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Leaching Behavior of Coal Combustion Products and the Environmental Implication in Road Construction

by

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16. Abstract

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SECTION I

INTRODUCTION

Coal fly ash is a common by-product of coal combustion, and it takes up to 70% of the total coal ash generation at coal fired power plants. In the United States, the average annual production of coal fly ash was 65.3 billion kilograms from years 2001 to 2008 (ACAA, 2009). The Energy Information Administration (EIA, 2010) suggested that coal will still be the primary fossil fuel for America's electricity needs in the near future. Therefore, the significant generation of fly ash from coal-burning power plants is expected to continue in the future. Due to the high content of silica and alumina, fly ash exhibits cementitious properties in the presence of water and calcium hydroxide (pozzolanic properties), making it useful as a substitute for portland cement in concrete products. In the United States, around 40% of the fly ashes were being beneficially used, mainly in concrete and cement industry, and the other 60% of fly ash is disposed of in landfills or ash ponds (ACAA, 2009).

1.1. COLA FLY ASH COMPOSITION

Coal fly ash is a fine powdery material. Up to 80-95% of the particles in fly ash were < 50 μm, and 14-28% of the particle masses were < 2 μm (EPRI, 1993). Solid spherical, amorphous (non-crystalline) particles dominate the fly ash morphology. Some other particles generally presents in minor amount, including cenospheres (caused by expansion of trapped volatile components), irregularly shaped unburned carbon and amorphous particles, agglomerates, and minerals and mineral aggregates (Kutchko and Kim, 2006). Quartz (SiO_2) and amorphous glass are the basic mineralogy in fly ash. Mullite ($3Al_2O_3$-$2SiO_2$) is also a dominant mineral phase of bituminous coal fly ashes (EPRI, 1993). More than half of fly ash particles (by mass) are in the 2.3-2.9 g/cm^3 density range; they are spherical particles containing high aluminum (Al) and silicon (Si), and dominated by mullite and quartz minerals. 14-33% of the mass of fly ash particles are heavier than 2.9 g/cm^3, and they are iron-rich magnetic particles. These particles are mainly spherical, with surface morphologies reminiscent of pyrite framboids (EPRI, 1993).

The predominant elements in the fly ashes were Si, Al, Fe, Ca and O (oxygen) in various compounds (Ctvrtnickov et al., 2009; Giere et al., 2003; Kutchko and Kim, 2006). Most fly ashes from lignites contain high contents of alkali oxides and significant quantities of anhydrous Ca- or Mg-sulfates, while fly ashes from bituminous coal are low in Ca, Mg, and sulfate (Evangelau, 1996). The concentrations of trace elements in fly ash are dependent on the composition of coal, and vary significantly among all types of coals. Generally, eastern bituminous coals have been found to contain higher amounts of several trace elements (e.g., As, Mo, and Zn) than the western subbituminous and lignite coals (EPRI, 1987).

1.2. COAL FLY ASH LEACHING

Based on their interaction with water, the solid components in fly ash can be divided into three groups: (1) components of low water reactive but possesses surface charge (may adsorb trace metals, e.g., Cd, Pb, Ni, As), including Al_2O_3, SiO_2, Fe_2O_3, and TiO_2; (2) metal and metalloids that adsorbed onto the oxide surfaces of (1), and most trace elements are of this category; (3) highly water reactive components, including oxides of Ca, Mg, K, Na, Ba, and gypsum ($CaSO_4.2H_2O$) and sulfite (Evangelau, 1996). The primary concern in fly ash management is the leaching of toxic trace elements.

Since many of the concerned trace elements, including As, Se, V, Mo, Pb, and Zn, and significant amount of Cr, Cu, and Ni mainly reside on the surface layer of fly ash (EPRI, 1993; Harris and Sllberman, 1983), upon weathering, these surface-condensed trace elements can be rapidly mobilized (because access by leaching solution is rapid) and in some cases may initiate the formation of secondary minerals (EPRI, 1993; Sandelin and Backman, 2001; EPRI, 2006; Wang et al., 2007). Due to the complex physical and chemical composition of fly ash, complicated reactions could occur when fly ash is exposed to water and air in the open environment. Therefore, knowledge of chemical composition of coal fly ash is not enough to predict the leaching potential of toxic constituents to soil and groundwater.

Among all the trace elements in fly ash, arsenic and selenium are of the most concern because of their concerned toxicity (Wang et al, 2009; EPRI, 2008). Other key oxyanionic elements such as chromium, molybdenum, antimony, and vanadium have also captured rising attentions due to their potential toxicity and the more stringent environmental standards (EPRI, 2010a). Therefore, understanding and predicting the leaching behavior of these oxyanions from coal fly ash are critical for addressing the environmental concerns during ash management. Exploratory studies on leaching mechanisms of trace cationic elements, such as cadmium, copper, and oxyanions such as arsenic and selenium, have been carried out for a few selected fly ashes. We (2008; 2009) developed a robust model which successfully predicted the partitioning of arsenic and selenium onto bituminous coal ashes. However, washed ashes were used in these studies, and the intrinsic leaching parameters including the total leachable arsenic and selenium from raw fly ash remained unsolved. Meanwhile, we (2007) used a similar approach successfully determined these intrinsic leaching parameters for trace cationic elements in raw fly ash. These studies provided promising insight into effectively predicting the leaching potential and stability of key oxyanions in fly ash.

1.3. CHANGES IN FLY ASH DUE TO SO_2 EMISSION CONTROL TECHOLOGIES

Sulfur dioxide (SO_2) emitted from coal fired power plants is a toxic inventory substance capped under the US EPA's Clean Air (US EPA, 2005), and therefore is the major target for emission treatment. Despite the effectiveness of various emission control technologies in reducing the SO_2 emission, they changed the coal ash characteristics and increased coal fly ash volumes. For example, due to the excess alkaline sorbent injected, flue gas desulfurization (FGD) leads to highly alkaline ash with high content of sulfate and cations such as calcium and magnesium (related to the sorbent used). Sodium sorbent injection (SSI, for flue gas desulfurization) has been estimated to produce about twice the amount of fly ash normally generated from a conventional coal combustion process burning the same coal (EPRI, 1997).

Depending on the emission control technologies being tested/applied at coal fired power plants, the coal fly ash generated from these processes may significantly different from the well characterized conventional fly ashes, and thus need different disposal practices. Therefore, studies on the composition and leaching characteristics of these new types of coal fly ash are important for risk assessment and choosing proper fly ash management methods, for groundwater protection and remediation requirements, and for sound engineering decisions at power plants.

1.4. ENVIRONMENTAL CONCERNS AND COAL ASH REGULATION

Many studies have found that a variety of toxic trace elements in coal fly ash may be leached into the environment, contaminating soil and water resources (Sandelin and Backman, 2001; EPRI, 2006; Wang et al., 2007). Field test of trace metals in coal ash ponds have demonstrated that water quality criteria violation may be an issue at some stations, and fly ash is the primary source of metals. In older facilities, releases of toxic metals to groundwater have occurred. Significant cancer risks and dangers to aquatic life from coal ash storage utilities were identified by US EPA in its screening study and comprehensive risk assessment that were carried out in year 2002 and 2007, respectively (EIP, 2009).

The Kingston ash spill in year 2008 warmed up the movement among general public and legislation bodies at both the federal and state level, to increase regulations over coal ash (TVA, 2009). North Carolina and Tennessee have passed bills changing their state regulations on coal ash storage facilities in year 2009. US EPA is currently in the process of creating the first-ever national rule on coal ash management, and proposed two options in June 2010: (1) US EPA would list coal ash as special wastes subject to regulation under subtitle C of the Resource Conservation and Recovery Act (RCRA), when they are destined for disposal in landfills and surface impoundments; (2) US EPA would regulate the disposal of such materials under subtitle D of RCRA by issuing national minimum criteria. Under both alternatives, US EPA proposed to remain the exempt of beneficially used coal combustion wastes from the hazardous waste regulations under Section 3001(b)(3)(A) of RCRA (US EPA, 2010). This proposed rule received little endorsement from coal energy industry and coal ash recycle industry, and extensive comments were raised on the uncertainties in US EPA's health risk assessment and the significant impact of such national rule on coal ash management cost and coal ash recycling industry (EPRI, 2010b; Kovacs, 2010). Therefore, it is still unclear what kind of coal ash regulation will be taken at the national level.

1.5. REMEDIATION OF TRACE CONTAMINANTS FROM COAL FLY ASH

With the change in fly ash regulation, simple and effective treatment methods may be needed to detoxify coal fly ash before disposal and/or utilization in concrete. Several physical, chemical, and phyoto- remediation methods in treating fly ash have been reported in the literature, and they mainly apply two principles: (I) stabilize the toxic trace elements inside coal fly ash by reducing their mobility and (II) extract the toxic trace elements from coal fly ash. The former includes methods that reduce the mobility of trace elements by adding precipitation agent to fly ash (e.g., lime, calcium aluminates, ferrous sulfate, geopolymers), or growing vetiver on fly ash to create a protective surface from percolation of water into fly ash (Evangelau, 1996; Bournonville et al., 2004, Phair et al., 2004, Bhattacharyya et al., 2008; Chakraborty and Mukherjee, 2011, Bankowski et al., 2006). The latter includes washing fly ash, and extracting trace metals with strong acid/base and chelating agents such as EDTA, and phytoextraction by Jatropha curcas (Kashiwakura et al., 2010; Jamil et al., 2009; Nugterena et al., 2001). Due to the high efficiency and stability in performance, chemical treatment methods generally prevalent in engineering practices.

The benefit of the chemical stabilization method is its convenience and effectiveness in treating large amounts of fly ash, and could be economic if the chemical is widely available (e.g., lime). However, larger amounts of solid waste maybe generated due to the large quantities of agents added. Meanwhile, because of the in-situ nature, change in fly ash characteristics and leaching condition may remobilize the initially stabilized toxins and retrieve the metal contamination issue. The chemical extraction method could be costly since large amounts of extraction agent are needed, and using strong acid/base may destroy the fly ash particle, resulting in greater ash dissolution, and have the subsequent burden for treating the extracted solution. However, it is a thorough treatment method (since toxic metals were extracted out), will likely end up with clean fly ash without long-term environmental concerns after treatment, and therefore could be a good option in treating small amounts of toxic fly ash. Compared to the acid/base extraction methods, extraction with EDTA uses less drastic solution and may have less impact on the fly ash particles.

EDTA is known as a strong chelating agent for most cationic elements, and has been used to remediate trace cationic elements of concern (e.g., Pb, Cd, Cu, Ni, Zn, etc.) in fly ash and contaminated soils. Theoretically, EDTA won’t react with anions, however, results of several studies demonstrated that, in the presence of EDTA, leaching of As, Sb, Cr and V from fly ash increased (Ahumada et al., 2004; Jegadeesan et al., 2008; Kim and Hesbach, 2009; Nugteren et al., 2002). Therefore, EDTA could also mobilize oxyanionic elements in fly ash. Extensive evaluation of the effectiveness of EDTA in extracting oxyanions is important for EDTA application in detoxifying coal fly ash.

1.6. GOAL AND OBJECTIVES

Little is known about the new types of coal fly ashes that are continuously generated as a result of the emission control technological evolution at coal energy industry. The uncertainties challenge the safe utilization and regulation decisions of coal fly ash. Up-to-date studies are needed to evaluate the emission control technology on the ashes produced in the power industry. For the key oxyanionic elements, especially arsenic and selenium, a model and protocol is needed to predict their leachability from the raw ash, and their treatability are also needed to be evaluated when using EDTA to remediate fly ash. The overall purpose of this study is to serve these needs, and the specific objectives are:

1. Assess the impact of trona injection for SO_2 emission control at coal power plants on the fly ash produced. The fly ash physical, chemical, and especially leaching characteristics are studied.
2. Develop a protocol to quantify the availability and stability of As and Se in raw bituminous fly ash under various field conditions.
3. Study the effectiveness of EDTA-washing in remediating fly ash, especially oxyanions such as arsenic and selenium.

SECTION II

IMPACT OF TRONA-BASED SO_2 CONTROL TECHNOLOGY ON FLY ASH LEACHING CHARACTERISTICS

ABSTRACT

Trona ($Na_3HCO_3CO_3 \bullet 2H_2O$) injection method has been tested to control SO_2 emissions in coal-fired power plants. Because of the strong alkaline nature of trona and the high solubility of sodium compounds, the fly ash generated from trona injection processes may have very different properties than conventional fly ash. This study investigated the impact of trona injection on the leaching characteristics of coal fly ash. Physical characterization and total chemical composition analysis indicated a significant change in the physical structures of the trona fly ash, and a consistent increase in sodium (Na), sulfur (S), and carbonate content, when compared to the conventional fly ash. Batch leaching results indicated that trona ash has much greater solubility, stronger alkaline leachate pH, and significantly enhanced leaching of anionic elements including fluoride, sulfate, chloride, and trace oxyanions of concern especially arsenic (As) and As (Se). Leaching of cationic elements of concern from trona ash were either undetectable or decreased compared to the ash without trona.

KEYWORDS

Coal fly ash; SO_2 control; trona; trace elements; leaching

1. Introduction

Currently, approximately 50% of the electricity in the United States is generated from coal-fired power plants, and it is predicted that coal will remain to be the dominant fuel for electricity production in the foreseeable future.[1, 2] However, many environmental concerns present major challenge in the future coal electricity production. SO_2 is generated in significant amount from coal-fired power plants and being capped under Title IV of the 1990 Clean Air Act Amendments (CAAA).[3] Meanwhile, coal-fired power plants generate about 72 million short tons of fly ash per year,[4] and fly ash contains a variety of trace elements of concern, including As, Se, Cr, Cu, Pb, Hg, and Zn. These elements can potentially be released to the environment through leaching process.[5-9] Following the catastrophic failure of a fly ash containment in Tennessee Valley Authority (TVA) Kingston Fossil Plant in December 2008, US EPA recently proposed the first-ever national rule to ensure the safe disposal and management of coal ash.[10]

To minimize environmental impacts and keep up with the stringent emission regulations, clean coal technologies such as sodium sorbent injection (SSI) are being tested or used to control SO_2 emission. It is reported that SSI can remove 70-90% of the S from the flue gas of coal-fired power plants.[11] Trona ($Na_3HCO_3CO_3\bullet 2H_2O$) is a naturally occurred fine power,[12] and it is one of the sodium sorbents used in SSI. When injected into the flue gas, trona calcines and transformed into sodium carbonate, sodium carbonate reacts with SO_2 to form fine sodium sulfite/sulfate particulates. The reaction products and unreacted sodium carbonate are then collected downstream with the fly ash in an electrostatic precipitator or baghouse. SSI process is estimated to produce about twice the amount of fly ash normally generated from a conventional coal combustion process burning the same coal.[11] Due to the excess amount of trona used and its strong alkaline nature, the fly ash from trona injection (trona ash) is expected to be significantly different from the conventional coal fly ash. Despite the extensive studies on coal fly ash, very limited information is currently available on the characterization of trona ash.[13, 14] With the tighten regulations, understanding of the impact of trona injection on the leaching characteristics of coal fly ash is necessary for sound engineering decisions at power plants and in the subsequent coal ash management processes. The objectives of this research were (1) to provide a comprehensive assessment of the impact of trona injection on the fly ash physical and chemical composition; (2) to evaluate the impact of trona injection on the fly ash leaching characteristics.

2. Experimental Section

2.1. Fly ash samples

Four fly ash samples were collected from three power plants testing trona injection for SO_2 control. Table 1 shows the ash information. Samples #182 and #183 are a set of paired samples collected from plant #1. Sample #182 was the control sample collected before trona injection, while sample #183 was the trona ash sample. Samples #258 and #259 are two individual trona ash samples generated during SO_2 control testing at plants #2 and #3, respectively. The exact trona injection rates at these power plants are not known at the time of sampling, but plant #1 is known to have the highest trona injection rates among the three plants.

While all 4 samples were studied on their leaching characteristics, the special focus of this study was given on the paired samples, ashes #182 and #183. Washed samples of #182 and #183 were also characterized for comparison during ash surface characterization. Ash washing was performed using deionized (DI) water at solid-to-liquid (L/S) ratio of 5 (200 g/L) following the method published by Wang et al..[8]

2.2. Ash chemical composition.

Important chemical characteristics, including the major chemical composition and total extractable Na, were determined for all samples. The total concentrations of major elements in all fly ashes were analyzed using XRF (XL3T 900, NITON Analyzer, Thermoscientific). Total content of extractable Na were determined for all the four ashes following EPA method 3051A.[15]

Total content of trace elements of concern were only determined for the set of paired samples following a microwave assisted acid digestion method developed based on EPA method 3052,[16] where 0.1 grams of fly ash was digested with 9 mL HNO_3, 3 mL HF, and 3 mL HCl, at 240^{o}C for 30 minutes. A Multiwave 3000 microwave digestion system (PerkinElmer, Waltham, Massachusetts, USA) was used and Table S1 in the Supplementary Material presents the summary of the digestion method. For each batch of digestion, sample duplicate, sample spike, reference material SRM1633b, and reagent blank were included for QA/QC check. After removal from the microwave, the digestate (crystal clear liquid) were then diluted to 50 mL using DI water, left settling for several hours or overnight, and then filtrated with 0.22 µm filters. The resulting solutions were then analyzed to determine trace element concentrations.

2.3. Ash physical and micro-physical/chemical characterization.

Both the raw and washed ash samples of #182 and #183 were determined for the specific surface area, micro structure, and micro chemical characteristics. The specific surface area was determined using a Quantachrome Autosorb-1-C high-performance surface area and pore size analyzer (Quantachrome Instruments). A Hitachi S-4700 Field Emission SEM was used to characterize the microstructure of the two ashes. It was equipped with an energy dispersive x-ray detector (EDS), which was used to obtain associated chemical information for the particles. The SEM was operated at an accelerating voltage of 15 kV for both imaging and EDS measurements.

2.4. Batch leaching experiment.

Batch leaching experiments using DI water under natural condition (e.g. without pH adjustment) were conducted in this study, to determine the leaching behavior of trace elements of concern from raw fly ashes.[17] Four L/S ratio were used: 2, 5, 10, and 20. These L/S ratios were created by adding 50 g, 20 g, 10 g, or 5 g ash into 100 mL of DI water, respectively, in four 125 mL LDPE bottles. The bottles were then sealed and shaken at 180 oscillations/min using an EBERBACH 6010 shaker for 24 hours. The supernatant was then collected after settling of 2 – 4 hours. The final pH in the remaining slurry was measured and recorded as the equilibrium pH.

The primary concern in coal fly ash management is the release of inorganic contaminants that may impair water quality. Therefore, this study examined most of the inorganic contaminants listed in the drinking water standards, including those in the primary drinking water standard, secondary drinking water standard, and drinking water contaminant candidate list 3 (CCL3), to screen for leachable species that might be problematic. A total of 25 elements/constituents were studied, including As, Se, Sb, Cr, Ba, Be, Cd, Cu, Pb, Hg, Tl, F^-, Al, Fe, Mn, Ag, Zn, Cl^-, SO_4^{2-}, pH, TDS, Co, Mo, Sr, and V.[18-20]

2.5. Chemicals, reagents, and analytical method.

Concentrations of Al, Fe, Na, and Sr in all aqueous samples were analyzed using a Perkin-Elmer ICP-OES or Flame AA. The total Hg concentrations in all samples were analyzed using a Tekran Series 2600 Ultra-trace Mercury Analysis System (Tekran Inc., Toronto, Canada), following EPA Method 1631.[21] SO_4^{2-}, F^-, and Cl^- in the leachate samples were analyzed using DX120 Ion Chromatograph. All other trace elements from microwave digested samples and leachate samples were analyzed using a Perkin-Elmer Elan DRCe ICP-MS (PerkinElmer SCIEX, Concord, Ontario., Canada) according to EPA Method 200.8.[22] An Orion pH meter (perpHecT LoR model 370) equipped with an Orion PerpHecT Triode pH electrode (model 9207BN) was used for pH measurement. A Fisher digital conductivity meter was used for TDS estimation.

Quality control (QC) and spike recovery were between 85% and 115% for all analyses. The QA/QC for the acid digestion was good for most elements, except for Sr and Ba, which had poor repeatability, and low QC and spike recovery. Compared to the certified total content of trace elements in SRM1633b,[23] the recovered Ba and Sr were only 39% and 26%, respectively. It should be noted that for the total digestion samples, white colloidal particulates was observed in some of the samples after settling overnight. The precipitates were separated from the liquid, and re-digested with 10 mL concentrated hydrofluoric acid on a hot plate at 105 ^{o}C for 2 hours, but no visible dissolution was observed. Therefore, it is suspected that these white particles are precipitates of fluoride (from the HF acid used for digestion) with some major cations (from fly ash), such as Ca, Mg, Ba and Sr. The fluoride precipitation effect may contribute to the poor QA/QC of Ba and Sr in the digestion method.

Trace metal grade nitric acid, hydrofluoric acid and hydrochloric acid for acid digestion/extraction, certified grade sodium sulfate, and sodium fluoride and sodium chloride for ion chromatograph standards preparation, and single metal standard solutions used on ICP-OES were purchased from Fisher Scientific. Multiple trace elements' standard solutions for ICP-MS were purchased from PerkinElmer (Waltham, Massachusetts, USA). DI water was generated from a Millipore water purification system with a conductivity of 18.2 MΩ/cm.

3. Results and discussion

3.1. Impact of trona injection on the chemical composition of fly ash.

The weight percentages of major elements detectable by XRF are summarized in Table 1. For the set of paired samples, concentrations of most elements in the trona ash #183 were lower than those of the control ash #182, except for Na, S, and Cl. If a stoichiometrically equivalent amount of SO_2 was reacted with trona, the final products would be sodium sulfate/sulfite, and the net increase in Na and S content in fly ash should follow the ratio Na:S = 2. Compared to the control ash #182, the net increases of Na and S in trona ash #183 were 2.67 wt% and 1.46 wt% respectively, corresponding to a Na:S molar ratio of 2.54. Therefore, it is likely that more than an equivalent amount of trona was injected to capture SO_2. Therefore, the increased content of Na was brought by reacted and unreacted sodium carbonate, while the higher contents of S and Cl in the trona ash were due to captured SO_2 and chlorine from the flue gas.

Al, Si, Ca and Fe are the major components of conventional fly ash.[24] The combined weight percentages of Al, Si, Ca and Fe in the trona ash #183 was 37.3% , which is lower than the 44.8% value of control ash #182. This reflects the fact that sodium carbonate, sodium sulfate, and/or sodium sulfite were captured in the ESP, so that the ratios of elements that dominate conventional fly ash decreased. The total extractable Na content determined after EPA method 3051A digestion was 460 mg/kg, 77,970 mg/kg, 61,860 mg/kg and 18,670 mg/kg, for ashes

#182, #183, #258 and #259, respectively. The Na concentration in extracts of these trona ash may be indicative of the amount of trona injection at the power plant.

Table 2 shows the total content of trace elements in the set of paired samples. Data of Hg, Ba, and Sr were not reported, because Hg in the digestates of ashes #182 and #183 were below the detection limit, and Ba and Sr had poor QA/QC due to suspected precipitation with added hydrofluoric acid during digestion. Compared to the control ash #182, trona ash #183 contained less amount of As, but much higher Se. Concentration differences of other trace elements in the paired samples were within the 30% analytical variance range, and thus considered insignificant. Different levels of trace elements in the two ashes could be attributed to their abundance variance in trona and coal, and/or the possible changes in their partitioning mechanism in the flue gas as a result of trona injection.

3.2. Impact of trona injection on ash surface physic-chemical characteristics.

The specific surface areas of raw and washed ashes #182 and #183 are tabulated in Table 3. It demonstrates that the specific surface area of both ashes increased slightly after washing, indicating that the raw fly ash surfaces were covered with some soluble substances. The specific surface area of the trona ash (#183) was about half of the control ash (#182), indicating trona injection for SO_2 control changed the fly ash surface structure significantly.

The micro-structure and micro-chemical composition of the paired samples were determined using SEM-EDS. Figure 1 illustrates the micro-structural information, with (a) and (b) showing SEM images of the raw ashes #182 and #183, (c) and (d) showing their corresponding washed samples, respectively. All these images were taken at a magnification of 250 times. Table 3 summarizes the EDS results of the circled areas in Figure 1. The micro-structures of the raw control ash #182 (Figure 1(a)) were largely composed of spheres, and most of these spheres are well below 20 μm. However, for the raw trona ash #183 (Figure 1(b)), three types of particles were observed: spheres, micrometer and sub-micrometer coalesce fragments (porous), and larger agglomerated ash fragments and microspheres. The later two types of particles were observed in significant amount during SEM scanning. A microstructure similar to that observed in #183 was reported by Greer and Zhang.[14] Comparison of the EDS results of the two raw ashes in Table 3 shows that, trona ash had increased levels of carbon, Na and S, but decreased levels of all the other major constituents which are typical of conventional fly ash chemistry.

SEM-EDS analysis on the major particles of these raw ashes was performed at higher magnifications (1300 times or 10000 times), and the results are presented in the Supplementary Materials. Figure S1 and Table S2 show the results of ash #182, and Figure S2 and Table S3 show the results of ash #183. For the dominant sphere particles in ash #182 morphology (Figure S1(c)), EDS result in Table S2 demonstrates that Al, Si and O take up more than 90% of the total weight percentage, indicating this type of particle are mainly consisted of Al and silicon oxides, which is typical of the fly ash composition reported.[24] The other two large particles, which are of irregular shapes, are presented in minor amounts in the fly ash. EDS result shows that the long layered particle (Figure S1(a)) is mainly composed of C (32 wt%) and O (53 wt%). The other large particle (Figure S1(b)) appears to be accumulated clusters of small particles on a crystal surface. As shown in Table S2, it is mainly composed of Al, Si, C, and O. The atomic percentage of C was more than 42% and 9% for the particle in Figure S1 (a) and (b), respectively. Therefore, these two types of large particles were probably generated from the incompletely-fused coal, and the lower content of C and higher content of Al and Si in the latter particle indicates that further agglomeration with coal fly may happened during the formation of the particle in Figure S1(b). It should be noted that trace elements including As, Se, and Mo, were also found in quantifiable amounts on these two large particles. For the trona ash particles shown in Figure S2, particles (a), (b), (c), (e) and (f) were observed in higher frequency in the raw trona ash #183. Figure S2(a) is a large particle with porous substances coated on a solid surface. Chemical analysis shows that the solid surface (EDS #1 of Table S3) is mainly composed of quartz, since Si and O take up to 97% of the total weight. The porous substances (EDS #2 of Table S3) are consisted of Si, Al, C, O, and minor amounts of Na, Mg, Fe, and K. It is probably the fused material of fly ash with minor amount of calcinated trona. The large particle in Figure S2(b) is mainly composed of Na, S, and O (EDS #3 of Table S3), indicating it is the trona and S reaction product, which could be sodium sulfate or sodium sulfite. Due to the high solubility of these sodium compounds, the particle in Figure S2(b) could be easily dissolved upon contact with water. Particle in Figure S2(c) is a crystal agglomerate consist of C, Na, S, Si, Al, and O (EDS #3 of Table S3), and C takes up more than 60% of the total atomic percentage. The chemical composition indicates that this particle is the agglomeration product of incompletely-fused coal with trona-sulfur reaction product. Figure S2(d) is unburned coal, with C taking up to 90% of the total weight. Figure S2(e) is an agglomeration product of trona reaction product (mainly with sulfur), because EDS #6 result shows that it is mainly composed of Na, S, C, and O. Figure S2(f) is a typical fly ash spheres, which resembles that of Figure S1(c) of ash #182. However, the chemical composition shows that the sphere in trona ash (EDS #7-#9) had increased content of Na and C. Comparison of the SEM-EDS results of ash #182 with ash #183 indicates that trona injection generates new agglomerates (particles in Figures S2(a), (b), (c), (e)), which are both physically and chemically different from the conventional fly ash, and even the similar spheres showed higher content of Na in the trona ash.

In both washed ashes #182 (Figure 1(c)) and #183 (Figure (1d)), spheres with particle sizes less than 20 μm are dominant. Comparison between the raw ash and corresponding washed ash images in Figure 1 shows no significant change in the microstructure for ash #182, and all the particles in Figure S1 can still be observed in the washed ash images of #182 (Figure 1(c)). For the trona ash #183, significant amount of fine fraction and some large coalesced fragments disappeared after washing, but some irregularly shaped large agglomerates and porous fragments were still reside in the washed ash. However, these particles occurred with much less frequency than in the raw trona ash (Figure 1(b)). This indicates that a significant amount of the fine spherical particles, micrometer coalesce fragments, and larger microspheres observed in raw trona ash #183 are soluble. In the washed ash #183, particles shown in Figures S2(b) and (e) disappeared, but particles in Figure S2(a), (c), (d) and (f) could still be observed. The porous substance on particles in Figure S2(a) seems to be more solid and the pore become larger after washing. This indicates that agglomerates of trona and sulfur reaction products (Figures S2 (b) and (e)) were soluble, and some other large agglomerates were coated with soluble deposits.

Comparisons of the EDS results (Table 3) of raw and washed ash #182 in Figure 1 show no significant change in the chemical composition, except for a slight decrease in C ratio after washing. However, for ash #183, the percentage of C, Na, and S significantly decreased after washing, while the percentage of other elements increased. This implies that the soluble components of the trona ash are composed of sodium carbonate and sodium sulfate/sulfite.

The above observation demonstrates that trona injection changed the fly ash physical characteristics and chemical composition, including reducing the specific surface area of fly ash, and bring significantly high amount of soluble materials into the trona ash. These changes may result in different leaching behavior of trona ash, and thus will impact the fly ash handling and management options.

