SAND REPORT

SAND2002-3641
Unlimited Release
Printed November 2002

Sorption of Arsenic from Drinking Water to Mg(OH)2, Sorrel's Cements, and Zirconium Doped Materials

Robert C. Moore, Kathleen Holt, Hongting Zhao, Fred Salas, Ahmed Hasan, and Dan Lucero

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online

SAND2002-3641
Unlimited Release
Printed November 2002

Sorption of Arsenic from Drinking Water to $Mg(OH)_2$, Sorrel's Cements, and Zirconium Doped Materials

Robert C. Moore, Kathleen Holt, Hongting Zhao,
Fred Salas, Ahmed Hasan, and Dan Lucero
Environmental Decisions and Program Development
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185-0779

Abstract

It was discovered that MgO or $Mg(OH)_2$ when it reacts with water is a very strong sorbent for arsenic. Distribution constants, or K_d values, are as high as 1×10^6 L/mole. In this work, $Mg(OH)_2$ and other compounds have been investigated as sorbents for arsenic and other contaminants. This work has resulted in several major accomplishments including: 1) design, construction, and testing of a pressure sand filter to remove $Mg(OH)_2$ after it has sorbed arsenic from water, 2) stabilization of $Mg(OH)_2$ as a Sorrel's cement against reaction with carbonate that results in $MgCO_3$ formation decreasing the efficiency of $Mg(OH)_2$ to sorb arsenic, and 3) the development of a new, very promising sorbent for arsenic based on zirconium. Zirconium is an environmentally benign material found in many common products such as toothpaste. It is currently used in water treatment and is very inexpensive. In this work, zirconium has been bonded to activated carbon, zeolites, sand and montmorillonite. Because of its high charge in ionic form (+6), zirconium is a strong sorbent for many anions including arsenic. In equilibrium experiments arsenic concentrations in water were reduced from 200 ppb to less than 1 ppb in less than 1 minute of contact time. Additionally, analytical methods for detecting arsenic in water have also been investigated. Various analytical techniques including HPLC, AA and ICP-MS are used for quantification of arsenic. Due to large matrix interferences HPLC and AA techniques are not very selective and are time consuming. ICP-MS is highly efficient, requires a low sample volume and has a high tolerance for interferences. All these techniques are costly and require trained staff, and with the exception of ICP-MS, these methods cannot be used at low ppb arsenic concentration without using a pre-concentration step. An alternative to these traditional techniques is to use a colorimetric method based on leucocrystal violet dye interaction with iodine. This method has been adapted in our facility for quantifying arsenic concentrations down to 14 ppb.

Acknowledgements

Sandia National Laboratory is operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Contents

Figures

Tables

Summary

Magnesium oxide has been discovered to be a very strong sorbent for arsenic in both the +3 and +5 oxidation states. K_d values are as high as 1×10^6 L/mole. However, a problem in using $Mg(OH)_2$ for arsenic sorption is removal of the $Mg(OH)_2$ after sorption has occurred. A pressure sand filter using a mixture of different sizes of sand (50 to 400 mesh) was constructed and effectively removed $Mg(OH)_2$ in bench scale tests. The filter was tested at flow rates from 2 to 4 gallons/minute and 0.1 to 0.5 g of $Mg(OH)_2$ per gallon of water. Once the filter reached its capacity the flow of water through the filter was reversed, fluidizing the sand bed, and washing the reacted $Mg(OH)_2$ and arsenic out the top of the filter.

Another problem with using $Mg(OH)_2$ in water treatment is its reaction with carbonate in water to form $MgCO_3$ which does not sorb arsenic. This problem has been almost eliminated by stabilizing the $Mg(OH)_2$ as a Sorrel's cement. Sorrel's cements are composed of $MgCl_2$ with $Mg(OH)_2$ in a polymerized form. Sorrel's cements are easily formed by mixing the two compounds in the proper ratio with water. Other compounds can be added to further stabilize the mixture. By using an $FeCl_3$ doped Sorrel's cement, we have been able to maintain the sorptive properties of $Mg(OH)_2$ and have almost eliminated the reaction of $Mg(OH)_2$ with carbonate.

Additionally, a new sorbent based on zirconium has been developed for arsenic sorption. Zirconium is an environmentally benign material found in many common products such as toothpaste. It is currently used in water treatment and is very inexpensive. In this work, zirconium has been bonded to activated carbon, zeolites, sand and montmorillonite. Because of its high charge in ionic form (+6), zirconium is a strong sorbent for many anions including arsenic. In equilibrium experiments arsenic concentrations in water were reduced from 200 ppb to less than 1 ppb in less than 1 minute of contact time.

Analytical methods for detecting arsenic in water have also been investigated. Various analytical techniques including HPLC, AA and ICP-MS are used for quantification of arsenic. Due to large matrix interferences HPLC and AA techniques are not very selective and are time consuming. ICP-MS is highly efficient, requires a low sample volume and has a high tolerance for interferences. All these techniques are costly and require trained staff, and with the exception of ICP-MS, these methods cannot be used at low ppb arsenic concentration without using a pre-concentration step. An alternative to these traditional techniques is to use a colorimetric method based on leucocrystal violet interaction with iodine. This method has been adapted in our facility for quantifying arsenic concentrations down to 14 ppb.

The major accomplishments for the work on arsenic sorbents include:

- The kinetic and sorption properties of $Mg(OH)_2$ for arsenic have been determined

- A 1-5 gallon/minute system for arsenic removal using $Mg(OH)_2$ and a pressure sand filter has been constructed, tested and the system presented to U.S. Senator Pete Domenici and the Mayor of Albuquerque, Jim Baca.

- $Mg(OH)_2$ has been incorporated into a Sorrel's cement where it is resistant to carbonate attack. The Sorrel's cement is a strong sorbent for arsenic but does not have the problem of pH adjustment and reaction with carbonate that $Mg(OH)_2$ does. Kinetic and equilibrium properties of Sorrel's cement with arsenic in water with and without carbonate have been determined.

- Proof-of-principle experiments have been performed with a new arsenic sorbent, zirconium doped activated carbon and zeolite. The results are very promising. The use of zirconium-based materials does not require a pH adjustment.

- A new analytical method for arsenic quantification using a pre-reduction step followed by colorimetric detection using leucocrystal violet dye interaction and iodine has been used to accurately quantify arsenic in Albuquerque tap water. The method is inexpensive, accurate, rapid and easy to use.

- The use of $Mg(OH)_2$ as an arsenic sorbent was presented at the 6th Annual New Mexico Environmental Health Conference, October 29-31, 2001 Albuquerque, NM and the ACS meeting in Orlando, Florida, August 2001.

