

Report as of FY2007 for 2006WV69B: "Evaluation of the Environmental Hazard of Selenium in Coal-Associated Rocks of the Southern WV Coal Basin (WRI-83)"

Publications

- Other Publications:
 - PUBLICATIONS 1. I. Pumure, J.J. Renton, and R.B. Smart, Accelerated aqueous leaching and speciation of selenium and arsenic from coal-associated rock samples using ultrasound extraction, Environmental Geology, submitted for publication, June, 2007. STUDENT SUPPORT Mr. Innocent Pumure, Ph.D. Candidate, West Virginia University, Department of Chemistry, \$4000, Summer, 2006.

Report Follows

Title: Evaluation of the Environmental Hazard of Selenium in Coal-Associated Rocks of the Southern WV Coal Basin

Annual Report: March 1, 2006 - February 28, 2007

Principal Authors: Dr. Ronald B. Smart and Dr. John J. Renton

Report Issued: May 31, 2007

USGS Award No. WRI-83

Submitting Departments: Department of Chemistry, West Virginia University, PO Box 6045
Department of Geology and Geography, West Virginia University, PO Box 6300

ABSTRACT

Mountaintop removal-valley fill coal mining involves the removal of the mountain top and the filling of nearby valleys with overburden to result in a level surface that can be used for a variety of purposes. According to a USEPA report, (Bryant et al. 2002) selenium concentrations in several streams and rivers associated with mountaintop removal-valley fill mining areas in southern West Virginia were found to contain up to 50 ng /L , a concentration that is ten times the West Virginia stream standard (5 ng /L). Pre-mining data indicated that the valley fills were responsible for the elevated selenium levels.

Our study focused on comparative ultrasound-assisted kinetics of the leaching of selenium and arsenic from pulverized samples of rock that are associated with coal mining activities. Most traditional batch extraction methods utilize lengthy mechanical shaking or soxhlet extractions that may take hours or days for a single extraction to be performed. For the ultrasound method, a five-minute application of ultrasound energy to a pulverized rock sample mixture in a 1:10 solid to solution ratio was found to produce useful results for a single extraction. The rock samples were collected from a core supplied by the West Virginia Geological and Economic Survey (WVGES). The samples were collected from Kayford Mountain in Kanawha County, West Virginia (USA).

The amount of arsenic extracted with ultrasound was three orders of magnitude greater than the selenium. No arsenic was previously detected in the stream waters (Bryant et al. 2002), even though the accelerated rate constants appeared to be ten times greater than those for selenium (Table 4), which suggests that arsenic is sequestered from the aqueous phase by a different mechanism compared to selenium. The rate of release of total arsenic and total selenium did not depend on their respective concentrations in rocks but rather on the type of rocks analyzed.

The reactivity and toxicity of arsenic and selenium depend on their oxidation states. The primary arsenic species found in the environment are inorganic As (III), arsenite, and As (V), arsenate, as well as several organoarsenic compounds. Selenium species include Se (IV), selenite, and Se (VI), selenate, Se (0) and Se (-II), as well as several organic forms. The most toxic species are Se (IV) and As(III), and Se (VI) and As (III) are more bioavailable compared to the other oxidation states. Sequential extractions of BT700 indicated that most of the extractable is Se (IV) whereas in BT571 the predominant extractable form is Se (VI).

TABLE OF CONTENTS

	Page No.
Title Page	1
Abstract	2
Introduction	4
Methods and Materials	6
Results and Discussion	8
Conclusions	12
References	14

Introduction

Temperature controlled ultrasound extractions provide important kinetic data that can be useful in describing the chemistry at the solid-solution interface. The solid – solution chemistry can then be used to infer the bioavailabilities of metals released into associated aquatic systems. Most traditional batch extraction methods utilize lengthy mechanical shaking or soxhlet extractions that may take hours or days for a single extraction to be performed. For the ultrasound method, a five-minute application of ultrasound energy to a pulverized rock sample mixture in a 1:10 solid to solution ratio was found to produce useful results for a single extraction. Ultrasonic extraction enhances dissolution process by causing acoustic cavitations that result in bubble formation and subsequent collapse generating high-pressure gradients, thereby increasing reactivities (Brunori et al. 2004; Suslick 1989).

The use of ultrasonic energy has been proven to be an easy, convenient, and fast way of desorbing inorganic (Luque-Garcia and de Castro 2003; Perez-Cid and Bola 2001; Perez-Cid et al. 1999) and organic pollutants (Tse and Lo 2002) from sediments, soil and biological samples (Arruda et al. 2003; Mierzwa et al. 1997). Focused ultrasonic probes enable efficient adjustment and monitoring of temperature in a water-jacketed extraction vessel and this methodology was used in this study to study the kinetic releases of arsenic and selenium from pulverized samples of rocks associated with coal mining activities. Since natural rock dissolution is a lengthy process (Sparks 1989), ultrasound extraction was used to mimic the natural weathering of coal associated rocks on a much shorter time scale.

Mountaintop removal-valley fill coal mining involves the removal of the mountain top and the filling of nearby valleys with overburden to result in a level surface that can be used for a variety of purposes. According to a USEPA report, (Bryant et al. 2002) selenium concentrations in several streams and rivers associated with mountaintop removal-valley fill mining areas in southern West Virginia were found to contain up to 50 ng /L , a concentration that is ten times the West Virginia stream standard (5 ng /L). Pre-mining data indicated that the valley fills were responsible for the elevated selenium levels.

Although low concentrations of selenium and arsenic are dietary essentials, higher concentrations pose a serious health risk to terrestrial and aquatic organisms (Jukes 1983; Yih et al. 2005). Elevated concentrations of these metalloids have also been shown to stunt the growth of some plants (Lejeune et al. 1996; Terry et al. 2000) which could inhibit a critical process required in the remediation of filled sites.

