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Characterization and modeling of toxic fly ash constituents in the environment

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I am submitting herewith a dissertation written by Zhenwei Zhu entitled "Characterization and modeling of toxic fly ash constituents in the environment." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Civil Engineering.

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Vice Provost and Dean of the Graduate School

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CHARACTERIZATION AND MODELING OF TOXIC FLY ASH CONSTITUENTS IN THE ENVIRONMENT

A Dissertation

Presented for the Doctor of Philosophy Degree

The University of Tennessee, Knoxville

Zhenwei Zhu
August 2011
Dedicated

to my parents, wife and young son whom I love the most
because they never lose faith in me and give me endless
support, encouragement and affection through my life.

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Finally, I greatly appreciate that my parents bring me up and support me continuously and selflessly and my wife trusts me all the time and make sacrifice to let me achieve this goal.
ABSTRACT

Coal fly ash is a by-product of coal combustion that has drawn renewed public scrutiny due to the negative environmental impacts from accidental release of this waste material from storage facilities. Historically, the leaching of toxic elements from coal fly ash into the environment has always been a major environmental concern. Despite extensive efforts into the characterization of coal fly ash, effective models for the fate and transport of toxic fly ash constituents have remained lacking, making it difficult to perform accurate environmental impact assessment for coal fly ash. To close this critical knowledge gap, the overall objective of this study was to develop a predictive model for the leaching of toxic elements from fly ash particles. First, physical properties of coal fly ash were characterized to evaluate their contribution to elemental transport. Unburned carbon was shown to contribute to the sorption of arsenic to fly ash, which slowed the release of arsenic from fly ash. In parallel, leaching properties of various elements were determined to differentiate species of varying leaching capacities, demonstrating that the majority of toxic elements were not mobile under environmentally relevant conditions. Subsequently, a mechanistic model for the dissolution of fly ash elements was developed and validated with batch kinetics studies. Furthermore, elemental dissolution was integrated with hydrodynamic modeling to describe the leaching of toxic elements from fly ash in dry disposal facilities, which was validated by column studies. The mechanistic model developed and validated in this research represents the first such model that successfully characterized the complex processes underlying the release and transport of toxic elements in coal fly ash, providing a valuable tool to predict the
environment impact of coal fly ash and develop more effective management practices for both the industry and regulators.
EXECUTIVE SUMMARY

This dissertation summarizes research efforts to the modeling of the release of toxic elements from coal fly ash based on the physical and chemical characterization of coal fly ash. Findings reported in this dissertation provide a much needed quantitative tool for environmental risk assessment associated with coal ash disposal practice.

Coal combustion products (CCPs) refer collectively to coal combustion residue including fly ash collected by flue gas emission control system and bottom ash dropped to the bottom of combustion chamber. Power plants are the most important source of CCPs and coal fly ash (CFA) represents the largest fraction of CCPs, which has historically drawn much scrutiny due to the potential release of toxic elements from CFA to the environment. Recent events of the accidental spill of large volumes of CFA from storage facilities have renewed public concerns of the safety of current CFA management practices. Extensive research has been conducted on the production, composition, and toxicity of CFA in the past several decades. However, a mechanistic predictive model for the transport of toxic elements in CFA remains unavailable, representing a major knowledge gap in the understanding of the environmental impact of CFA, which is critical for the development of more effective CFA management and regulatory strategies.

Therefore, with the overall goal of this doctoral study to develop an effective transport model for the prediction of the mobility of toxic fly ash constituents in aqueous environments, the following objectives were achieved to obtain physical, chemical, and kinetics parameters followed by the quantitative validation of the transport model:
1. Characterization of the physical properties of CFA and investigate the linkage between unburned carbon and particle size distribution, surface area, and adsorption capacity of CFA;

2. Characterization of the chemical properties of CFA with a focus on the elemental distribution and speciation in fly ash size fractions, providing the linkage between chemical properties and leaching behavior under distinct environmental conditions.

3. Evaluation of processes underlying elemental release from CFA and the development and validation of a quantitative model accurately describing elemental release from CFA.

4. Develop and validate a mechanistic model capable of quantitatively predict the mobilization and transport of fly ash constituents in aqueous systems in a packed column leaching study.

Results from this study show that unburned carbon dictates the surface area and sorption capacity of CFA, which is subsequently implicated in reducing the rate of release of arsenic from CFA. Sequential extraction of size-fractionated fly ashes further indicates that a large majority (~60—80%) of total arsenic in CFA is present in forms not prone to immobilization.

The release of trace elements such as arsenic from CFA involves complex processes that can only be described by a multi-order dissolution model. For elements As, Cd, and Se, diffusive mass transfer does not play a major role in elemental mobilization. Subsequently, leaching of toxic elements from fly ash in packed columns was studied as a model system simulating the release of CFA constituents to demonstrate the utility of the elemental mobilization model. Integrated with hydrodynamic modeling, the coupled physicochemical
transport model was successfully validated and capable of predicting the leaching behavior of trace elements in CFA.

The mechanistic model developed and validated in this research represents the first such model that can successfully characterize the complex processes underlying the release and transport of toxic elements in coal fly ash, providing a valuable tool to predict the environment impact of coal fly ash and develop more effective management practices for both the industry and regulators.

However, since large variations in physical and chemical properties have been observed in CFAs from different sources. It is likely that the importance of multiple processes controlling the mobilization of toxic elements in CFA may shift. Future studies are needed to study the applicability of the transport model developed in this study for fly ashes of distinct properties. Furthermore, the transport of toxic elements from fly ash is only studied in packed columns which are only relevant for fly ash in dry disposal. It is important that similar efforts to be devoted to the modeling of elemental transport under environmental conditions relevant to the wet disposal of fly ash, particularly for scenarios when fly ash is accidentally released into a waterbody from wet disposal facilities.
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<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross-sectional area, m²</td>
</tr>
<tr>
<td>C</td>
<td>Liquid concentration of interested element, g/m³</td>
</tr>
<tr>
<td>C_b</td>
<td>Bulk concentration of element, g/m³ bulk volume</td>
</tr>
<tr>
<td>C_b(t)</td>
<td>Bulk concentration of element at time t, g/m³ bulk volume</td>
</tr>
<tr>
<td>C_bmax</td>
<td>Maximum bulk concentration of element, g/m³ bulk volume</td>
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<td>C_i</td>
<td>Dynamic state liquid concentration of interested element, g/m³</td>
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<tr>
<td>C_in</td>
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<tr>
<td>C_max</td>
<td>Maximum liquid concentration of interested element, g/m³</td>
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<tr>
<td>D</td>
<td>Dispersion coefficient</td>
</tr>
<tr>
<td>f</td>
<td>Mathematic function</td>
</tr>
<tr>
<td>I_in,i</td>
<td>Total mass input of the element, g/m³</td>
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<tr>
<td>k</td>
<td>Dissolution coefficient, hour⁻¹</td>
</tr>
<tr>
<td>k'</td>
<td>Constant, as C_bmax×k</td>
</tr>
<tr>
<td>k_d</td>
<td>Dissolution coefficient</td>
</tr>
<tr>
<td>k_n</td>
<td>Constant, as k×C_bmax×(C_bmax×V/w)^n-1</td>
</tr>
<tr>
<td>K_d</td>
<td>Sorption coefficient</td>
</tr>
<tr>
<td>K_p</td>
<td>Partition equilibrium coefficient</td>
</tr>
<tr>
<td>m</td>
<td>Mass of dissolved element, g</td>
</tr>
<tr>
<td>q</td>
<td>Lateral inflow, m³/hour</td>
</tr>
<tr>
<td>Q</td>
<td>Water discharge, m³/hour</td>
</tr>
<tr>
<td>n</td>
<td>Exponential constant</td>
</tr>
<tr>
<td>r_i</td>
<td>Difference between prediction and measurement</td>
</tr>
<tr>
<td>r_Ci</td>
<td>Liquid transformation rate, g element/m³·hour⁻¹</td>
</tr>
<tr>
<td>r_Ssi</td>
<td>Solid transformation rate, g element/kg·hour⁻¹</td>
</tr>
<tr>
<td>S</td>
<td>Leach square</td>
</tr>
<tr>
<td>S_s</td>
<td>Solid surface concentration, g element/kg coal fly ash</td>
</tr>
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<td>S_s(t)</td>
<td>Solid surface concentration at time t, g element/kg coal fly ash</td>
</tr>
<tr>
<td>S_seq</td>
<td>Solid surface concentration at equilibrium state between liquid and solid</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>$S_{\text{max}}$</td>
<td>Maximum solid surface concentration, g element/kg coal fly ash</td>
</tr>
<tr>
<td>$S_{\text{si}}$</td>
<td>Dynamic state solid concentration, g element/kg solid</td>
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<tr>
<td>$t$</td>
<td>Time, hour</td>
</tr>
<tr>
<td>$w$</td>
<td>Weight of coal fly ash, kg</td>
</tr>
<tr>
<td>$x$</td>
<td>Column length, m</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Independent variable</td>
</tr>
<tr>
<td>$y_i$</td>
<td>Dependent variable</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of batch reactor, m$^3$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Bulk liquid density, kg/m$^3$ liquid</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Solid particle density, kg/m$^3$ solid</td>
</tr>
</tbody>
</table>
NOMENCLATURE

AASHTO = American Association of State Highway and Transportation officials
ASTM = American Society for Testing and Materials
B.E.T. = Brunauer, Emmett and Teller
CCD = Charge-Coupled Device
CCPs = Coal Combustion Product
CFA = Coal Fly Ash
CFM = Cubic Foot per Minute
ESP = Electrostatic Precipitator
ICP-AES = Inductively Coupled Plasma-Atomic Emission Spectrometry
LOI = Loss On Ignition
MARS = Microwave Accelerated Reaction System
PFA Teflon = Perfluoroalkoxy Teflon
PVC = Polyvinyl Chloride
RCRA = Resource Conservation and Recovery Act
SCR = Selective Catalytic Reduction
SEM = Scanning Electron Microscopy
SI = Saturation Index
TCLP = Toxicity Characteristic Leaching Procedure
TEM = Transmission Electron Microscopy
USEPA = United States Environmental Protection Agency
CHAPTER 1 INTRODUCTION

1.1. Statement of the problem

Coal fly ash (CFA) represents the most abundant form of Coal Combustion Products (CCPs) in coal-fired power plant, which also includes bottom ash, boiler slag, and flue gas desulfurization material [1, 2]. In 2008, 72.4 million tons of CFA, approximately 53.2% of CCPs, were produced in the United States, in which only 41.6% of CFA was reused, according to American Coal Ash Association CCPs Production & Use Survey [2]. The rest of CFA is either stored onsite, in fly ash impoundment ponds and dry fly ash silos, or disposed offsite in landfills, presenting well known environmental risks as a result of the potential leaching of toxic elements from CFA. Therefore, it remains the priority to develop fly ash disposal options that minimize environmental impacts. The formation of fly ash is complicated and affected by many factors, such as coal properties, combustion temperature, and furnace types, which subsequently influence the mobility of toxic elements in CFA. The primary concern of CFA has been the potential environmental risks associated with the release of heavy metals and inhalable particulate matter. Specially, the interaction between fly ash and the aqueous phase is the main pathway for the release of toxic constituents from fly ash to the environment, posing potential harms to human beings and other living organisms. Since fly ash contains heavy metals which are naturally present in coal and subsequently concentrated through the combustion process, the heavy metals and their leaching behavior are critical for the understanding of the environmental impact of CFA. This study establishes the linkage between fly ash and its environmental behavior in order to answer those questions mentioned above.
In general, CFA is a heterogeneous solid waste which has been studied extensively on physiochemical properties and potential beneficial applications. Both physical and chemical properties of CFA are found to be dependent on many factors, including coal source and type, combustion process, furnace temperature and flue gas emission control processes. As a result, studies of CFA are frequently focused on selected fly ash characteristics of fly ashes from particular sources. One of the objectives of this study is to overcome these limitations by studying CFA in a systematic manner using consistent technical approaches. In this study, CFA was sorted into more homogeneous fractions according to particle sizes, providing a better understanding of the distribution of fly ash properties. Furthermore, this study also addresses the challenge to develop a predictive model to describe the leaching behavior of fly ash under environmentally-relevant conditions, providing a useful tool for the prediction of the transport of CFA toxic constituents and the assessment of the environmental risks of fly ash disposal practices.