- The use of MgO/CaO or $Mg(OH)_2/Ca(OH)_2$ to Concentrate Arsenic and Remove Impurities in Water Samples for Analysis was presented at the 6th Annual New Mexico Environmental Health Conference, October 29-31, 2001 Albuquerque, NM

- Three patent applications have been filed on the use of $Mg(OH)_2$ and zirconium doped materials for water treatment to remove arsenic from drinking water.

Introduction

Arsenic (As) has long been known as a highly toxic element. Recently, the United States Environmental Protection Agency (EPA) adopted a regulation to reduce the public health risks from arsenic in drinking water. The EPA set the new arsenic standard for drinking water at 10 ppb down from the original 50 ppb to protect consumers against the effects of long-term, chronic exposure to arsenic in drinking water.

A survey conducted by the American Water Works Association (AWWA) for inorganic contaminants in water supplies in the United States revealed 34 violations for arsenic (maximum contaminant level (MCL) 0.05 mg/L), with concentration values ranging from 0.052 to 0.190 mg/L and a mean concentration of 0.083 mg/L (American Water Works Association Committee, 1985). Arsenic cannot be destroyed; it can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron.

Higher levels of arsenic are generally found in ground water rather than in surface water sources. In the United States, western states have more systems with arsenic levels greater than 10 ppb. In order to reach the new arsenic standard in drinking water, cost-effective technologies are needed. In this work $Mg(OH)_2$, Sorrel's cements, and zirconium doped activated carbon, zeolite, sand and montmorillonite are being investigated as sorbents for arsenic. Kinetic and equilibrium experiments have been performed that indicate these materials are rapid acting, strong sorbents for arsenic. $Mg(OH)_2$ was used with a pressure sand filter to remove arsenic in a 1 to 5 gallon per minute bench scale system. Using a mixture of sand sizes, 50 to 400 mesh, $Mg(OH)_2$ with sorbed arsenic was easily removed at levels from 0.1 to 0.5 g $Mg(OH)_2$ per gallon of water.

One of the problems with the use of $Mg(OH)_2$ for arsenic sorption is the reaction of $Mg(OH)_2$ with carbonate in the water to form $MgCO_3$. $MgCO_3$ does not sorb arsenic therefore reducing the efficiency of the process. Another problem with the use of $Mg(OH)_2$ is the pH change of the water to be treated. With $Mg(OH)_2$ solid present, water pH is set at 10.6. The acid required to reduce pH back to levels of drinking water, around 6.5 to 9, would add to the cost of the treatment process. To overcome these problems we have incorporated $Mg(OH)_2$ into the form of Sorrel's cement. Sorrel's cement is a mixture of $Mg(OH)_2$, $MgCl_2$ and water. Other compounds can be added to affect the physical and chemical properties of the Sorrel's cement. In this work, we have identified $FeCl_3$ as a compound that increases the resistance of Sorrel's cement to react with carbonate and lowers the equilibrium pH of water in contact with Sorrel's cement.

In addition to developing a Sorrel's cement for arsenic sorption, we are also examining zirconium doped activated carbon, zeolite, sand and montmorillonite. Recently, zirconium bound to activated carbon tubules has been used in analysis by atomic adsorption spectroscopy as a pre-concentration step. In our work we have attached zirconium to activated carbon and zeolite particles and used the material to sorb arsenic from water. Zirconium doped materials do not have the drawback reactions with carbonate and pH adjustment which is required for $Mg(OH)_2$ based compounds. Additionally, the use of zirconium attached to zeolite is very economical.

The technique for quantifying arsenic in water is based on reducing all arsenic to the +3 oxidation state and reacting the As(III) with potassium iodate. Arsenic reacts with potassium iodate in the presence of HCl to liberate iodine. The librated iodine oxidizes leucocrystal violet to form crystal violet dye in the presence of sodium hydroxide. The dye can be quantified using a

UV/VIS Spectrophotometer set at 595 nm. This method is low cost, simple, and can be performed in 1 hour. In our facility we have adapted the method for measuring arsenic concentration down to 10 ppb. For water samples containing both As(III) and As(V), $SnCl_2$ is used to reduce all arsenic to the +3 state for analysis.

Experimental

Batch and Equilibrium Experiments

Arsenate ($NaAsO_3•H_2O$) or arsenite ($NaAsO_2•H_2O$) were obtained from Aldrich and used as received. Batch kinetic and equilibrium sorption experiments were performed in the same manner. Solid sorbents were equilibrated with water at a set pH. The pH was adjusted using either NaOH or HCl. Arsenic in either the +3 or +5 oxidation state was added to the solutions and agitated for a specific time or until equilibrium was reached. The solid sorbents were removed by centrifugation and filtration. Arsenic concentrations were determined by ICP-MS. For kinetic experiments, the concentration of arsenic sorbed was determined over time.

NSF challenge water was used in the batch and equilibrium experiments and made using the following components:

Na^+:	73.7 ppm	Ca^{2+}:	40.1 ppm	Mg^{2+}:	12.6 ppm
HCO_3^-:	183.0 ppm	Cl^-:	71.0 ppm	SO_4^{2-}:	50.0 ppm
NO_3^-:	2.0 ppm	F^-:	1.0 ppm	HPO_4^{2-}:	0.04 ppm

Zr-Doped Zeolite(ZrDZ) and Activated Carbon (ZrDC)

Zeolite (St. Cloud clinoptilolite - 14x40 mesh) was obtained from St. Cloud Mining Company, Truth or Consequences, NM. Activated carbon was obtained from Fisher Scientific and ground and separated into two fractions: coarse (~2 mm) and fine powder. Zirconium oxychloride hydrate (98%) was obtained from Aldrich as received. ZrDZ and ZrDC were synthesized by immersing 10-100 g solid in 25-50 mL 0.1 M $ZrOCl_2$ solution for 1-2 days, filtered and rinsed extensively with deionized water, air-dried and stored in polyethylene bottles before use.

Zr-pillared montmorillonite (ZrPM)

Reference montmorillonite clay, SWy-1 (Source Clay Repository of the Clay Mineral Society) was dispersed in water using Na_2CO_3 and the <2 μm fractions separated using wet sedimentation. ZrPM was synthesized by titrating freshly prepared 0.25 M $ZrOCl_3$ into a well-dispersed clay suspension (1g/100 mL) to reach a final concentration of 0.25 mmol Zr/g clay. The suspension was continuously stirred at room temperature (23°C) for 2 hours, then filtered, washed and dialyzed extensively against deionized water (DI) until the conductivity was below 0.01 *ds* m^{-1}. The samples were dried at 40°C, ground and stored in polyethylene bottles before use. A portion of the sample was calcined at 400°C for 2 hours.

