

Report for 2005SD37B: Development of an Agglomeration Process to Increase the Efficiency of Limestone-Based Material to Remove Metals from Drinking Water

Publications

- Other Publications:
 - Sorensen, J.L., Davis, A.D., Webb, C.J., and Dixon, D.J., 2005, Engineering design considerations for using limestone-based material to remove arsenic from drinking water: Presented at 17th Annual South Dakota Ground-Water Quality Conference, March, 2005, Pierre, South Dakota.
 - Webb, C.J., Davis, A.D., and Dawadi, S., 2005, Investigation of the formation of arsenic-containing minerals on a limestone base: Presented at Geological Society of America, Annual Meeting, Division of Geochemistry, Denver, Colorado.
 - Webb, C.J., and Davis, A.D., 2005, Arsenic remediation of drinking water using modified limestone: American Chemical Society, Anaheim, California.
 - Sorensen, J.L., Davis, A.D., Dixon, D.J., Webb, C.J., and Hocking, C.M., 2005, Arsenic removal demonstration project at Keystone, South Dakota: Presented at Western South Dakota Hydrology Conference, Rapid City, South Dakota, April, 2005.
 - 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 (submitted in 2005).
- Unclassified:
 - Webb, C.J., Davis, A.D., Dixon, D.J., Sorensen, J.L., and Dawadi, S., 2005, Limestone-based material for arsenic removal from drinking water (abstract): Geological Society of America, Abstract No. 95792.
 - 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.

- 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, Symposia Paper (paper submitted in 2005).
- 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: SME Paper TP-05-025, Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, 4 p. [Paper submitted in 2005.]

Report Follows

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Title: *Development of an Agglomeration Process to Increase the Efficiency of Limestone-Based Material to Remove Metals from Drinking Water*

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ABSTRACT

Metals contamination of drinking water is a major problem facing many areas of the United States and the world. There is a need for an inexpensive remediation technology for the removal of metals in drinking water that can be applied to small rural water systems. The metals in drinking water considered for this research included arsenic, cadmium, and lead. All three are toxic in the environment and cause both acute and chronic toxicity in humans at elevated concentrations.

Limestone-based material has demonstrated the potential to reduce select metals in drinking water. Earlier research by the principal investigators of this grant and others has demonstrated arsenic removal of greater than 95 percent by limestone. The purpose of this study was to develop a technique to agglomerate powdered limestone into granules and characterize the ability of the manufactured granules to remove metals from solution using both batch and column adsorption experiments. Limestone is readily available and its use for metals removal is relatively inexpensive.

Three specific objectives were achieved during this research: 1) development and testing of a bench-scale agglomeration process for granulating limestone-based material as a filter media for metals adsorption, 2) development of a mixture formula for the limestone-based granules and a manufacturing protocol, and 3) investigation of the adsorption capacity of manufactured granules to remove metals from solution using batch and column experiments.

This project investigated the technique of agglomeration as a method to improve the metals removal efficiency of limestone-based material. Agglomeration is the process of taking fine materials and forming them into spherical granules. Magnesium carbonate powder was tested as an additive to enhance metals removal and was found to be effective. Portland cement was added as an insoluble binder to the limestone mix to bond the individual particles together and to strengthen the granules. Agglomeration increased material surface area as compared to crushed limestone without compromising water flow through rates.

Using batch and column experiments, it was shown that limestone-based granules effectively remove arsenic, cadmium, and lead from water. The adsorption of arsenic by limestone follows the Langmuir isotherm model and arsenic removal by limestone does

not show pH dependence in the pH range from 4 to 10. Arsenic adsorption capacity of 1-2 mm sized manufactured granules at a starting concentration of 100 ppb arsenic was 5.4 ug arsenic per gram granules. In comparison, an equal mass of limestone powder has an arsenic capacity of 5.9 ug/gram and 1-2 mm crushed limestone chips have a capacity of 4.2 ug/gram. Column experiments showed that 1-2 mm limestone-based granules had an adsorption capacity about four times greater than crushed limestone chips of the same diameter. Arsenic adsorption capacity by the granules dropped from 22 to 9.8 ug/gram when naturally occurring groundwater with arsenic at 50 ppb was tested as the influent solution.

Limestone-based granules also showed a very high adsorption capacity for both cadmium and lead. At concentrations from 5 to 50 ppm, greater than 99 percent of the cadmium was removed by the granules in batch experiments. Lead was removed to below detection limits for all concentrations measured (up to 3 ppm).

INTRODUCTION

Metals contamination of drinking water is a major problem facing many areas of the United States and the world. The problem has been highlighted by the U.S. EPA's decision to mandate the reduction of the maximum contaminant level of arsenic from 50 to 10 parts per billion (ppb) in January 2006. There is a need for an inexpensive remediation technology for the removal of metals in drinking water that can be applied to small rural water systems. There are at least five benefits to the drinking water community by which an effective rural water treatment method can be evaluated: 1) reasonable removal efficiency as compared to material and operation costs, 2) broad geographic and water system applicability, 3) compatibility with other water treatment processes, 4) ease of technical use, and 5) low-cost disposal in ordinary landfills. This research focused on the removal of three inorganic metal contaminants from drinking water: arsenic (in the arsenate form), cadmium (Cd(II)), and lead ((Pb(II))).

Mineral surfaces such as carbonates, which include limestone, dolomite, and aragonite (another form of calcium carbonate), regulate the concentrations of dissolved trace metals in natural aqueous environments. Concentrations of trace metals are usually less than the solubilities of the pure solid phases which contain the metal ion. Processes such as adsorption and ion exchange are used to explain this discrepancy (Drever, 1982). The mineral calcite (calcium carbonate) is the main constituent of limestone and is the mineral surface considered when discussing metals adsorption mechanisms by limestone.

The purpose of this study was to develop a technique to agglomerate powdered limestone and additives into granules and characterize the ability of the manufactured granules to remove metals from solution using adsorption studies. These macroscopic adsorption studies were carried out in both stirred reactors (batch experiments) and flow-through column studies. Batch and column experiments place an aqueous solution of the metal of interest (the adsorbate) in contact with the adsorbent, in this case limestone-based media. Batch and column experiments monitor changes in solution chemistry and provide indirect information on the nature of the adsorption process. However, they do not provide enough information to characterize the identity and stoichiometry of the adsorbed species (Brown et al., 1995). To better understand the molecular-level interactions between the aqueous metals and the limestone-based material, microscopic

studies of adsorption processes previously published by other researchers were reviewed and summarized.

Chemistry of Arsenic

Arsenic is a persistent, bio-accumulative toxin. The maximum contaminant level for arsenic, formerly 50 parts per billion (ppb), will be lowered to 10 ppb in 2006 because of links to cancer. In South Dakota alone, about 30 (8.6 percent) of the state's public water supply systems will not be in compliance with this mandate. 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).

An example of the impact of elevated arsenic levels on a small rural drinking water system is the Grass Mountain area on the Rosebud Reservation of South Dakota. Elevated arsenic levels (greater than 80 ppb) were first observed in 1990 at two production wells, and local residents were supplied with an alternate water supply in 1993. A study by the United States Geological Survey (Carter et al., 1998) characterized the extent of arsenic in the study area and attributed the primary source of arsenic to arsenic-rich volcanic ash, which is abundant in the Arikaree Formation and White River Group.

Arsenic in the aquatic environment has very complex chemistry that is dependent on a number of factors, including pH, redox potential, ions present, and adsorbing surfaces. The speciation of arsenic governs its availability, accumulation, and toxicity to living organisms as well as its mobility in the environment. Inorganic arsenic has two oxidation states – arsenate (As(V)) and arsenite (As(III)). Arsenate forms four different oxyanions in water, depending on pH. At pH less than two, the dominant form is H_3AsO_4 . For the pH range from 3 to 6, the dominant form is H_2AsO_4^- . For the pH range from 8 to 10 dominant form is HAsO_4^{2-} . For pH values greater than 12, arsenate takes the form AsO_4^{3-} . Arsenite forms three different oxyanions, depending on pH. For the pH range from 7 to 8, the dominant form is H_3AsO_3 . For the pH range from 10 to 11, the dominant form is H_2AsO_3^- . For the pH range from 12 to 13, the dominant form is HAsO_3^{2-} . The arsenite form of arsenic is about sixty times more toxic than arsenate. Arsenate is the most stable form in oxidized environments, although significant amounts of arsenite can also exist in oxidizing environments (Seyler and Marin, 1989). Arsenate is the form of arsenic examined during this research.

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; Karcher et al., 1999), 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. 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. Other processes that are generally less effective than coagulation-filtration and ion exchange are reverse osmosis, activated alumina, and lime softening.

Chemistry of Cadmium and Lead

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)

Cadmium in the aquatic environment has a +2 oxidation state. The solubility and partitioning of cadmium depends on a number of factors including pH, cations present, organic carbon present, and adsorbing surfaces (Davis et al., 1987; Filius et al., 1998; Fuller and Davis, 1987; Johnson, 1990; Seco et al., 1999). Cadmium carbonate (CdCO_3) has a very low solubility, with a solubility product (K_{SP}) equal to $10^{-13.7}$. Observations of CdCO_3 (otavite) and CaCO_3 solid solution formation on calcareous aquifer material show that cadmium is initially adsorbed during a fast adsorption stage and then forms a regular solid solution where Cd^{2+} is incorporated into calcium carbonate by direct growth of a $(\text{Cd,Ca})\text{CO}_3$ solid solution (Davis et al., 1987).

Lead is a well-known toxin that causes delays in the physical and mental development of children that are exposed to elevated levels. Lead poisoning causes anemia, damage to the central nervous system, mental deterioration, and can impact all major body systems (Mohd et al., 1998). The action limit for lead is 15 ppb. Lead was historically widely used in plumbing, and older plumbing systems provide the opportunity for lead to dissolve into drinking water, especially by waters with low pH (Hem, 1978). Lead is used in a number of products including lead crystal and flint glass, paint pigment, lead-acid storage batteries (PbO_2), insecticide ($\text{Pb}_3(\text{AsO}_4)_2$), fireworks, ammunition, and building construction materials.

The oxidation state of lead in water is +2. Lead concentrations in natural oxidized waters are mainly controlled by the formation of lead carbonate (cerussite) (Hem, 1978). Lead carbonate (PbCO_3) has a very low solubility, with a solubility product (K_{SP}) equal to 7.4×10^{-14} .