1.2. Background knowledge on coal and coal combustion
1.2.1. Coal properties and classification

Coal is a brown-to-black readily combustible, sedimentary rocklike material altered from the buried prehistoric plant under the exposure to extreme pressure and temperature during geological transition in earth [3]. Coal has a highly variable composition, affecting both its chemical and its physical properties. It may contain significant amounts of sulfur, arsenic, and other materials that can lead to environmental concerns as the coal residue is produced [4]. In regard to chemical composition, coal is a complex composite primarily composed of carbon, hydrogen, oxygen, nitrogen with variable amount of dozens of trace elements, such
as heavy metals [5]. From the emission point of view, the elements, such as sulfur, nitrogen, and mercury which are converted to chemical forms as pollutants in air and water, are the major concern. As for as the environmental impact from disposing coal combustion residue is concerned, toxic metals, especially heavy metals, leached from coal ash have always been the primary target [5].

Based on the fixed carbon and heating value of coal, a classification system is established by the ASTM and accepted universally, which categorizes coal into four types, anthracitic coals (15000Btu/lb or more), bituminous coals (between 10500 and 14000Btu/lb), subbituminous coals (from 8300 to 11500Btu/lb), and lignite (8300Btu/lb or less), in the descendent order of heating value. 

1.2.2. Coal combustion technologies

Many industrial and utility boilers use coal as the primary source of fuel. The boiler is the unit that encloses the furnace, where the fuel is combusted. When coal is fed into the furnace, the heat generated is used to heat water circulating in tubes surrounding the furnace. As the water heats, it turns to steam. The steam is captured and used within the facility to turn the blades of an electricity generator or a compressor for refrigeration, to heat a process or a building, or for many other uses.

There are three primary coal combustion technologies, as shown in Fig.1.1.

A. Grate firing, where coal is combusted while residing on a grate within the furnace. Grate firing technology was the first combustion system used for solid fuels. It now is used mainly for burning waste and biomass, but also for smaller coal furnaces.
B. Fluidized bed firing, where coal is crushed to a fine powder prior to entering the combustion chamber. In the combustion chamber, the solid fuels form fluidized bed from the suspension created by upward-blowing air. It results in a turbulent mixing of air and fuels, which provides more effective chemical reactions and heat transfer.

C. Pulverized fuel firing is a solid fuel burning technique in which the fuel is pulverized before being ignited. It is the most common method of burning coal for power generation. The basic idea of a firing system using pulverized fuel is to use the whole volume of the furnace for the combustion of solid fuels. Coal is ground to the size of a fine grain, mixed with air and burned in the flue gas flow. Biomass and other materials can also be added to the mixture. Coal contains mineral matter which is converted to ash during combustion. The ash is removed as bottom ash and fly ash. The bottom ash is removed at the furnace bottom.

Figure 1.1: Combustion systems for solid fuels, such as coal.
1.2.3. Description of fly ash formation

In pulverized coal boilers, fly ash formation involves a complex series of processes. As coal burns out, inorganic mineral starts fragmentation followed often by coalescence on the char surface. The molten ash particles, entrained in the combustion gases after char fragmentation, are rapidly quenched to primarily spherical, glassy particles as they are swept away from the flame region. Microanalysis of ash collected in flue gas cleaning plant shows that it consists primarily of spherical particles of impure aluminosilicate glass. The particle size varies from sub-micrometer to $> 100$ pm [6]. As the carbonaceous material is consumed and recedes, the major inorganic constituents are exposed, while the atomically dispersed elements are released by the oxidation of the organic matter. Much of the exposed mineral matter remains attached to the char surface as glassy spheres or at high melting point, irregularly shaped particles. Particle size growth can occur as a result of mineral matter agglomeration. In the extreme, the maximum initial size of an individual ash particle may be proportional to the total inorganic content of the original coal particle (e.g., one ash particle generated per coal particle). However, in reality, because of the char particle's increasing porosity as the coal particle burns, a critical porosity is reached which results in fragmentation into new ash particles of various sizes. Typically, spherical ash particles are created which may subsequently undergo other transformation processes, such as coalescence with other particles or swelling due to release of volatiles. Hollow cenosphere may also be generated via the expansion of trapped volatiles within melted particles. It can be concluded that the great overall variation in the size of the larger ash particles, which is significantly greater than that of the feed coal particles, is mostly attributed to the ash content
of individual coal particles, the fragmentation phenomena, and cenosphere formation [7]. Conventionally, particulate matter from pulverized coal combustion is considered to be bimodally distributed, including an ultrafine mode (~0.1 μm) formed primarily by the vaporization-condensation mechanism and a coarse mode (1-20 μm) produced mainly by the coalescence of molten ash droplets and char fragmentation [8].

The typical coal combustion facility, seen in Fig.1.2, consists of a coal pulverizer, a furnace with three burners and a gas treatment system, including selective catalytic reduction (Flue-gas denitrification), electrostatic precipitator or bag filter (fly ash removal) and wet limestone scrubber (Flue-gas desulfurization).

Bottom ash typically consists of large ash residues that accumulate at the bottom of the boiler. Boiler slag is a molten inorganic material that is collected at the bottom of the boiler and discharged into a water-filled pit, where it is cooled with water (quenched) and removed as glassy particles resembling sand. The form of the bottom ash or slag is dependent on the type of furnace and the fusion temperature (or melting point) of the ash or slag generated from the coal. Some pulverized coal (PC) furnaces fire coals of high ash-fusion temperatures and use a dry ash removal technique [9]. Others fire coal with a low ash-fusion temperature causing much of the ash to form a liquid slag, which is then drained from the bottom. Boiler slag is a coal combustion residue that is expected to be produced in diminished quantities in the future because of the retirement of the older boilers that produce liquid slag in significant quantities.
1.3. Review of the literature

Essentially, CFA is a coal combustion residual when carbon in coal is burned out and minerals are exposed at high temperature and then melted into liquid state or gasified into gas phase. The mineral residue will form into solid state when temperature plummets along the post-combustion processes. However, CFA is not pure mineral residual but a mixture of coal char, other type of carbon debris and mineral. The process of ash formation varies due to many factors. Short retention time of pulverized coal particle in the combustion zone is one of the major factors contributing to the inconsistency of CFA production and the increase of unburned carbon content in CFA. The unburned carbon residual directly results in degrading CFA quality for construction purpose. The unburned carbon has great impact on fly ash characterization and other beneficial use of CFA.

1.3.1. Carbon effect of unburned carbon on the characterization of coal fly ashes

CFA utilization is the major motivation for scientists and engineers to study its property and characteristic as they think CFA as “a valuable industrial by-product” defined by Lindon...
K. A. Sear [10]. The primary market of fly ash utilization is as pozzolanic additive in concrete production. However, fly ash is not always a good material from the beneficial utilization point of view despite its inexpensive and abundant characters. The presence of unburned carbon is the main hindrance to its beneficial application. As it is well known that the presence of unburned carbon in fly ash can significantly reduce the effect of air entrainment agents added into fresh concrete, subsequently affecting the durability of concrete [11]. Therefore, American Society for Testing and Materials [12] and American Association of State Highway and Transportation Officials (AASHTO) specify carbon content in fly ash once it is used as an admixture in Portland cement concrete. In the United States, ASTM limits fly ash that is used as cement replacement in concrete having under 6% of unburned carbon as Loss On Ignition (LOI) according to ASTM C618 [12]. The excess unburned carbon in the fly ash greatly restricts extensive CFA utilization in concrete and concrete products. According to American Coal Ash Association CCPs Production & Use Survey, in 2008, 72.4 million tons of fly ash were produced, of which only 17.4% was reused in concrete and concrete related product [2]. In order to facilitate the use of fly ash in concrete industry, in general, there are two types of approaches that have been taken advantaged of improving the fly ash quality by removing unburned carbon from fly ash. One is to manipulate the coal combustion process to minimize unburned carbon in the fly ash. Unburned carbon in the fly ash can be influenced by three major categories, including coal preparation and grinding, selection of coals of specific properties, and adjustments of burner and furnaces [13]. By optimizing those factors, theoretically it can greatly improve the quality of final fly ash. However, in reality, the coal properties are inconsistent from source
to source which significantly undermines the efforts that have been done to improve the combustion process. The other approach is to implement fly ash post-treatment to achieve a better quality of fly ash. It can be done either through oxidation or separation. Fly ash oxidation could be done at either low or high temperature, with oxygen or ozone, to burn out unburned carbon. Physical separation can recover carbon from fly ashes and enrich mineral fraction suitable for concrete application [11]. Even though it is technically feasible for carbon removal, it has not universally utilized either on-site or off-site of coal combustion facilities. There are various other factors that are playing important roles in decision-making process, for example, economical assessment, technical complexity, current regulation and practice, etc.

There are also other types of beneficial use for fly ash, for example, contaminant removal by adsorption. The adsorption application for fly ash utilization becomes attractive mainly because of its low cost compared with other types of adsorbent, such as activated carbon. Fly ash as an adsorbent has been reported in applications for removing organic compounds, such as PCB and phenolic compounds from wastewater [14-17], herbicides adsorption from soil-fly ash mixtures [18], and heavy metals from industrial waste streams [19]. Many studies already showed the potential of fly ash as low-cost adsorbent [19-22] although the efficiency of fly ash being an absorbent is not as high as activated carbon or other types of carbon absorbent. As fly ash inevitably contains unburned carbon, one could logically reason that the adsorption capacity for fly ash may be mainly due to the presence of carbon in the raw fly ash. Wang et al. suggest that the adsorption capacity of fly ash is dominantly contributed by
the porous unburned carbon rather than the fly ash itself [23]. Researchers have realized that unburned carbon is critical for adsorption application.