UV/VIS Colorimetric Quantification of Arsenic

A UV-VIS Spectrometer with quartz cells was used for quantification. Stock solution of arsenic (1000 ppm) was prepared from sodium arsenite (Merk). Leucocrystal violet was obtained from Schmid and Co., West Germany. Potassium iodate was obtained from Fisher. All the reagents used were of A.R. grade. Double distilled deionized water was used for all measurements.

Preparation of Calibration Curve

To a 25 mL aliquot of solution containing 5-500 ppb arsenic, 2 mL of 1% potassium iodate and 1 mL of 0.5 M HCl was added and the mixture was shaken gently for 5 minutes followed by addition of 1 mL of leucocrystal violet and 5 drops of 2 M NaOH solution. The solution was kept in a thermostat oven at 45–48°C for 15 minutes. The pH was adjusted between 5.5 to 6.5 before the colorimetric measurement. The absorbance was measured at 592±2 nm against a reagent blank that was prepared in the same manner as mentioned above.

Determination of total As in Albuquerque tap water

To one liter of tap water 0.001g of $SnCl_2$ was added to convert all As(V) to As(III). Air was then bubbled through the sample to convert all remaining $SnCl_2$ to SnO. The procedure described above was then used to measure the As(III) in solution.

Results and Discussion

$Mg(OH)_2$ for Arsenic Sorption

The kinetics of arsenic sorption onto $Mg(OH)_2$ are very rapid (Figure 1). Concentrations of 200 ppb can be reduced to less than 10 ppb using 0.3 g of $Mg(OH)_2$ per liter of water. Lesser amounts of $Mg(OH)_2$ require more time. $Mg(OH)_2$ has the advantage of sorbing arsenic in the +3 and +5 oxidation state, although sorption of +3 arsenic proceeds slower and equilibrium constants are not as high as with arsenic in the +5 state.

At this time we are not modeling the reactions kinetics because the stoichiometry of the $Mg(OH)_2$-arsenic compound is unknown. We are currently looking at using XAFAS for examining the surface of the $Mg(OH)_2$ with sorbed arsenic. These experiments should be completed this summer. The equilibrium constant for arsenic(V) sorption to $Mg(OH)_2$ is extremely high with values as high as 968000 L/mole (Table 1). These values are significantly decreased by the presence of carbonate in the water.

Thus far the mechanism of sorption of arsenic(V) onto $Mg(OH)_2$ is unknown. A plot of final concentration of arsenic in solution vs. $1/K_d$ is close to linear and does not confine to any conventional isothermal models (Figure 2).

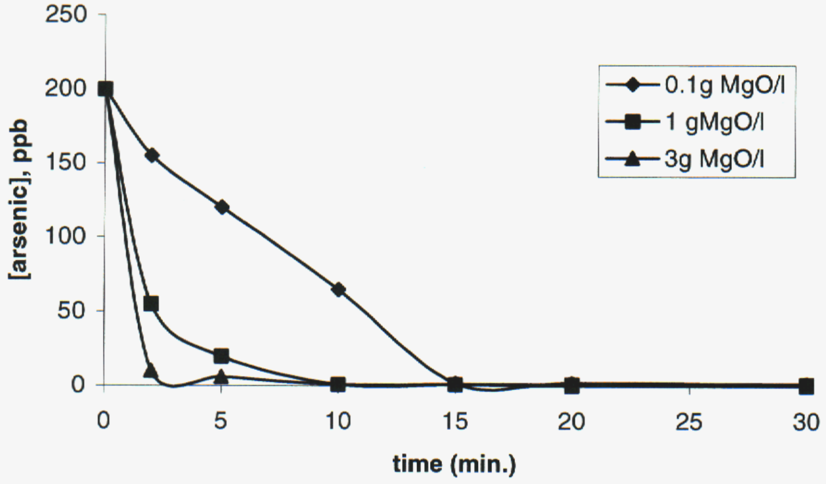

Figure 1. Sorption kinetics of arsenic (V) onto $Mg(OH)_2$ in water. $Mg(OH)_2$ was added as MgO. Samples were analyzed by ICP-MS.

Table 1. Equilibrium constant, K_d, for arsenic sorption to MgO. 0.5 g/liter of water

[As] initial (ppb)	[As] final (ppb)	K_d (L/mole)
1000	1	580800
5000	3	968000
6000	7	497700
7000	7	369000
8500	43	114000
10000	121	47500

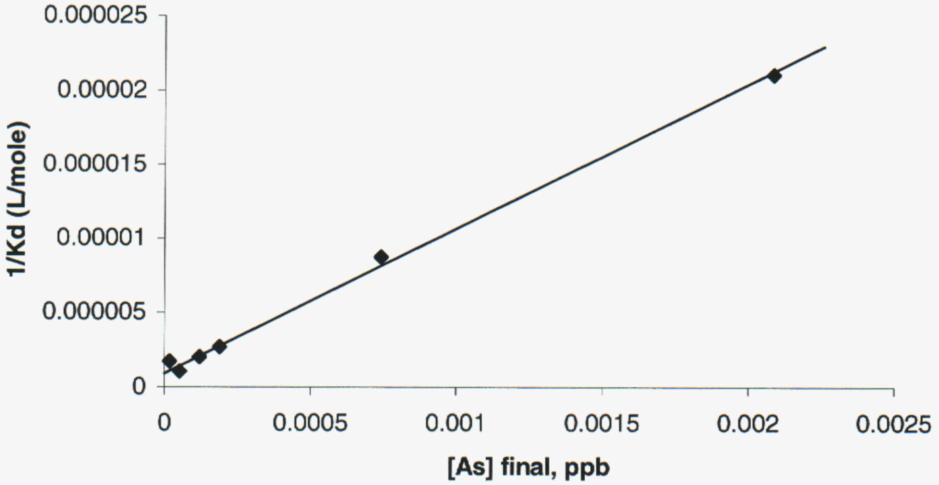

Figure 2. Plot of final concentration vs. $1/K_d$ for $Mg(OH)_2$ sorption of arsenic(V). 0.1 g of MgO added to 1 L of solution. Y-intercept = .0000011, slope = .0095

In addition to reagent grade $Mg(OH)_2$, commercial $Mg(OH)_2$ from Martin Marietta was tested for use as an arsenic sorbent (Table 2). The commercial product was sized to that of reagent grade material (200-400 mesh size) and tested in batch experiments. The commercial material reduced 100 ppb arsenic to approximately 46 ppb while the reagent grade material reduced arsenic concentrations to approximately 5 ppb. The decreased sorptive ability of the commercial material is likely due to the method of manufacture. Reagent grade material is precipitated from an over saturated solution while commercial material is produced by calcining $MgCO_3$ ore. The calcining results in a much more crystalline MgO that requires much more time to convert to $Mg(OH)_2$ in water. Granular MgO had very little effect on arsenic concentrations.