Our study focused on comparative ultrasound-assisted kinetics of the leaching of selenium and arsenic from pulverized samples of rock that are associated with coal mining activities. The most common models used to describe the kinetics for the release of inorganic and organic substances from solids into solution are parabolic diffusion, Elovich, power function and first and second order kinetic models. (Aharoni et al. 1991; Goh and Lim 2004; Kithome et al. 1998; Shimizu et al. 2004). These models are often used to approximate the overall chemical kinetics of intricate reactions occurring in complex matrices that are often unknown. Although the first order and parabolic diffusion models are both very important in describing the surface film diffusion or intraparticle diffusion of materials from rocks into solution (Sparks 1989), the first order

kinetic model was found to be most useful in comparing the rates of accelerated rock disintegration and the concomitant release of arsenic and selenium from coal-associated rocks. Thus, the ultrasound assisted extraction rate is proportional to the following parameters: 1) the mobility of the selenium and arsenic compounds from the solid to liquid phase, 2) the chemical potential of these species, 3) lithology of rocks extracted, 4) the surface area of particles, and 5) the level of ultrasonication power.

Methods and materials

An Ultrasonic Sonicator (Misonix, Model XL 2020) with a 0.3 mm diameter titanium probe was used to deliver sound energy (200 W/cm^2) to a mixture of 1g of pulverized sample and 10 mL water. A 38-ml capacity water-jacketed extraction vessel (22mm ID x 10 cm quartz tube) was designed. The ultrasonic power was measured by calorimetry (Contamine et al. 1995; Mason et al. 1992). A thermocouple was immersed into the extraction solution to monitor the temperatures during extraction and ultrasound energy measurement processes. The water/pulverized rock mixture was ultrasonicated for a period of five minutes followed by centrifugation for 20 minutes at 3400g. The supernatant solution was decanted and placed in a 25-mL polyethylene vial. The solid residue was returned back to the sonication vessel followed by the addition of a fresh 10-mL aliquot of water for the second ultrasonication step. The process was repeated seventeen times for a total 90 minutes of sequential extraction. Each extract was analyzed for total selenium and arsenic by graphite furnace atomic absorption spectrophotometry and Se (IV) and As (III) were measured by hydride generation atomic spectrophotometry. A Varian atomic absorption spectrometer (Model 55B) was used to analyze all the samples.

The total arsenic and selenium concentrations in the unextracted rocks were determined after microwave digestion. Each of the three samples (0.5g) were digested in triplicate using 5 ml concentrated HNO₃ , 5 ml concentrated HF and 3 mL concentrated HCl in a microwave oven (CEM Corporation MARS-5- Explorer version 194A04) followed by analysis of digests using graphite furnace atomic absorption spectrophotometry.

Sampling

The rock samples were collected from a core supplied by the West Virginia Geological and Economic Survey (WVGES). The samples were collected from Kayford Mountain in Kanawha County, West Virginia (USA). The core was obtained by drilling from the mountaintop down to 270 m below the surface. Three samples (BT60, BT571 and BT700) were analysed. These samples were collected at depths of 18 meters (BT60), 174 meters (BT571) and 214 meters (BT700), respectively. Each sample was subdivided lengthwise, pulverized and passed through a 60 mesh sieve. The sieved rock powders were then subjected to ultrasonic extraction.

Mineralogical examination of pulverized rocks

Lithologic analyses of the rocks were performed by analysts at WVGES. The results obtained indicated that BT60 was sandstone, while BT571 and BT700 were claystones. Sample BT60 was comprised of 81% SiO₂ , most of which was present as quartz as shown in Tables 1 and 2. Samples BT571 and BT700 had 62.25 % and 63.83 % SiO₂ of which about half of BT571 and about a third of BT700 was quartz. The two claystone samples had about six times the percentage of illite as that in BT60. There were

no significant differences in kaolin composition in the three samples as indicated in Table 1. The Fe_2O_3 and % chlorite compositions in BT60 were below 0.01% as shown in Tables 1 and 2.

Results and discussion

Comparison of extraction methods

Most kinetic batch extraction experiments reported in the literature are carried out at aqueous concentrations that are higher than those found in natural environments. In these studies pure solids (e.g. kaolin, silica, illite, iron oxides) are equilibrated with organic or inorganic substances of interest to allow them to adsorb onto the solid surfaces prior to performing desorption experiments. Because ionic concentrations used in such adsorption and desorption experiments are too high, kinetic studies are limited due to equilibrium conditions that are quickly established during the onset of extractions (Skopp 1986). The reason most workers in this area prefer to use continuous flow methods is that there is no flow back or re-adsorption of the materials that had been released earlier into the solution (Barry et al. 1993; Huertas et al. 1999; 2002). The initial extractions in kinetic batch experiments are known to release most of the metals being extracted, therefore during the first extraction, there is a greater chance of establishing equilibrium between the adsorbed and free metals in solution. Thus, concentrations so obtained cannot be used to describe the kinetics of extraction but rather only provide equilibrium conditions (Sabbah et al. 2005). Such conditions prompted the use of temperature-jump experiments (Zhang and Sparks 1990) to study the adsorption and desorption kinetics of selenate and selenite at the goethite surface.

In order to establish that equilibrium was not reached during the first 5 minutes of ultrasonic extraction, results for 120 minutes of continuous sonication were compared with those obtained from the initial 5 minutes of sonication of a 90-minute sequential extraction experiment consisting of 5 minute ultrasonics. The concentrations of total arsenic and selenium obtained by different extraction methods and microwave digestions are summarized in Table 3.

Although there was a large initial increase for both the arsenic and selenium concentration obtained during the first five minutes of the 90-minute sequential extraction, there is a statistically significant difference in the values obtained after first 5 minutes of the 90 minute sequential extraction to the Se concentration that was extracted after 120 minutes of continuous sonication ($P \leq 0.11$, $n = 9^*$). Based on this, it can be concluded that the concentration of both metals in solution obtained after five minutes would not have reached equilibrium with arsenic and selenium still encapsulated, sorbed or remaining within the pulverized rock particles.