On the other hand, the major hindrance to the beneficial use of fly ash in cementitious materials is the presence of unburned carbon. Possible technologies that can be used for carbon removal include electrostatic separation and microwave heating [24]. Given the importance of unburned carbon, research conducted in this study examined the unburned carbon distribution and evaluate the relationship between physical adsorption capacity and quantitative mass of unburned carbon at different particle size fractions of fly ash.

Besides the unburned carbon in fly ash, the mineral ash, also referred to as fly ash particle, is the major part of CFA. Its chemical properties and elemental distribution, especially heavy metals, are critical for the assessment of CFA management practices because the leaching and transport of toxic constituents in fly ash present major environmental risks.

1.3.2. Characterization of pulverized coal fly ashes and evaluation of elemental distribution and speciation in fractionated CFAs

CFA is generated through coal combustion process. The majority of CFA is in perfect solid spherical shape, mixed with other combustion residues in minimal fraction, for example, unburned carbon, cenospheres, and amorphous particles. CFA is an extremely complex mixture, containing SiO$_2$, Al$_2$O$_3$, CaO, MgO, Fe$_2$O$_3$, K$_2$O, Na$_2$O, SO$_3$ and other oxides, and heavy metals such as As, Cd, and Se [25]. Due to the presence of hazardous elements, like heavy metals, in large amounts of coal fly ash, fly ash disposal has drawn great attention regarding public health and environmental conservation. As conventional disposal approaches for fly ash disposal, either in landfill or on-site impoundment storage, cannot
circumvent the interactions between fly ash and the aqueous phase, metal or toxic elements leaching is inevitable throughout the time of storage. Therefore, contamination of water, soil, and sediment resulting from the released toxic constituents has become a major concern.

Because fly ash is a heterogeneous material which contains fly ash particles of different sizes, it will provide insightful understanding to study the elemental distribution among different sizes of fly ash particle. The elemental distribution not only determines the leaching potential of toxic compound but also implies the leaching characteristic of fly ash. Therefore, studying the characteristics of fractionated fly ash provides more detailed data for the development of quantitative predictive models capable of accurately describe the mobilization and transport of toxic constituents in fly ash in the environment.

Davison et al [26] reported that fine particle fraction of fly ash could be enriched in trace elements compared with the fraction of trace elements in the parent coal. This is due to the volatilization of some elements in the boiler and their subsequent condensation in the cooler sections of the flue gas stream. Many of the most toxic elements, significant enrichment is observed in the fine particle of coal fly ash [27]. Karayigit et al [28] indicated that some volatile elements, notably As, Cd, and Zn, had increasing concentrations from coarse to finer particle size fly ash. Similar observations with As, Cd, Pb and Zn have also been reported by Hower et al [29].

While the concentration and mobility of toxic elements in fly ash may be influenced by particle size distribution, the structure of particle size and the pattern of elemental incorporation may also affect the mobility of fly ash constituents. Domka [30] pointed out that fly ash is formed mainly by a certain matrix (i.e. SiO$_2$, Al$_2$O$_3$, CaO). It also contains
other elements which are embedded into the silica skeleton and the rest of the elements in trace amount sitting on the surface of the ash molecules. The presence and quantity of major and trace elements in coal fly ash depend on the type of coal and conditions of combustion. Furthermore, the elemental distribution is also affected by other factors, such as organic matter and carbonate species etc. Mardon et al [31] summarized that organic-, sulfide-, and carbonate-bound elements are generally more easily volatilized than silicate-bound elements.

Elemental speciation, defined by the approach of sequential extraction [32], differentiates chemical fraction of elements into five categories, (i) water-soluble; (ii) acid-soluble; (iii) oxide; (iv) difficult reducible; and (v) residual. This approach has been widely used to investigate elemental leaching behavior and mobility in environmental conditions [33-35]. The elemental speciation has a direct connection with the potential leaching capacity of toxic constituents in fly ash. Therefore, analysis of elemental speciation gives insightful understanding of elemental behavior in environment, especially elemental mobility.

Researchers have conducted extensive studies on fly ash characterization from different sources. Due to the complex properties of coal, especially chemical composition, and the difference of coal combustion technologies, the coal fly ashes show considerably variations in physical and chemical properties. Up to date, there is no mechanistic model capable of accurately describing the mobilization of toxic elements from fly ash, representing a major knowledge gap in the understanding of the fate and transport of fly ash constituents in the environment.
1.3.3. Elemental leaching and mobility in environmental conditions

Fly ash leaching involves both chemical and physical transport/leaching processes, which can be schematically presented in Fig. 1.3. When the heavy metal-containing solid matrix, i.e. fly ash, is exposed to aqueous solution, mobile fly ash constituents enter the pore water due to desorption of metals or/and dissolution of metal compounds. The desorption process for metals or dissolution of metal compounds in the pore water is called “solubilization”. The difference in chemical potential between the pore fluid and the fluid surrounding the porous matrix induces diffusion of metals through pore fluid and causes leaching. As the aqueous solution or water passes through the porous matrix, contaminant transports due to advection along with dispersion (which includes molecular diffusion) of contaminants through pore water [36]. The solubility of heavy metals in water depends on hydrolysis, and the presence of other organic and inorganic ligands, their coordinate chemistry, and the pH of the solution. The desorption of metals depends on the properties of the solid (particle size, nature inorganic oxide coating, organic carbon content, and zero point charge of the solid) as well as the properties of the liquid, include pH and total dissolved metal concentrations. The effect of pH on desorption is generally dominant, because pH has a major influence on solubility of most chemical species [37].

Fly ash leaching test has been extensively conducted over the past fifty years to study the mobility of heavy metals in fly ash in particular. Coal ash leachate is generated by the contact of water with the ash. The water soluble oxides on the surface of the ash particles are dissolved into solution, creating a potentially high salinity leachate. The chemistry of the leachate varies quite considerably, with pH ranging from acidic to alkaline. The majority of
fly ash leachate is prone to be alkaline due to the presence of lime while fly ash with high Fe can lead to an acidic leachate through oxidation and the release of hydrogen ions. Batch and column leaching are the most commonly approaches to investigate the mobility of major and trace elements in coal ash, assess ash disposal options, and even study the impact of field relevant leaching conditions (e.g. low flow, intermittent flow scheme) [38-40].

The duration of test is usually selected so it can represent a period of time when the material would become stable. Duration of the column experiments ranges from 48 hours to 7 years. Another way of determining the duration of the test has been by cumulative LS ratio or pore volume flowing through the column combined with the flow rate. Column tests are usually carried out from \( \frac{1}{2} \) pore volume to 10 pore volumes. The controlled amounts of leachate were usually based on an average monthly or yearly rainfall amount.

Column tests have been studied as both closed systems [41] and open systems [42]. In closed systems, the material in the column has no contact with the atmosphere, so carbonation of the sample and evaporation and transpiration losses from the column do not represent an extra variable to consider. In open systems evaporation and transpiration, as well as carbonation, cannot be ignored. The packing of the column also varies between experiments. In most cases, a layer of glass beads or ceramic material is placed underneath and above the material of interest. The top layer, usually consisting of glass beads, helps distribute the flow above the column evenly [43, 44]. The bottom layer, typically consisting of sand or glass beads, nylon mesh, filter paper, glass wool or synthetic cloth, helps filter the leachate and prevent the material inside the column from exiting the system [43-45].
1.3.4. AQUASIM software and its applications

AQUASIM was first developed in 1994 by Peter Reichert who emphasized that it is a tool for simulation and data analysis of aquatic systems [46]. In the program, the spatial configuration of a model system is represented by compartments, which are connected by links. It also allows user to define an arbitrary number of substances to be modeled and it is extremely flexible in the formulation of transformation processes. The model structure is shown in Fig.1.4. It not only offers the possibility of performing simulations of the time evolution of the user-specified system, but it provides also methods for system identification (sensitivity analysis and automatic parameter estimation) and it allows us to estimate the uncertainty of calculated results.

In the process of model creation, the key component is to choose compartments. There are 6 compartments defined in the software: Mixed Reactor Compartment, Biofilm Reactor Compartment, Advective-Diffusive Reactor, Saturated Soil Column compartment, River Section compartment and Lake Compartment. There are many applications utilizing AQUASIM to simulate specific process in aqueous phase [47-49], to simulate dynamic
process in a complex reactor [50-53], to simulate dynamic process in a column reactor [48],
even to simulate substance transport in a river system [54, 55] or lake system [56].

1.4. Research incentive

Despite numerous studies on the characterization of various fly ashes, we still lack the
ability to predict the fate and transport of toxic fly ash elements in natural environments and
subsequent impact on public health, representing a critical knowledge gap that needs to be
closed for the development of effective strategies for risk assessment and management
decision-making. This study will be dedicated to fulfilling this need through developing an
experimentally validated mechanistic model to quantitatively characterize the mobilization
and transport of toxic elements in fly ash, which could be used to simulate and predict the
environmental impact of fly ash.

Figure 1.4: Main elements of model structure in AQUASIM program.
CHAPTER 2 LINKAGES BETWEEN UNBURNED CARBON AND CHARACTERIZATION OF COAL FLY ASHES

2.1. Introduction

Coal fly ash is the predominant by-product of coal-fired power generation processes worldwide. Due to the potential environmental risks associated with the disposal of coal fly ash as a waste stream, major efforts have been devoted to the beneficial use of coal fly ash as a sustainable management strategy [57]. Currently, the primary market for coal fly ash utilization is as a pozzolanic additive in concrete, reducing the use of energy-intensive Portland cement and improving the properties of concrete with the pozzolanic characteristic of coal fly ash [58].

Despite these benefits, one of the challenges to promoting the beneficial use of fly ash is the presence of the unburned carbonaceous fraction of coal fly ash and its adsorption capacity [11]. In concrete production, air entrainment agents are added to the concrete admixture to stabilize air bubbles for improved freeze-thaw resistance of the hardened concrete and workability of the concrete while in a plastic state. When present at high levels in coal fly ash used in concrete, unburned carbon, possessing considerable surface area, is considered to provide adsorption sites for air entrainment agents, lowering their availability to stabilize air bubbles, and subsequently reducing the durability of concrete [59].

While the negative impact of unburned carbon in coal fly ash on concrete property could be mitigated by adding extra air entrainment agents to offset the adsorption by unburned carbon, previous studies have found significant variations in the content of unburned carbon of different fly ashes, which increase the operational complexity of concrete production and
reduce the marketability of coal fly ash for beneficial use in concrete [60]. Previous research efforts have been directed toward the characterization of residual carbon in coal fly ash to understand the causes of the inconsistency in unburned carbon content, which has shown that unburned carbon distribution is correlated to fly ash particle size [61, 62]. To further assess the implications of these findings on the conventional use of coal fly ash in concrete and more innovative applications in pollutant removal as low-cost sorbents [63], the objective of this study is to characterize the linkages between fly ash particle size, unburned carbon content, surface area, and adsorption capacity.

