

Leachability of Arsenic and Selenium in Submicron Coal Fly Ash

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ABSTRACT

The leaching of arsenic (As) and selenium (Se) from coal combustion fly ash for the submicron particle size range was assessed using a modified Toxicity Characteristic Leaching Procedure (TCLP) protocol. Size segregated fly ash samples were collected from the combustion of Powder River Basin (PRB) subbituminous coal at 1723 K and 1838 K. These ash samples were leached under acidic, neutral and basic pH conditions. Qualitative data on the solubility of As and Se for each pH environment were determined as a function of combustion temperature for submicron particle sizes. For both temperature samples, arsenic showed slight to moderate mobility under acidic conditions and was not mobile in basic and neutral mediums. Selenium, on the other hand, was found in the 1723 K samples to be highly soluble in an acidic medium but mobility decreased as the pH increased towards basic conditions. And in samples from the 1838 K run Se was found to be highly soluble under all three pH conditions.

INTRODUCTION

Coal fly ash contains trace elements such as arsenic and selenium which are typically found in the submicron size range^{1,2}. Particles in this size range are not efficiently captured by particulate control equipment^{1,3} and have the ability to affect air pollution devices such as selective catalytic reduction (SCR)⁴. Arsenic and selenium are highly volatile but when they are associated with inorganic materials, such as pyrite, they may not undergo complete vaporization during combustion. In the PRB coal used in this study arsenic is largely associated organically and during combustion will experience very high temperatures and vaporize completely^{5,6,7}. Some of it may also be associated as arsenates which will be less likely to vaporize. Selenium is also almost entirely – up to 90% - organically associated with a small percentage associated with pyrite⁸. As the flue gas cools, As and Se vapors can homogeneously nucleate, heterogeneously condense on fine particulate fly ash surfaces or continue as vapor phase species^{7,9,10}. Partitioning of these two elements back to solid particle surfaces depends not only on the gas - solid equilibrium but also on other minor cations such as calcium and iron¹¹. Calcium is a refractory element that volatilizes only at high combustion temperatures^{7,12} and can repartition back to the solid phase on particle surfaces⁹. It also plays an

important role in arsenic partitioning in coal flue gas. Reactions between arsenic and calcium form calcium arsenate which remains non volatile even at temperatures up to 1573 K¹³. Understanding the physical and chemical composition of size segregated fly ash will help determine the fate of trace elements in air pollution control devices and in the environment.

Leaching tests are qualitative means to estimate the mobility of trace elements and potential environmental impacts. Of particular concern are submicron particles because they are difficult to collect in air pollution control devices. In addition, the solubility of the elements is dependent on the pH of environment where the particles are deposited.

RESEARCH OBJECTIVE

The objective of this research is to assess the solubility of trace metals – arsenic and selenium – present in the submicron range of coal combustion fly ash. The effect of combustion temperature on the leachability of arsenic and selenium from submicron particles was studied under acidic, neutral and basic pH conditions.

EXPERIMENTAL METHODS

Fly ash samples were collected from a 19 kW vertical downflow laboratory combustor which is 6 m tall with a 0.15 m ID. The combustor consists of a burner cap, a 1.8 m long burn chamber with 4 sample ports, a 4.2 m long post combustion zone with 7 additional sample ports and an ash trap located directly below the bottom of the post combustion zone. The schematic for the combustor is shown in Figure 1. The burner cap contains a top port for a water cooled fuel probe and a side port through which hot secondary air is introduced. A honeycomb flow straightener (0.08 m long and 0.16 m diameter) helps streamline the flow of secondary air as it enters the combustor. It is made from alumina and can withstand temperatures as high as 1973 K. The top half of the flow straightener is encased in the furnace cap and is located just below the port where secondary air is introduced to the furnace. The other half of the flow straightener sits inside the combustion chamber. The flow straightener has a 0.03 m opening in the center through which the water cooled fuel injector is inserted into the furnace. Hot secondary air and fuel do not mix until they are both delivered inside the furnace. The fuel probe (0.72 m long) has an inner 0.015 m diameter tube surrounded by an outer 0.03 m diameter tube that is water cooled to keep the probe from overheating. Fuel is injected from the top into the inner tube and room temperature primary air is introduced to the side of the inner tube just below fuel injection. Primary air is used as transport air and is usually not more than 20 % of the total air required for the combustion process, including excess air supplied. Air to the system is delivered by a compressor operating at a 1 MPa. Rotometers (Dwyer Inc) control the rate of air flow into the system.