REVIEW OF RELATED RESEARCH

Arsenic Literature Review

Limited research has been completed examining arsenic adsorption by calcite, lime, and limestone. Bothe and Brown (1999) studied the types of hydrated calcium arsenates that form when high concentrations of arsenic are exposed to lime for extended time periods. Non-hydrated forms of calcium arsenate were not observed. Their efforts focused on the immobilization of arsenic in lime as a treatment method for solutions containing high arsenic concentrations. Cheng et al. (1999) studied the incorporation of arsenite at the calcite surface using microscopic techniques. Their study showed that arsenite is incorporated at carbonate sites, although the exact speciation of the arsenite was not determined. Arsenite is incorporated into calcite in a dissolution/precipitation mechanism similar to that for the otavite/calcite solid solution, and surface dissolution or precipitation of one monolayer of calcite is estimated to take only several seconds. Other studies (House and Donaldson, 1986; Karaca et al., 2004) have examined the nature of phosphate adsorption on calcite and dolomite, which is significant in that the chemistry of phosphate is similar in nature to the chemistry of arsenate.

A study by Ongley et al., (2001) examined the used of untreated, crushed limestone as a simple method of arsenic water treatment in Mexico, and demonstrated the material's efficacy. Maeda et al. (1992) used iron(III) hydroxide-loaded coral limestone and Ohki et al. (1996) used aluminum-loaded coral limestone to adsorb arsenic. While both materials improved removal efficiency over untreated limestone, the iron-treated material performed significantly better. Reardon and Wang (2000) have tested limestone as a removal agent for fluoride from wastewaters, and Wang and Reardon (2001) used siderite (iron carbonate) in a column to elevate the low initial pH of an influent arsenic solution and simultaneously dissolve the siderite material. Iron-arsenic compounds precipitated out of solution onto the surface of the siderite, removing the arsenic in solution. Mackintosh et al. (2002), using a limestone contactor to harden soft water, observed that metals concentrations in the water stream were also removed by the limestone. This was an unintended benefit of the water softening treatment.

Surface complexation modeling of dissolved metals on oxide surfaces has been extensively studied and used as a template for predicting surface complexation reactions on carbonate surfaces. Although calcium and magnesium carbonates make up about 20 percent of sedimentary rocks and the reactivity of these minerals (adsorption, dissolution/precipitation) plays an important role at the solid/water interface in soils and aquifers, the exact surface species that control the reactivity of carbonates in water are not established (Pokrovsky et al., 2000). Van Cappellen et al. (1993) developed a surface complexation model for the reactivity of the carbonate-water interface. Surface complexation theory is based on the concept that water molecules and dissolved species (such as metals) form chemical bonds with ions at the mineral lattice surface. A series of reactions were proposed to model surface speciation in the metal ion – carbonate - water system. The metal ions considered were Ca^{2+} , Mn^{2+} , and Fe^{2+} , which combine with the carbonate ion (CO_3^{2-}) to form carbonate minerals. Surface complexation models for dolomite (calcium-magnesium carbonate) (Pokrovsky et al., 1999a) and magnesite (pure magnesium carbonate mineral) (Pokrovsky et al., 1999b) have also been developed.

Surface adsorption of arsenic to iron oxides, iron hydroxides, and clay minerals has been extensively characterized (Goldberg, 1986; Goldberg, 2002; Holm, 2002; Manning and Goldberg, 1996; Pierce and Moore, 1982). Other iron-based media that adsorb arsenic include granulated ferric hydroxide (Driehaus et al., 1998; Thirumavukkarasu et al., 2003), red mud (bauxsol) (Genc et al., 2003; Genc-Fuhrman et al., 2004), ferrihydrite (Jain and Loeppert, 2000; Raven et al., 1998), goethite (Fendorf et al., 1997; Gao and Mucci, 2001; Grossel et al., 1997), iron-treated activated carbon (Huang and Vane, 1989), and zero-valent iron (Farrell et al., 2001; Melitas et al., 2002; Nikolaidis et al., 2003). Aluminum-based adsorbents, such as aluminum hydroxides and oxides (Anderson et al., 1976; Arai et al., 2001, Ladeira et al., 2001), activated alumina (Lin and Wu, 2001), and aluminum-loaded zeolites (Xu et al., 1998) are also shown to remove arsenic. Other, more novel arsenic adsorbents include hardened Portland cement (Kundu et al., 2004), manganese-dioxide coated sand (Bajpai and Chaudhuri, 1999), titanium dioxide (Dutta et al., 2004), and ettringite (Myneni et al., 1997). Although extensive, the above list is only a portion of the literature available on the chemistry of arsenic adsorption.

Cadmium Literature Review

Zachara et al (1991) examined the uptake of cations, including cadmium, onto calcite, and proposed the following order of cation affinity for calcite: cadmium > zinc ≥ manganese > cobalt > nickel >> barium = strontium. Several possible mechanisms have been proposed for the uptake of cadmium by calcite: ionic radius and the solubility product of the cadmium carbonate solid (Zachara et al, 1991), ion exchange of Cd^{2+} for Ca^{2+} at the mineral-water interface (McBride, 1980; Davis et al., 1987), defect-enhanced diffusion into the calcite lattice (Stipp et al., 1992), and co-precipitation (Zachara et al., 1991). The formation of $\text{CaCO}_3\text{-CdCO}_3$ solid solutions and the crystal growth of CdCO_3 (otavite) on calcite during cadmium uptake from solution has been confirmed through spectroscopic studies (Chiarello and Sturchio, 1994; Stipp et al., 1992).

Cadmium uptake has been shown to occur in two steps: 1) fast adsorption of dissolved cadmium onto the calcite surface, and 2) slower solid phase incorporation (Davis et al., 1987; Martin-Garin et al., 2003; Stipp et al., 1992). The rate of solid phase incorporation was found to be independent of the amount of adsorbed cadmium (Davis et al., 1987) and initial migration of the cadmium ions into the calcite lattice is limited to a few angstroms (Martin-Garin et al., 2003). Stipp et al (1992) showed that solid phase incorporation sequestered the cadmium in the calcite permanently and surface uptake ranged from the equivalent of about one to four monolayers. Martin-Garin et al. (2003) found that adsorption of cadmium ions inhibits the dissolution of calcite and the degree of inhibition increases with the surface density of adsorbed cadmium and reaches a maximum of about 75 percent when maximum cadmium adsorption is reached. Ion interference by increasing phosphate and sulfate concentrations was shown to decrease cadmium adsorption by calcite and also affected the sorption reversibility of cadmium (Van der Weijden et al., 1997). Wang and Reardon (2001) showed that crushed limestone is effective at removing dissolved cadmium, while siderite (iron carbonate) has no influence on cadmium concentrations.

A number of studies have been completed examining cadmium uptake by a variety of adsorbents other than calcium carbonate. Commonly known adsorbents that

also adsorb cadmium include but are not limited to: activated carbon (Leyva-Ramos et al., 1997; Marzal et al., 1996; Rangel-Mendez et al., 2002; Seco et al., 1999), iron oxide (Cowan et al., 1991), aluminum oxide (Floroiu et al., 2001), goethite (Johnson, 1990; Venema et al., 1996), hematite (Davis and Bhatnagar, 1995; Pivovarov, 2001), red mud (Apak et al., 1998), gibbsite (Weerasooriya et al., 2002), and clays, including kaolinite (Angove et al., 1997; Suraj et al., 1998) and montmorillonite (Barbier et al., 2000). Also, articles have been published examining cadmium adsorption onto calcium-rich materials, including calcareous soils and sands (Fuller and Davis, 1987; Martin-Garin et al., 2002).

Lead Literature Review

Although it is well known that lead is a common, toxic, heavy metal contaminant in the environment, there are limited atomic-scale studies of the adsorption of lead onto minerals such as calcium carbonate (calcite). An investigation using synchrotron X-ray standing wave, X-ray reflectivity techniques, and atomic force microscopy showed that most (60 percent) of the lead adsorbed on the calcite occupied the calcium (Ca^{2+}) site in the calcite surface (40 percent of the adsorbed lead was disordered). There was a total of 0.08 equivalent monolayers of adsorbed lead at the calcite-water interface, and 70 percent of the ordered lead found in the calcium sites in the calcite lattice was in the surface atomic layer (Sturchio et al., 1997). This is interesting since divalent metals strongly sorbed by calcite (Mn, Co, Ni, Zn, and Cd) tend to have ionic radii less than or about equal to the calcium ion (0.99 Å). In contrast, the ionic radius of lead is 1.20 Å, indicating more complex reasons for this observation than ionic radius alone (Davis et al., 1987; Lorens, 1981; McBride, 1980; Zachara et al., 1991).

Additional recent studies have furthered the understanding of lead adsorption onto calcite at the atomic level. Godelitsas et al. (2003) have shown that the lead sorption process by calcite is mainly surface precipitation leading to overgrowth of lead carbonate (cerussite) and hydrated lead carbonate (hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). The resulting calcite surface with the adsorbed lead may have an aragonite-type character. At low lead concentrations (1 μM) using X-ray absorption fine structure instrumentation, Rouff et al. (2004) observed that lead forms mononuclear inner-sphere complexes at the surface. At higher lead concentrations (20 and 60 μM), precipitation of hydrocerussite and cerussite was observed. A study comparing lead and cadmium uptake by calcite determined that the uptake of cadmium was greater than lead under similar experimental conditions (Chada et al., 2005). A study examining the effects of interference ions and pH on lead adsorption by calcite (Rouff et al., 2005) showed that nitrate and chloride interference ions showed no significant effect on lead adsorption. Lead adsorption increased from pH 7.3 to 8.5, with a decrease from 8.5 to pH 9.4.

A number of studies have been completed examining lead uptake by a variety of adsorbents other than calcium carbonate. Well-known adsorbents found in the literature to adsorb lead include but are not limited to: activated carbon (Gomez-Serrano et al., 1998; Reed et al., 1996), zeolite (Al-Haj-Ali and El-Bishtawi, 1997; Scott et al., 2002), clay materials such as montmorillonite (Barbier et al., 2000), bentonite (Naseem and Tahir, 2001), and kaolinite (Orumwense-Faraday, 1996), and slag materials such as activated slag (Srivastava et al., 1997), electric furnace slag (Curkovic et al., 2001), and granulated blast-furnace slag (Dimitrova and Mehandgiev, 1998). Adsorbents such as

ferrihydrate (Scheinost et al., 2001), manganese and iron hydroxides (Yarrow et al., 2002), red mud (Gupta et al., 2001), and oxide surfaces (Strawn et al., 1998) are also effective lead adsorbents. Other more novel lead adsorbent materials described in the literature include manganese oxyhydroxide (Matocha et al., 2001), diatomite (Al-Degs et al., 2001), mackinawite ((Fe,Ni)₉S₈) (Coles et al., 2000), hydroxyapatite (Ma, 1996), and peat (Ho and McKay, 1999).