2.2. Methodology

2.2.1. Source of fly ash

Fly ash samples were taken from the electrostatic precipitators of four coal-fired power plants in Tennessee, abbreviation as AL, BR, CO, GA, all equipped with selective catalytic reduction systems for the reduction of nitrogen oxide emission. A blend of low-sulfur coal was used for the pulverized coal combustion process in four power plants. Dry fly ash samples were collected in sealed plastic buckets, shipped to the laboratory, stored at room temperature before use.

2.2.2. Fly Ash Particle Size Fractionation

Size fractionation for each fly ash sample was conducted following a previously described procedure [64]. Briefly, fly ash was first dried at 105 °C overnight and then cooled down to room temperature in a desiccator before size fractionation. Subsequently, the dried fly ash sample was mechanically passed through a stainless-steel sieve tower on a Humboldt motorized sieve shaker (Humboldt Mfg. Co., Schiller Park, IL) (Fig. 2.1). The sieve tower
consisted of five U.S. standard sieves: No. 100, 140, 200, 325, and 635, equivalent to opening sizes of 150, 106, 75, 45, and 20 microns, respectively. The fly ash particles retained by each sieve were collected, weighed, and stored in zip-lock plastic bags.

2.2.3. Fly Ash Characterization

The unburned carbon content of fly ash was measured as loss-on-ignition (LOI) using standard methods detailed in ASTM C618 as previously described [65]. Scanning Electron Microscopy (SEM) analysis of the morphology of fly ash particles was conducted with a LEO 1550 field emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany) (Fig. 2.2). Specific surface area of fly ash samples was quantified with a Micromeritics TriStar 3000 analyzer (Micromeritics Instrument, Norcross, GA) (Fig. 2.3), using the BET method as previously described [66].

2.2.4. Quantification of Sorption Capacity with the Methylene Blue Adsorption Assay

The sorption capacity of fly ash was quantified using methylene blue, which has been frequently used as a model compound to study the adsorption capacity of porous materials in aqueous solutions [67, 68], as the sorbate. The batch methylene blue adsorption assay was conducted following a previously described protocol [67]. Briefly, varying quantities of fly ash (0.1-1.0 g) were added as the sorbent into solutions containing 100 mg/L methylene blue. The suspensions were allowed to reach equilibrium with shaking at 150 rpm (25 °C) for 5 days. Subsequently, the aqueous phase was separated from fly ash by centrifugation at 9,000 × g for 10 minutes. Aqueous concentration of methylene blue was quantified colorimetrically at 668 nm on a UV/VIS spectrophotometer (Fig. 2.4). The methylene blue adsorption
capacity for each fly ash sample was determined following the Langmuir model as previously described [69].

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Figure 2.1: Humboldt® Motorized Sieve Shaker and 3” U.S.A. Standard Sieves.

Figure 2.2: ZEISS LEO 1550 Scanning Electron Microscopy.
2.3. Results and Discussion

2.3.1. Size Distribution of Coal Fly Ash

In order to study the relationship between particle size and adsorptive properties of fly ash, each fly ash sample was separated into six size fractions by sieving (Fig. 2.5). The particle size fraction with the smallest size (<20 μm) predominated in four fly ashes, comprising greater than 58% of the total fly ash mass. In general, the relative abundance of
fly ash fractions showed a steady decrease with increasing particle size (Fig. 2.5). A noticeable exception to this pattern was observed in Fly Ash-AL, where the particle fraction with the largest size (>150 µm) was the third most abundant, accounting for 11.1% of the total fly ash mass. In contrast, the same particle fraction in other fly ashes (>150 µm) accounted for the least in total fly ash mass, the least of all particle size fractions.

Interestingly, the contrast in coloration was more evident following particle size fractionation. While the coloration turned darker in particle fractions as particle size increased in four fly ashes, particle size fractions of Fly Ash-AL&CO showed more intense black coloration in comparison with particle fractions of Fly Ash-BR&GA with the same size range (Fig. 2.6). Since unburned carbon is reported to be associated with the black coloration of fly ash [70], these results suggest that particle fractions with larger size might contain more unburned carbon and Fly Ash-AL&CO could have higher unburned carbon content than Fly Ash-BR&GA.

2.3.2. Particle Morphology of Fly Ash Size Fractions

Given the changes in coloration in fly ash fractions of different particle sizes, the fly ash particles in each fraction were further examined with SEM. It is evident that fly ash particles were well separated according to the expected size ranges, confirming the effectiveness of the size fractionation procedure in this study (Fig. 2.7). It is noted that the fly ash fraction of the finest size (< 20 µm) consisted of mostly smooth spherical particles. The increase in the particle size range to 75-106 µm resulted in the presence of a significant number of irregularly-shaped grains in the fly ash. In the particle fraction with the largest size (> 150
µm), irregularly-shaped vesicular grains appeared to have become the dominant constituents of fly ash with few smooth spherical particles.

These results are consistent with previous observations that fly ash particles of irregular shape tend to be larger in size than those of smooth spherical shape [71, 72]. Furthermore, these irregularly-shaped fly ash particles have been indicated to be associated with unburned carbon [72, 73]. More importantly, the irregularly-shaped fly ash particles were also reported to have high surface area [74]. Thus, the fly ash fractions of large particle sizes, where irregularly-shaped particles were enriched, could have important impact on the unburned carbon content and surface properties of fly ash.

2.3.3. Distribution of Unburned Carbon

To further study the significance of unburned carbon in fly ash properties, unburned carbon content was measured as Loss on Ignition (LOI) in all fly ash particle fractions. For four fly ashes tested, unburned carbon content was higher in particle fractions of larger size (Fig. 2.8), which is consistent with previous observations on unburned carbon distribution [61]. In fact, unburned carbon content in the particle fractions of the largest size (>150 µm) was more than 20 times higher than that of the finest particles (<20 µm), supporting the association of unburned carbon with irregularly-shaped grains enriched in fly ash fractions of large particle size as suggested by SEM particle morphological analysis (Fig. 2.7). Since unburned carbon is linked particularly to surface properties of fly ash [75], coarse fly ash fractions with high unburned carbon content could have disproportionately greater impact on fly ash property despite being the minor constituents by total mass (Fig. 2.5).

2.3.4. Linkage between Unburned Carbon Content and Surface Area
Surface properties are critical for the potential beneficial use of fly ash as an additive to cement or as adsorbents for pollutant removal. Therefore, specific surface area of fly ash was investigated as a key parameter of surface property. In general, specific surface area increased as particle size increased in four fly ashes (Fig. 2.9), following the same trend of increases in unburned carbon content as a function of particle size (Fig. 2.8). Similarly, fly ash fractions of four fly ashes, particularly those of larger particle sizes, had greater specific surface area (Fig. 2.9), which mirrored the same pattern regarding unburned carbon (Fig. 2.8). Evidently, these results pointed to a direct link between unburned carbon and surface area. However, the carbon content from different fly ashes makes significant difference on specific surface area because the mass of carbon content is not proportional to the surface area among fractionated fly ashes from all four plants.

To determine the contribution of unburned carbon to the surface area of fly ash, the unburned carbon in fly ash fractions were removed by combustion and specific surface area quantified again. Following adjustment to pre-combustion basis, the specific surface area before and after the removal of unburned carbon was compared to estimate the relative contributions to total surface area from unburned carbon and the mineral phase, i.e. non-combustible inorganic portion of fly ash. Notably, the large majority of surface area in all fly ashes could be attributed to unburned carbon in all particle fractions (Fig. 2.10). A general observation was that the contribution from unburned carbon to surface area was higher in fly ash fractions with increasing particle size and unburned carbon content.

Indeed, a strong correlation was found between unburned carbon content and specific surface area in four fly ashes (Fig. 2.11), a further indication that unburned carbon was an
important determinant of surface property. Regression analysis of specific surface area as a function of unburned carbon content revealed a steeper slope in Fly Ash-AL&GA than Fly Ash-BR&CO, suggesting the unburned carbon among fly ashes might have distinct characteristics, which is likely as different forms of unburned carbon in fly ash have been shown to differ considerably in surface area and adsorptive behavior [76, 77].

2.3.5. Fractional Sorption Capacity of Fly Ash

While unburned carbon content is an indicator of fly ash property, sorption capacity is a more direct parameter for the beneficial use of fly ash. The sorption of methylene blue as a model compound indicates that fly ash fractions of larger particle size exhibited higher capacity of sorption (Fig. 2.12), likely the result of higher unburned carbon content and surface area associated with larger fly ash particles (Fig. 2.8 & 2.9). The sorption of methylene blue to Fly Ash-AL&GA was more effective than sorption to Fly Ash-BC&CO, consistent with the higher unburned carbon content and specific surface area observed in Fly Ash-AL (Fig. 2.12). A surprising finding was that even the particle fraction (< 20 μm) with the least sorption capacity in Fly Ash-AL exhibited greater methylene blue sorption than the particle fraction (> 150 μm) with the most sorption capacity in Fly Ash-AL (Fig. 2.12), suggesting potentially substantial differences among the physicochemical characteristics of the four fly ashes.

A strong correlation was observed between sorption capacity and unburned carbon content in four fly ashes (Fig. 2.13A), corroborating the linkage of surface characteristics to unburned carbon. Similarly, regression analysis also found sorption capacity to correlate strongly with specific surface area (Fig. 2.13B), demonstrating that unburned carbon in fly
ash was the dominant contributing factor to surface area, which in turn governed the sorption capacity of fly ash. However, the slopes of the regression analysis differ considerably among four fly ashes (Fig. 2.13), evidence that the properties of the unburned carbon in the four fly ashes were vastly different. Given that sportive characteristics are critical to the beneficial use of fly ash in concrete production and the removal of environmental pollutants via adsorption [57], further efforts are needed to elucidate the mechanisms underlying the marked differences in surface properties between unburned carbon in fly ashes from various sources.

Results from this study systematically established the linkage between fly ash particle size, particle morphology, unburned carbon content, surface area, and sorption capacity, which could facilitate the development of strategies for the optimization of beneficial use of fly ash. The excessive adsorption of air entrainment agents by unburned carbon has been a major challenge to the use of fly ash in concrete production [11]. Analysis in this study has demonstrated that the majority of the unburned carbon and sorption capacity could be attributed to the larger fly ash particles. Among the various factors influencing unburned carbon content, size of pulverized coal particles has been shown to affect the size of the ash particles [78]. Thus, the optimization of coal processing could potentially improve the properties of fly ash for use in concrete. In contrast, previous studies on the use of coal fly ash as the sorbent for pollutant removal have found unburned carbon as the primary components responsible for adsorption capacity [79, 80]. Thus, for the application of fly ash for the adsorptive removal of pollutants, it would be desirable to develop techniques capable of efficient separation of fly ash fractions enriched with unburned carbon.
Figure 2.5: Mass distribution of fly ash particle size fractions.

Figure 2.6: Appearance of the bulk fly ashes and particle size fractions.
Figure 2.7: SEM micrographs of the fractionated coal fly ashes at sizes of below 20, 20 to 45, and 45 to 75 micrometers. The left-side pictures show raw fractionated particles and the right-side pictures are treated after LOI test.
Figure 2.8: SEM micrographs of fractionated coal fly ashes at sizes of 75 to 106, 106 to 150 and above 150 micrometers. The left-side pictures show raw fractionated particles and the right-side pictures are treated after LOI test.
Figure 2.9: Distribution of unburned carbon content (LOI) of fly ash particle fractions.

