Arsenic Remediation of Drinking Water

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ABSTRACT

The recent reduction of the U.S. EPA's maximum contaminant level for arsenic has prompted increased research into methods for removing it from drinking water. Previous work has indicated the possibility that limestone is capable of arsenic removal. This research is a preliminary investigation of the feasibility of a limestone-based arsenic removal process.

Research summarized in this work includes batch and column experiments. A significant literature review also was conducted on arsenic's uses, history, background exposure, toxicity, and distribution. The experiments primarily investigated the ability of Minnekahta Limestone to remove arsenic from a solution of arsenic and deionized water, hereafter referred to as standard solution.

Minnekahta Limestone was successful in effectively removing arsenic from standard solutions. This held true regardless of the water's pH, within the normal range of drinking water sources. All four grain sizes, ranging from 0.5 to 6.7 mm in diameter, of limestone successfully reduced arsenic concentrations from ~100 parts per billion to less than 5 parts per billion. The greatest efficiency of arsenic removal was achieved with limestone of the smallest grain size.

The series of experiments raised some areas of concern. Arsenic was not removed as efficiently from water with high total dissolved solids concentrations as from prepared standard solutions. The process's waste product, arsenic-saturated limestone, may be susceptible to leaching. Arsenic was partially remobilized when deionized water was used to rinse the waste product. Preliminary Toxic Characteristic Leaching Procedure tests, performed according to U.S. Environmental Protection Agency protocols, indicate that the waste is stable. However, additional research on disposal or reuse of the waste product is needed.

Limestone-based arsenic removal appears to have merit. Minnekahta Limestone consistently removed arsenic from solution. If and when it is made applicable to a variety of natural waters, limestone-based arsenic removal could provide a simple, inexpensive method for dealing with elevated arsenic concentrations.

ACKNOWLEDGEMENTS

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INTRODUCTION

Arsenic, while common in many environments, 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 reduction reflects the potentially harmful nature of arsenic, especially inorganic arsenic. The lower MCL will affect a significant number of water suppliers and users in many regions of the United States. Figure 1 shows those counties which have water supplies that will be affected by the lower arsenic MCL; darker shaded counties have higher arsenic concentrations (Focazio et al., 2000).

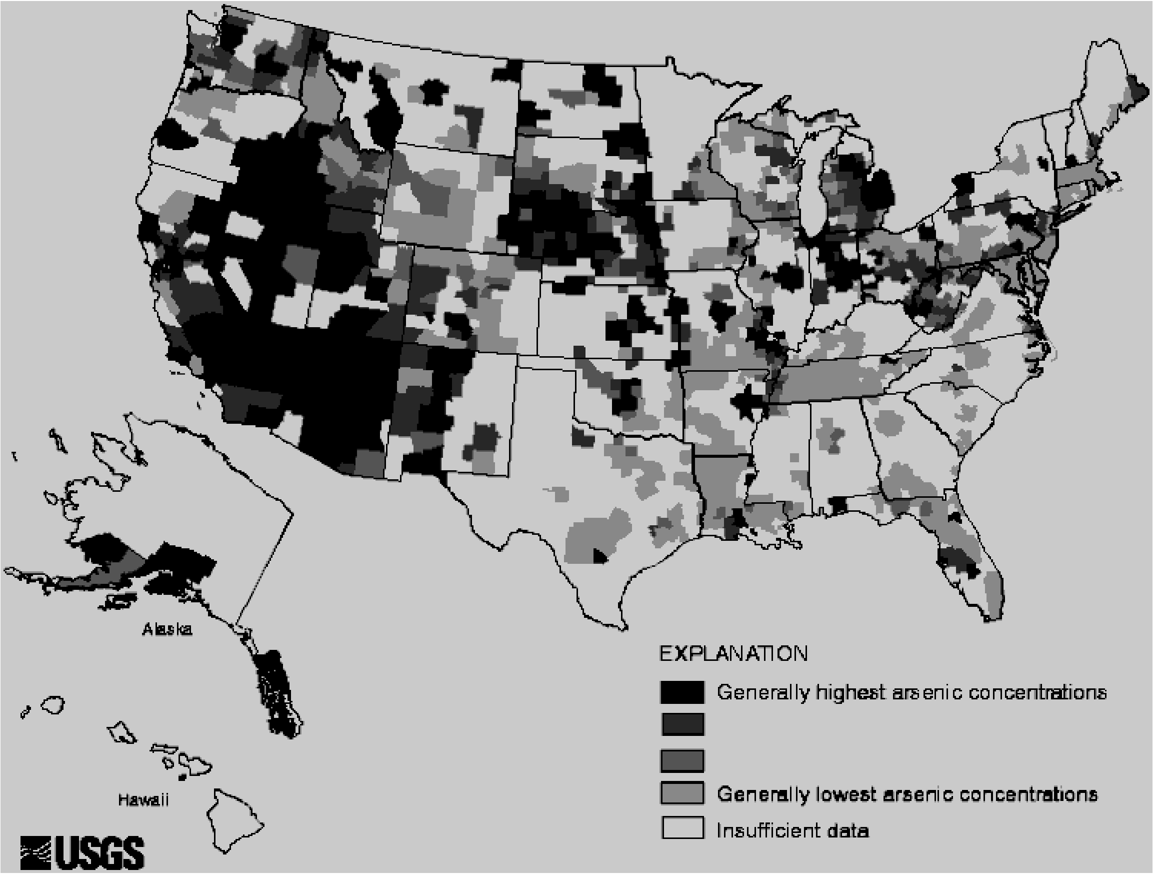


Figure 1. Counties in the U.S. with elevated arsenic concentrations (from Focazio et al., 2000).

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.

ARSENIC

History and Present Uses

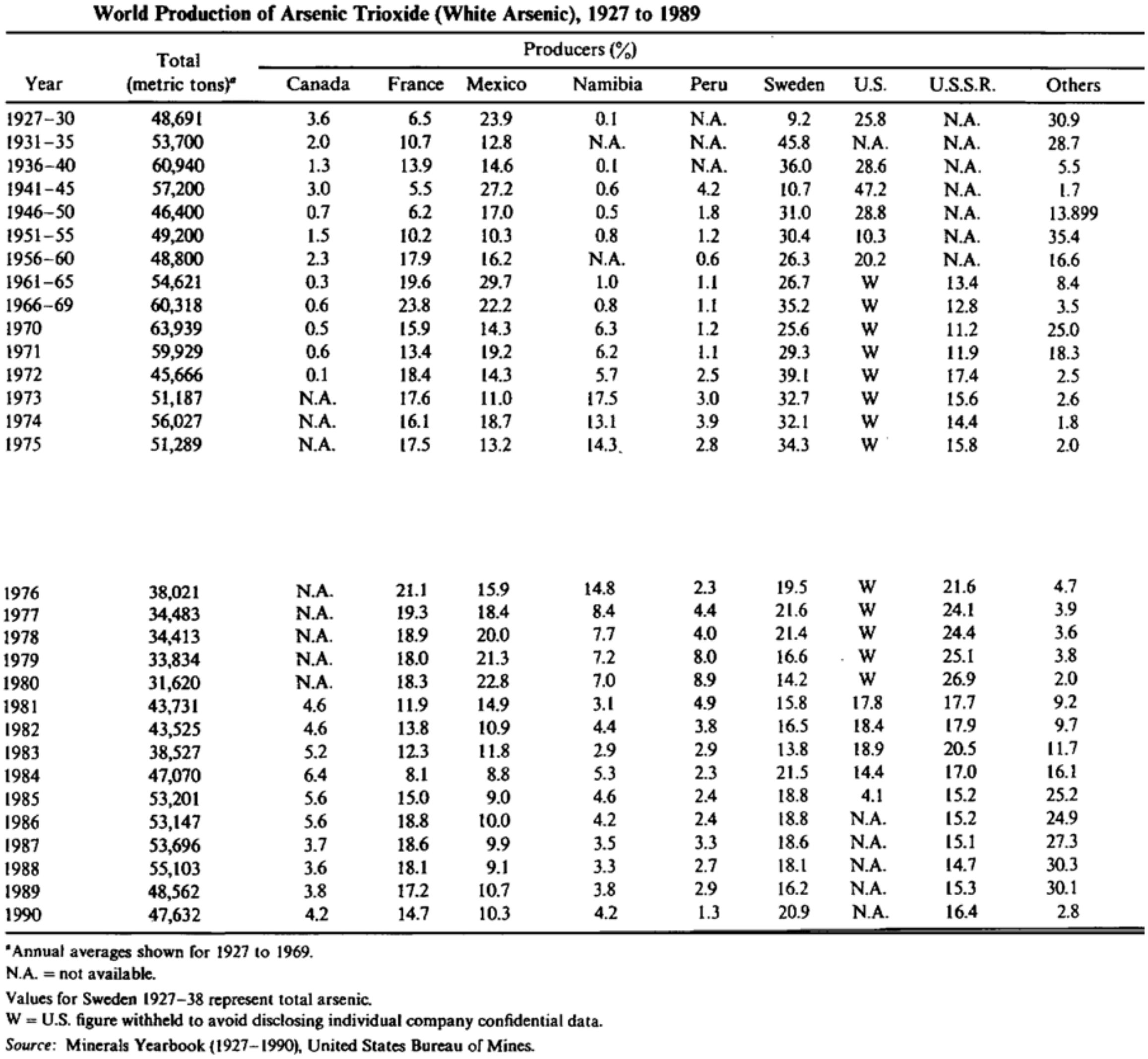
The discovery of elemental arsenic occurred during the 13th century and is usually attributed to Albertus Magnus. However, references to arsenic compounds were common much earlier. Aristotle wrote of arsenic's toxicity in 34 BC. Much of the early interest in arsenic was related to alchemy. The writings of Pliny claim that Caligula extracted gold from the yellow-colored arsenic sulfide, orpiment. Arsenic oxides also were a key ingredient in a supposed transmutation of copper to silver (Azcue and Nriagu, 1994).

Arsenic has been used for decorative and medicinal uses. The bright red and yellow arsenic sulfides were used to color paints, inks, and cosmetics. It was used as a fluxing agent in early glass production. Medical uses varied extensively and included supposed cures for syphilis, anemia, leprosy, and many other afflictions. As Fowler's solution, 1% potassium arsenite solution, arsenic remained a common medicine into the early 20th century. By the late 1800s, however, London's medical community recommended reduced arsenic exposure (Azcue and Nriagu, 1994).

Arsenic is most widely known as a poison. Arsenic trioxide (As_2O_3), also known as white arsenic, is a metallurgical by-product of the refining of ores, hence the industrial form. Because it is odorless, tasteless, and toxic, arsenic has long been a favorite murder weapon. The French termed it *poudre de succession*, or inheritance powder. Its widespread use as a poison resulted in laws banning the possession of white arsenic (Azcue and Nriagu, 1994). Alternatives to oral arsenic poisoning included poisonous candles since white arsenic sublimates when heated. Arsenic has been suggested as the cause of death for Napoleon, Leopold I of Austria, and Clare Boothe Luce, a former U.S. Ambassador to Italy (Azcue and Nriagu, 1994). The assumed prevalence of arsenic poisoning sometimes adversely affected rationality, as in the Maybrick case. In late 19th century England, Mrs. Maybrick was found guilty of murdering her husband. The case was built on circumstantial evidence of arsenic in the household. She is now thought to have been innocent (JAMA, 1995). The Maybrick case typifies the widespread belief that arsenic was, first and foremost, a poison.

Currently arsenic production is a by-product of ore smelting. White arsenic production grew quickly in the first quarter of the last century as a result of an increased demand for insecticides. Recent arsenic production totals are shown in Table 1 (Azcue and Nriagu, 1994).

Table 1. World-wide white arsenic production (from Azcue and Nriagu, 1994).



World Production of Arsenic Trioxide (White Arsenic), 1927 to 1989

Year	Total (metric tons)[a]	Producers (%)								
		Canada	France	Mexico	Namibia	Peru	Sweden	U.S.	U.S.S.R.	Others
1927–30	48,691	3.6	6.5	23.9	0.1	N.A.	9.2	25.8	N.A.	30.9
1931–35	53,700	2.0	10.7	12.8	N.A.	N.A.	45.8	N.A.	N.A.	28.7
1936–40	60,940	1.3	13.9	14.6	0.1	N.A.	36.0	28.6	N.A.	5.5
1941–45	57,200	3.0	5.5	27.2	0.6	4.2	10.7	47.2	N.A.	1.7
1946–50	46,400	0.7	6.2	17.0	0.5	1.8	31.0	28.8	N.A.	13.899
1951–55	49,200	1.5	10.2	10.3	0.8	1.2	30.4	10.3	N.A.	35.4
1956–60	48,800	2.3	17.9	16.2	N.A.	0.6	26.3	20.2	N.A.	16.6
1961–65	54,621	0.3	19.6	29.7	1.0	1.1	26.7	W	13.4	8.4
1966–69	60,318	0.6	23.8	22.2	0.8	1.1	35.2	W	12.8	3.5
1970	63,939	0.5	15.9	14.3	6.3	1.2	25.6	W	11.2	25.0
1971	59,929	0.6	13.4	19.2	6.2	1.1	29.3	W	11.9	18.3
1972	45,666	0.1	18.4	14.3	5.7	2.5	39.1	W	17.4	2.5
1973	51,187	N.A.	17.6	11.0	17.5	3.0	32.7	W	15.6	2.6
1974	56,027	N.A.	16.1	18.7	13.1	3.9	32.1	W	14.4	1.8
1975	51,289	N.A.	17.5	13.2	14.3	2.8	34.3	W	15.8	2.0
1976	38,021	N.A.	21.1	15.9	14.8	2.3	19.5	W	21.6	4.7
1977	34,483	N.A.	19.3	18.4	8.4	4.4	21.6	W	24.1	3.9
1978	34,413	N.A.	18.9	20.0	7.7	4.0	21.4	W	24.4	3.6
1979	33,834	N.A.	18.0	21.3	7.2	8.0	16.6	W	25.1	3.8
1980	31,620	N.A.	18.3	22.8	7.0	8.9	14.2	W	26.9	2.0
1981	43,731	4.6	11.9	14.9	3.1	4.9	15.8	17.8	17.7	9.2
1982	43,525	4.6	13.8	10.9	4.4	3.8	16.5	18.4	17.9	9.7
1983	38,527	5.2	12.3	11.8	2.9	2.9	13.8	18.9	20.5	11.7
1984	47,070	6.4	8.1	8.8	5.3	2.3	21.5	14.4	17.0	16.1
1985	53,201	5.6	15.0	9.0	4.6	2.4	18.8	4.1	15.2	25.2
1986	53,147	5.6	18.8	10.0	4.2	2.4	18.8	N.A.	15.2	24.9
1987	53,696	3.7	18.6	9.9	3.5	3.3	18.6	N.A.	15.1	27.3
1988	55,103	3.6	18.1	9.1	3.3	2.7	18.1	N.A.	14.7	30.3
1989	48,562	3.8	17.2	10.7	3.8	2.9	16.2	N.A.	15.3	30.1
1990	47,632	4.2	14.7	10.3	4.2	1.3	20.9	N.A.	16.4	2.8

[a] Annual averages shown for 1927 to 1969.
N.A. = not available.
Values for Sweden 1927–38 represent total arsenic.
W = U.S. figure withheld to avoid disclosing individual company confidential data.
Source: Minerals Yearbook (1927–1990), United States Bureau of Mines.

Lead and copper ores often contain 2 to 3% arsenic, while gold ores can contain up to 11%. The vast majority, 97%, of arsenic produced is As_2O_3. Three-fourths of the amount produced is used by agriculture in pesticides and animal feed additives. The United States uses about half of the world production and is a net importer (U.S. Environmental Protection Agency, 1980). Seventy percent of U.S. demand is for use as a wood preservative. The remaining 3% of total arsenic production is metallic arsenic, which is used in some lead and copper alloys. The electronics industry uses high-purity

(99.999%) metallic arsenic in the manufacture of semiconductors (Azcue and Nriagu, 1994).

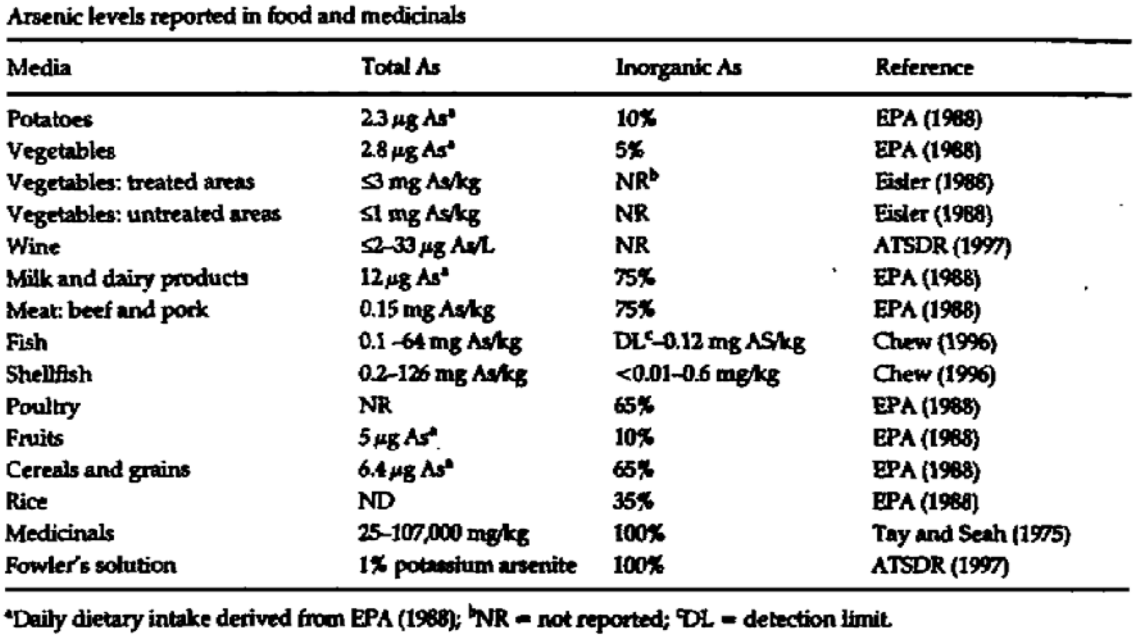
Distribution

Arsenic is abundant and widespread in the environment. At a concentration of 5 mg/kg, it is the 20th most common element in the earth's crust (U.S. Environmental Protection Agency, 1980). Arsenic is the 14th most common element in seawater and the 12th most common element in the human body (Nagui et al., 1994). Mispickel, also known as arsenopyrite, is the most common arsenic-bearing mineral (Bhumbla and Keefer, 1994). Arsenic tends to concentrate in four environments: lacustrine, volcanic, geothermal, and mineral ores (Welch et al., 1988). Arsenic's ability to substitute for ferric iron, aluminum in silicates, and silicon leads to high arsenic concentrations in iron oxides, aluminosilicates, and volcanic glasses. Sedimentary rocks, especially those derived from clays, are higher in arsenic concentration than are igneous or metamorphic rocks. Increased retention of arsenic by smaller grains, hence larger surface area per weight, is the leading cause of arsenic concentrations in sediment. Human exposure to arsenic from rocks is minimal except in a few mining and industrial situations.

Food can contain high levels of arsenic. Seafood, especially shellfish, can contain more than 100 parts per million (ppm) arsenic. Fortunately this arsenic is almost entirely of the safer organic form. Beef and pork have relatively high inorganic arsenic concentrations. Vegetables, grains, and fruits also contribute significant inorganic arsenic to the diet (Grissom et al., 1999). Dairy products also have significant inorganic arsenic content.

Table 2 (Grissom et al., 1999) lists these and other dietary sources of arsenic.

Table 2. Amounts of arsenic found in various foods (from Grissom et al., 1999).



Arsenic levels reported in food and medicinals

Media	Total As	Inorganic As	Reference
Potatoes	2.3 μg As[a]	10%	EPA (1988)
Vegetables	2.8 μg As[a]	5%	EPA (1988)
Vegetables: treated areas	≤3 mg As/kg	NR[b]	Eisler (1988)
Vegetables: untreated areas	≤1 mg As/kg	NR	Eisler (1988)
Wine	≤2–33 μg As/L	NR	ATSDR (1997)
Milk and dairy products	12 μg As[a]	75%	EPA (1988)
Meat: beef and pork	0.15 mg As/kg	75%	EPA (1988)
Fish	0.1 –64 mg As/kg	DL[c]–0.12 mg AS/kg	Chew (1996)
Shellfish	0.2–126 mg As/kg	<0.01–0.6 mg/kg	Chew (1996)
Poultry	NR	65%	EPA (1988)
Fruits	5 μg As[a]	10%	EPA (1988)
Cereals and grains	6.4 μg As[a]	65%	EPA (1988)
Rice	ND	35%	EPA (1988)
Medicinals	25–107,000 mg/kg	100%	Tay and Seah (1975)
Fowler's solution	1% potassium arsenite	100%	ATSDR (1997)

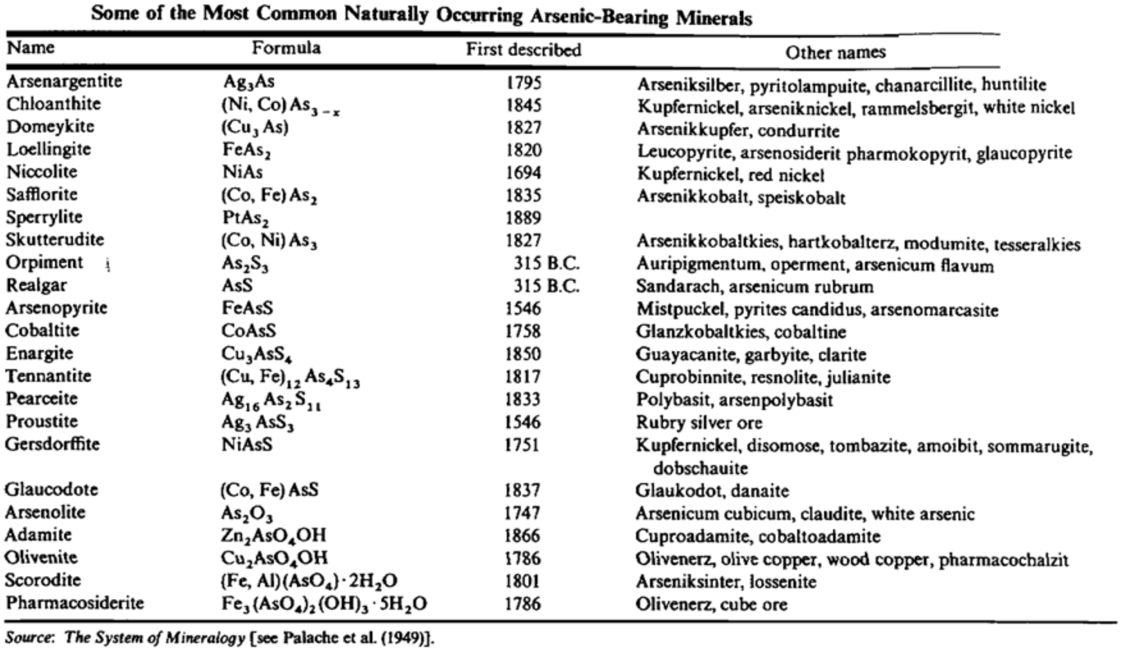
[a]Daily dietary intake derived from EPA (1988); [b]NR = not reported; [c]DL = detection limit.

