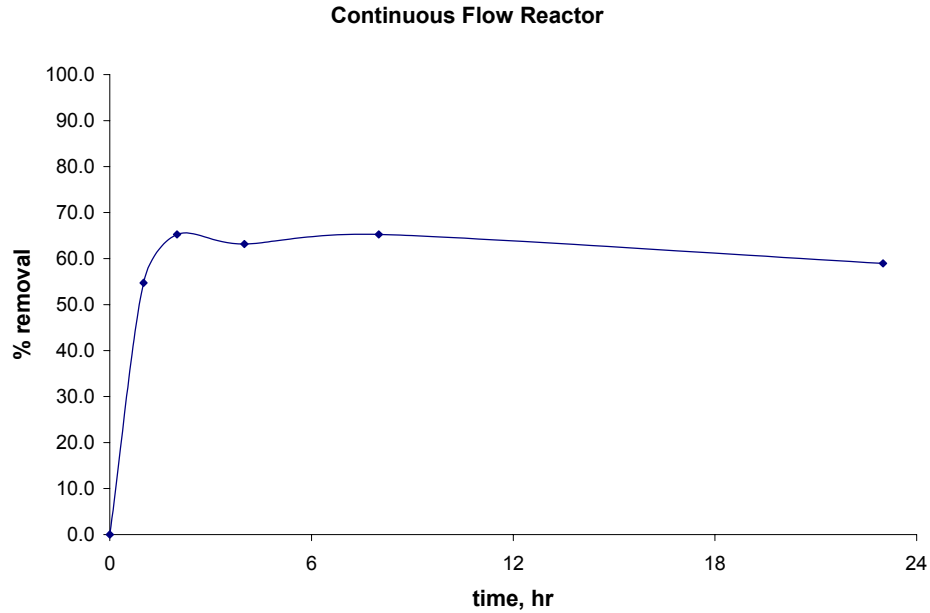


FIGURE 4. Continuous flow reactor arsenic removal with respect to time.

PLATE-AFFIXED BATCH REACTOR

Initial difficulties encountered with binding of material in the pelletization process (described below) prompted investigation of affixing methods for the limestone. This included the use of a silicone sealant/adhesive to affix sulfonated biomasses to Plexiglas plates for cadmium removal of aqueous solutions. A 100% silicone rubber sealant (food grade) DAP (Dow Chemical Corp.) was spread on a Plexiglas plate and limestone was attached as evenly as possible to the glued surface. The plate was allowed to dry overnight, and then was rinsed in DI-H₂O, to remove any non-affixed limestone. It is believed that approximately < 1.0 g of adsorbent actually adhered to the plate. The plate then was submerged in 400 mL (600 mL beaker) of 100ppb arsenic solution and placed upon a magnetic stir plate. Figure 5 shows the setup.



FIGURE 5. The plate affixed batch reactor.

The stir rate was sufficient enough to produce continuous surface motion. The batch reactor then was covered with plastic wrap and allowed to stir for 48 hours. An aliquot was taken for elemental analysis. Results are shown below in Table 3.

TABLE 3. Plate affixed batch reactor results (48hrs.).

Sample #	Residual Arsenic ppb	% removal
Standard	89	
S1	66	25.8

The plate-affixed batch reactor result indicates modest arsenic removal. Assuming that one gram of adsorbent was affixed to the plate, it removed a considerable amount of arsenic compared to the volume of solution (400 mL). The plate reactor method could be explored further by submerging additional plates (three or more) simultaneously, and exploring the application of recycling of the adsorbent plates for arsenic removal.

PELLETIZATION AND ARSENIC REMOVAL

A long-term goal of this research project is to develop a marketable product for arsenic removal in domestic drinking water supplies that are contaminated with arsenic concentrations exceeding U.S. EPA drinking water quality regulations. Pelletization of limestone fines is a step toward the overall goal because it could improve adsorption efficiency and handling. Various methods of pelletizing and sintering limestone and other materials are described in sections below.

This research also explored binders including bentonite clay, cement, and gypsum as possible agents to bind limestone particles into pellets. The attempts of these “natural binders” was to find a binding agent that could be added to the limestone, mixed with water, and pelletized under low pressure.