Figure 2.10: Specific surface area of fly ash particle fractions.
Figure 2.11: Relative contribution to surface area in fly ash particle size fractions from the mineral phase and unburned carbon.
Figure 2.12: Correlation between unburned carbon content and specific surface area of fly ash particle size fractions.

Figure 2.13: Sorption capacity of fly ash particle size fractions measured as the sorption of methylene blue (MB) to fly ash.
Figure 2.14: Correlation between the sorption capacity and A) unburned carbon content, and B) specific surface area of fly ash particle size fractions.
2.4. Conclusions

Adsorptive behavior is critical for the beneficial use of coal fly ash, either as a pozzolanic additive in cement or as a sorbent for contaminant removal. A systematic analysis of fly ash particle size fractions established linkages between particle size, particle morphology, unburned carbon content, surface area, and sorption capacity. Unburned carbon was enriched in fly ash fractions of the largest particle sizes and associated with irregularly-shaped particles. Further, the majority of surface area and sorption capacity of fly ash could be attributed to unburned carbon. More importantly, unburned carbon content, specific surface area, and methylene blue sorption capacity were strongly correlated to each other as revealed by regression analysis, providing a potentially quantitative basis for understanding the surface properties of fly ash and developing more effective practices for the beneficial use of fly ash.
CHAPTER 3 PARTICLE SIZE FRACTIONATION AND ELEMENTAL SPECIATION IN COAL FLY ASHES

3.1. Introduction

CFA is anthropogenic engineering product generated through coal combustion process. The majority of CFA is in perfect solid spherical shape, mixed with other combustion residues in minimal fraction, for example, unburned carbon, cenosphere, amorphous particle. CFA is an extremely complex mixture, mainly including SiO$_2$, Al$_2$O$_3$, CaO, MgO, Fe$_2$O$_3$, K$_2$O, Na$_2$O, SO$_3$ and other oxides, heavy metals as well [25]. Due to the presence of toxic constituents, like heavy metals, and the magnitude of coal ash generation and accumulation, fly ash disposal has drawn great attention regarding public health and environmental conservation. As conventional approaches for fly ash disposal, either in landfill or on-site impoundment storage, cannot avoid interaction between fly ash and aqueous solution, metal or toxic elements leaching is inevitable throughout the time of storage. Therefore, environment problem related to fly ash disposal that may hazard surface water and subsurface water becomes major concern nowadays.

Since fly ash is a heterogeneous material which contains different sizes of fly ash particles, fractionation of fly ashes will provide insightful understanding to study the elemental distribution among different sizes of fly ash particle. The elemental distribution not only determines the leaching potential of toxic compound but also implies the leaching characteristic of fly ash. Therefore, studying the fractionated fly ash can differentiate the fly ash problem to seek solution in controlling the toxic contaminants and further understand its leaching behavior in nature in order to better manage the fly ash disposal.
Davison et al [26] reported that fine particle fraction of fly ash could be enriched in trace elements compared with the fraction of trace elements in the parent coal. This is due to the volatilization of some elements in the boiler and their subsequent condensation in the cooler sections of the flue gas stream. Many of the most toxic elements, significant enrichment is observed in the fine particle of coal fly ash [27]. Karayigit et al [28] indicated that some volatile elements, notably As, Cd, Zn increases from coarse to finer particle size fly ash. Similar observation on As, Cd, Pb and Zn have been also indicated by Hower et al [29]. The concentration of volatile trace elements increases with an increase in fly ash surface area. Volatile elements such as Zn and As will increase in concentration as a function of the decreasing particle size and consequently enhanced surface area of the fly ash.

Beside particle size mattering with the elemental distribution, the structure of particle size and the trace elemental incorporation pattern also affect the mobility of elements. Domka summarized that fly ash is formed mainly by certain matrix (SiO$_2$, Al$_2$O$_3$, CaO). It also contains other elements dominant fraction of which are embedded into the silica skeleton and the rest of the elements in trace amount sitting on the surface of the ash molecules [30]. The dominant and trace elements occur mostly in compounds, whose chemical composition depends on the kind of coal and conditions of combustion. Furthermore, the elemental distribution is also affected by other factors, like organic matter, carbonate species etc. Mardon et al summarized that organic-, sulfide-, and carbonate-bound elements are generally more easily volatilized than silicate-bound elements [31].

Elemental speciation, defined by the approach of sequential extraction [32], differentiates chemical fraction of elements into five categories, water-soluble(i), acid-soluble(ii), oxide(iii),
difficult reducible (iv) and residual (v) which has been widely used to investigate elemental leaching behavior and their mobility in environmental conditions [33-35]. The elemental speciation has a direct connection with the potential leaching capacity of toxic constituents in fly ash. Through the analysis of speciation on different source of fly ash, it can better explain the difference on their environmental behavior, especially elemental mobility.

Therefore, this study was dedicated to the characterization of pulverized CFA especially elemental distribution in term of different particle sizes and in different formations. What’s more important is to explain the leaching characteristics based on the particle size distribution and elemental speciation in fly ash. The last task was to utilize the knowledge about fly ash obtained from fly ash characterization to explain the column leaching pattern and behavior.

3.2. Methodology

3.2.1. Source of fly ash

The fly ashes were obtained from two fossil fuel power plants in eastern Tennessee, named as BR and CO respectively. Both plants are equipped with single coal-fired generating unit and burn a blend of low-sulfur bituminous coal from eastern Kentucky. Fly ash was collected from the hopper underneath the ESP in dry form and shipped to laboratory in a sealed plastic bucket.

3.2.2. Fly ash fractionation method

Size fraction was used not only to collect the fractionated fly ashes for other analysis but also to measure particle size distribution of fly ashes. This test was modified from the method described by Liu [81]. In the pretreatment step, the raw fly ash sample was dried at 105°C in
oven over night and then cooled down to room temperature in a desiccator. 1 gram dried fly ash was mechanically sieved through a stainless-steel sieve tower coupled with a 3” U.S.A. Standard Sieves and Humboldt® Motorized Sieve Shaker. The sieve tower is comprised of five different sieves, from top to bottom, No. 100, 140, 200, 325 & 635 as US standard sieves or 150, 106, 75, 45, 20 microns in sieve sizes. The retained fly ash particles by sieves were collected, weighted and stored in a zip-lock plastic bag.

3.2.3. Metals and trace elemental analysis

Major, trace and heavy metal concentrations were determined with Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES). The samples were digested with aqua regia and hydrofluoric acid mixture. Then the digested liquid and debris are rinsed with 1% nitric acid solution and filtrated with 0.2 micron polycarbonate filter. The collected filtrate was filled up to 20 mL with 1% nitric acid to be ready for ICP analysis. Analytical errors were estimated at <5% for most of the elements. As a quality control measure, selenium standards were added into the acid-digestion solution for total element analysis.

3.2.4 Fly ash microwave acid digestion

Microwave acid digestion is more recommended instrumentation to perform chemical analysis on elemental composition, which is implemented on SEM® Microwave Accelerated Reaction System (MARS). A 0.4000±0.0050 gram of ash sample was treated with 3mL of HF and 9mL of HCl and 3mL of HNO₃ in a close PFA vessel under microwave heating program that vessel was heated to 180°C in 15 minutes and kept then the temperature for another 30 minutes. After cooling down, the vessel was uncapped and 10mL of boric acid neutralization solution was quickly added. The vessel was then replaced, returned to the
microwave oven and changed to another heating program that the vessel was heated to 170°C in 15 minutes and then the temperature was held for another 20 minutes. The digested solution was analyzed with ICP-AES for elemental concentration determination.

3.2.5. Fly ash sequential extraction

Sequential extraction has been universally accepted for speciation of trace metals in particle matter. Sequential extraction was initially utilized in soil chemical analysis and broadened its application into sediments [32]. In natural environment, the heavy metals in solid material can be partitioned into five fractions, exchangeable (water-soluble), bound to carbonates (acids-soluble), bound to iron and manganese oxides (oxides), bound to organic matter (difficult reducible) and residual fraction. Conceptually the sequential extraction is to quantify the distribution of heavy metals in solid material. It also helps estimate the mobility of heavy metals in soil and water system. The procedure used here were adjusted accordingly from the method given by Tessler [32]. (a). Weight about 1.0 gram pre-dried (105°C) fly ash in centrifuge tubes (polypropylene, 50 mL), add into 8 mL of 1.0 mol/L MgCl₂ at pH 7.0 with agitation at 150 rpm for 1h at 24°C. Then filter the sample on vacuum filtration station through 0.2 μm carbon filter, collect the filtrate into centrifuge tube and fill up to 10ml with 1% nitric acid solution. The solid residue on the filter and filtration cup needs to be washed with the following extraction solution. (b). The washed residue from (a) was extracted with 10 mL of 1mol/L NaOAc at pH = 5 (adjusted pH by acetic acid) with agitation for 5 h at 25°C. Warning: volume is critical so write the volume of each solution added into sample. Then separate liquid and particle by filtration station. The filtrate is preserved with 1% nitric acid solution and fill up to 10 ml. The residue was washed with next extraction solution and
collected in the same extraction tube. (c). The residue washed with 20 mL 0.1mol/L NH₂OH·HCl (pH=4) are transferred into a glass Erlenmeyer flask, then was extracted for 3h at 96°C in a water bath with occasional agitation. Then separate liquid and particle by filtration station, the filtrate was preserved with 1% nitric acid and filled up 20 mL. The residue was washed with washed with next extraction solution. (d).The washed residue from (c) was added 3 mL of 0.02 M HNO₃ and 8mL 30% H₂O₂ at pH=2 and shaken for 5 h at 85°C. After cooling, 5 mL of 3.2M NH₄OAc in 20% (v/v) HNO₃ was added and separate the sample, then dilute the filtrate to 10 mL with 1% nitric acid solution. The residue was collected in a crucible and dry in 105°C for 2 hours. (e). The dried residual from step (d) cools down in the desiccator and weight about 0.2 gram was transferred to 50 mL Teflon reactor. By using microwave assistant acid digestion method, described in 2.2.2.6, to complete the residual digestion. Filtrate the liquid and collect the filtrate and then fill up 20mL with 1% nitric acid solution. All extraction liquids were analyzed on ICP-AES to obtain the metal concentration for all interested elements.

### 3.3. Results and discussion

#### 3.3.1. Correlation of major oxides in fractionated fly ashes and particle sizes

Fly ashes from pulverized coal combustion have a dominant fraction of less than 20 microns, as seen in Fig.3.1. Considering the fractions of less than 54 microns, more than 80% of fly ashes are present in finer size. Therefore, the particle size is the major factor in determining the distribution of major oxides in fractionated fly ashes, as shown in Fig.3.2 and Fig.3.3. The majority of oxides in fly ash from 45% to 70% are in the form of fine particle with size of less than 20 microns. As known that smaller particle has larger surface
area, the larger contact surface of fly ash particle will facilitate its dissolution in liquid solution. Therefore, pulverized coal fly ashes are more active in term of elemental mobility under environmental conditions.