There is an apparent three orders of magnitude (ng/g vs. $\mu\text{g/g}$) difference between the Se and As concentrations extracted from the rock samples. The values obtained after 2 hours of continuous sonication were smaller than the values obtained by the 90-minute sequential sonication. These data indicate equilibration and/or reabsorption could have been established during the course of the 2-hour extraction. In order to promote the non-equilibrium conditions needed for kinetic studies it was found necessary to use the sequential extraction method. Thus the observed non-equilibrium conditions at 5 minutes of ultrasonication time could be described in terms of a slow reabsorption process of the released metals compared to a faster desorption rate at 200W/cm^2 of ultrasonication

power. These extraction conditions were used to simulate the accelerated kinetic release of selenium and arsenic from valley fills into streams.

The amount of arsenic extracted with ultrasound was three orders of magnitude greater than the selenium as shown in Figures 2 and 3. No arsenic was previously detected in the stream waters (Bryant et al. 2002), even though the accelerated rate constants appeared to be ten times greater than those for selenium (Table 4), which suggests that arsenic is sequestered from the aqueous phase by a different mechanism compared to selenium.

Sample BT60 was found to have the lowest concentrations of arsenic and selenium compared to BT571 and BT700 as shown in Table 1. Although BT700 had the highest total and extractable arsenic and selenium species, the rates of their releases from the solid into the solution were smaller than those of BT571 and BT60 as shown in Table 4.

The rate of release of total arsenic and total selenium did not depend on their respective concentrations in rocks but rather on the type of rocks analysed. Sample BT60, a sandstone had the lowest amounts of selenium yet it was all extracted during the first three extractions. Jenkins and Schaer (2005) found that darker overburden with large amounts of humic and fulvic substances had the highest selenium concentrations. These observations were consistent with our findings in that the claystones (BT700 and BT571) were dark in appearance and had the highest amounts of selenium and arsenic (Table 3).

Organic acids which originate from dead plants are often incorporated into rock lattices during rock formation. Any selenium that is bound to organic acids will become part of the rock and some of this sorbed selenium can become bioavailable as the rocks

weather (Liu et al. 2006). In the rocks analysed, it appears there are two forms of organic bound selenium, with one weakly sorbed and the other strongly sorbed. The weakly sorbed forms are readily available and the strongly sorbed take more time and energy to become bioavailable. This information could explain the fact that samples BT571 and BT700 had more selenium which was not readily leachable compared to BT60.

Peak and Sparks (2002) found that selenate and selenites both bind strongly to iron oxides and this could be the reason the selenium in BT60 was easily extracted compared to BT571 and BT700 (Table 2). Such kinetic information is useful in determining procedures that are necessary to be undertaken when disposing different types of mining waste. Another complication is that the toxicity and bioavailability of the released metalloids depend on chemical speciation which suggests the need to differentiate the selenium and arsenic compounds released.

The reactivity and toxicity of arsenic and selenium depend on their oxidation states. The primary arsenic species found in the environment are inorganic As (III), arsenite, and As (V), arsenate, as well as several organoarsenic compounds. Selenium species include Se (IV), selenite, and Se (VI), selenate, Se (0) and Se (-II), as well as several organic forms. The most toxic species are Se (IV) and As(III), and Se (VI) and As (III) are more bioavailable compared to the other oxidation states.

Effects of ultrasonic power on the speciation studies for Se (IV)/ Se (VI) and As (III)/As (V)

In order to determine the effects of ultrasonic power on the stability of arsenic and selenium, 10 ml of 5 ng/mL solutions of As (III)/As (V) and Se (IV)/Se (VI) in a 1:1 ratio were separately monitored as a function of ultrasonication time using 200W/cm² power

intensity. A fresh 10-ml solution of 5 ng/L arsenic /selenium was sonicated for each of the following sonication times (5 min, 10 min, 15 min ... up to 2 hours). All experiments were done in triplicates. As illustrated in Figure 4, As (III) concentration decreased by 70% after only five minutes of sonication followed by a slow decrease to reach values that are 96 % lower than the initial concentration within a period of two hours. Solutions containing 1:1 mixtures of 5, 10 and 15 ng/mL of As (III) and As (V) also showed similar trends. Hence, ultrasonication extraction cannot be applied for the speciation studies of As in rocks. Analysis of the total arsenic in the ultrasonicated solutions revealed no arsenic losses due to evaporation.

On the other hand Se (IV) concentration remained constant over the entire 120 minutes of continuous sonication. No significant changes in total selenium concentrations were observed after a two-hour continuous sonication of 5, 10 and 15 ng/mL of 1:1 Se (IV)-Se (VI) mixtures. Hence, Se (IV) solutions are not easily oxidized under the experimental conditions used.

Comparison of the extraction of Se (IV) and total Se in samples

Sequential extractions of BT700 indicated that most of the extractable is Se (IV) whereas in BT571 the predominant form is Se (VI), as shown in Figures 5 and 6. The Se (IV) concentration increased in the order $BT60 < BT571 < BT700$.

Conclusions

Ultrasound dissolution is a useful tool for the kinetic extraction of arsenic and selenium and the speciation of selenium from coal-associated rocks. The release of arsenic and selenium from coal-associated rocks depend both the type of rock and the

concentrations found in rocks. These metalloids are released at different rates indicating that they bound at different sites and by different mechanisms.

The extracted arsenic concentrations are 3 orders of magnitude higher than selenium concentrations, and the speciation of the extracted selenium is also dependent on the rock material. Additional work is currently in progress to determine the type of binding and the locations of arsenic and selenium in these coal-associated rocks as well as the fate of arsenic and selenium that has been leached from valley fills.