Several pellets of different percentage compositions of limestone and selected binders were attempted with nominal success. Pellets of satisfactory structural integrity were obtained (bentonite was the most successful binder), but dissolution was observed when pellets were subjected to water submersion. Portland cement (Hills Materials Mortar Reddi-Mix, Rapid City, South Dakota) was a poor binder of limestone. Because cement is partially the product of limestone decomposition, it is likely that a chemical reaction occurred between cement and limestone in slurry, degrading the structural integrity of the concrete.

Ball-Milling Procedure

In order to begin research on the pelletization process of limestone, fines were prepared from limestone rocks. To do this, limestone rocks were crushed with a rock

crusher. Then they were put through a sieve and separated, with the following grain diameters: fines greater than 2.362 mm in diameter, fines between 2.362 mm in diameter and 1.18 mm in diameter, fines between 1.18 mm in diameter, and 0.425 mm in diameter, and fines with a diameter less than 0.425 mm. For the ball-milling procedure, the fines with a diameter less than 0.425 mm were used.

In preparation for ball-milling the fines, a ceramic container was rinsed with water, approximately one cup of the fines to be ball-milled, and ceramic beads. This container was placed on a bottle roller for six hours. These rinse fines were filtered out with de-ionized distilled water. Next, the container was refilled, first with the ceramic beads and fines and then with de-ionized distilled water, leaving approximately one inch of air at the top of the container before putting the lid on and placing it onto the bottle roller for six hours. When this was complete, the fines were separated and dried.

Sintering

Sintering was used to make pellets for an adsorption column. Sintering essentially welded the limestone fines together, creating a stronger pellet that would hold together in water yet contain pore spaces for water to flow through. Sintering was performed at high temperatures just below the melting point of the limestone. Sintering decreased surface energy by decreasing the surface area present as the fines welded together. This improved the mechanical and physical properties of the limestone fines, in this case increasing strength and preventing disintegration in water. Previous research indicated that 850° C would be a good temperature at which to begin sintering trials on the limestone fines.

Trials P5, P6, and P7

Initial trials, P5, P6, and P7, were unsuccessful. These pellets were heated to approximately 820° C for about one hour. Each pellet showed signs of decomposition. The pellets were white and crumbly. To test for problems, the pellet was dissolved in water. It had a very basic pH, leading to the conclusion that calcium carbonate had decomposed in the heating process to become calcium oxide or lime.

Trial P8

Trial P8 provided the first successful experiment in pellet preparation. Twenty grams of limestone fines and three milliliters of de-ionized H₂O were combined using a hydraulic press with a pressure of 10,000 lb/in² for one minute. The pellet then was placed in an oven and heated to a temperature of 570° C over a four hour and fifty-two minute time period. The pellet was then cooled in a CO₂ environment for 24 hours. This procedure produced a noticeably harder and stronger pellet. P8 also was placed in water to see if it would disintegrate. It held its shape and remained hard. Pellets similar to P8 were produced for later comparison experiments to test the arsenic adsorption abilities of this pellet.

Trials P9 and P11

Trials P9 and P11 explored whether the pellet could be strengthened at temperatures lower than 500° C. Although heating the pellets to 430° and 300° C made them harder, when compared to P8, they broke more easily and disintegrated in water more readily.

Trials P10, P12, P13, and P14

Trials P10, P12, P13, and P14 were unsuccessful. They involved the use of a polyethylene glycol (PEG) in combination with the limestone, held together using paraffin wax. Originally, the plan was to heat the pellet enough to volatilize the wax and then heat it to a slightly higher temperature, allowing sintering to occur. However, these pellets crumbled after heating, leading to the conclusion that the wax had not been completely volatilized during the heating process. Trial P12 had to be cancelled in the heating process because it released large amounts of smoke and vapor when heated to about 200°C and there was concern about a fire. It was hypothesized that the wax caused the problems; therefore, successive polymer trials were completed by using water and pressure to produce pellets rather than using waxes for binding.

Trials P21a, P22a, P23a, P24a, P25a, P26a, and P27a

Trials P21a, P22a, P23a, P24a, P25a, P26a, and P27a explored the temperature limit for sintering by heating to a temperature of 630°C. This temperature appeared to be too high for successful pelletization. All the pellets looked very much like the calcium oxide results from P5, P6, and P7.