![Particle size distribution of pulverized fly ashes.](image)

**Figure 3.1: Particle size distribution of pulverized fly ashes.**

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>Fe₂O₃ (%)</th>
<th>Na₂O (%)</th>
<th>K₂O (%)</th>
<th>P₂O₅ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>52.99</td>
<td>25.88</td>
<td>1.33</td>
<td>1.10</td>
<td>8.72</td>
<td>1.42</td>
<td>5.84</td>
<td>3.55</td>
</tr>
<tr>
<td>20~45</td>
<td>53.20</td>
<td>25.37</td>
<td>1.50</td>
<td>1.48</td>
<td>8.16</td>
<td>1.41</td>
<td>5.57</td>
<td>3.05</td>
</tr>
<tr>
<td>45~75</td>
<td>53.27</td>
<td>25.68</td>
<td>1.81</td>
<td>2.09</td>
<td>7.61</td>
<td>1.12</td>
<td>5.61</td>
<td>2.44</td>
</tr>
<tr>
<td>75~106</td>
<td>53.35</td>
<td>26.28</td>
<td>2.16</td>
<td>2.93</td>
<td>6.43</td>
<td>1.24</td>
<td>5.34</td>
<td>2.40</td>
</tr>
<tr>
<td>106~150</td>
<td>53.38</td>
<td>23.93</td>
<td>3.65</td>
<td>4.20</td>
<td>6.56</td>
<td>0.60</td>
<td>5.81</td>
<td>2.78</td>
</tr>
<tr>
<td>&gt;150</td>
<td>50.50</td>
<td>25.58</td>
<td>4.11</td>
<td>4.42</td>
<td>6.27</td>
<td>0.58</td>
<td>6.25</td>
<td>2.92</td>
</tr>
</tbody>
</table>

*Unit: in %.*
Table 3.2: Trace elements distribution in concentration in fractionated BR fly ashes.

<table>
<thead>
<tr>
<th>Particle size(µm)</th>
<th>As (mg/g)</th>
<th>Ba (mg/g)</th>
<th>Cr (mg/g)</th>
<th>Mn (mg/g)</th>
<th>V (mg/g)</th>
<th>Zn (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>0.1272</td>
<td>1.1438</td>
<td>0.2763</td>
<td>0.0150</td>
<td>0.2875</td>
<td>0.3650</td>
</tr>
<tr>
<td>20–45</td>
<td>0.1507</td>
<td>1.2307</td>
<td>0.2283</td>
<td>0.0153</td>
<td>0.2565</td>
<td>0.1833</td>
</tr>
<tr>
<td>45–75</td>
<td>0.1250</td>
<td>0.8414</td>
<td>0.2081</td>
<td>0.0157</td>
<td>0.2226</td>
<td>0.2862</td>
</tr>
<tr>
<td>75–106</td>
<td>0.1154</td>
<td>0.9408</td>
<td>0.2267</td>
<td>0.0186</td>
<td>0.2130</td>
<td>0.1374</td>
</tr>
<tr>
<td>106~150</td>
<td>0.1022</td>
<td>0.4643</td>
<td>0.2499</td>
<td>0.0129</td>
<td>0.1920</td>
<td>0.1024</td>
</tr>
<tr>
<td>&gt;150</td>
<td>0.1619</td>
<td>0.3186</td>
<td>0.1849</td>
<td>0.0190</td>
<td>0.1918</td>
<td>0.0947</td>
</tr>
</tbody>
</table>

Unit: mg/g.

Table 3.3: Trace elements distribution in concentration in fractionated CO fly ashes.

<table>
<thead>
<tr>
<th>Particle size(µm)</th>
<th>As (mg/g)</th>
<th>Ba (mg/g)</th>
<th>Cr (mg/g)</th>
<th>Mn (mg/g)</th>
<th>V (mg/g)</th>
<th>Zn (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>0.1904</td>
<td>1.3874</td>
<td>0.1091</td>
<td>0.0173</td>
<td>0.0794</td>
<td>0.1174</td>
</tr>
<tr>
<td>20–45</td>
<td>0.1739</td>
<td>2.0601</td>
<td>0.1912</td>
<td>0.0155</td>
<td>0.1117</td>
<td>0.2252</td>
</tr>
<tr>
<td>45–75</td>
<td>0.1703</td>
<td>0.7644</td>
<td>0.0784</td>
<td>0.0162</td>
<td>0.0268</td>
<td>0.0826</td>
</tr>
<tr>
<td>75–106</td>
<td>0.1946</td>
<td>0.9737</td>
<td>0.0777</td>
<td>0.0146</td>
<td>0.0318</td>
<td>0.0750</td>
</tr>
<tr>
<td>106~150</td>
<td>0.2105</td>
<td>0.8980</td>
<td>0.0765</td>
<td>0.0118</td>
<td>0.0389</td>
<td>0.1001</td>
</tr>
<tr>
<td>&gt;150</td>
<td>0.2436</td>
<td>1.9937</td>
<td>0.3533</td>
<td>0.0309</td>
<td>0.1187</td>
<td>0.3400</td>
</tr>
</tbody>
</table>

Unit: mg/g.

3.3.2. Trace elemental distribution in fractionated fly ashes

According to US EPA report, some trace metals become concentrate in certain particle streams from a combustor while others do not. There are classification schemes describe the pattern of different elements: Class 1: Elements that are approximately equally concentrated in the fly ash and bottom ash and show little or no small particle enrichment, for example, manganese and chromium. Class 2: Elements that are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size, for instance, arsenic.

As seen in Tables 3.1 and 3.2, arsenic did not show significant enrichment as particle size decreases. There may be other factors, unburned carbon, for instance, affecting arsenic distribution in fly ash, which has been thoroughly discussed in Chapter 2.3. Barium shows
apparent enrichment in both fly ashes as particle size decreases, especially, in BR fractionated fly ashes. Chromium, manganese, zinc seems to be relatively homogeneous distribution among different particle sizes of fractionated BR fly ashes. The finer particles have slightly higher elemental concentration but it may not be statically significant. For the same elements mentioned above, they did not present any significant trend among different particle size of fractionated CO fly ashes. Therefore, it is hard to generalize the elemental distribution pattern for each element among fly ashes. The elemental distribution was affected by many factors thus the elemental distribution has to draw conclusion on the base of case study.

3.3.3 Elemental partitioning of pulverized CFA

Aluminum is hardly exchangeable in the smaller particle sizes of fly ashes. The fractions with particle size more than 106 microns shows some exchangeable aluminum which may not be associated with spherical shape of fly ash. The major reason is that the fractions of fly ash with particle sizes less than 45 microns, mainly spherical shape of fly ash shows no exchangeable aluminum. For spherical shape of fly ash, the aluminum is mainly present in the stable form, which is less prone to be dissolved in the natural environment. Furthermore, the smaller particle size of fly ashes contains more aluminum content in the residue.

Arsenic seems to be barely exchangeable, partially bounded with carbonate species, iron and manganese oxides and organic matter. Significantly, arsenic is mainly present in the residue, which still maintains 70 to 90% elemental reservoir in the inactive form in the mineral. In other words, fly ash has efficiently stabilized the hazardous element of arsenic during the combustion process.
The extraction results show that barium presents in an active form, which can be exchanged by ions, loosely bounded with carbonate species, iron and manganese oxides and organic matter. The spherical shape of fly ash has a certain level of barium stabilization as the barium in the residue mainly shows up in the smaller size of particle.

Calcium is the most active element which gradually dissolves into aqueous phase and only about 20% of total amount is indissolvable, present in the residue. In acid solution (not HF), only mineral in glass phase can survive from harsh condition. It is known that crystalline is more easily dissolvable in aqueous solution. Therefore it is most likely that calcium are incorporated into crystalline type of mineral, present in coal fly ash.

Aluminum, Chromium, iron, manganese and vanadium are mainly present in the inactive form, can hardly be released into environment from the mineral. Zinc shows solubility to limited extent and become more mobile as extraction liquid increase acidity. However, there are still about 80 percentage of elemental reservoir are in inert form in the fly ash particle.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>As</th>
<th>Ba</th>
<th>Cr</th>
<th>Mn</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-soluble</td>
<td>BR</td>
<td>0.02</td>
<td>0.19</td>
<td>26.96</td>
<td>0.01</td>
<td>0.85</td>
<td>4.00</td>
<td>0.12</td>
<td>1.07</td>
<td>0.00</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0</td>
<td>0.14</td>
<td>27.50</td>
<td>0.02</td>
<td>0.00</td>
<td>1.55</td>
<td>4.11</td>
<td>2.88</td>
<td>0.96</td>
<td>0.48</td>
</tr>
<tr>
<td>Acids-soluble</td>
<td>BR</td>
<td>0.08</td>
<td>0.62</td>
<td>16.81</td>
<td>0.64</td>
<td>12.00</td>
<td>6.47</td>
<td>2.34</td>
<td>0.86</td>
<td>3.43</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0.18</td>
<td>0.55</td>
<td>14.42</td>
<td>0.71</td>
<td>0.10</td>
<td>1.02</td>
<td>1.77</td>
<td>3.78</td>
<td>6.49</td>
<td>3.35</td>
</tr>
<tr>
<td>Oxides</td>
<td>BR</td>
<td>0.15</td>
<td>1.77</td>
<td>22.67</td>
<td>0.97</td>
<td>9.30</td>
<td>3.66</td>
<td>1.53</td>
<td>1.00</td>
<td>3.14</td>
<td>7.31</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0.40</td>
<td>2.92</td>
<td>25.61</td>
<td>1.16</td>
<td>1.92</td>
<td>0.47</td>
<td>4.58</td>
<td>8.15</td>
<td>21.76</td>
<td>4.42</td>
</tr>
<tr>
<td>Difficult reducible</td>
<td>BR</td>
<td>0.18</td>
<td>2.65</td>
<td>12.46</td>
<td>1.09</td>
<td>6.67</td>
<td>6.94</td>
<td>1.32</td>
<td>0.84</td>
<td>1.53</td>
<td>9.61</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0.31</td>
<td>2.03</td>
<td>13.51</td>
<td>0.70</td>
<td>0.84</td>
<td>3.09</td>
<td>3.47</td>
<td>2.68</td>
<td>2.39</td>
<td>6.47</td>
</tr>
<tr>
<td>Residual</td>
<td>BR</td>
<td>99.56</td>
<td>94.77</td>
<td>21.10</td>
<td>97.28</td>
<td>71.18</td>
<td>78.93</td>
<td>94.69</td>
<td>96.22</td>
<td>91.90</td>
<td>80.23</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>99.11</td>
<td>94.36</td>
<td>18.96</td>
<td>97.41</td>
<td>96.13</td>
<td>93.87</td>
<td>86.08</td>
<td>82.51</td>
<td>68.41</td>
<td>85.28</td>
</tr>
</tbody>
</table>
3.4. Conclusions