3.3. Ash leaching characteristics.

3.3.1 Fly ash pH.

The pH is one of the most important factors determining the leaching behavior of coal fly ash.[8, 25-27] Figure 2 shows the leachate pH of the four ashes at four liquid/solid ratios (L/S =2, 5, 10, and 20) under natural pH. The natural pH of each ash remained nearly constant at different L/S ratios. However, trona injection increased ash pH of plant #1 from 7.6 (control ash) to 11 (trona ash). Trona is strongly alkaline. Discussions in Section 3.1 have indicated that significantly excess amount of trona was injected to capture SO_2. Therefore, the greater pH of trona ash #183 was probably due to the excess trona residual. The pH values of the other two trona ashes from plants #2 and #3 were also in the strong alkaline pH range, with pH values of 13 for ash #258, and 10.6 for ash #259. For these ashes, large amounts of acid may be needed to neutralize the leachate before it could be discharged. Meanwhile, due to the amphoteric characteristics of fly ash particles, more fly ash components may dissolve in these strongly alkaline pH conditions, and cause greater leaching of trace elements of concern.

3.3.2 Leachate TDS.

Figure 2 also shows that TDS of the four ashes generally decreased with the increase of L/S ratio. TDS concentrations of all the three trona ashes are significantly greater than the conventional fly ash #182. For example, at L/S=10, the TDS of #182, #183, #258 and #259 are 285 mg/L, 12,680 mg/L, 12,610 mg/L and 3,710 mg/L, respectively. Converting to dissolved ash weight percentage, at L/S=10, the dissolved ashes were 12.7 %, 12.6 % and 3.7 % for #183, #258 and #259, respectively, while that value was only 0.27 % for control ash #182. This indicates that trona ash has much higher solubility than the conventional fly ash. EPRI's study in 1989 also showed similar trend.[13] It was found that the TDS in the column leaching test was so high even after four months of leaching, and re-crystallization occurred before the sample could be analyzed. It was also reported that sodium sorbent injection resulted in fly ash fluidization at low levels of added moisture, and up to half of the waste may be dissolved when it encounters water.[13]

The high solubility of trona ash could be ascribed to its strong alkaline pH and the high content of sodium compounds, because the high pH results in greater dissolution of fly ash particle, and sodium compounds are generally very soluble. It was reported that dissolved sodium can also disperse other substances therefore fluidize the sodium injection waste.[13] Based on the comparison of EDS results of the raw and washed ashes in Section 3.2, soluble sodium compounds including excess trona and trona–S reaction products are likely the most significant contributors to the elevated TDS in trona ash leachates.

3.3.3 Fluoride, chloride, and sulfate.

F^- is regulated in both the primary and secondary drinking water standards, and the limits are 4 mg/L and 2 mg/L, respectively.[18, 19] The secondary drinking water standard sets the limits for both Cl^- and SO_4^{2-} at 250 mg/L.[19] Figure 2 shows that leaching of all these elements was much higher for the trona ashes than the control ash #182. As a strong alkaline sorbent, trona not only reacts with SO_2 in the flue gas, it also captures some other acidic gases including chlorine and fluorine. The high concentrations of these three anions in trona ash leachates are likely contributed by their soluble sodium compounds, which were generated by the reaction of trona with their corresponding acidic gases.

3.3.4 Barium, beryllium, cadmium, cobalt, copper, iron, lead, manganese, mercury, silver, strontium, thallium and zinc.

Among these 13 cationic elements, concentrations of Be, Cd, Co, Hg, Pb, Ag and Tl from all ash leachates were below or close to the detection limits at all the four L/S ratios, and they were generally well below the limits in the drinking water standards.[18, 19] The low leachate concentrations of these seven elements could be attributed to their low content in the fly ash (Table 2), and the alkaline pHs of these ashes. High pH significantly improved cationic metal uptake due to the increased concentration of deprotonated surface sites, which act as the cationic metal binding sites, and increased concentrations of metal-hydroxide species that are more adsorbable than the free metal ions.[28]

Figure 2 illustrates the results of other cationic elements that are above the method detection limits. It demonstrates that leaching of all these elements were generally decreasing with the increase of L/S ratio, which is typical of an adsorption/desorption controlled leaching process. However, at the natural pHs of the four ashes, Sr, Zn, Cu, Fe and Mn could precipitate with hydroxide, Sr and Ba can also precipitate with sulfate, and all these elements can form precipitates with carbonate. Therefore, co-precipitation may also impact the availability of these elements in the leachate. Calculation of $[Fe] \times [OH]^3$ indicates that Fe is oversaturated in the leachate of #258. Similarly, Ba, Cu, and Zn in all the ash leachates are oversaturated based on the K_{sp} values of their hydroxide compounds. Fe, Ba, Cu, and Zn ions could form soluble complexes with other ligands (such as ammonia), therefore increase the solubility. For these more soluble ions, adsorption/desorption on fly ash surface may play an important role in their leaching.

Leaching of Sr, Fe, and Mn from trona ash #183 was lower than that of the control ash #182. As have been demonstrated earlier, trona ash had greater pH (higher hydroxide concentration) and higher content of soluble carbonate and sulfate (Section 3.2). These anions could facilitate the precipitation of these cationic elements. Therefore, the trona ash #183 leached less amounts of Sr, Fe, and Mn. For the same reason, the leaching of these elements from the other two trona ashes (#258 and #259) was also insignificant. Ba leaching from all ashes was low and without consistent trend. Trona ash #183 leached a greater amount of Cu and Zn than the control ash #182, which was probably caused by the significant dissolution of the trona ash. Leaching of Cu from ash #259 was the highest among the four ashes, while those of ash #258 fell between ashes #182 and #183. Zn concentrations in the leachates of both #258 and #259 were less than those in the leachates of the other two ashes.

3.3.5 Aluminum.

Figure 2 shows Al leaching from all ashes generally decreased with the increase of L/S ratio, except for ash #183, which showed a slightly different trend. Al concentrations in leachates of #182 were close to or below the detection limit, but its concentrations in leachates of the three trona ashes (#183, #258 and #259) at all L/Ss were much higher. Since Al is generally associated with fly ash particles, increased pH enhanced Al dissolution. Based on Al speciation calculation (not shown), at pH>9, which is the case for the three trona ashes, soluble $Al(OH)_4^-$ is the dominant Al species. However, at 5<pH<8, which is the case of #182, $Al(OH)_3$ is dominant species. Therefore, Al dissolution from trona ashes was significant while that from the control ash was limited. Leachate from trona ash #258 had the strongest ash pH, therefore had the highest Al concentration. At L/S=2, the Al concentration was more than 1,851 mg/L. Leachate pH of ash #183 was slightly higher than that of ash #259, however the soluble Al concentration was slightly lower. Since ash #183 had the highest level of sulfate, secondary mineralization of Al with sulfate and calcium may form ettringite,[29] resulting in relatively less leaching of Al from #183. The formation of ettringite could also resulted in the increased leaching of Al as the L/S ratio increases, because at high L/S ratios, the leachate is more diluted, and the secondary mineralization effect would be reduced.

3.3.6 Arsenic, chromium, molybdenum, antimony, selenium and vanadium.

Oxyanions including As, Cr (could also be a cation), Mo, Sb, Se, and V have drawn increased interest due to their potential carcinogenic effects.[18-20] As, Cr, Sb, and Se are regulated on the primary drinking water standard, and the MCLs are 0.01 mg/L, 0.1 mg/L, 0.006 mg/L and 0.05 mg/L, respectively.[18] V and Mo are on the drinking water contaminant candidate list CCL3, and California has set a notification level of 0.05 mg/L for V for the state.[20, 30] Figure 2 demonstrates that leaching of these elements from all ashes generally decreased with the increase of L/S ratio, indicating an adsorption/desorption controlled leaching mechanism as reported in earlier studies. [25-27, 31]

Figure 2 demonstrates that the trona ash (#183) leached much larger quantities of all these oxyanions than the control (#182). Take leachate composition at L/S=10 for example, As concentration increased from 0.094 mg/L in the control ash leachate to 3.319 mg/L in the trona ash leachate, while Cr increased from 0.002 mg/L to 0.069 mg/L, Mo increased slightly from 0.473 mg/L to 0.498 mg/L (or at the same level), Sb increased from 0.046 mg/L to 0.096 mg/L, Se increased from 0.005 mg/L to 1.611 mg/L, and V increased from 0.115 mg/L to 1.218 mg/L. High Se leaching was also reported in EPRI's earlier study where column leaching test with neutral water was performed on an individual trona ash.[13] Comparing the leachate As concentration at L/S ratio=10 with the total As content in the fly ash (Table 2) for the paired samples, 1.5% of the total As was leached from the control ash #182, while 83% of the total As was leached from the trona ash #183. Similarly, the leached Cr, Mo, Sb, Se and V from the control ash #182 were 0.02%, 46.2%, 7.2%, 21.4% and 0.5%, respectively, while for the corresponding trona ash #183, these values were 0.7%, 73.1%, 21.7%, 96.4% and 4.8%, respectively. These comparisons indicate that trona fly ash has significantly enhanced mobility all these six oxyanions, and particularly in the case of As and Se.

Multiple reasons could enhance the leaching of these oxyanions. Previous leaching studies using bituminous coal fly ashes reported that the leaching of oxyanions increases as the pH increases from 7 to12.[26, 27, 31] This behavior may contribute to the enhanced leaching of As, Cr, Mo, Sb, Se ,and V in trona ash #183 compared to control ash #182, where the ash pH was increased from 7.5 (#182) to 11 (#183). In addition, Table 3 shows that trona ash #183 had much less specific surface area, therefore the total surface adsorption sites could be much less than the control ash. This may also contribute to the enhanced leaching of these elements. Moreover, As, V, Cr, As, and Mo, together with sulfate and phosphate, have been reported to compete for adsorption onto various sorbent.[32, 33] Sb has very similar chemistry properties with that of As, and could be impacted by the same competitive adsorption effect as As.[34] EDS results of the raw and washed ashes in Table 3, and the leaching profiles in Figure 2 have demonstrated that #183 had much higher content of competing anions, which may significantly contribute to the enhanced leaching of these oxyanions of concern. The high solubility of the trona ash as discussed earlier may also greatly contribute to the significant increase in the leaching of trace oxyanions from trona ash.

Concentrations of the six oxyanions in the leachates of the three trona ashes generally follow the order of #183 > #258 > #259. However, ash #258 leached the highest concentrations of Cr and V. Besides the factors discussion above, the greater dissolution of this ash and the higher ash pH (pH=13.2), could have contributed to the high Cr and V concentrations in the leachate. The concentrations of As, Se, and Sb in all trona ash leachates are significantly greater than the MCLs in the primary drinking water standard, and Cr from #258 is also much greater than 0.1 mg/L (MCL) at all L/S ratios. Therefore, avoiding water contact is important in the safe management of trona ash.

4. Conclusions

Compared to control ash, trona ash has less specific surface area, different fly ash morphology, much greater solubility, and higher leachate pH. The leaching of cationic elements of concern, including Ag, Be, Cd, Co, Hg, Mn, Pb, Sr, and Tl either decreased or not detectable after trona injection. However, the leaching of major oxyanions of concern, especially As and Se, significantly increased after the trona injection. Many factors, including the elevated pH, reduced specific surface area, increased concentrations of other competing anions, and increased solubility of the trona ash could contribute to the enhance leaching of oxyanions of concern

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Table 1. Fly ash samples and chemical composition of major elements.

Ash Information			Chemical composition determined with XRF (wt%)											
Ash ID	**Ash Type**	**Plant ID**	**Al**	**Si**	**Ca**	**Fe**	**Mg**	**Na**	**S**	**Ba**	**Sr**	**Ti**	**Cl**	**P**
#182	Control	#1	12.60	26.73	0.64	4.86	ND	0.20	0.17	0.07	0.30	0.87	0.03	0.19
#183	Trona	#1	10.22	22.28	0.60	4.25	ND	2.87	1.76	0.03	0.26	0.75	0.31	ND
#258	Trona	#2	6.73	15.80	9.29	3.47	0.84	NM	2.38	0.55	1.32	0.73	0.16	0.37
#259	Trona	#3	4.59	12.29	1.62	2.60	ND	NM	2.16	0.03	0.78	0.51	0.39	0.34

Control - sample collected when trona was not injected;

Trona - sample collected during trona testing (trona ash);

ND- not detectable;

NM- not measured.

Table 2. Total composition of trace elements of concern (mg/kg ash) in ashes #182 and #183.

Ash ID	Ag	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Pb	Sb	Se	Tl	V	Zn
#182	1.0	63.5	20.2	0.7	35.2	92.7	131.4	103.3	10.2	62.6	6.4	0.2	3.3	235.7	93.3
#183	0.9	39.9	15.9	0.5	26.7	104.5	102.4	83.7	6.8	45.8	4.5	15.4	2.4	254.9	91.1

Table 3. Specific surface area and EDS spectrum results for ashes #182 and #183.

Ash ID		BET (m^2/g)	O wt %	C	Si	Al	K	Fe	Mg	Na	S	Ca	Ti
#182	Raw	8.9	52.2	10.2	17.3	12.2	2.3	3.2	0.8	0.4	ND	ND	0.8
	Washed	10	53.0	9.2	17.5	12.4	2.3	3.4	0.7	0.5	ND	ND	0.8
#183	Raw	4.3	50.3	19.7	11.7	8.1	1.5	2.4	0.5	4.3	1.5	ND	ND
	Washed	4.7	51.7	16.9	14.3	10.1	1.8	2.6	0.7	0.6	0.3	0.5	0.6

Weight percentage (wt%).

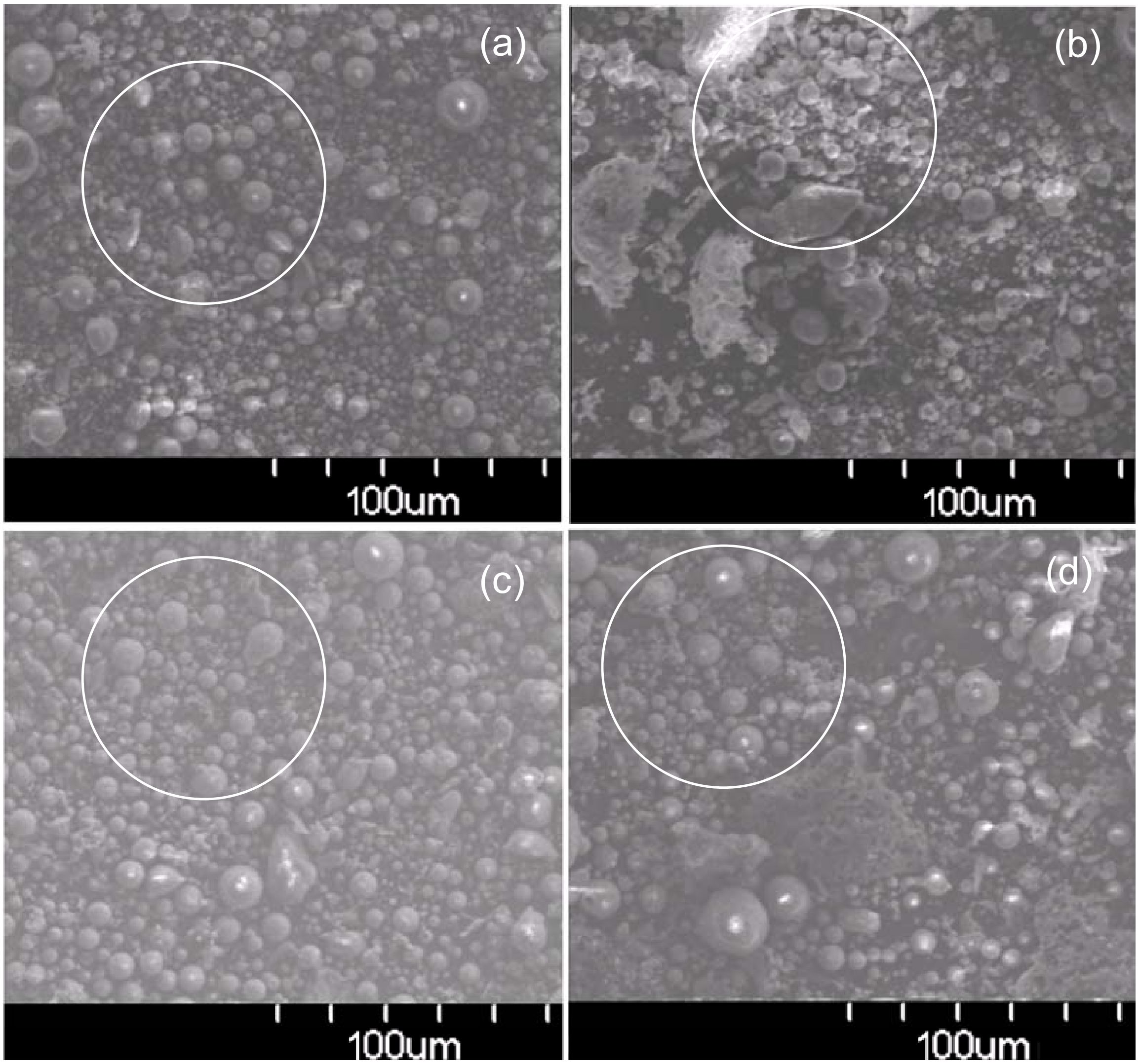

Figure 1. SEM images of paired samples at original magnification of 250X. (a) and (b) are raw ashes #182 and #183, (c) and (d) are washed ashes #182 and #183, respectively. The circled areas indicate the position of EDS analysis.

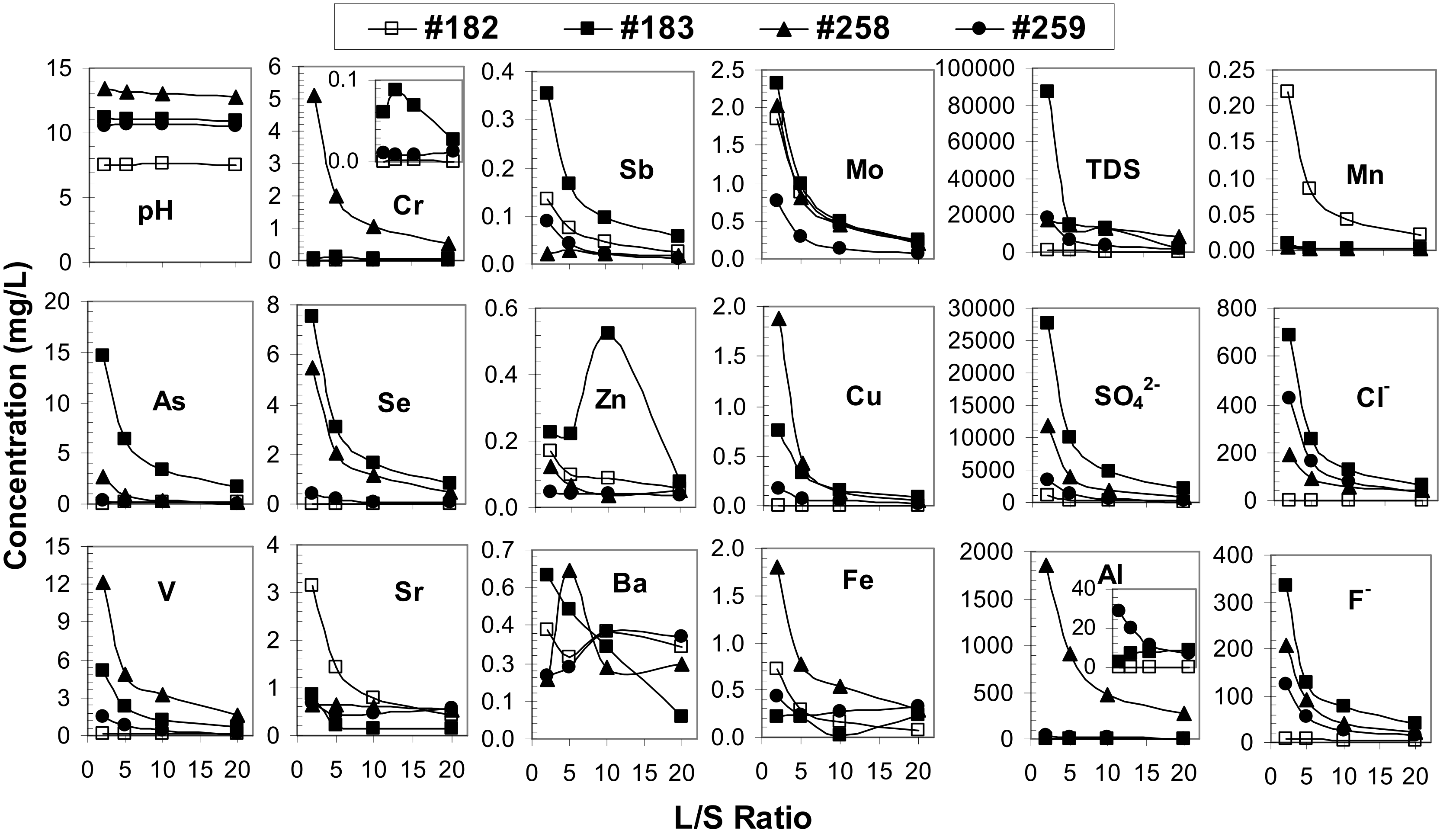

Figure 2. Natural leaching results of ashes #182, #183, #258 and #259. Concentrations of Tl, Pb, Be, Cd, Co, Ag, and Hg are below or close to the detection limit for all 4 ashes. Experimental conditions: temperature = 21 oC; leaching time = 24 hours.

Supporting Information:

Table S1. Microwave assisted acid digestion procedure.

Method	**Sample weight**	**Acid**	**Microwave procedure**
Complete Digestion	0.1 g	HNO_3 9mL HCl 3mL HF 3mL	Temperature 240°C Ramp Time 10min Hold Time 30min
EPA 3051A[15]	0.1 g	HNO_3 9mL HCl 3mL	Temperature 175°C Ramp Time 5.5 min Hold Time 4.5min

Table S2. Summarized EDS spectrum results for raw ash #182 in Figure S1, unit is in wt%.

EDS#	**O**	**Al**	**Si**	**C**	**K**	**Fe**	**Mg**	**Se**	**Cl**	**Mo**	**As**
1	53.06	1.6	2.2	32.11				1.6	1.1	2.8	0.9
2	51.54	16.3	16.1	5.56	2.0	1.9		1.3		1.3	
3	60.65	21.0	10.7	1.27	3.0	2.3	1.1				

Table S3. Summarized EDS spectrum results for raw ash #183 in Figure S2, unit is in wt%.

EDS#	**O**	**Si**	**Al**	**C**	**Na**	**S**	**K**	**Mg**	**Mo**	**Fe**	**Se**	**Sb**
1	61.54	36.0	1.1	1.38								
2	52.4	18.6	14.6	4.2	2.1		1.0	3.53		2.2		
3	50.8			1.5	32.4	8.9			1.9		0.6	0.6
4	32.61	3.0	2.3	50.16	8.8	3.2						
5		7.3	2.8	89.87								
6	53.58		0.6	3.44	31.6	10.7						
7	56.0	18.1	10.6	2.5	1.3		2.4	1.5	2.3	1.5	1.3	
8	60.7	21.2	13.6	1.7			2.8					
9	60.3	17.0	11.6	3.7	1.6		1.9	1.43		2.4		

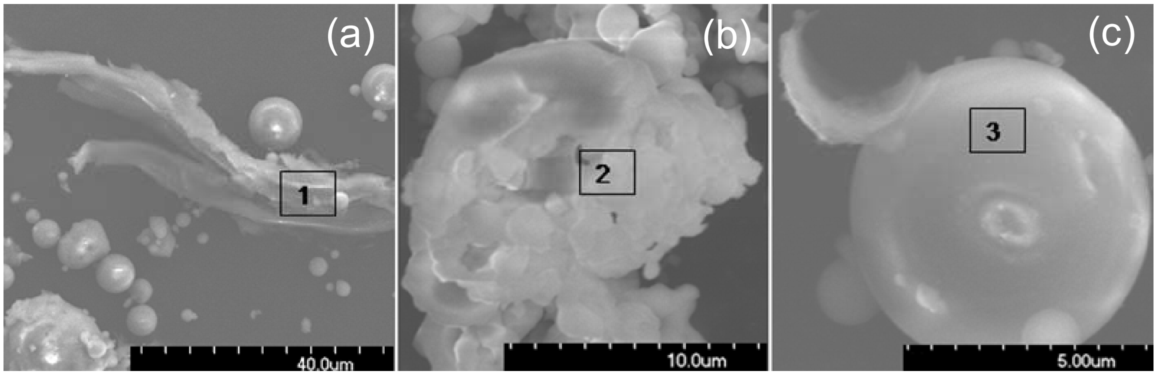

Figure S1. SEM images of particles from raw ash #182 at higher magnifications. The magnifications of (a), (b) and (c) are 1300x, 5000x and 10000x, respectively. The numbered areas indicate the positions of EDS analysis.

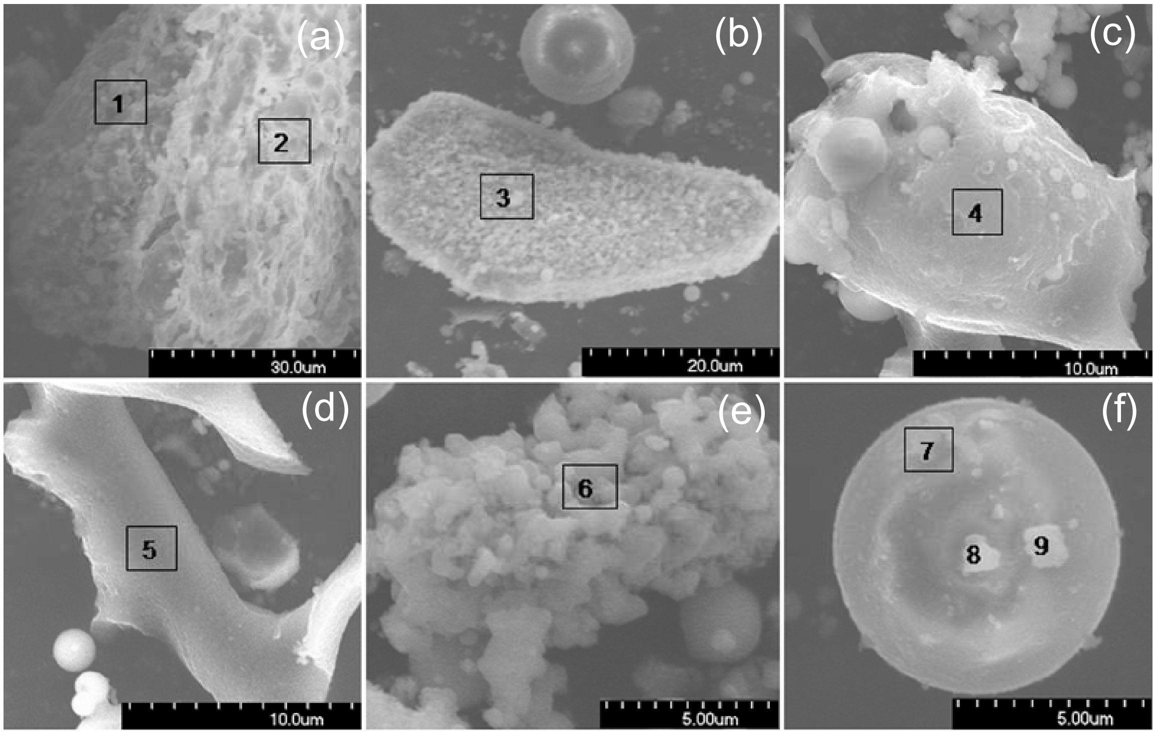

Figure S2. SEM images of particles from raw ash #183 at higher magnification. The magnifications of (a), (b), (c), (d), (e) and (f) are 1490x, 2000x, 5000x, 5000x, 7000x and 8000x, respectively. The numbered areas indicate the positions of EDS analysis.

SECTION III

UNDERSTANDING THE ENHANCED ARSENIC AND SELENIUM LEACHING BEHAVIOR OF TRONA ASH GENERATED FROM A SO_2 CONTROL PLANT

ABSTRACT

Arsenic (As) and selenium (Se) are two important elements regulated by EPA drinking water regulations, and their leaching from coal fly ash could impair groundwater quality. Our previous study indicated that the trona-based SO_2 control process significantly enhanced leaching of As and Se from coal fly ash under natural conditions. This study presents detailed information relating to As and Se leaching from trona ash. Bach leaching methods were used for both equilibrium and kinetic studies. The results demonstrated that multiple factors contributed to the enhanced As and Se leaching from trona ash, including more alkaline pH, greater ash solubility, reduced surface site density, presence of high concentrations of competing anions (such as sulfate and carbonate), increased background concentration of Se, and a greater Se(VI) fraction in the trona ash. Leaching data also showed that As(V) was the only species in both fresh and stored trona ashes, while Se(IV) was gradually converted to more leachable Se(VI) with increases in storage time and leaching time.

KEYWORDS

Trona ash; arsenic; selenium; speciation; leaching

1. Introduction

As the prices of pollution credits continue to rise under the cap and trade program, many coal fired power plants are implementing SO_2 control as part of the business decision. Trona ($Na_3HCO_3CO_3 \bullet 2H_2O$) is a strongly alkaline sorbent, which can be injected into the flue gas at coal fired power plants to control SO_2 emission. It was reported that trona injection can remove 70-90% of the sulfur in flue gas. However, trona injection could significantly increase fly ash production.[1] Coal fly ash, which accounts for about 60% of the 126 million short tons (1.14×10^{11} kg) of coal combustion by-products, may be subject to a new national rule on coal ash disposal and management in the future.[2, 3] The primary concern in the disposal and beneficial use of fly ash has been the leachability of trace elements that may contaminate soil and groundwater.