Trials P16a, P16b, P17a, P17b, P18a, P18b, P19, and P20

Trials P16a, P16b, P17a, P17b, P18a, P18b, P19, and P20 involved experimentation with pellet shape and less pressure during pellet formation. This technique used more water to hold the pellets together and hand pressure to roll the pellets into a spherical shape. These pellets were placed in the oven for heating to a

temperature of 500° and 550° C. Then the pellets were cooled in a CO₂ environment. These pellets were strong and did not disintegrate when placed in water. They were not as strong as the pellets produced using the hydraulic press, but they retained strength. It was hoped that these pellets could be made more porous, enabling them to adsorb arsenic better. Further trials, making pellets in a similar manner, were conducted to test the ability of these pellets to adsorb arsenic.

Trials P21b, P22b, P23b, P24b, P25b, P26b, and P27b

Trials P21b, P22b, P23b, P24b, P25b, P26b, and P27b were experiments to compare different compositions of limestone, limestone and bentonite, and limestone and polymer. All pellets were prepared in the same way using the hydraulic press providing 10,000 lb/in² for one minute. Pellets were placed in the same oven and heated to 530° C over a time period of approximately six hours. The pellets were placed in a vacuum CO₂ chamber upon removal for approximately 24 hours. A sample then was taken from each of these pellets for SEM analysis. The pellets all were chiseled so that the mass size for each would be 2.42 g. These pellets were placed in a static batch test with 100 ppb arsenic contaminated water to test their adsorption abilities. During this batch experiment, P23b and P24b disintegrated in the water, so the five percent and ten percent bentonite compositions did not hold together.

Trials P29 a, b, c through P35 a, b, c

Trials P29 a,b,c through P35 a,b,c attempted to repeat the comparison experiment using the different compositions of limestone, limestone and bentonite, and limestone and

polymer. This time, however, more de-ionized water was added and spherical pellets were formed with hand pressure. However, there was experimental interference with all of the “c” trials of this experiment. Therefore, the results of this part of the experiment could not be determined. Pellets P33, P34, and P35 disintegrated in water. Once again, as observed earlier, these pellets did not seem as strong as the ones created by using a hydraulic press.

Trials P36 a, b, c, d through P38 a, b, c, d

Trials P36 a,b,c,d through P38 a,b,c,d involved a comparison of the amount of heating time in the oven. Three different pellets, composed of limestone, two weight percent bentonite, and two weight percent PEG, were made by using the hydraulic press and applying 10,000 lb/in² for one minute. The oven containing these pellets then was heated to 500° C. The “a” pellets were removed after one hour, the “b” pellets were removed after one hour and thirty minutes, the “c” pellets were removed after two hours, and the “d” pellets were removed after two hours and thirty minutes. All pellets were cooled in a CO₂ environment. Batch experiments explored the adsorption capabilities of these pellets. For regular limestone after one hour, the pH was very basic and specific conductance was high. It was concluded that decomposition was still occurring even though there were no visible signs of it. PEG seemed to retard decomposition because this did not occur until the two-hour mark with these pellets. The results of this experiment were very encouraging. Although arsenic does not adsorb as readily as with un-sintered fines, a significant amount of arsenic was adsorbed on these pellets. It had

been feared that less would be adsorbed on these pellets because the decreased surface area available for adsorption, as compared to other pellets and the fines.

Trials P39 and P40

Trial P39 and P40 involved a comparison of a pellet made with a hydraulic press (at 10,000 lb/in²) and a pellet made with hand pressure to create a spherical shape. At the time of this experiment, it was not known that heating the oven to 500° C for more than one hour would lead to decomposition. Therefore, the results of the batch experiment showed high pH and specific conductance readings. The results of this experiment were interesting because it appeared that the pellet prepared with a hydraulic press adsorbed arsenic much better than the one prepared with hand pressure.

Results of Sintering Experiments

Several pellets prepared by research assistants appeared to be of such structural integrity that arsenic removal testing was required to determine their removal effectiveness. As mentioned above, numerous variations of binder materials including water, bentonite, PEG (polyethylene glycol), were used.

Variations of temperatures as well as sintering time were used systematically to determine the best overall binder and removal efficiency. Variations are described in Table 4, as well as arsenic removal efficiencies. All arsenic solutions were prepared at 100 ppb, unless otherwise noted.