Acknowledgements

We wish to express our sincere gratitude to the following: 1) the WVGES for providing the pulverized coal-associated rock samples, Dr. Louis McDonald, WVU Department of Plant and Soil Sciences, for providing the opportunity to use the CEM microwave oven and for assistance in the preparation of this manuscript and, 3) the United States Geological Survey - State Water Resources Research Institute Program for providing financial assistance for this research.

References

- Aharoni C, Sparks DL, Levinson S, Ravina I. 1991. Kinetics of Soil Chemical-Reactions - Relationships between Empirical Equations and Diffusion-Models. *Soil Science Society of America Journal* 55(5):1307-1312.
- Alaejos MS, Romero CD. 1995. Analysis of Selenium in Body-Fluids - a Review. *Chemical Reviews* 95(1):227-257.
- Arruda SCC, Rodriguez APM, Arruda MAZ. 2003. Ultrasound-assisted extraction of Ca, K and Mg from in vitro citrus culture. *Journal of the Brazilian Chemical Society* 14(3):470-474.
- Barry DA, Parlange JY, Hensley PJ. 1993. Calculation of Kinetic Rate Constants from Steady-State Soil-Profile Concentration Measurements. *International Journal for Numerical and Analytical Methods in Geomechanics* 17(4):243-254.
- Brunori C, Ipolyi I, Macaluso L, Morabito R. 2004. Evaluation of an ultrasonic digestion procedure for total metal determination in sediment reference materials. *Analytica Chimica Acta* 510(1):101-107.
- Bryant G, McPhilliamy S, Childers H. 2002. A Survey of the water Quality of Streams in the Primary Region of Mountaintop /Valley Fill Coal Mining. WVGES.
- Contamine RF, Wilhelm AM, Berlan J, Delmas H. 1995. Power Measurement in Sonochemistry. *Ultrasonics Sonochemistry* 2(1):S43-S47.
- Goh KH, Lim TT. 2004. Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. *Chemosphere* 55(6):849-859.
- Gu BH, Schmitt J, Chen ZH, Liang LY, Mccarthy JF. 1994. Adsorption and Desorption of Natural Organic-Matter on Iron-Oxide - Mechanisms and Models. *Environmental Science & Technology* 28(1):38-46.
- Huertas FJ, Chou L, Wollast R. 1999. Mechanism of kaolinite dissolution at room temperature and pressure Part II: Kinetic study. *Geochimica Et Cosmochimica Acta* 63(19-20):3261-3275.
- Jenkins G, Schaer N. 2005. The occurrence of Selenium in the upper Kanawha formation of the pennsylvanian system in the Southern West Virginian Coals. WVDEP.
- Jukes TH. 1983. Selenium, an essential poison. *Journal of Applied Biochemistry* 5:233-234.
- Kithome M, Paul JW, Lavkulich LM, Bomke AA. 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Science Society of America Journal* 62(3):622-629.
- Lejeune K, Galbraith H, Lipton J, Kapustka LA. 1996. Effects of metals and arsenic on riparian communities in southwest Montana. *Ecotoxicology* 5(5):297-312.
- Ling YH, Jiang JD, Holland JF, Perez-Soler R. 2002. Arsenic trioxide produces polymerization of microtubules and mitotic arrest before apoptosis in human tumor cell lines. *Molecular Pharmacology* 62(3):529-538.
- Liu G, Zhang Y, Qi C, Zheng L, Chen Y, Peng Z. 2006. Comparative on Causes and Accumulation of Selenium in the Tree-rings Ambient High-selenium Coal Combustion Area from Yutangba, Hubei, China. *Environ Monit Assess.*
- Luque-Garcia JL, de Castro L. 2003. Ultrasound: a powerful tool for leaching. *Trac-Trends in Analytical Chemistry* 22(1):41-47.

- Mason TJ, Lorimer JP, Bates DM. 1992. Quantifying Sonochemistry - Casting Some Light on a Black Art. *Ultrasonics* 30(1):40-42.
- Mierzwa J, Adeloju SB, Dhindsa HS. 1997. Ultrasound accelerated solid-liquid extraction for the determination of selenium in biological samples by electrothermal atomization atomic absorption spectrometry. *Analytical Sciences* 13(2):189-193.
- Niu C, Yan H, Yu T, Sun HP, Liu JX, Li XS, Wu W, Zhang FQ, Chen Y, Zhou L and others. 1999. Studies on treatment of acute promyelocytic leukemia with arsenic trioxide: Remission induction, follow-up, and molecular monitoring in 11 newly diagnosed and 47 relapsed acute promyelocytic leukemia patients. *Blood* 94(10):3315-3324.
- Peak D, Sparks DL. 2002. Mechanisms of selenate adsorption on iron oxides and hydroxides. *Environmental Science & Technology* 36(7):1460-1466.
- Perez-Cid B, Bola C. 2001. Comparison between total determination and extractable heavy metals from river sediments using conventional and microwave accelerated leaching tests. *International Journal of Environmental Analytical Chemistry* 81(2):101-115.
- Perez-Cid B, Lavilla I, Bendicho C. 1999. Use of ultrasonic energy for shortening the sequential extraction of metals from river sediments. *International Journal of Environmental Analytical Chemistry* 73(2):79-92.
- Sabbah I, Ball WP, Young DF, Bouwer EJ. 2005. Misinterpretations in the modeling of contaminant desorption from environmental solids when equilibrium conditions are not fully understood. *Environmental Engineering Science* 22(3):350-366.
- Shimizu K, Hasegawa K, Nakamuro Y, Kodama T, Komarneni S. 2004. Alkaline earth cation exchange with novel Na-3-mica: kinetics and thermodynamic selectivities. *Journal of Materials Chemistry* 14(6):1031-1035.
- Skopp J. 1986. Analysis of Time-Dependent Chemical Processes in Soils. *Journal of Environmental Quality* 15(3):205-213.
- Sparks DL. 1989. *Kinetics of Soil Chemical Processes*: Academic press, San Diego, CA.
- Suslick KS. 1989. The Chemical Effects of Ultrasound. *Scientific American* 260(2):80-86.
- Terry N, Zayed AM, de Souza MP, Tarun AS. 2000. Selenium in higher plants. *Annual Review of Plant Physiology and Plant Molecular Biology* 51:401-432.
- Tse KKC, Lo SL. 2002. Desorption kinetics of PCP-contaminated soil: effect of temperature. *Water Research* 36(1):284-290.
- Wen B, Shan XQ, Lin JM, Tang GG, Bai NB, Yuan DA. 2002. Desorption kinetics of yttrium, lanthanum, and cerium from soils. *Soil Science Society of America Journal* 66(4):1198-1206.
- Yih LH, Hsueh SW, Luu WS, Chiu TH, Lee TC. 2005. Arsenite induces prominent mitotic arrest via inhibition of G(2) checkpoint activation in CGL-2 cells. *Carcinogenesis* 26(1):53-63.
- Zhang PC, Sparks DL. 1990. Kinetics of Selenate and Selenite Adsorption Desorption at the Goethite Water Interface. *Environmental Science & Technology* 24(12):1848-1856.