Extensive leaching studies have been carried out on conventional coal fly ashes. However, very limited information is available on the characterization of ashes generated from plants employing trona injection to control SO_2 emission (e.g., trona ash). [4] We have conducted a screening study using a set of paired samples generated from a power plant, with and without trona injection. In the screening study, 25 inorganic elements/constituents, all of which are listed in the national drinking water standards, were analyzed in leachates of the trona ash and the corresponding control ash (conventional ash without trona injection). These leachates were generated under natural pH conditions. The results demonstrated that trona ash had significantly higher leachability of most anionic elements, especially As and Se. Two other trona ashes were studied by us recently (data not shown) and another trona ash was studied by EPRI in 1989, [4] all the data demonstrated that As and Se leaching from these trona ashes were significant, even with neutral water leachant (e.g., DI water). Because As and Se have very low maximum contaminant levels (MCL) in the primary drinking water standard,[5-12] understanding the enhanced leaching behavior of As and Se from trona ash is very significant in assessing the potential environmental impact of fly ashes generated from power plants employing the trona-injection process. Further, this information is necessary for developing sustainable strategies at power plants on both SO_2 control options and fly ash management/disposal methods.

The leaching of As and Se from fly ash is affected by fly ash physical and chemical characteristics, pH, liquid-to-solid (L/S) ratio, leaching time, speciation of As and Se, and presence of competing anions such as sulfate. [5, 6, 9-19] Meanwhile, the speciation of As and Se may change during the storage or leaching, which further changes their leaching characteristics. The objectives of this study were to (1) investigate the impact of different conditions, such as pH, L/S ratio, presence of competing anions, storage time, and leaching time on the leaching of As and Se from trona ash; and (2) determine the As and Se speciation in the trona ash leachate, and the impact of storage or leaching time on the speciation. A conventional ash collected from the same location right before trona injection was used as a control for comparison.

2. Experimental Section

2.1. Fly ash samples. .

Table 1 shows the fly ash physical and chemical information Samples #182 and #183 are paired samples collected from a power plant burning bituminous coal. Sample #182 was a conventional ash collected before trona injection (control sample), while sample #183 was the trona ash. Trona was injected into the boiler at a rate of 13 to 51 lbs per hour per megawatt during SO_2 control testing. The specific surface area (BET) of raw trona ash #183 was about half that of control ash #182. Compared to the control ash, the trona ash contained lower amounts of typical fly ash constituents (e.g., Al, Si) listed in Table 1, and higher amounts of LOI (Loss-on-Ignition, an indicator of carbon content), Na, S, and Se. This is because excess trona and trona reaction products decreased the conventional fly ash content, and increased the amount of Na, S, and C in the trona ash. Previous studies demonstrated that the increased Na, S and C are likely sodium sulfate and carbonate, which are readily soluble upon contact with water. [1, 4]

While this study was focused on the leaching of As and Se from raw ash samples, washed ash samples were also studied for surface site characterization. Ash washing was performed using deionized (DI) water at a L/S ratio of 5 (200 g/L) following an established method by Wang et al.[9, 11]

2.2. Reagents and chemicals.

DI water (18.2 MΩ-cm at 25°C) was used throughout this research. A multiple trace elements standard with 100 mg/L As and Se was purchased from PerkinElmer (Waltham, Massachusetts, USA). Monosodium acid methane arsonate sesquihydrate (MMA) and arsenobetaine (AsB) were purchased from Sigma Aldrich. Cacodylic acid (DMA) and 1000 mg/L Se(IV) standard were purchased from Fisher Scientific. Individual standard solutions of 1000 mg/L As(III), As(V), and Se(VI) were purchased from SPEX CertiPrep. HPLC grade ammonium phosphate (monobasic), trace metal grade nitric acid, high purity ammonium hydroxide, HPLC grade methanol, certified grade sodium hydroxide stock solutions (1 N and 10 N), sodium sulfate, and sodium carbonate were also purchased from Fisher Scientific. During speciation analysis, a 20 mg/L intermediate standard (including all As and Se species) was made from the corresponding 1000 mg/L standard solutions. Calibration standards (5, 20, 50, and 100 μg/L) were freshly prepared by serial dilution of the intermediate standards with mobile phase A (see Table 2). The mobile phases were filtered with a 0.22 μm membrane filter, and then sonicated before use.

2.3. Analytical method.

An Orion pH meter (perpHecT LoR model 370) equipped with an Orion PerpHecT Triode pH electrode (model 9207BN) was used for pH measurements. Concentrations of total As and Se in all leachate samples were analyzed using a Perkin-Elmer Elan DRCe ICP-MS (PerkinElmer SCIEX, Concord, Ontario., Canada) according to EPA Method 200.8.[20] Five As species and two Se species, including AsB, As(III), As(V), DMA, MMA, Se(IV), and Se(VI), were analyzed in leachates from ash #182 and ash #183, using a PerkinElmer 200 Series high performance liquid chromatography (HPLC) coupled with the ICP-MS system. The speciation analysis was carried out in both years 2007 and 2010. An isocratic method (published by Wang et al.) was used in the year 2007, with a Hamilton PRP-X100 (4.1 × 150 mm, 3 μm particle size) anion-exchange column. [5] That column was clogged and the same product had been phased out of the market. A new gradient method (developed by the authors) was used for the analysis in the year 2010. Table 2 summarizes the details of the gradient method. Both methods were able to simultaneously detect five As species and two Se species. The chromatography of the gradient method was presented in Figure S1 of the Supporting Information. For all samples quantified for As and Se speciation with HPLC-ICP-MS, the total concentrations of different As and Se species were in generally good agreement with the total As and Se concentrations determined with ICP-MS only, except very few samples that had As and Se concentrations that were close to the detection limit. Spiking recovery was between 85% and 115% for all analyses.

2.4. Batch leaching experiment.

Three types of batch leaching experiments were conducted in this study using a series of 125 mL LDPE bottles. The Type I experiment was to determine the leaching of As and Se under different pH conditions. The Type II experiment was to determine the impact of sulfate and carbonate on the leaching of As and Se from fly ash. The Type III experiment was to determine the leaching rate and speciation of As and Se. Type I and Type III experiments were conducted for both the control ash #182 and the trona ash #183, while the Type II experiment was only conducted with the control ash #182. Both Type I and Type III experiments used DI water, under two L/S ratios, i.e., 10:1 and 20:1. Type II experiments used stock solutions of 46 mM sodium sulfate or 23 mM sodium carbonate, with a L/S ratio of 10:1.

Take the batch leaching experiment at L/S = 10:1, for example: 10 g ash and 100 mL DI water or stock solution were added to each of the series of bottles. For Type I and Type II experiments, 6-10 bottles were prepared for each L/S ratio, and stock solutions of HNO_3 and NaOH were used to adjust the pH of the series of bottles to cover a pH range of 2-12. For the Type III experiment, six bottles were used for each batch, corresponding to six leaching times, 4, 12, 24, 48, 120, and 720 hours. The pH of the Type III experiment was not adjusted (natural leaching). The bottles were then sealed and shaken at 180 oscillations/min on an EBERBACH 6010 shaker. The leaching time was 24 hours for the Type I and Type II experiments. The shaker was then stopped after a pre-selected leaching time and supernatants were collected and filtered through 0.22 μm syringe filters. The final pH in the remaining slurry was measured and recorded. Nitric acid (1%) was used to preserve the samples for total As and Se determination on ICP-MS. The samples for speciation analysis were not acidified but were refrigerated immediately after sampling, and analyzed on the HPLC-ICP-MS as soon as possible.

3. Results and Discussion

3.1. Fly ash surface site characterization.

Adsorption/desorption have been reported to be a controlling mechanism in As and Se leaching from bituminous coal ashes.[5, 6, 9, 11, 21-24] Therefore, surface site characterization is important in determining the leaching of As and Se from ashes #182 and #183. A batch acidimetric–alkalimetric titration method was employed to quantify the surface site density and acidity constant of the washed ashes #182 and #183. [25, 26] Two L/S ratios, 10:1 and 20:1 for ash #182, and 10:1 and 100:1 for ash #183, were used in this study. Symbols in Figure S2 (Supporting Information) show the net titration data, which are the differences between the overall acid/base consumption by the ash slurry and that by water only. The solid curves are curve fitting results using an equation developed by Wang et al. [25, 26] Table 3 shows the values of constants obtained through curve fitting - the surface site density and acidity constant. It demonstrates that there are three types of acid sites for both ashes, with similar acidity constants (pK_H) of 4, 7, and 10.6 for site S_1, S_2 and S_3, respectively. While the estimated values of the surface site densities have relatively large error, they still indicate that trona ash has significantly less surface sites than the control ash does. Therefore, less As and Se would be constrained on the trona ash surface than there would be on the control ash surface.

3.2. Impact of pH on As and Se leaching.

The speciation of As, Se, fly ash surface sites, and the dissolution of fly ash are pH dependent. Therefore, pH is one of the most important factors determining the leaching of As and Se from fly ash. [9, 11, 27, 28] Figure 1 shows the leaching of As and Se from both ashes over pH 2-12, for L/S of 10:1 and 20:1. Figures 1(a) and 1(b) demonstrate that As leaching from both ashes decreased with the increase of pH in the very acidic pH range, reached a minimal level, and then increased with the increase of pH in the alkaline pH range. Se leaching from the control ash #182 (Figure 1(c)) followed the same trend as that of As over pH 2-12, but Se leaching from #183 (Figure 1(d)) generally increased with the increase of pH. As leaching was minimal between pH 3-7.5 and pH 4-6 for ashes #182 and #183, respectively, while Se leaching was minimal between pH 4.5-7 for ash #182. There was no minimal pH of Se for ash #183. For the entire pH range studied, the maximal leaching of both As and Se from the two ashes occurred at the most alkaline pH (close to pH 12). Figure 1 demonstrates that, in general, the leaching of As and Se from the trona ash was greater for L/S 10:1 than for L/S 20:1, which is consistent with earlier findings. [5] However, the leaching curves for the control ash under two L/S ratios almost overlapped. The As and Se leaching profiles as a function of the pH and L/S ratio, are typical of an adsorption/desorption controlled process. Since all As and Se species are soluble over pH 2-12, there would not be a minimum leaching pH range if no adsorption occurred.

Figure 1 also demonstrates that, over pH 2-12, As and Se leaching from trona ash was significantly greater than that from the control ash #182. Table 1 shows that the total As content of trona ash #183 was about the same as that of control ash #182. Therefore, the greater As leaching from trona ash indicates that As was more mobile after trona addition. Meanwhile, the total Se content of ashes #182 and #183 was 0.0006% (6 mg/kg) and 0.003% (30 mg/kg), respectively. Therefore, trona injection enhanced Se capture from the flue gas. According to the data in Figure 1, at L/S 10:1, the maximal leachate Se concentration of control ash #182 was 26 μg/L (0.26 mg/kg), while the minimal leachate Se concentration of #183 was 1123 μg/L (11.23 mg/kg). Therefore, the maximal leached Se was 4% for the control ash #182, while the minimal leached Se from trona ash #183 was 37%. This demonstrates that Se was also significantly more mobile in the trona ash than in the control ash.

As indicated in Figure 1, As and Se are significantly more leachable from trona ash than from the control, and have a narrower minimal leaching pH range. One of the major reasons is that trona ash has significantly less surface sites (therefore less adsorption capacity) than the control ash does. Previous studies have demonstrated that increasing surface loading narrows the maximal adsorption plateaus of As and Se, corresponding to a narrow minimal leaching pH range in this study. [27, 28] Other important reasons are that trona ash has greater solubility, and a higher content of sulfate and carbonate that may compete with As and Se for adsorption sites on the ash surface. As demonstrated in Figure S3 in the Supporting Information, concentrations of total dissolved solids (TDS), sulfate, and total inorganic carbon (TIC) in the leachate of trona ash #183 were significantly greater than that of control ash #182. The impact of sulfate and carbonate on the leaching of As and Se will be discussed in the next section.

The MCLs of As and Se in the primary drinking water standard are 10 µg/L and 50 µg/L, respectively. [7] Figure 1 demonstrates that concentrations of As and Se in leachates of trona ash #183 were significantly higher than 10 µg/L and 50 µg/L, respectively, over pH 2-12. Beyond the minimal leaching pH range of 3-7.5, the concentrations of As in the leachates of the control ash were also significantly greater than 10 µg/L. Se leaching from the control ash was below the MCL of 50 µg/L over pH 2-12. At a L/S of 10:1, the maximal leachate concentrations of As and Se were 5253 µg/L and 2264 µg/L, respectively, for trona ash, and 3084 µg/L and 26 µg/L, respectively, for control ash.

3.3. Impact of sulfate and carbonate on As and Se leaching.

Sulfate and inorganic carbon (in carbonate and bicarbonate form) are anions that may compete with As and Se for the same adsorption sites. [29-37] Figure S3 demonstrates that sulfate concentrations were almost constant over pH 2-12 for both ashes, with approximately 4622 mg/L for trona ash, and approximately 162 mg/L for control ash. Concentrations of TIC in leachates increased with the increase of pH, and the maximal TIC was 1412 mg/L for trona ash and 4.5 mg/L for control ash. Based on the speciation of carbonic acid ($pK_{a1} = 6.4$ and $pK_{a2} = 10.3$), carbonate ion (CO_3^{2-}) is the major inorganic carbon species for these maximal TIC pH points. Based on the data in Figure S3, at L/S 10:1, the differences between the leachates of trona ash #183 and control ash #182 are 4460 mg/L of sulfate (46 mM), and a maximal 1421 mg/L of TIC (23 mM carbonate).

To evaluate the impact of sulfate and carbonate on As and Se leaching, batch leaching experiments using stock solutions of 46 mM sodium sulfate and 23 mM sodium carbonate as leachants were carried out for control ash #182. Figure 2 compares the leaching results of As and

Se from control ash #182 with and without the addition of sulfate/carbonate, plus the leaching data from the trona ash. It demonstrates that spiking of 46 mM sulfate or 23 mM carbonate significantly increased the leaching of both As and Se from the control ash. This confirms that the larger amount of sulfate and inorganic carbon in trona ash have contributed to the greater leaching of As and Se. Figure 2 also demonstrates that 23 mM carbonate increased As leaching more significantly, while 46 mM sulfate increased Se leaching more significantly. This indicates that carbonate is more competitive than sulfate in releasing As, while the increased sulfate may have played a more important role than carbonate in releasing Se from the trona ash. It should be noted that neither the spiked 46 mM sulfate, nor the spiked 23 mM carbonate increased the As and Se leaching from the control ash to the same levels as those of the trona ash. Therefore, the significantly greater leaching of As and Se from the trona ash could also be attributed to some other factors, such as the much smaller surface site density, greater ash solubility, and more availability of Se in the trona ash.

3.4. Impact of leaching time on As and Se leaching

3.4.1. Total As and Se.

The impacts of leaching time on As and Se release and speciation were investigated under natural pH conditions (e.g., without pH adjustment). Figure 3 demonstrates the pH and total As and Se in the leachates of both ashes over leaching times of between 4 to 720 hours. Figures 3(a) and 3(d) demonstrate that, despite the changes in leaching time and L/S ratio, the leachate pH of the control ash remained at around 7.7, and those of the trona ash remained at about 11. Figures 3(b) and 3(c) demonstrate that As and Se leaching from the control ash increased significantly in the first 48 hours. The increase then slowed down and reached equilibrium at around 240 hours. In addition, As and Se leaching curves from the control ash were almost the same for L/S 10:1 and L/S 20:1 in the first 24 hours. After 24 hours, the concentrations of both elements were generally higher in the L/S of 10:1 batch than in the L/S of 20:1 batch.

Figures 3(e) and 3(f) demonstrate that the leaching rate of As and Se from the trona ash is very fast within the first few hours, and then slowed down with the increase of leaching time before reaching the maximal value at around 240 hours. However, concentrations of As and Se in leachates of the trona ash decreased slightly with the further increase in leaching time. Results also show that concentrations of both As and Se in the L/S 10:1 batch were about twice those in the L/S 20:1 batch. For example, at 240 hours, the As concentrations in the L/S 10:1 and 20:1

batches were 3665 μg/L and 1847 μg/L, respectively, while the Se concentrations were 1798 μg/L and 826 μg/L, respectively. The proportional leaching of As and Se, as a function of ash concentration, indicates that these two elements are readily releasable from the trona ash.

Figure 3 also demonstrates that concentrations of both As and Se in the leachate of trona ash were hundred times greater than their corresponding MCLs. For example, at L/S 10:1, the maximal As and Se concentrations were 3665 μg/L and 1798 μg/L, respectively. The maximal concentration of As in the control ash was 188 μg/L, exceeding the 10 μg/L MCL in a much smaller magnitude than that of the trona ash. The concentration of Se in the control ash #182 leachate was below the MCL of 50 μg/L for all conditions.

3.4.2 As and Se speciation.

Figure 4 shows the detectable As and Se species in samples shown in Figure 3. Consistent with the literature, [5, 38-40] only inorganic As and Se species were detected in the leachates of these two ashes. They were As(III), As(V), and Se(IV) for control ash #182, and As(V), Se(IV) and Se(VI) for trona ash #183. More oxidized forms of As (As(V)) and Se (Se(VI)), were presented in larger ratios in the trona ash than in the control ash. Concentrations of both As(III) and Se(IV) in the leachate of the control ash were less than 10 μg/L, which is close to or below the detection limit after dilution. Figure 4(a) demonstrates that As(III) only existed in a short period of time during leaching, and became undetectable when leaching time was more than 24 hours. The decreased As(III) concentration is probably due to the oxidation of As(III) into As(V), since As(V) is a more stable species than As(III) in aqueous solutions, [5, 41] and its concentration increased with the increase in leaching time. Concentrations of As(V) and Se(IV) in control ash #182 generally increased with the increase in leaching time, and followed the same trend as the leaching of total As and Se (Figure 3). Leaching of As(V) from trona ash generally followed the same trend as the total As leaching shown in Figure 3(e). The concentrations of Se(IV) in trona ash leachates decreased with an increase in leaching time before reaching a constant level at 240 hours, while the concentration of Se(VI) increased with the increase of leaching time over 4 - 120 hours, reached a peak at 120 hours, and then decreased slightly and reached a constant level at 240 hours. Comparison of Figures 4(e) and 4(f) shows that, Se(IV) was the dominant Se species in the leachate of trona ash for the first 48 hours. After 48 hours, Se(VI) became the dominant species. This implies that the released Se(IV) was oxidized to Se(VI) as the leaching time increased.

Consistent with the leaching result in Figure 3, all detectable As and Se species in leachates of both ashes were higher in the L/S = 10:1 batch than in the L/S=20:1 batch, except for some discrepancy in the leaching of Se(IV) from the control ash. This could be attributed to the analytical variance due to the low concentration after needed dilution for speciation analysis. For the control ash, concentrations of As and Se species in L/S = 10:1 leachates were only slightly higher than those in L/S = 20:1 leachates. However, for the trona ash, concentrations of As and Se species in L/S = 10:1 leachates were almost twice those in L/S = 20:1 leachates. For example, at 240 hours, concentrations of As(V), Se(IV), and Se(VI) at L/S 10:1 were 3276 μg/L, 618 μg/L, and 757 μg/L, respectively; while these values for L/S 20:1 were 1672 μg/L, 306 μg/L, and 331 μg/L, respectively. This is consistent with the trends of total As and Se leaching from the trona ash, which were proportional to the ash concentration. Compared to the leaching results of control ash (Figure 4(a)-(c)), trona ash (Figure 4(d)-(f)) consistently leached significantly greater amounts of As(V), Se(IV), and Se(VI) over the entire leaching time period.

The pH, ash surface site density, ash solubility, and loading of competing adsorbate are major factors impacting the release of As and Se. Based on the impact of pH on As and Se leaching, demonstrated in Section 3.2 and previous reports, [5, 6, 9, 14, 17, 19] the trona injection increased ash leachate pH from 7.7 to 11, should have significantly contributed to the greater release of As and Se species. Meanwhile, Se(VI) has a much weaker affinity than Se(IV) on fly ash. [5, 11, 42, 43] The greater Se(VI)/Se(IV) ratio in the trona ash leachate also contributed to the greater release of Se from trona ash. In summary, the greater leaching of As and Se from trona ash than from control ash could be attributed to a number of reasons, including the increased ash pH, increased concentration of competing adsorbates, fewer adsorption sites, and greater solubility of the trona ash. In the case of Se (besides the above factors), the higher Se content in the trona ash and the larger fraction of Se(IV) also contributed to the greater release of Se.

3.5. Impact of storage time on As and Se leaching.

All of the above results were generated in the year 2007. After being kept in the original container (with the bucket cap on, but no air proof seal) for 3 years in the laboratory, As and Se speciation in both ashes #182 and #183 was analyzed again in the year 2010, under the same natural pH leaching condition. One-day and 6-day leaching experiments were carried out this time, and the results at L/S 2:1 and 5:1 were compared. Figures 3 and 4 show that the leaching of all As and Se species from ashes #182 and #183 almost equilibrated after 5 days. Therefore, the

6-day leaching data for the year 2010 can be considered as parallel to the 5-day leaching data for the year 2007. New data indicate that, for each ash, the leachate pH was still independent of the L/S ratio and the leaching time. However, the leachate pH for the control ash decreased from 7.7 in 2007 to 7.0 in 2010. For the trona ash, however, the leachate pH remained at around pH 11 for both 2007 and 2010. The reduced pH of the control ash #182 can possibly be contributed to the carbon dioxide in the air, which could slowly react with calcium in the ash. In the case of trona ash, the high carbonate concentration in the ash may have resisted the uptake of carbon dioxide from the air.

Figure 5 compares the leaching results of As and Se for control ash #182 in 2007 and in 2010, and Figure 6 compares the leaching results for trona ash #183. Only inorganic As and Se species were detected in all leachates. The total concentrations of different As and Se species generally agreed with their corresponding total concentrations, except for the Se results of control ash #182. The total concentrations of Se species in control ash leachates (Figures 5(e) and 5(f)) were lower than the total Se concentration (Figure 5(d)). This is because Se concentrations were below the quantification limit of the speciation method after needed dilution. Therefore, the data shown in Figures 5(e) and 5(f) are best applied to understand the relative magnitude of Se(IV) and Se(VI) in the control ash.

Figures 5(a) and 5(d) demonstrate that 3 years' storage time decreased the As leaching while Se leaching from the control ash increased. Figures 5(b) and 5(c) demonstrate that both As(III) and As(V) were present in the 1-day leachates of control ash #182, but only As(V) was detected in the 5-day or 6-day leachates. Therefore, As(III) was converted to As(V) during the leaching. Figures 5(e) and 5(f) demonstrate that Se speciation of control ash changed from Se(IV) in the year 2007 and to Se(VI) in the year 2010. Since Se(VI) is less adsorbable, the total Se leaching increased after 3 years of storage.

For the trona ash, Figures 6(a) and 6(d) demonstrate that 3 years of storage time increased leaching of both As and Se. Take the 1-day leaching data at L/S = 2:1, for example. The As and Se concentrations in 2007 were 13,785 µg/L and 7229 µg/L, respectively; those values for 2010 were 15,497µg/L and 9477µg/L, respectively. Figures 6(b) and 6(c) show that As(V) was the only As species in the leachate for both 2007 and 2010, but its concentration increased in 2010. A significant decrease in the leachate Se(IV) concentration and a significant increase in the leachate Se(VI) concentration was observed after 3 years of storage. Take the 1-day leaching data, for example. Se(IV) was the dominant Se species in 2007, and the Se(IV) and Se(VI) concentrations at L/S=2 were 4355 µg/L and 2420 µg/L, respectively. These Se(IV) and Se(VI) values changed to 1454 µg/L and 6802 µg/L in 2010, respectively. Therefore, the Se(IV)/Se(VI) ratio changed from 1.8 in 2007 to 0.2 in 2010. When the 5-day leaching data in 2007 is compared to the 6-day leaching data in 2010, the Se(IV)/Se(VI) ratio at L/S 2:1 changed from 0.76 to 0.18. These results indicate that Se(VI) is more stable than Se(IV). Comparison of the decrease in Se(IV) concentration after 5-day or 6-day leaching with the 1-day leaching also indicates that the conversion of Se(IV) to Se(VI) continued during the leaching experiment. The conversion from Se(IV) to the less adsorbable Se(VI) increased leaching of total Se from the trona ash after storage.

4. Conclusions

Compared to the conventional ash, trona ash leached significantly more As and Se in all conditions. Multiple factors may contribute to the enhanced As and Se leaching from trona ash, including more alkaline pH, greater ash solubility, reduced surface site density, presence of high concentrations of competing anions (such as sulfate and carbonate), increased background Se concentration, and a greater Se(VI) fraction in trona ash.

Ash storage time and leaching time impact As and Se speciation and, therefore, change the leaching characteristics of As and Se. While As(V) was the only As species in trona ash before and after 3 years of storage, both Se(IV) and Se(VI) were detected in leachates of fresh and stored trona ashes. A 3-year storage time significantly increased the fraction of Se(VI) while decreasing the fraction of Se(IV). In addition, increased leaching time also converted Se(IV) to more leachable Se(VI). For the control sample, both As(III) and As(V) were initially detected in leachates of fresh and stored ashes. However, As(III) was converted to less leachable As(V) within several days of leaching time. Se(IV) was the only detectable Se species in the fresh control sample, but it was totally converted to Se(VI) after 3 years of storage. As a result, the more oxidized forms of As and Se are more stable species in both trona ash and conventional ash.

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Table1. Fly ash sample information.

Ash ID	**Ash Type**	**BET**	**LOI**	**Al**	**Si**	**Ca**	**Fe**	**Mg**	**Na**	**S**	**As**	**Se**
		(m^2/g)	**wt%**									
#182	Control	8.9	8.7	13.1	23.7	0.4	4.9	0.5	0.2	0.2	0.007	0.0006
#183	Trona	4.3	11.2	10.1	18.9	0.4	4.4	0.4	2.9	1.8	0.006	0.003

Table 2. HPLC-ICP-MS conditions for As and Se speciation analysis.

Column	Hamilton PRP-X100 (4.1 × 150 mm, 10 µm particle size), PRP-X100 guard column (2.3 mm × 25 mm)				
Flow rate	1.2 mL/min				
Injection volume	100 µL				
ICP-MS mode	Standard mode				
m/z ratio	As 74.9, Se 81.9, In 114.9				
Mobile phase	(A) 10 mM $NH_4H_2PO_4$, 10 mM NH_4NO_3, 2% MeOH, pH 8.9; (B) 100 mM $NH_4H_2PO_4$, 100 mM NH_4NO_3, 2% MeOH, pH 8.91.				
Gradient	0-3min 100% A	3-5 min 50% A, 50% B	5-9 min 50% A, 50% B	9-10 min 100% A	9-10 min 100% A

Table 3. Surface site density and acidity constant of ashes #182 and #183.

Ash ID	**Parameter**	**S_1**	**S_2**	**S_3**
#182	Site Density (10^{-4} mol/g)	24.9±10.3	22.5±11.7	27±12.8
	Acidity constant (pK_H)	4.23±0.84	7.35±0.62	10.22±0.76
#183	Site Density (10^{-4} mol/g)	1.63±0.35	1.26±0.33	1.88±0.29
	Acidity constant (pK_H)	3.72±0.41	6.89±0.44	10.99±0.41

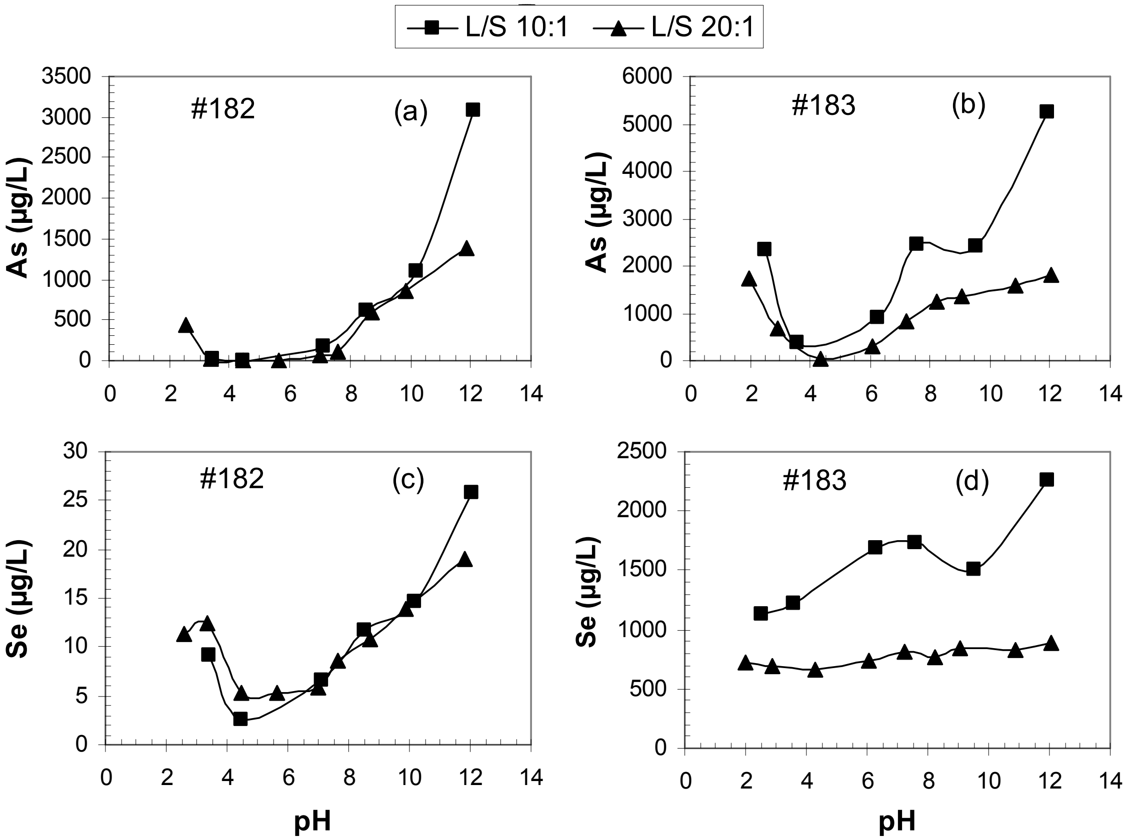

Figure 1. Leaching of As and Se over pH 2-12, and at L/S 10:1 and 20:1. Natural pH = 7.5 for #182 and 11.0 for #183. Experimental conditions: temperature = 21 oC, leaching time = 24 hours.