Table 2. Commercial and chemical grade MgO for arsenic sorption.
Reaction time was 10 minutes. with 1 gram of MgO in 1 liter of water.

MgO	**[As] initial (ppb)**	**[As] final (ppb)**
Fisher Scientific (reagent grade)	100	5.2
Commercial powder (Martin Marietta)	100	45.8
Granular MgO (Martin Marietta) treated at different temperature		
700°C	100	97.6
500°C	100	95.3
300°C	100	90.5

The use of $Mg(OH)_2$ for arsenic sorption requires a method of mixing the $Mg(OH)_2$ in the water and removing it after sorption of arsenic has taken place. It is not practical to use $Mg(OH)_2$ in a packed column configuration because of the reaction of $Mg(OH)_2$ with carbonate. After a relatively short time all MgO in the column would be converted to $MgCO_3$ and all arsenic would be released back into the water. Mixing the $Mg(OH)_2$ with water is a trivial task, but because of its very small size, 200 to 400 mesh, separating the $Mg(OH)_2$ from water after reaction can be difficult. In this work, we constructed a flow system using a pressure sand filter for removing the $Mg(OH)_2$ after reaction with arsenic (Figure 3). The sand is a mixture of different sizes ranging from 50 to 200 mesh. The system has a variable flow rate from 0.1 to 5 gallon per minute. The system was tested using deionized water and NSF challenge water with an initial arsenic concentration of 100 ppb and a flow rate of 2 gallons per minute (Table 3). For the deionized water, arsenic concentrations decreased to 1 to 12 ppb depending on the amount of MgO added. For NSF challenge water, arsenic concentrations decreased to 8 and 14 ppb using 0.5 and 0.2 g MgO per gallon of water respectively. The NSF

Figure 3. 1 to 5 gallon/minute process using $Mg(OH)_2$ and pressure sand filtration for arsenic removal.

water contained 200 ppm of carbonates and required more MgO for arsenic sorption.

Table 3. Results from 1 to 5 gallon/minute arsenic removal process

Water	MgO (g/gallon)	Flow rate (gallons/min)	Reaction time (min)	Initial Arsenic (ppb)	Final Arsenic Treatment (ppb)
Deionized	0.1	2	1 to 10	100	12
Deionized	0.2	2	1 to 10	100	6
Deionized	0.5	2	1 to 10	100	1
NSF Challenge Water	0.2	2	1 to 10	100	14
NSF Challenge Water	0.5	2	1 to 10	100	8

Stabilization of $Mg(OH)_2$ against reaction with CO_3^{2-}

As previously stated, a major problem in using $Mg(OH)_2$ is the reaction of $Mg(OH)_2$ with carbonate in water to form $MgCO_3$ that decreases the efficiency of the process. In order to stabilize the $Mg(OH)_2$ against reaction with carbonate we have stabilized the $Mg(OH)_2$ in the form of a Sorrel's cement. Sorrel's cements are composed of MgO and $MgCl_2$. When mixed with water the MgO reacts with the water converting to $Mg(OH)_2$ in a polymerized form when $MgCl_2$ is present. This produces a hard, more stable form of $Mg(OH)_2$ (Figure 4). Other compounds can be added to the mixture to change the physical and chemical properties of the Sorrel's cement. In this work we have identified $FeCl_3$ and SiO_2 as two compounds that can be mixed with Sorrel's cement to produce a sorbent for arsenic that is much more resistant to reaction with carbonate than $Mg(OH)_2$ but still strongly sorbes arsenic. Table 4 gives results for arsenic sorption using 1 g of sorbent per liter of solution. With a reaction time of 5 minutes, the doped Sorrel's cements performed almost as well as $Mg(OH)_2$. However, in the presence of carbonate the Sorrel's cements perform much better than $Mg(OH)_2$ (Table 5). With carbonate concentrations between 200 to 700 ppm the Sorrel's cements sorb a order-of-magnitude more than $Mg(OH)_2$. Of the types of doped Sorrel's cements tested, the $FeCl_3$ doped Sorrel's cement proved to be the best material. Although the SiO_2 doped material was just as effective in removing arsenic it was much more soluble in water.

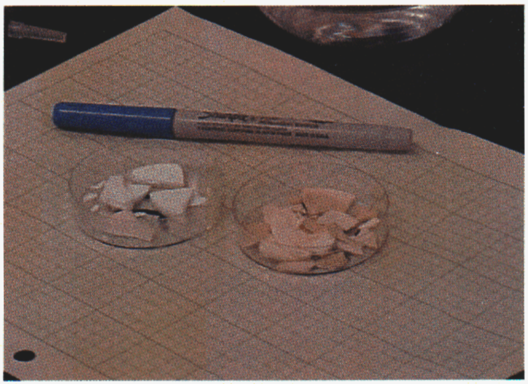

Figure 4. Sorrel's cement prepared from MgO and $MgCl_2$ (l) and MgO/$MgCl_2$ mixed with $FeCl_3$ (r).

Table 4. Removal of arsenic using MgO, MgO + CaO, and Sorrel's cement doped with $FeCl_3$ and SiO_2.

Sorbent	[As V] initial, ppb	[As V] final, ppb
MgO (1g/L)	200	0.7
Sorrel's cement type F5* + $FeCl_3$ (1 g/L)	200	4.5
Sorrel's cement type F5* + SiO_2 (1 g/L)	200	3.2

*Sorrel's cement type F5 (4g of MgO + 4g of $MgCl_2$ + 20mL water)

Table 5. Effect of carbonate concentration on removal of arsenic by MgO and Sorrel's cement. 1 g of sorbent per L of solution. Reaction time was 15 minutes.