Water, particularly ground water, is often the greatest source of human exposure to inorganic arsenic. The arsenic content of seawater averages 2 μg/L. Freshwater arsenic concentrations often are higher. A 1969 survey conducted by the U.S. Geological Survey found 21% of 727 river water samples had arsenic levels above 10 μg/L. Ninety-four percent of lake water samples had arsenic concentrations above 10 μg/L; high 340 μg/L. Even rainwater contains measurable arsenic, 0.46 μg/L for rain from land-derived evaporation (Welch et al., 1988). Ground-water arsenic concentrations are typically greater than those for surface water. While up to 46% of ground-water supplies have arsenic levels > 5 μg/L, only 11% of surface water supplies exceed that level (Frey and Edwards, 1997). Barring geothermal and mining areas, aquifers with elevated arsenic levels are most often related to the presence of volcanic sediments (Welch et al., 1988).

Chemistry and Cycling

Arsenic is a metalloid that occurs most commonly in a combined form with other elements. It occurs only rarely as the dull, gray, brittle native element. Arsenic is often associated with the metals of lead, tin, silver, or antimony (Azcue and Nriagu, 1994). It is found in compounds with iron, nickel, and sulfur. Arsenic is especially concentrated in iron ores and sulfides including FeAsS, also known as arsenopyrite or mispickel, As_4S_4, also known as realgar, and As_2S_3, also known as orpiment. Other arsenic-bearing minerals are shown in Table 3 (Azcue and Nriagu, 1994).

Table 3. Arsenic-bearing minerals (from Azcue and Nriagu, 1994).



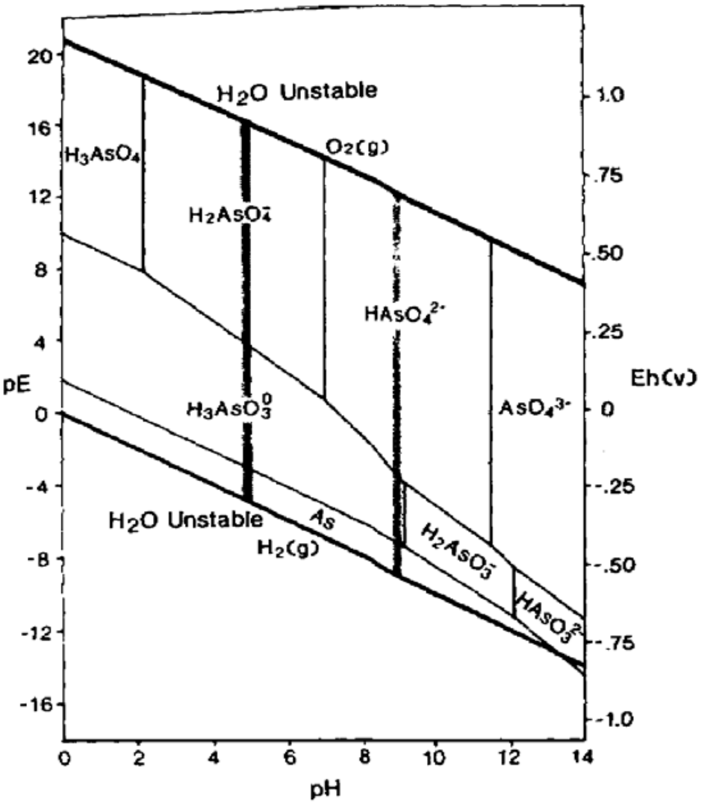
Some of the Most Common Naturally Occurring Arsenic-Bearing Minerals

Name	Formula	First described	Other names
Arsenargentite	Ag_3As	1795	Arseniksilber, pyritolampuite, chanarcillite, huntilite
Chloanthite	$(Ni, Co)As_{3-x}$	1845	Kupfernickel, arseniknickel, rammelsbergit, white nickel
Domeykite	(Cu_3As)	1827	Arsenikkupfer, condurrite
Loellingite	$FeAs_2$	1820	Leucopyrite, arsenosiderit pharmokopyrit, glaucopyrite
Niccolite	NiAs	1694	Kupfernickel, red nickel
Safflorite	$(Co, Fe)As_2$	1835	Arsenikkobalt, speiskobalt
Sperrylite	$PtAs_2$	1889	
Skutterudite	$(Co, Ni)As_3$	1827	Arsenikkobaltkies, hartkobalterz, modumite, tesseralkies
Orpiment	As_2S_3	315 B.C.	Auripigmentum, operment, arsenicum flavum
Realgar	AsS	315 B.C.	Sandarach, arsenicum rubrum
Arsenopyrite	FeAsS	1546	Mistpuckel, pyrites candidus, arsenomarcasite
Cobaltite	CoAsS	1758	Glanzkobaltkies, cobaltine
Enargite	Cu_3AsS_4	1850	Guayacanite, garbyite, clarite
Tennantite	$(Cu, Fe)_{12}As_4S_{13}$	1817	Cuprobinnite, resnolite, julianite
Pearceite	$Ag_{16}As_2S_{11}$	1833	Polybasit, arsenpolybasit
Proustite	Ag_3AsS_3	1546	Rubry silver ore
Gersdorffite	NiAsS	1751	Kupfernickel, disomose, tombazite, amoibit, sommarugite, dobschauite
Glaucodote	(Co, Fe) AsS	1837	Glaukodot, danaite
Arsenolite	As_2O_3	1747	Arsenicum cubicum, claudite, white arsenic
Adamite	Zn_2AsO_4OH	1866	Cuproadamite, cobaltoadamite
Olivenite	Cu_2AsO_4OH	1786	Olivenerz, olive copper, wood copper, pharmacochalzit
Scorodite	$(Fe, Al)(AsO_4)\cdot 2H_2O$	1801	Arseniksinter, lossenite
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3\cdot 5H_2O$	1786	Olivenerz, cube ore

Source: *The System of Mineralogy* [see Palache et al. (1949)].

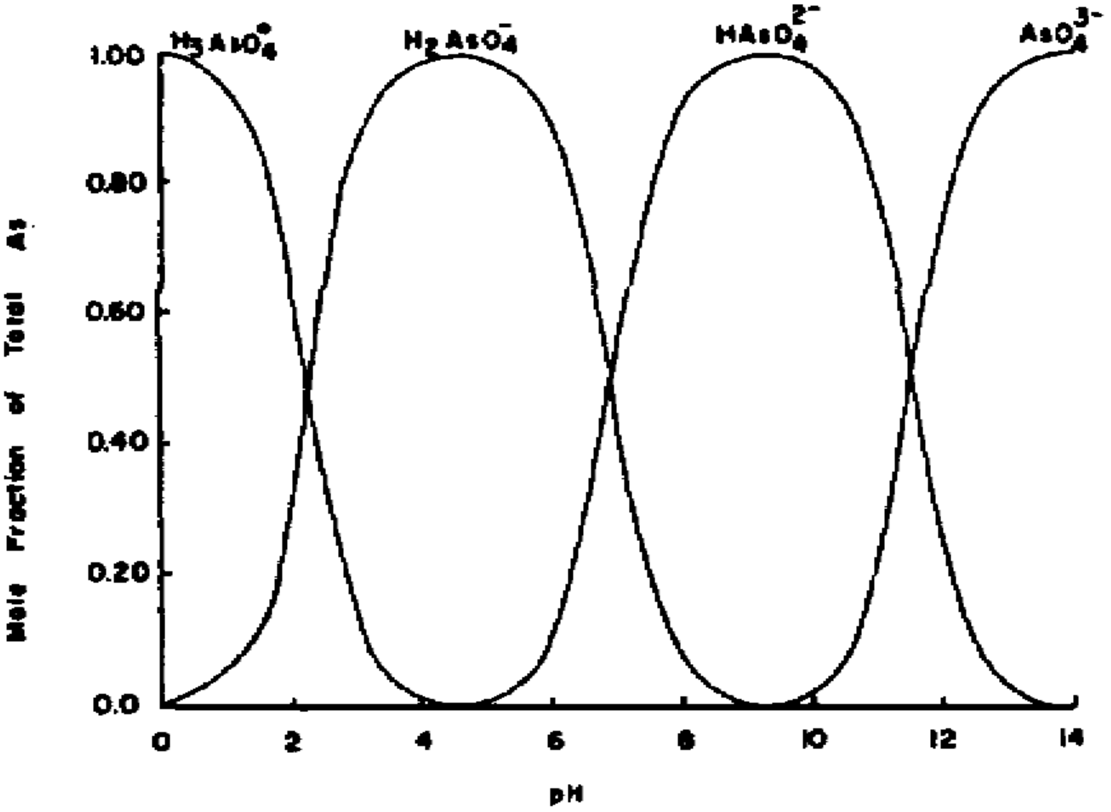
Soils average 5 to 6 ppm arsenic, range 1 to 50 ppm. Some areas of recent volcanism have soils averaging 20 ppm arsenic (Yan-Chu, 1994).

Arsenic is present in both organic, meaning with carbon and hydrogen, and inorganic compounds. Organic arsenic is present in soils as cocodylic acid, also known as dimethylarsenic acid or DMA (Bhumbla and Keefer, 1994). It also is a minor component of many foods. Inorganic arsenic is much more detrimental to human health. The common species of inorganic arsenic are As(III), or arsenite, and As(V), or arsenate. An acidic, reducing environment leads to formation of the more dangerous arsenite by the following redox reaction: $H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$ (Jekel, 1994). Predictably, arsenate is the dominant species in oxidized environments, while arsenite dominates in anoxic environments. Figure 2, a pE-pH diagram (Cherry et al., 1979) and Figure 3, a dominant species diagram (Sadiq et al., 1983), show the prominent ionic species of arsenic under various pH and redox conditions.



pE—pH diagram for the As—H_2O system at 25°C. Total dissolved As species is set at $10^{-6.176}$ mol/l (50 μg/l). The *area* within the *vertical bars* represents the common pE—pH domains for natural waters.

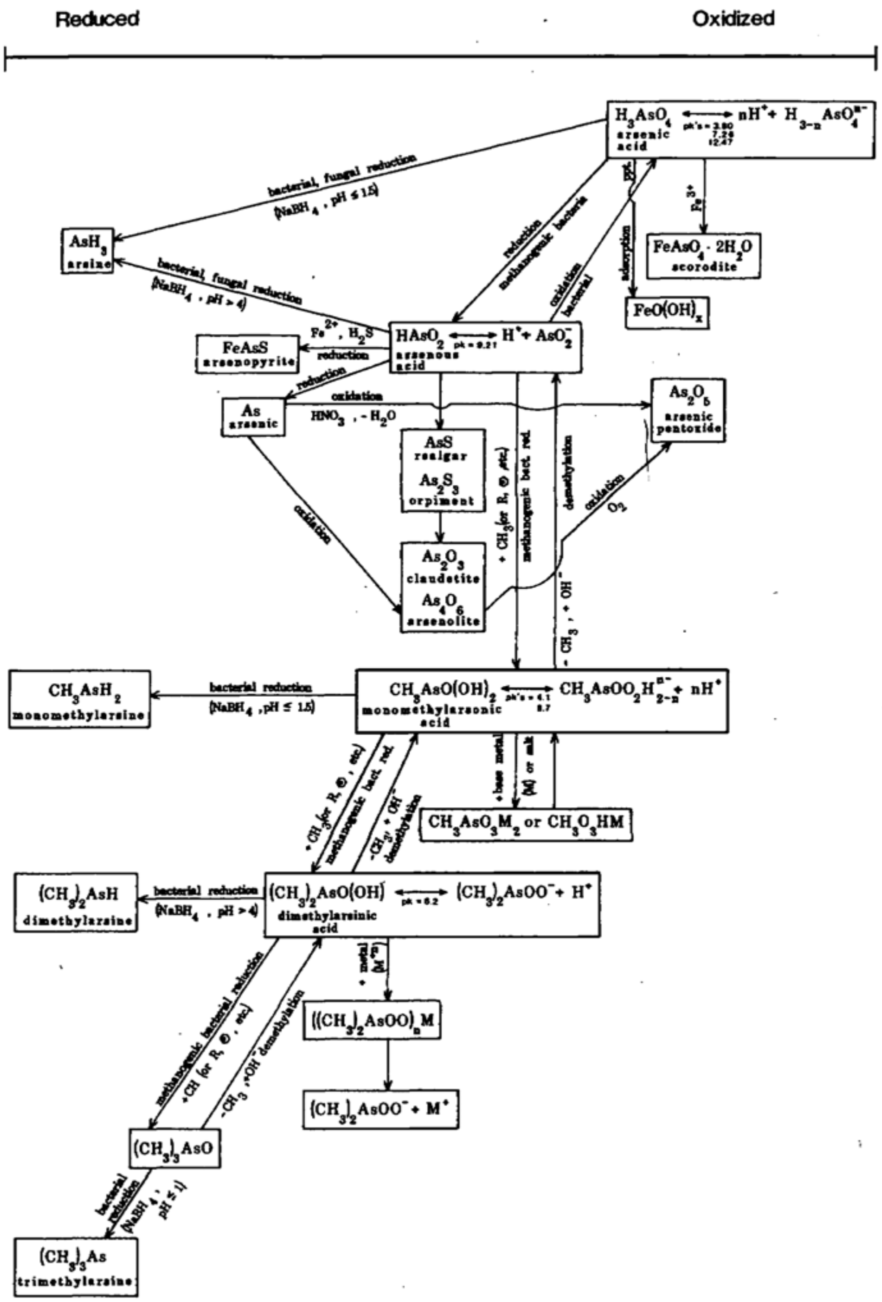
Figure 2. Diagram of pE-pH stability fields for arsenic-water system (from Cherry et al., 1979).



The mole fraction distribution of arsenic acid species.

Figure 3. Dominant arsenic species across a range of pH (from Sadiq et al., 1983).

The entire natural cycle of arsenic is shown by Figure 4 (Welch et al., 1988).



Forms of naturally occurring arsenic found in the natural environment (after Braman, 1975; and Irgolic, 1982). Chemical formulas of stable phases are shown in boxes with common names adjacent to box. Reaction paths are shown by arrows with conditions necessary to allow reaction to occur. Relative oxidation state of arsenic in the compounds is shown at the top of the diagram.

Figure 4. Natural arsenic cycle (from Welch et al., 1988).

ARSENIC AND THE HUMAN BODY

Exposure

Arsenic exposure pathways include dermal contact, inhalation, and ingestion. Contact with the skin is by far the least effective of these pathways. Some skin adsorption of arsenite, As (III), oxides has been documented (Morton and Dunnette, 1994). This preferential adsorption of arsenite over arsenate, As (V), is caused by the greater lipid solubility of arsenite (Saha et al., 1999). As well as presenting a relatively low risk, dermal exposure is easily detected and avoided. .

Inhalation of arsenic is a very effective exposure pathway. Serious exposure is most often encountered in industrial settings. Routine exposure in the U.S. is believed to be 0.006 μg As/m^3, of which 30 to 85% is adsorbed upon inhalation. The U.S. EPA estimates the general public is exposed to 0.04 to 0.09 μg/day of arsenic simply by breathing (Pontius et al., 1994). As_2O_3, arsenic trioxide, is the most common arsenic form in air (Naqui et al., 1994). Arsine gas, AsH_3, is very dangerous. It is difficult to detect physically. However a garlic odor and irritation of moist surfaces can indicate exposure (Harbison and Garvey, 1983). Smoking has been an inhalation exposure method, especially when lead arsenate pesticides were used in tobacco fields. In the 1950s a typical cigarette contained > 40 μg of arsenic. This number is now below 8 μg/g of tobacco (Ishinishi et al., 1986).

Ingestion of arsenic can occur with either eating or drinking. Both organic and inorganic forms of arsenic often are ingested. Organic arsenic, often eaten in seafood as arsenobetaine (Ishinishi et al., 1986), changes to cacodylic acid and is quickly excreted (Morton and Dunnette, 1994). Inorganic arsenic, typified by arsenite and arsenate, is more problematic. The U.S. Food and Drug Administration (FDA) estimates arsenic exposure from food in the U.S. at 53 μg/day. In food, estimates of the proportion of inorganic arsenic to total arsenic vary from 20 to 75% (Pontius et al., 1994). Once ingested, 40 to 100% of the soluble arsenic is adsorbed, with a preference for arsenate adsorption. This is fortunate because arsenate is only 1/10 as toxic as arsenite. Water is the other major contributor of ingested inorganic arsenic. The arsenic concentration of drinking water is highly variable, depending upon the water's source. The World Health Organization (WHO) recommends limiting total inorganic arsenic exposure to 2 μg/kg of body weight (Saha et al., 1999).

Toxicity

The forms and species of arsenic vary considerably with regard to toxicity. Forms of arsenic listed by decreasing toxicity are as follows: arsine gas, arsenite, arsenoxides, arsenates, arsenium compounds, and metallic arsenic (Morton and Dunnette, 1994). A fatal dose of the common industrial form of arsenic, As_2O_3 or white arsenic, is believed to be 0.1 to 0.2 grams. However, the lethal dose can vary. Much less arsenic could cause death. In at least one instance, though, survival has occurred after the ingestion of greater than one gram of white arsenic, albeit with severe complications (Kamijo et al., 1998).

Acute poisoning from ingestion shows symptoms within 30 minutes. Initial symptoms include metallic taste, trouble swallowing, dry mouth, muscle pain, and weakness. Nausea, vomiting, abdominal pain, and diarrhea follow. Victims also might complain of muscle cramps, thirst, body rash, numb extremities, cold and clammy skin, and decreased urine output. Drowsiness, delusion, hallucination, seizures, coma, and death from shock can occur within hours. Circulatory collapse, with accompanying heart problems, or kidney and liver failure will cause death in a matter of days (Saha et al., 1999). Inhalation of arsine gas also can quickly cause death. Symptoms quickly progress from headache, dizziness, and stomachache to vomiting, bloody urine, jaundice, and a decreased red blood cell count. Death results from heart attack or renal failure (Harbison and Garvey, 1983).

Chronic arsenic poisoning is more insidious. Symptoms can occur after anywhere from six months to ten years of subacute levels of exposure. The average onset of symptoms requires two years of exposure. Chronic arsenic poisoning, also known as arsenicosis, affects all body systems, particularly the organs (Saha et al, 1999). Because no medications are effective for arsenicosis, the only practical course is to treat the symptoms and reduce arsenic intake.

Skin effects consist of raindrop pigmentation as well as roughening and thickening of the skin. This is called melano-keratosis or arsenical dermatosis. A higher incidence of skin cancer is also present in instances of prolonged (15 to 20 years) exposure (Saha et al., 1999).

Respiratory effects from inhalation include laryngitis, bronchitis, and rhinitis (i.e. cold symptoms). High exposure rates, > 1 mg/m^3, can result in a perforated septum and death by mucosal sloughing, hemorrhaging, and pulmonary edema. Drinking water with an elevated arsenic content also can cause chronic asthma and bronchitis (Saha et al., 1999).

Effects on the cardiovascular and circulatory systems are numerous. Bone marrow depression, anemia, luekopenia, and red cell hemolysis are possible. Chronic inhalation of arsenic trioxide raises the incidence of cardiovascular disease. Chronic ingestion causes heart arrhythmia, vascular damage (e.g. Blackfoot disease), and vessel thickening (Saha et al., 1999).

The liver and kidneys are sites of arsenic accumulation. As such, they are particularly vulnerable to the chronic effects of arsenic. Arsenic was the first compound known to cause liver disease. Jaundice and liver tenderness occur as manifestations of cirrhosis of and lesions on the liver. The kidneys are a major site of arsenate to arsenite conversion. Oliguria can occur, eventually resulting in kidney failure (Saha et al., 1999).

Although little information exists regarding ingested arsenic's effect on fetal development (Saha et al., 1999), in-utero child development is inhibited by arsenic inhalation. Low birth weights and spontaneous abortions are thus more prevalent. Genetic effects are supported by the literature yet are not well understood. No evidence of gene mutations exists, but arsenic prevents deoxyribonucleic acid (DNA) repair and alters chromosomes. Arsenite is more a genotoxin than arsenate (Saha et al., 1999).

Arsenic is a known carcinogen. Chronic inorganic arsenic exposure is strongly associated with an increased incidence of cancer. Patients with arsenical keratosis are 5 to 10 times more likely to die from lung cancer. Various skin cancers can occur; the most common is basal cell carcinoma (Saha et al., 1999). Evidence indicates a link between ingesting inorganic arsenic and death by lung or bladder cancer. Ten percent of all deaths in a Chilean community having a 500 μg/L level of arsenic in their water supply are attributed to lung or bladder cancer. A study in England reported three times the incidence of bladder cancer in a population exposed to a dose equivalent to two liters of water per day with an arsenic concentration of 100 μg/L for 30 years (Smith et al., 1999).

Although the exact mechanism by which arsenic contributes to cancer risk is in debate, arsenic is believed to promote but not actually initiate tumors (Morton and Dunnette, 1994).

Metabolization and Methylation

Arsenic is transformed chemically by the human body through reduction and a methylation process. When arsenic is ingested, 40 to 100% of the soluble arsenic is adsorbed into the circulatory system (Pontius et al., 1994). Arsenate is adsorbed more efficiently than arsenite. Arsenate may cause problems by replacing phosphate in normal cell reactions. Upon entering a cell, arsenate is reduced to arsenite. Arsenite has an affinity for thiol groups. It can separate them from proteins, thus deactivating enzymes. Arsenite may be capable of disrupting more than 200 human enzymes (Abernathy et al., 1999).

In the liver, a methyl transfer reaction involving S-adenosylmethioine occurs. This reaction produces methylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Abernathy et al., 1999). Neither MMA nor DMA interfere with molecular function. Therefore, MMA and DMA are considered less toxic than As(V). Arsenic and the resulting acids leave the body via the urinary tract. About 50 to 90% of blood-borne arsenic exits the body within 2 to 4 days (Saha et al., 1999).

Testing for Arsenic in the Body

Arsenic can be detected in blood, urine, and hair samples. Some testing methods do not differentiate between organic and inorganic arsenic. For this reason, consumption of seafood should be avoided for 48 hours before urine or blood tests. Hair analysis is the recommended method to detect arsenic exposure that occurred more than one week prior to the test. The normal arsenic concentrations in blood, urine, and hair are < 5 μg/L, < 10 μg/L, and 0.03 to 3 μg/g hair, respectively (NMS Laboratories).