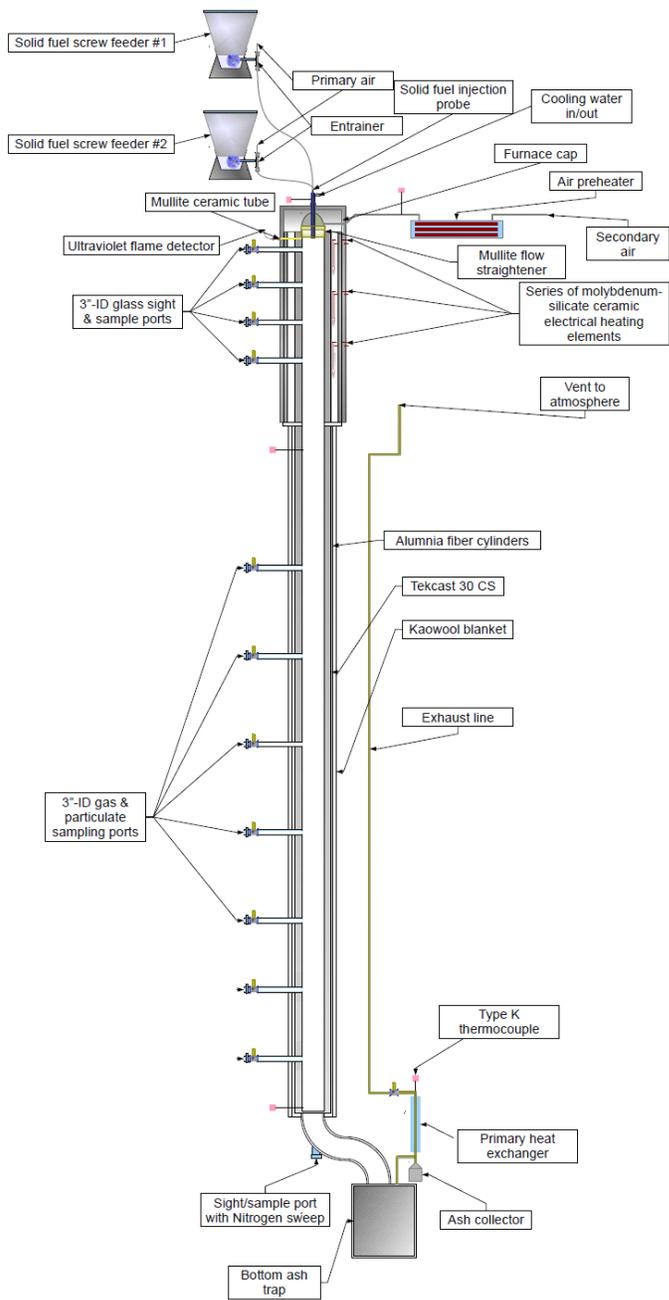


Figure 1: Schematic of furnace with sample ports.

Prior to introducing solid fuel the furnace is preheated with external heating elements followed by natural gas. Heating elements are installed on all three zones of the combustion chamber. Each zone is heated by 4 heating elements in series and a Watlow controller is used to control the heating rate for each zone. The elements are used to preheat the furnace to approximately 1373 K. Once the elements reach the desired set point, natural gas is combusted to slowly increase the inside temperature of the furnace. Natural gas is fed through a probe very similar to the one used for solid fuel injection but with a slightly smaller (0.013 m) internal diameter. Once steady state conditions are achieved with natural gas, the delivery line is shut and the natural gas probe is quickly replaced by the solid fuel probe. Solid fuel is fed into the furnace using an Acrison series 105 volumetric screw feeder with feed rate adjusted using a variable voltage controller. After the furnace reaches steady state operating conditions, a temperature profile is measured along the length of the furnace. A high velocity temperature probe measures the gas centerline temperature.