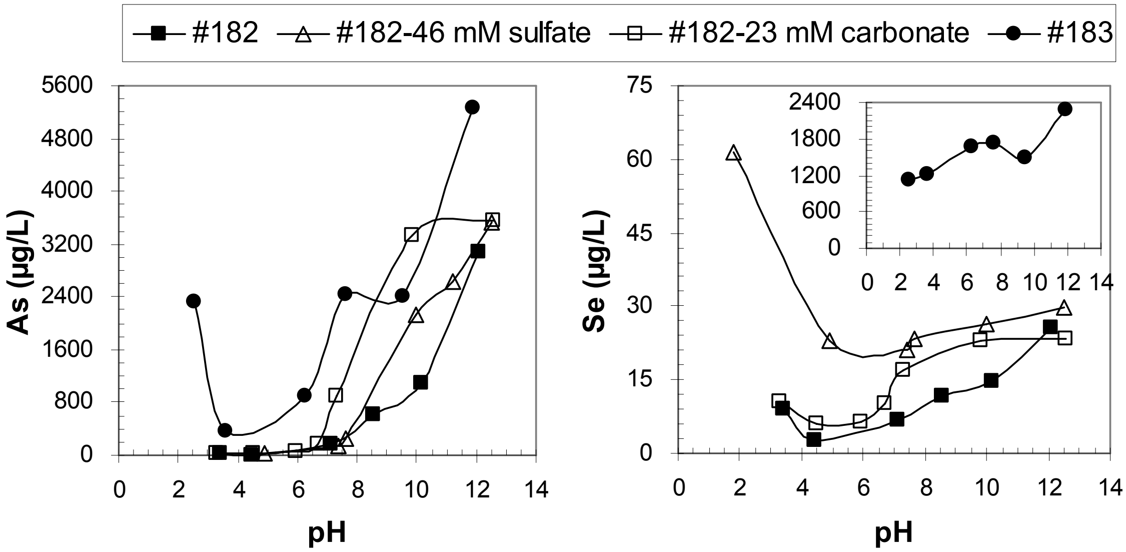

Figure 2. Impact of sulfate and carbonate on As and Se leaching. Experimental conditions: L/S = 10:1, temperature = 21 °C, leaching time = 24 hours.

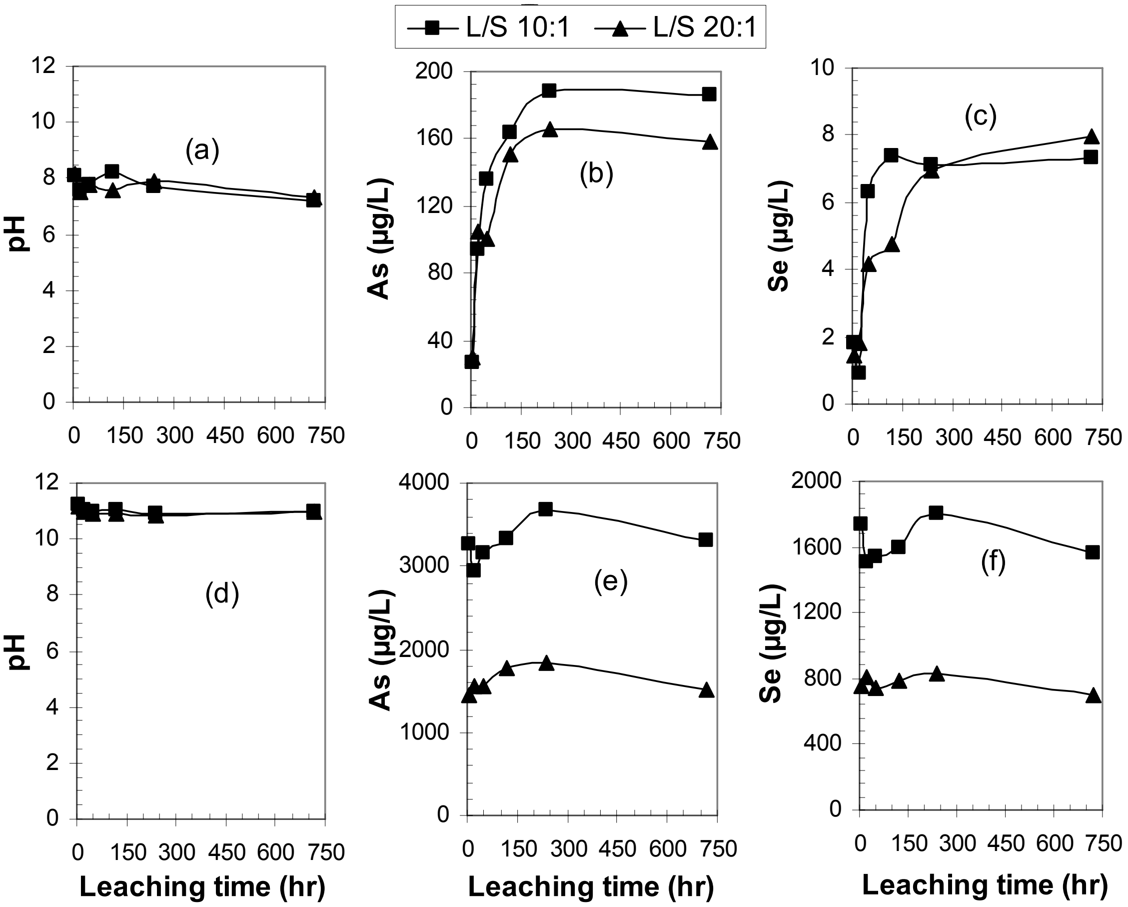

Figure 3. Impact of leaching time on the pH and concentrations of As and Se in leachates of ashes #182 and #183. Plots (a)-(c) are the results of control ash #182; and plots (d)-(f) are the results of trona ash #183. Experimental conditions: temperature = 21 oC, no pH adjustment. Data were obtained in 2007.

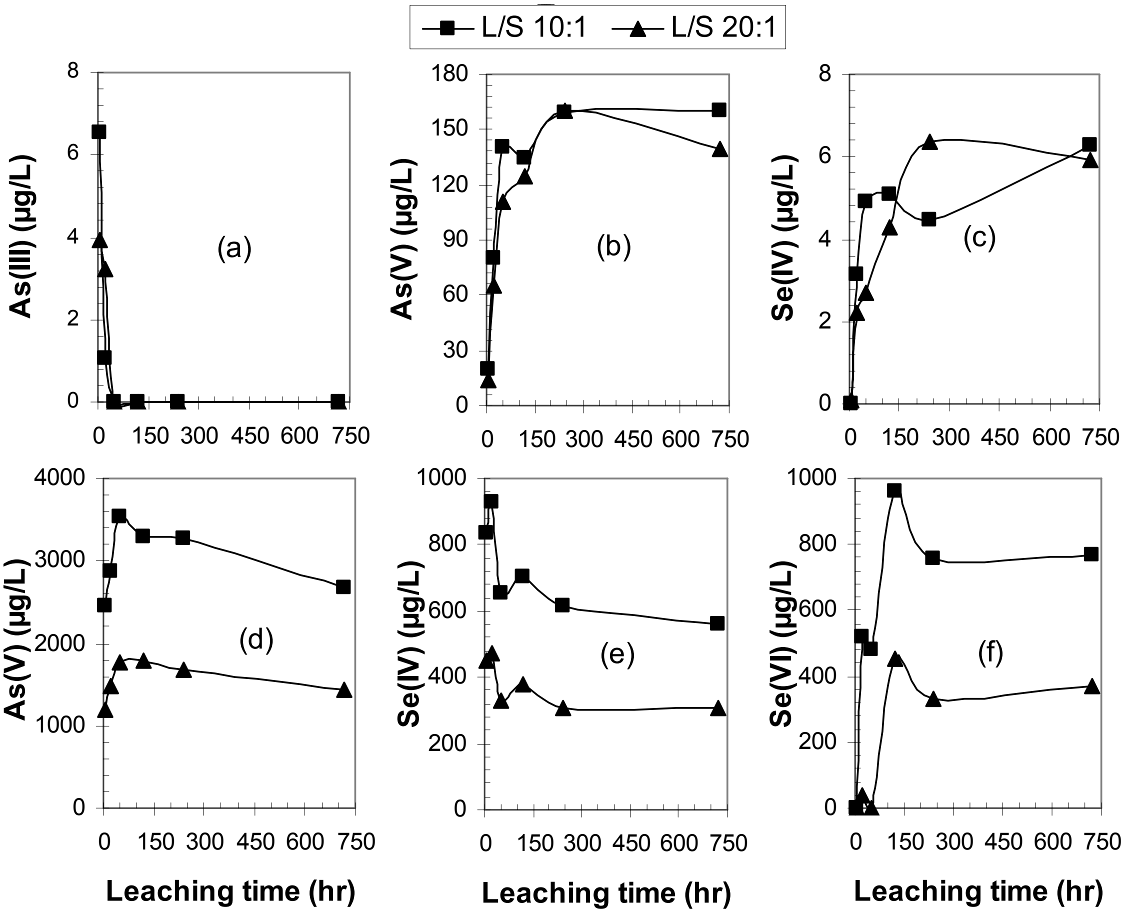

Figure 4. As and Se speciation in leachates of ashes #182 and #183 over a leaching time of 4 to 720 hours. Plots (a)-(c) are the results of control ash #182; plots (d)-(f) are the results of trona ash #183. Experimental conditions: temperature = 21 °C, no pH adjustment. Data were obtained in 2007.

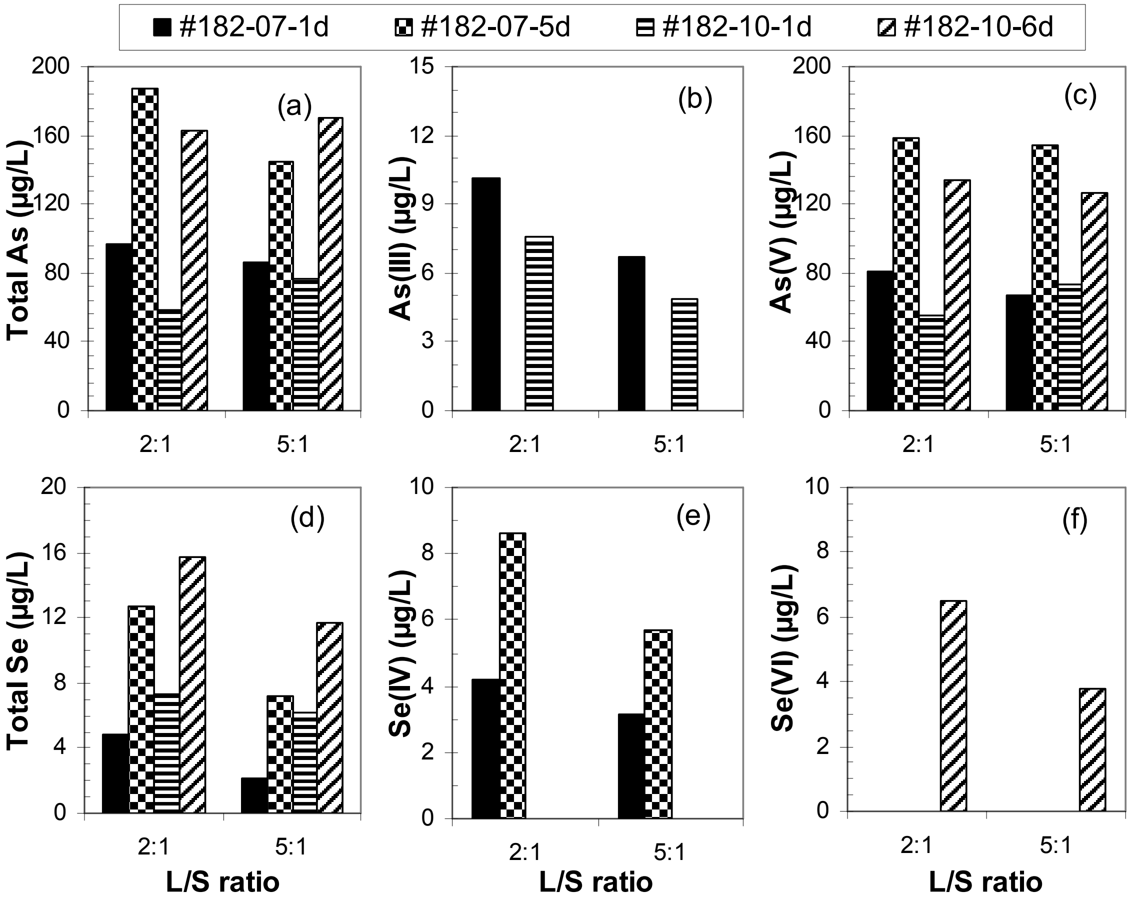

Figure 5. Impact of storage time on As and Se leaching and speciation in control ash #182. Experimental conditions: temperature = 21 ^{o}C, no pH adjustment. Se(IV) and Se(VI) in plots (e) and (f) were close to or below the method quantification levels.

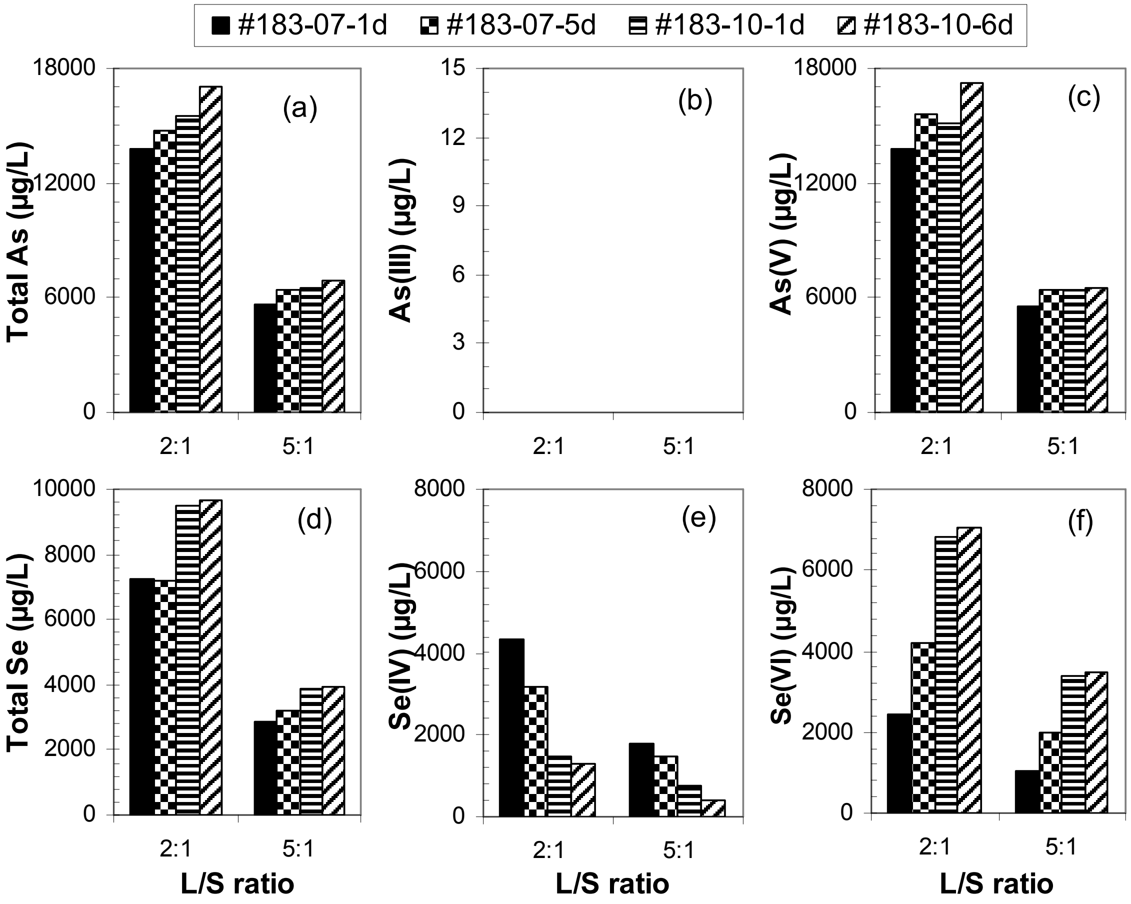

Figure 6. Impact of storage time on As and Se leaching and speciation in trona ash #183. Experimental conditions: temperature = 21 °C, no pH adjustment.

Supporting Information:

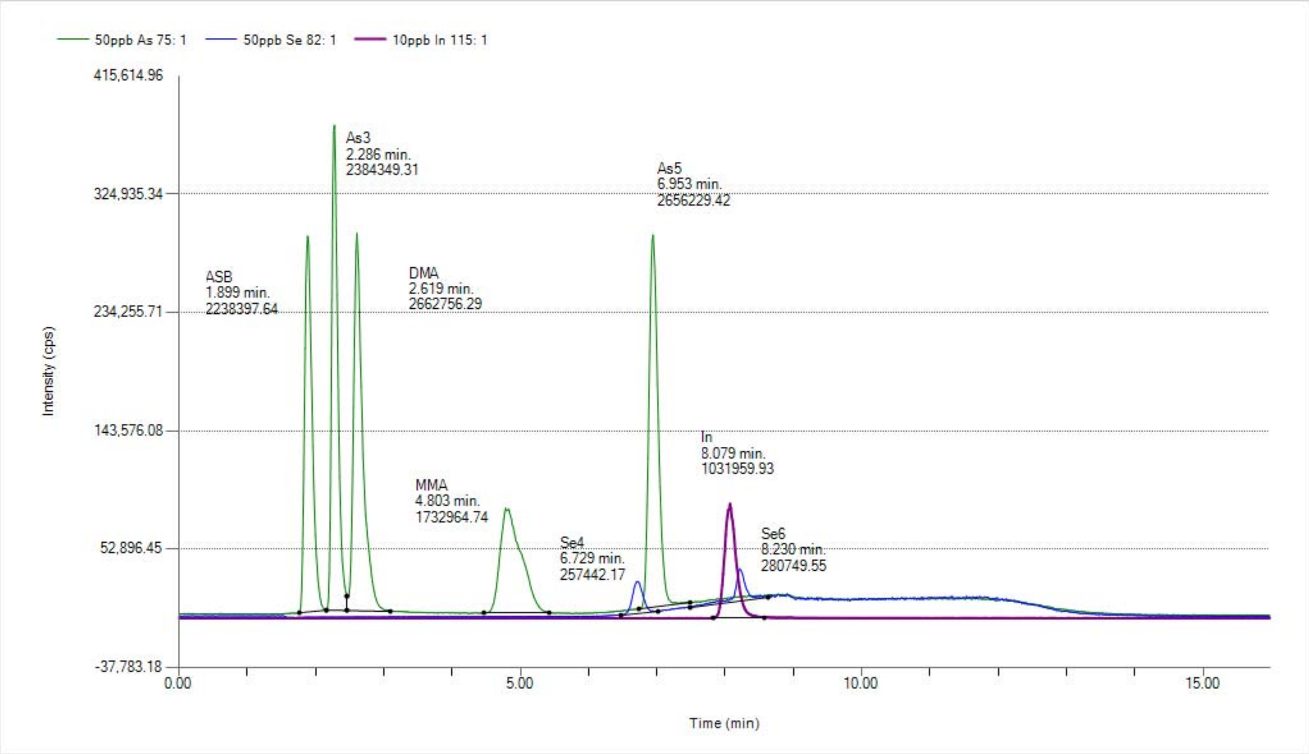

Figure S1. HPLC-ICP-MS Chromatogram of 50 µg/L arsenic and 50 µg/L selenium species and 10 µg/L Indium. The green peaks are arsenic species with the elution order from left to right are: ASB, As(III), DMA, MMA, and As(V); the blue peaks are selenium species with the elution order from the left to the right are Se(IV) and Se(VI); the purple peak is In.

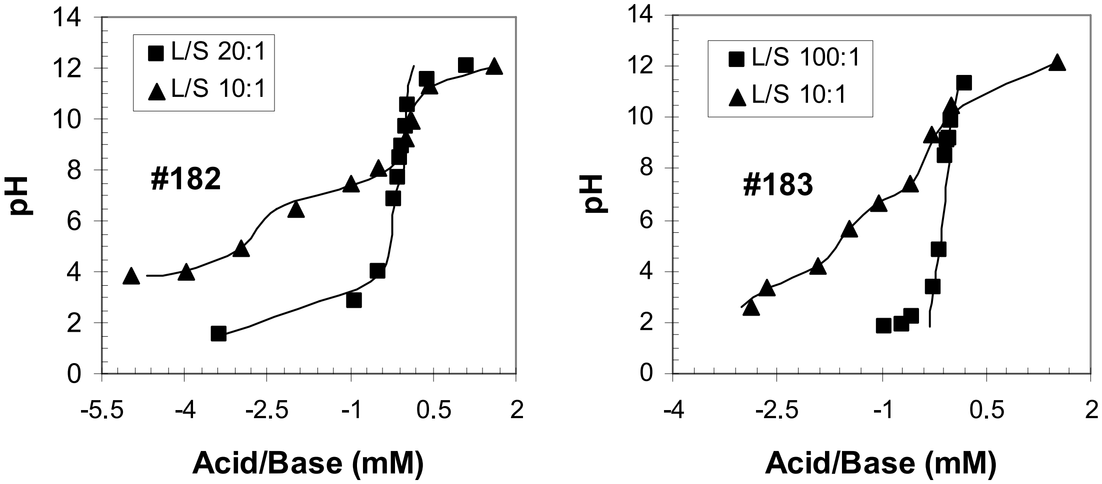

Figure S2. Titration results of washed ashes #182 and #183. Experimental condition: temperature 21 ^{o}C, reaction time = 24 hours.

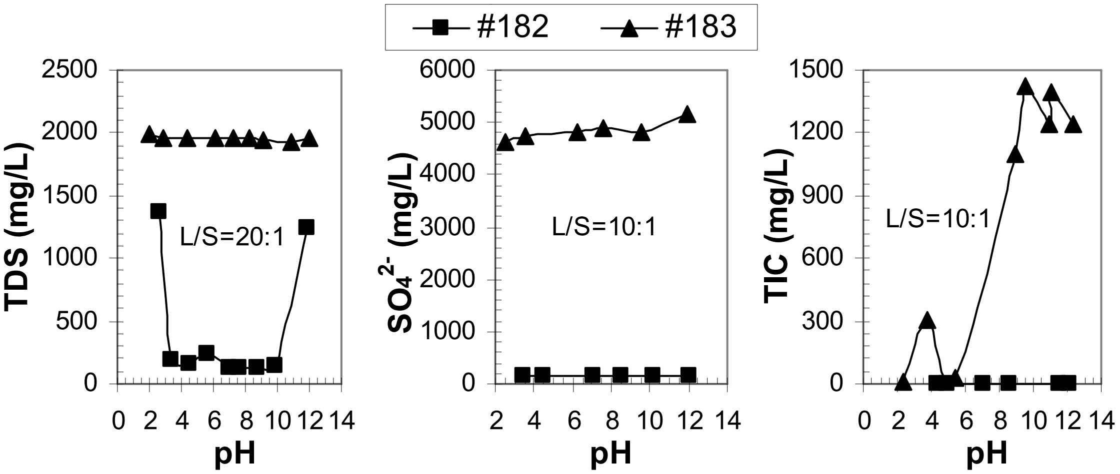

Figure S3. Concentrations of total dissolved solids (TDS), sulfate and total inorganic carbon (TIC) in leachates of raw ashes #182 and #183. Experimental condition: temperature 21 ^{o}C, reaction time = 24 hours.

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SECTION IV

MODELING BATCH LEACHING BEHAVIOR OF ARSENIC AND SELENIUM FROM RAW BITUMINOUS COAL FLY ASHES

Abstract

Impacts of pH, leaching time, and ash washing on the batch leaching behavior of arsenic (As) and selenium (Se) from bituminous coal fly ashes were investigated. As and Se leaching decreased with the increase of pH in the very acidic pH range, reached their minimal levels in the intermediate pH range, and increased with the increase of pH in the alkaline pH range. Increasing leaching time increased As leaching but slightly decreased Se leaching in alkaline pH conditions. DI-water washing may increase the leaching concentrations of As and Se. A speciation-based adsorption model was used to quantify the batch leaching data. Intrinsic leaching parameters, including the total batch leachable concentration and the adsorption constant of As or Se were determined through curve fitting. These constants were validated by correctly predicting the leaching concentrations of As and Se from fly ashes under different experimental conditions. Modeling results also demonstrated that ash washing did not change the adsorption strength of As and Se on the fly ash surface, and that the externally added As and Se had similar adsorption/desorption behavior as those originally presented in bituminous fly ashes.

Keywords

Arsenic, selenium, leaching, bituminous coal fly ash, speciation-based model

Introduction

Arsenic (As) and selenium (Se) are important oxyanions regulated by the primary drinking water standard with MCLs of 10 µg/L and 50 µg/L, respectively (*1*). Coal fly ash, which contains As and Se, is generated at a rate of 653 billion kilograms per year in the US (*2*). For different types of coal fly ashes, the As and Se contents vary significantly, from µg/g to mg/g (*3*-*7*). As and Se leaching from coal fly ash has raised major environmental concerns during fly ash management (*6*-*11*). Studies have shown that factors such as pH, leaching time, liquid-to-solid (L/S) ratio, and ash type significantly impact the leaching of As and Se (*6, 7, 9*). Bituminous coal ashes generally leach significantly more As and Se than sub-bituminous coal ashes (*7, 12*). Therefore, understanding the leaching behavior of As and Se from bituminous coal ash is critical for addressing the environmental concerns during ash management.

As(V) and Se(IV) are the dominant As and Se species in raw ashes (*7, 13-15*), and adsorption/desorption are major control mechanisms for As and Se leaching from bituminous coal ashes (*6, 9, 12, 16-18*). Therefore, the total leachable concentrations of As and Se in fly ash, and their adsorption constants are key parameters in determining the leachability of As and Se. We developed a speciation-based model to quantify the adsorption behavior of added As and Se onto washed, clean bituminous coal ashes (*6, 12*). In these studies, the adsorption ratio was calculated based on the equilibrium, total added, and estimated background concentrations of As or Se in the system. In practice, the background concentrations of As and Se available for leaching are unknown. In addition, no study has compared raw ash versus washed ash with regard to the adsorption constants of As and Se. While we have successfully used a speciation-based approach to predict the leaching of selected cations from raw ashes (*19*), the effectiveness of the similar speciation-based approach in quantifying the leaching of oxyanions (such as As and Se) from raw ash needs to be validated.

The goal of this study was to exemplify the speciation-based approach in quantifying the batch leaching behavior of As(V) and Se(IV) in raw bituminous coal fly ashes under different pH and L/S ratio conditions.

Materials and methods

Fly ash. Two bituminous coal fly ash samples used in this study, #034 and #094, were generated from power plants equipped with electrostatic precipitators. Table 1 shows the ash information. It demonstrates that ash #034 is acidic and ash #094 is alkaline, with a natural pH of 4.0 and 8.4, respectively. Al, Si, and Fe are the top three components in both ashes, and their total amount accounts for more than 42% of the total ash weight.

While this study focused on the leaching of As and Se from raw ash samples, washed ash samples were also studied for surface site characterization, and to compare the leaching behavior of As and Se with that of raw ash. Ash washing was performed using deionized (DI) water at an L/S ratio of 5 (e.g. 200 g/L). Five washing cycles, each including approximately 20 hours of mixing and 2-4 hours of settling, were performed. Washed ashes were dried in a 105 °C oven for at least 24 hours to remove all moisture, and then stored in air tight containers before use (*7, 12, 19*).

Chemicals, reagents, and analytical method. DI water (18.2 MΩ·cm at 25 °C) was used throughout the research. A multiple-trace elements standard with 100 mg/L As and Se was purchased from PerkinElmer (Waltham, Massachusetts, USA). Trace metal grade nitric acid and certified grade sodium hydroxide stock solutions (1 N and 10 N) were purchased from Fisher Scientific. Sodium hydrogen arsenate (heptahydrate), purchased from Alfa Aesar, and sodium selenite, purchased from MP Biomedicals, were used to prepare the stock solutions of As(V) and Se(IV) in batch leaching experiments.

An Orion pH meter (perpHecT LoR model 370) coupled with an Orion PerpHecT Triode pH electrode (model 9207BN) was used for pH measurement. Concentrations of total As and Se in all leachate samples were analyzed using a graphite furnace atomic absorption spectrometer (AAnalyst 600, Perkin–Elmer Corp., Norwalk, Connecticut, USA). Quality control (QC) and spike recovery were between 85% and 115% for all analyses.

Batch leaching experiment. Batch leaching experiments were conducted for both raw ash and washed ash, under different L/S ratio and pH conditions. Besides the background leaching using DI water (BKGD), stock solutions containing preselected contents of As(V) and Se(IV) were also used as leachants, so as to generate more data for leaching modeling. For a batch of experiments with an L/S ratio of 10, 10 g ash (raw or washed) and 100 mL leachant (DI water or As/Se solution) were placed in each of a series of 125 mL LDPE bottles. Stock solutions of HNO_3 and NaOH were then used to adjust the pH in each bottle so that the batch of bottles could cover a pH range of 2-12. The bottles were then sealed and shaken at 180 oscillations/min on an EBERBACH 6010 shaker. After 24 hours, the shaker was stopped and the mixture in the bottles was settled for 2 – 4 hours. The supernatant samples were then collected and filtered through 0.45 μm syringe filters. Strong nitric acid (1%) was used to preserve the samples before analysis. The pH of the slurry remaining in the bottles was measured and recorded as the final pH.