Fine particle determine the chemical and physical properties as more than 90% of coal fly ash particle is under 45 micrometer therefore the fine particle contains main fraction of major oxides. Fine particle accumulate 90% of trace elements, like Arsenic, Barium, Chromium, Manganese, Vanadium and Zinc therefore they are most environmental hazardous. Sequential extraction concluded that minor and trace elements are relative inert in environmental condition because major part of the element presents in the residue. Only less than 40% of total amount of elements might be mobilized under certain conditions by ion exchange, acid dissolution. For those elements whose are in indissoluble form, Aluminum, Arsenic, Barium, Chromium, Vanadium and Zinc, they are incorporated into glass phase of minerals in the coal fly ash. While calcium is present in a crystalline form mostly, it easily leaches out as sequential extraction proceeds with lower pH solution.
CHAPTER 4 DISTRIBUTION AND MOBILITY OF ARSENIC IN COAL FLY ASH

4.1. Introduction

Arsenic is one of the potentially occurring toxic trace elements in coal fly ash. It has drawn great attention due to its mobility and toxicity though there are numerous reports that concluded the amount of arsenic released from coal ash never exceed the EPA regulation on hazardous waste [82]. During coal combustion process, arsenic is released from the minerals and oxidized to form gaseous As$_2$O$_3$ or its dimer form As$_2$O$_6$. Subsequently, the arsenic vapor interacts with other gaseous species and ash particles in the furnace and ash in post-combustion flue gas. There are two theoretical paths in explaining arsenic removal from flue gas, one is heterogeneous condensation and the other one is surface reaction on the ash particle [83, 84]. There are two oxidation states of arsenic, As$^{3+}$, and As$^{5+}$, corresponding two speciation of arsenic, arsenate and arsenite. Arsenate is the predominant species. Frank et al [85] concluded post-combustion behavior and capture of arsenic are likely controlled by the element or phase in fly ash after analyzed different types of fly ashes.

The major concern about arsenic is the potential contamination of groundwater and surface water from any activities related to fly ash disposal and beneficial usages. The potential leachability of arsenic from fly ash may pose health risks on human beings directly or indirectly exposed. Arsenic mobility in aqueous solution is controlled by two processes that include: (1) adsorption and desorption reactions and (2) solid-phase precipitation and dissolution reactions. Once it is leached out from fly ash in aqueous phase, it will interact with other elements and be affected by other environmental factors, for example pH, organic
matters. It has reported arsenic can form precipitate with iron, calcium in aqueous solution which will directly affect the dissolution of arsenic and leaching from fly ash particle [86]. Wang et al., studied the pH effect on arsenic solubility and concluded that strong acid and base condition facilitate arsenic soluble and at neutral condition arsenic has the lowest solubility [86, 87]. Due to the complex factors affecting arsenic leaching and solubility, Ghosh et al., [88] drawn the conclusion that traditional leaching method (TCLP) may underestimate the leaching of arsenic from solid residual.

This research studies the concentration distribution of arsenic in different particle size and its leaching behavior among the size-fractionated fly ash. Furthermore, the factors that affect the arsenic leachability from both physical and chemical characteristics are also taken into consideration.

4.2. Methodology

4.2.1. Source of fly ash

The fly ashes were obtained from a fossil fuel power plant in eastern Tennessee. This plant is equipped with single coal-fired generating unit and burns a blend of low-sulfur bituminous coal from eastern Kentucky. Fly ash was collected from the hopper underneath the ESP in dry form and shipped to laboratory in a sealed plastic bucket.

4.2.2. Fly ash fractionation method

Size fraction was used not only to collect the fractionated fly ashes for other analysis but also to measure particle size distribution of fly ashes. In the pretreatment step, the raw fly ash sample was dried at 105°C in oven over night and then cooled down to room temperature in desiccators. one gram dried fly ash was mechanically sieved through a stainless-steel sieve
tower coupled with a 3" U.S.A. Standard Sieves and Humboldt® Motorized Sieve Shaker. The sieve tower is comprised of five different sieves, from top to bottom, No. 100, 140, 200, 325 & 635 as US standard sieves or 150, 106, 75, 45, 20 microns in sieve sizes. The retained fly ash particles by sieves were collected, weighted and stored in a zip-lock plastic bag.

4.2.3. Six-Stage Viable particle sampler and inhalable fly ash particle separation

The New Star Six-Stage Viable Sampler is a multi-orifice, cascade impactor which simulates human respiratory system so all particle collected the calibrated sampler, regardless of particle size, shape, or density are sized aerodynamically and can be directly related to human lung deposition. The sampler was connected to the flow meter using 9.5 mm outer diameter and 6.4 mm inner diameter (3/8 inch outer diameter and ¼ inch inner diameter) plastic (polyethylene) tubing. To effectively use the sampler, the vacuum on the apparatus must be maintained at a flow of 28.3 liter per minute (1 CFM) [89]. As the sampler is applied a vacuum and air suspended particle flows through the top of the sampler and then filters downward. Particles are collected on the six different stages using Petri dishes. From the top to the bottom, there are six stages where each stage collects a certain size of fly ash particle. The particle size ranges collected on the stages from top to down are 7.0 to 10, 4.7 to 7.0, 3.3 to 4.7, 2.1 to 3.3, 1.1 to 2.1 and 0.7 to 1.1 micrometers, respectively. Due to the limitation of reparable fly ash particle and the amount of samples required for certain analysis, only the fly ash samples collected from first three stages were quantitatively enough to fulfill the following test. Fly ash particles under 3.3 microns did not take into consideration in this paper.
CFA were dried at 105°C in oven for at least 10 hours and then cooled down to room temperature in desiccators, sealed in a zip-lock plastic bag for further test. In the laboratory, an inhalable particle separation system was built up, which is composed of a 40×25×25cm Plexiglass chamber (1), a six-stage viable sampler (2), a vacuum pump (3), an electric fan (4), a plastic funnel (5) and PVC pipe (6). The CFA was sparsely fed from the funnel into the PVC pipe. The Massey 4” high velocity metal fan blows enough air into PVC pipe to create turbulence inside the pipe tunnel in mobilize CFA dropped from the feeding funnel. The suspended light fly ash particle will travel from one end to the other end of chamber where a six-stage viable sampler, namely cascade impactor manufactured by New Star Environmental, was used to separate CFA particle. As the sampler is applied with negative pressure, the suspended particle inside the chamber will be inhaled into impactor from top opening and filter downward. Inside the impactor, there is a Petri dish on each stage. The targeted fly ash particle hit on Petri dish and is collected on the dish surface. The schematic graph of laboratory setup was shown in the Fig.4.1.

Figure 4.1: Schematic graph of inhalable fly ash particle separation system.
4.2.4. B.E.T. surface area analysis

Surface area is one of important parameters to quantitatively characterize physical properties of coal fly ash, which can be used to differentiate the contribution of total surface area from both mineral particle and unburned carbon content. \( \text{N}_2 \) gas adsorption isotherms were measured at 77K using Tristar 3000 from Micromeritics. Samples were degassed for two hours at 393K in vacuum prior to adsorption measurement. 20 adsorption and desorption points were set up for each sample [90]. The Brunauer-Emmett-Teller [91] theory was used for calculating surface area [92].

4.2.5. Metals and trace elemental analysis

Major, trace and heavy metal concentrations were determined with Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES). The samples were digested with aqua regia and hydrofluoric acid mixture. Then the digested liquid and debris were rinsed with 1% nitric acid solution and filtrated with 0.2 micron polycarbonate filter. The collected filtrate was filled up to 20mL with 1% nitric acid to be ready for ICP analysis. Analytical errors were estimated at <5% for most of the elements. As a quality control measure, selenium standards were added into the acid-digestion solution for total element analysis and extraction solution for TCLP analysis, respectively.

4.2.6 Fly ash microwave acid digestion

The chemical composition analysis of coal fly ash was performed with microwave acid digestion method, which was implemented on SEM® Microwave Accelerated Reaction System (MARS). A 0.4000±0.0050 gram of ash sample was treated with 3mL of HF and 9mL of HCl and 3mL of HNO₃ in a close PFA vessel under microwave heating program that
vessel was heated to 180°C in 15 minutes and kept then the temperature for another 30 minutes. After cooling down, the vessel was uncapped and 10mL of boric acid neutralization solution was quickly added. The vessel was then replaced, returned to the microwave oven and changed to another heating program that the vessel was heated to 170°C in 15 minutes and then the temperature was held for another 20 minutes. The digested solution was analyzed with ICP-AES for elemental concentration determination.

4.2.7. Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This is usually used to determine if a waste may meet the definition of EPA Toxicity that is carrying a hazardous waste code under RCRA (40CFRPart261) of D004 through D052. If a “Solid Waste” fails the test for one or more of these compounds, the waste is considered to be a characteristic hazardous waste—unless there is an exemption that applies.

According to USEPA TCLP method 1311, the solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. A 0.5000±0.0030 gram of pulverized CFA was weighted in 50 mL polypropylene centrifuge tube. 10 mL extraction fluids, freshly prepared at pH 4.93±0.05 and 2.88±0.05, were added to those sample tube. The mixture was then agitated in an end-over-end fashion rotation at 30 ± 2 rpm for 20 h at room temperature. After agitation, the mixture was centrifuged for 10 minutes at 5000 rpm. The supernatant was separated and then further filtrated with syringe filter with size of 0.2 micrometers. A fixed volume of 6ml filtrate then was acidified by adding 0.3 ml of
concentrated nitric acid. The samples were analyzed by ICP-AES to determine elemental concentration.

4.2.8. Fly ash sequential extraction

Sequential extraction has been universally accepted for speciation of particulate trace metals in particle matter. Sequential extraction was initially utilized in soil chemical analysis and broadened its application into sediments and other [32]. In natural environment, the heavy metals in solid material can be partitioned into five fractions, exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual fraction. Conceptually the sequential extraction is to quantify the distribution of heavy metals in solid material. It also helps estimate the mobility of heavy metals in soil and water system. The procedure used here were adjusted accordingly from the method given by Tessler [32].

(a). Weight about 1.0 gram pre-dried (105°C) fly ash in centrifuge tubes (polypropylene, 50mL), add into 8mL of 1.0mol/L MgCl$_2$ at pH 7.0 with agitation at 150 rpm for 1h at 24°C. Then filtrate the sample on vacuum filtration station through 0.2 μm carbon filter, collect the filtrate into centrifuge tube and fill up to 10ml with 1% nitric acid solution. The solid residue on the filter and filtration cup needs to be washed with the following extraction solution.