A total of 11 specially installed sample ports along the length of the furnace allow temperature measurements at different zones of the furnace. For this study ash samples were extracted at port 11, located near the end of the combustor but sufficiently far upstream from the un-insulated ash trap. A Dekati Low Pressure Impactor (DLPI) and a pre-separator cyclone were used to collect ash samples. The DLPI can segregate ash in 13 different size fractions between 0.03 and 10 microns. Samples were collected with and without the pre separator cyclone and the combined data from both the runs are used to generate a particle size distribution (PSD) curve. When the pre-separator cyclone is used, it removes a majority of particles larger than one μm from the sample gas stream. This allows a sufficient quantity of smaller particles to be collected and minimizes any bounce-off of larger particles which skews the data. Sampling without the pre-separator cyclone allows larger particles to be collected. Isokinetic conditions were maintained during the entire sampling time.

Collected ash samples from each stage were digested in an acidic mix of $\text{HF} + \text{HNO}_3 + \text{HCl}$ in distilled water, to determine the total concentration of elements for that particular size fraction. For leaching studies, ash samples collected under the same furnace operating conditions, were extracted with acidic ($\text{pH} = 2.88$), neutral ($\text{pH} = 7$) and basic ($\text{pH} = 11$) leaching solutions. The samples were placed in an auto shaking apparatus for about 18 hours. A modified TCLP procedure, as suggested by Seames and Wendt¹⁴ is used to determine trace element leachability in the submicron particle regime. The EPA recommended TCLP Improved Method 1311 requires the use of about 100 g of fly ash and a L/S ratio of 20. Submicron particles account for only a small percentage in the total ash and collecting 100 g would require extremely long sampling times, especially in a lab scale system that burns fuel at a rate less than 5 lb/hr. Additionally, the TCLP Method 1311 requires loose ash samples to carry out leaching studies. Submicron particles for this study are collected using greased membranes in an impactor. Hence the modified procedure serves as a better protocol for ash in a desired size fraction, in particular the smaller particles. Sample pH was continuously monitored and appropriate buffers were added to maintain a constant pH value. Total digestion and leaching

solution samples were analyzed using a Graphite Furnace Atomic Absorption Spectrometer (GFAAS) capable of measuring concentration levels as low as 1 ppb for As and 2 ppb for Se. The coal used for this study was a PRB subbituminous coal that had a high weight percent of sodium in ash. Calcium in ash was high compared to bituminous coals but arsenic and selenium levels were only present in extremely trace amounts. This may be due to low levels of pyrite in the fuel. Some of the relevant properties of the coal used are shown in Table 1.

Table 1: Relevant properties of the partially dried PRB Coal.

Proximate Analysis	Weight %	Analyte (in ash)^a	Weight %
Total moisture	11.28		
Ash	8.96	Silicon Dioxide	45.57
Volatile matter	33.54	Aluminum Oxide	15
Fixed Carbon	46.22	Titanium Dioxide	0.78
Higher heating value (BTU/lb)	10015	Iron Oxide	5.27
		Calcium Oxide	12.61
Ultimate Analysis	Weight %	Magnesium Oxide	3.62
Ash	8.96	Potassium Oxide	1.16
Carbon	60.11	Sodium Oxide	2.94
Hydrogen	5.11	Sulfur Trioxide	11.52
Nitrogen	0.87	Phosphorous Pentoxide	0.56
Total Sulfur	0.76	Strontium Oxide	0.41
Oxygen by difference	24.43	Barium Oxide	1.88
Trace element composition	(ppmw)	Manganese Dioxide	0.08
Arsenic	1.83		
Selenium	2.21		

^aExpressed as wt% equivalent oxide.

RESULTS

Samples were collected for combustion temperatures of 1723 and 1838 K. Typical temperature profiles for the furnace are shown in Figure 2. The respective sample port temperatures were 894 and 980 K. Figure 3 shows the particle size distribution (PSD) curves for ash samples collected at 1723 K and 1838 K. Peaks were observed in the submicron size range for both 1723 K and 1838 K runs. Vaporized species, including arsenic and selenium, will condense on these small particles due to their large surface area. For analysis, stages 3, 4, 5 and 6 of the DLPI (corresponding to sizes 0.108, 0.17, 0.26 and 0.4 μm) were used to characterize submicron particulate. Error bars were added to the data points to show variability in the total digestion and leaching measurements.