Raw ash #034 was used to conduct different types of leaching experiments to generate leaching data. Some data were used to determine the model constants through curve fitting, while the rest were used to validate the model. Washed ash #034 was also used to generate leaching data that were compared to those from the raw ash. Both the raw ash and the washed ash #094 were used to validate the modeling approach developed using ash #034.

Results and discussion

As and Se leaching from fly ash.

Impact of pH. Symbols in Figure 1 demonstrate the leaching results of raw ash #034 in three batches, with a leaching period of 1-day and an L/S ratio of 10, over pH 2-12. Figures 1(a) and 1(b) are the As and Se concentrations in the leachate. These figures demonstrate that As and Se leaching decreased with the increase of pH in the very acidic pH range, reached minimal levels in the intermediate pH range, and increased with the increase of pH in the alkaline pH range. The minimal leaching pH for As was between 3.5-7.5 in all batches, while that for Se spanned various pH ranges with different leachants. For example, the pH range of the minimal Se leaching of the batch with DI water was 3-8, that of the batch with 1.97 mg/L As(V) and 2.28 mg/L Se(IV) addition (e.g., using the leachant containing 1.97 mg/L As(V) and 2.28 mg/L Se(IV)) was 3-7, and that of the batch with 4.75 mg/L As(V) and 5.31 mg/L Se(IV) addition was 3-6. The As and Se leaching profiles shown in Figure 1 are typical of an adsorption/desorption controlled process, and are consistent with the results of previous studies (*6, 7, 9, 20*). Because As and Se species are very soluble over the entire pH range, there would not be a minimal leaching pH range if there is no adsorption. Meanwhile, previous studies also demonstrated that increasing the surface loading of adsorbates narrows down the maximal adsorption pH range (*21, 22*), which, in this study, corresponds to the minimal leaching pH range (Figure 1(b)). This further indicates that adsorption/desorption controlled the leaching of As and Se from raw ash #034.

In Figures 1(a) and 1(b), the three batches of leaching data of As and Se overlap in the minimal leaching pH range, but beyond that pH range, the soluble As and Se concentrations are greater in the batches with the addition of more As(V) and Se(IV). For the two batches with external As and Se additions, the soluble As and Se concentrations in the leachate were less than the added values, indicating that part of the added As(V) and Se(IV) were adsorbed onto the fly ash surface. Subtracting the background leaching data (with DI water as the leachant) from the batches with As(V) and Se(IV) addition, the net adsorption of added As(V) and Se(IV) by the raw ash was obtained. Symbols in Figures 1(c) and 1(d) demonstrate the adsorption ratio of the added As(V) and Se(IV). The adsorption ratio data for different As(V) and Se(IV) additions overlapped over pH 2-12, indicating that the adsorption was in the linear range of the Langmuir isotherm.

Impact of leaching time. Figure 2 shows 1-day and 1-month leaching data for raw ash #034 at L/S 10, using DI water or As/Se solution as leachants. The parallel comparison of the 1-day and 1-month leaching data was to determine the impact of leaching time on As and Se leaching; the result may also imply the impact of ash aging in the field (e.g. ash pond) on As and Se leaching characteristics.

Figures 2(a) and 2(b) show that, for the two batches of background leaching data, at a pH of <8, the 1-month leaching curve (1m-BKGD) overlapped the 1-day leaching curve (1d-BKGD); but at a pH of >8, the 1m-BKGD leached more As but less Se than the 1d-BKGD. Therefore, the leaching time has more effect on As and Se leaching when in the alkaline pH condition. The comparative magnitude of soluble As and Se concentrations in 1-day and 1-month batches with As(V) and Se(IV) additions followed the same trend as those of background batches.

Figures 2(c) and 2(d) show the net adsorption data generated by subtracting the 1-day or 1-month background leaching data from the batches with As(V) and Se(IV) addition. The results demonstrate that, despite the different leaching times of 1 day and 1 month, the adsorption behaviors of the added As(V) and Se(IV) onto the raw fly ash are the same. This has several implications: (a) adsorption/desorption of As(V) and Se(IV) on fly ash have equilibrated after 1 day; (b) increasing the leaching time from 1 day to 1 month did not change the adsorption strength of As(V) and Se(IV) on fly ash; and (c) As and Se speciation did not change over the 1-month leaching period. If there was any speciation change during the leaching, for example, As(V) changed to As(III), or Se(IV) changed to Se(VI), the adsorption ratio of the added As or Se would be reduced for the 1-month batch. As reported in the literature, As(III) is less adsorbable than As(V), and Se(VI) is almost not adsorbable on fly ash (*7, 12, 23-25*).

Impact of ash washing. Figure 3 shows the 1-day leaching results of As and Se from washed ash #034 at L/S=10, using two As/Se solutions as leachants. Compared to the 1-day As and Se leaching profiles for the raw ash at L/S 10 (Figure 1), the As and Se leaching from the washed ash followed the same trend. However, for a similar amount of added As(V) and Se(IV), the washed ash yielded greater soluble As and Se concentrations than the raw ash did. For example, when 4.08 mg/L of As(V) and 3.96 mg/L of Se(IV) were added to the washed ash, the soluble As and Se concentrations in the leachate at pH 12 were 2.7 mg/L and 4.5 mg/L, respectively. When 4.75 mg/L of As(V) and 5.31 mg/L of Se(IV) were added to the raw ash (a larger addition than for the washed ash), the soluble As and Se concentrations in the leachate at pH 12.34 were 1.6 mg/L and 3.8 mg/L, respectively. Therefore, the DI-water washing process exposed more As and Se for leaching from the ash, or made less As and Se adsorbed from the solution. DI-water washing has also been found to enhance the leaching of Hg from fly ash (*20*).

Figure 4 compares the leaching of As and Se from washed ash #094 with that from raw ash. Symbols in the figure are the experimental results. Figures 4(a) and 4(b) demonstrate that the As and Se leaching curves from the raw ash generally overlapped that of the washed ash over pH 2-12. Therefore, the DI-water washing process had no significant effect on the leachability of As and Se in ash #094. Figures 4(c) and 4(d) illustrate the net adsorption ratios of added As and Se onto the raw and washed ashes of #094, showing that the adsorption data of As and Se by raw ash also overlapped those of the washed ash. Therefore, washing with DI water did not change the adsorption strength of As and Se on the surface of ash #094.

Modeling As and Se leaching/adsorption in fly ash.

Fly ash surface characterization. Characterization of the surface adsorption site is important for determining the leaching of As and Se from fly ash. A batch acidimetric–alkalimetric titration method was employed to quantify the surface site density and acidity constant of washed ashes (*26*). Two L/S ratios, 10 and 100, were used in this study. Figure S1 (Supporting Information) shows the net titration data, where the symbols are the differences between the overall acid/base consumption by ash–water mixture and that by water only. The solid curves are the curve fitting results using an equation we developed (*26*). Table S1 (Supporting Information) shows the parameters generated through curve fitting, e.g., the surface site density and acidity constant. It demonstrates that there are three types of adsorption sites on ash #034, sites S_1, S_2, and S_3, with the corresponding acidity constants (pK_H) of 2.82, 8.11, and 11.34, respectively. Ash #094 only has two types of surface sites, S_1 and S_2, and the pK_H values are 3.2 and 12.59, respectively.

Fly ash is known to be amphoteric due to the significant content of Al and Si (the two major components of fly ash). Figure S2 (Supporting Information) demonstrates the Al and Si leaching from ashes #034 and #094 as a function of pH. It shows that the dissolution of Al and Si was significant at a pH of <4, minimal at a pH of 4-10, and only started to increase to relatively low levels at around pH 10. This indicates that fly ash dissolution was significant in the extreme acidic pH conditions, but minor in the alkaline pH ranges (especially for pH < 10). The experimental data in Figures 1, 2, and 4 demonstrate that the maximal uptake of As and Se onto ashes #034 and #094 occurred over a pH of 3-8, and decreased in other pH ranges. The decreased adsorption over pH <3 was probably caused by the ash dissolution and element speciation change. Neutral species of As and Se, which are dominant species at pH less than 3, are considered non-adsorbable (*6, 12, 21, 22*). Based on data in Figure S2, the decrease in As and Se adsorption at around pH 8 were not caused by fly ash dissolution, but more likely caused by the reduction of protonated adsorption sites. As shown in Table S1, sites S_2 ($pK_H = 8.11$) and S_3 ($pK_H = 11.34$) are dominant over pH >8 for ash #034. These two surface sites are, therefore, unlikely to be responsible for the adsorption of As and Se. Otherwise, the adsorption ratio curves would not start to drop from pH 8. Similarly, the surface site S_2 of ash #094 is unlikely to be responsible for the As and Se adsorption either. As a result, only the protonated surface site S_1 in each ash was responsible for As and Se adsorption (*6, 12*). As shown in Table S1 (Supporting Information), the S_1 site density for ash #034 is 9.81×10^{-4} mol/g, and that for ash #094 is 3.2×10^{-4} mol/g.

Model development. For the adsorption/desorption controlled leaching process, the total available concentration and the adsorption constant of As and Se are intrinsic parameters that determine their leaching behavior under different environmental conditions. The following section will take As(V) as an example for developing the adsorption model, which is used to determine these intrinsic leaching parameters and further, predicting batch leaching behavior of As and Se using these constants under different conditions.

If the total element loading is less than 10% of the total surface site concentration, the adsorption of the target element is in the linear range of the Langmuir isotherm (*26*). The following equation developed by us (*6*) was used to express the adsorption ratio of As(V) in fly ash:

$$R = \frac{\alpha_+ S_T (K_{S1}\alpha_1 + K_{S2}\alpha_2 + K_{S3}\alpha_3)}{1 + \alpha_+ S_T (K_{S1}\alpha_1 + K_{S2}\alpha_2 + K_{S3}\alpha_3)} \qquad \text{Eq. [1]}$$

where R is the adsorption ratio, α_+ is the ratio of the protonated surface site to the total surface site determined by the pH condition, $\alpha_+ = \frac{K_H}{[H^+] + K_H}$; K_H is the surface acidity constant (M); $[H^+]$ is the proton concentration in the bulk solution (M); S_T is the total surface site concentration (M), $S_T = \Gamma_m \times SS$; Γ_m is the surface site density (mol/g); SS is the concentration of fly ash (g/L); α_1, α_2, and α_3 are fractions of $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}, respectively; K_{S1}, K_{S2}, and K_{S3} are adsorption constants of $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} on surface sites, respectively.

Meanwhile, the overall adsorption ratio of an element can be expressed as a function of the total dissolved element concentration and the total added element concentration (*6, 19*):

$$R = 1 - \frac{M_d}{M_b + M_{add}} \qquad \text{Eq. [2]}$$

where M_d is the total soluble concentration (mg/L), M_b is the maximal background concentration that is carried to the system by fly ash under a specific L/S ratio (mg/L), and M_{add} is the total externally added concentration (mg/L).

Combining Eq. [1] and Eq. [2] generates the following model for As(V):

$$M_d^{As} = \frac{M_b^{As} + M_{add}^{As}}{1 + \alpha_H S_T (\alpha_1^{As} K_{S1}^{As} + \alpha_2^{As} K_{S2}^{As} + \alpha_3^{As} K_{S3}^{As})} \qquad \text{Eq. [3]}$$

where the superscript ^{As} in Eq.[3] denotes the parameters of As(V).

The relationship of M_d as a function of pH under different M_{add} concentrations can be determined experimentally. In Eq. [3], the only unknown parameters are M_b and adsorption constants (K_{S1}, K_{S2} and K_{S3}). By fitting experimental data M_d^{As} – (pH, M_{add}^{As}) using Eq. [3] with a multiple variable nonlinear regression program such as SigmaPlot (Systat Software Inc., San Jose, CA) or NLREG (Phillip H. Sherrod, Brentwood, TN), the background As concentration and adsorption constants of different As species can be determined.

Similarly, the model for Se(IV) is:

$$M_d^{Se} = \frac{M_b^{Se} + M_{add}^{Se}}{1 + \alpha_H S_T (\alpha_1^{Se} K_{S1}^{Se} + \alpha_2^{Se} K_{S2}^{Se})} \quad \text{Eq. [4]}$$

where the superscript ^{Se} in Eq.[4] denotes the parameters of Se(IV). α_1^{Se} and α_2^{Se} are fractions of $HSeO_3^-$ and SeO_3^{2-}, respectively. K_{S1}^{Se} and K_{S2}^{Se} are the adsorption constants of $HSeO_3^-$ and SeO_3^{2-} on surface sites, respectively.

Since batch leaching method is used in this study, the total concentration of As or Se carried to the system by the ash is defined as the total batch leachable concentration, and it is a constant for a given batch. The total batch leachable mass (TBLM) of As and Se (mg/kg) can be calculated as: TBLM $= M_b \times L/S$.

The total batch leachable mass of As(V) and Se(IV) and the adsorption constant. The 1-day total batch leachable concentration and the adsorption constant of As and Se were determined for the raw and washed ash #034, by regressing Eq. [3] and Eq. [4] with the experimental data generated from 1-day batch leaching at L/S 10 (symbols in Figure 1 for raw ash, and symbols in Figure 3 for washed ash, respectively).

When modeling the parameters for As(V), the adsorption constant K_{S1}^{As} was not convergent, and it did not impact the regression coefficient either. To reduce the number of parameters in Eq. [3], $K_{S1}^{As} = K_{S2}^{As}$ was assumed. When modeling Se leaching data from raw ash #34 using Eq. [4], a negative value for the total batch leachable concentration was obtained. This indicates that raw ash #034 contained very low levels of leachable Se, which is consistent with the low background Se concentrations carried in by the ash, as shown in Figure 1 and Figure 2. The negative value suggests that other factors such as other cations or anions in the system, promoted the Se uptake by the fly ash.

Table 2 shows the values of the intrinsic leaching parameters of As and Se. It demonstrates that ash #034 has similar adsorption constants for As or Se before and after washing, indicating that DI-water washing did not affect the affinity of As or Se on the ash surface of #034, e.g., same surface complexes were formed on both the raw ash surface and the washed ash surface. However, the 1-day total batch leachable mass of As or Se from the raw ash is significantly smaller than that from the washed ash, which is consistent with the experimental data, that show that the ash washing process made more As or Se available for leaching from ash #034.

The smooth lines in Figure 1 and Figure 3 are the curve fitting results. Compared to the original leaching data (symbols), the model could well describe the soluble As concentration data over a wide pH range, with or without external As addition. It also reasonably predicted the soluble Se concentration data for the batches with external Se addition in a broad pH range, except that, for the batch with the addition of 4.75 mg/L As(V) and 5.31 mg/L Se(IV), the modeling results slightly overestimated the Se(IV) leaching from the raw ash over pH >10.5. This can be ascribed to the precipitation or mineralization effect with cations, i.e., $CaSeO_3$ ($K_{SP}= 10^{-7.27}$ at $I = 0$), or the formation of ettringite (*10, 11*), so that additional Se was stabilized. Due to the very low background of Se in fly ash, the Se leaching data without external Se addition were extremely low and, therefore, could not be modeled. Figures 1(c) and 1(d) show that, based on the adsorption constants generated from the leaching data, one could accurately predict the adsorption behavior of externally added As over pH 3-12, and that of externally added Se over pH <10.5. This indicates that the externally added As and Se had similar adsorption and desorption behavior as those originally presented in fly ash.

Method verification with independent leaching data. For ash #034, the adsorption constants of As and Se in Table 2 were used to predict the adsorption ratio of the added As and Se for the 1-month leaching batches (smooth curves in Figures 2(c) and (d)). As indicated, the model prediction matches the experimental data. Therefore, the adsorption behavior of the fly ash for As(V) and Se(IV) after 1 month of leaching did not change.

The total batch leachable mass and adsorption constants of As and Se in Table 2 were used to predict the As and Se leaching data at L/S 5 (smooth curves in Figure 5). As indicated, the model accurately predicted the experimental data (symbols) obtained from this independent experiment in a broad pH range.

Method verification with a different ash. Ash #094 was used to further verify the effectiveness of the speciation-based approach in quantifying As and Se leaching. The experimental data (raw and washed ash combined) in Figures 4(a) and 4(b) were fit with Eqs. [3] and [4], respectively, to generate the intrinsic leaching parameters of As and Se. However, to eliminate the interference from ash dissolution and cation precipitation in extreme pH conditions, only the experimental data over pH 4-10 was used. The values of the intrinsic leaching parameters generated from curve fitting are also listed in Table 2.

The solid curves in Figure 4 are the curve fitting results. Compared to the experimental data (symbols), over pH 4-10, the model accurately quantified the leaching and adsorption of As and Se. This demonstrates that the speciation-based approach developed in this study also worked well for ash #094. Beyond pH 4-10, some discrepancies were observed between the modeling data and the experimental results in Figure 4. The significant dissolution of ash in acidic pH condition could have contributed to the underestimated release of As and Se. While over pH >10, as discussed above, ash dissolution could release excess As and Se, but precipitation and/or secondary mineralization with cation could stabilize As from leaching. The relative significance of these conflicting effects could not be quantified at this time.

The capability of the speciation-based modeling approach for predicting independent leaching data at a different L/S ratio and for different ashes validated the approach for quantifying the batch leaching behavior of raw bituminous coal fly ashes under different pH conditions. It should be noted that, in Table 2, the values of adsorption constants of As and Se on ash #034 are close to those on ash #094. It is meaningful to study whether this applies to other raw bituminous fly ashes in the future, because it may lead to the generalization of the adsorption of As and Se in bituminous fly ashes. At minimum, the intrinsic leaching parameters obtained through the speciation-based modeling approach can be used to quantify the leaching behavior of the same ash under different pH and L/S ratio conditions, which is critical for evaluating the potential impact of coal fly ash on groundwater quality in field.

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Supporting Information Available

Additional two figures and one table are available in the supporting materials.

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Table 1. Characteristics of bituminous fly ash samples.

Ash ID	**pH**	**Total[a] (wt%)**							**Total Acid Extractable[b] (mg/kg ash)**	
		LOI	**Al**	**Si**	**Ca**	**Fe**	**Sr**	**S**	**As**	**Se**
#034	4.0	5.2	12.4	23.1	1.3	6.5	1.2	0.4	145.1	2.66
#094	8.4	2.0	12.0	25.5	0.9	4.5	0.4	0.2	38.4	15.4

[a] Except for LOI, total contents of other constituents were determined with XRF.

[b] Total extractable As and Se were determined with EPA method 3051A.

Table 2. Adsorption constants and 1-day total batch leachable concentration of As and Se in fly ash.

Ash		**Element**	**log K_{S1}**	**log K_{S2}**	**log K_{S3}**	**M_b(mg/L)**	**R^2**	**TBLM (mg/kg)**
#034	Raw	As	7.55±0.73	7.55±0.73	11.07±0.13	2.87±1.62	0.87	28.7
	Washed	As	6.79±0.22	6.79±0.22	10.89±0.1	9.92±3.66	0.91	99.2
	Raw	Se	2.86±0.67	7.86±0.1	--	-0.87±0.13	0.90	--
	Washed	Se	2.98±0.49	7.46±0.06	--	0.56±0.31	0.97	5.6
#094	Raw/	As	7.98±0.05	7.98±0.05	10.20±0.03	1.22±0.19	0.97	12.2
	Washed	Se	4.68±0.13	6.75±0.04	--	1.00±0.09	0.98	10

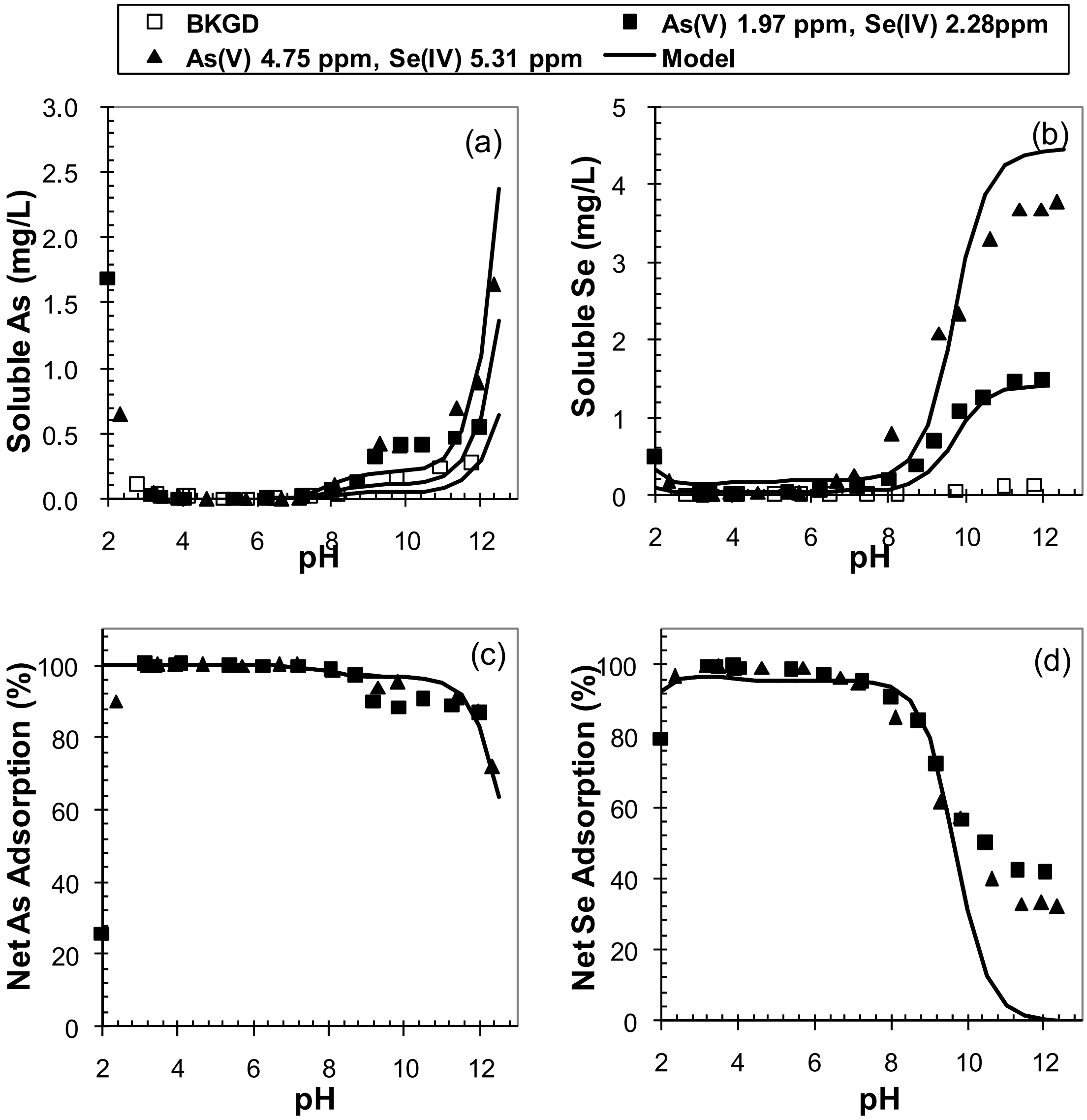

Figure 1. As and Se leaching and adsorption from raw ash #034. Symbols are experimental data, solid curves are modeling results. Experimental conditions: L/S = 10, temperature = 20–25 oC, leaching time = 24 hours.

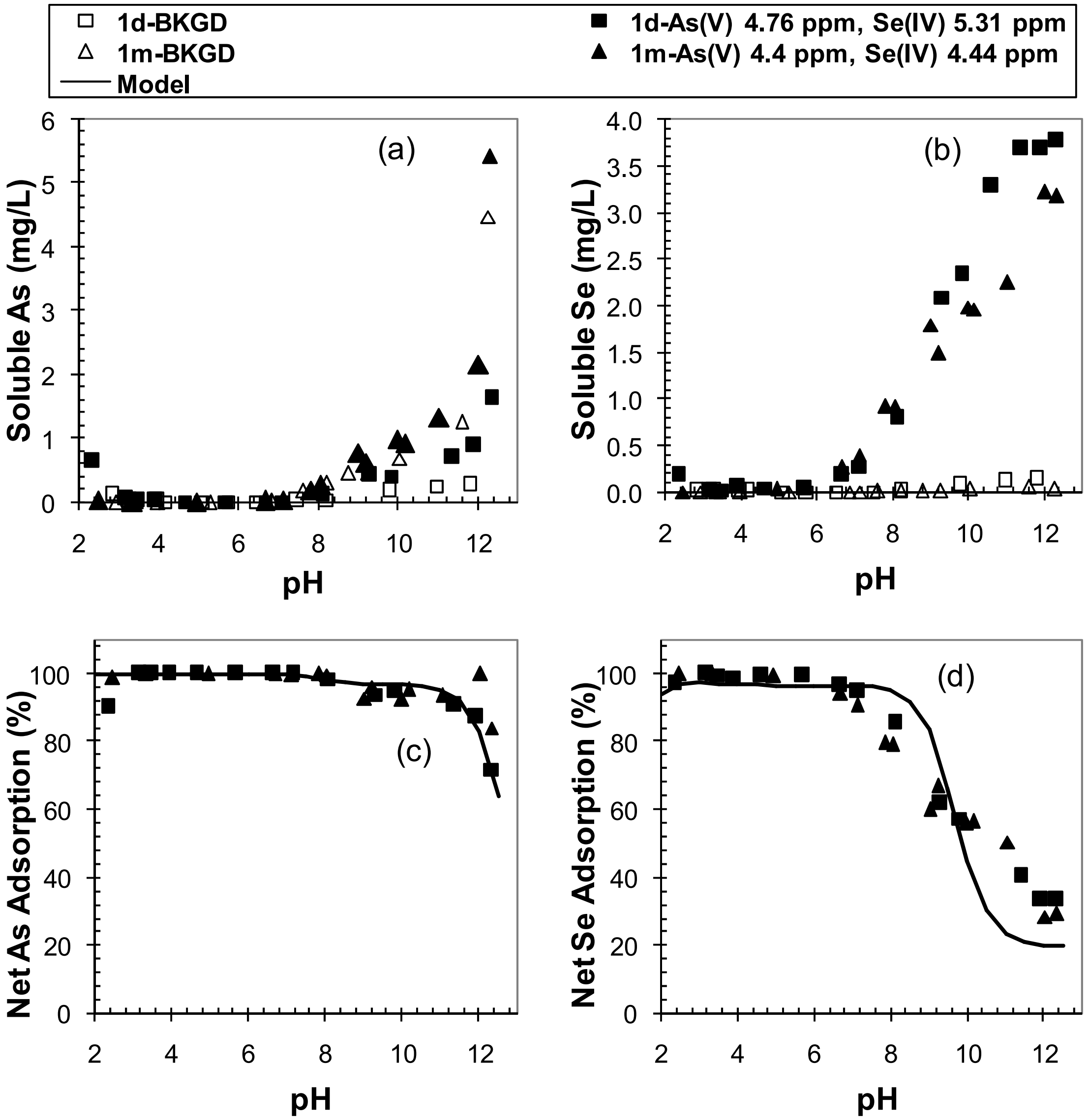

Figure 2. Comparison of the 1-day and 1-month leaching of As and Se from raw ash #034. Symbols are experimental data, solid curves in plots (c) and (d) are modeling results of the 1-month adsorption data. Experimental conditions: L/S = 10, temperature = 20–25 °C

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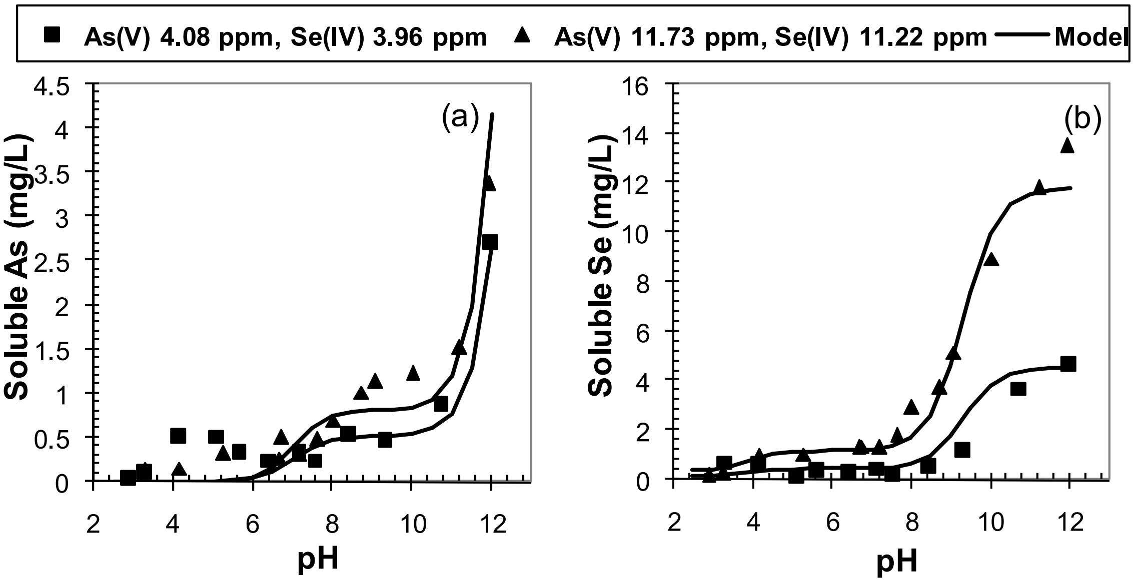

Figure 3. Leaching of As and Se from washed ash #034 using As/Se solutions as leachants. Symbols are experimental data, solid curves are modeling results. Experimental conditions: L/S = 10, temperature = 20–25 oC, leaching time = 24 hours.