Sorbent	CO_3^{-2}, ppm	[As(V)] initial (ppb)	[As(V)] final (ppb)
MgO	700	200	101
MgO	500	200	92.5
MgO	300	200	102
MgO	200	200	100
Sorrel's cement F5 + $FeCl_3$	700	200	8.9
Sorrel's cement F5 + $FeCl_3$	500	200	8.3
Sorrel's cement F5+ $FeCl_3$	300	200	<1
Sorrel's cement F5+ $FeCl_3$	200	200	<1

Because of its effectiveness, resistance to carbonate attack, and stability in water, the $FeCl_3$ doped Sorrel's cement was further investigated. Kinetic and equilibrium experiments were performed. Kinetic experiments indicate the material can be used to significantly reduce arsenic concentrations (Figure 5). Using 0.5 g per liter of 550 ppb arsenic and 200 ppm carbonate, arsenic concentrations were decreased to approximately 150 ppb in 10 minutes of contact time. Values of equilibrium constants, K_d, are given in Table 6 and range from 631 to over 35,000. Although these values are not as high as $Mg(OH)_2$, they indicate the $FeCl_3$ doped Sorrel's cements are very strong sorbents for arsenic. Additionally, the materials to manufacture the Sorrel's cements are very inexpensive and do not require a large energy input (i.e. heating). A plot of final arsenic concentration versus $1/K_d$ is given in Figure 6. The plot is similar to the one for arsenic sorption to $Mg(OH)_2$. As with $Mg(OH)_2$, the data can not be modeled using any conventional isothermal model for sorption.

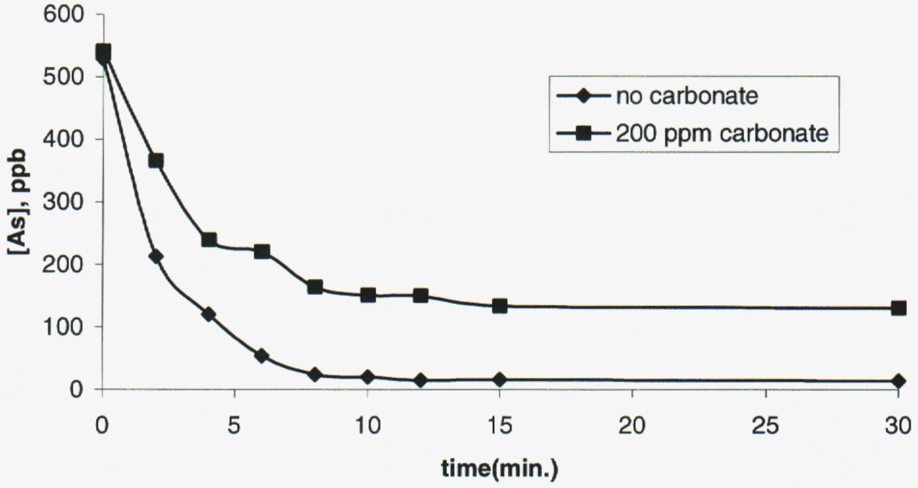

Figure 5. Kinetics of arsenic (V) sorption using Sorrel's cement doped with $FeCl_3$. 0.5 g or sorbent per liter of solution.

Table 6. Equilibrium constant for Sorrel's cement sorption of arsenic(V). 1.0 g of F5 Sorrel's cement doped with $FeCl_3$ in 1 liter of water.

[As] initial (ppb)	[As] final (ppb)	K_d (L/mole)
200	2	35145
300	3.3	35100
500	8.7	19400
700	9.6	24495
1000	14	25002
5000	78	22401
10000	516	6524
20000	880	4250
40000	1160	870
50000	2200	631

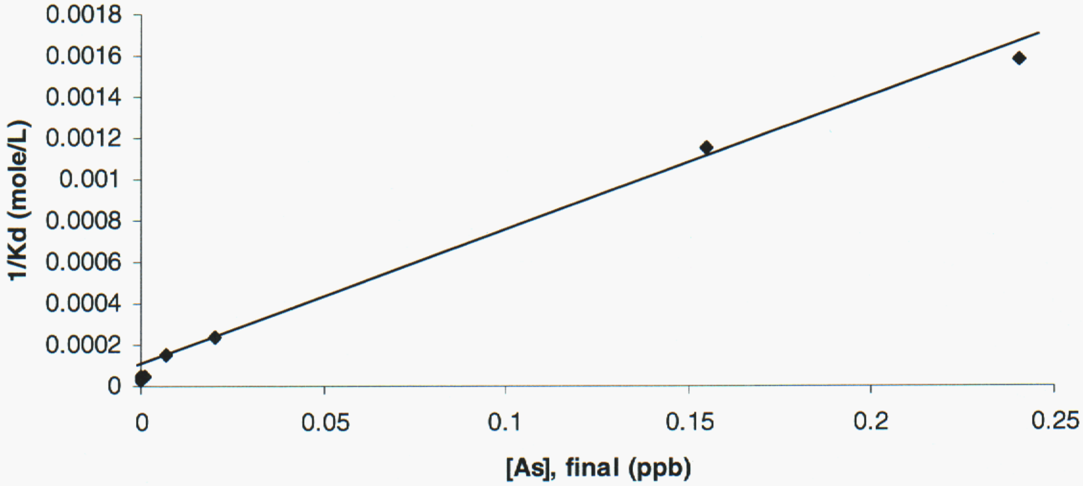

Figure 6. Plot of 1/K_d vs. final arsenic concentration in solution for $FeCl_3$ doped Sorrel's cement. y-intercept = 0.00008, slope = 0.07

Chromium Sorption

In addition to sorption of arsenic, Sorrel's cement is also a strong sorbent for chromium. In batch tests with 0.5 g of Sorrel's cement in 500 mL of water containing 500 or 1000 ppb chromium concentrations decreased to 17 and 36 ppb respectively in 15 minutes time (Table 7).

Table 7. Sorption of chromium onto Sorrel's cement in water. 0.5 g of Sorrel's cement in 500 mL of Cr solution.

Adsorbent	[Cr] initial concentration (ppb)	[Cr] final concentration (ppb)
Sorrel's cement	500	17
Sorrel's cement	1000	36

Zr-Doped Clays and Activated Carbon as Effective Adsorbents for Trapping Trace Arsenic in Drinking Water

Rare earth elements have been found to have a high affinity for fluoride, phosphate, and other weaker conjugate acids such as arsenic and selenium. Due to their high affinity for these elements, rare earths have been used as solution modifiers, pre-concentrators, and furnace coatings for As, Se and Hg for analysis by atomic absorption spectroscopy (AA). Zirconium-doped materials were synthesized using zeolite, montmorillonite and activated carbon and tested for their ability to remove trace amounts of arsenic from water (Table 8). A single column experiment has been performed to date using zirconium doped zeolite (Table 9). The results indicate the material can rapidly reduce arsenic concentrations from high levels of 100 ppb to less than 1 ppb with a residence time of only 45 seconds. Additionally, the cost of zirconium doped zeolite is very low. A pound of the material can be produced for approximately $0.70 (Table 10).