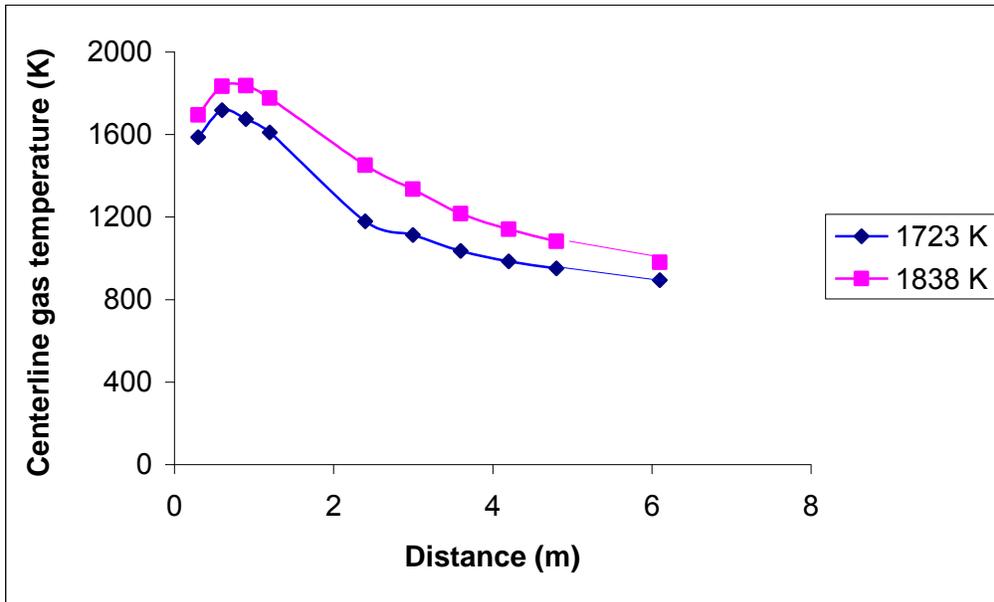


Figure 2: Temperature profiles of the furnace

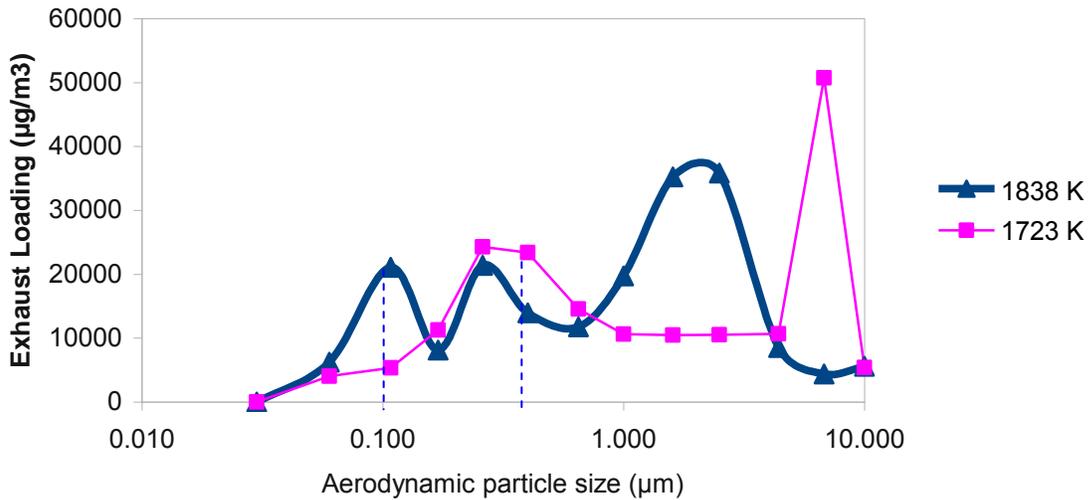


Figure 3: Typical particle size distribution for fly ash at 1723 K and 1838 K

Figure 4 shows the total concentration of arsenic at 1723 and 1838 K for particles collected on the 0.108, 0.17, 0.26 and 0.4 µm size stages. Arsenic concentration showed higher levels at 1838 K than at 1723 K for all four particle sizes. This may be due to an even higher degree of vaporization at 1838 K than 1723 K. Condensation by a purely physical phenomenon will drive vapors towards smaller particles as they have a higher specific surface area compared to large particles. The availability of calcium plays an important role in arsenic partitioning as calcium arsenate is the most likely species formed when arsenic vapors heterogeneously condense on fly ash surfaces^{8,10}.