Adsorption of lead onto oxide surfaces has been modeled by Davis and Kent (1990) using a surface complexation approach. X-ray adsorption fine structure (XAFS) studies of oxides and hydrous oxides have shown that lead generally forms monodentate or bidentate inner-sphere complexes with oxide surfaces at low surface coverage (submonolayer) and may form multinuclear lead complexes at higher surface coverage (near monolayer) (Chisholm-Brause et al., 1990; Manceau et al., 1992; Roe et al., 1991)

Agglomeration Process Literature Review

The science of agglomeration has been described extensively by Pietsch (2001). McClellan et al. (2002) have researched the granulation of limestone fines for purposes of producing a concrete aggregate from quarry waste materials. In their study, three insoluble granule binders were tested and the manufactured granules were tested for strength. The manufactured material was incorporated into concrete and observed by scanning electron microscopy to see how the material changed the quality of concrete when it was incorporated in the mix.

Previous Work by This Research Group Using Limestone-Based Material

Previous research completed by the principal investigators of this grant and others during Phase I and Phase II U.S. EPA Small Business Innovation Research (SBIR) grants and other grants demonstrate arsenic removal of greater than 95 percent by limestone. Some of the research completed so far is presented in Fivecoate (2004), a M.S. thesis in Geological Engineering from the South Dakota School of Mines and Technology.

Research completed used arsenate as the primary form of arsenic tested. Past experiments using arsenite and limestone have shown that limestone does not significantly remove arsenite. An experiment was completed using arsenite that was oxidized prior to contact with limestone in batch experiments and percent arsenic removal was comparable to that seen when arsenate is used.

Materials used for testing arsenic removal (numerous limestone rock types and reagent grade calcium and magnesium carbonates) were characterized using BET specific 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.

Toxicity Characteristic Leaching Procedure (TCLP) tests of arsenic-treated material have shown that final arsenic concentration of the extraction fluid was 24 ppb, well within the standards set for disposal in ordinary landfills. Also, thermal stability tests

of arsenic-treated limestone have shown that the product is thermally stable and can be used as a raw material in cement kilns for manufacturing cement.

Batch experiments were used to examine the impacts of interference ions on arsenic removal. Both chloride and nitrate ions showed interference with arsenic removal. Sulfate did not show much impact to arsenic removal, even at concentrations greater than 1000 ppm. Batch experiments were also completed, using additives to the limestone powder, including magnesium carbonate, iron oxide, titanium oxide, and activated alumina. Iron oxide was found to improve removal significantly, but addition of the material to batch experiments iron-stained the effluent water. Magnesium carbonate was also an effective additive, improving arsenic removal. One drawback to adding magnesium carbonate is that it increases the effluent pH to about 10.

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.

RESEARCH OBJECTIVES

The purpose of this research was to develop a granular adsorbent product that removes dissolved metals and that can be manufactured and sold for use at the drinking water source, at point-of-use, or point-of-entry. This technology has been designed for use by small, rural water supply systems. The major benefit of this research is the development of a low-cost treatment technology for source reduction that will reduce select metals to below drinking water standards. Limestone agglomeration efforts built on the work described in McClellan et al. (2002), in which limestone was granulated for purposes of producing an aggregate for incorporation into concrete. The manufacturing of limestone-based granules was completed on a bench-scale level and did not require specialized equipment.

During earlier phases of this on-going project, laboratory research has indicated improvements in metals removal with finer grain sizes of limestone and the addition of magnesium carbonate. Agglomeration has provided a means to utilize the increase in surface area of powdered material while not compromising filter flow through rates.

The specific objectives, tasks, and criteria for success of this research included:

Objective 1: Development and testing of an agglomeration process for granulating limestone-based material as a filter media for metals adsorption.

Tasks:

- Determine optimum granule grain size, binder, and manufacturing method.

Criteria for Success:

- Development of a bench-scale agglomeration process for granulating powdered limestone mixed with enhancing additives and binder to produce a granulated water filter media.

Objective 2: Development of a mixture formula and manufacturing process for granulation, and production of sufficient quantities for use in batch and column experiments.

Tasks:

- Test the granule mixture formula at different percentages of limestone, additive, and binder to determine the optimum formula for metals removal while still maintaining granule strength and material surface area.
- Perform batch experiments to compare the performance of the different granule mixture formulas.

Criteria for Success:

- Successful production of agglomerated granules with sufficient strength to withstand use in batch and column experiments.
- At a minimum, metals removal efficiency of the manufactured granules will be comparable in efficiency to an equal mass of powdered limestone.

Objective 3: Investigation of the efficiency of the manufactured granules to remove select metals (arsenic, cadmium, and lead) using batch and column experiments.

Tasks:

- Perform batch experiments with granules and varying concentrations of arsenic, cadmium, and lead.
- Develop isotherm models to determine if the metals removal follows an adsorption type model.
- Determine mass of metals removal per gram of material at different metals concentrations.
- Perform column experiments to compare the rate of metals removal by granules versus crushed native limestone of similar size.

Criteria for Success:

- Isotherm models will be developed and mass of metal removed per gram of granule material will be determined.

MATERIALS CHARACTERIZATION AND METHODS

Materials Characterization

Minnekahta Limestone from the Pete Lien and Sons Quarry in Rapid City, South Dakota, was used as the limestone source for this research. Limestone fines were collected from the quarry and sieved to a size of less than 74 microns (sieve mesh #200). Based on X-ray diffraction analysis, Minnekahta Limestone is composed of about 95 percent calcite, 4 percent quartz, and 1 percent microcline. Surface area of the powdered Minnekahta Limestone used in manufacturing the granules was about 1 m²/gram (although this measurement is for ball-milled limestone, as measurements for the sieved powder are not available). Reagent-grade magnesium carbonate, MgCO₃, (source: Fisher Scientific), used as an additive in the granules to enhance arsenic removal, has a specific surface area of about 22 m²/gram. The surface area of the Portland cement used as an insoluble binder in the granules is about 1 m²/g. Portland cement is a hydraulic cement that sets and hardens by reacting chemically with water, a process called hydration. Portland cement is composed of tricalcium and dicalcium silicates, tricalcium aluminoferrite, tricalcium aluminate, and calcium sulfate.

Figure 1 is a photo of manufactured granules after drying. Granules in the red circle are about 1-2 mm in diameter. Table 1 lists specific surface area measurements for three of the granule formulations tested during this research. Overall, granules appear to have a surface area of 4 to 6 m²/gram. In comparison, the surface area of crushed limestone chips of the same diameter (1-2 mm) is about 0.3 m²/gram. Some of the increase in surface area of the granules is likely due to the nature of the granule surface itself – the granules abrade easily, forming powder.



Figure 1. Photo of manufactured limestone-based granules. Granules in the red circle are about 1-2 mm in diameter.

Sample Description	BET Surface Area (m ² /g)
Manufactured granules composed of 10% Portland cement and 90% Minnekahta Limestone	5.3
Manufactured granules composed of 15% Portland cement and 85% Minnekahta Limestone	6.4
Manufactured granules composed of 10% Portland cement, 87% Minnekahta Limestone, and 3% reagent grade MgCO ₃	4.4

Table 1. BET surface area measurements of three formulas of manufactured limestone-based granules.

Scanning electron micrograph (SEM) images of the surfaces of manufactured limestone-based granules were taken to visually characterize the granule surfaces. Figure 2 shows the surface of a manufactured granule of limestone with 10 percent Portland cement binder. Surface area appears to be increased over that of limestone chips, but the granules also seem to be coated, perhaps with the binder. Figure 3 shows the surface of a limestone granule with 15 percent Portland cement binder. In this portion of the granule, it appears that nanometer-sized crystals formed on the surface of the granules. X-ray fluorescence indicated that these crystals are composed of calcium carbonate. This type of crystallization was not observed on all the granules and was not widespread.

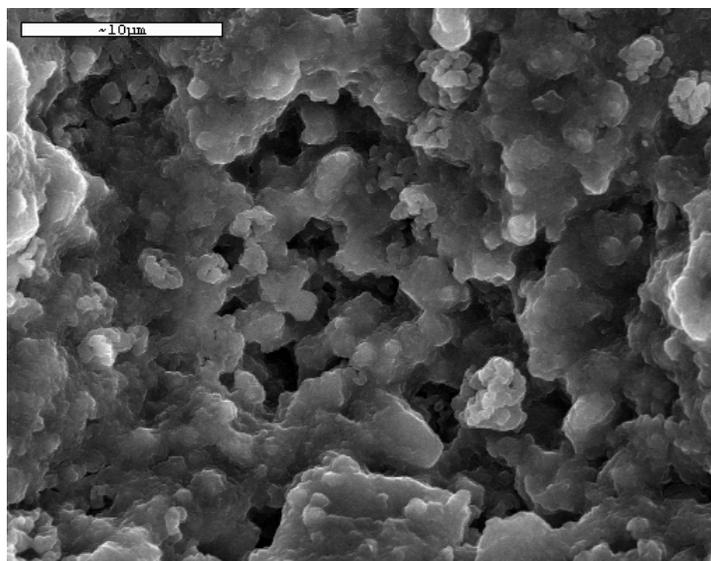


Figure 2. Limestone granule with 10 percent Portland cement binder, taken at 3,500x magnification.

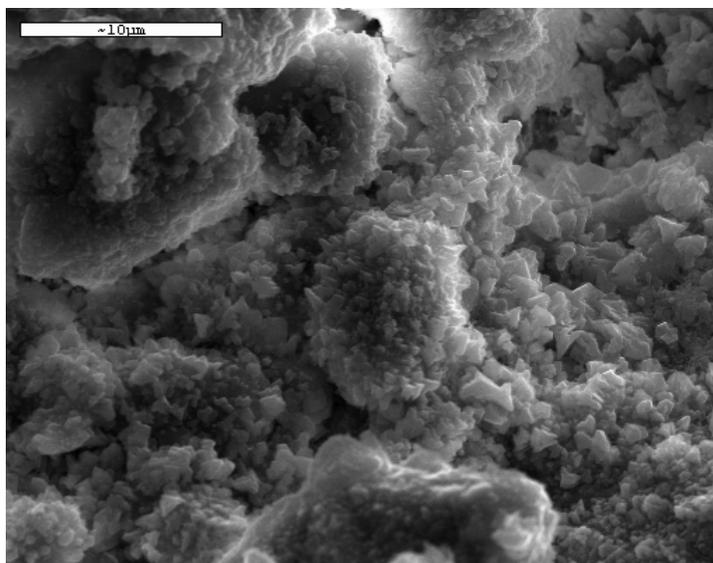


Figure 3. Limestone granule with 15 percent Portland cement binder, taken at 3,500x magnification.