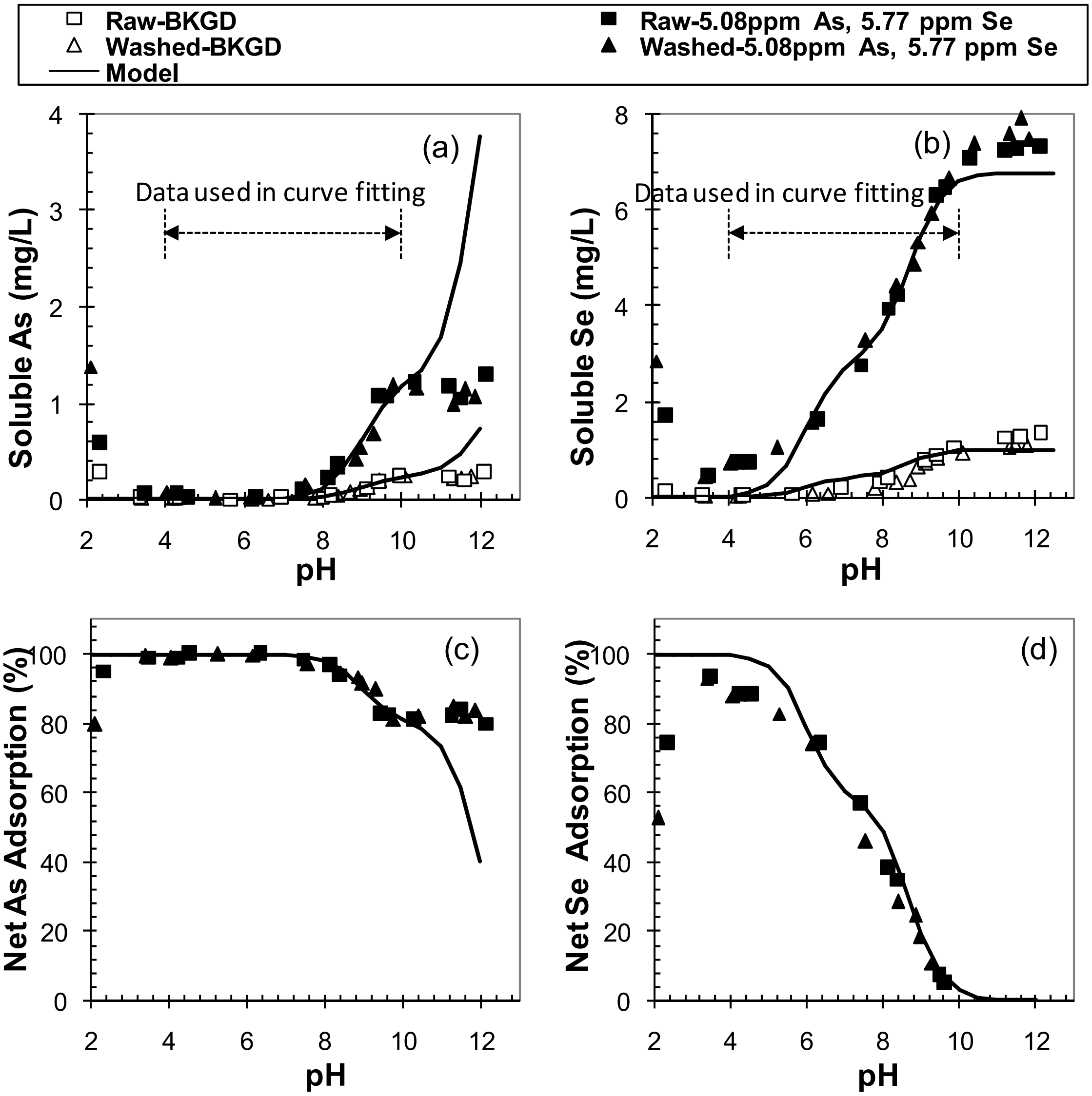

Figure 4. Comparison of the raw and washed ashes of #094 on As and Se leaching and adsorption. Symbols are experimental data, solid curves are modeling results. Experimental conditions: L/S = 10, temperature = 20–25 oC, leaching time = 24 hours.

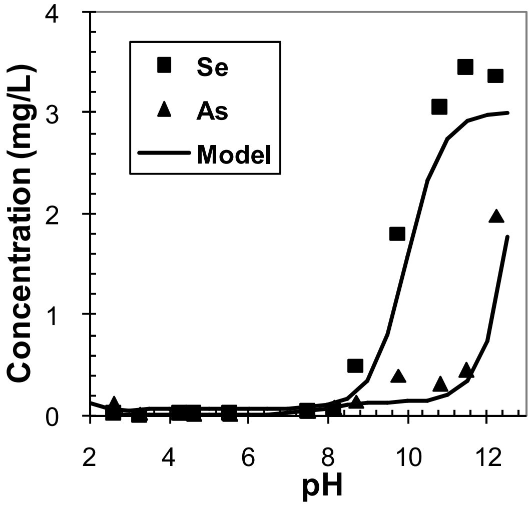

Figure 5. As and Se leaching from raw ash #034 at L/S 5 using As/Se as a leachant. Symbols are experimental data, solid curves are modeling results. Experimental conditions: leachant = 4.43 mg/L As(V) and 4.74 mg/L Se(IV), temperature = 20–25 oC, leaching time = 24 hours.

Supporting Information:

Table S1. Surface site density and acidity constants of fly ash samples.

Ash ID	Parameter	S_1	S_2	S_3	R^2
#034	Site Density(10^{-4} mol/g)	9.81±1.25	0.43±0.24	1.68±0.44	0.98
	pK_H	2.82±0.01	8.11±1.08	11.34±0.45	
#094	Site Density(10^{-4} mol/g)	3.20±0.30	8.82±42.37	--	0.93
	pK_H	3.20±0.14	12.59±2.33	--	

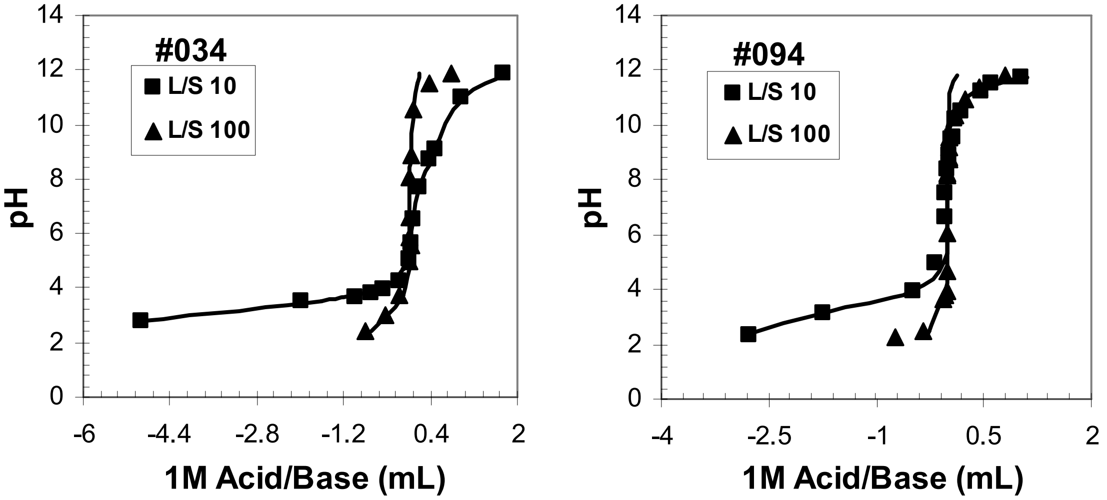

Figure S1. Net titration results of washed ashes #034 and #094. Symbols are experimental data, solid curves are modeling results. Experimental condition: temperature = 21 °C, reaction time = 24 hours.

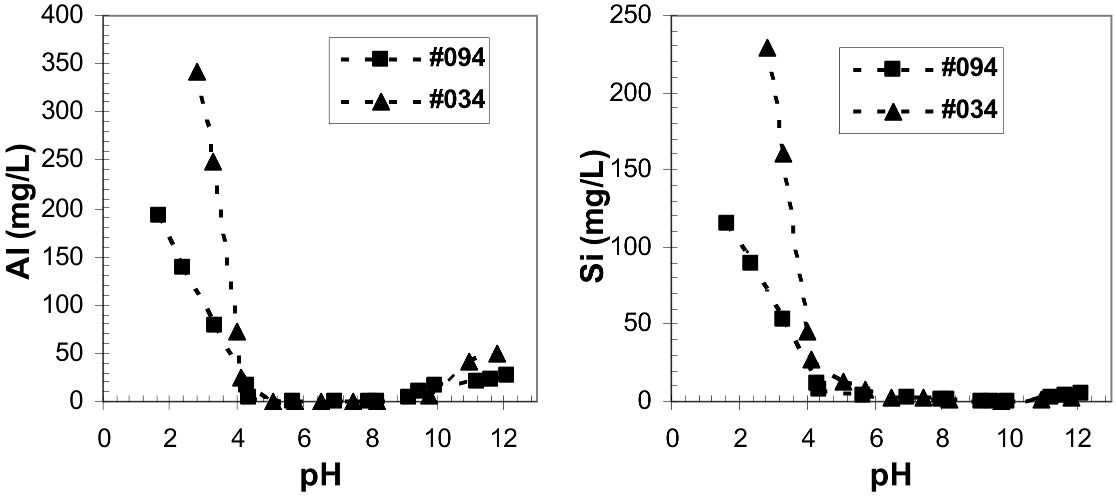

Figure S2. Al and Si leaching from raw ashes #034 and #094 over pH 2-12. Experimental condition: L/S = 10, temperature = 20–25 ^{o}C, leaching time = 24 hours.

SECTION V

EXTRACTION OF AS AND SE FROM COAL FLY ASH USING EDTA

Abstract

Effect of EDTA on arsenic (As) and selenium (Se) leaching from different types of coal fly ashes was studied at a liquid-to-solid ratio (L/S) of 10 using batch methods. The results showed that EDTA significantly increased the leaching of As and Se from low-Ca ashes (Ca<5%) over pH 2-12. With 50 mM EDTA, up to 75% of As and 100% of Se could be leached from low-Ca ashes under natural pH conditions. The leaching of As was not dependent on pH, but the leaching of Se slightly increased with the increase of pH. The leached amounts of As and Se significantly correlated to the total As and Se contents in the ash sample. However, for high-Ca ashes (Ca>5%), As and Se were relatively stable under natural pH conditions, and the EDTA effect in releasing As and Se was lower than that for low-Ca ashes. The mechanisms of the EDTA effect on As and Se leaching were discussed. In addition, the EDTA effect on the leaching of other 15 trace elements of concern from low-Ca fly ashes was also presented. This study demonstrates that the EDTA extraction might be useful for estimating the total available As and Se in low-Ca fly ash, and for remediating this class of coal fly ash in removing As and Se, together with other trace elements of concern.

Keywords:

EDTA, fly ash, As, Se, extraction

1. Introduction

Each year, coal-fired power plants in US generate approximately 653 billion kilograms of coal fly ash. Currently, approximately 40% of the fly ash is beneficially utilized, while the other 60% is disposed of in impoundments or landfills [1]. A variety of toxic trace elements, including Pb, Hg, Cd, Cr, As, Se, Cu, and Zn, are present in the fine fly ash particles [2][5]. These elements may impair the environmental quality through leaching or spill from impoundments and landfills, the un-encapsulated uses in mines, and the structural failures of impoundments [2][6]. The catastrophic fly ash spill at Tennessee Valley Authority’s plant in Kingston (TN) in

December 2008 aroused immense interests on coal ash regulation [7][8]. US EPA proposed the first-ever national rule on coal ash in June of 2010, to address risks from the disposal of wastes generated by electric utilities and independent power producers [8]. A stringent regulation may require extensive environmental risk assessment, and even necessary treatment (e.g., detoxification) of fly ash, during coal ash management and utilization.

As and Se are regulated in the US EPA Primary Drinking Water Standard [9] with very low maximum contaminant levels (MCLs) of 10 μg/L and 50 μg/L, respectively. Therefore, their releases are of the greatest concern in fly ash management [11][13]. As and Se mainly exist in the outer layer of the fly ash particle [13], and their mobility is significantly relies on the fly ash's surface characteristics and leaching chemistry [12][13]. Earlier studies have found that the leaching of As and Se from fly ashes were controlled by adsorption/desorption on Fe-oxides (and very minor on Al-oxides) in a broad pH range [15][17], but under strongly alkaline pH conditions ($pH > 12$), sorption of As and Se was very limited due to the deprotonation of surface sites and the transformation of Fe-oxides into crystalline oxides [18][19]. However, calcium and its minerals (e.g., calcite and ettringite) can restrict As and Se from leaching in the strongly alkaline pH conditions [18][20]. In fact, As and Se leaching from high-Ca ashes was significantly reduced by Ca minerals [13][20][21].

EDTA is a strong chelating agent for most cationic elements, and has been used to remove Pb, Cd, Cu, Ni, Zn, etc. [13][22]. Theoretically, As and Se could not directly react with EDTA due to their anionic nature. However, by chelating the major and trace cationic elements, EDTA may change the fly ash's surface property and the leaching chemistry, and thereby directly or indirectly impact the leachability of As and Se [23]. Results of several studies demonstrated that, in the presence of EDTA, leaching of As, Sb, Cr, and V from fly ash increased [2][15][25],[23]. However, systematic investigations of the effect of EDTA on the release of As and Se under different conditions (such as leaching time, pH, and ash type) are still lacking [25][27].

The objective of this study was to investigate the effect of EDTA on the release of As and Se from various types of fly ashes under varying experimental conditions, so as to evaluate the effectiveness of the EDTA extraction method in removing toxic trace elements, especially As and Se from coal fly ash.

2. Materials and methods

2.1. Fly ash samples

A total of 14 fly ash samples were used in this study. These samples covered all possible ash types generated from different coals in US. Table 1 shows the detailed sample information. Except for ash #186, which was collected from a fabric filter, all other 13 ashes were collected from units with an Electrostatic Precipitator (ESP). Ashes #1021 and #186 were generated from plants burning sub-bituminous coal. Ashes #1020 and #189 were from two different processes at plant #35085 that burned a combination of bituminous and sub-bituminous coals. The other 10 samples were all generated from bituminous coals.

2.2. Ash characterization

Major chemical composition was determined for all ashes. The total concentrations of major elements were analyzed using XRF (XL3T 900, NITON Analyzer, Thermoscientific). The total amounts of 17 trace elements of concern, including As, Se, Cr, V, Mo, Sb, Ba, Cd, Cu, Ni, Tl, Mn, Pb, Zn, Ag, Be, and Co were also determined, using a microwave-assisted complete acid digestion method, developed based on EPA method 3052 [28], where 0.1 grams of fly ash were digested with 9 mL of HNO_3, 3 mL of HF, and 3 mL of HCl. A Multiwave 3000 microwave digestion system (PerkinElmer, Waltham, Massachusetts, USA) was used, and the digestion process included 10 minutes' ramp time and then holding at 240 ^oC for 30 minutes. Sample duplicate, sample spike, reference material SRM1633b, and reagent blank were included for QA/QC check. After digestion, the digestates (crystal clear liquid) were diluted to 50 mL using deionized (DI) water, left to settle for overnight, and then filtrated with 0.22 μm syringe filters. The filtrates were then analyzed for trace elements concentrations.

2.3. Batch leaching kinetics

The batch method was used to investigate the leaching rates of As and Se from ashes #034, #094 and #1021 under natural pH, at L/S = 10, and using 50 mM EDTA as the leachant. For each ash, 10 g ash and 100 mL EDTA solution were placed in a series of 125 mL LDPE bottles. The bottles were then sealed and shaken at 180 oscillations/min on an EBERBACH 6010 shaker. Six to eight bottles, each corresponding to a selected shaking time (e.g. leaching time) between 2 to 72 hours, were prepared for each ash. After its preselected leaching time, the bottle was removed from the shaker, and the supernatant was collected and filtered immediately for metal analysis. The pH of the slurry remaining in the bottle was recorded as the final pH.

2.4. Batch leaching equilibrium

Batch leaching experiments were conducted for all 14 ashes over pH 2-12, under L/S 10, and with a leaching time of 24 hours. Two batches of experiments were carried out for each ash, one batch used DI water as the leachant, e.g., background leaching (BKGD), and the other batch used a stock solution containing 50 mM or 200 mM EDTA as the leachant. The experimental set up and sampling procedure were the same as those of the batch kinetic leaching experiment, except that pH adjustment was involved and the shaking time was fixed at 24 hours for all bottles. At least 12 bottles were used for each batch of ashes #034, #094, and #1021, and at least three bottles were used for each batch of the other 11 ashes. In each batch, the pH of one bottle was not adjusted (natural pH), and those of the other bottles were adjusted with stock solutions of HNO_3 or NaOH, to represent the leaching performance under low and high pH conditions.

2.5. Chemicals, reagents, and analytical methods

DI water (18.2 MΩ·cm at 25 °C) was used throughout the research. A 100 mg/L multiple-trace elements standard solution (containing As, Se, Fe, and other elements) was purchased from PerkinElmer (Waltham, Massachusetts, USA). Trace metal grade nitric acid, certified grade sodium hydroxide stock solutions (1 N and 10 N), and EDTA disodium salt ($Na_2EDTA.2H_2O$, for preparation of the EDTA stock solutions) were purchased from Fisher Scientific.

An Orion pH meter (perpHecT LoR model 370), coupled with an Orion PerpHecT Triode pH electrode (model 9207BN) was used for pH measurement. A graphite furnace atomic absorption spectrometer (AAnalyst 600, Perkin–Elmer Corp., Norwalk, Connecticut, USA) and a Perkin-Elmer Elan DRCe ICP-MS (PerkinElmer SCIEX, Concord, Ontario., Canada) was used to analyze the total As, Se, and other trace elements of concern in the leachate and digested samples, according to EPA Method 200.8 [29]. QC and spike recovery were between 85% and 115% for all analyses.

3. Results and discussion

3.1 Fly ash composition

Bulk contents of Al, Si, Ca, Fe, S, Mg, Ba, Sr, P, Cl, Pb, Zn, Cr, Mo, V, Nb, Zr, Rb, Cu, Ni, Mn, Ti, K, and Na were determined for the 14 ashes using XRF. Among the 24 elements tested, Al, Si, Ca, and Fe were the four major elements in all ashes, and their total content accounted for 36-52% of the total ash weight. Table 1 shows the major chemical composition of the 14 ashes.

Of all these ashes, the Ca contents of #169, #1021, #186, and #170 were the highest (≧ 5%), and those of the other 10 ashes were less than 5%. In the following sections of this paper, the former are denoted as high-Ca ashes, while the latter are denoted as low-Ca ashes. The pH values listed in Table 1 were the natural pH of ash leachate at L/S =10 (with a leaching time of 24 hours). Table 1 demonstrates that all 4 high-Ca ashes were strongly alkaline (pH>12.3), while the pH of the 10 low-Ca ashes ranged from 4.08 to 12.7.

Table 1 also shows the total amounts of As and Se determined using the complete acid digestion method. It demonstrates that the concentration range for As was 7.6-172.5 mg/kg in these 14 ashes, and that for Se was 0.5-15.4 mg/kg. Ash #034 had the highest concentration of As, while ash #094 had the highest concentration of Se.

3.2. Leaching rate of As and Se in the presence of 50 mM EDTA

Figures 1 shows the soluble concentrations of As and Se and the leachate pH, for ashes #034, #094, and #1021 in the presence of 50 mM EDTA, as a function of leaching time. All experiments were conducted under natural pH conditions (without pH adjustment). Figure 1 demonstrates that As, Se, and pH levels in the leachates of all ashes equilibrated after 24 hours. Before reaching equilibrium, As leaching from the two low-Ca ashes (#034 and #094) generally increased, while that from the high-Ca ash #1021 decreased with the increase of leaching time (Figure 1(a)). The leached Se concentration from ash #034 was close to the detection limit after necessary dilution. Se leaching from #094 increased, while that from #1021 decreased with the increase of leaching time (Figure 1(b)). Figure 1(c) demonstrates that with the increase of leaching time from 2 hours to 24 hours, the pH of all leachates increased. The pHs of low-Ca ashes increased from pH 3.7 to pH 4.4 for #034, and from pH 4.2 to pH 4.7 for #094, respectively, while for the high-Ca ash #1021, the pH increased from pH 9 to pH >12. With the increase in leaching time, the increased pH and greater leaching of As and Se from low-Ca ashes #034 and #094 may be attributed to the ash dissolution, which released more alkalis (e.g., lime and MgO) [30] and reduced the adsorption sites for As and Se. On the other hand, the decreased leaching of As and Se from alkaline ash #1021 may be attributed to the increased pH and the high Ca concentration, which caused secondary stabilization of the initially released As and Se; i.e., through the formation of $Ca_3(AsO_4)_2$, ettringite, or gypsum, that either precipitated or encapsulated the dissolved oxyanions [20][31][32]. This also indicated that for the high-Ca ash #1021, 50 mM EDTA was not sufficient to chelate all dissolved Ca.

Compared to the total amount of As and Se in these ashes (Table 1), the 50 mM EDTA-extracted amount of As and Se at equilibrium were 95% and 89% for ash #034, 79% and 86% for ash #094, and 4% and 12% for ash #1021, respectively. These data indicate that 50 mM EDTA is very effective in extracting As and Se from low-Ca ashes, but is not as effective for the high-Ca ash.

3.3. Equilibrium extraction of As and Se with EDTA

3.3.1 Low-Ca ashes

Figure 2 shows the leaching of As and Se from two low-Ca ashes, #034 and #094 over pH 2-12, with and without the presence of EDTA. For both ashes, As and Se leaching in the BKGD batch demonstrated a typical adsorption/desorption controlled process: there was a minimal leaching pH range, and As/Se leaching increased beyond the minimal leaching pH range [11][12][13]. The greatest As and Se leaching in the BKGD batches occurred in extreme pH conditions (pH <2 or pH >12), with 108 μg/L of As and 143 μg/L of Se leached from ash #034, and 2,272 μg/L of As and 1,256 μg/L of Se from ash #094, respectively. In the 50 mM EDTA batches, As leaching remained almost constant over pH 2-12, which was approximately 12,236 μg/L for #034 and approximately 3,607 μg/L for #094, respectively. These values were significantly greater than the maximal As concentrations in their corresponding BKGD batches. Se leaching from the 50 mM EDTA batch generally increased with the increase of pH for both ashes. However, the slope of the leaching curve was much smaller than that of the BKGD, and the Se leaching from ash #034 decreased over pH >10. Over pH 2-12, the average Se concentrations were 129 μg/L for ash #034 and 1,374 μg/L for ash #094. These values were also significantly greater than the maximal Se concentrations of their corresponding BKGD batches. The comparison between the 50 mM EDTA batch with the BKGD batch demonstrated that 50 mM EDTA significantly enhanced the leachability of As and Se in these low-Ca ashes.

Figures S1 and S2 compare the As and Se leaching in the 50 mM EDTA batch with that in the BKGD batch for the other 8 low-Ca ashes. Except for the Se leaching from ash #189, the leaching profiles of As and Se from these ashes were consistent with those observed with ashes #034 and #094: 50 mM EDTA enhanced the As and Se leaching significantly, and the leached As remained constant under different pH conditions, while the leached Se slightly increased with the increase of pH. For ash #189, 50 mM EDTA increased Se leaching in the acidic pH range, but decreased the Se leaching over pH >8 when compared to the background. Under the natural pH, the leached As concentration by 50 mM EDTA from the 10 low-Ca ashes followed the order of #034 > #089 > #189 > #104 > #182 > #1020 > #103 > #183 > #094 > #153, while the leached Se follow the order of #183 > #094 > #153 > #189 > #103 > #089 > #104 > #1020 > #182 > #034. These sequences generally agree with the sequences of the total As and Se contents in these ashes (Table 1).

The impact of a higher EDTA concentration (200 mM) on As and Se leaching was also determined for ash #094. The adjustment of pH was difficult for this batch due to the slow drifting during the experiment. Therefore, the final pH range used in this experiment was much narrower than other experiments, as shown in Figure 2. Results show that As and Se leaching from ash #094 also remained constant between pH 3-6 in the 200 mM EDTA batch. For the same pH condition, the As and Se leached by 200 mM EDTA were slightly lower than that by 50 mM EDTA. Therefore, increasing the EDTA concentration did not increase the leaching of As and Se from ash #094. Nugteren et al. [23] reported that after reaching the optimal extraction, increasing the extraction reagent-to-ash ratio only resulted in greater leaching of major elements, but did not improve the trace element extraction. Therefore, 50 mM EDTA is probably sufficient to reach the maximal As and Se leaching in the low-Ca ash #094.

3.3.2 High-Ca ashes

For the high-Ca ash #1021, pH adjustment in the presence of 50 mM EDTA was extremely difficult, and the pH of all 14 reactors drifted to around pH 12 after 24 hours of shaking. Therefore, a higher EDTA concentration of 200 mM was used for the experiment. Figure 3 shows the leaching profiles of As and Se from ash #1021 over pH 2-12, with and without the presence of 200 mM EDTA. In the BKGD batch, leaching of both As and Se decreased with the increase of pH, and the As concentration was very low over the entire pH range. Under the natural pH of 12.6, the leached concentrations of both As and Se were much lower than their corresponding MCLs (10 μg/L for As and 50 μg/L for Se) of the US primary drinking water standard [9]. In the batch with 200 mM EDTA, As leaching increased significantly compared to the background leaching. It decreased with the increase of pH that was over pH <4, remained almost constant over pH 4-10, decreased with pH of over 10-12, and then sharply increased when pH was >12. Se leaching was undetectable when pH was <4 (e.g., EDTA reduced Se leaching under acidic pH conditions), increased with the increase of pH that was over 4-7, remained almost constant when the pH was over 7-10, and then decreased when the pH was >10.

The scales in Figure 3 demonstrate that 200 mM EDTA generally extracted significantly greater amounts of As over pH 2-12, and significantly greater amounts of Se over pH > 7, than DI water did (BKGD). Therefore, EDTA also enhanced As and Se leaching from the high-Ca ash #1021, and changed their leaching profiles as a function of pH.

Figure S3 compares the As and Se extracted by DI water and by 50 mM EDTA from the other three high-Ca ashes, #169, #170, and #186. It demonstrates that 50 mM EDTA generally extracted much greater amounts of As and Se from all these ashes than DI water did. Except for the Se leaching from ash #169, the leaching of As/Se followed a similar pH dependency in the 50 mM EDTA batch as in the corresponding BKGD batch of these ashes: As leached less in higher pH conditions for all ashes, as did Se from ash #186. Se leaching in the BKGD batch of ash #170 reached a peak at around pH 9, and reduced when the pH was beyond 9, while Se leaching in the 50 mM EDTA batch of #170 generally increased with the increase of pH (similar to those of the low-Ca ashes). Se leaching from the BKGD batch of ash #169 followed the same trend as those of ashes #186 and #1021, but that of the 50 mM EDTA batch followed a leaching trend similar to that of ash #170. For the same pH condition, the As and Se leaching profiles depicted in Figure S3 were generally consistent with those of ash #1021. It should be noted that, for all of these high-Ca ashes (including ash #1021), the adjustment of pH was extremely difficult and sometimes unrepeatable, due to their strong alkaline nature and high Ca content. This may have contributed to some discrepancy of the leaching profiles among the ashes shown in Figures 2 and S3. Under the natural pHs, the As extracted by 50 mM EDTA followed the sequence of #170 > #1021 > #186 > #169, while that of Se was #170 > #169 > #1021 > #186. These sequences are not in the same order as the corresponding total As and Se contents in these ashes.

It should be noted that, the BKGD leaching data for all high-Ca ashes (Figures 2 and S3) indicate that the leaching of As and Se from this type of ash under natural pH conditions was minimal (close to or below their MCLs in drinking water). This finding was consistent with our previous studies [13][21]. Therefore, As and Se were relatively stable in high-Ca ashes, and the post-removal of As and Se from high-Ca ashes using other methods may not be necessary.

3.3.3. Mechanisms of EDTA-enhanced leaching of As and Se

The above results demonstrate that EDTA significantly changed As and Se leaching profiles and enhanced their leaching from both the low-Ca and high-Ca fly ashes. Several mechanisms could have contributed to the EDTA-enhanced As and Se leaching:

(a) EDTA can form stable complexes with Fe and Al [34]. Therefore, through chelating these major cationic elements of fly ash, EDTA increased ash dissolution and reduced surface binding sites for As and Se, thereby inducing the increased release of As and Se. Figure 4 shows the Fe leaching profile from ash #094, with and without 50 mM EDTA. It demonstrates that 50 EDTA significantly enhanced leaching of Fe over pH 2-12. It was reported that EDTA-treated fly ash showed increased particle volume, mean pore radius, and surface area [35], which also confirmed that EDTA changed the fly ash surface property and improved ash dissolution. Therefore, EDTA could mobilize elements originally covered under the top layer (including As and Se), and remove As/Se binding sites from the ash surface.

(b) EDTA may form strong surface complexes with As and Se binding sites on ash surface, and block the adsorption sites (Fe-oxide and Al-oxide) that formerly used for As and Se adsorption. Figure 5 shows the TDS of ashes #034 and #094, with and without the addition of EDTA. Compared to the BKGD batches, the net increases of TDS concentrations in the 50 mM EDTA batches were about 5,383 mg/L for ash #034 and 5,324 mg/L for ash #094, and those of the 200 mM EDTA batch were about 12,764 mg/L for ash #094, respectively. In all cases, the net TDS increases were less than the corresponding 14,511 mg/L (50 mM) and 58,046 mg/L (200 mM) of EDTA added. This indicates that a significant amount of the added EDTA was either adsorbed on the fly ash surface, or precipitated by cations. Both cases would have competed with As and Se, and thereby enhanced As and Se leaching from the fly ash.