Additionally the availability of extra calcium rich particles at 1838 K may have increased the concentration of arsenic at this temperature. In contrast total selenium levels (Figure 5) did not show any significant change with difference in temperature. Selenium has a higher volatility than arsenic¹⁵ and appears to vaporize equally well at either temperature. Much of the Se is expected to remain as flue gas vapor

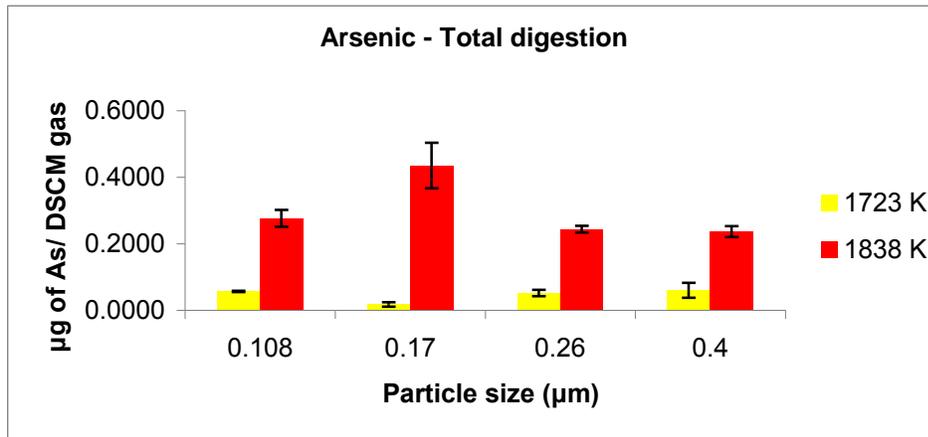


Figure 4: Total concentration of arsenic in submicron fly ash

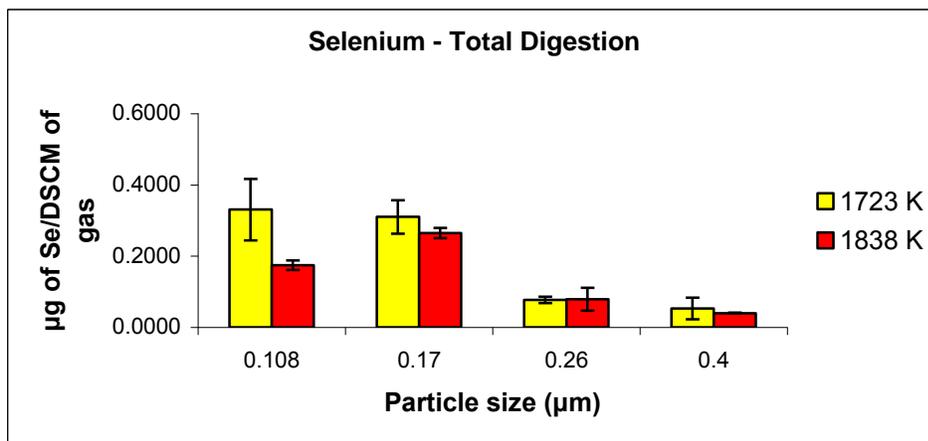


Figure 5: Total concentration of Selenium in submicron fly ash

Results from the leaching studies are presented in Figures 6-10. Leached concentration is expressed as µg of element leached/ DSCM of gas. Due to the small quantities of As and Se present, these results are qualitative in nature. A figure for leaching in a basic medium is not included because no As was detected at either temperature. As shown in these figures, 1838 K samples released more Se and As than 1723 K samples and this was observed under all pH conditions. Elements present on the surface of ash particles are more easily available for leaching and vaporized trace elements enrich on the surfaces of submicron particles due to their higher surface areas. Percentage leachability was calculated as the ratio of concentration of metal that leached for a particular size to the total concentration of metal for the same size. Table 2 expresses

leachability of arsenic and selenium in terms of percent solubility for the total of all four particle sizes.