Batch Experiment Methodology

Weighed samples of the limestone-based material are placed in labeled round-bottomed flasks. One-hundred milliliters of metals solution (concentrations vary depending on the experiment and the metal being examined) is added to each flask. The metals solutions are pH-balanced to a pH of 8 ± 2 prior to mixing with the adsorbent using either concentrated nitric acid (HNO_3) or sodium hydroxide (NaOH). The flasks are secured to the wrist shaker (Figure 4) and agitated for 48 hours (or two hours in the case of limestone-based granules). After mixing, the samples are filtered with a $0.45 \mu\text{m}$ filter. The pH and conductivity of the effluent solution are measured. The samples were analyzed by MidContinent Testing in Rapid City, South Dakota for metals concentration.



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

Column Experiment Methodology

The columns are constructed of PVC pipe of varying diameters and lengths, depending on the column design. Influent metals solution is 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 is 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 are collected regularly and the pH and conductivity of the effluent are measured. Samples are filtered with a $0.45 \mu\text{m}$ filter and are then analyzed by MidContinent Testing for metals concentration. Figure 5 shows a typical column set up.



Figure 5. Photo of column experiments being run.

Development of the Agglomeration Process

An investigation of methods for agglomerating powdered limestone into granules was completed for this research. The purpose of agglomeration is to increase the limestone surface area relative to the size of the limestone particles. Since 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 the diameter of sand), efforts were made to granulate powdered limestone, in order to maintain high surface area but allow flow through of water.

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. One advantage of the agglomeration process is that it allows the addition of additives to the limestone that improve removal efficiency. Magnesium carbonate was added to the limestone/binder mix to enhance metals removal efficiency. Limestone agglomeration techniques were derived from the work of McClellan et al. (2002), in which limestone powder was granulated for purposes of producing an aggregate for incorporation in concrete.

The agglomeration was done at bench-scale using a metal coffee can with three paddles attached on the inside as the granulator. Mixed powdered materials were placed in the can and the can was rotated on a bottle roller at about 50 revolutions per minute (rpm). As the can rotated around, water was sprayed into the can using a spray bottle. The process of rotating the can while adding water allowed for the agglomeration to occur and the formation of a wide size range of granules. The granules were wet sieved, spread out on screens, and set in a cement curing room with elevated levels of humidity for several days to promote further hydration of the cement binder. The granules were then air-dried and sieved for use in experiments. After drying, the granules are firm enough to hold their shape in a column and do not disintegrate when exposed to water because the binder

is insoluble. Over time (several weeks), the cement continues to cure and the granules become harder.

RESEARCH RESULTS

Preliminary Batch Experiments to Determine Granule Formulation

Manufactured granules of limestone with Portland cement binder and two different additives (magnesium carbonate and calcium carbonate) were manufactured. Batch experiments using arsenic solution as the dissolved metal were performed to compare arsenic removal by granules with five percent, 10 percent, and 15 percent binder. Batch experiments were also done with one percent and three percent of each additive added to see how this improved arsenic removal efficiency. Each batch experiment with the granules used 1.5 grams of granules as the adsorbent and 100 mL of 100 ppb arsenic solution. The granules used were 2 to 4 mm in size and were made using ball-milled Minnekahta Limestone. Figure 6 shows final arsenic concentrations of each batch experiment. Batch experiments were also completed with 1.5 grams of ball-milled limestone (not granulated) and 90 percent limestone/10 percent binder (not granulated) as a performance comparison for the manufactured granules.

The batch experiment that showed the highest removal efficiency (lowest final arsenic concentration) was the ungranulated mixture of Minnekahta Limestone powder (90 percent by weight) Portland cement powder (10 percent by weight). Powdered cement performs well as an arsenic removal agent, but causes the pH and conductivity of the final solution to be significantly elevated. Final pH values were about 11.5 and conductivity values about 1,800 $\mu\text{mhos/cm}$ for this powdered mixture.

As the percent Portland cement binder was increased in the manufactured granules, final arsenic concentration increased. With 5 percent binder, final arsenic concentration averaged 58 ppb. With 10 percent binder, final concentration increased to 60 ppb and with 15 percent binder, final arsenic concentration was 68 ppb. Research by Kundu et al (2004) shows that at pH values above 7, arsenic removal by hardened cement decreases. Optimum pH for arsenic removal by hardened cement is 4 to 5. Final pH of the batch experiments using limestone granules was about 10. With more binder added to the granules, the Portland cement could also be coating more of the surface area of the powdered limestone and reducing its effectiveness as an arsenic removal agent. Also, as additional binder is added to the mixture, there is less limestone in the mix, which may also reduce arsenic removal.

Manufactured granules with reagent-grade magnesium carbonate as an additive showed promise as an arsenic removal agent. Final arsenic concentration of the batch experiment with one percent MgCO_3 averaged 43 ppb, while the batch experiment with three percent MgCO_3 averaged 32 ppb. This final concentration is similar to the batch experiment of an equal mass of ball-milled limestone (not granulated), which had a final arsenic concentration of 33 ppb. Thus, using granulation and three percent by weight of

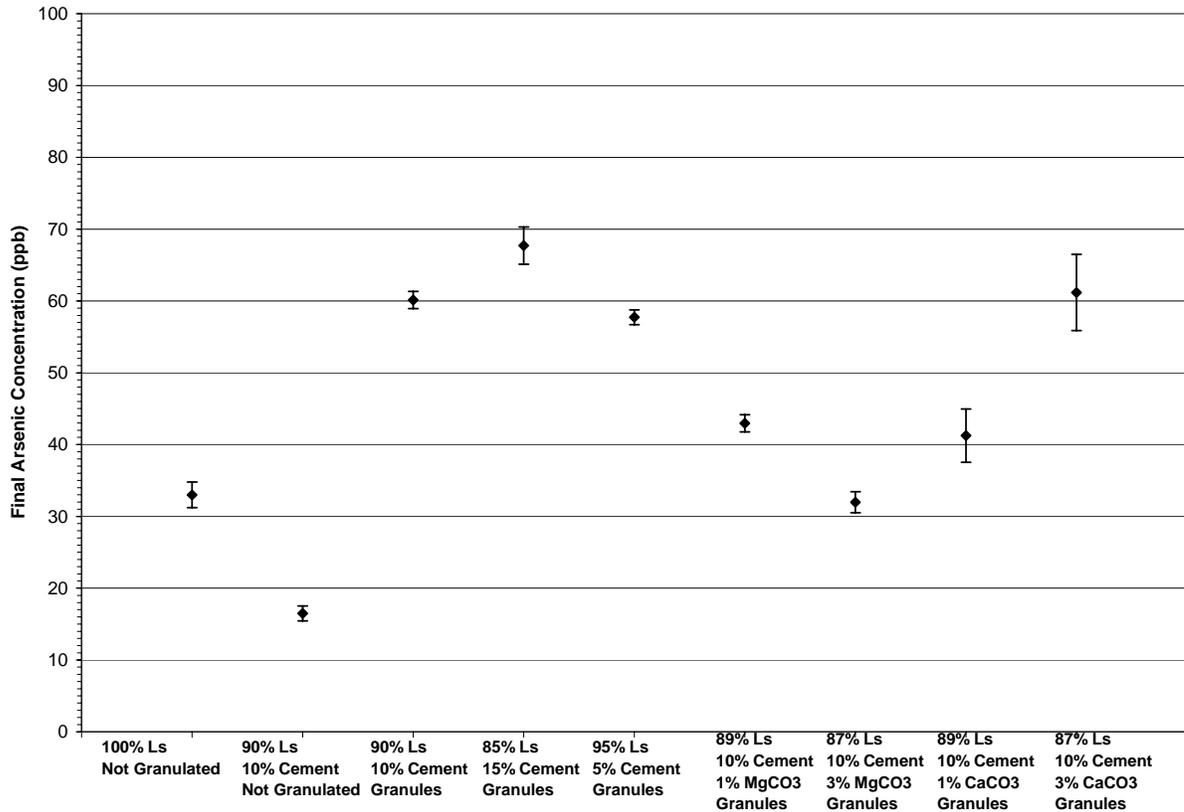


Figure 6. Arsenic removal by different limestone-based granule formulations. Initial batch experiment conditions: 1.5 grams of 2-4 mm sized manufactured granules or powdered limestone-based media in 100 mL 100 ppb arsenic solution, initial solution pH 8 ± 0.2 pH units, room temperature, duration 2 hours.

magnesium carbonate as an additive achieved the same level of arsenic removal as powdered limestone, with the added benefit of being in a form that can be readily used as a filter media. The final pH of solutions treated with granules containing magnesium carbonate ranged from about 10 to 10.5 and conductivity ranged from 100 to 125 $\mu\text{mhos/cm}$. The final pH of solutions treated with limestone powder was 9.6 and had a conductivity of about 60 $\mu\text{mhos/cm}$.

Reagent-grade calcium carbonate, CaCO_3 , as an additive in granules did not perform as well as magnesium carbonate. The batch experiment with one percent CaCO_3 had a final arsenic concentration of 41 ppb, while the batch experiment with three percent CaCO_3 had a final concentration of 67 ppb. The reason for this increase in final arsenic concentration is unclear, although batch experiments with CaCO_3 completed previously have shown that arsenic removal using this additive varies unpredictably and is consistently a poorer performer than magnesium carbonate.

Granule Attrition Resistance Test

The granule attrition resistance test completed for this investigation is based on a method described by Brady and McKay (1996). The purpose of the test is to measure the

amount of fines generated during batch experiments using limestone-based granules due to sample agitation. Two sizes of limestone granules were tested: 1 – 2 mm and 0.5 – 1 mm. The tests used 100 mL of deionized water pH-adjusted to 8.0 ± 0.2 pH units and 1.0 gram of limestone-based granules (87 % limestone sieved to < 74 microns, 3 % magnesium carbonate, and 10 % Portland cement binder). Each test was repeated in triplicate and results averaged. The experiments were completed in 500 mL round bottomed flasks placed on a wrist shaker. The flasks were shaken for two hours. Following agitation, the granules and fines (material < 0.2 mm) were sieved, dried, and weighed. Attrition resistance was then determined as percent granule loss due to production of fines using the equation:

$$\frac{\text{weight of fines (grams)}}{\text{weight of starting granules (grams)}} \times 100 \text{ percent}$$

For the 1-2 mm granules, attrition resistance averaged about 35 percent. For the 0.5 – 1 mm granules, attrition resistance averaged about 42 percent. The smaller granules (0.5 – 1 mm) abraded about six percent more than the 1 – 2 mm granules. For both sizes of granules tested, at least half of the granules remaining after agitation sieved to the starting size range. However, the level of attrition resistance observed for granule testing under batch experiment conditions is significant. This information must be taken into consideration when evaluating data results from batch experiments using granules.