Table 8. Preliminary results using zirconium doped materials to sorb arsenic from water

Matrix per 250 mL	Adsorbent	Amount	Initial [As] (ppb)	Final [As] (ppb)
Tap Water + As(V)	Zr-Coarse AC	5 g	206	11.5
Tap Water + As(III)	Zr-Coarse AC	5 g	193	11.5
Tap Water + As(V)	Untreated AC	5 g	193	194
Challenge Water + As(V)	Zr-Coarse AC	5 g	185	4.6
Challenge Water + As(III)	Zr-Coarse AC	5 g	182	5.3
Challenge Water + As(V)	Zr-Fine AC	0.5 g	185	9.3
DW + As(V)	Zr-zeolite	5 g	200	1.7
Challenge Water + As(V)	Zr-zeolite	5 g	185	7.8
Challenge Water + As(V)	Untreated zeolite	5 g	185	182

DW=deionized water; AC=activated carbon

Table 9. Column study using zirconium doped zeolite to remove arsenic from water. Residence time was 45 seconds in a column 6 inches long by 1/2 inch I.D.

Adsorbent	Amount / 250 mL Water	Initial [As] (ppb)	Final [As] (ppb)
Zr-zeolite	17.6 cm x 0.7 cm	100	0.24

Table 10. Cost of zirconium doped zeolite for arsenic sorption

Reagent	Cost
Zeolite (New Mexico)	$0.02/lb
ZrOCl2	$0.70/lb if purchased in bulk
Total cost	Approx. $0.10/lb

The results from arsenic sorption experiments for arsenic in its various forms sorbed to Zr doped montmorillonite in simulated groundwater are given in Table 11. Initial arsenic concentrations below 500 ppb are reduced well below the new EPA limit of 10 ppb. For activated carbon more sorbent was required to remove the same amount of arsenic than for the Zr doped montmorillonite

Table 11. Sorption of Arsenite, Arsenate and Organoarsenic by Zr-Montmorillonite. 50 mg Zr-montmorillonite in 25 mL simulated ground water. Numbers in parentheses are sorption using 50 mg calcined Zr-montmorillonite.

Initial As (ppb)	Final As Concentration (ppb)		
	As (V)	As(IV)	Organoarsenic
100	0.92		
250	1.7		
500	5.4		
1000	19.2	38	160
2000	30.1 (180a)	101 (320)	420
5000	52.0 (1310)	380 (990)	1560
10000	125	1050	3970

Table 12. Preliminary Sorption Study of Arsenite/Arsenate by Zr-tailored Activated Carbon from Simulated Groundwater

Adsorbent	Amount	Initial [As] (ppb)	Final [As] (ppb)
Zr-Coarse AC	5 g	185 As(V)	4.6
Zr-Coarse AC	5 g	182 As(III)	5.3
Zr-Fine AC	0.5 g	185 As(V)	9.3

Figure 7 gives the results for a kinetic study of arsenic sorption to Zr-tailored materials. Both As(III) and As(V) were sorbed in the study and completely removed in 60 minutes. Figure 8 is the sorption isotherm of arsenate and arsenite by Zr-zeolite from simulated groundwater.

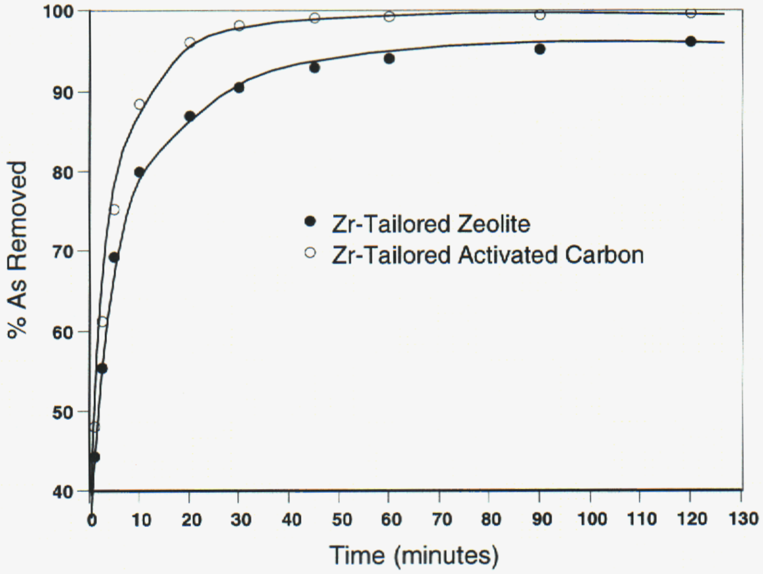

Figure 7. As(III)/As(V) Sorption Kinetics by Zr-tailored materials. The kinetic study was carried out using 10 g Zr-zeolite in 400 mL simulated groundwater.

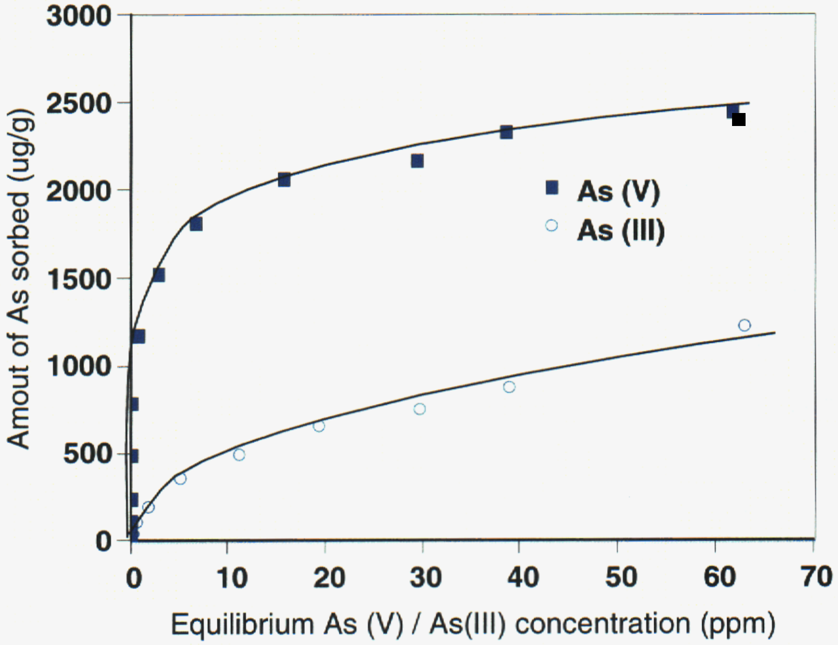

Figure 8. Sorption isotherm of arsenate and arsenite by Zr-zeolite from simulated ground water.