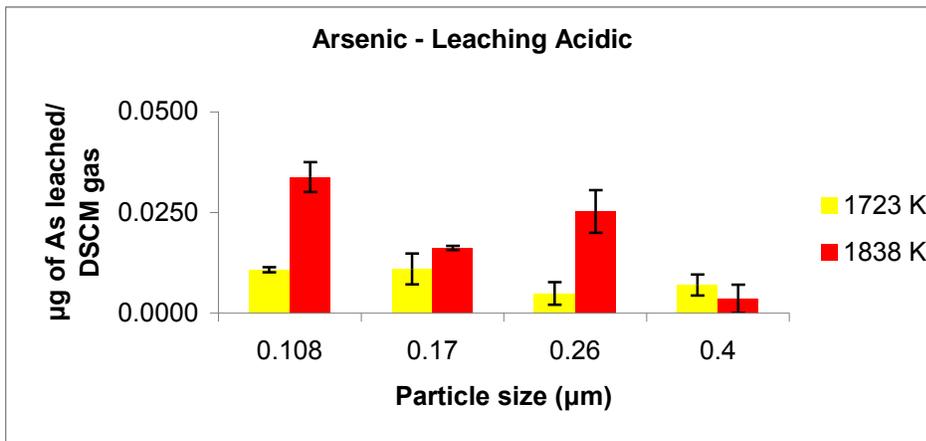


Figure 6: Concentration of arsenic leached in an acidic medium (pH = 2.88)

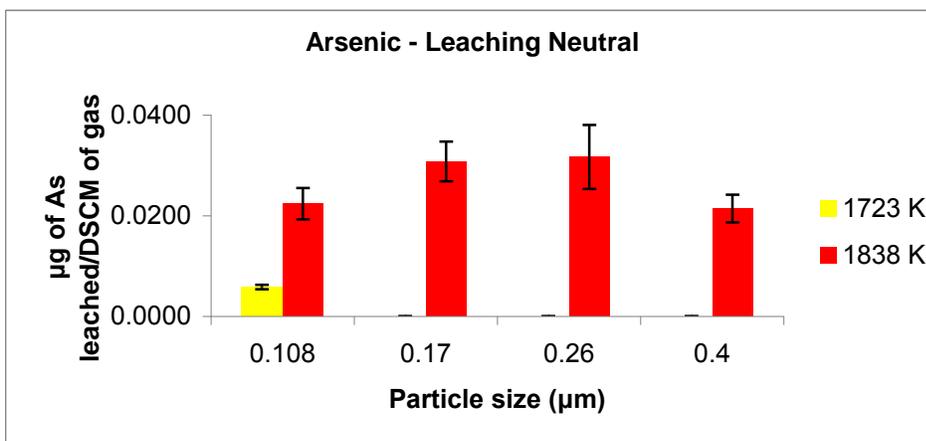


Figure 7: Concentration of arsenic leached in a neutral medium (pH = 7)

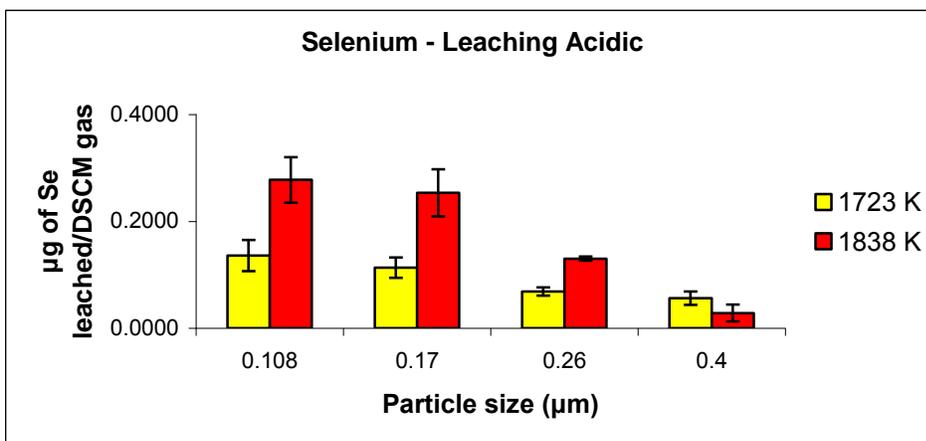


Figure 8: Concentration of selenium leached in an acidic medium (pH = 2.88)