Effect of Granule Size on Arsenic Removal

Batch experiments were completed to compare the effect of the size of the limestone-based granules on arsenic adsorption capacity at three initial arsenic concentrations (50, 100, and 500 ppb). Granules composed of 87 percent Minnekahta Limestone, three percent reagent grade magnesium carbonate, and 10 percent Portland cement as binder were tested at two different granule sizes: 1-2 mm and 0.5-1 mm. The results of this study are shown in Figure 7. It is clear that as initial arsenic concentration increases, adsorption capacity increases for both granule sizes. For 1-2 mm size granules, the increase in adsorption capacity from 100 to 500 ppb arsenic is from 5.4 to 20 ug arsenic per gram limestone-based granules, whereas the increase for 0.5-1 mm size granules is from 8.6 to 37 ug arsenic per gram granules. At an initial concentration of 50 ppb arsenic, there was a difference of 1.1 ug/g between the adsorption capacities of the two granule sizes, with 0.5-1 mm size granules having the greater adsorption capacity. However, because the 1-2 mm size granules are more durable during batch experiments, this granule size was chosen for subsequent batch experiments.

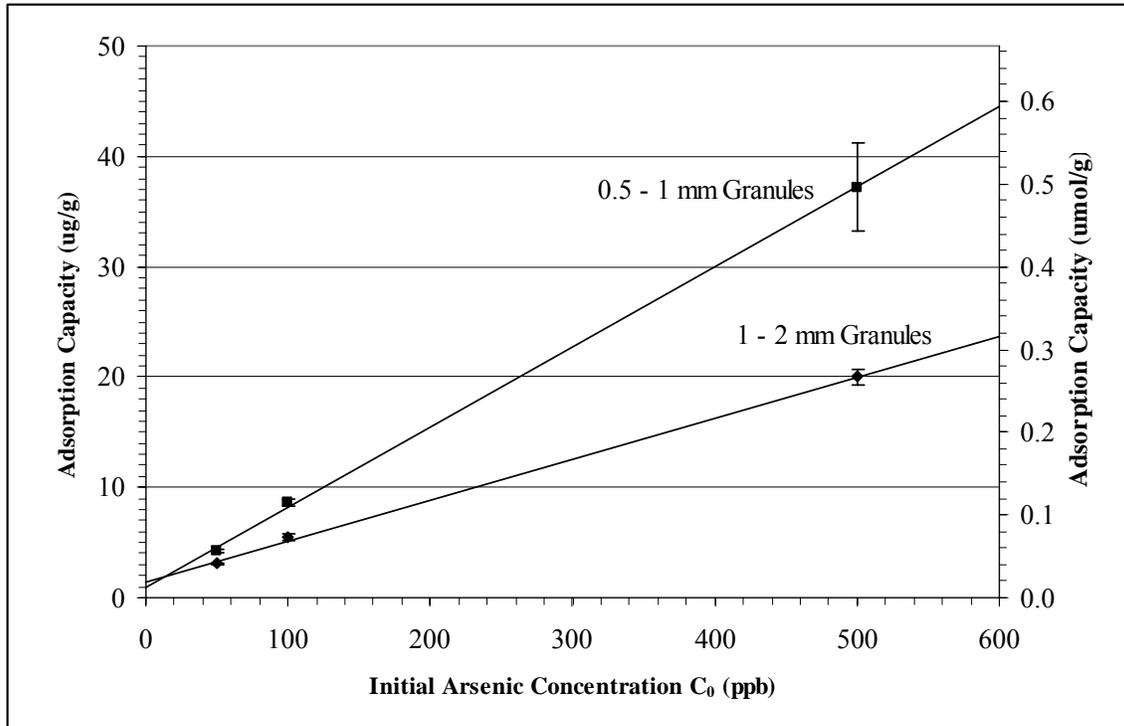


Figure 7. Adsorption capacity of two limestone-based granule sizes at three arsenic concentrations. Initial batch experiment conditions: 1.0 gram of granules (either 0.5-1 or 1-2 mm in size) in 100 mL arsenic solution of three concentrations (50, 100, and 500 ppb), initial solution pH 8 ± 0.2 pH units, room temperature, duration 2 hours.

Adsorption Isotherm Study Using Limestone Powder

There are three main processes by which an aqueous metal solute (such as arsenic, cadmium, or lead) reacts with the surface of a solid phase such as limestone: adsorption, absorption, and surface precipitation (Sposito, 1986). Absorption refers to the diffusion of an aqueous solute into a solid phase to form a solid solution (Sposito, 1986). The bonding mechanisms of adsorption and surface precipitation are similar – adsorption is two-dimensional and surface precipitation is three-dimensional (Corey, 1981). In order for surface precipitation to occur, the aqueous solution must be supersaturated with respect to the solubility of the solid phase. In systems which are undersaturated, either adsorption or absorption will control the concentration of solute. Surface precipitation means that a solid phase grows by the propagation of a molecular unit that repeats itself in three dimensions (Sposito, 1986). The time scale of metal adsorption onto mineral surfaces has typically been found to be in the range of minutes (Davis et al., 1987; McBride, 1980), and is followed by a slow removal step on the time scale of hours to days. This slow step may be due to surface precipitation, co-precipitation, or diffusion of previously adsorbed ions into the existing solid (Martin-Garin et al., 2003).

An adsorption isotherm consists of batch equilibrium experiments that provide data relating the amount of adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in solution. Factors that affect an isotherm model include adsorbent preparation and dosage, pH, temperature, and contact time (Bernardin, 1985).

When examining an isotherm plot, slope provides a visual estimation of the affinity of the adsorbate for the adsorbent. An isotherm with a steeper slope indicates that the adsorbent in that experiment has a greater affinity for the adsorbate than an isotherm with a shallower slope (Deutsch, 1997). A linear (straight line) adsorption isotherm implies that the process of adsorption is not affected by adsorbate concentration in solution and that the surface of the solid has unlimited capacity for adsorption. Such adsorption isotherms are appropriate at low concentrations of adsorbate, but are not appropriate at higher concentrations when the surface sites for adsorption become filled (Deutsch, 1997). Also, isotherm models should be developed for the concentration range likely to be encountered in practice, because the extrapolation of isotherm data can lead to errors and may overestimate adsorption (Kinniburgh, 1986).

The Langmuir isotherm is a commonly used adsorption isotherm for assessing the potential use of an adsorbent material for removal of metals such as arsenic, cadmium, and lead. Based on the results of adsorption studies done for this research, limestone powder as an adsorbent obeys the Langmuir isotherm model and the results show high correlation coefficients with the model.

For adsorption by solid adsorbents from solution, the Langmuir adsorption isotherm is expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

This equation indicates that q_e approaches Q_0 asymptotically as C_e approaches infinity (Faust and Aly, 1987). The linearized form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where:

q_e = adsorption capacity (amount of solute adsorbed per unit weight of adsorbent), $\mu\text{mol/g}$

C_e = equilibrium concentration, $\mu\text{mol/L}$

Q_0 = adsorption capacity required for surface monolayer coverage, $\mu\text{mol/g}$

b = adsorption constant related to the enthalpy of adsorption [$b \propto (\exp(-\Delta H/RT))$], $1/\mu\text{mol}$

When C_e/q_e is plotted against C_e , a straight line, having a slope $1/Q_0$ and an intercept $1/bQ_0$ is obtained. Obtaining slope and intercept values graphically, the constant b can be determined. The monolayer adsorption capacity, Q_0 , defines the total capacity of the adsorbent for a specific adsorbate. However, reliable Q_0 values can only be obtained

if the system exhibits the Type 1 isotherm of the Brunauer's classification (Faust and Aly, 1987).

Linearized isotherms with respect to the Langmuir model are shown in Figure 8 and the calculated Langmuir isotherm constants are tabulated in Table 2. These Langmuir isotherm plots were derived from a series of batch experiments with initial arsenic concentrations varying from 100 to 1000 ppb and amounts of Minnekahta Limestone powder varying from 0.5 to 6.0 grams. Results show that adsorption of arsenic on Minnekahta Limestone conforms to the Langmuir isotherm model at concentrations from 100 to 1000 ppb arsenic.

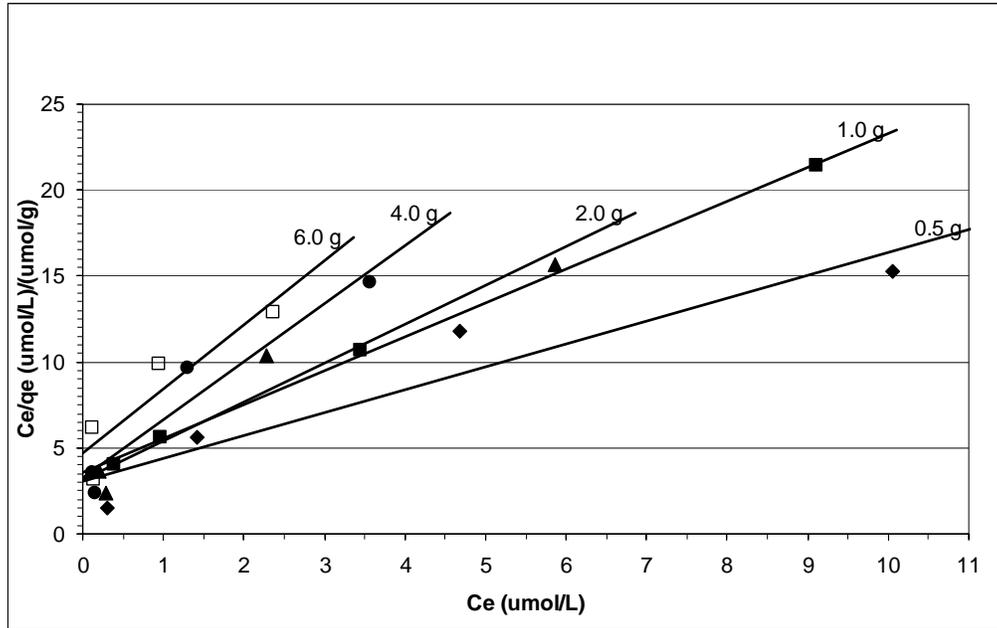


Figure 8. Langmuir adsorption plots for arsenic adsorption on Minnekahta Limestone powder (sieved to less than 74 microns). Batch experiment conditions: 0.5 to 6.0 grams of adsorbent in 100 mL of arsenic solution ranging from 100 to 1000 ppb, initial solution pH 8 ± 0.2 pH units, room temperature, duration 48 hours.

Initial Adsorbent Amount (grams)	Correlation Coefficient R^2	b (1/umol)	Q_0 (umol/g)
0.5	0.8955	0.438	0.75
1.0	0.9989	0.549	0.51
2.0	0.9413	0.725	0.44
4.0	0.9318	1.05	0.29
6.0	0.8481	0.788	0.27

Table 2. Langmuir isotherm parameters for arsenic adsorption on limestone powder as shown in Figure 8.