ARSENIC REMOVAL

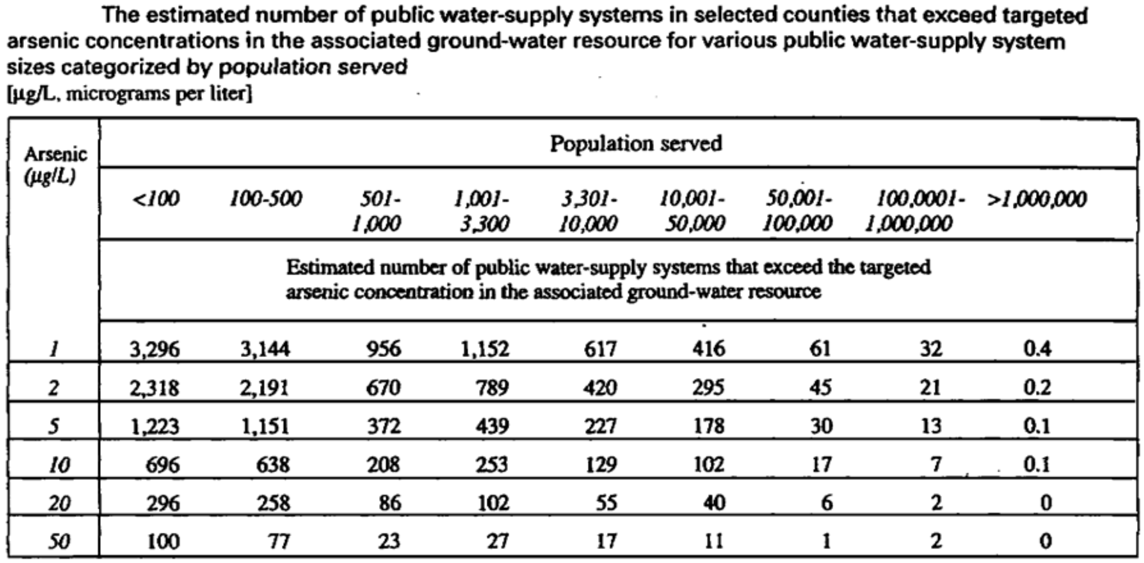
New Maximum Contaminant Level

The U.S. EPA's maximum contaminant level (MCL) for arsenic formerly was 50 μg/L or parts per billion (ppb). Canada's MCL is 25 μg/L, and Australia's is 7 μg/L (Smith et al., 1999). The EPA in November, 2001, announced the lowering of the U.S. MCL. The new level is 10 μg/L and is to take effect by 2006. It is believed that this will reduce arsenic-attributable skin cancer risk to 1 in 10,000 (Frey and Edwards, 1997). Below 10 μg/L of arsenic in water, food becomes the major inorganic arsenic source (Smith et al., 1999).

The ability of water suppliers to comply with the new standard understandably varies, based on the raw water's arsenic concentration. Forty percent of water supplies have arsenic concentrations > 1 μg/L, and 5% are > 20 ppb (Welch et al., 1999). Another source indicates that 25% of water supplies exceed 2 ppb, 6 to 17% exceed 5 ppb, and 1 to 3% exceed 20 ppb. Also, 20.7% of suppliers would not meet a 2 ppb standard, 9.3% would not meet a 5 ppb standard, 3.6% would not meet a 10 ppb standard, and 1.7%

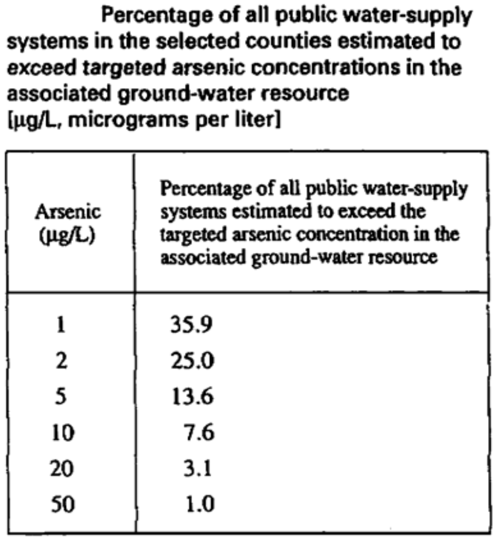
would not meet a 20 ppb standard (Frey and Edwards, 1997). Ground water averages even higher: 36% > 1 ppb, 25% > 2 ppb, 14% > 5 ppb, 8% > 10 ppb, 3% > 20 ppb, and 1% > 50 ppb (Focazio et al., 2000). Tables 4 and 5 (Focazio et al, 2000) show the number and percentage of water systems that exceed various arsenic concentrations.

Table 4 and 5. Number and percentage of water supplies exceeding various arsenic concentrations (from Focazio et al., 2000).



The estimated number of public water-supply systems in selected counties that exceed targeted arsenic concentrations in the associated ground-water resource for various public water-supply system sizes categorized by population served
[µg/L, micrograms per liter]

Arsenic (µg/L)	Population served								
	<100	100-500	501-1,000	1,001-3,300	3,301-10,000	10,001-50,000	50,001-100,000	100,0001-1,000,000	>1,000,000
	Estimated number of public water-supply systems that exceed the targeted arsenic concentration in the associated ground-water resource								
1	3,296	3,144	956	1,152	617	416	61	32	0.4
2	2,318	2,191	670	789	420	295	45	21	0.2
5	1,223	1,151	372	439	227	178	30	13	0.1
10	696	638	208	253	129	102	17	7	0.1
20	296	258	86	102	55	40	6	2	0
50	100	77	23	27	17	11	1	2	0



Percentage of all public water-supply systems in the selected counties estimated to exceed targeted arsenic concentrations in the associated ground-water resource
[µg/L, micrograms per liter]

Arsenic (µg/L)	Percentage of all public water-supply systems estimated to exceed the targeted arsenic concentration in the associated ground-water resource
1	35.9
2	25.0
5	13.6
10	7.6
20	3.1
50	1.0

Lowering the MCL will increase costs for many water suppliers and consequently their customers. Industry analysts predict a cost of \$600 million/year and \$5 billion in capital costs to meet a 10 ppb arsenic standard. EPA believes the same standard can be met at a cost of \$187 million/year (WaterWorld, 2000). Another study predicts costs of \$330 million/year to achieve a 20 ppb standard. Most industry estimates are 10 to 20 times the EPA's cost predictions. Regardless of actual cost, ground-water suppliers will bear the majority, 62 to 82%, of the cost (Frey et al., 1998).

Current Arsenic Removal Technologies

Widespread variations in the projected costs of arsenic removal are partially attributable to the large number of possible arsenic removal technologies. All of the following methods are intended to remove As(V). As(III) can be oxidized to As(V) by using ferric chloride, potassium permanganate, or chlorine. Ferric sulfate coagulation works well for removing arsenic at nearly neutral pH values, but sludge disposal can be a problem. Lime softening is effective, especially at pH > 10.5. This could be a good first step, but extremely low arsenic concentrations cannot be achieved. Activated aluminum is very good for waters with high total dissolved solids (TDS) concentrations, but ion competition and regeneration difficulties must be overcome. Ion exchange's drawbacks include ion competition and iron precipitate clogging. Reverse osmosis can remove 95% of the arsenic; however a significant amount of water is concentrated with arsenic and therefore wasted. Nanofiltration can be > 90% effective, but 80% of the water is wasted. Iron coagulation and filtering work well given tight control of parameters, most notably iron content, time, and pH. Arsenic often is bound to iron or manganese, so traditional

Fe/Mn removal methods work well for some waters (WaterWorld, 2000). In 1978, Jones and others suggested Fe(II) and lime for the removal of As(V) from acidic solutions (Prasad, 1994). At present lime softening and iron coprecipitation appear to be the most effective removal technologies barring the wasteful membrane separation methods. Arsenic removal methods and their effectiveness are shown in Table 6.

Table 6. Arsenic removal methods and their effectiveness (from Torrens, 1999).

Arsenic removal in drinking water – summary of available data

Treatment technology	Arsenic in (ppb)	arsenic out (ppb)	% removal
Chemical precipitation			
Oxidation/iron coprecipitation	110	10-85	23-91
Oxidation/iron coprecipitation	200	80-200	0-60
Oxidation/iron coprecipitation	1100	<5	>99
lime softening	220	30	86
lime softening (pH > 10.5)	75	<5	>95
lime softening	100	<5	>95
iron coprecipitation	50	<5	>90
iron coprecipitation	21	<2	>90
iron coprecipitation	377	11	95
Adsorption			
Activated alumina	88	<50	>43
Activated alumina	103	<50	>51
ion exchange	92	<50	>45
ion exchange	103	<50	>51
Manganese green sand	110	6.8-37.7	64-94
Membrane separation			
Reverse osmosis	91	1	99
Electrodialysis	85	23	73
Reverse osmosis	260	2.6	99
Coagulation/microfiltration	50	<5	>90

ARSENIC IN GROUND WATER IN SOUTH DAKOTA

The State of South Dakota will be affected by the lower arsenic standard for drinking water. Figure 5 (Welch et al., 1999) shows locations of water samples with elevated arsenic levels. The darkest marks represent samples above 50 ppb.

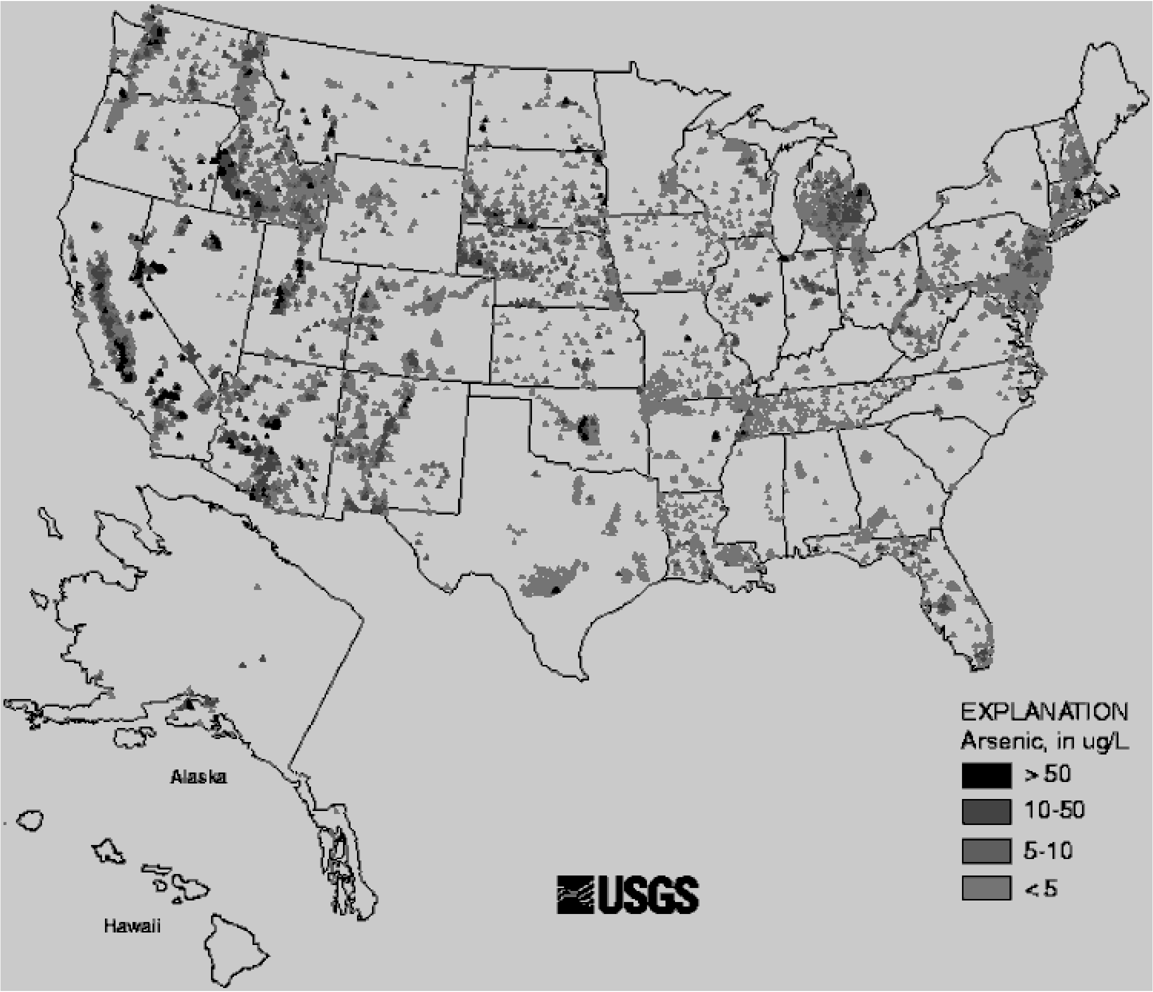


Figure 5. Locations in the U.S. of arsenic-rich water samples (from Welch et al., 1999).

A substantial number of water samples with elevated arsenic concentrations are from South Dakota. Information from the South Dakota Department of Environment and Natural Resources (DENR) shows the state's public water systems with arsenic concentrations greater than 5 ppb. Table 7 lists these systems and their arsenic concentrations, as measured during the late 1990s.

Table 7. South Dakota water supplies with arsenic levels above 5 ppb.

Public water supply system	As content (ppb)	Public water supply system	As content (ppb)
B&J Mobile Home Park	8	Martin	13.9
Batesland	6.4	Marvin	7.7
Bestgen Water Company	5.9	Memorial Christian School	13.5
Boulder Park Water Users Association	7.2	Merchen's Mobile Home Acres	6.72
Brandon	44.9	Midland Heights	12
Britton	5.1	Newdale Colony	32.2
Carriage Hills	7	Newport Colony	16.5
Castlewood	5.5	Peaceful Pines	5.2
Centennial Hills Water Company	5.9	Pine Hills Park	6
Central Elementary School	9.55	Pineview Water Association	10
Chapel Lane Water Company	7.7	Provo Township Water	9.65
Cimarron Park	8	Ree Heights	14.3
Colton	29.5	Saint Lawrence	14.1
CPH – Whispering Pines	6.3	Saint Onge Sewer & Water Company	5.73
Desmet	10	Selby	6.4
East Ridge Acres	7	Sioux San Hospital	8.2
Edgemont	10	Spring Canyon Water Company	6.4
Edgemont	10	Spring Creek Elementary School	10.7
Edgemont	10	Stagebarn Subdivision	9
Elk Creek Water Company	10	State Veterans Home	6.6
Golden Meadows	6	Sturgis	13
Grant – Roberts Rural Water System	7.4	Sunset Colony	33.8
Happy Holiday Incorporated	6.3	Sunshine Bible Academy	10.8
Hecla	27.5	VA Medical Center - Hot Springs	6
Highland Hills	5.5	Valley View Mobile Home Park	6.3
Hill City	10	Veblen	25
Hill City	7.9	Wharf - Terry Valley	21
Hill City	12	Whispering Pines Water Association	6
Hot Springs	6.2	White Rock Colony	44.5
Hutterville Colony	14	Wilhelm Court	11.4
Interior	5.27	Willow Lake	9.77
Lake city	15.9	Winner	5.09
Lakeview Elementary School	10.7	Wolf Creek Elementary School	7.2
Littleburg Elementary School	10.7	Wonderland Homes	11
Long Valley Elementary School	6.4		

Rosebud Indian Reservation and the Grass Mountain Area

The Grass Mountain area on the Rosebud Indian Reservation, South Dakota, has elevated arsenic concentrations in Arikaree aquifer wells. The Grass Mountain area is five miles northwest of Rosebud, South Dakota. It is located along the Little White River south of the North Ironwood Creek confluence on Tribal Highway 5. The source of arsenic in the Grass Mountain area is believed to be volcanic ash in the Arikaree aquifer (Carter et al., 1998). The positive correlation between uranium, with only natural sources in the area, and arsenic is indicative of a volcanic source. USGS has concluded the high arsenic content, up to 100 ppb, of ground water in the Grass Mountain area is likely to be caused by leaching of these volcanic sediments (Carter et al., 1998). The arsenic is dissolved from the ash and enters solution at pH > 8, presumably as arsenate. As the water moves downgradient, dissolved oxygen decreases and the arsenate is converted to arsenite. As the water enters the Little White River alluvium, the dissolved oxygen can further decrease because of contact with carbonaceous organic material. Eventually pH and dissolved oxygen can drop enough to allow adsorption onto clays or precipitation, often with iron or magnesium. Local surface water samples do not have unusually high arsenic concentrations (Carter et al., 1998). The solution implemented at the Grass Mountain area was to discontinue the domestic use of the Arikaree aquifer. A pipeline that carries water from the Ogallala aquifer now supplies the community (Syed Huq et al., Rosebud Sioux Water Resources, personal communication).

Arikaree Formation and Aquifer

The Arikaree Formation is a medium to fine-grained tuffaceous sandstone and siltstone of Miocene age. Volcanic ash fell episodically throughout the deposition of the Arikaree and underlying White River group (Carter et al., 1998). The Arikaree group consists of the Sharps and overlying Monroe Creek formations. The Sharps Formation has 40 feet of reworked ash topped by 350 feet of silt, clay, and ash. Pinkish color and small concretions also are characteristic. The Monroe Creek Formation is 100 feet of eolian silt and ash (Gries, 1996).

The Arikaree aquifer consists of the saturated sandstones and siltstones of the Arikaree Formation. Along with the Ogallala aquifer, it is considered part of the High Plains aquifer system. The Arikaree aquifer averages 270 feet in thickness. It thickens southward. The aquifer yields from 1 to 1000 gal/min, though it is not as productive as some parts of the Ogallala aquifer (Carter, 1998). Nonetheless, the Arikaree is an important aquifer in parts of Todd and Mellette counties, South Dakota. Unfortunately, parts of it contain water that is high in arsenic, making continued domestic use of the aquifer somewhat questionable.

LIMESTONE-BASED ARSENIC REMOVAL METHODS

Experiments were performed using Minnekahta Limestone to remove arsenic from water. This approach was supported by previous research regarding the removal of arsenic by the formation of calcium arsenate (Bothe and Brown, 1999). Mobilization of arsenic from sediment is most likely when the sediment is low in iron and calcium carbonate (Brannon and Patrick, 1987). A reasonable conclusion is that arsenic is immobilized in iron and/or calcium compounds. Work on arsenic-rich mine drainage and the subsequent decrease of arsenic content down gradient from where discharges crossed limestone outcrops indicated that limestone is a possible arsenic removal medium (Davis et al., 1999).

Both batch and column experiments were completed as part of this research. Batch experiments tested various combinations of rock material and arsenic-rich waters. Shake time, mass of rock material, and pH also were varied in the batch experiments. The column experiments tested the effectiveness of different grain sizes of Minnekahta Limestone in removing arsenic. Subsequently, one arsenic-saturated column was slowly rinsed in an attempt to determine the mobility of arsenic after removal by limestone. The limestone used in all experiments was crushed and then sieved to separate the various grain sizes. Spreadsheets located in the appendix contain the raw data from all the experiments.

Batch experiments involved the use of flasks containing a solution and a rock material, usually Minnekahta Limestone. The solution normally consisted of deionized water and arsenic. The flasks were placed on a shaker to facilitate mixing. Samples of the resulting solution were tested for conductivity, pH, temperature, and arsenic content. Eighteen batch experiments were performed to define the parameters that had the greatest effect on arsenic removal.

Column experiments consisted of running arsenic-rich water through a polyvinyl chloride (PVC) pipe column filled with Minnekahta Limestone. This was accomplished by adding arsenic-rich water to the top of the column while draining an equivalent amount of water from the bottom of the column. The resulting sample was tested for pH, conductivity, temperature, and arsenic content. This process was repeated twice a day for the duration of the column experiment. Five column experiments were run to test the effectiveness of various grain sizes of limestone in removing arsenic from both standard solutions and natural water. One column experiment tested the ability of limestone to retain arsenic when rinsed with deionized water.

RESULTS

Batch Experiments

General Procedure

Samples of crushed limestone (different grain sizes) with masses of 1, 5, 10, 40, and 100 grams were each combined with 100 mL of approximately 100 ppb arsenic solution set at pH = 8 +/- 0.2. A duplicate 10-gram limestone sample also was prepared for each batch experiment. A 10-gram limestone sample using 100 mL of deionized water rather than the arsenic solution was used as the blank for each batch experiment. The limestone sample material and arsenic solution were combined in a 250-mL round-bottomed flask and shaken for two days, then allowed to settle for about one hour. An aqueous sample was collected and tested for pH and conductivity. A filtered portion (0.45 μm filter) of the sample was taken to Mid-Continent Laboratories in Rapid City, South Dakota, for determination of the dissolved arsenic concentration. The initial arsenic solution of approximately 100 ppb was prepared by a 1:100 dilution of a 10 ppm arsenic solution, which in turn, was prepared by a 1:100 dilution of a 1000 ppm arsenic standard. A sample of the original arsenic solution was also sent for analysis to determine the exact initial arsenic concentration. The detection limit for arsenic at Mid-Continent Laboratories is 5 ppb. Samples testing below detection limit (BDL) were plotted within the shaded area on the graphs.

Four batch experiments, using the batch experiment procedure previously described, were used to test the effect of grain size on arsenic removal. Crushed and sieved Minnekahta Limestone samples with grain sizes of 4.7 - 6.7, 2 - 4.7, 1 - 2, and 0.5 - 1 mm were prepared. Batches with smaller grain size limestone were more effective in removing arsenic. All four experiments showed effective removal of arsenic, resulting in observed final arsenic concentrations at or below 5 ppb when using 40 grams of limestone of any grain size. The data (Figures 6, 7, 8, and 9) indicate that much less than 40 grams would have been sufficient.

100 ppb Arsenic Solution

Batch experiment 2

Batch experiment 2 was performed using 4.7 - 6.7 mm limestone and 109 ppb arsenic solution. The initial pH of the solution was 7.9. Data from batch experiment 2 are shown on Figure 6.

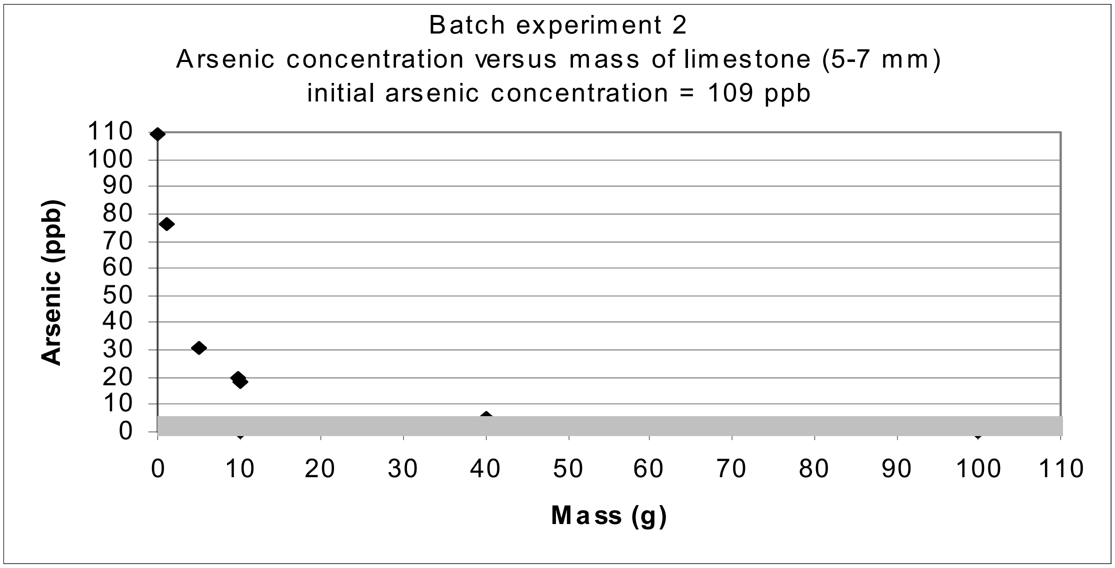


Figure 6. Experiment B2 using 4.7 - 6.7 mm limestone. Shaded area is BDL (below detection limit).