TABLE 4. Static pellet arsenic removal experiments.

Sample #	Time at 500C Time (hr)	final pH	TDS	Description	% removal
P21	1	9.4	70	Pelletized Limestone	54.8
P22	1	9.3	70	Limestone + 2% Bentonite	35.6
P25	1	9.2	60	Pelletized Limestone	> 93.2 *
P26	1	8.9	60	Limestone + 2% PEG	> 93.2 *
P27	1	8.9	60	Limestone + 5% PEG	> 93.2 *
P36 S1	1	8.8	80	Pelletized Limestone	26.0
P36 S2	1.5	10.4	210	Pelletized Limestone	29.0
P36 S3	2	10.8	410	Pelletized Limestone	43.0
P36 S4	2.5	11.3	440	Pelletized Limestone	35.0
P37 S5	1	10.0	100	Limestone + 2% Bentonite	11.0
P37 S6	1.5	10.1	100	Limestone + 2% Bentonite	**
P37 S7	2	10.9	270	Limestone + 2% Bentonite	30.0
P37 S8	2.5	10.7	190	Limestone + 2% Bentonite	24.0
P38 S9	1	9.67	80	Limestone + 2% PEG	7.8
P38 S10	1.5	9.72	90	Limestone + 2% PEG	21.1
P38 S11	2	9.74	100	Limestone + 2% PEG	8.9
P38 S12	2.5	10.44	180	Limestone + 2% PEG	40.0

* This experiment should be replicated to ensure the validity of the data.

** Arsenic concentration increased from 100 ppb to almost 1 ppm, an obvious anomaly of the data set.

As expected, the static pellet results were mixed. Excluding P25-P27, the removal efficiencies of the pellets are typically below 40%. This is attributable to the decreased exposed surface area and reduced porosity of the pellets.

Interesting observations of the data are the final pH and total dissolved solids (uS/cm). Observed final pH of limestone batch experiments typically ranged from 8.5 to 9.5. Values of pH in the pellet experiments, above, indicate that some pellets have undergone partial decomposition to lime CaO, which is strongly basic in solution ($9.5 < \text{pH} < 13$). The high TDS recorded for the pellets also indicates dissolution of lime, increasing the pH.

Sintering time appears to play a significant role in the pelletization process, especially relating to limestone decomposition. There were no significant differences

among physical strengths of the pellets tested. This indicates that although heating is necessary for pelletization and sintering, limiting the heating time is desirable.

Of the two binders tested, polyethylene glycol (PEG) appeared to resist the decomposition of limestone more effectively than bentonite, with respect to time. The binders also seemed to slightly hamper the removal characteristics of the limestone. It is possible that the addition of a doping compound such as Fe_2O_3 or MgCO_3 could be used to increase the arsenic removal of the pellets.

Problems Encountered While Making Pellets

An important finding encountered during this research is the decomposition of calcium carbonate at high temperatures. At temperatures above 630°C , the pellets decomposed, releasing CO_2 and converting to calcium oxide (lime). To eliminate this problem, several methods could be tested. The pellets could be heated in a vacuum oven with CO_2 pumped into it. It is believed that the CO_2 environment could prevent the decomposition reaction from occurring. However, this would be expensive and might not be practical for this application. Therefore, future experiments could be conducted to find the maximum temperature to which the pellets could be heated without causing decomposition.

Doping Experiments

Trials P41- P46

Trials P41, P42, P43, P44, P45, and P46 were conducted to examine the addition of other metals to the limestone, in order to increase the adsorption efficiency of the limestone. At the time of these experiments, it was not known that one hour at 500° C would cause decomposition of calcium carbonate. The pellets were heated at 500° C for 1.5 hours. After analysis of the samples from this experiment, it was discovered that MgCO₃ appears to help the sintered pellets to adsorb arsenic, while Fe₂O₃ appears to hinder the ability of the pellet to adsorb arsenic.

ELEMENTAL DETERMINATIONS

Residual arsenic in batch and column experiments was analyzed with two methods. Samples were sent to Mid-Continent Testing Laboratories in Rapid City, South Dakota, for arsenic analysis by graphite furnace atomic absorption (Varian GFAA). Graphite furnace AA is the preferred method for arsenic determinations, according to EPA methods (Total Arsenic EPA Method 206.2). Typical detection limits by this method are 5 µg/L (5 ppb).