Table 1: X-ray diffraction results

Sample	Lithology	% Quartz	% Orthoclase Feldspars	% Plagioclase (Na/K Feldspar)	% Illite	% Kaolinite	% Chlorite
BT60	Sandstone	81.0	3.2	< 0.1	6.8	9.1	< 0.01
BT571	Claystone	32.1	0.4	0.5	40.1	12.2	14.7
BT700	Claystone	22.6	0.5	0.9	46.6	7.5	21.9

Courtesy, West Virginia Geological and Economic Survey

Table 2: X-ray fluorescence results

	% MnO	% K ₂ O	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% Na ₂ O	% MgO	% TiO	% CaO
BT60	0.01	2.48	81.05	15.28	< 0.01	0.07	0.48	0.86	0.22
BT571	0.04	4.91	62.25	23.95	5.17	0.05	2.15	1.34	0.04
BT700	0.03	5.52	63.83	23.28	4.16	0.19	1.97	1.27	<0.01

Courtesy, West Virginia Geological and Economic Survey.

Table 3: Comparison of extraction techniques

Sample	Total available Selenium	Total Selenium Extracted			Total available Arsenic	Total Arsenic extracted		
	Microwave digestion ng/g	120 min continuous sonication* ng/g	Partial 5 minute of the 90 minute sequential sonication* ng/g	Total 90 minute sequential sonication ng/g	Microwave digestion µg/g	120 min continuous sonication* µg/g	Partial 5 minute of the 90 minute sequential sonication* µg/g	Total 90 minute sequential sonication µg/g
BT60	93.3 ± 3.7	78.4 ± 3.1	69.7 ± 2.5	93.2 ± 3.4	5.05 ± 0.15	2.19 ± 0.55	0.78 ± 0.11	4.15 ± 0.4
BT571	1088 ± 18	261.1 ± 15	208.3 ± 35	387.0 ± 14.5	48.2 ± 5.9	8.71 ± 1.07	9.07 ± 0.67	11.6 ± 1.4
BT700	1126 ± 122	153.8 ± 9.6	101.7 ± 10.1	428.8 ± 20.2	61.8 ± 5.4	15.7 ± 1.4	4.55 ± 1.76	27.7 ± 2.21

Table 4: Accelerated first order kinetic modeling for the extraction of total Se and total As

Sample	Se		As	
	^b Rate constant min ⁻¹	R ² value	^b Rate constant min ⁻¹	R ² value
BT60 ^a	-	-	0.050 ± 0.003	0.9404
BT571	0.0089 ± 0.0002	0.9474	0.013 ± 0.003	0.9847
BT700	0.0052 ± 0.0001	0.9949	0.034 ± 0.001	0.9950

^aNot enough data points were available for total Se kinetic modeling. All Se was leached out in the first three extractions.

^bAccelerated extraction rate constant ± standard error of the slope obtained from First order model $\ln(1 - C_t / C_\infty) = -kt$, where C_t is the concentration of extracted species at sonication time t and C_∞ is the extracted species concentration at infinite sonication, k is the accelerated extraction rate constant

Table 5: First order kinetic modeling for the release of Se (IV)

Sample	Rate constant (min ⁻¹)	R ² value
BT571	0	0.9837
	.034 ± 0.002	
BT700	0.026 ± 0.001	0.9905