Batch experiment 3

Batch experiment 3 was performed using 2 - 4.7 mm limestone and 108 ppb arsenic solution. The initial pH of the solution was 8.0. Data from batch experiment 3 are shown on Figure 7.

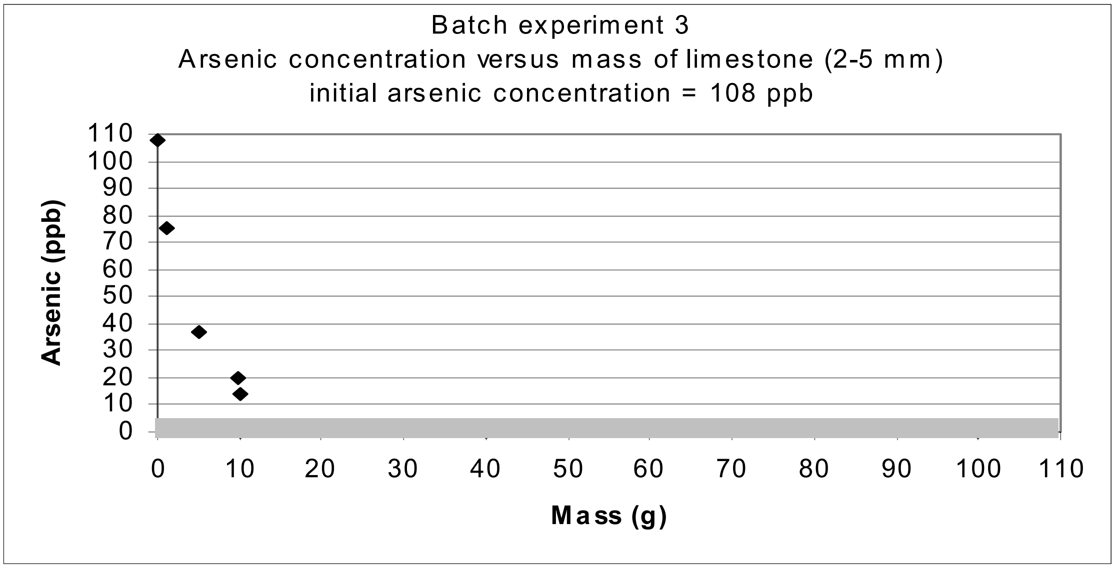


Figure 7. Experiment B3 using 2 - 4.7 mm limestone. Shaded area is BDL.

Batch experiment 4

Batch experiment 4 was performed with 1 - 2 mm limestone and 106 ppb arsenic solution. The initial pH of the solution was 8.0. Data from batch experiment 4 are shown on Figure 8.

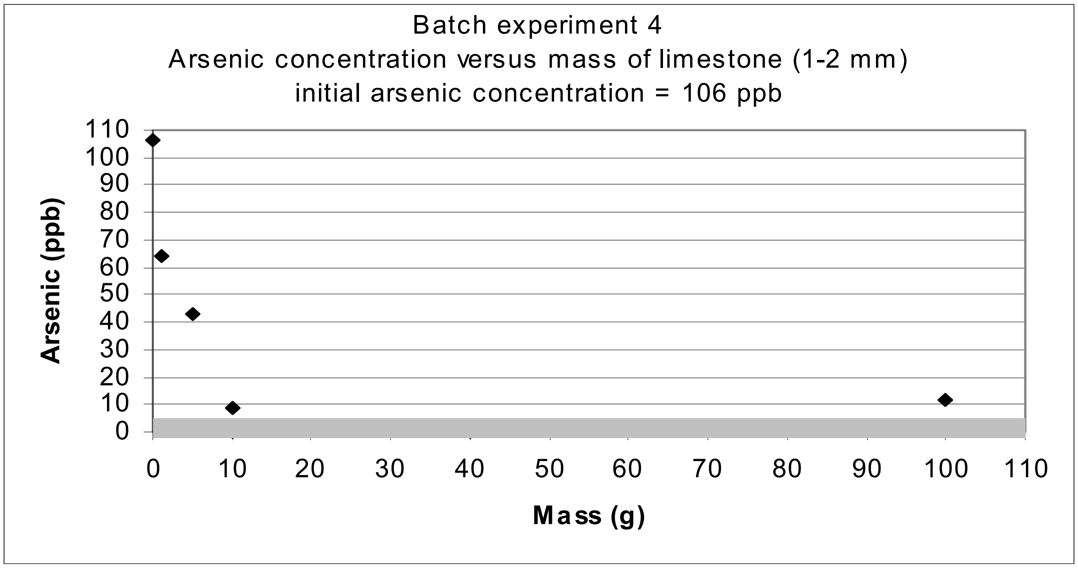


Figure 8. Experiment B4 using 1 - 2 mm limestone. Shaded area is BDL.

Batch experiment 5

Batch experiment 5 was performed using 0.5 - 1 mm limestone and 91 ppb arsenic solution. The initial pH of the solution was 8.0. Data from batch experiment 5 are shown on Figure 9.

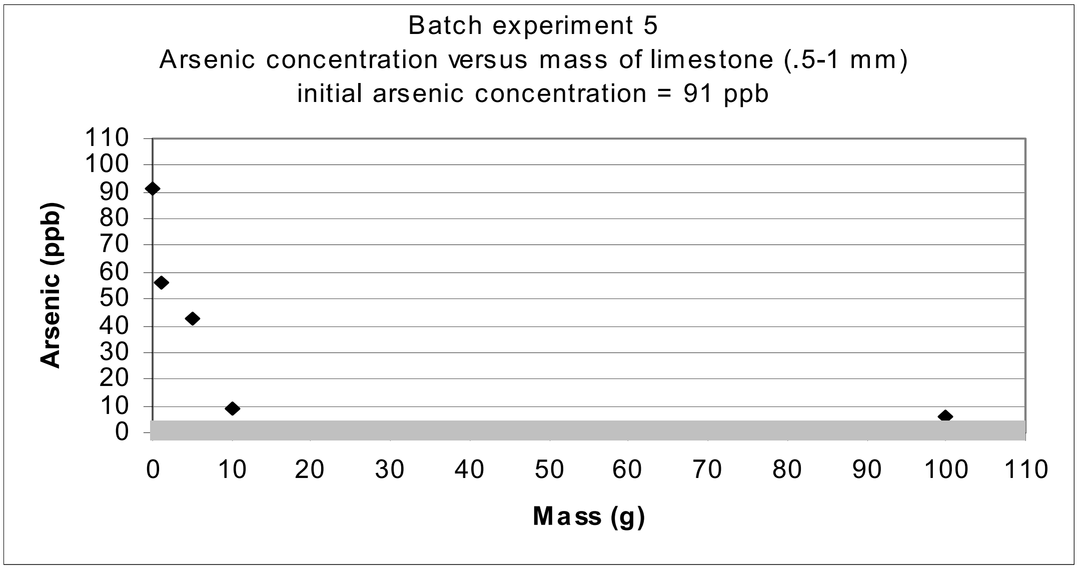


Figure 9. Experiment B5 using 0.5 - 1 mm limestone. Shaded area is BDL.

20 ppb Arsenic Solution

The batch experiments that tested the effect of grain size on arsenic removal at an initial concentration of 100 ppb were repeated with a 20 ppb arsenic solution. A lower arsenic concentration was used to better approximate natural conditions. The majority of water systems affected by a reduction in the MCL will be dealing with arsenic concentrations well below 100 ppb. Once again the smaller grain size limestone removed more arsenic per unit mass of limestone than the larger grain sizes. Generally only 5 grams of limestone were needed to reduce the arsenic content to about 5 ppb.

Batch experiment 10

Batch experiment 10 was performed with 4.7 - 6.7 mm limestone and 20 ppb arsenic solution. The initial pH of the solution was 7.9. The seven bottles were shaken for two days. Ten grams of limestone were sufficient to reduce the arsenic content of the solution below 5 ppb. Data from batch experiment 10 are shown on Figure 10.

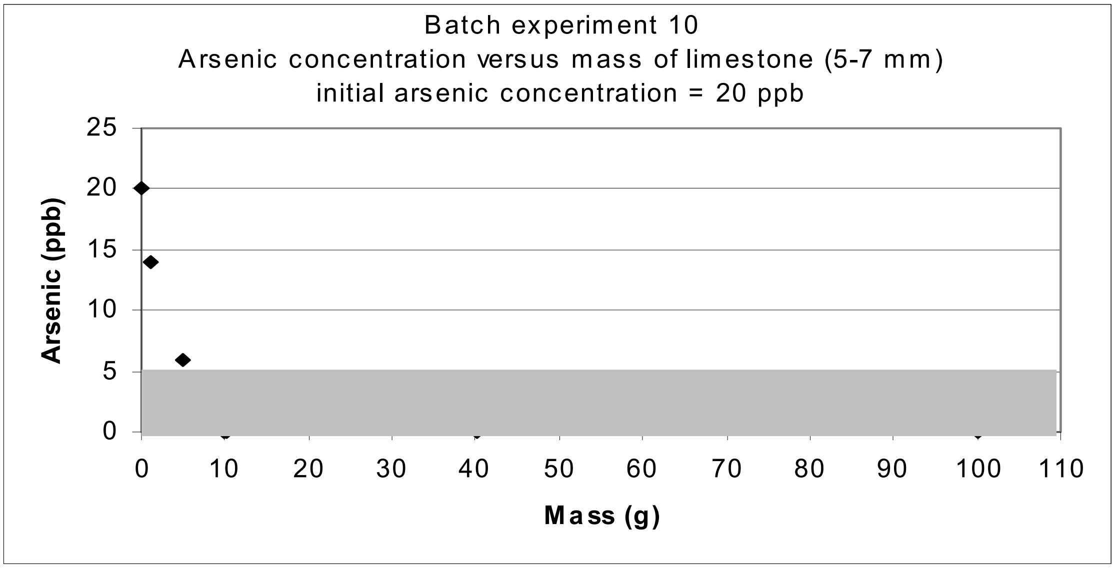


Figure 10. Experiment B10 using 4.7 - 6.7 mm limestone. Shaded area is BDL.

Batch experiment 11

Batch experiment 11 was performed with 2 - 4.7 mm limestone and 18 ppb arsenic solution. The initial pH of the solution was 8.0. Five grams of limestone were sufficient to reduce the arsenic content of the solution to 5 ppb. Data from batch experiment 11 are shown on Figure 11.

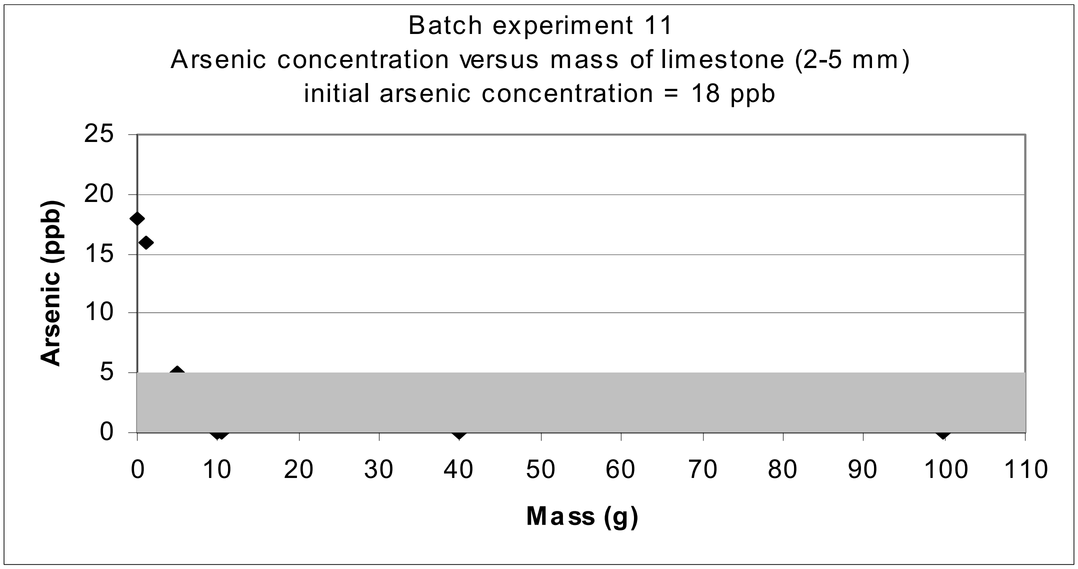


Figure 11. Experiment B11 using 2 - 4.7 mm limestone. Shaded area is BDL.

Batch experiment 13

Batch experiment 13 was performed with 1-2 mm limestone and 21 ppb arsenic solution. The initial pH of the solution was 7.8. Five grams of limestone were sufficient to reduce the arsenic content of the solution below 5 ppb. Data from batch experiment 13 are shown on Figure 12.

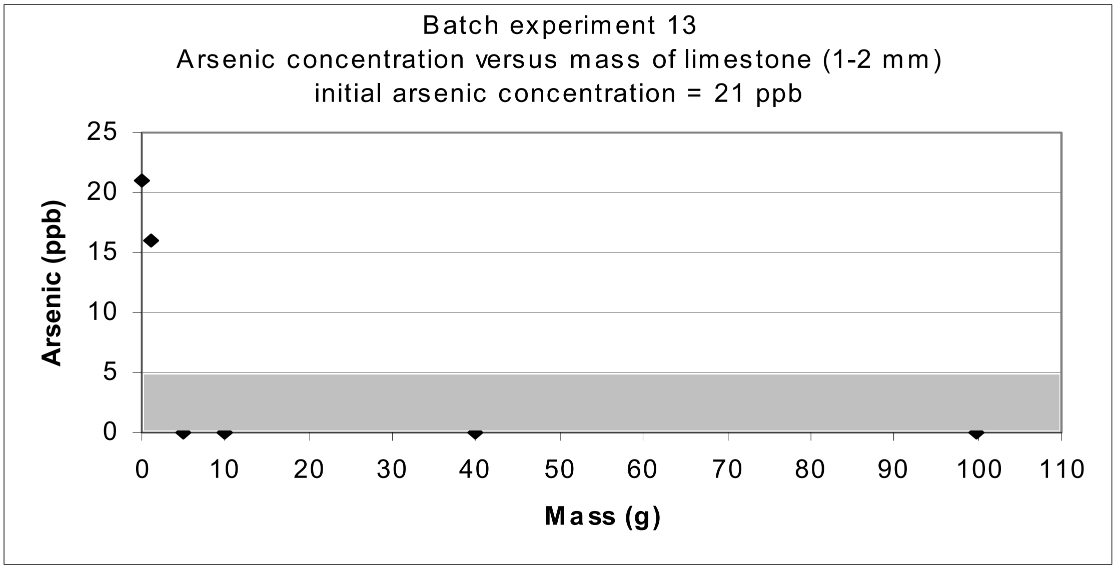


Figure 12. Experiment B13 using 1 - 2 mm limestone. Shaded area is BDL.

Batch experiment 14

Batch experiment 14 was performed with 0.5-1 mm limestone and 20 ppb arsenic solution. The initial pH of the solution was 8.2. Five grams of limestone were sufficient to reduce the arsenic content of the solution to 5 ppb. Data from batch experiment 14 are shown on Figure 13.

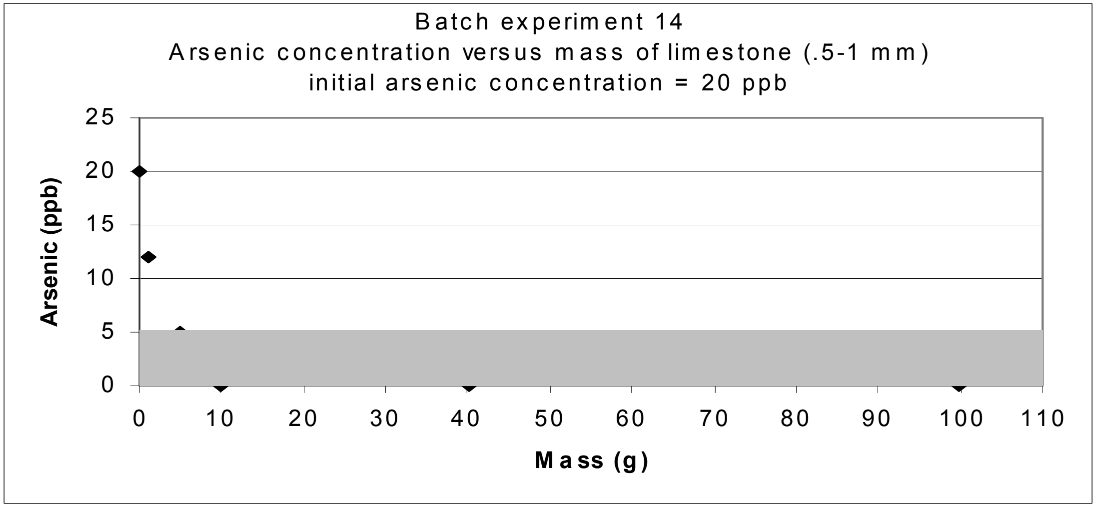


Figure 13. Experiment B14 using 0.5 - 1 mm limestone. Shaded area is BDL.

Other Materials

Batch experiments were run to test the ability of materials other than limestone to remove arsenic. The materials included very fine calcium carbonate, sea sand, Arikaree aquifer material, and agricultural limestone. The results of the pure calcium carbonate batch experiment were inconsistent and thus inconclusive. The sea sand nominally removed some arsenic; however, the chemical makeup of the sand is unknown. The Arikaree material added arsenic to solution. This was expected, based on conditions in the Grass Mountain area. After being exposed to the Arikaree material, the deionized water used in the blank contained more than 30 ppb arsenic. The agricultural limestone consistently reduced arsenic to some extent. An apparent clay fraction of the material led to clumping of the 40 and 100 gram agricultural limestone samples.

Batch experiment 1

Batch experiment 1 was performed with several quantities of 10 micron $CaCO_3$ mixed with 100 mL of ~100 ppb arsenic solution. Batch experiment 1 was inconclusive. Some samples were preserved with nitric acid while others were not. Very little can be concluded, except perhaps a general relationship between greater masses of calcium carbonate and further reduction in arsenic content. Data from batch experiment 1 are shown on Figure 14.

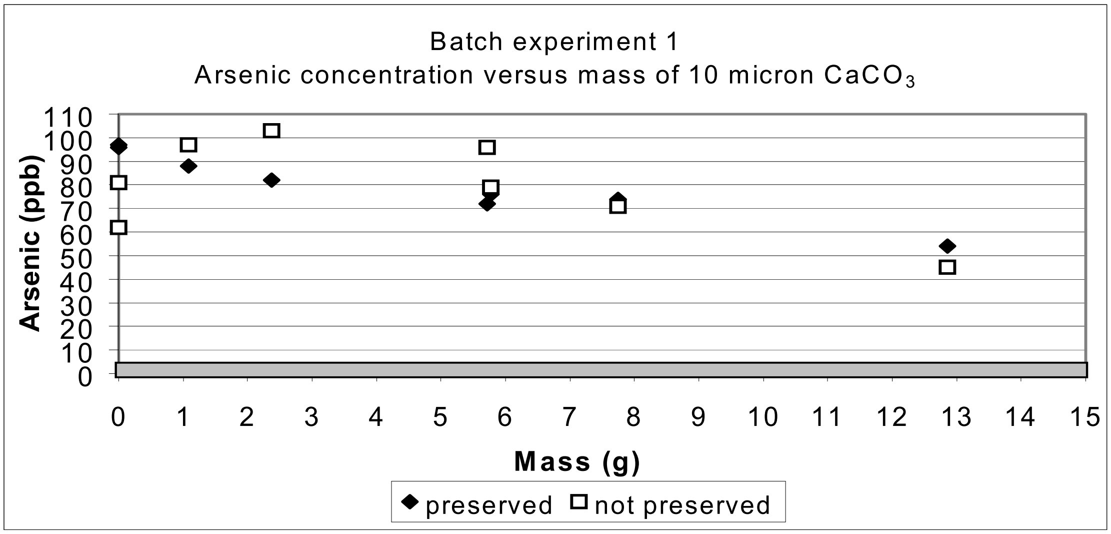


Figure 14. Experiment B1 using 10 micron calcium carbonate. Shaded area is BDL.

Batch experiment 6

Batch experiment 6 was performed with several quantities of sea sand mixed with 100 mL of 99 ppb arsenic solution. The initial pH of the solution was 8.0. Arsenic content was consistently reduced after two days of constant agitation. However 100 grams of limestone only reduced the arsenic content of the solution to 30 ppb. Data from batch experiment 6 are shown on Figure 15.

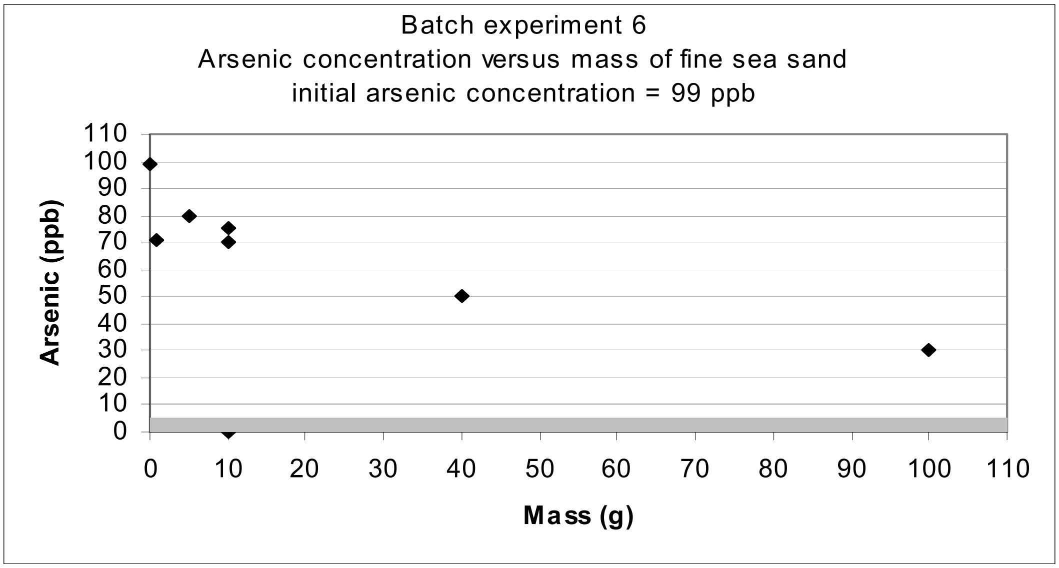


Figure 15. Experiment B6 using sea sand. Shaded area is BDL.