Samples also were sent to the Engineering Mining and Experiment Station (EMES) at South Dakota School of Mines and Technology in Rapid City, South Dakota, for analysis by Inductively Coupled Plasma Mass Spectrometry (Agilent Technologies, HP 4500 ICP-MS). The ICP-MS was explored as an alternative method because of its increased detection limits over GFAA (~X pptr = part per trillion ng/L).

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The Toxicity Characteristic Leaching Procedure (TCLP) test is a method used to determine the relative stability of a waste component. EPA protocol SW-846 1311 describes the procedure and is available online at <http://www.epa.gov/sw-846/4xxx.htm> (9). The EPA has devised methods such as the TCLP to predict the leaching properties of waste in the landfill/ waste management environment.

Conditions in a landfill are simulated through the preparation of an acidic extraction fluid, based upon the properties of the waste being analyzed. A known quantity of the waste is then bottle-rolled with the prepared extraction fluid for 18 ± 2 hrs. Aliquots of the solution then were withdrawn and acidified with nitric acid prior to elemental analysis.

Two samples of limestone were analyzed with the TCLP test. Prior column work in Phase I of this research provided limestone wastes saturated with arsenic. Solids samples were extracted from column #1 (~ 0.5-1.0 mm sands) and column #4 (0.5-1.0 cm coarse sands). Waste samples (~150 g) were filtered with an 11-cm ceramic Buchner filtration apparatus with 2.0 L of DI-H₂O to remove any interstitial arsenic. The waste then was subjected to the TCLP, and sample aliquots were withdrawn for analysis (GFAA MC testing). Table 5 lists results from the TCLP tests.

TABLE 5. Residual arsenic concentrations from the TCLP.

Sample #	final pH	Residual Arsenic ppb
Col 1 TCLP	6.4	8
Col 4 TCLP	6.2	< 5.0

The leaching potential of column 4 waste was at or below the detection limit for Total Arsenic EPA method 206.2 by GFAA. Results from this procedure indicate that the waste rock is relatively stable, and could be disposed by normal means in a landfill.

SCANNING ELECTRON MICROSCOPY

A scanning electron microscope (SEM) was used to view materials under high magnification (up to 300,000 X). Several samples of limestone were examined with the SEM to determine particle size and the potential effects of pressure and heat that could occur during the sintering and pelletization process.

Limestone samples that were used in the arsenic removal process also were examined, but little or nothing was visible that could relate to surface bonding or interactions. At the ppb level, it is very difficult if not impossible to find any arsenic formation or complexes on the surface of limestone. Figure 6 shows an image of the limestone fines under SEM at 1000x. Note that although particle size is variable, there appears to be a semi-homogenous particle distribution.

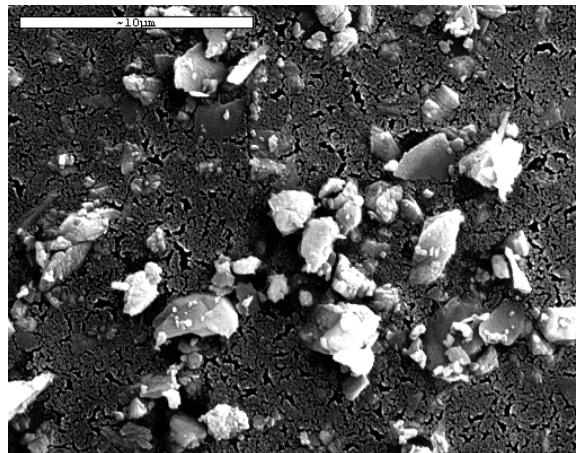


FIGURE 6. Limestone fines at 1000x.

CONCLUSIONS AND RECOMMENDATIONS

Findings from this work have several implications for continuing research on arsenic removal from drinking water. Minnekahta Limestone has been shown to be effective in the removal of arsenic from aqueous solutions, as demonstrated by batch experiments. The composition of the limestone appears to be a controlling factor in the removal of arsenic. The isolation of specific compounds within the limestone will provide insight into unlocking the responsible mechanism or processes for arsenic removal.