The effect of ions that could interfere with the sorption of arsenic to Zr doped zeolites is given graphically in Figure 9. As seen in the figure, only phosphate is a significant competitor for sorption. However, typically groundwater contains only a trace amount of phosphate. Figure 10 and 11 are plots of arsenic concentration in the effluent of column experiments for by Zr-activated carbon and Zr-tailored zeolite respectively. As seen in Figure 11, more than 1500 pore volumes passed through the column with no breakthrough. The experiments had to be terminated because of equipment failure at this point.

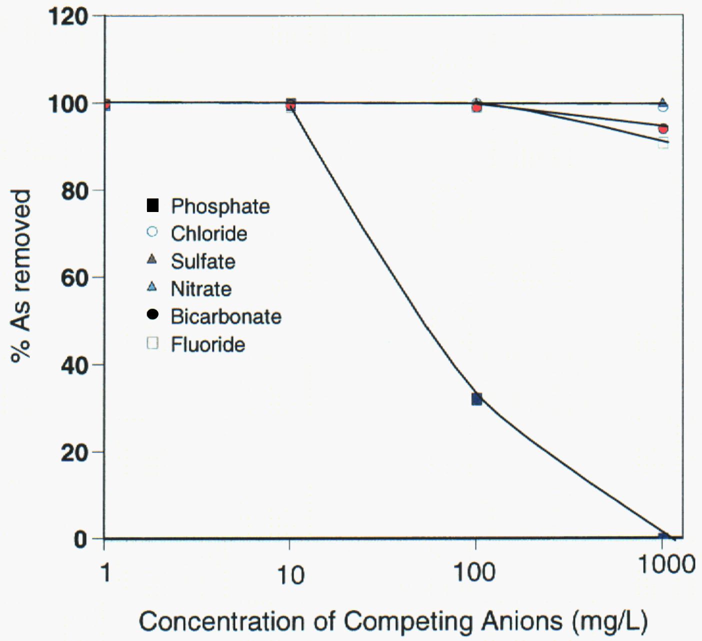

Figure 9. Effect of Various Anions on As(V) Sorption by Zr-Tailored Zeolite. 500 mg Zr-zeolite in 25 mL deionized water containing 1.0 mg/L arsenate.

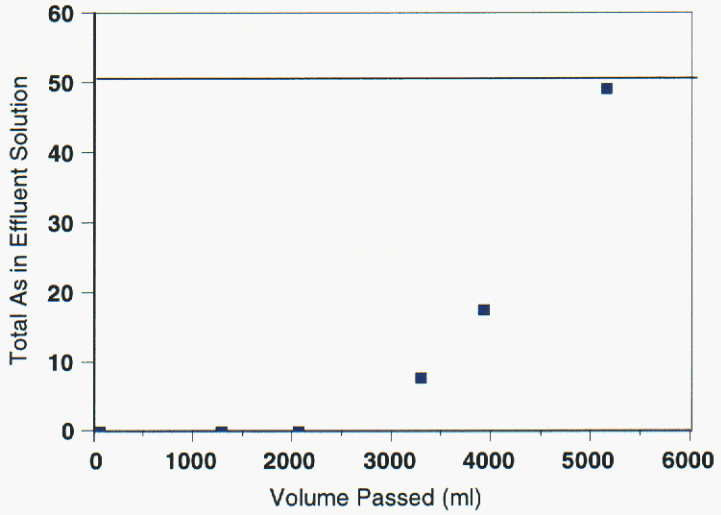

Figure 10. Column Study of As(V)/As(III) removal using Zr-Activated Carbon. Initial As(III)=25ppb; As(V)=25 ppb in simulated ground water. Flow rate=0.08 mL/min. Column length=12.5 cm. Column diameter=1.5 cm. Zr-AC mass=10.5 g.

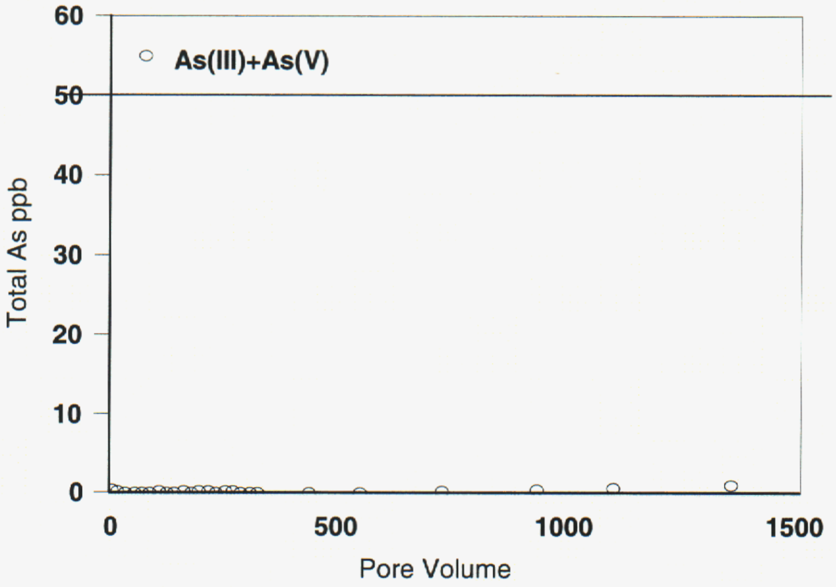

Figure 11. Column Study of As(III)/As(V) removal by Zr-Tailored Zeolite. After 40 L of solutions passed through the column breakthrough still had not occurred. Initial As(III) = 25 ppb; As(V) = 25 ppb in simulated ground water. Flow rate = 0.8 mL/min. Column length = 12.5 cm. Column diameter = 1.5 cm. Zr-zeolite mass = 20.5 g.

UV Colorimetric Quantification of ppb Levels of Arsenic in Water

After testing the colorimetric method, the method was used to determine the concentration of arsenic in Albuquerque tap water, which was compared to results from ICP-MS analysis (Table 13). The results indicate the method is highly accurate for quantification of arsenic. However, much more work is needed including a test for compounds that could interfere with the method.

Table 13. Comparison of ICP-MS results and colorimetric method for quantification of arsenic in water.

Water	ICP-MS analysis (ppb)	Colorimetric method (ppb)
Albuquerque tap water	13	14
Albuquerque tap water + 20 ppb arsenic	35	30
Albuquerque tap water + 50 ppb arsenic	65	68

Conclusions

The results from this work indicate both $Mg(OH)_2$ and zirconium doped clays, minerals, and activated carbon will strongly sorb arsenic. For $Mg(OH)_2$, the material is best used in the form of Sorrel's cement to prevent reaction with carbonate to form non-arsenic sorbing $MgCO_3$. The use of $Mg(OH)_2$ or Sorrel's cement is best suited to operations where the sorbent is contacted with arsenic containing water and then removed from the system before excessive reaction with carbonate can occur.