Batch experiment 8

Batch experiment 8 evaluated sediment from the Arikaree Formation as a potential absorbate of arsenic. The general procedure described previously was followed. The initial arsenic concentration was 102 ppb arsenic solution. The initial pH of the solution was 8.0. The Arikaree Formation material was obtained along the Little White River near the Grass Mountain Community on the Rosebud Indian Reservation. This material had a significant silt and clay fraction, making the filtering of these samples very difficult. The Arikaree material contributed additional arsenic to the solution. Sample 2 had an arsenic content greater than the initial arsenic solution. Sample 3b, the blank sample mixing Arikaree material with deionized water, contained 32 ppb arsenic, all of which came from the Arikaree Formation. Data from batch experiment 8 are shown on Figure 16.

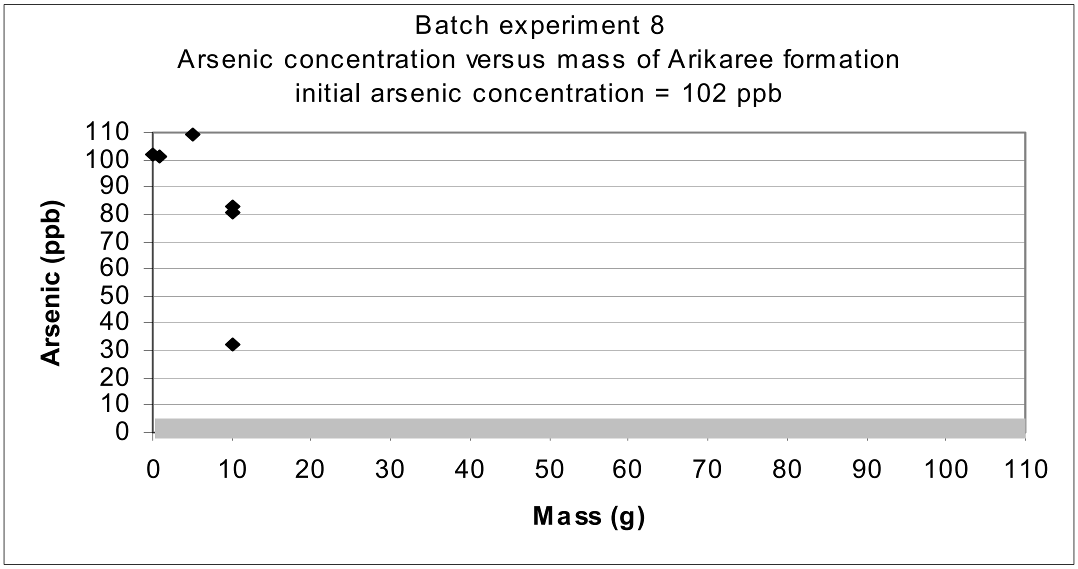


Figure 16. Experiment B8 using Arikaree material. Shaded area is BDL.

Batch experiment 17

Batch experiment 17 was performed with several quantities of agricultural limestone, including 48% calcite and 34% magnesite, and 100 mL of 87 ppb arsenic solution. The initial pH of the solution was 7.9. The seven bottles were shaken for two days. Even 100 grams of agricultural limestone were not quite sufficient to reduce the arsenic content of the solution below 5 ppb. However the agricultural limestone stuck together in the 40-gram and 100-gram bottles. This obviously reduced the effective surface area in those samples. Data from batch experiment 17 are shown on Figure 17.

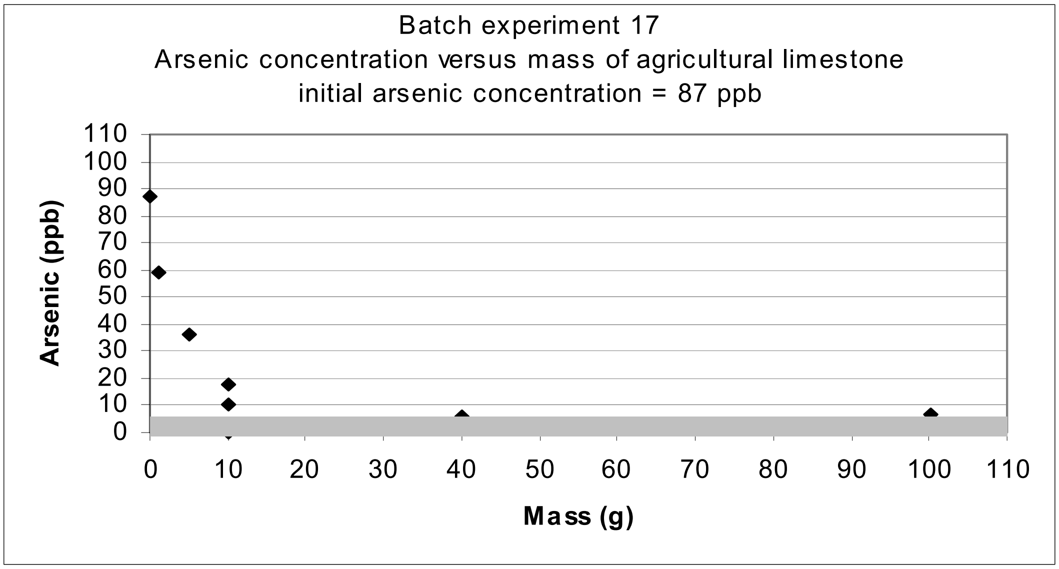


Figure 17. Experiment B17 using agricultural limestone. Shaded area is BDL.

Variations of Shaking Time

Shaking time was varied to test the rate at which arsenic was removed from solution. The results showed a quick initial reduction in arsenic concentration. After one hour the concentration was reduced to about a third of the original concentration. Subsequent reductions in arsenic concentration occurred at a slower rate. Semi-log plots of this data are also included.

Batch experiment 7

Batch experiment 7 was performed with 10 grams of 1 - 2 mm limestone mixed with 100 mL of ~100 ppb arsenic solution. The initial pH of the solution was 8.0. The seven bottles were shaken for 1, 2, 4, 8, 12, 24, or 48 hours. This experiment was designed to determine how quickly limestone removed arsenic from solution. The majority of arsenic is removed within one hour. The concentration of arsenic continued to slowly decrease linearly throughout the two-day period. Data from batch experiment 7 are shown on Figure 18. Shaded areas are BDL.

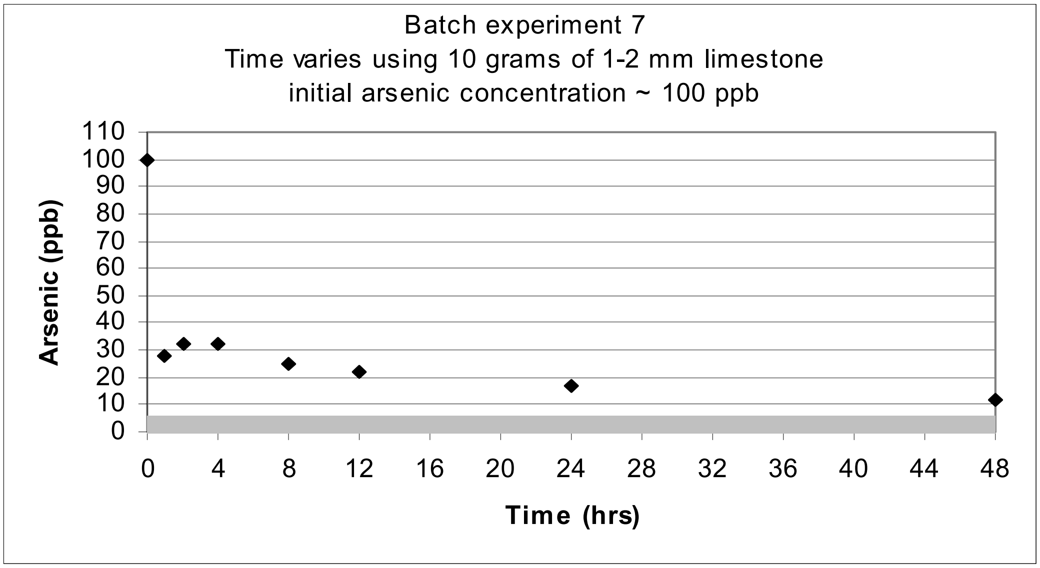


Figure 18a. Experiment B7 using 10 g of 1 - 2 mm limestone and 100 ppb arsenic. Shaded area is BDL.

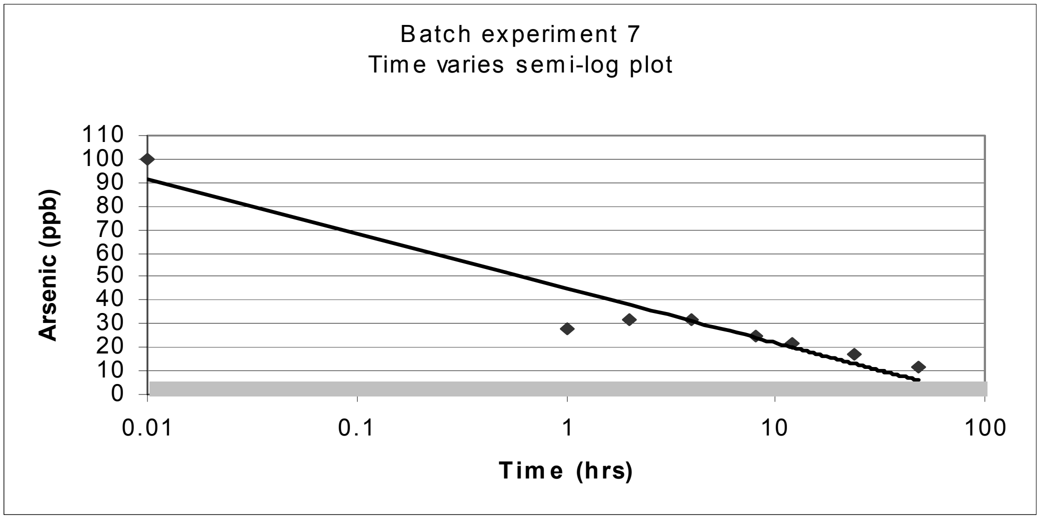


Figure 18b. Experiment B7 graphed as a semi-log plot. Shaded area is below BDL.

Batch experiment 18

Batch experiment 18 was performed with 5 grams of 1 - 2 mm limestone mixed with 100 mL of 23 ppb arsenic solution. The initial pH of the solution was 8.2. The seven bottles were shaken for 1, 2, 4, 8, 12, 24, or 48 hours. This experiment was designed to determine how quickly limestone removed arsenic from solution. The majority of arsenic was removed within one hour. Two hours of shaking time was sufficient to reduce the arsenic content to less than 10 ppb. Data from batch experiment 18 are shown on Figure 19. Shaded areas are below the detection limit (BDL).

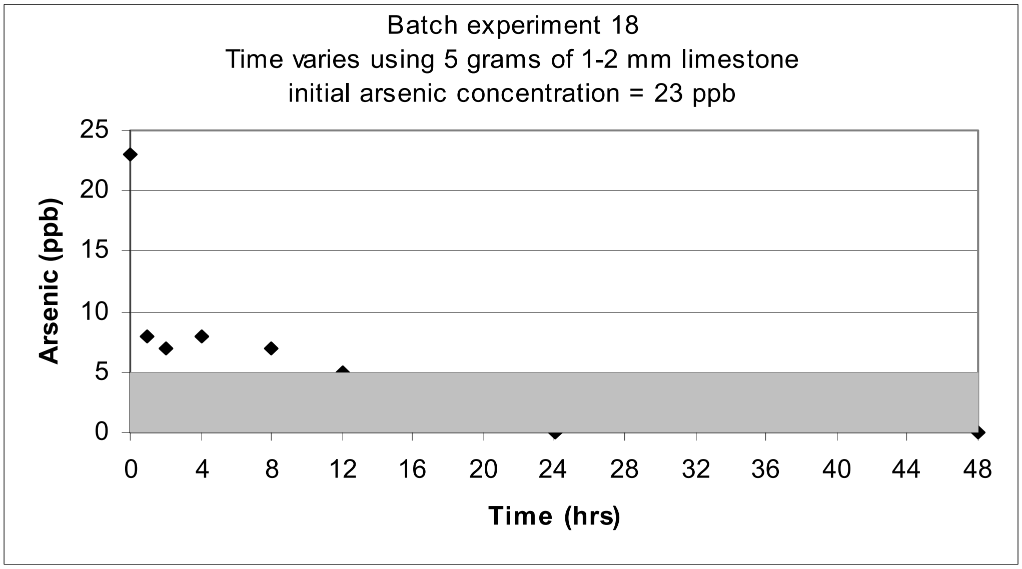


Figure 19a. Experiment B18 using 5 g of 1 - 2 mm limestone and 20 ppb arsenic. Shaded area is BDL.

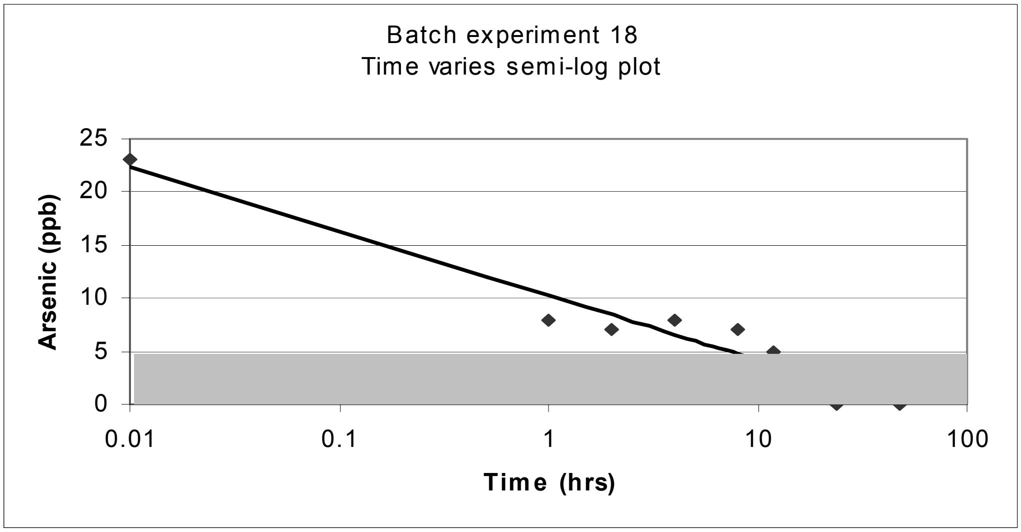


Figure 19b. Experiment B18 graphed as a semi-log plot. Shaded area is BDL.

Role of Fine-Grained Material

A batch experiment was conducted to test the effect of fine-grained material on arsenic removal. The fine-grained material present in the limestone is a result of the crushing and sieving process. Crushing produces a range of grain sizes, including some very fine material. Sieving is intended to separate these grain sizes. However, dry sieving cannot remove all of the fines. Therefore, some particulate matter is present in all grain sizes. Some samples were rinsed and dried before the solution was added. This removed most of the small particulate matter. Other samples were not rinsed. The unrinsed samples were better at removing arsenic.

Batch experiment 9

Batch experiment 9 was performed with 10 grams of 1 - 2 mm limestone (rinsed and unrinsed) mixed with 100 mL of 90 ppb arsenic solution. The initial pH of the solution was 8.0. The unrinsed (with fines) limestone was slightly more effective at removing arsenic from solution (< 10% more arsenic removed). Nevertheless, the rinsed (without fines) limestone also was quite effective. The data from batch experiment 9 are shown on Figure 20.

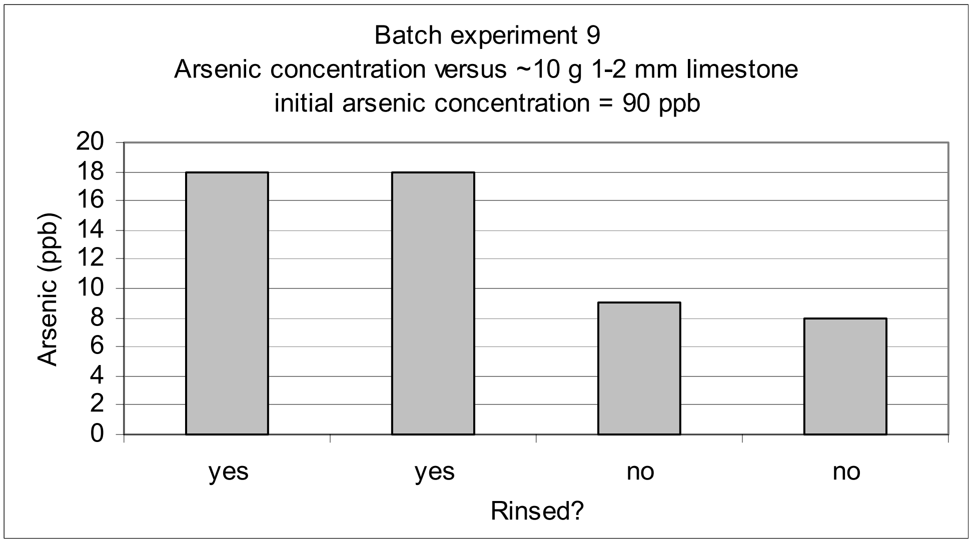


Figure 20. Experiment B9 using 10 g of 1 - 2 mm limestone, rinsed and unrinsed.

Sequential Limestone Addition

A batch experiment involving the sequential addition of limestone was conducted. One gram of limestone was added every two hours. Consistent reduction in arsenic content occurred throughout the test. By the end of ten hours, two hours after the fifth gram had been added, the arsenic concentration had been reduced to between 40 and 50 ppb. This is the same decrease in concentration that was generated by using five grams of the same limestone and shaking for 48 hours.

Batch experiment 12

Batch experiment 12 tested 1-2 mm limestone mixed with 100 mL of 92 ppb arsenic solution. One gram of limestone was added sequentially every two hours. Eventually five grams of limestone was added over the course of 10 hours. An aqueous sample was collected every two hours just prior to adding the next gram of limestone. The arsenic content consistently decreases with time. Data from batch experiment 5 are shown on Figure 21.

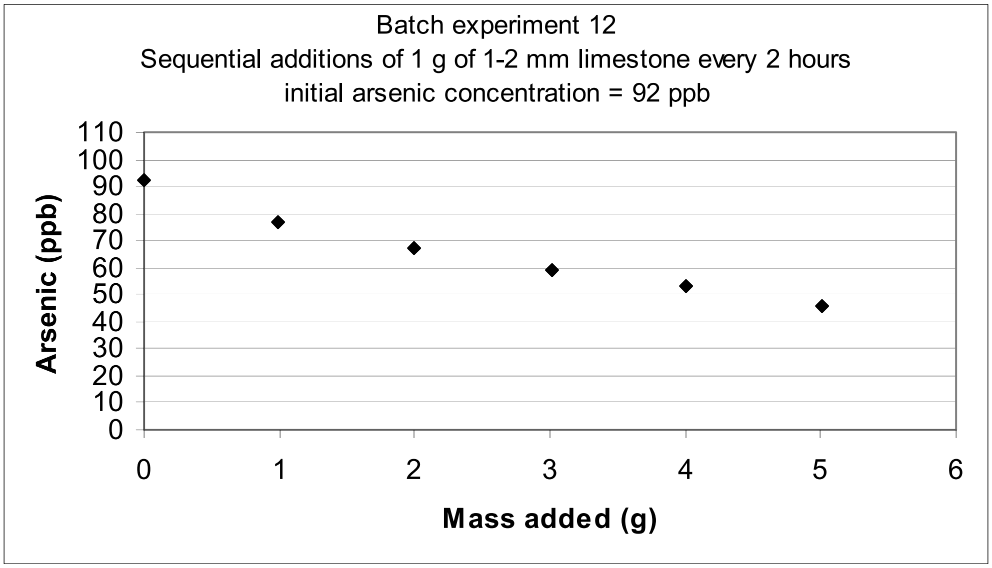


Figure 21. Experiment B12 using sequential additions of 1 - 2 mm limestone.

Natural Water with High Total Dissolved Solids Concentration

A batch experiment used arsenic-rich water (arsenic concentration = 25 ppb) from a well located near the Grass Mountain Community to test the ability of limestone to remove arsenic from natural water. Arsenic concentrations were consistently reduced, but not as efficiently as had been predicted. The elevated level of total dissolved solids, or TDS, is believed to have been a factor. The No Heart well water had a TDS value of 1020 mg/L in the fall of 1995. This is by far the highest TDS of any water tested in the Grass Mountain area. All other wells in the area tested below 700 mg/L, with most below 400 mg/L (Carter et al., 1998). Presumably waters with a more moderate TDS level would be better suited to the limestone-based arsenic removal process because of less interference from dissolved ions in solution.

Batch experiment 15

Batch experiment 15 tested several quantities of 1 - 2 mm limestone mixed with 100 mL of No Heart well water. The No Heart well is located on the Rosebud Indian Reservation. The initial pH of the No Heart well water was 7.6. Seven bottles were shaken for two days. The conductivity, and hence the total dissolved solids, was quite high (>1100 µS) for the No Heart well water. This results in increased competition for adsorption sites and is the likely reason for the reduced effectiveness of limestone in removing arsenic from the No Heart well water. One hundred grams of limestone were sufficient to reduce the arsenic content below 5 ppb. Forty grams of limestone were nearly as effective, reducing the arsenic content to 6 ppb. Data from batch experiment 15 are shown on Figure 22.

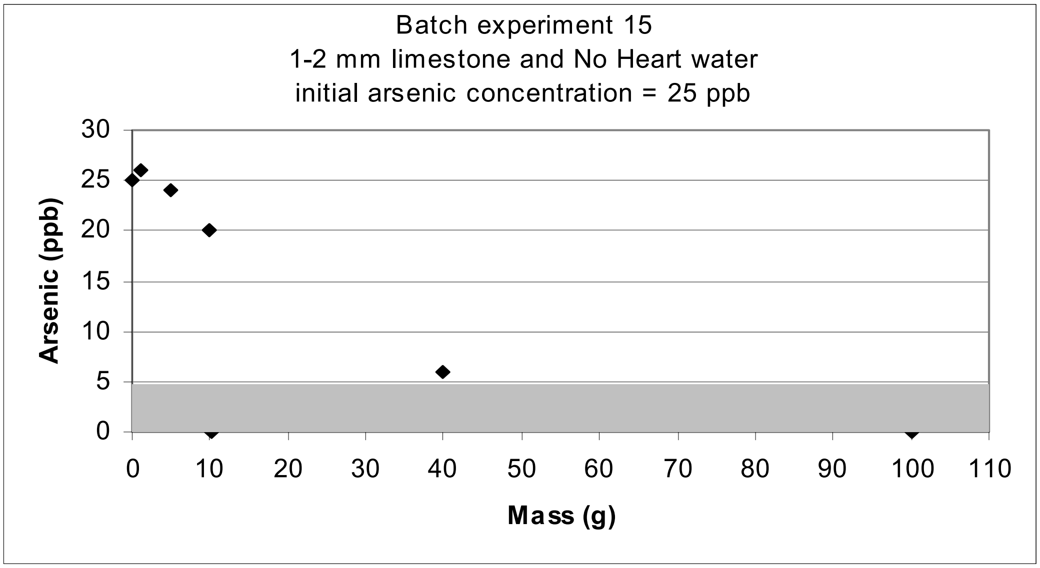


Figure 22. Experiment B15 using No Heart well water and 1 - 2 mm limestone. Shaded area is BDL.