The starting pH of the solution played an insignificant role in arsenic removal ($4 \leq \text{pH} \leq 10$), and post treatment pH values remained predominantly in the range of $8.0 < \text{pH} < 9.5$. A pH value of 8 is reasonable for drinking water quality. The characteristic pH values for surface-water and ground-water supplies are within the range of 6 to 8; therefore this technology will be applicable to domestic water treatment.

Results from the introduced interference studies indicate that additional chloride and sulfate species in solution did not appear to affect the arsenic removal properties of the limestone. Although “real world” water conditions can include high total dissolved solids, introduced chlorides and sulfates, in the ppm level, were of no consequence in this study. If necessary, high TDS concentrations could be reduced through the addition of a flocculent such as activated alumina before arsenic remediation.

Industrial large-scale application of the continuous flow reactor or the plate affixed batch reactors could merit consideration. Unless refined, however, the processes described above might not sufficiently reduce the arsenic concentration in solution. Application of limestone fines to a large continuously mixed reactor, followed by

filtration, could be an effective application of the small-scale experiments employed in the laboratory.

Pelletization and sintering should be explored further for use of limestone fines in a column application. Several variables must be considered in this process, including time, sintering temperature, limestone composition, and binder properties. Ultimately, the addition of any heating process or binding material adds complexity and cost to the development of a limestone adsorbent. This should be balanced between the overall removal efficiency and the costs as well as the complexity of the process.

The Toxic Characteristic Leaching Procedure indicates that the waste is relatively stable. The leaching potential of the arsenic on the waste rock is low, which is encouraging for considerations of disposal of the rock in a normal waste facility.

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APPENDIX A

Standard Methods for Arsenic Batch Removal Process

Standard Methods for Arsenic Batch Removal Process

Equipment Required

prepared limestone adsorbent

micro-spatula

arsenic standard (1000 ppm)

analytical balance

Burrell wrist action shaker

150-200 mL round bottom flasks w/stoppers

~10% conc. nitric acid (glassware cleaning)

distilled water

distilled-deionized water

disposable plastic cups ~1-2 oz. (sample analysis)

glass vials 3-5 mL (final elemental analysis)

disposable glass micro-pipets

pH meter and buffers 4, 7, and 10

total conductivity meter

30 mL plastic syringe

0.45 μm small volume filtration apparatus

5, 10, 100 mL volumetric pipets

pipet bulb

aqueous NaOH (standardized pH pre-adjustment of arsenic solution)

0.5, 1.0 L volumetric flasks

1.0 L NALGENE storage vessel

rubber gloves

safety goggles

Preparation for Batch Process

In order for elemental arsenic analysis to be reproducible at the part-per-billion (ppb) level, special precautions need to be taken. *All labware used in the procedure must be rigorously washed using the following procedure.*

- 1) All labware must be triple rinsed with ~10% conc. nitric acid.
- 2) After acid wash, triple rinse labware with distilled water (d-H₂O).
- 3) Follow the d-H₂O rinse with a triple rinse of distilled-deionized water (DI-H₂O).

Limestone Sample Preparation

In order to determine the effectiveness of a limestone adsorbent in the batch process, it is often necessary to vary the quantities used. Prior to setup of the batch procedure, weigh out various quantities of crushed limestone. Typical gram quantities could include: 0.5, 1.0, 5.0, and 10.0. Using the analytical balance, carefully weigh out the desired quantity of adsorbent using a pre-tared disposable cup and micro-spatula. Measure out all quantities using this procedure.

It is also desired to include a duplicate as well as a blank sample in the batch process. The duplicate sample is prepared to check the process by reproducibility. The blank sample (limestone adsorbent + DI-H₂O) is for quality control of the experiment, a

method to detect any cross-contamination. The duplicate and blank samples are prepared at a sample quantity at the middle of the desired experiment. For example, in the gram quantities listed above, the duplicate and blank samples would be prepared at 5.0 g.

Arsenic Solution Preparation

For the experiments performed in this laboratory, a 100 ppb solution was used during testing. Chemical supply companies readily sell arsenic standards for HPLC analysis as 1000 ppm. Two dilutions are necessary for solution preparation. The 100 ppb solution is prepared using the procedure below.