(c) Xu and Nakajima [17] reported that EDTA chelated metal ions (such as Fe and Al), which are in the dissolved phase, could serve as a bridge to promote As and Se leaching. Therefore, another possible mechanism of the EDTA-enhanced leaching of As and Se was that the EDTA-Fe or EDTA-Al complexes served as active binding sites for As and Se anions, which retained As and Se on soluble phase.

3.4. The extent of As and Se extraction by 50 mM EDTA

The extracted As and Se by 50 mM EDTA under natural pH conditions were plotted as a function of the total As and Se content (determined using the complete digestion method). Figure 6 shows data from low-Ca ashes, demonstrating that the EDTA-extracted As and Se were linearly correlated to the total As and Se. The slope of the trend line indicates the ratio that can be extracted. The slope of the line for As in Figure 6(a) is 0.75, while that for Se in Figure 6(b) is approximately 1. Therefore, 50 mM EDTA can extract about 75% of the total As, and almost

100% of the total Se from low-Ca ashes under natural pH conditions. No correlation was found for high-Ca ashes #169, #170, #186 and #1021 (data not shown).

This and earlier studies have found that As and Se leaching from low-Ca ashes can be significant, while that from high-Ca ashes is generally very minor [13][21]. Therefore, environmental concerns of As and Se leaching from coal fly ashes is mostly for low-Ca ashes. The significant correlations between the EDTA-extracted As and Se with the total As and Se content are very meaningful for future toxicity assessment and field management of fly ash. First, the 24-hour extraction using 50 mM EDTA may be used to estimate the total content of As and Se, or, at a minimum, the total leachable As and Se that are meaningful to environment. Because the complete acid digestion method involves many experimental steps, it may result in analyte losses, high reagent consumption (implying a large amount of toxic wastes), high dependence on instrumentation (need a microwave digester or hot plate digester; instrument should be HF proof), and high risks (handling HF and strong acid). It is also very labor intensive. In contrast, the EDTA extraction method under the natural pH condition is very convenient to use and can provide similar information. Second, if the As and Se contents of the fly ash have to be reduced before disposal or beneficial use, EDTA-washing could be used to extract most of the As and Se from the fly ash.

3.5. Equilibrium extraction of other trace elements of concern with EDTA

Cr, V, Mo, Sb, Ba, Cd, Cu, Ni, Tl, Mn, Pb, Zn, Ag, Be, and Co are also trace elements of concern that may impair water quality. They are regulated in the primary or secondary drinking water standards, or are listed in the drinking water candidate list [9][10]. Figure S4 compares their leaching profiles from #034 and #094 with and without the addition of 50 mM EDTA. It demonstrates that 50 mM EDTA significantly enhanced the leaching of all these 15 elements from both ashes over pH 2-12. In the 50 mM EDTA batch, except for Sb, concentrations of all elements remained constant when over pH >4 (when over pH <4, their concentrations are generally higher due to greater ash dissolution). Mechanisms, similar to those of As and Se, could have contributed to the EDTA-enhanced leaching of Cr, V, Mo, and Sb, since these oxyanions have similar chemical and leaching characteristics [36][38]. For other elements (trace cations), besides EDTA-enhanced ash dissolution and surface adsorption site reduction, the strong affinity of these cations with EDTA is another contributor to their enhanced leaching in the 50 mM EDTA batch [13][22][34].

Compared to the total content of these trace elements (data not shown), when under natural pH, 50 mM EDTA extracted about 80% of Mo from both ashes, with the naturally extracted amounts of the other 14 elements being below 40%. The percentages of these elements extracted by EDTA are consistent with their reported enrichment ratios in the surface layers of fly ash, which represents their most mobile fraction and environmentally significant fraction [27]. Therefore, EDTA-washing could be a feasible method to significantly detoxify fly ash of most heavy metals of concern. However, the dissolution of major calcium, Al, and iron minerals may impact the physical, chemical, and engineering properties of the fly ash after EDTA-washing and, consequently, impact the application of fly ash in some beneficial usages currently underway. Further study is recommended to investigate the significance of the EDTA impact on fly ash engineering properties. In addition, cost-effective methods for leachate treatment need to be investigated before EDTA-washing method is implemented.

4. Conclusions

EDTA can significantly enhance the leaching of As, Se, and other trace elements of concern from coal fly ash, especially from low-Ca ashes. At L/S 10, 50 mM EDTA can extract about 75% As and 100% Se from low-Ca ashes, under the natural pH condition. For high-Ca ashes, however, this is no such correlation. The EDTA extraction could be a convenient alternative for assessing the total leachable As and Se, and to remediate fly ash for the removal of As and Se, and other trace elements of concern.

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Table 1. Sample information of fourteen fly ashes.

Plant ID	Ash ID	Coal type	Fly Ash Control	pH	Al	Si	Ca	Fe	As	Se
					wt%				mg/kg	
33103	#183	Bit[a]	ESPh[d]	10.8	10.2	22.3	0.6	4.3	46.9	15.4
33103	#182	Bit	ESPc[e]	7.5	12.6	26.7	0.6	4.9	53.3	0.6
35406	#153	Bit	ESPc	4.2	13.7	28.7	0.7	2.9	19.4	10.3
33102	#094	Bit	ESPc	8.8	12.0	25.6	0.9	4.5	38.4	15.4
40109	#034	Bit	ESPh	4.3	12.5	23.1	1.3	6.5	172.5	0.6
35015	#089	Bit	ESPc	9.3	12.5	21.8	1.4	17.3	102.9	4.2
35085	#1020	Subbit& Bit[b]	ESPc	9.4	11.4	20.1	1.8	20.7	48.1	2.8
35085	#189	Subbit& Bit	ESPc	8.5	11.3	19.7	1.9	18.4	57.2	10.2
17154	#104	Bit	ESPc	12.4	11.0	24.8	2.6	13.6	66.4	2.3
17154	#103	Bit	ESPc	12.2	10.5	23.4	3.5	13.3	61.2	8.3
14650	#170	Bit	ESPc	12.5	11.0	20.6	5.0	10.7	55.1	7.6
6191	#186	Subbit[c]	FF[f]	12.4	6.4	14.6	13.2	1.9	7.6	5.7
50207	#1021	Subbit	ESPc	12.3	9.2	16.5	14.2	3.4	25.2	9.6
14650	#169	Bit	ESPc	12.5	8.0	13.3	20.4	5.0	36.4	9.1

[a]Bit-bituminous coal; [b]Subbit&Bit - blend of sub-bituminous and bituminous coal; [c]Subbit- sub-bituminous coal; [d]ESPh- Electrical Static Precipitator hot side; [e]ESPc- Electrical Static Precipitator cold side; [f]FF- Fabric Filter.

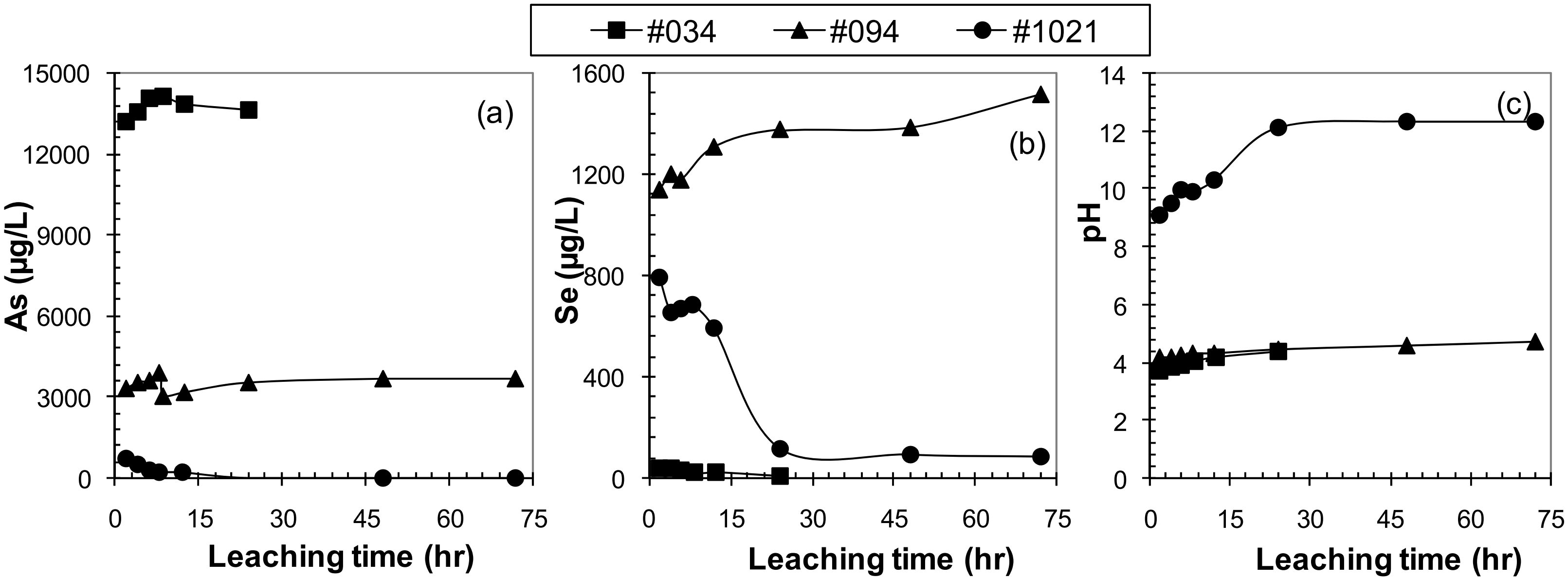


Figure 1. Changes of As, Se and pH in fly ash leachates as a function of leaching time. Experimental conditions: leachant = 50 mM EDTA, L/S =10, temperature = 21-25 °C.

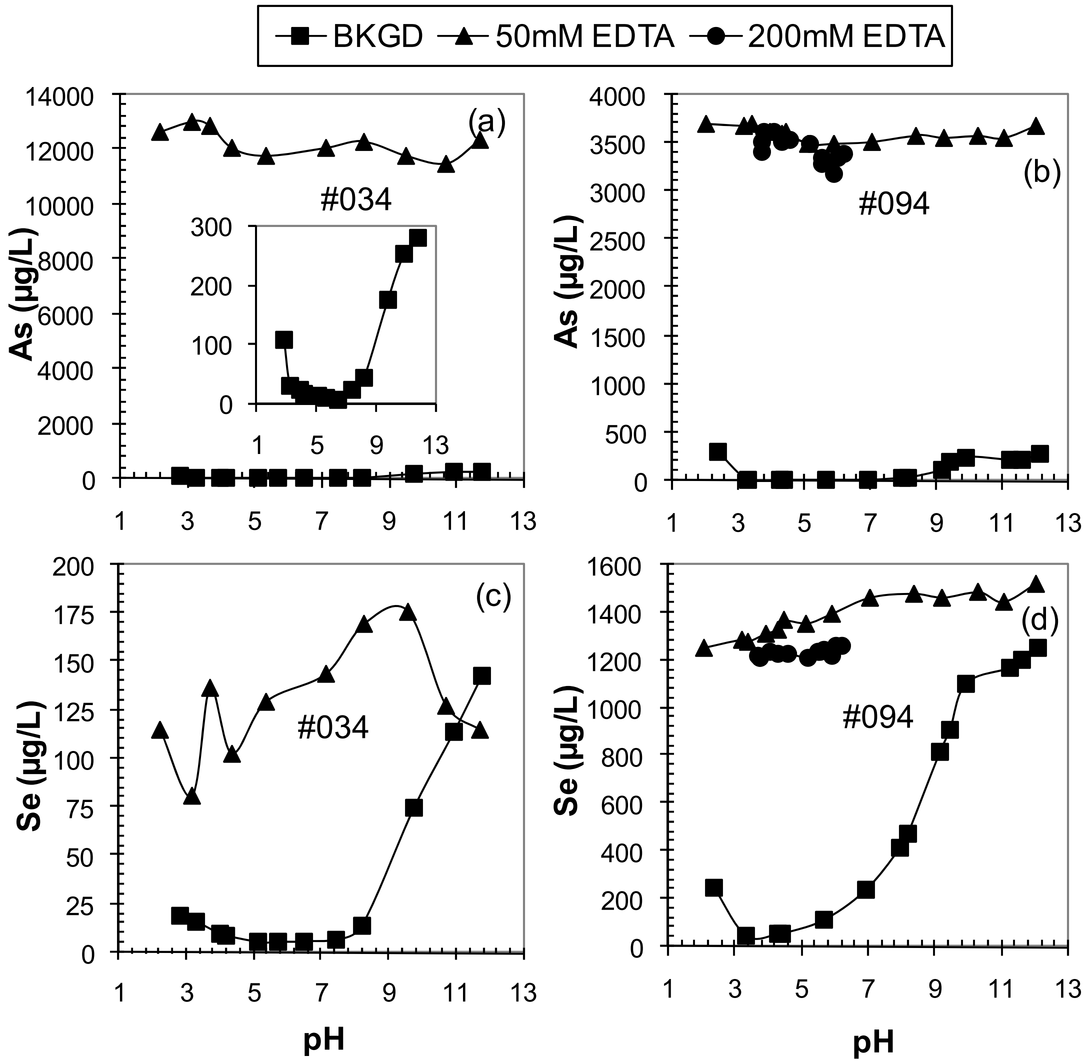


Figure 2. Leaching of As and Se from low-Ca ashes #034, and #094, with and without presence of EDTA. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hours.

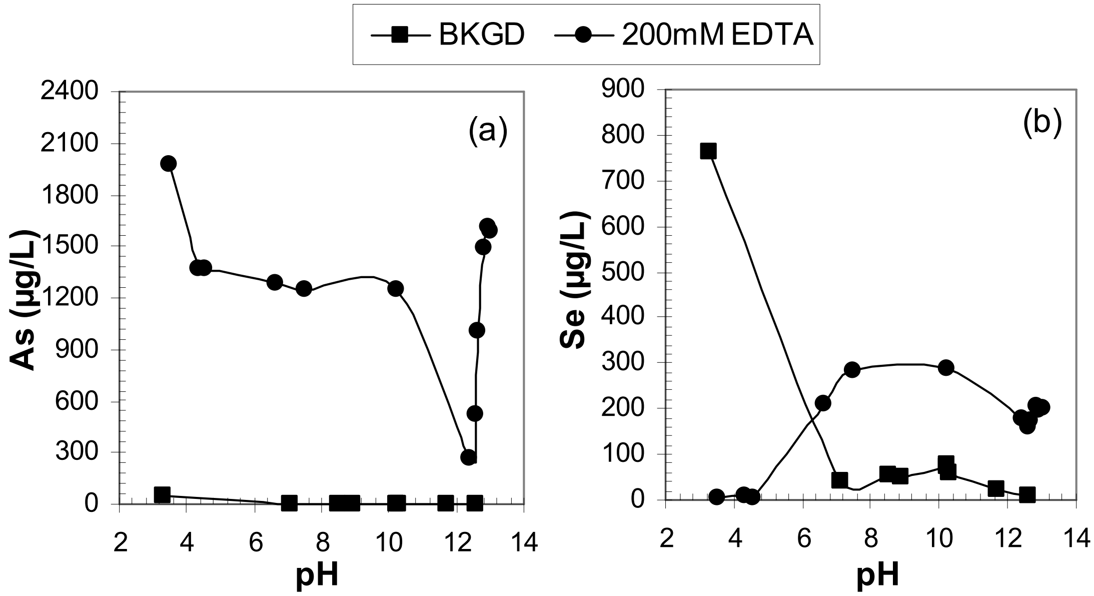


Figure 3. Leaching of As (a) and Se (b) from high-Ca ash #1021, with and without the presence of EDTA. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hours.

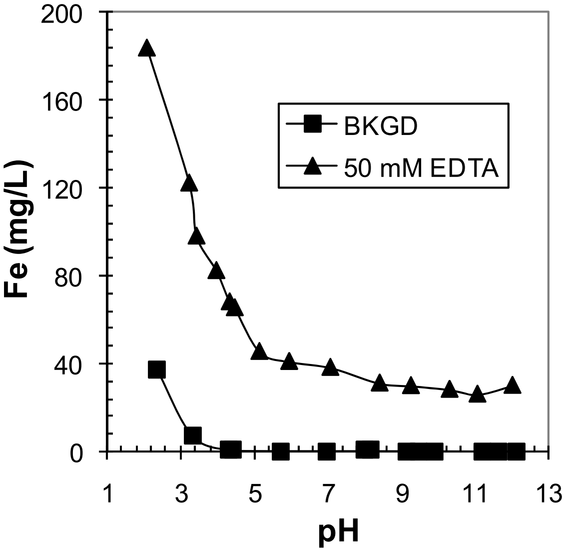


Figure 4. Leaching of Fe from ash #094 with and without 50 mM EDTA. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hrs.

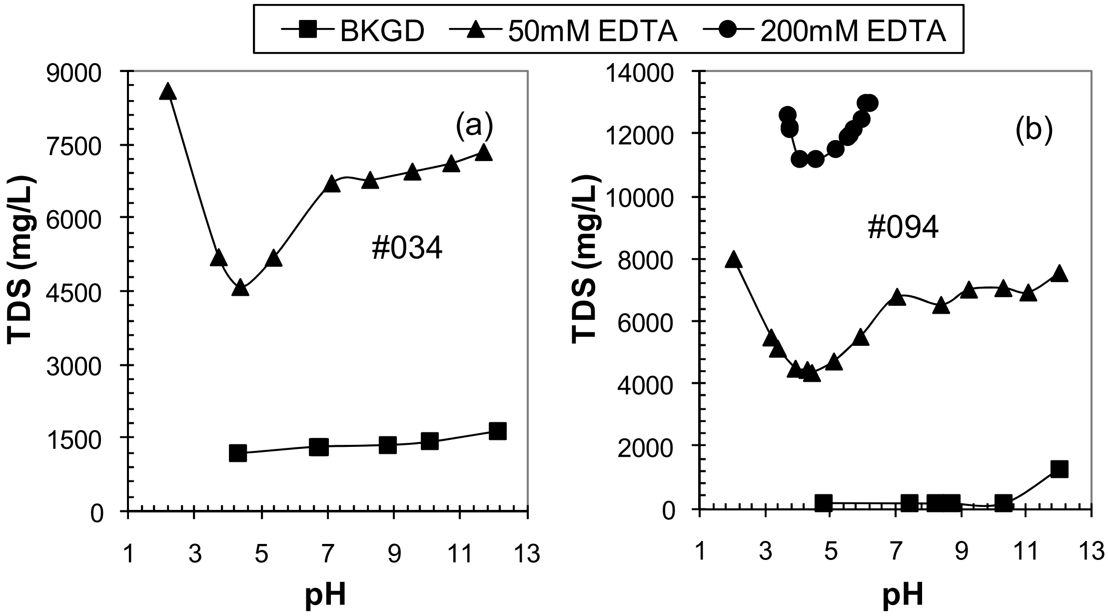


Figure 5. Leachate TDS of ashes #034 and #094, with and without EDTA addition. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hrs.

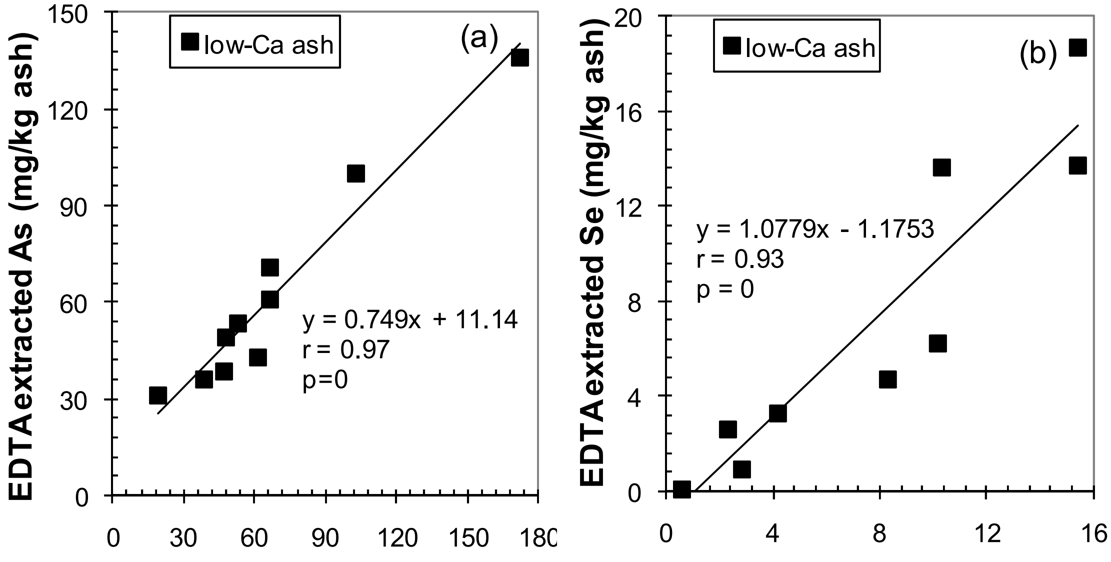


Figure 6. Correlation analysis of total extracted As and Se by 50 mM EDTA with the total As and Se for low-Ca ashes under natural pH at L/S 10.

Supporting Information:

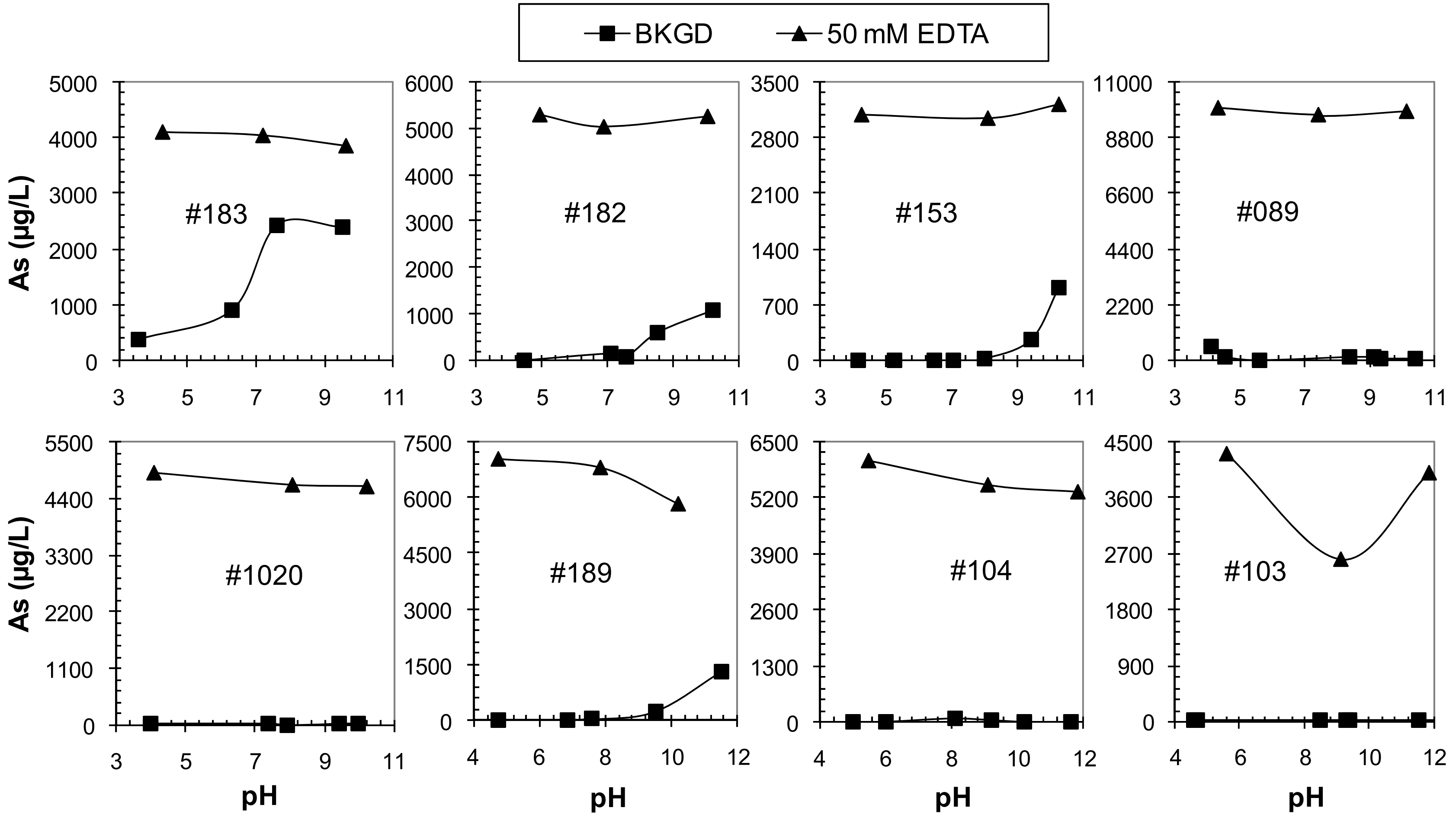


Figure S1. Leaching of As from eight low-Ca ashes with and without 50 mM EDTA. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hours.

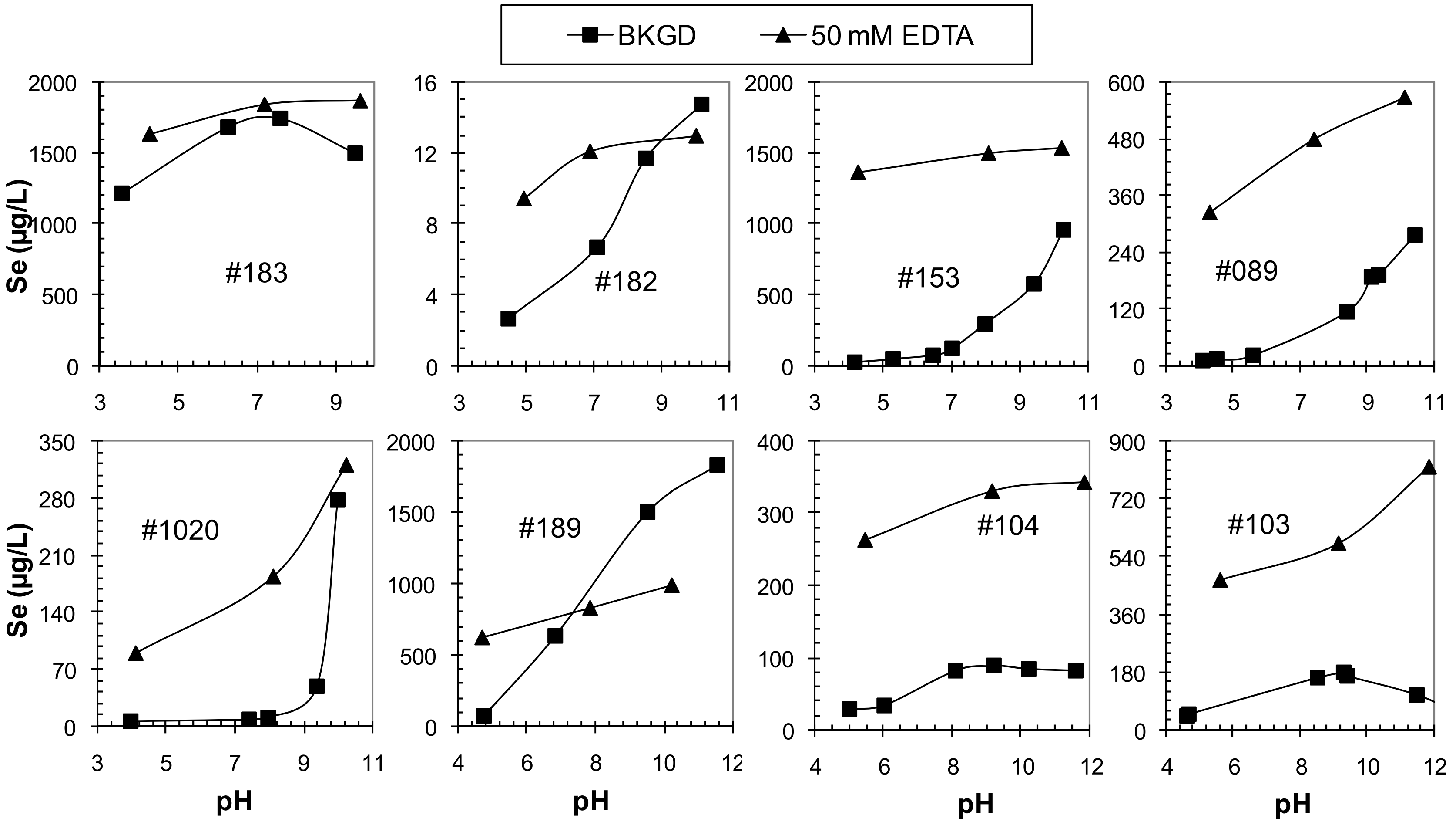


Figure S2. Leaching of Se from eight low-Ca ashes with and without 50 mM EDTA. Experimental conditions: L/S =10, temperature = 21-25 ^{o}C, leaching time = 24 hours.