Variations of pH

A batch experiment was conducted using arsenic solutions that were adjusted to different pH values. The varying pH, within the range normally seen in ground water, had no effect on the amount of arsenic removed.

Batch experiment 16

Batch experiment 16 used 10 grams of 1-2 mm limestone mixed with 100 mL of ~100 ppb arsenic solution. The initial pH of the solution varied from 6 to 8.4. All six bottles were shaken for two days. Variations of pH throughout the range of natural waters had little effect on the reduction of arsenic content. Each sample was reduced to or slightly below 10 ppb. Data from batch experiment 16 are shown in Figure 23.

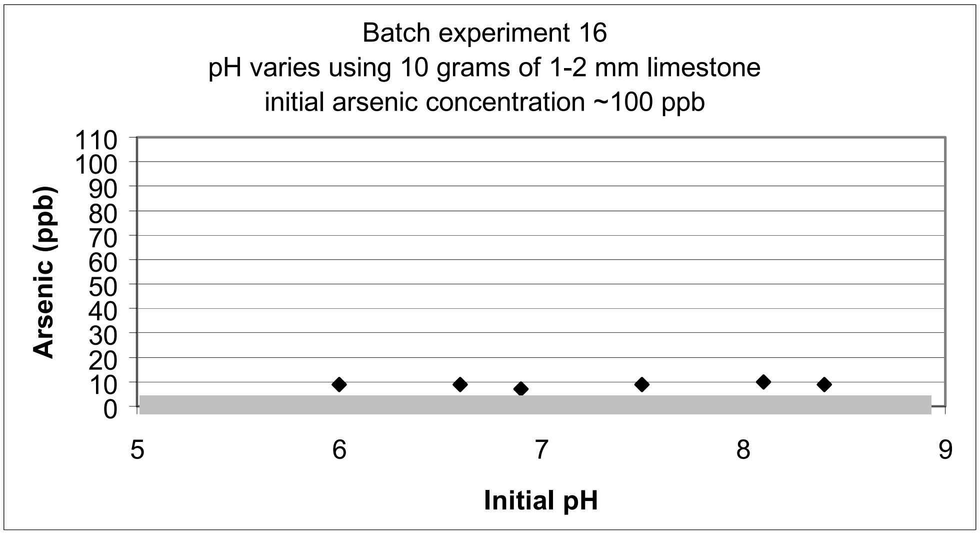


Figure 23. Experiment B16 using 10 g of 1 - 2 mm limestone. Shaded area is BDL.

Discussion of Batch Experiments

The batch experiments successfully demonstrated the removal of arsenic by Minnekahta Limestone. Smaller grain size limestone removed more arsenic per unit weight of limestone. None of the other materials tested removed arsenic as efficiently as did Minnekahta Limestone. Most of the arsenic removal occurred quickly; additional removal continued at a slower rate. Fine particulate matter was beneficial in further reducing arsenic concentrations. Increased high ionic activity, indicated by high TDS values, reduced the ability of limestone to preferentially remove arsenic. The arsenic removal process was unaffected by the standard solution's initial pH, within the natural range for ground water.

Batch experiments 2 through 5, as well as 10, 11, 13, and 14, tested the effect of grain size on the effectiveness of arsenic removal. Based on the results of the tests, it can be concluded that less of the smaller grain size limestone is necessary to reduce the arsenic content of the solution below the new MCL levels announced by the EPA. This appears to result because smaller grain sizes have a greater effective surface area. This series of experiments indicates that surface area, rather than mass alone, is an important controlling parameter.

Batch experiments 1, 6, 8, and 17 tested the arsenic-removal ability of sea sand, very fine calcium carbonate, Arikaree material, and agricultural limestone. None of these materials was as effective as Minnekahta Limestone at removing arsenic. The Arikaree material actually added arsenic to solution, presumably from the volcanic ash sediments present. This strongly supports the belief, as offered by previous research, that the Arikaree aquifer is a source of arsenic.

Batch experiments 7 and 18 provide results indicating the majority of arsenic removal occurs very quickly upon exposure to limestone. Batch experiment 12 involved the sequential addition of limestone. A similar amount of arsenic was removed by sequential addition as by the standard method of adding all the limestone at the start. All three experiments provide evidence that arsenic removal and quasi equilibrium occur in a relatively short time, probably within one hour.

Batch experiment 9 tested the effect of rinsing the limestone on arsenic removal. It indicated fine particulate material enhances the efficiency of arsenic removal. About 10% of the total arsenic was removed by the fine particles. Using larger samples, thus removing more particulate material by rinsing, would likely result in a more noticeable variation in the samples' efficiency. The reason for the enhanced efficiency appears to be a greater effective surface area of the fine particles.

Batch experiment 15 used a high TDS natural water instead of a standard arsenic solution. All of the arsenic was removed from the high TDS water, albeit by use of relatively large quantities of limestone. However, the process was not as effective with natural water from the No Heart well as it had been with standard solutions. Ionic interference is believed to be the reason for this pronounced difference in efficiency.

Batch experiment 16 was undertaken to determine the effect of varying the pH of the initial solution. Results of the experiment show there is no change in the amount of arsenic removal when the initial pH of the standard solution is varied. This result supports the applicability of the process for a wide range, at least with regards to pH, of waters.

Column Experiments

General Procedure

The column experiments used four PVC pipe columns, each approximately 4 inches in diameter and 3 feet long, filled with Minnekahta Limestone. The columns contained the same grain sizes of Minnekahta Limestone (0.5-1 mm, 1-2 mm, 2-5 mm, and 5-7 mm) as used in the batch experiments. Each column was saturated with distilled water. A slug of either standard solution or No Heart well water was added to the top of the column. A sample of the slug was collected and sent to the lab once a week for the period of time the experiment was conducted. Fluid level was maintained at the top of the column by simultaneously taking a sample from the bottom of the column. Subsequently, 500 mL of slug (or distilled water for the nitrate tracer experiments) was added to the column and resulting samples were taken twice a day. Sample volume, pH, conductivity, temperature, and time of day were recorded. A small part of the sample was filtered (0.45 um filter) and sent to Mid-Continent Laboratories for analysis of arsenic concentration. The experiment ended when sample concentration began to approach slug concentration, i.e. material was becoming chemically saturated. Data points in the shaded area on the graphs were below the detection limit (BDL) of 5 ppb.

Nitrate Tracer Tests

Columns 1, 2, 3, and 4 were subjected to a tracer test to show the behavior of a non-reactive species as it was flushed through the column. A single 250 mL slug of 100 parts per million (ppm) nitrate solution was added to the water-saturated column. Subsequently, 500 mL of water was added to the top of the column while an equal size sample was removed from the bottom of the column. Conductivity measurements were taken from each sample. A series of solutions of varying concentrations were made to relate nitrate concentration and conductivity. Using a calibration curve, estimates of nitrate concentration for each sample were determined. These resulting concentrations, in ppm, were shown as open squares on the graphs prepared for the later column experiments.

100 ppb Arsenic Solution

Column experiments using the four grain sizes were run to determine the limestone's ability to remove arsenic without agitation. These tests simulated the proposed implementation of the limestone-based arsenic removal process as a water line cartridge. The smaller grain sizes reduced arsenic to below 5 ppb for a longer period of time; thus, removing arsenic from a much larger volume of water. The finest grain size was the most effective for arsenic removal.

Column experiment 1

Column 1 contained 5725 grams of 0.5 - 1 mm limestone. A solution of ~100 ppb arsenic at pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 66 days and approximately 34 pore volumes. The limestone adsorbed approximately 0.0065 grams of arsenic prior to the occurrence of breakthrough. On the average, it is estimated that 1.1 x 10^{-6} grams of arsenic per gram of limestone was absorbed. Data from column experiment 1 are shown on Figure 24.

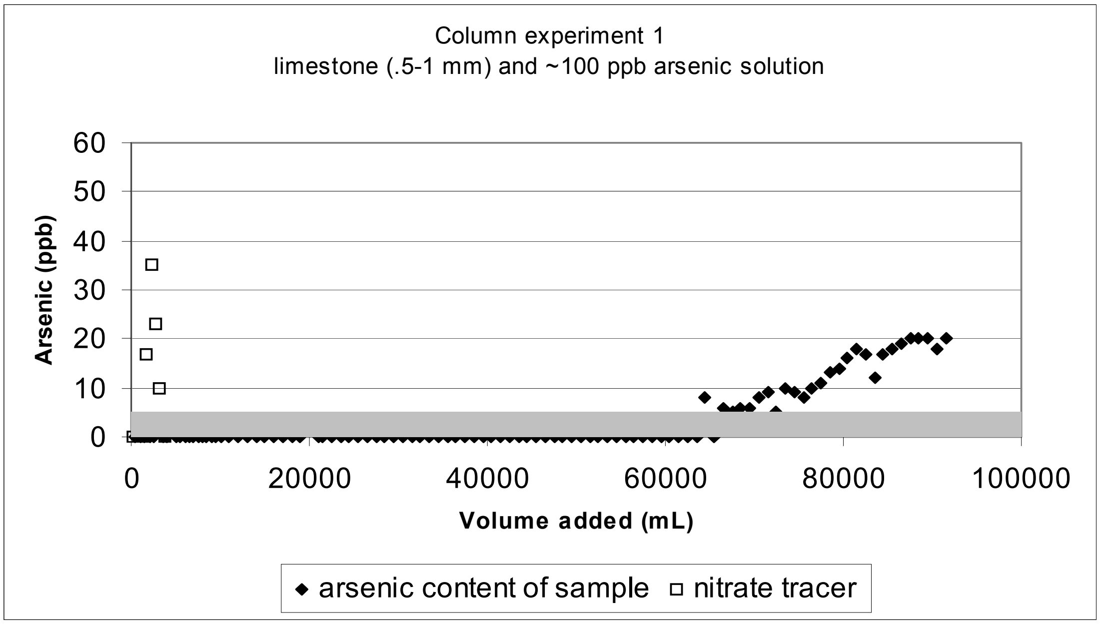


Figure 24. Experiment C1 using 0.5 - 1 mm limestone and 100 ppb arsenic. Shaded area is BDL.

Column experiment 2

Column 2 contained 5590 grams of 1-2 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 25 days and approximately 13 pore volumes. The limestone adsorbed approximately 0.0024 grams of arsenic before breakthrough occurred (4.3×10^{-7} grams of arsenic per gram of limestone). Data from column experiment 2 are shown on Figure 25.

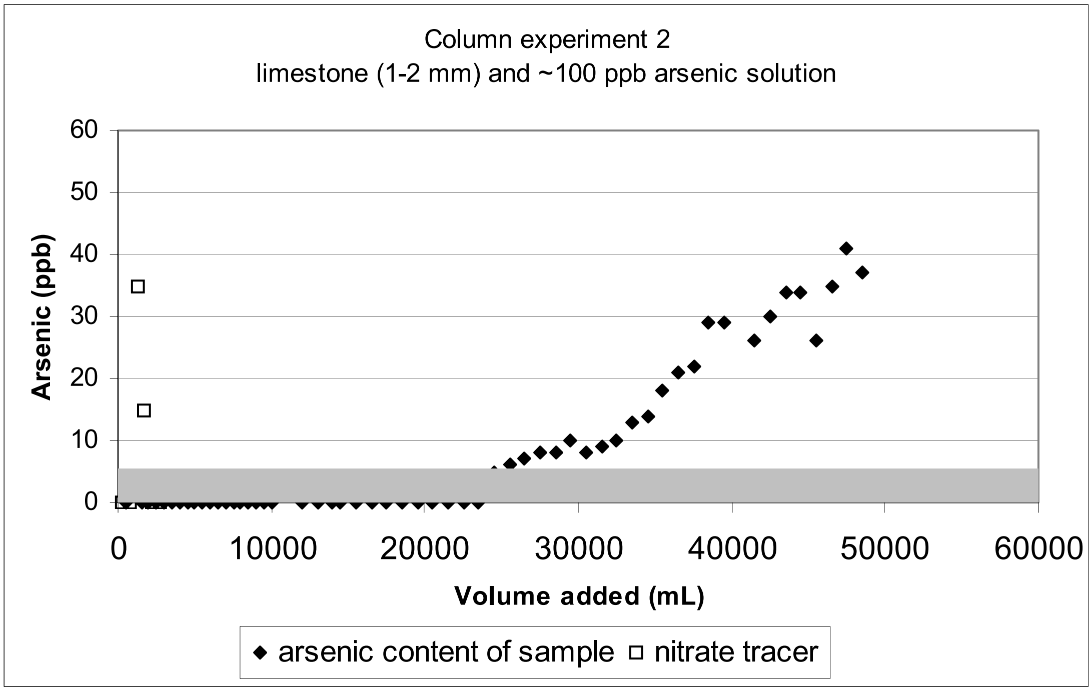


Figure 25. Experiment C2 using 1 - 2 mm limestone and 100 ppb arsenic. Shaded area is BDL.

Column experiment 3

Column 3 contained 5989 grams of 2 - 4.7 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 13 days and approximately seven pore volumes. The limestone adsorbed approximately 0.0012 grams of arsenic before breakthrough occurred (2×10^{-7} grams of arsenic per gram of limestone). Data from column experiment 3 are shown on Figure 26.

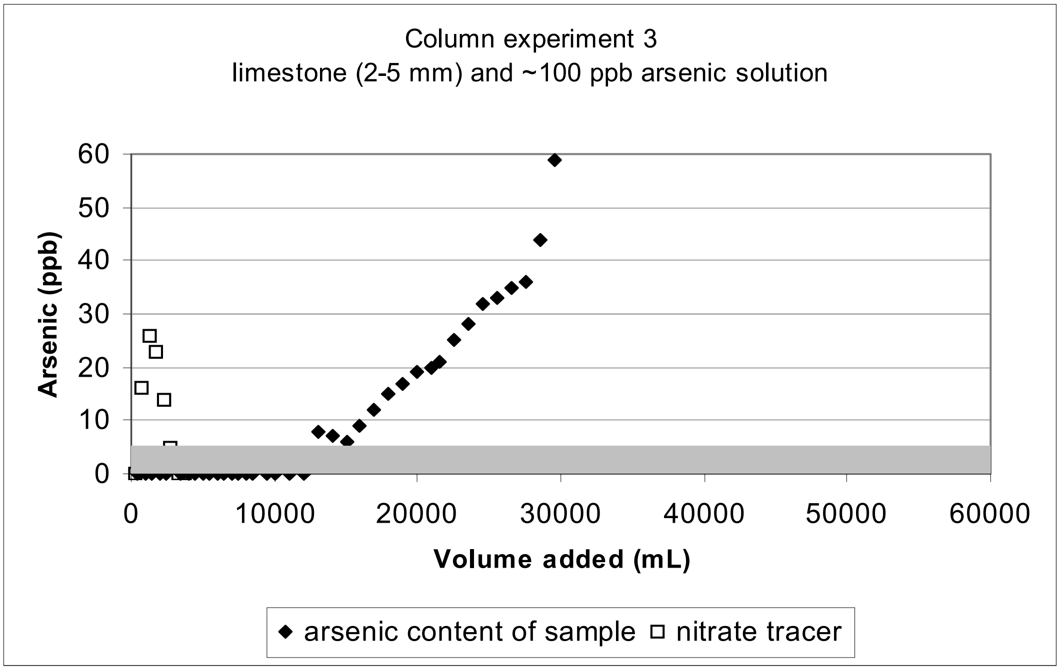


Figure 26. Experiment C3 using 2 - 4.7 mm limestone and 100 ppb arsenic. Shaded area is BDL.

<u>Column experiment 4</u>

Column 4 contained 6343 grams of 4.7 - 6.7 mm limestone. A solution of ~100 ppb arsenic at a pH of 8 +/- 0.2 was run through the column at a rate of one liter per day. Arsenic breakthrough occurred after 10 days and approximately six pore volumes. The limestone adsorbed approximately 0.0009 grams of arsenic prior to breakthrough (1.4 x 10^{-7} grams of arsenic per gram of limestone). Data from column experiment 4 are shown on Figure 27.

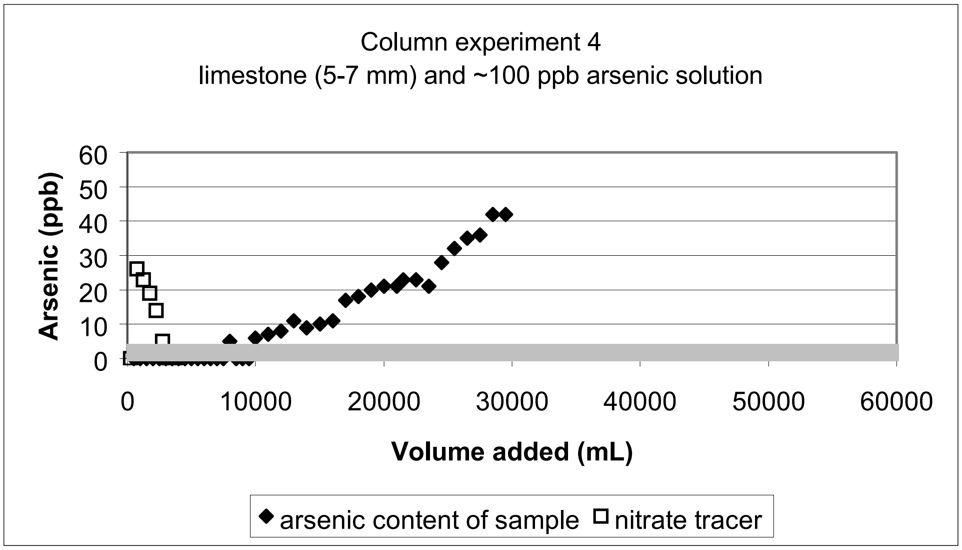


Figure 27. Experiment C4 using 4.7 - 6.7 mm limestone and 100 ppb arsenic. Shaded area is BDL.

Natural Water with High Total Dissolved Solids Concentration

A column experiment using natural water with elevated levels of total dissolved solids was conducted. Arsenic breakthrough occurred after three days. Apparently the other ions in the water also bound to the limestone and limited the amount of arsenic that could be taken out of solution, i.e. the amount of water that could be treated.

Column experiment 5

Column 5 contained 6579 grams of 1 - 2 mm limestone. No Heart well water, with an arsenic content of about 30 ppb, was run through the column at a rate of two liters per day. Three samples of No Heart well water tested at 25, 26, and 36 ppb arsenic. Breakthrough occurred in three days. The limestone adsorbed approximately 0.0001 grams of arsenic prior to breakthrough (1.5 x 10^{-8} grams of arsenic per gram of limestone). The well water did not exit the column at a pH of ~9.5 as expected from previous column experiments. Instead the pH stayed at ~7. The conductivity of the well water was approximately 1200 µS. Data from column experiment 5 are on Figure 28.

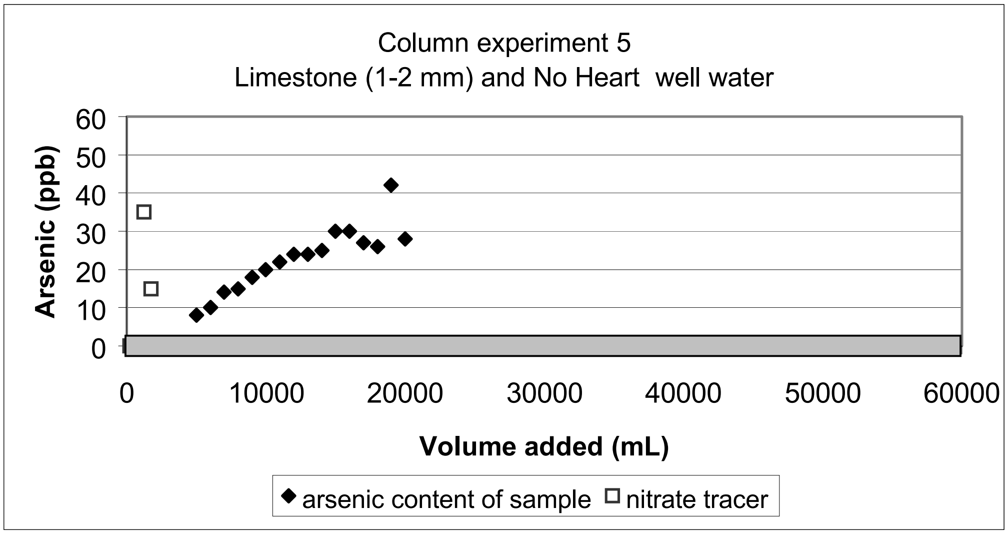


Figure 28. Experiment C5 using 1 - 2 mm limestone and No Heart well water. Shaded area is BDL.

Data from the construction of the columns (Adel Heriba, personal communication) and from the column experiments were used to determine adsorption ratios for the various columns. All columns contained Minnekahta Limestone. Columns 1 through 4 used a prepared standard solution, while column 5 used No Heart well water. Mass balance data are shown in Table 8.

Table 8. Limestone and arsenic mass balance for columns 1 through 5.

Column	Vol filled (cc)	wt LS (g)	LS dens (g/cc)	LS vol (cc)	porosity	Time (d)	ppb As (g/d)	As out (g)	As/LS (g/g)
1	4104	5725	2.625	2181	0.4686	66	0.0001	0.0065	1.14E-06
2	4104	5590	2.625	2130	0.4811	25	0.0001	0.0024	4.29E-07
3	4150	5989	2.625	2282	0.4502	13	0.0001	0.0012	2E-07
4	4172	6343	2.625	2416	0.4208	10	0.0001	0.0009	1.42E-07
5		6579	2.625	2506		3	0.00005	0.0001	1.52E-08

Rinsing Arsenic-Saturated Column with Deionized Water

After saturation with arsenic, Column 3 was rinsed with deionized water. The resulting samples continued to be high in arsenic throughout the test.

Column experiment 3r

Column experiment 3r was a continuation of column experiment 3. The arsenic-saturated limestone was rinsed by running one liter of deionized water per day through the column for 20 days. The purpose of experiment 3r was to test the stability of the arsenic-saturated limestone. The arsenic content of the resulting samples remained in the 30-ppb range even after the addition of 20 liters of deionized water. This is approximately 11 times the pore volume of the column. Therefore, some arsenic is being released back into solution by the limestone. Data from column experiment 3r are shown on Figure 29.