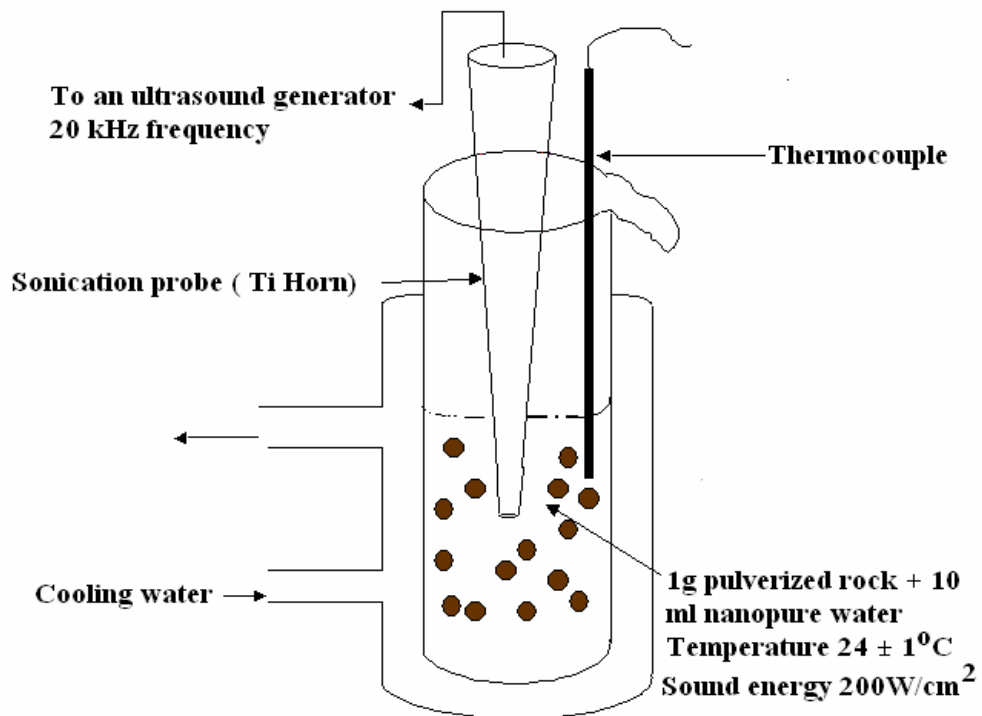


Figure 1: Ultrasound extraction experimental set up

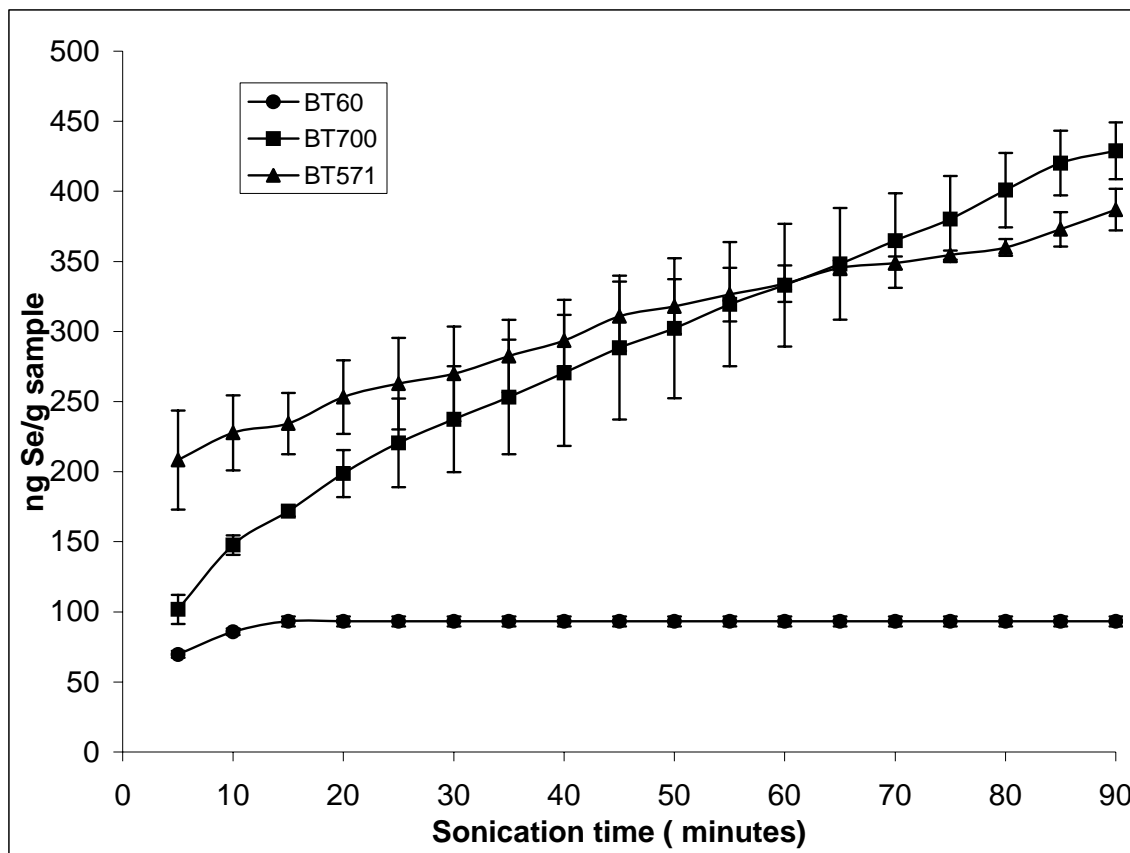


Figure 2: Release of total Se (ppb) as a function of sonication time

Conditions: Sequential five minute ultrasonic extractions, ultrasound pulse 40 %, probe diameter 0.3 cm, sonication power 200 watts/cm², temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.