Zirconium doped materials have a very high capacity for arsenic sorption and do not suffer from the drawbacks of $Mg(OH)_2$ or Sorrel's cement. The zirconium doped materials do not effect water pH or add any additional species to the water. The only significant interfering species is phosphate that is typically not present in groundwater to any appreciable extent. A significant advantage of zirconium doped materials is cost. The raw materials necessary to produce zirconium doped materials are very inexpensive. Lastly, zirconium is environmentally benign and poses no health hazards and is easily disposed in a municipal landfill.

The adaptation of a colorimetric technique for quantification of As(III) along with the use of stannous chloride as an arsenic reducing agent was successful at quantifying arsenic in drinking water to the 14 ppb level. Further investigation of this method is needed before it can be properly applied.

References

Samanta,G., Chakraborti, D. Fresenius (1997*) J. Anal. Chim.* 357, pp. 827

Ybanez, N., Cervera, M. L., Montro, R. (1992) *Anal.Chim Acta* 258, pp.61

Narro, M., Lopez, H.., Lopez, M.C. Sanchez, M. (1992) *J.Anal.Toxicol.* 16 pp.169

Samanta, G., Chatterrjce, A.., Das, D., Chowdhury, P. Chanda, C. R., Chakraborti, D. (1995) *Environmental Technology* 16, pp.223

Das, D., Chatterjee, A., Samanta, G., Chakraborti, D., (1992) *Chem. Environ. Res.* 1(3) pp.279

Zmijeska, W. J. (1977) *Radional.Chem.* 35 pp. 389.

Shull, M., Winefordner , (1984) *J.D. Anal.Chem.* 56 pp. 2617.

Madride,Y., Chakraborti, D.; Camara, *C. Microchimica Acta* 1995,120,63.

Patterson, J.W. (1985) Industrial Wastewater Treatment Technology, Butterworth Publishers. pp.11-21.

Agrawal, Omi , Sunita,G and Gupta,V.K. (1999) *Journal of the Chinese Chemical Society*, 46, 641-645

Gupta, S.K. and Chen, K.Y. (1978). *Journal Water Pollution Control Federation*, 50(3),4930-506.

American Water Works Association Committee (1985). An AWWA survey of inorganic contaminates in water supplies. *Journal American Water Works Association*, 77(5), 67-72.

Reese Jr ,R.G., Geol. Surv., U.S., Miner. Commodity Summ, (1998) 23.

Loebenstein J.R., Proceedings, Workshop on Removal, Recovery, Treatment and Disposal of Arsenic and Mercury, USEPA Report EPA / 600/R-92? 105, 1992, pp.8-9.

Hering J., Chen P., Wilkie J., Elimelch M., and Liang J., *J. Am. Water Works* 88 (1996) 155.

Cliffored, D., G. Ghurye and A. Tripp (1998). " Arsenic removal by Ion Exchange with and without Brine Reuse," AWWA Inorganic Contaminates Workshop, San Antonio, TX, February 23-24, 1998.

Cliffored, D., G. Ghurye and A. Tripp (1998) Final Report: Phase 3 City of Albuquerque Arsenic Study Field Studies on Arsenic Removal in Albuqurque, New Mexico using the University of Houston / EPA Mobile Drinking Water Treatment Research Facility. Houston, TX: University of Houston, August 1998.

EPA (1994). Review of the Draft Drinking Water Criteria Document on Inorganic Arsenic , EPA SAB-DWC-94-004.

Agrawal, Omi , Sunita,G and Gupta,V.K. " *Journal of AOAC International* " vol.18, No. 4, 1998

BermejoBarrera P, MoredaPineiro J, MoredaPineiro A. .BermejoBarrera *Fresenius Journal Of Analytical Chemistry* 355(#2):174-179, 1996.

Burch R and C.I. Warburton (1986) *Journal Of Catalysis*. 97(2) pp.503-510

Chen YL, Qi WQ, Cao JS, Chang MS. *Journal Of Analytical Atomic Spectrometry* 8(#2):379-381, 1993.

Farfantorres Em, Sham E, Grange P. *Catalysis Today* 15(#3-4):515-526, 1992

Gandia LM, Toranzo R, Vicente MA, Gil *Applied Catalysis A-General.* 183(#1):23-33, 1999.

Gandia LM, Vicente MA, Gil A. *Applied Catalysis A-General* 196(#2): 281-292, 2000.

Garbos S, Walcerz M, Bulska E, Hulanicki. *Spectrochimica Acta Part B-Atomic Spectroscopy* 50(#13):1669-1677, 1995.

Gil A, Vicente MA, Gandia LM *Microporous and Mesoporous Materials* 34(#1):115-125, 2000.

Jiang JQ. *Water Science And Technology* 44(#6):89-98, 2001.

MieheBrendle J, Khouchaf L, Baron J, LeDred R, Tuilier MH *Microporous Materials* 11(#3-4): 171-183, 1997.

Peraniemi S, Ahlgren M. *Analytica Chimica Acta* 302(#1): 89-95, 1995.

Peraniemi S, Hannonen S, Mustalahti H, Ahlgren M. *Fresenius Journal Of Analytical Chemistry* V. 349(#7): 510-515. 1994.

Pereira PR, Pires J, de Carvalho MB. *Separation and Purification Technology* 21(#3): 237-246, 2001.

Pereira PR, Pires J, deCarvalho MB. *Langmuir,* 14(#16): 4584-4588, 1998.

Pires J, Carvalho A, de Carvalho MB *Microporous And Mesoporous Materials* 43(#3):277-287, 2001.

Suzuki TM, Bomani JO, Matsunaga H, Yokoyama T *Reactive & Functional Polymers* 43(#1-2):165-172, 2000

Toranzo R, Vicente MA, BanaresMunoz MA, Gandia LM, Gil. M*icroporous and Mesoporous Materials* 24(#4-6): 173-188, 1998

Viraraghavan T, Subramanian KS, Aruldoss JA. *Water Science And Technology* 40(#2): 69-76, 1999,

Volzone C, Hipedinger NE Influence of hydrolyzed zirconium solutions on the OH-Zr-montmorillonite. *Clays And Clay Minerals* 47(#1):109-111,1999.

Yamanaka, S., Brindley GW. High Surface-area solids obtained by reaction of montmorillonite with zirconyl Chloride. *Clays And Clay Minerals* 27(#2):119-124 1979

You YW, Zhao HT, Vance GF. Removal of arsenite from aqueous solutions by anionic clays. *Environmental Technology.* 22(#12):1447-1457, 2001.