Effect of pH on Arsenic Removal by Limestone Powder

Arsenic removal by limestone is a process that operates effectively over a wide range of pH values. Figure 9 shows that arsenic removal has limited dependence on initial solution pH over a range from pH 4 to 10. The pH range of natural ground water is from about pH 6 to 8. Batch experiments were completed over a range of pH values, using either nitric acid (HNO_3) or sodium hydroxide (NaOH) to adjust initial solution pH. At the extremely low pH value of 2, dissolution of limestone by the acidic solution occurred. The pH values of the effluent solutions at the end of the experiment were about 7, indicating that limestone dissolution continued throughout the duration of the batch experiment. Final pH values for the pH 4 experiments were an average of 9.3. The two unit drop from pH 4 to pH 2 had a significant impact on system dynamics, causing pH to be suppressed throughout the duration of the experiment. Above pH 10, it appears that the hydroxide ions added to the solutions to adjust pH created ion interference and suppressed arsenic adsorption by the limestone.

Batch experiments were also completed to compare limestone arsenic adsorption capacity at three arsenic concentrations (100, 200, and 500 ppb) and at three pH values (4, 8, and 12). Figure 10 shows the results of this study. Adsorption capacity of the limestone increased as arsenic solution concentration increased. Significant influences of pH on adsorption capacity were limited and were observed at pH 12, where ion interference was seen due to the addition of hydroxide ions for pH adjustment. Also, the drop in arsenic adsorption capacity from pH 4 to 8 for the 500 ppb arsenic solution was greater than at lower arsenic concentrations.

Effect of Initial Arsenic Concentration on Removal by Limestone Powder

The results of this study show that arsenic uptake by limestone powder increases for increasing arsenic concentrations and increasing limestone dosages. In Figure 11, initial arsenic concentration values (100, 200, 500, and 1000 ppb) are plotted versus adsorption capacity at five different adsorbent dosages (0.5, 1.0, 2.0, 4.0, and 6.0 grams). For example, for $C_0 = 100$ ppb, capacity is 0.21 $\mu\text{mol/g}$ by 0.5 grams limestone and 0.020 $\mu\text{mol/g}$ by 6.0 grams limestone, whereas at $C_0 = 1000$ ppb, adsorption capacity is 0.66 $\mu\text{mol/g}$ by 0.5 grams limestone and 0.18 $\mu\text{mol/g}$ by 6.0 grams limestone. The data presented in Figure 11 fits the trend lines well (all R^2 values > 0.9) and this data may be useful in predicting limestone arsenic capacities for batch experiments under similar conditions at other arsenic concentrations between 100 and 1000 ppb for the five adsorbent dosages presented.

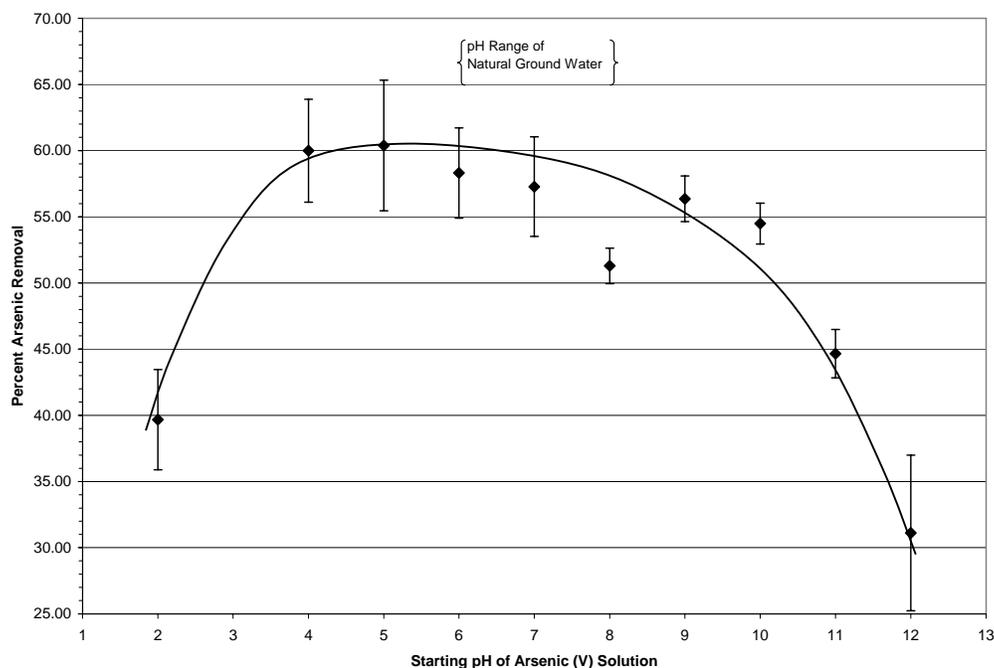


Figure 9. Influence of initial solution pH on arsenic removal. Initial batch experiment conditions: 0.5g ball-milled Minnekahta Limestone in 100 mL 100 ppb arsenic solution, room temperature, duration 48 hours.

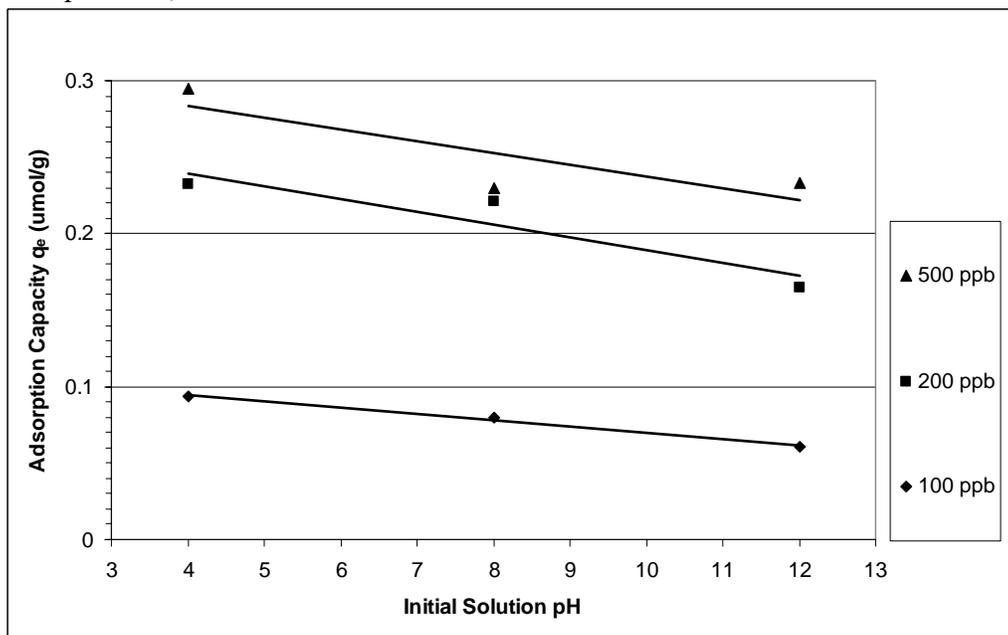


Figure 10. Adsorption capacity of limestone as initial solution pH and starting arsenic concentration are varied. Initial batch experiment conditions: 0.5 mg Minnekahta Limestone (sieved to less than 74 microns) in 100 ml arsenic solution, room temperature, duration 48 hours.

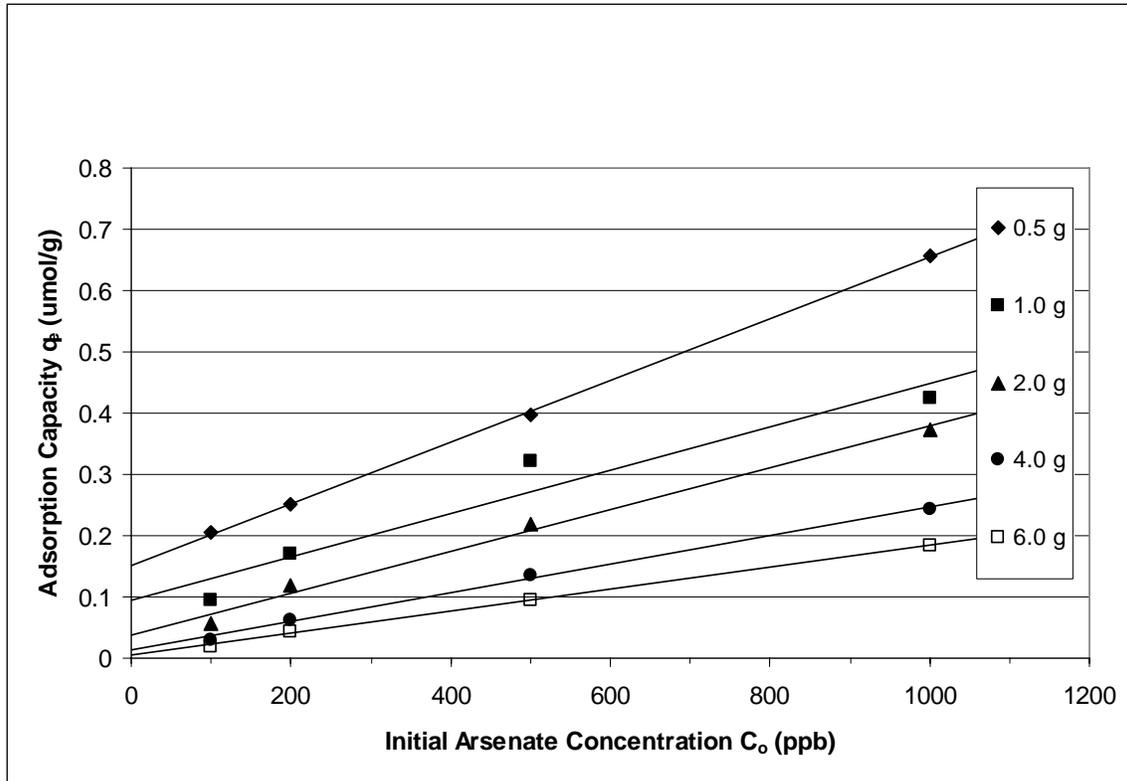


Figure 11. The effect of initial arsenic concentration on arsenic removal at different dosages of Minnekahta Limestone (sieved to less than 74 microns). Initial batch experiment conditions: Minnekahta Limestone (0.5, 1.0, 2.0, 4.0, 6.0 grams) in 100 mL of arsenic solution (100, 200, 500, and 1000 ppb), initial solution pH 8 ± 0.2 pH units, room temperature, duration 48 hours.