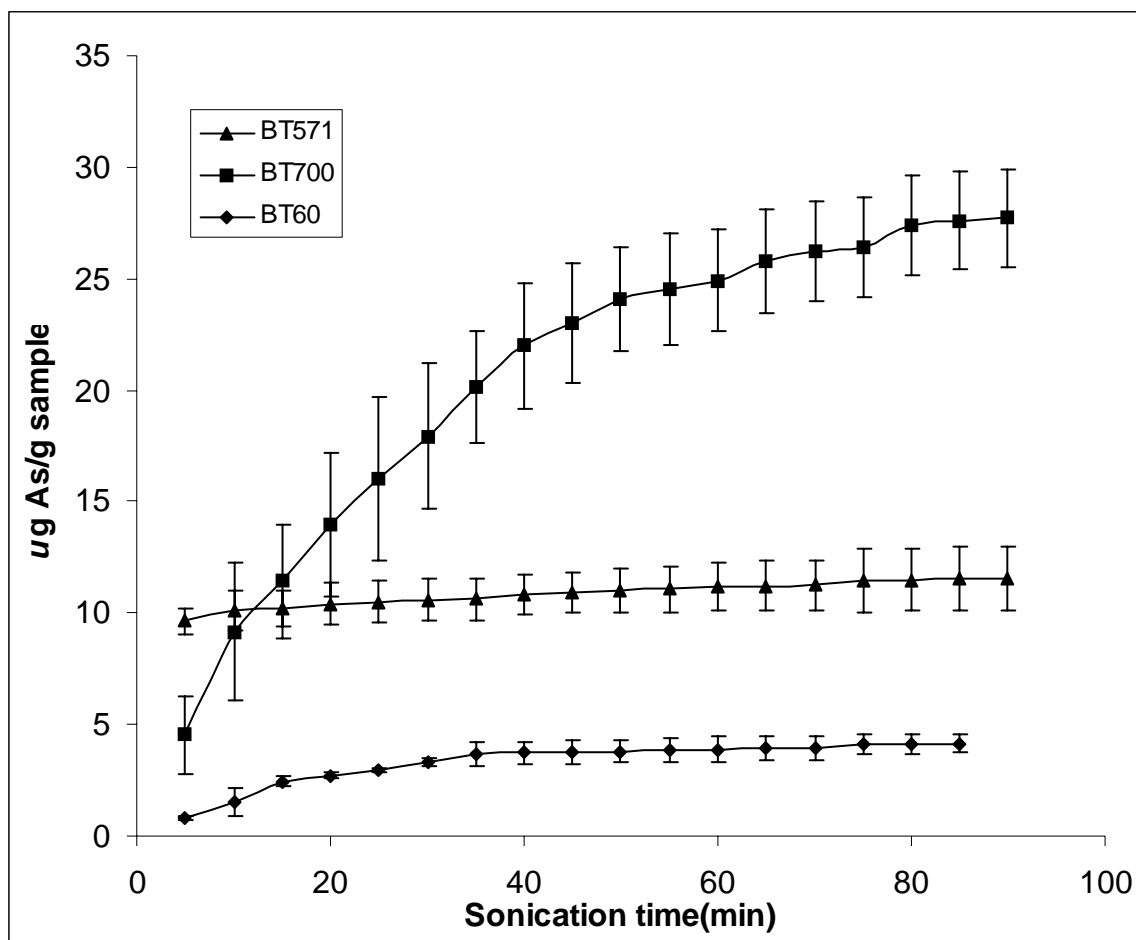


Figure 3: The release of total Arsenic (ppm) as a function of sonication time

Conditions: Sequential five minute ultrasonic extractions, ultrasound pulse 40 %, probe diameter 0.3 cm, sonication power 200 watts/cm², temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.

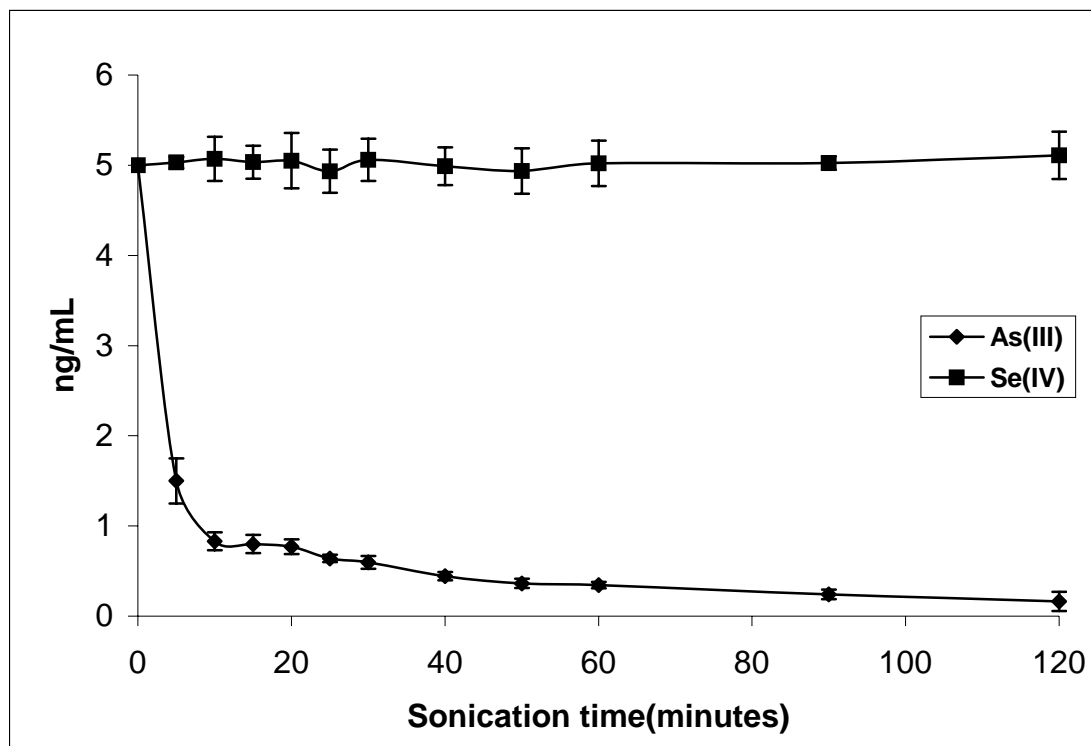


Figure 4: Variation of Se (IV) and the disappearance of As (III) as a function of sonication time

Conditions: 10 ml solutions of 5 ng/ml of 1:1 Se (IV)/Se (VI) and As (III)/As (V) sonicated at $200\text{W}/\text{cm}^2$, continuous sonication, ultrasound pulse 40 %, probe diameter 0.3 cm, $24 \pm 1^\circ\text{C}$.