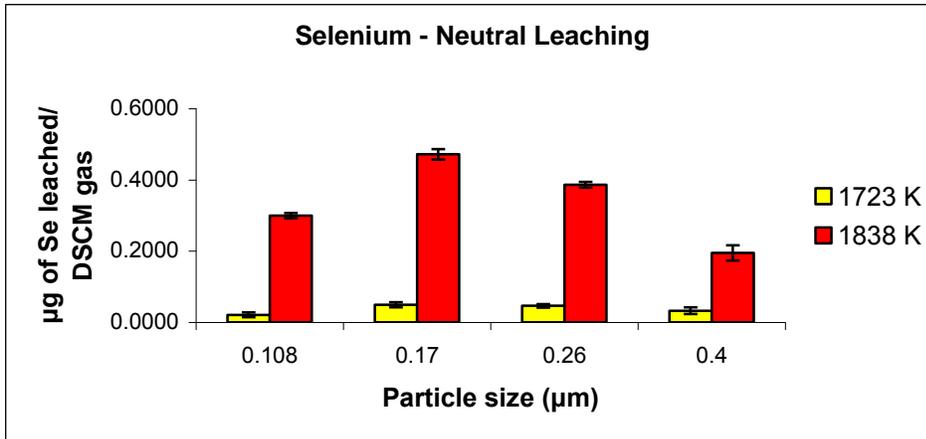


Figure 9: Concentration of selenium leached in a neutral medium (pH = 7)

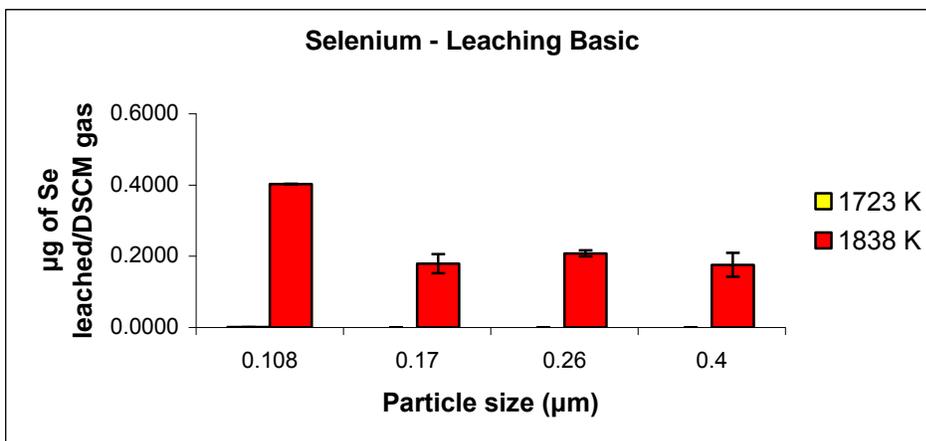


Figure 10: Concentration of selenium leached in a basic medium (pH = 11)

Arsenic showed some mobility under acidic conditions for 1723 K but it was only slightly mobile for 1838 K. Under neutral conditions, arsenic was only slightly mobile for both temperatures. And in basic conditions arsenic did not leach out for either temperature. One possible reason for lack of mobility at higher pH may be the formation of insoluble precipitates such as calcium arsenate $[\text{Ca}_3(\text{AsO}_4)_2]$ which is not very soluble under alkaline conditions. Formation of ettringite (calcium aluminate sulfate hydroxide hydrate) at high pH can also reduce arsenic mobility^{16,17}. Leaching results for selenium indicate the 1838 K samples were highly soluble for all pH conditions, whereas in the 1723 K samples Se was highly soluble only for acidic conditions with mobility decreasing entirely as pH increases to basic conditions.

Table 2: Leachability of Arsenic and Selenium in submicron particles – Weight percent of total element mass soluble in leaching fluid

Element	Acidic pH = 2.88	Neutral pH = 7	Basic pH = 11
Arsenic			
1723 K	30	2	0
1838 K	10	8	0
Selenium			
1723 K	100	30	0
1838 K	100	100	100

CONCLUSIONS AND FUTURE WORK

Fly ash samples were collected from the combustion of PRB coal at two different combustion temperatures. The leachability of As and Se in the submicron size under three different pH conditions was determined using a modified TCLP protocol. Selenium was found to be mobile under all pH conditions for the high temperature samples but had high solubility only under acidic conditions for the low temperature run. Arsenic showed some solubility under acidic conditions for 1723 K samples, was only slightly soluble in a neutral medium for both temperatures, and did not leach out at all in a basic environment for either sample.

The results presented here are the preliminary findings of a more comprehensive study. Analysis is ongoing for the remaining particles in the fine fragment and bulk size regimes that were collected during the sample runs described here. Additionally, experiments will be carried out using another PRB coal that has different ash chemistry. Ash samples from the co-combustion of coal and wood chips will also be characterized to determine leachability of trace elements under mixed fuel conditions.

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