Arsenic Removal by Manufactured Granules

The adsorption capacity of 1-2 mm sized limestone-based granules (87 percent Minnekahta Limestone powder, 3 percent magnesium carbonate, and 10 percent Portland cement binder) at three arsenic concentrations (50, 100 and 50 ppb) was shown in Figure 7. Arsenic adsorption capacity of the 1-2 mm granules at 100 ppb starting solution is 5.4 ug arsenic/gram granules. In comparison, an equal mass of limestone powder, ungranulated, has an arsenic capacity of 5.9 ug arsenic/gram limestone, and crushed limestone sieved to 1-2 mm has an adsorption capacity of 4.2 ug arsenic/ gram limestone. Overall, in batch experiments, granulation improves arsenic capacity of the limestone media about 30 percent over the capacity of limestone chips of equal diameter. The arsenic capacity of limestone-based granules is about equal to the capacity of powdered limestone in batch experiments, with the added benefit that granules can be used as a filter media in a column-type filter device without impairing flow-through rates.

Cadmium Removal by Manufactured Granules

Initial batch experiments with cadmium solutions in the range of parts per billion removed all cadmium in solution. Batch experiments with 0.5 grams powdered limestone

and 60 to 80 ppb cadmium at three pH values (5, 8, and 10) removed cadmium to below analysis detection limits (10 ppb). Solution concentrations were increased to part per million levels in order to reach effluent cadmium concentrations greater than 10 ppb.

Batch experiments were completed using 1.0 gram of limestone-based granules and 100 mL of solution with cadmium concentrations of 5, 20, and 50 ppm. At these concentrations, cadmium removal by the granules was greater than 99 percent for all three concentrations. Because cadmium removal was greater than 99 percent, an adsorption isotherm could not be developed.

Adsorption capacities of the granules at the three concentrations show that cadmium uptake increases dramatically for increasing cadmium concentrations. In Figure 12, initial cadmium concentration values (5, 20, and 50 ppm) are plotted versus adsorption capacity at an adsorbent dosage of 1.0 gram. 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 12 fits the trend line well (R^2 value > 0.9) and it follows that this figure may be useful in predicting limestone cadmium capacities for batch 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-based granules to remove cadmium is much greater than the capacity for arsenic removal by granules.

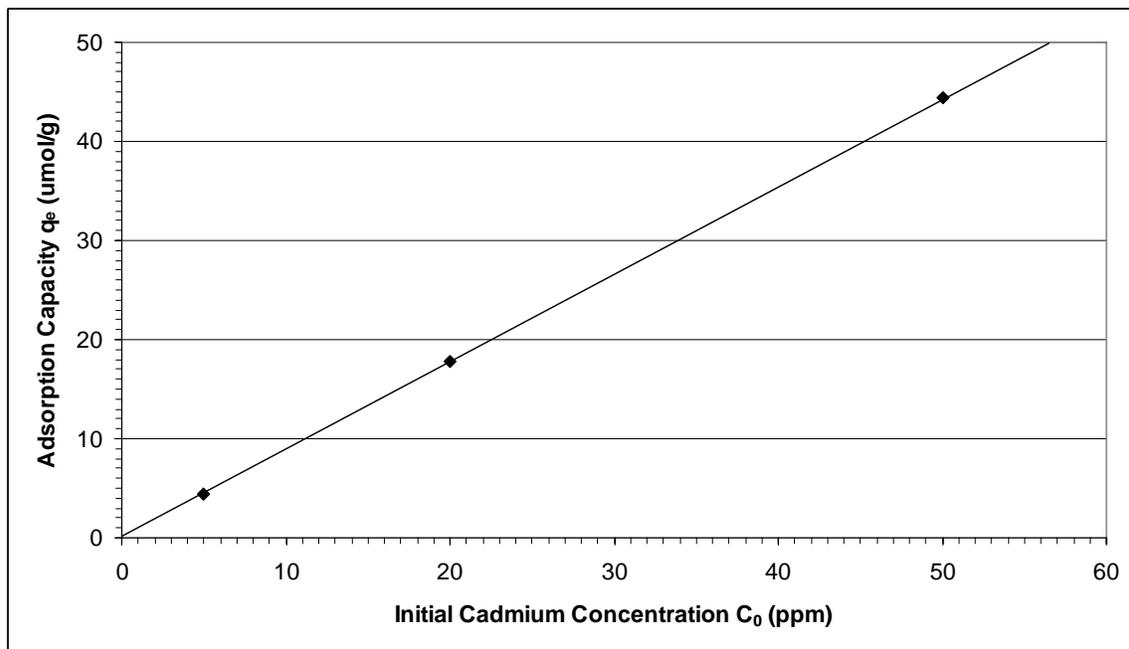


Figure 12. Cadmium adsorption capacity of limestone-based granules for initial cadmium concentrations of 5, 20, and 50 ppm. Initial batch experiment conditions: 1.0 g granules in 100 mL cadmium solution of three concentrations (5, 20, and 50 ppm), initial pH 8.0 ± 0.2 pH units, room temperature, duration 2 hours.

Lead Removal by Manufactured Granules

Initial batch experiments with lead solutions in the range of parts per billion removed all lead in solution. Batch experiments with 0.5 grams powdered limestone and 80 to 100 ppb lead removed lead to below analysis detection limits (10 ppb). Solution concentrations were increased to part per million levels to try to obtain effluent lead concentrations greater than 10 ppb. However, batch experiments using 1.0 gram of limestone-based granules and 100 mL of lead at concentrations of 0.5 ppm, 2 ppm, and 3 ppm, also resulted in lead concentrations below the analysis detection limits. From these results it is clear that the capacity for lead removal by limestone-based granules is much greater than the capacity for arsenic removal. Because adsorption at all lead concentrations was below analysis detection limits, an adsorption isotherm for lead could not be developed.

An interesting phenomenon occurred when mixing the lead solutions. The solutions were initially mixed to concentrations of 5, 20, and 50 ppm. The solutions were pH-adjusted to about 8 using small quantities of concentrated sodium hydroxide. After pH-adjustment, it was noted that a fine white precipitate formed in the solutions. It is thought that this was a precipitate of lead hydroxide ($\text{Pb}(\text{OH})_2$) that formed, reducing the dissolved lead concentrations of the mixed solutions. Lead hydroxide has a very low solubility, with a solubility product (K_{SP}) equal to 2.5×10^{-16} .

Arsenic Removal: Limestone Chips Versus Manufactured Granules - Column Experiments

Two column studies were completed to compare the efficiency of manufactured limestone-based granules to crushed limestone chips. One column was run with 1-2 mm sieve size untreated limestone and the other column was run with 1-2 mm size manufactured limestone-based granules (containing 87 percent Minnekahta Limestone, 10 percent Portland cement binder, and three percent reagent-grade magnesium carbonate) as a comparison. Both columns used a starting solution containing 100 ppb arsenic. Column size was 12 inches long by 1 inch in diameter.

The column of 1-2 mm washed Minnekahta Limestone chips was packed with 249.6 grams of material. Figure 13 is a plot of the measured effluent arsenic concentration during the total run time of 720 minutes (12 hours). Based on this graph, the time of breakthrough at 10 ppb occurred prior to the first sampling at 60 minutes. Flow through the column was 1.2 liters per hour (eight bed volumes per hour). About 14.5 liters of water passed through the column before complete exhaustion of the column material. This corresponds to about 97 bed volumes.

The column of 1-2 mm diameter manufactured limestone-based granules was packed with 159.248 grams of material. Figure 14 is a plot of the measured effluent arsenic concentration during the total run time of 1,740 minutes (29 hours). Based on this graph, the time of breakthrough at 10 ppb was about 600 minutes (10 hours). Flow through the column was 1.2 liters per hour (eight bed volumes per hour). About 12 liters of water passed through the column before breakthrough occurred. This corresponds to about 80 bed volumes. About 35 liters of water passed through the column before complete exhaustion of the column material. This corresponds to about 233 bed volumes.

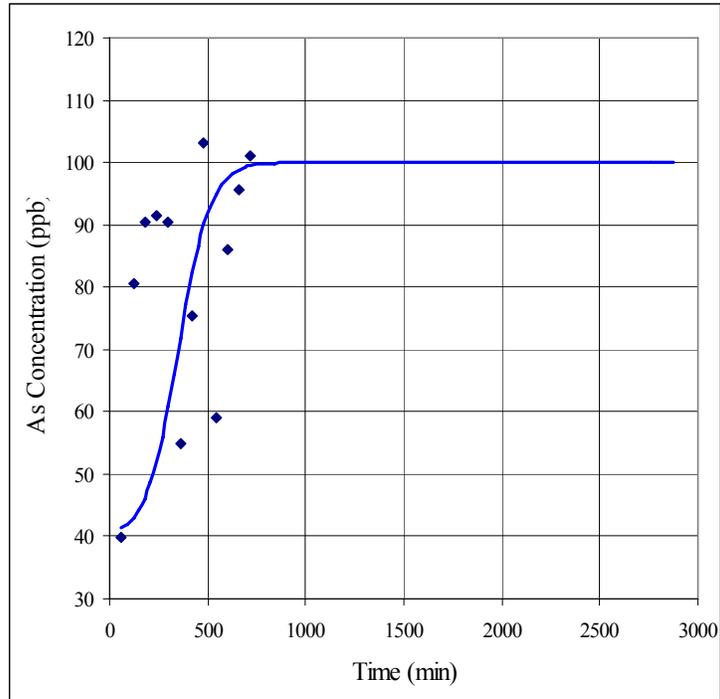


Figure 13. Results of column study using 12 inch by 1 inch diameter column, with Minnekahta Limestone, sieve size 1-2 mm, as the adsorbent, influent arsenic concentration of 100 ppb, and a flow rate of eight bed volumes per hour (1.2 L/hr)

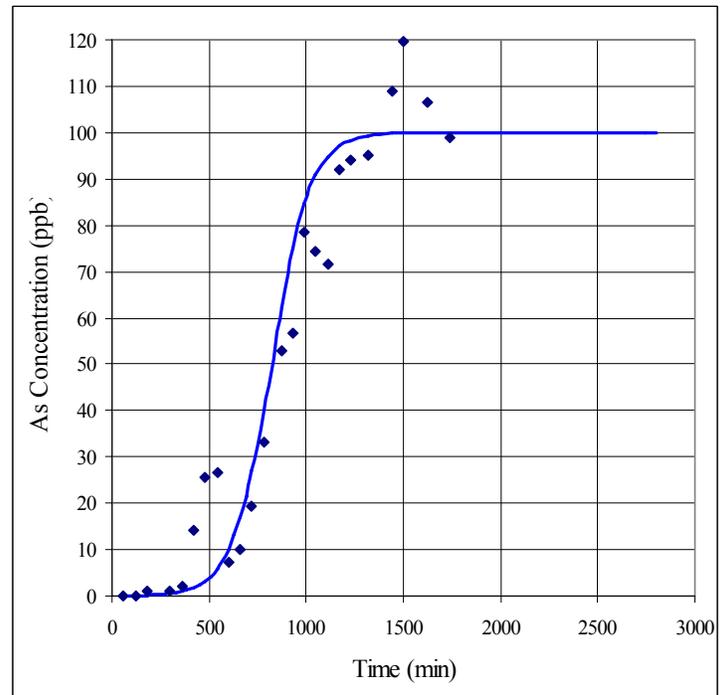


Figure 14. Results of column study using 12 inch by 1 inch diameter column, with limestone-based manufactured granules as the adsorbent, influent arsenic concentration of 100 ppb, and a flow rate of eight bed volumes per hour (1.2 L/hr).