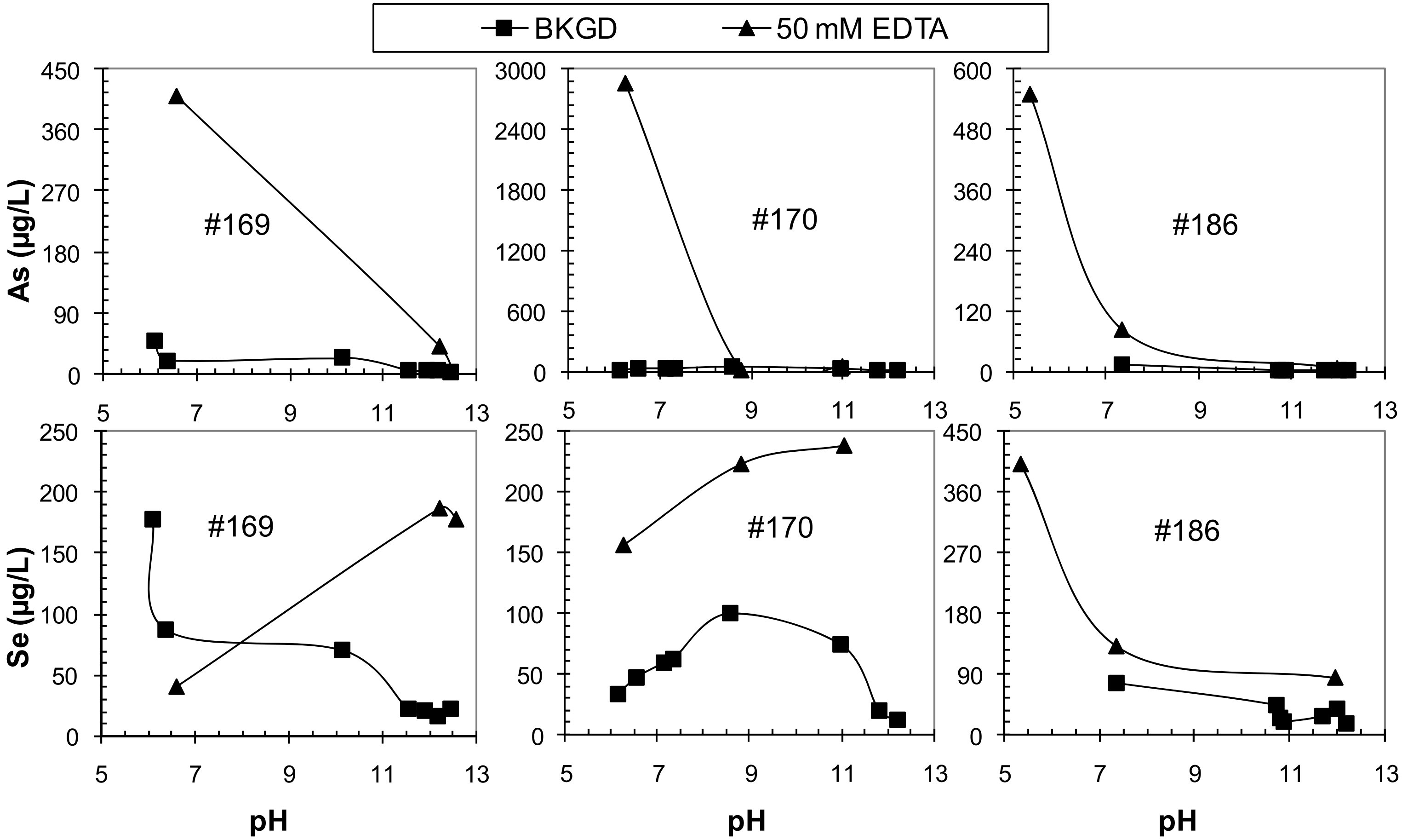
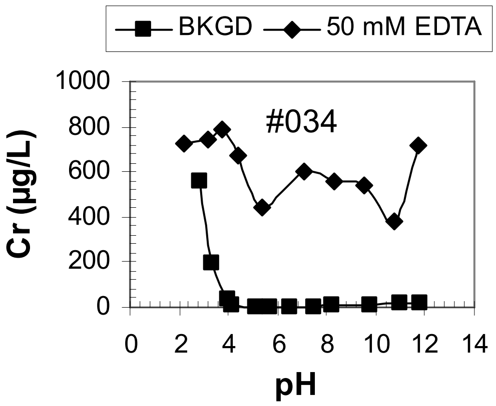
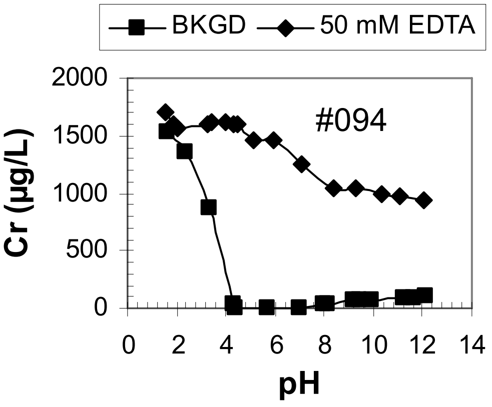
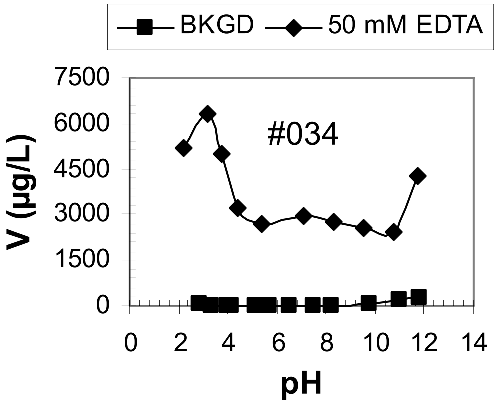


Figure S3. Leaching of As and Se from three high-Ca ashes with and without 50 mM EDTA. Experimental conditions: L/S =10, temperature = 21-25 °C, leaching time = 24 hours.


BKGD
50 mM EDTA
#034
Cr (µg/L)
0
200
400
600
800
1000
pH
0
2
4
6
8
10
12
14


BKGD
50 mM EDTA
#094
Cr (µg/L)
0
500
1000
1500
2000
pH
0
2
4
6
8
10
12
14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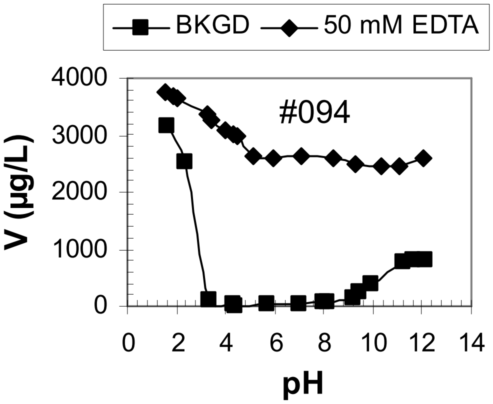
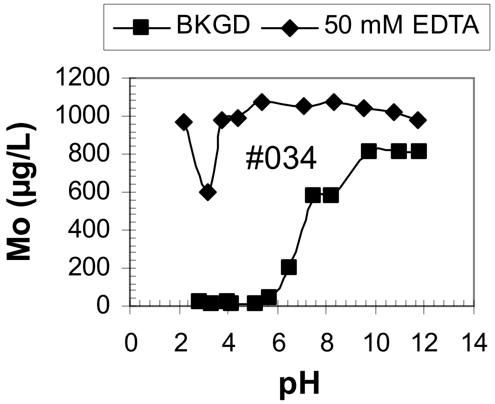
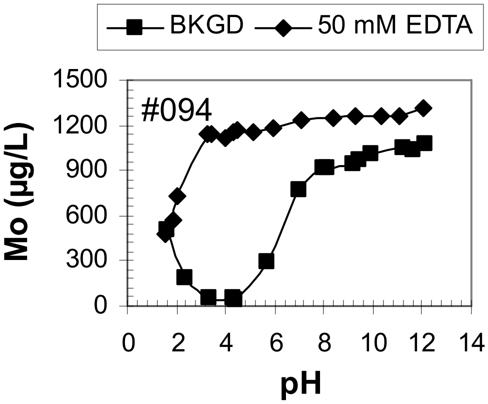
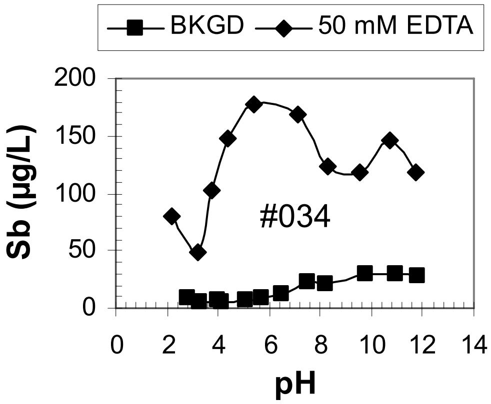
50 mM EDTA
#034
V (µg/L)
0
1500
3000
4500
6000
7500
pH
0
2
4
6
8
10
12
14


BKGD
50 mM EDTA
#094
V (µg/L)
0
1000
2000
3000
4000
pH
0
2
4
6
8
10
12
14


BKGD
50 mM EDTA
#034
Mo (µg/L)
0
200
400
600
800
1000
1200
pH
0
2
4
6
8
10
12
14


BKGD
50 mM EDTA
#094
Mo (µg/L)
0
300
600
900
1200
1500
pH
0
2
4
6
8
10
12
14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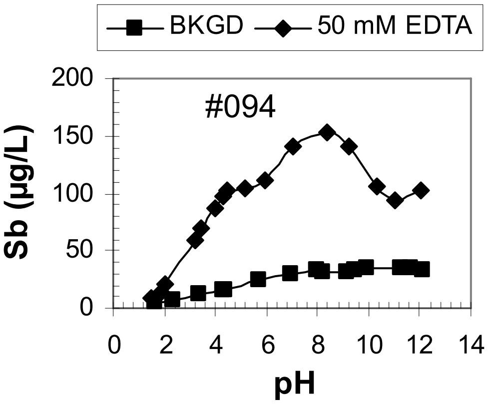
50 mM EDTA
#034
Sb (µg/L)
0
50
100
150
200
pH
0
2
4
6
8
10
12
14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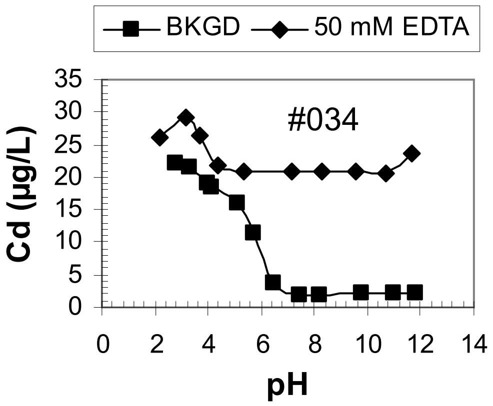
50 mM EDTA
#094
Sb (µg/L)
0
50
100
150
200
pH
0
2
4
6
8
10
12
14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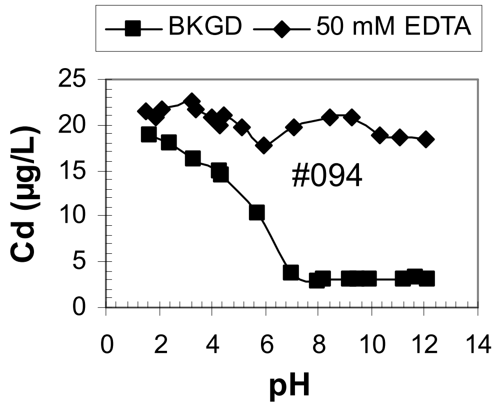
50 mM EDTA
#034
Cd (µg/L)
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
14
pH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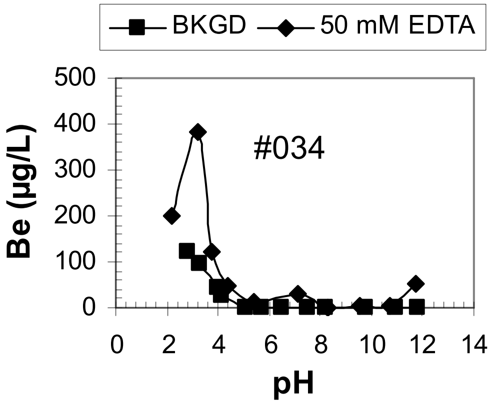
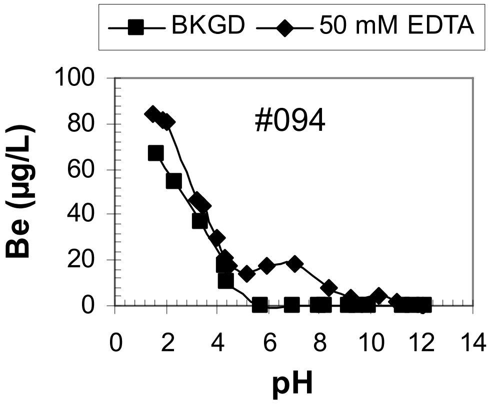
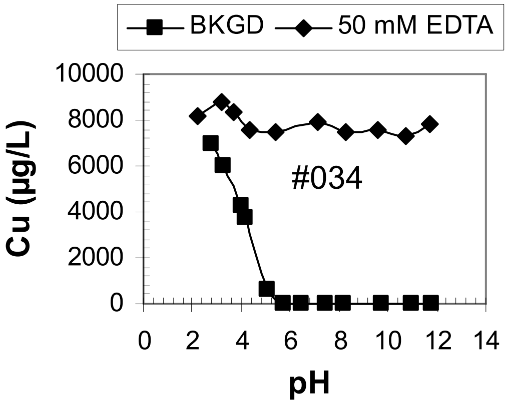
#094
Cd (µg/L)
25
20
15
10
5
0
0
2
4
6
8
10
12
14
pH


BKGD
50 mM EDTA
#034
Be (µg/L)
500
400
300
200
100
0
0
2
4
6
8
10
12
14
pH


BKGD
50 mM EDTA
#094
Be (µg/L)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
pH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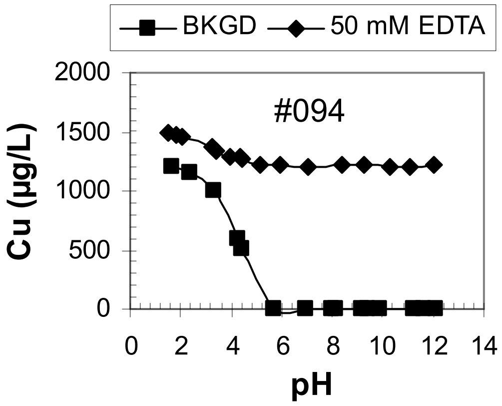
50 mM EDTA
#034
Cu (µg/L)
10000
8000
6000
4000
2000
0
0
2
4
6
8
10
12
14
pH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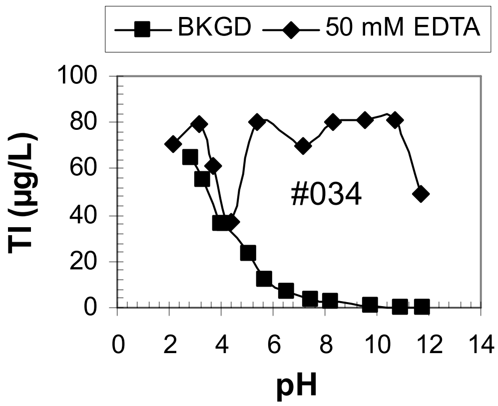
50 mM EDTA
#094
Cu (µg/L)
2000
1500
1000
500
0
0
2
4
6
8
10
12
14
pH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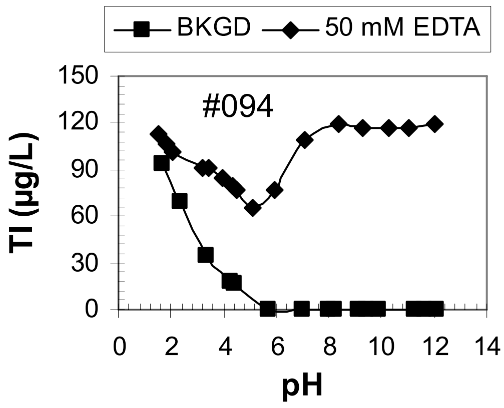
50 mM EDTA
#034
Tl (µg/L)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
pH


BKGD
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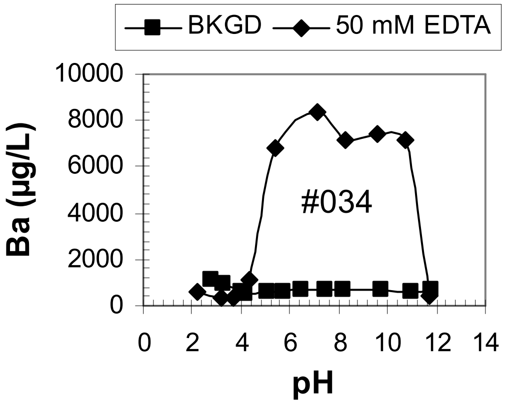
#094
Tl (µg/L)
150
120
90
60
30
0
0
2
4
6
8
10
12
14
pH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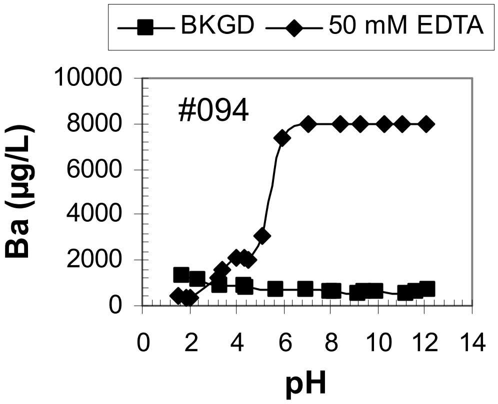
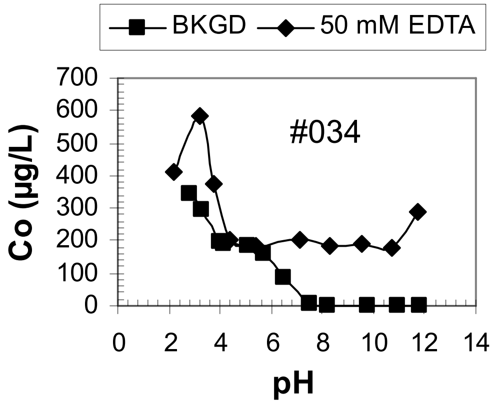
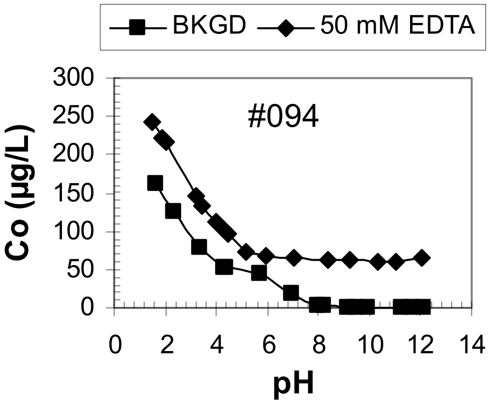
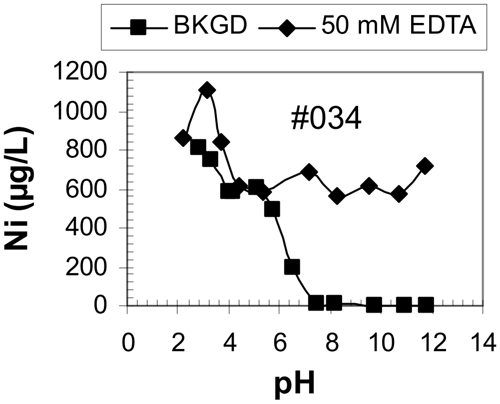
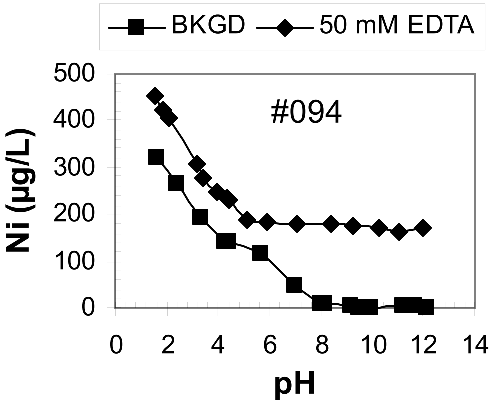
50 mM EDTA
Ba (µg/L)
10000
8000
6000
4000
2000
0
#034
0 2 4 6 8 10 12 14
pH


BKGD
50 mM EDTA
Ba (µg/L)
10000
8000
6000
4000
2000
0
#094
0 2 4 6 8 10 12 14
pH


BKGD
50 mM EDTA
Co (µg/L)
700
600
500
400
300
200
100
0
#034
0 2 4 6 8 10 12 14
pH


BKGD
50 mM EDTA
Co (µg/L)
300
250
200
150
100
50
0
#094
0 2 4 6 8 10 12 14
pH


BKGD
50 mM EDTA
Ni (µg/L)
1200
1000
800
600
400
200
0
#034
0 2 4 6 8 10 12 14
pH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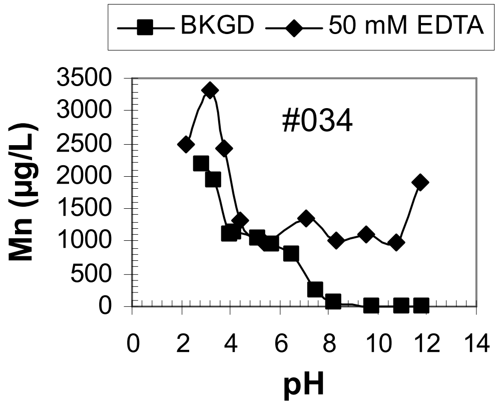
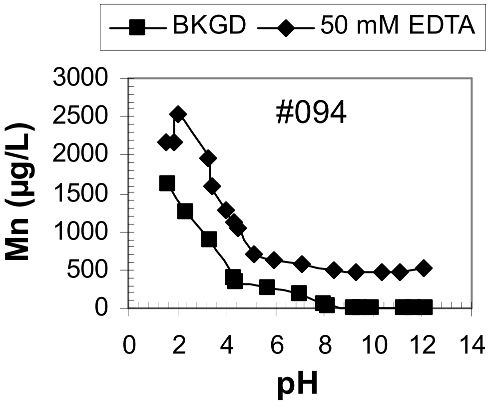
50 mM EDTA
Ni (µg/L)
500
400
300
200
100
0
#094
0 2 4 6 8 10 12 14
pH


BKGD
50 mM EDTA
Mn (µg/L)
3500
3000
2500
2000
1500
1000
500
0
#034
0 2 4 6 8 10 12 14
pH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Mn (µg/L)
3000
2500
2000
1500
1000
500
0
#094
0 2 4 6 8 10 12 14
pH

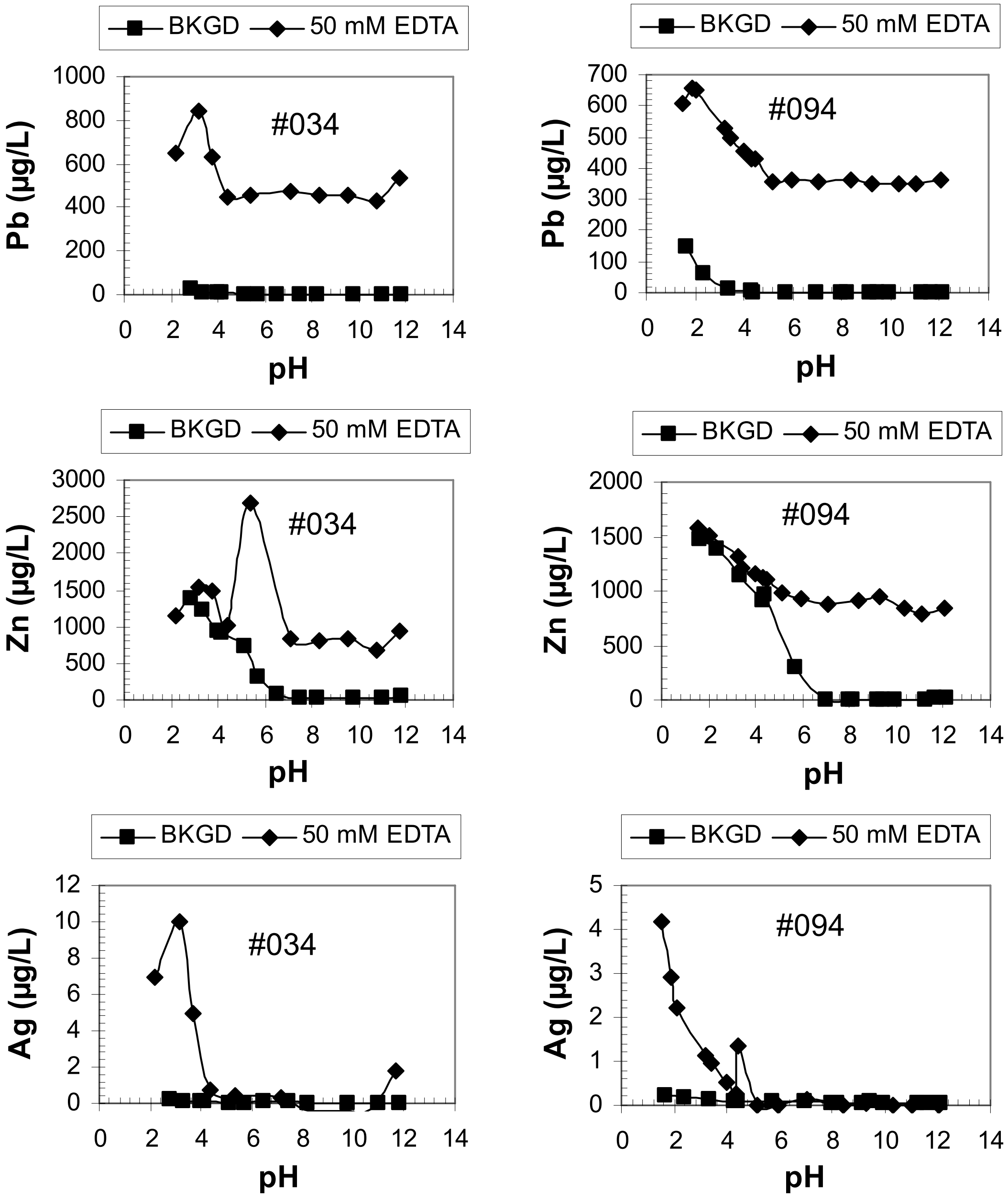

Figure S4. 50 mM EDTA extraction of 15 trace elements from ashes #034 and #094 over pH 2-12. Expereimental condition: L/S 10, room temperature, leaching time =24 hours.

SECTION VI

CONCLUSIONS

The primary results of this work are presented in four manuscripts to be submitted to peer-reviewed journals. Conclusions from this work have been reported in each paper, respectively, and have also been compiled and reported below.

Key conclusions on assessing the impact of trona-based SO_2 control technology on coal fly ash (Paper I):

1. Trona injection for SO_2 emission control significantly changed the fly ash physical characteristics, including reduced specific surface area, and changed particle morphology and microstructure.
2. Trona injection for SO_2 emission control significantly increased the bulk contents of sodium, sulfur, and carbonate in the fly ash, and brought great amount of soluble materials into the fly ash.
3. Trona injection for SO_2 emission control greatly increased the fly ash solubility, pH, and leachability of anionic elements including fluoride, sulfate, chloride, and trace oxyanions of concern especially As and Se. Leaching of cationic elements of concern from trona ash were either undetectable or decreased compared to the ash without trona.

Key conclusions on understanding the enhanced arsenic and selenium leaching behavior of trona ash generated from SO_2 control plant (Paper II):

1. Compared to the conventional fly ash, trona ash leached significantly more As and Se in all conditions, including varying leaching time, L/S, pH, storage time conditions.
2. Multiple factors may contribute to the enhanced As and Se leaching from trona ash, including more alkaline pH, greater ash solubility, reduced surface site density, presence of high concentrations of competing anions (such as sulfate and carbonate), increased background Se concentration, and a greater Se(VI) fraction in trona ash.
3. Ash storage time and leaching time also impacted As and Se speciation and, therefore, changed the leaching characteristics of As and Se. As(V) was the only species in both

fresh and stored trona ashes, while Se(IV) was gradually converted to more leachable Se(VI) with increases in storage time and leaching time. Both As(III) and As(V) were initially detected in leachates of fresh and stored control ash, but As(III) was converted to less leachable As(V) within several days of leaching time. Se(IV) was the only detectable Se species in the fresh control sample, but it was totally converted to Se(VI) after 3 years of storage. As a result, the more oxidized forms of As and Se are more stable species in both trona ash and conventional ash.

Key conclusions on modeling the batch leaching behavior of arsenic and selenium from raw bituminous coal fly ashes (Paper III):

1. As and Se leaching decreased with the increase of pH in the very acidic pH range, reached their minimal levels in the intermediate pH range, and increased with the increase of pH in the alkaline pH range..
2. Increasing leaching time increased As leaching but slightly decreased Se leaching in alkaline pH conditions.
3. DI-water washing may increase the leaching concentrations of As and Se.
4. The modeling protocol developed in this research is appropriate to determine the intrinsic leaching parameters of As(V), Se(IV), and other trace oxyanionic elements in raw bituminous fly ash, and to quantify their leaching under different pH and L/S ratios.
5. The modeling results demonstrated that ash washing did not change the adsorption strength of As and Se on the fly ash surface, and that the externally added As and Se had similar adsorption/desorption behavior as those originally presented in bituminous fly ashes.

Key conclusions on extraction of As and Se from coal fly ash using EDTA (Paper IV):

1. EDTA can significantly increase the leaching of As and Se from coal fly ash over pH 2-12. For low-Ca ashes (Ca<5%), the extraction of As was not dependent on pH, but the extraction of Se slightly increased with the increase of pH.
2. With 50 mM EDTA, up to 75% of As and 100% of Se could be extracted from low-Ca ashes under the natural pH condition. The EDTA effect in removing As and Se from high-Ca ashes was lower than that for low-Ca ashes.

3. As and Se were relatively stable in high-Ca ashes, and their leaching are minimal under natural pH. Therefore, the removal of As and Se from high-Ca ashes may not be necessary.
4. The extracted amount of As and Se significantly correlated to the total As and Se content in the low-Ca ash sample. However, no such correlation was observed for high-Ca ashes (Ca>5%). EDTA extraction may replace the complete acid digestion methods in assessing the total content and/or the total leachable arsenic and selenium in low-Ca fly ashes.
5. For low-Ca coal fly ashes, the EDTA extraction could be a convenient alternative for assessing the total leachable As and Se, and remediate fly ash of As, Se, and other toxic trace-element contaminants.

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