- 1) The first dilution is made to 10 ppm. Using appropriate volumetric pipets, transfer the amount of arsenic standard required to the respective volumetric flask. For example, if 500mL of 10 ppm was desired

$$(500\text{mL}) * (10 \text{ ppm}) = (X \text{ mL}) * (1000 \text{ ppm})$$

$$X = 5 \text{ mL}$$

The 5 mL of 1000 ppm arsenic solution is transferred to the 500mL volumetric flask using a 5 mL pipet. The flask is then filled with DI-H₂O to the dilution mark and shaken vigorously.

- 2) The second dilution is made to 100 ppb or 0.1 ppm. Using appropriate volumetric pipets, transfer the amount of arsenic standard required to the respective volumetric flask. For example if 1.0 L of 100 ppb was desired,

$$(1000 \text{ mL}) * (0.1 \text{ ppm}) = (X \text{ mL}) * (10 \text{ ppm})$$

$$X = 10 \text{ mL}$$

The 10 mL of 10 ppm arsenic solution is transferred to the 1000mL volumetric flask using a 10 mL pipet. The flask is then filled with DI-H₂O to the dilution mark and shaken vigorously. After the arsenic solution is prepared to 100 ppb, it is then necessary to pH pre-adjust the solution before the batch process.

- 1) Transfer ~900mL of the 100 ppb arsenic solution to the 1.0 L NALGENE container.
- 2) Calibrate the pH meter using the buffers required and appropriate methods.
- 3) Measure the pH of the arsenic solution.
- 4) The first typical pH measurement of the arsenic solution will be approximately pH = 4.3-5.0.
- 5) Carefully add NaOH dropwise, to increase the pH to the desired level. For the course of these experiments, the desired range was pH = 7.8-8.3.
- 6) Shake the solution adequately.
- 7) Measure the pH after the addition of NaOH. The pH of the solution can change readily due to the acid equilibrium of arsenic in solution. Consequently, if the pH is too alkaline >8.3, Nitric acid can be heavily diluted with DI-H₂O, and added to the solution to decrease pH.
- 8) When appropriate pH is reached, set solution aside for the batch procedure.

Batch Procedure

Transfer the samples of limestone adsorbent to the appropriately labeled round bottom flasks from the plastic cups using the micro-spatula. Ensure that all adsorbent is carefully transferred to the r-b flasks.

Assuming a blank is being run in the batch experiment, pipet 100mL of DI-H₂O into the flask. All other samples and the duplicate sample must be filled with 100mL of the pH pre-adjusted arsenic solution described above. Pipet 100mL of arsenic solution to each of the samples, including the duplicate.

All samples must then be secured to the Burrell wrist action shaker. Ensure that the clamps holding the round bottom flasks are secure, as the motion of the shaker can loosen the clamp. Turn the dial to HOLD, and allow the shaker to continuously agitate the samples for a predetermined period (~48 hours).

Laboratory Preparation of Samples

After the predetermined agitation period, turn the dial on the wrist action shaker to OFF. Allow the samples to settle for a period of approximately 30 minutes. After settling, remove the sample from the wrist action shaker. Decant the solution into a disposable plastic cup.

Place an unused 0.45 μ m filter in the small volume filtration apparatus.

Withdraw ~10 mL of solution using the 30mL syringe. Affix the filtration apparatus to the syringe. Apply pressure to the syringe to begin filtration. Transfer this solution directly to the appropriately labeled vial. Cap or stopper the vial and set aside for

elemental analysis. After use, discard the filter and acid wash the syringe and filtration device.

If necessary, transfer additional solution from the round bottom flask to the disposable plastic cup. Measure and record pH and total conductivity of the solution. After the measurement has been made, dispose of solution and clean glassware accordingly. *In order to avoid cross-contamination of the samples, the sampler should change gloves after each sample has been prepared.* Perform the exact same procedure for all samples as described above.

Additional Comments

For the course of the experimental procedures outlined above, it was noted that a duplicate as well as a blank sample was to be run during the batch process. It is also important to prepare an additional vial for a standard arsenic sample. Using a disposable glass micro-pipet, carefully transfer ~5mL of the arsenic solution described above in “Arsenic solution preparation” into a labeled vial and include it in the elemental analysis as the standard solution.