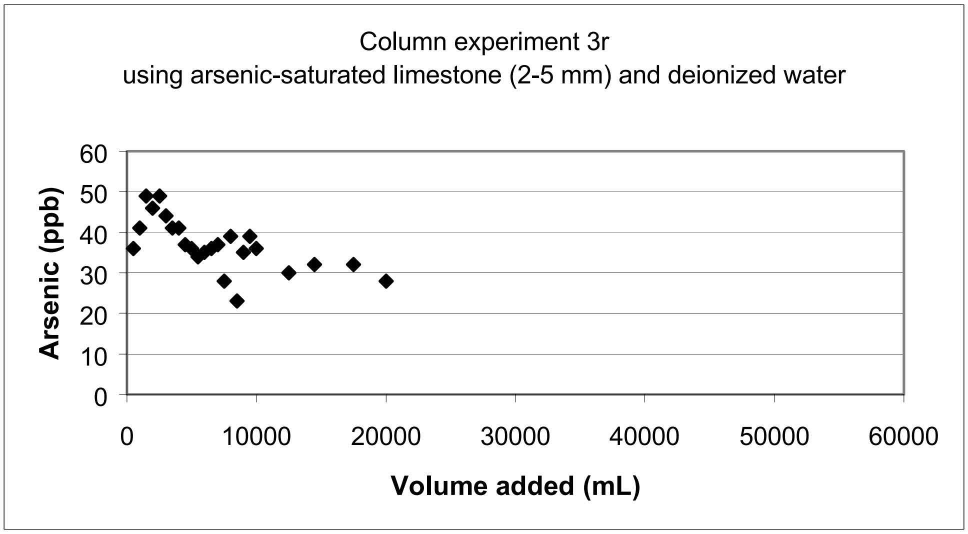


Figure 29. Experiment C3r rinsing column 3 with deionized water.

Discussion of Column Experiments

Column experiments are a more realistic representation of the type of device necessary for implementation of the process in a residential situation. Columns 1 through 4 all effectively reduced the arsenic concentration of the standard solution. These columns confirmed the importance of grain size identified during the batch tests, that is, the smaller the grain size, the more efficient the arsenic removal. Ultimately the limiting factor controlling grain size will be the required flow velocity through a column of limestone. At some lower limit of permeability, water will not flow through the column, or cartridge, at a sufficient rate. An important, related factor is the residence time necessary to reduce arsenic to an acceptable level. All else being equal, the shorter the necessary residence time, the greater the rate of flow and the greater the amount of water that can be treated in a given amount of time. Maximizing the flow rate will be of utmost importance when developing a marketable product.

Column experiment 5 indicated that high TDS concentrations hinder the arsenic removal process. It is proposed that the large number of other ions present compete with arsenic for available reaction sites on the surface of the limestone. The lower than expected pH values from column experiment 5, along with the early breakthrough, indicate that less chemical interaction occurs between the limestone and the well water compared to that which occurred between the limestone and the standard solution in column experiments 1 through 4. The reduced chemical interaction is likely to have resulted from ionic interference. The identity of the ions that are causing the problem is unknown. The No Heart well water has the highest TDS concentration of any well in the Grass Mountain area. It is higher than is recommended for domestic use. Hopefully waters of more moderate TDS concentrations will provide less ionic interference. Further tests are needed and are scheduled for the near future.

In column experiment 3r, the arsenic did not appear to be sufficiently bound to the limestone to prevent some remobilization. However, we attribute these results primarily to dissolved arsenic in the interstitial pores in the column.

Related work at South Dakota School of Mines and Technology, as part of the Research Experiences for Undergraduates program of the National Science Foundation (Pogany, 2001), used a leaching test to examine stability of the waste. The Toxicity Characteristic Leaching Procedure (TCLP) was conducted on two samples of limestone waste from column tests, following methods outlined by EPA protocol SW-846-1311. Solid samples were extracted from two spent columns that held 0.5 – 1 mm particles. Waste samples were filtered with an 11-cm ceramic Buchner filtration apparatus and 2 liters of de-ionized water to remove any interstitial arsenic. The waste then was subjected to the TCLP test, and sample aliquots were withdrawn for analysis. Results showed arsenic concentrations of 8 ppb from the first column and less than 5 ppb from the second. The leaching potential of the waste was lower than the new MCL of 10 ppb for arsenic, so the waste appears to be stable and potentially could be placed in a landfill.

SUMMARY AND CONCLUSIONS

The results of the series of experiments conducted are encouraging. Minnekahta Limestone consistently removed arsenic from water. Exposure to the limestone routinely reduced arsenic concentrations from ~100 ppb to less than 5 ppb. However, implementation of a limestone-based arsenic removal process for natural waters will take much additional work.

Surface area of the limestone is a key parameter controlling the efficiency of the process. The smaller grain sizes provided a greater surface area per unit weight; thus, better arsenic removal was demonstrated by the batch experiments and confirmed by the column experiments. The 0.5 - 1 mm grain size column reduced arsenic concentrations below 5 ppb in 66 liters of ~100 ppb standard solution. The 4.7 - 6.7 mm grain size column reduced the arsenic concentration of only 10 liters of the same standard solution to less than 5 ppb.

An area of concern is the stability of the arsenic-saturated limestone waste product. Preliminary TCLP tests indicate that the waste is stable. However, additional research on disposal or reuse of the waste product is needed.

While arsenic is consistently removed by limestone, widespread use of the process will require its applicability to a sufficient range of natural water conditions. The pH of the arsenic-rich water did not affect the efficiency of the process. Arsenic was consistently reduced in solutions with pH values from 4 to 10. This is encouraging for application of the process to natural waters. However, the elevated TDS (> 1000 mg/L) of the No Heart well water reduced the effectiveness of the process. Additional work is necessary to quantify the ionic effect and identify the specific ions responsible for the interference. Overall, the limestone-based arsenic removal process shows promise but will require a significant amount of further work to implement at the Rosebud Indian Reservation or elsewhere.

RECOMMENDATIONS

The areas of major concern regarding feasibility of a limestone-based arsenic removal process are ionic interference, the stability and disposal of arsenic-saturated limestone, and the rate at which the process can treat water. Each of these concerns should be addressed.

The process should be studied at the molecular level regarding what compound is formed on or within the limestone. A better understanding of the entire process and the composition of the arsenic-rich limestone waste product would likely result from such a study. Perhaps a material other than limestone needs to be added to the process to enhance waste product stability. Based on previous research, iron oxide seems an appropriate choice. Other limestones should be tested. A rock unit can contain various constituents and still qualify for classification as limestone. One of these minor constituents could greatly enhance the process.

Various other natural waters should be used in upcoming work with a batch reactor. Chemical analyses of these natural waters should be done in an attempt to identify which ions preferentially interfere. Column experiments using a constant flow rate are needed. Understanding the flow mechanics of the process will be essential to development of a prototype.

A prototype cartridge must be designed. Experimental data regarding mass adsorption ratios and necessary residence times, hence indicating an appropriate cartridge size and flow rate, would assist in the design of a prototype. The intent of any design should be to maximize the efficiency of the limestone-based arsenic removal process with regard to both limestone mass and water volume or flow rate. This assumes the use of the smallest feasible limestone grain size. Cost and availability factors could affect that assumption.

Initial experimental work has been successful in demonstrating the use of limestone to reduce the arsenic concentrations of a prepared standard solution. Prototype design and arsenic-rich limestone disposal must be addressed before the ultimate feasibility of applying limestone-based arsenic removal systems can be determined. Further work should focus on expanding the applications of the process, namely to include removing arsenic from natural waters as well as standard solutions.

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APPENDIX

Spreadsheets of experimental data

b1 CaCO3 10 micron + 100 mL As standard

preserved sample	As ppb	Mass (g)	PH
standard	96	0	
s1	88	1.08	8.82
s2	82	2.37	9.36
s3	76	5.77	9.35
s3d	72	5.71	9.35
s4	74	7.74	9.35
s5	54	12.85	9.27
s6	97	0	

not preserved sample		
standard	81	0
s1	97	1.08
s2	103	2.37
s3	79	5.77
s3d	96	5.71
s4	71	7.74
s5	45	12.85
s6	62	0

b2 4.7-6.7 mm LS + 100 mL As standard

sample	As ppb	Mass (g)	PH	Cond	temp=26.2
standard	109	0	7.9		
s1	76	1.02	9.3	150	
s2	31	5.03	9.4	150	
s3	20	9.87	9.4	150	
s3b	<5	9.94	9.1	60	
s3d	18	10.05	8.9	160	
s4	5	40.14	9.1	170	
s5	<5	99.91	9.1	210	

b3 2-4.7 mm LS + 100 mL As standard

sample	As ppb	Mass (g)	PH	Cond	temp
standard	108	0	8		
s1	75	1.01	9.7	60	
s2	37	4.99	9.3	60	
s3	20	9.93	9.6	80	22
s3b	<5	10.09	8.6	50	21
s3d	14	9.99	9.3	60	21
s4	<5	39.96	8.8	100	
s5	<5	99.98	9.3	140	

b4 1-2mm LS 100 mL 100ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	106	0	8		
s1	64	1	9.7	60	24
s2	43	4.97	9.3	70	24
s3	9	10.02	9.4	120	24
s3b	<5	10.03	9.5	50	
s3d	9	9.99	9.5	70	
s4	<5	40	9.1	130	
s5	12	100.02	8.6	210	

b5 LS .5-1mm + 100 mL As standard

sample	As ppb	Mass (g)	PH	Cond	temp
standard	91	0			
s1	56	1.05	9.5	50	26.5
s2	43	5.03	9.5	60	26
s3	9	10.01	9.4	80	26
s3b	<5	10.02	9.2	80	26
s3d	9	9.99	9.4	80	
s4	<5	40.02	9	160	26
s5	6	100.03	8.6	280	25.5

b6 fine sea sand + 100 mL 100 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	99	0			
s1	71	0.95	6.6	20	21.5

s2	80	4.93	6.9	30	22
s3	75	10.07	7.6	30	21
s3b	<5	10.02	7.6	30	22
s3d	70	10.17	7.4	30	22
s4	50	40	8.5	90	21
s5	30	99.82	8.4	200	21

b7 time variable 10 g 1-2 mm LS +100 mL of ~100 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp	shake time (hrs)
	100					0.01
s1	28	9.99	9.7	50	21	1
s2	32	10.03	9.7	70	21	2
s3	32	10.01	9.7	70	21	4
s4	25	10	9.6	60	23	8
s5	22	10.02	9.7	80	20	12
s6	17	9.99	9.5	60	20	24
s7	12	10.01	9.5	70	18	48

b8 arikaree + 100 mL standard

sample	As ppb	Mass (g)	PH	Cond	temp
standard	102	0	8		
s1	101	0.97	7.9	30	19
s2	109	5.12	7.9	60	19
s3	83	10.05			
s3b	32	10.2			
s3d	81	9.98	8.4	60	20
s4	not tested	40.31	8.2	140	20
s5	too hard to filter	100.06	8.2	490	20

all samples very cloudy and difficult to filter
As ppb results are from 5X dilutions.

b9 LS 1-2mm + 100 mL standard fines?

sample	As ppb	Mass (g)	PH	Cond	temp	rinsed?
standard	90	0	8			
s1	18	10.22	9.6	60	20	yes
s1d	18	10.12	9.6	60	20	yes
s2	9	9.99	9.5	70	20	no

s2d	8	9.99	9.5	60	20	no

b10 5-7 mm LS 100 mL 20 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	20	0	7.9		
s1	14	1.05	9.5	60	20
s2	6	4.97	9.5	50	20
s3	<5	9.98	9.3	60	20
s3b	<5	10.04	9.5	60	20
s3d	<5	9.96	9.3	70	20
s4	<5	40.02	9.1	90	20
s5	<5	100.02	8.8	170	21

b11 2-5 mm LS 100 mL 20 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	18	0	8		
s1	16	0.99	9.7	50	18
s2	5	4.95	9.5	50	18
s3	<5	10	9.5	50	18
s3b	<5	10.33	9.5	50	18
s3d	<5	10	9.4	60	18
s4	<5	39.96	9.1	100	18
s5	<5	99.94	8.9	160	18

b12 sequential 1-2 mm LS 100 mL 100 ppb As
1 g LS every 2 hrs

sample	As ppb	Mass in (g)	Mass added (g)	vol out (mL)	time (hr)
standard	92	0	0.99	0	0
s1	77	0.99	1.01	8	2
s2	67	2	1.01	13	4
s3	59	3.01	0.99	10	6
s4	53	4	1.01	6	8
s5	46	5.01	0	All	10

b13 1-2 mm LS 100 mL 20 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	21	0	7.8		
s1	16	0.98	9.3	50	18
s2	<5	4.96	9.6	50	18
s3	<5	9.99	9.5	50	19
s3b	<5	9.96	9.5	60	19
s3d	<5	9.95	9.5	60	18
s4	<5	40	9.1	110	19
s5	<5	99.94	8.9	170	19

b14 .5-1 mm LS 100 mL 20 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp
standard	20	0	8.2		
s1	12	1.03	9.6	50	18
s2	5	5	9.5	60	18
s3	<5	9.98	9.3	80	19
s3b	<5	9.95	9	80	18
s3d	<5	10.01	9.4	70	19
s4	<5	40.02	9	150	19
s5	<5	99.96	8.6	210	19

b15 1-2 mm LS 100 mL no heart water

sample	As ppb	Mass (g)	PH	Cond	temp
standard	25	0	7.6	1280	
s1	26	1	7.7	1270	19
s2	24	5.06	7.6	1260	19
s3	20	9.99	7.4	1180	19
s3b	<5	10.05	9.3	60	19
s3d	20	10.03	7.4	1190	19
s4	6	39.97	7.3	1150	19
s5	<5	99.99	7.3	1130	19

b16 pH varies 1-2 mm LS 100 mL 100 ppb As

sample	As ppb	Mass (g)	pH in	pH out	cond	temp
standard	~100	0	~8			
s1	9	10.06	6	9.5	60	15
s2	9	10.05	6.6	9.5	50	15

s3	7	10.08	6.9	9.4	60	15
s4	9	10.07	7.5	9.5	50	15
s5	10	10.09	8.1	9.5	70	16
s6	9	10.1	8.4	9.4	70	16

b17 agri LS 100 mL 100 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp	
standard	87	0	7.9			
s1	59	0.98	9.5	50	24	
s2	36	5.05	9	70	24	
s3	18	10	9.2	80		
s3b	<5	9.97	9.5	70		
s3d	10	10	9.2	90		
s4	6	40.08	8.9	180		LS stuck
s5	7	100.28	8.3	360		together

b18 time variable 5 g 1-2 mm LS +100 mL of 20 ppb As

sample	As ppb	Mass (g)	PH	Cond	temp	shake time (hrs)
standard	23	0	8.2			0.01
s1	8	4.98	9.5	60	22	1
s2	7	5	9.8	50	21	2
s3	8	4.99	9.7	50	22	4
s4	7	5.04				8
s5	5	4.98	9.4	80	23	12
s6	<5	5.01	9.4	60	26	24
s7	<5	4.96	9.5	60	27	48

c1 LS .5-1mm 100 ppb As at pH=8

column	sample	Vin	Vout	pH	cond	temp	time	date	ppb As	cum. Vin
c1-	1	500	480	9.5	50	24		8/9/00	<5	500
c1-	2	500	510	9.4	50	20		8/10/00	<5	1000
c1-	3	500	510	9.5	80	24		8/10/00	<5	1500
c1-	4	500	490	9.5	60	22		8/11/00	<5	2000
c1-	5	500	500	9.5	70	25		8/11/00	<5	2500
c1-	6	500	510	9.4	60	20		8/12/00	31	3000
c1-	7	500	500	9.5	70	20		8/12/00	<5	3500
c1-	8	500	500	9.5	60	18		8/13/00	<5	4000
c1-	9	500	500	9.3	60	19		8/13/00	6	4500
c1-	10	500	500	9.3	60	19		8/14/00	<5	5000
c1-	11	500	520	9.1	60	22		8/14/00	<5	5500

c1-	12	500	500	9.5	60	19	8/15/00	<5	6000
c1-	13	500	500	9.5	60	20	8/15/00	<5	6500
c1-	14	500	510	9.5	60	18	8/16/00	<5	7000
c1-	15	500	530	9.4	80	19	8/16/00	<5	7500
c1-	16	500	490	9.5	60	18	8/17/00	<5	8000
c1-	17	500	510	9.1	50	18	8/17/00	<5	8500
c1-	18	500	495	9.5	60	18	8/18/00	<5	9000
c1-	19	500	490	9.5	50	20	8/18/00	<5	9500
c1-	20	500	550	9.3	60	18	8/19/00	<5	10000
c1-	21	500	490	9.1	60	18	8/19/00		10500
c1-	22	500	500	9.3	60	18	8/20/00	<5	11000
c1-	23	500	500	9.2	50	19	8/20/00		11500
c1-	24	500	510	9.3	50	18	8/21/00	<5	12000
c1-	25	500	500	9.5	50	18	8/21/00		12500
c1-	26	500	500	9.5	50	18	8/22/00	<5	13000
c1-	27	500	500	9.5	50	19	8/22/00		13500
c1-	28	500	500	9.5	60	17	8/23/00	<5	14000
c1-	29	500	490	9.3	50	20	8/23/00		14500
c1-	30	500	500	9.5	60	19	8/24/00	<5	15000
c1-	31	500	480	9	70	21	8/24/00		15500
c1-	32	500	540	9.1	60	19	8/25/00	<5	16000
c1-	33	500	500	9.5	60	22	8/25/00		16500
c1-	34	500	490	9.5	50	19	8/26/00	<5	17000
c1-	35	500	480	8.5	60	20	8/26/00		17500
c1-	36	500	490	9.5	60	19	8/27/00	<5	18000
c1-	37	500	510	9.5	60	19	8/27/00		18500
c1-	38	500	500	9.6	60	18	8/28/00	<5	19000
c1-	39	500	500	9.3	60	19	8/28/00		19500
c1-	40	500	500	9.4	50	18	8/29/00	10	20000
c1-	41	500	500	9.2	60	19	8/29/00		20500
c1-	42	500	520	9.2	60	18	8/30/00	<5	21000
c1-	43	500	480	9.5	90	19	8/31/00	<5	21500
c1-	44	500	490	8.4	60	18	8/31/00		22000
c1-	45	500	500	9.5	60	18	9/1/00	<5	22500
c1-	46	500	490	9.4	60	19	9/1/00		23000
c1-	47	500	550	9.3	60	17	9/2/00	<5	23500
c1-	48	500	520	9.1	50	18	9/2/00		24000
c1-	49	500	530	9.4	60	17	9/3/00	<5	24500
c1-	50	500	490	9.5	50	18	9/3/00		25000
c1-	51	500	500	9.1	60	18	9/4/00	<5	25500
c1-	52	500	490	9.4	50	19	9/4/00		26000
c1-	53	500	500	9.5	50	18	9/5/00	<5	26500
c1-	54	500	490	9.3	60	21	9/5/00		27000
c1-	55	500	510	9.4	50	19	9/6/00	<5	27500
c1-	56	500	490	9.4	60	20	9/6/00		28000
c1-	57	500	490	9.5	50	19	9/7/00	<5	28500
c1-	58	500	500	9.5	50	17	9/7/00		29000
c1-	59	500	500	9.5	60	18	9/8/00	<5	29500
c1-	60	500	520	9.3	60	18	9/8/00		30000
c1-	61	500	500	9.2	50	17	9/9/00	<5	30500

c1-	62	500	500	9.3	50	17	9/9/00		31000
c1-	63	500	500	9.6	60	19	9/10/00	<5	31500
c1-	64	500	490	9.5	50	17	9/10/00		32000
c1-	65	500	490	9.5	60	19	9/11/00	<5	32500
c1-	66	500	490	9.5	50	18	9/11/00		33000
c1-	67	500	500	8.7	50	19	9/12/00	<5	33500
c1-	68	500	490	9.5	50	18	9/12/00		34000
c1-	69	500	490	9.5	50	18	9/13/00	<5	34500
c1-	70	500	500	9.5	60	19	9/13/00		35000
c1-	71	500	530	9.5	50	18	9/14/00	<5	35500
c1-	72	500	500	9.5	50	17	9/14/00		36000
c1-	73	500	520	9.5	60	18	9/15/00	<5	36500
c1-	74	500	510	9.6	50	18	9/15/00		37000
c1-	75	500	500	9.5	50	18	9/16/00	<5	37500
c1-	76	500	500	9.5	50	18	9/16/00		38000
c1-	77	500	490	9.6	50	18	9/17/00	<5	38500
c1-	78	500	510	9.6	50	18	9/17/00		39000
c1-	79	500	500	9.6	50	18	9/18/00	<5	39500
c1-	80	500	510	9.5	70	21	9/18/00		40000
c1-	81	500	480	9.6	60	19	9/19/00	<5	40500
c1-	82	500	510	9.6	60	18	9/19/00		41000
c1-	83	500	500	9.7	70	18	9/20/00	<5	41500
c1-	84	500	480	9.6	60	18	9/20/00		42000
c1-	85	500	510	9.7	70	16	9/21/00	<5	42500
c1-	86	500	510	9.5	60	18	9/21/00		43000
c1-	87	500	480	9.5	50	16	9/22/00	<5	43500
c1-	88	500	510	9.5	50	13	9/22/00		44000
c1-	89	500	500	9.7	40	10	9/23/00	<5	44500
c1-	90	500	410	9.7	50	10	9/23/00		45000
c1-	91	500	520	9.6	40	9	9/24/00	<5	45500
c1-	92	500	510	9.6	50	10	9/24/00		46000
c1-	93	500	510	9.7	50	11	9/25/00	<5	46500
c1-	94	500	510	9.5	70	14	9/25/00		47000
c1-	95	500	500	9.5	130	21	9/26/00	<5	47500
c1-	96	500	410	9.5	90	24	9/26/00		48000
c1-	97	500	510	9.4	100	26	9/27/00	<5	48500
c1-	98	500	510	9.5	100	25	9/27/00		49000
c1-	99	500	500	9.5	110	28	9/28/00	<5	49500
c1-	100	500	510	9.5	80	23	9/28/00		50000
c1-	101	500	510	8.7	50	20	9/29/00	<5	50500
c1-	102	500	500				9/29/00		51000
c1-	103	500	510	9.4	80	28	9/30/00	<5	51500
c1-	104	500	500	9.2	60	22	9/30/00		52000
c1-	105	500	500	9.3	100	28	10/1/00	<5	52500
c1-	106	500	500	9.4	50	22	10/1/00		53000
c1-	107	500	480	9.4	80	26	10/2/00	<5	53500
c1-	108	500	500	9.5	60	22	10/2/00		54000
c1-	109	500	500	9.5	60	20	10/3/00	bad	54500
c1-	110	500	480	9.3	60	21	10/3/00		55000
c1-	111	500	500	9.3	60	21	10/4/00	<5	55500