This preliminary comparison column study shows that limestone-based granules with magnesium carbonate added as an additive performed about four times as well as the limestone chips of equal diameter. In these two column studies, the 1-2 mm limestone chips removed a total of about 5.8 ug arsenic/gram limestone while the 1-2 mm limestone-based granules removed about 22 ug arsenic/gram limestone.

Two column studies were completed to compare the capacity of arsenic removal by crushed limestone chips and manufactured limestone-based granules from water from a city well in Keystone, South Dakota. One column experiment was run with 0.2-0.5 mm sieve size untreated Minnekahta Limestone using a 12 inch long by 1.5 inch diameter column and the other experiment was run with manufactured limestone-based granules (containing 87 percent Minnekahta Limestone, 10 percent Portland cement binder, and three percent reagent-grade $MgCO_3$) in a 12 inch long by 1 inch diameter column. Both columns were run using water sample KEY-2 (water analysis shown in Table 3), which contained 50 ppb dissolved arsenic. Arsenic in the Keystone well is naturally occurring.

For the first column experiment, a column was packed with 587.208 grams of 0.2-0.5 mm sieve size washed Minnekahta Limestone. Figure 15 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 (at which point the 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 6.4 ug arsenic were treated by each gram of limestone.

For the second experiment, the column was packed with 168.681 grams of 1-2 mm diameter manufactured limestone-based granules. Figure 16 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 9.8 micrograms of arsenic were treated by each gram of limestone-based granules. This sorption capacity estimate indicates that the limestone under these conditions had a low capacity, although it is an improvement of about 1.5 times over the sorption capacity of the column experiment that was run with 0.2-0.5 mm 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. A preliminary examination of the water quality analysis completed for the Keystone City well (Table 3) does not provide a clear explanation as to why arsenic removal capacity of limestone decreases when using natural well water as compared to arsenic-spiked deionized water solutions.

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

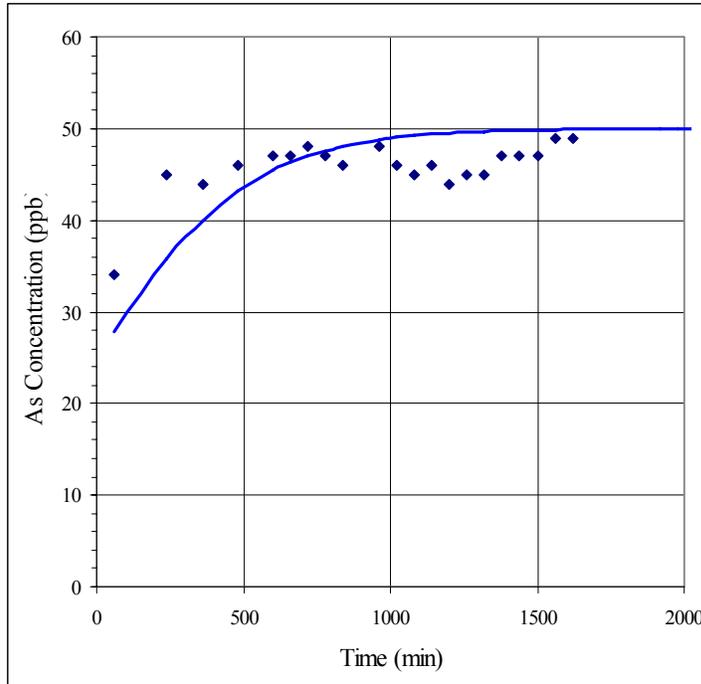


Figure 15. Results of column study using 12 inch by 1.5 inch diameter column, Minnekahta Limestone, sieve size 0.2-0.5 mm, influent arsenic concentration 50 ppb in KEY-2 water sample (source: Keystone No. 4 City Well), and a flow rate of 8 bed volumes/hour (2.8 L/hr).

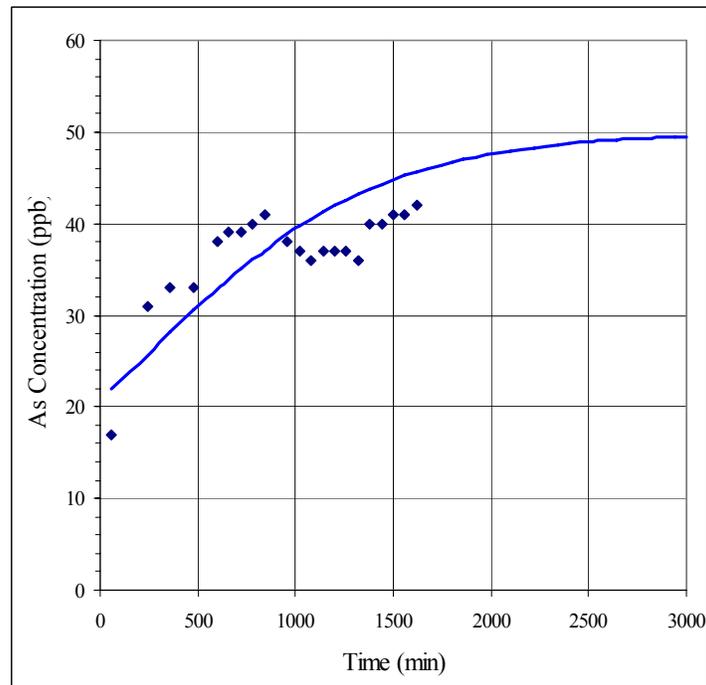


Figure 16. Results of 12 inch by 1 inch diameter column with manufactured 1-2 mm size limestone-based granules as the adsorbent, and influent arsenic concentration 50 ppb in the KEY-2 water sample (source: Keystone No. 4 City Well, Keystone, South Dakota), and a flow rate of 8 bed volumes/hour (1.23 L/hr).

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research was to develop an agglomeration process to increase the efficiency of limestone-based material to remove metals from drinking water. The end goal was to develop a granular adsorbent product that removes dissolved metals and that can be manufactured and sold for use at the drinking water source, at point-of-use, or point-of-entry. During earlier phases of this on-going project, laboratory research has shown improvements in metals removal with finer grain sizes of limestone.

Agglomeration, the process of taking fine materials and forming them into larger spherical granules, provided a means to utilize the increase in surface area acquired through agglomeration while not compromising water flow through rates of the adsorbent material.

This research had three specific objectives, each of which was met during this research. Objective 1 was the development and testing of an agglomeration process for granulating limestone-based material as a filter media for metals adsorption. A bench scale agglomeration process was developed for granulating limestone powder using a coffee can, bottle roller, and water spray bottle. No specialized equipment was required to complete the process.

Objective 2 was the development of a granule formula. To develop the formula, several mixtures of limestone powder, binder, and additives were tested. It was found that cement works as an insoluble binder and can be added in powdered form to the limestone. Two additives were tested: magnesium carbonate and calcium carbonate. Magnesium carbonate was found to be the better additive for increasing arsenic removal. The granule formula chosen contained 87 percent powdered limestone (sieved to less than 74 microns), 10 percent Portland cement binder, and three percent reagent-grade magnesium carbonate powder. Preliminary testing found that limestone-based granules with three percent magnesium carbonate remove about the same quantity of arsenic as an equal mass of limestone powder.

Objective three was the investigation of the efficiency of the manufactured granules to remove arsenic, cadmium, and lead, using batch and column experiments. By performing an isotherm study, it was found that the adsorption of arsenic by limestone follows the Langmuir isotherm model. Arsenic removal by limestone does not show a pH dependence in the pH range from 4 to 10. Arsenic adsorption capacity of 1-2 mm sized manufactured granules at a starting concentration of 100 ppb arsenic was 5.4 ug arsenic per gram granules. In comparison, an equal mass of limestone powder has an arsenic capacity of 5.9 ug/gram and 1-2 mm crushed limestone chips have a capacity of 4.2 ug/gram. Agglomeration provides a means of maintaining the arsenic adsorption capacity of powdered limestone while providing a means for water flow-through in a column-type water treatment unit. This was demonstrated by column experiments which showed that 1-2 mm limestone-based granules had an adsorption capacity about four times greater than crushed limestone chips of the same diameter. Arsenic adsorption capacity by the granules dropped from 22 ug/gram to 9.8 ug/gram when naturally occurring groundwater with arsenic at 50 ppb was tested as the influent solution.

Limestone-based granules showed a very high adsorption capacity for both cadmium and lead. At concentrations from 5 to 50 ppm, greater than 99 percent of the

cadmium was removed by the granules in batch experiments. Lead was removed to below detection limits for all concentrations measured (up to 3 ppm).

There are a number of directions in which this research may be expanded:

1. Test additional granule formulas. Materials such as granulated activated carbon, activated alumina, silica gel, or iron hydroxides (such as granulated ferric hydroxide) are known to remove arsenic, cadmium, and lead from drinking water. These materials could be added to the limestone granules to enhance metals removal. Also, a technique for loading iron onto the limestone surface (both crushed limestone chips and limestone powder) could be developed.
2. Test additional cation metals such as nickel, cobalt, zinc, manganese, and iron. These metals all have +2 oxidation states similar to cadmium and lead and would be expected to be removed by a limestone-based adsorbent.
3. Perform further batch experiments using naturally-occurring groundwater spiked with metals to develop isotherm models for removal by limestone powder and limestone-based granules. Naturally occurring water samples typically do not remove as much dissolved metals from solution as a starting solution of deionized water spiked with metals because of high total dissolved solids and multiple ion interferences. Further testing would quantify removal capacity of the limestone-based materials from natural waters, information that is important when designing full-scale treatment systems.
4. Perform additional column studies using naturally occurring groundwater for engineering scale-up purposes. Column experiments with multiple columns could be performed (increasing the material bed length) and the results used to scale-up a treatment unit for installation at an onsite pilot study. Column studies could be done using both crushed limestone chips and limestone-based granules as a comparison. Different metals could be tested by spiking the influent groundwater solution with the metals.
5. Test adsorption capacity with more than one metal in solution using batch and/or column studies to see if adsorption interference is observed between the metals.

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