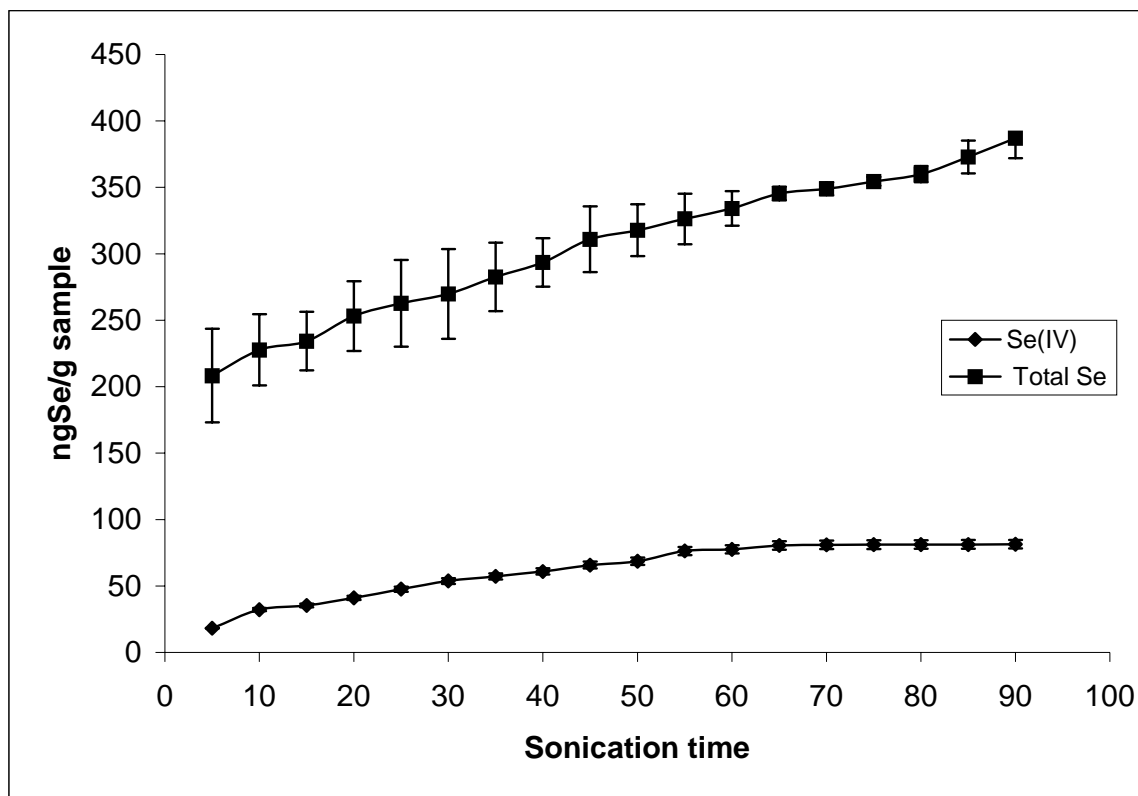


Figure 5: The release (ppb) of total Se and Se (IV) from BT571 as function of sonication time

Conditions: Sequential five minute sonications, sonication pulse 40 %, probe diameter 0.3 cm, Sonication power 200 watts/cm², temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.

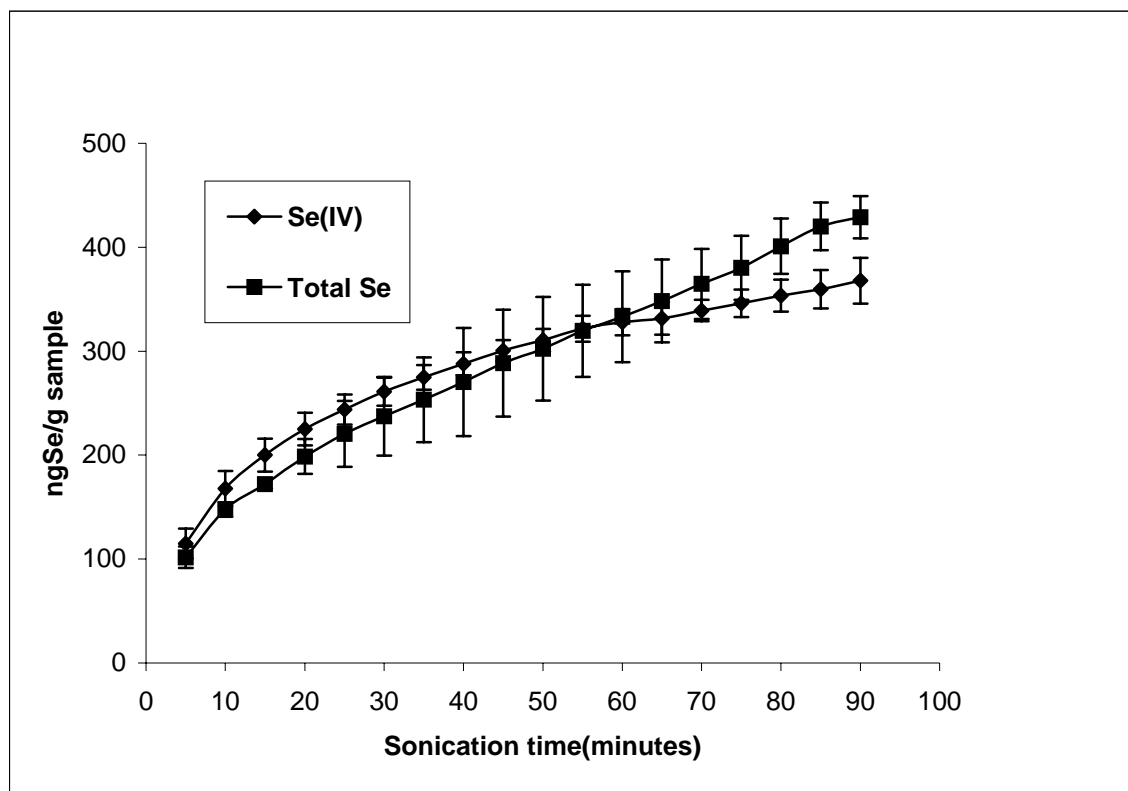


Figure 6: The release of total and Se (IV) from BT700 as a function of sonication time.

Conditions: Sequential five minute ultrasonifications, sonication pulse 40 %, probe diameter 0.3 cm, Sonication power 200 watts/cm², temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.