c1-	112	500	480	9.4	60	20	10/4/00		56000
c1-	113	500	500	9.4	60	20	10/5/00	<5	56500
c1-	114	500	510	9.4	60	21	10/5/00		57000
c1-	115	500	470	9.2	70	21	10/6/00	<5	57500
c1-	116	500	490	9.4	60	23	10/6/00		58000
c1-	117	500	500	9.4	60	21	10/7/00	<5	58500
c1-	118	500	500	9.5	50	21	10/7/00		59000
c1-	119	500	510	9.4	100	21	10/8/00	<5	59500
c1-	120	500	510	9.5	60	20	10/8/00		60000
c1-	121	500	500	9.5	80	21	10/9/00	<5	60500
c1-	122	500	500	8.5	90	21	10/9/00		61000
c1-	123	500	510	9.3	90	21	10/10/00	<5	61500
c1-	124	500	500	9.3	80	24	10/10/00		62000
c1-	125	500	510	9.4	80	23	10/11/00	<5	62500
c1-	126	500	500	9.4	80	26	10/11/00		63000
c1-	127	500	510	9.4	110	28	10/12/00	<5	63500
c1-	128	500	500	9.5	60	24	10/12/00		64000
c1-	129	500	490	9.3	80	25	10/13/00	8	64500
c1-	130	500	500	9.4	70	26	10/13/00		65000
c1-	131	500	490	9.4	70	24	10/14/00	<5	65500
c1-	132	500	490	9.5	70	23	10/14/00		66000
c1-	133	500	490	9.5	60	22	10/15/00	6	66500
c1-	134	500	500	9.5	70	23	10/15/00		67000
c1-	135	500	500	9.5	60	21	10/16/00	5	67500
c1-	136	500	500	9.4	90	24	10/16/00		68000
c1-	137	500	500	9.5	70	23	10/17/00	6	68500
c1-	138	500	490	9.5	60	24	10/17/00		69000
c1-	139	500	500	9.5	80	22	10/18/00	6	69500
c1-	140	500	500	9.5	80	23	10/18/00		70000
c1-	141	500	490	9.5	70	22	10/19/00	8	70500
c1-	142	500	500	9.5	60	23	10/19/00		71000
c1-	143	500	500	9.5	60	22	10/20/00	9	71500
c1-	144	500	500	9.5	70	22	10/20/00		72000
c1-	145	500	490	9.5	90	21	10/21/00	5	72500
c1-	146	500	490	9.5	80	22	10/21/00		73000
c1-	147	500	510	9.6	70	20	10/22/00	10	73500
c1-	148	500	500	9.5	60	19	10/22/00		74000
c1-	149	500	500	9.5	50	19	10/23/00	9	74500
c1-	150	500	510	9.3	50	21	10/23/00		75000
c1-	151	500	500	9.6	70	19	10/24/00	8	75500
c1-	152	500	500	9.5	70	21	10/24/00		76000
c1-	153	500	500	9.5	70	20	10/25/00	10	76500
c1-	154	500	500	9.4	700	21	10/25/00		77000
c1-	155	500	500	9.5	70	20	10/26/00	11	77500
c1-	156	500	500	9.5	60	21	10/26/00		78000
c1-	157	500	500	9.6	60	19	10/27/00	13	78500
c1-	158	500	500	9.7	70	20	10/27/00		79000
c1-	159	500	500	9.6	60	18	10/28/00	14	79500
c1-	160	500	510	9.6	60	19	10/28/00		80000
c1-	161	500	500	9.2	50	19	10/29/00	16	80500

c1-	162	500	500	9.6	70	19		10/29/00		81000
c1-	163	500	490	9.5	60	18		10/30/00	18	81500
c1-	164	500	500	9.6	60	20		10/30/00		82000
c1-	165	500	490	9.6	50	18		10/31/00	17	82500

c2 LS 1-2 mm 100 ppb As at pH=8 +/- .2

column	sample	Vin	Vout	pH	Cond	temp	time	date	As ppb	cum. Vin
c2-	1	500	510	9.5	60	19		8/16/00	<5	500
c2-	2	500	500	9.5	70	18		8/17/00	23	1000
c2-	3	500	500	9.4	50	18		8/17/00	<5	1500
c2-	4	500	515	9.5	50	18		8/18/00	<5	2000
c2-	5	500	490	9.5	50	19		8/18/00	<5	2500
c2-	6	500	530	9.6	60	18		8/19/00	<5	3000
c2-	7	500	510	9.5	70	18		8/19/00	<5	3500
c2-	8	500	530	6.9	50	18		8/20/00	<5	4000
c2-	9	500	480	9.5	50	18		8/20/00	<5	4500
c2-	10	500	490	9.2	50	18		8/21/00	<5	5000
c2-	11	500	490	9.3	70	18		8/21/00	<5	5500
c2-	12	500	520	9.5	100	18		8/22/00	<5	6000
c2-	13	500	500	9.6	70	19		8/22/00	<5	6500
c2-	14	500	490	9.1	90	17		8/23/00	<5	7000
c2-	15	500	500	9.1	80	20		8/23/00	<5	7500
c2-	16	500	520	8.6	50	19		8/24/00	<5	8000
c2-	17	500	500	9.5	70	21		8/24/00	<5	8500
c2-	18	500	500	9.3	80	19		8/25/00	<5	9000
c2-	19	500	510	9.3	50	22		8/25/00	<5	9500
c2-	20	500	490	8.8	50	19		8/26/00	<5	10000
c2-	21	500	490	9.5	70	19		8/26/00		10500
c2-	22	500	510	9.5	90	19		8/27/00	18	11000
c2-	23	500	500	9.5	70	19		8/27/00		11500
c2-	24	500	500	9.6	70	18		8/28/00	<5	12000
c2-	25	500	500	9.5	80	19		8/28/00		12500
c2-	26	500	450	9.3	50	18		8/29/00	<5	13000
c2-	27	500	500	9.5	80	19		8/29/00		13500
c2-	28	500	500	9.5	80	18	a.m.	8/30/00	<5	14000
c2-	29	500	540	9.5	50	18		8/31/00	<5	14500
c2-	30	500	500	9.1	50	18		8/31/00		15000
c2-	31	500	490	9.5	70	18		9/1/00	<5	15500
c2-	32	500	510	9.5	60	18		9/1/00		16000
c2-	33	500	510	9.5	60	17		9/2/00	<5	16500
c2-	34	500	500	8.4	50	17		9/2/00		17000
c2-	35	500	500	9.5	60	17		9/3/00	<5	17500
c2-	36	500	450	9	80	18		9/3/00		18000
c2-	37	500	490	9.5	70	18		9/4/00	<5	18500
c2-	38	500	510	9.5	60	19		9/4/00		19000
c2-	39	500	520	9.5	70	18		9/5/00	<5	19500
c2-	40	500	490	9.5	70	21		9/5/00		20000

c2-	41	500	490	9.5	70	18	9/6/00	<5	20500
c2-	42	500	500	9.5	60	20	9/6/00		21000
c2-	43	500	500	9.5	60	19	9/7/00	<5	21500
c2-	44	500	490	9.5	40	17	9/7/00		22000
c2-	45	500	510	9.5	70	18	9/8/00	<5	22500
c2-	46	500	530	9.5	60	18	9/8/00		23000
c2-	47	500	510	9.6	50	17	9/9/00	<5	23500
c2-	48	500	490	9.5	50	17	9/9/00		24000
c2-	49	500	480	9.6	60	19	9/10/00	5	24500
c2-	50	500	520	9.6	40	17	9/10/00		25000
c2-	51	500	480	9.7	60	19	9/11/00	6	25500
c2-	52	500	480	9.6	70	18	9/11/00		26000
c2-	53	500	510	9.6	60	19	9/12/00	7	26500
c2-	54	500	500	9.5	40	18	9/12/00		27000
c2-	55	500	500	9.5	60	18	9/13/00	8	27500
c2-	56	500	500	9.5	70	19	9/13/00		28000
c2-	57	500	500	9.6	60	18	9/14/00	8	28500
c2-	58	500	510	9.5	50	17	9/14/00		29000
c2-	59	500	500	9.7	50	18	9/15/00	10	29500
c2-	60	500	530	9.7	50	18	9/15/00		30000
c2-	61	500	500	9.6	80	18	9/16/00	8	30500
c2-	62	500	480	9.5	50	18	9/16/00		31000
c2-	63	500	480	9.7	60	18	9/17/00	9	31500
c2-	64	500	510	8.8	60	18	9/17/00		32000
c2-	65	500	490	9.7	60	18	9/18/00	10	32500
c2-	66	500	500	9.5	50	21	9/18/00		33000
c2-	67	500	490	9.5	50	19	9/19/00	13	33500
c2-	68	500	500	9.5	40	18	9/19/00		34000
c2-	69	500	500	9.7	50	18	9/20/00	14	34500
c2-	70	500	500	9.7	50	18	9/20/00		35000
c2-	71	500	500	9.7	40	16	9/21/00	18	35500
c2-	72	500	500	8.5	50	18	9/21/00		36000
c2-	73	500	500	9.5	40	16	9/22/00	21	36500
c2-	74	500	500	9.4	40	12	9/22/00		37000
c2-	75	500	490	9.3	40	10	9/23/00	22	37500
c2-	76	500	500	9.7	40	10	9/23/00		38000
c2-	77	500	600	9.5	40	9	9/24/00	29	38500
c2-	78	500	400	9.5	40	10	9/24/00		39000
c2-	79	500	500	9.7	40	11	9/25/00	29	39500
c2-	80	500	500	9.3	40	14	9/25/00		40000
c2-	81	500	510	9.5	50	21	9/26/00	bad	40500
c2-	82	500	510	9.5	50	24	9/26/00		41000
c2-	83	500	500	9.4	50	26	9/27/00	26	41500
c2-	84	500	500	9.4	50	24	9/27/00		42000
c2-	85	500	500	9.2	60	27	9/28/00	30	42500
c2-	86	500	490	9.2	50	23	9/28/00		43000
c2-	87	500	500	8.5	50	19	9/29/00	34	43500
c2-	88	500	500	9.5	70	22	9/29/00		44000
c2-	89	500	500	9.4	50	27	9/30/00	34	44500
c2-	90	500	480	8.6	50	21	9/30/00		45000

c2-	91	500	500	9.4	60	28		10/1/00	26	45500
c2-	92	500	530	9.5	50	21		10/1/00		46000
c2-	93	500	490	9.2	60	26		10/2/00	35	46500
c2-	94	500	500	7.8	50	21		10/2/00		47000
c2-	95	500	490	9.5	50	20		10/3/00	41	47500
c2-	96	500	500	9.3	50	21		10/3/00		48000
c2-	97	500	500	9.4	50	21		10/4/00	37	48500

c3 LS 2-5 mm 100 ppb As at pH=8 +/- .2

column	sample	Vin	Vout	pH	Cond	temp	time	date	As ppb	cum. Vin
c3-	1	500	490	9.3	50	24		8/9/00	<5	500
c3-	2	500	500	9.3	40	20		8/10/00	<5	1000
c3-	3	500	510	9.3	50	24		8/10/00	<5	1500
c3-	4	500	500	9.3	60	21		8/11/00	<5	2000
c3-	5	500	500	9.1	50	25		8/11/00	<5	2500
c3-	6	500	510	9.3	50	19		8/12/00	14	3000
c3-	7	500	500	9.3	50	20		8/12/00	<5	3500
c3-	8	500	520	9.1	50	18		8/13/00	<5	4000
c3-	9	500	460	9.1	50	19		8/13/00	<5	4500
c3-	10	500	500	9.3	50	19		8/14/00	<5	5000
c3-	11	500	500	9.2	50	22		8/14/00	<5	5500
c3-	12	500	530	9.5	50	18		8/15/00	<5	6000
c3-	13	500	500	9.5	50	20		8/15/00	<5	6500
c3-	14	500	500	9.5	50	18		8/16/00	<5	7000
c3-	15	500	500	9.5	50	19		8/16/00	<5	7500
c3-	16	500	500	9.5	50	18		8/17/00	<5	8000
c3-	17	500	490	9.2	40	18		8/17/00	<5	8500
c3-	18	500	490	9.5	50	18		8/18/00	21	9000
c3-	19	500	490	9.3	50	20		8/18/00	<5	9500
c3-	20	500	500	9.4	50	18		8/19/00	<5	10000
c3-	21	500	490	9.1	40	18		8/19/00		10500
c3-	22	500	500	9.3	50	18		8/20/00	<5	11000
c3-	23	500	500	9.4	40	18		8/20/00		11500
c3-	24	500	500	8.9	40	18		8/21/00	<5	12000
c3-	25	500	500	9.5	40	18		8/21/00		12500
c3-	26	500	510	9.5	40	18		8/22/00	8	13000
c3-	27	500	500	9.5	50	19		8/22/00		13500
c3-	28	500	520	9.5	40	17		8/23/00	7	14000
c3-	29	500	490	9.5	40	20		8/23/00		14500
c3-	30	500	500	9.5	50	19		8/24/00	6	15000
c3-	31	500	480	9.5	50	21		8/24/00		15500
c3-	32	500	520	9.3	50	19		8/25/00	9	16000
c3-	33	500	490	9.3	50	22		8/25/00		16500
c3-	34	500	530	9.3	40	19		8/26/00	12	17000
c3-	35	500	490	9.3	40	19		8/26/00		17500
c3-	36	500	520	9.1	40	19		8/27/00	15	18000
c3-	37	500	500	9.1	50	19		8/27/00		18500

c3-	38	500	500	9.5	50	18		8/28/00	17	19000
c3-	39	500	500	9.5	40	19		8/28/00		19500
c3-	40	500	490	9.2	40	18		8/29/00	19	20000
c3-	41	500	500	9.5	50	19		8/29/00		20500
c3-	42	500	510	9.1	40	17		8/30/00	20	21000
c3-	43	500	480	9.4	50	19		8/31/00	21	21500
c3-	44	500	500	8.9	40	18		8/31/00		22000
c3-	45	500	500	9.5	40	18		9/1/00	25	22500
c3-	46	500	500	9.3	40	18		9/1/00		23000
c3-	47	500	510	9.1	50	17		9/2/00	28	23500
c3-	48	500	490	9.1	40	17		9/2/00		24000
c3-	49	500	490	9	50	17		9/3/00	32	24500
c3-	50	500	500	9.4	40	18		9/3/00		25000
c3-	51	500	510	9.1	40	17		9/4/00	33	25500
c3-	52	500	500	9.3	40	19		9/4/00		26000
c3-	53	500	470	9.4	40	18		9/5/00	35	26500
c3-	54	500	500	8.9	50	21		9/5/00		27000
c3-	55	500	520	9.4	40	18		9/6/00	36	27500
c3-	56	500	490	9.5	50	20		9/6/00		28000
c3-	57	500	490	9.4	40	19		9/7/00	44	28500
c3-	58	500	500	9.3	40	17		9/7/00		29000
c3-	59	500	490	9.5	50	18		9/8/00	59	29500

c3r LS 2-5 mm Di water rinse

column	sample	Vin	Vout	pH	Cond	temp	time	date	As ppb	cum. Vin
c3r-	1	500	600	9	60	21		9/18/00	36	500
c3r-	2	500	390	9	60	19		9/19/00	41	1000
c3r-	3	500	500	9.1	60	17		9/19/00	49	1500
c3r-	4	500	500	9.2	60	18		9/20/00	46	2000
c3r-	5	500	500	9.4	40	18		9/20/00	49	2500
c3r-	6	500	500	9.2	40	16		9/21/00	44	3000
c3r-	7	500	500	9	40	18		9/21/00	41	3500
c3r-	8	500	500	9.3	40	16		9/22/00	41	4000
c3r-	9	500	500	9.1	30	13		9/22/00	37	4500
c3r-	10	500	500	8.9	30	10		9/23/00	36	5000
c3r-	11	500	520	9.3	30	10		9/23/00	34	5500
c3r-	12	500	500	9.5	30	9		9/24/00	35	6000
c3r-	13	500	520	9.5	30	10		9/24/00	36	6500
c3r-	14	500	500	9.7	30	11		9/25/00	37	7000
c3r-	15	500	500	9.4	30	14		9/25/00	28	7500
c3r-	16	500	500	8.8	40	21		9/26/00	39	8000
c3r-	17	500	500	9.5	40	24		9/26/00	23	8500
c3r-	18	500	500	9.4	50	26		9/27/00	35	9000
c3r-	19	500	500	9	40	24		9/27/00	39	9500
c3r-	20	500	530	9.2	50	27		9/28/00	36	10000
c3r-	21	500	~500					9/29/00		10500
c3r-	22	500	~500					9/29/00		11000

c3r-	23	500	~500					9/30/00		11500
c3r-	24	500	~500					9/30/00		12000
c3r-	25	500	490	9.3	50	28		10/1/00	30	12500
c3r-	26	500	~500					10/1/00		13000
c3r-	27	500	~500					10/2/00		13500
c3r-	28	500	~500					10/2/00		14000
c3r-	29	500	540	8.1	40	20		10/3/00	32	14500
c3r-	30	500						10/3/00		15000
c3r-	31	500						10/4/00		15500
c3r-	32	500						10/4/00		16000
c3r-	33	500						10/5/00		16500
c3r-	34	500						10/5/00		17000
c3r-	35	500	500	9.3	50	21		10/6/00	32	17500
c3r-	36	500						10/6/00		18000
c3r-	37	500						10/7/00		18500
c3r-	38	500						10/7/00		19000
c3r-	39	500						10/8/00		19500
c3r-	40	500	510	9.3	40	20		10/8/00	28	20000

c4 LS 5-7 mm 100 ppb As at pH=8 +/- .2

column	sample	Vin	Vout	pH	Cond	temp	time	date	As ppb	cum. Vin
c4-	1	500	500	9.2	50	24		8/9/00	<5	500
c4-	2	500	520	9.1	50	20		8/10/00	<5	1000
c4-	3	500	500	9.1	60	24		8/10/00	<5	1500
c4-	4	500	500	9.1	60	21		8/11/00	<5	2000
c4-	5	500	500	9.1	60	25		8/11/00	<5	2500
c4-	6	500	500	9.3	50	19		8/12/00	<5	3000
c4-	7	500	500	8.9	50	20		8/12/00	<5	3500
c4-	8	500	500	8.8	50	18		8/13/00	<5	4000
c4-	9	500	490	8.6	50	19		8/13/00	<5	4500
c4-	10	500	500	8.7	50	19		8/14/00	<5	5000
c4-	11	500	500	9.3	50	22		8/14/00	<5	5500
c4-	12	500	500	8.5	50	19		8/15/00	<5	6000
c4-	13	500	520	9.1	50	20		8/15/00	<5	6500
c4-	14	500	510	9.4	50	18		8/16/00	<5	7000
c4-	15	500	500	9.5	50	19		8/16/00	<5	7500
c4-	16	500	490	9.3	50	18		8/17/00	5	8000
c4-	17	500	500	9.1	40	18		8/17/00	<5	8500
c4-	18	500	500	9.5	40	18		8/18/00	<5	9000
c4-	19	500	490	9.2	50	20		8/18/00	<5	9500
c4-	20	500	560	9.3	50	18		8/19/00	6	10000
c4-	21	500	490	9.2	50	18		8/19/00		10500
c4-	22	500	500	9.1	50	18		8/20/00	7	11000
c4-	23	500	500	9.4	40	19		8/20/00		11500
c4-	24	500	500	9.2	50	18		8/21/00	8	12000
c4-	25	500	500	9.3	40	18		8/21/00		12500
c4-	26	500	520	9.5	40	18		8/22/00	11	13000

c4-	27	500	500	9.5	40	19		8/22/00		13500
c4-	28	500	510	8.8	40	17		8/23/00	9	14000
c4-	29	500	500	9.5	40	20		8/23/00		14500
c4-	30	500	500	9.5	40	19		8/24/00	10	15000
c4-	31	500	490	9.1	40	22		8/24/00		15500
c4-	32	500	510	9.3	50	19		8/25/00	11	16000
c4-	33	500	440	9.3	50	22		8/25/00		16500
c4-	34	500	580	9.3	50	19		8/26/00	17	17000
c4-	35	500	450	9	40	19		8/26/00		17500
c4-	36	500	500	8.5	50	19		8/27/00	18	18000
c4-	37	500	520	9	50	19		8/27/00		18500
c4-	38	500	500	9.5	50	18		8/28/00	20	19000
c4-	39	500	500	9.5	40	19		8/28/00		19500
c4-	40	500	490	9.3	40	18		8/29/00	21	20000
c4-	41	500	500	9.1	40	19		8/29/00		20500
c4-	42	500	500	9.3	50	18		8/30/00	21	21000
c4-	43	500	560	9.3	40	19		8/31/00	23	21500
c4-	44	500	500	8.9	50	18		8/31/00		22000
c4-	45	500	480	9.3	40	18		9/1/00	23	22500
c4-	46	500	500	8.9	40	18		9/1/00		23000
c4-	47	500	500	9.4	40	17		9/2/00	21	23500
c4-	48	500	500					9/2/00		24000
c4-	49	500	500	9.3	40	17		9/3/00	28	24500
c4-	50	500	490	9.2	40	18		9/3/00		25000
c4-	51	500	500	9.3	40	17		9/4/00	32	25500
c4-	52	500	500	9.2	40	19		9/4/00		26000
c4-	53	500	500	9.1	40	18		9/5/00	35	26500
c4-	54	500	500	9.3	40	21		9/5/00		27000
c4-	55	500	500	9.4	40	18		9/6/00	36	27500
c4-	56	500	510	9.4	50	20		9/6/00		28000
c4-	57	500	480	9.4	40	19		9/7/00	42	28500
c4-	58	500	500	8.9	40	17		9/7/00		29000
c4-	59	500	490	9.5	40	18		9/8/00	42	29500

c5 LS 1-2 mm no heart water

column	sample	Vin	Vout	pH	cond	temp	time	date	ppb As	cum. Vin
c5-	1	1000	1000	9.4	50	26		9/18/00	<5	1000
c5-	2	1000	1000	7.5	610	24		9/19/00	<5	2000
c5-	3	1000	1010	7.4	1090	17		9/19/00	<5	3000
c5-	4	1000	1010	7.3	1160	18		9/20/00	<5	4000
c5-	5	1000	1000	7.3	1160	18		9/20/00	8	5000
c5-	6	1000	1080	7.4	1160	16		9/21/00	10	6000
c5-	7	1000	1010	6.9	1170	18		9/21/00	14	7000
c5-	8	1000	990	7.2	1170	16		9/22/00	15	8000
c5-	9	1000	1010	7.3	1160	13		9/22/00	18	9000
c5-	10	1000	910	7.3	1140	10		9/23/00	20	10000
c5-	11	1000	1010	7.4	1150	10		9/23/00	22	11000

c5-	12	1000	1000	7.1	1130	9	9/24/00	24	12000
c5-	13	1000	1010	7.4	1140	10	9/24/00	24	13000
c5-	14	1000	1010	7.4	1150	11	9/25/00	25	14000
c5-	15	1000	1010	7.3	1140	14	9/25/00	30	15000
c5-	16	1000	1010	7.2	1150	21	9/26/00	30	16000
c5-	17	1000	1000	7.1	1220	24	9/26/00	27	17000
c5-	18	1000	1000	7.1	1220	26	9/27/00	26	18000
c5-	19	1000	1010	7.2	1200	24	9/27/00	42	19000
c5-	20	1000	990	7.1	1230	27	9/28/00	28	20000