(b). The washed residue from (a) was extracted with 10 mL of 1mol/L NaOAc at pH= 5 (adjusted pH by acetic acid) with agitation fro 5 h at 25°C. Warning: volume is critical so write the volume of each solution added into sample. Then separate liquid and particle by filtration station. The filtrate is preserved with 1% nitric acid solution and fill up to 10 ml. The residue was washed with next extraction solution and collected in the same extraction tube. (c). The residue washed with 20 mL 0.1mol/L NH$_2$OH.HCl (pH=4) are transfer into a
glass Erlenmeyer flask, then was extracted for 3h at 96°C in a water bath with occasional agitation. Then separate liquid and particle by filtration station, the filtrate was preserved with 1% nitric acid and filled up 20 mL. The residue was washed with washed with next extraction solution. (d). The washed residue from (c) was added 3 mL of 0.02 M HNO₃ and 8mL 30% H₂O₂ at pH=2 and shaken for 5 h at 85°C. After cooling, 5 mL of 3.2M NH₄OAc in 20% (v/v) HNO3 was added and separate the sample, then dilute the filtrate to 10mL with 1% nitric acid solution. The residue was collected in a crucible and dry in 105°C for 2 hours. (e). The dried residual from step (d) cools down in desiccators and weight about 0.2 gram was transferred to 50mL Teflon reactor. By using microwave assistant acid digestion method, described in 2.2.2.6, to complete the residual digestion. Filtrate the liquid and collect the filtrate and then fill up 20mL with 1% nitric acid solution. All extraction liquids were analyzed on ICP-AES to obtain the metal concentration for all interested elements.

4.2.9. Mineral phase equilibrium assessment

As elements dissolve into solution from coal fly ash, the dissolved elements or species may form other type of mineral or precipitate in the solution. The mineral dissolution, solution speciation can be performed with the geochemical computer model PHREEQC for windows (an extended version of PHREEQC-2 [93]). The thermodynamic database of the geochemical speciation code MINTEQA2 version 3.11 [94] was used for phase equilibrium calculation [95]. Saturation indices were calculated using the theoretical concentrations of the elements, known from sequential extraction, listed in Table 4.6 as input in the model. The pH was fixed at pH = 5 and fly ash dissolved in an acetic-based buffer solution.
4.3. Results and discussion

4.3.1 Chemical and physical characteristics of pulverized CFA

The chemical compositions of raw and fractionated fly ashes selected in this study are summarized in Table 4.1. As Querol et al concluded that the fractionation of the major elements varies very slight [96], it is likewise in this study, seen in the size-fractionated fly ashes with size of less than 75 micrometers and having lower LOI as well. For those fly ash particles with size of more than 75 micrometers and having higher LOI, silicon and aluminum oxides are significantly less than the ones in other fractions. The physical characterization for size-fractionated fly ashes is summarized in Table 4.2. As the particle size distribution results show that dominant fraction of fly ash by size is under 20 micrometers, which is typical for fly ash from pulverized coal combustion process. LOI values are generally correlated with carbon contents in fly ash which also reflect combustion efficiencies [97]. The LOI values in Table 4.2 show the distribution of carbon contents in size-fractionated fly ashes which indicates that the larger the particle size for fractionated fly ash, the more unburned carbon it contains in that fraction. The carbon content in the fractionated fly ashes is also confirmed by B.E.T. surface area measurement and pore volume results. As it has been well known that fly ash particle is spherical shape and can be treated as solid sphere. Theoretically, the fine spherical particles have larger surface area than the course particles. In contrast with the theoretical deduction of surface area on spherical particles, the fractionated fly ash shows a reverse trend of surface area with particle size due to the presence of unburned carbon. It is likewise for pore volume in fractionated fly ashes.
Table 4.1: Major element oxides and LOI of raw and fractionated fly ashes.

<table>
<thead>
<tr>
<th>Sample Name (μm)</th>
<th>LOI</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw PCFA</td>
<td>2.82</td>
<td>51.1</td>
<td>25.3</td>
<td>1.09</td>
<td>1.50</td>
<td>7.55</td>
<td>1.44</td>
<td>5.61</td>
<td>3.23</td>
</tr>
<tr>
<td>3.3~4.7</td>
<td>0.97</td>
<td>52.9</td>
<td>25.4</td>
<td>1.01</td>
<td>0.96</td>
<td>9.67</td>
<td>1.14</td>
<td>5.59</td>
<td>3.28</td>
</tr>
<tr>
<td>4.7~7.0</td>
<td>1.27</td>
<td>52.7</td>
<td>26.0</td>
<td>0.94</td>
<td>1.01</td>
<td>9.85</td>
<td>1.17</td>
<td>5.13</td>
<td>3.08</td>
</tr>
<tr>
<td>7.0~10</td>
<td>0.92</td>
<td>53.0</td>
<td>25.1</td>
<td>1.00</td>
<td>0.95</td>
<td>10.3</td>
<td>1.13</td>
<td>4.85</td>
<td>3.49</td>
</tr>
<tr>
<td>&lt;20</td>
<td>1.04</td>
<td>52.4</td>
<td>25.6</td>
<td>0.95</td>
<td>1.61</td>
<td>7.75</td>
<td>1.40</td>
<td>4.75</td>
<td>2.69</td>
</tr>
<tr>
<td>20~45</td>
<td>1.99</td>
<td>52.1</td>
<td>24.9</td>
<td>0.93</td>
<td>1.57</td>
<td>8.00</td>
<td>1.38</td>
<td>5.07</td>
<td>2.29</td>
</tr>
<tr>
<td>45~75</td>
<td>3.88</td>
<td>51.2</td>
<td>24.7</td>
<td>0.73</td>
<td>1.50</td>
<td>7.32</td>
<td>1.07</td>
<td>4.25</td>
<td>1.99</td>
</tr>
<tr>
<td>75~106</td>
<td>6.40</td>
<td>49.9</td>
<td>24.6</td>
<td>0.72</td>
<td>1.22</td>
<td>6.02</td>
<td>1.16</td>
<td>5.22</td>
<td>2.02</td>
</tr>
<tr>
<td>106~150</td>
<td>12.8</td>
<td>46.5</td>
<td>22.4</td>
<td>0.66</td>
<td>1.16</td>
<td>5.72</td>
<td>0.52</td>
<td>3.69</td>
<td>3.20</td>
</tr>
<tr>
<td>&gt;150</td>
<td>21.1</td>
<td>43.0</td>
<td>20.2</td>
<td>0.61</td>
<td>0.89</td>
<td>5.75</td>
<td>0.45</td>
<td>3.53</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Unit: concentrations are in % wt.

Table 4.2: Physical characteristics of fractionated fly ashes in this study.

<table>
<thead>
<tr>
<th>Fractionated Fly Ash (μm)</th>
<th>PSD (%)</th>
<th>LOI (%)</th>
<th>B.E.T. (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Collection approaches</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3~4.7</td>
<td>n/a</td>
<td>0.97</td>
<td>n/a</td>
<td>n/a</td>
<td>Cascade Impactor</td>
</tr>
<tr>
<td>4.7~7.0</td>
<td>n/a</td>
<td>1.27</td>
<td>n/a</td>
<td>n/a</td>
<td>Cascade Impactor</td>
</tr>
<tr>
<td>7.0~10</td>
<td>n/a</td>
<td>0.92</td>
<td>n/a</td>
<td>n/a</td>
<td>Cascade Impactor</td>
</tr>
<tr>
<td>&lt;20</td>
<td>58.5</td>
<td>1.04</td>
<td>1.06</td>
<td>0.0025</td>
<td>Mechanical Sieve</td>
</tr>
<tr>
<td>20~45</td>
<td>23.8</td>
<td>1.99</td>
<td>1.60</td>
<td>0.0036</td>
<td>Mechanical Sieve</td>
</tr>
<tr>
<td>45~75</td>
<td>8.3</td>
<td>3.88</td>
<td>1.82</td>
<td>0.0036</td>
<td>Mechanical Sieve</td>
</tr>
<tr>
<td>75~106</td>
<td>4.4</td>
<td>6.40</td>
<td>2.31</td>
<td>0.0047</td>
<td>Mechanical Sieve</td>
</tr>
<tr>
<td>106~150</td>
<td>3.4</td>
<td>12.8</td>
<td>5.28</td>
<td>0.0094</td>
<td>Mechanical Sieve</td>
</tr>
<tr>
<td>&gt;150</td>
<td>1.6</td>
<td>21.1</td>
<td>6.99</td>
<td>0.0114</td>
<td>Mechanical Sieve</td>
</tr>
</tbody>
</table>

Note: n/a: not available.

4.3.2. Total content of arsenic, iron and calcium in size-fractionated fly ashes

Disregarding the effect of carbon (due to insignificant percentage and minimal amount in mass) in size-fractionated fly ashes, fly ashes with size of below 20 microns have an inclined trend of arsenic enrichment as shown in the Table 4.3. Arsenic enrichment on finer particle has been reported by various studies [98-100]. It is well known that volatilized elements, such as arsenic, apt to condense on the surface of the fine particles due to a larger surface
area. Therefore, the coarse particle supposed to have significantly less arsenic content than
the finer particle. In fact, the arsenic distribution among fly ash particle size from 20 to 150
microns in this case did not show considerable difference. Furthermore, the relation between
particle size and B.E.T. surface area was positive correlated, converse to theoretical
predication based on particle size. This trend is mainly resulted from the presence of
unburned carbon. Therefore, taking the carbon content in fly ash particle into consideration is
critical in order to reason why the arsenic content in coarse particle is not lower, supposedly.
Previous study by Lopez-Anton et al [101] on arsenic capture by activated carbon in post-
combustion flue gas has proved that arsenic can be retained on the carbon. Therefore, it is
obvious that the carbon plays a role in adsorbing arsenic in those fractions with presence of
carbon. Calcium and iron distributions among different particle sizes are also reported in
Table 4.3. It seems that calcium and iron contents are higher in finer particles. Calcium and
iron concentrations in dry weight are 20 and 100 more times, respectively, than arsenic
concentration in fractionated fly ash.

<table>
<thead>
<tr>
<th>Fractionated Fly Ash particle size in μm (d)</th>
<th>As (μg/g)</th>
<th>Ca (mg/g)</th>
<th>Fe (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3~4.7</td>
<td>205</td>
<td>7.26</td>
<td>37.0</td>
</tr>
<tr>
<td>4.7~7.0</td>
<td>239</td>
<td>6.81</td>
<td>36.9</td>
</tr>
<tr>
<td>7.0~10</td>
<td>170</td>
<td>7.22</td>
<td>38.6</td>
</tr>
<tr>
<td>&lt;20</td>
<td>177</td>
<td>6.77</td>
<td>36.2</td>
</tr>
<tr>
<td>20~45</td>
<td>180</td>
<td>6.63</td>
<td>30.8</td>
</tr>
<tr>
<td>45~75</td>
<td>173</td>
<td>5.21</td>
<td>30.9</td>
</tr>
<tr>
<td>75~106</td>
<td>177</td>
<td>5.16</td>
<td>29.6</td>
</tr>
<tr>
<td>106~150</td>
<td>164</td>
<td>4.75</td>
<td>22.9</td>
</tr>
<tr>
<td>&gt;150</td>
<td>170</td>
<td>4.33</td>
<td>22.7</td>
</tr>
</tbody>
</table>
### Table 4.4: Arsenic distributed fractions in size-fractionated fly ashes.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Water-soluble</th>
<th>Acids-soluble</th>
<th>Oxides (Fe&amp;Mn)</th>
<th>Difficult reducible</th>
<th>Residual</th>
<th>Total mass/Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>1.0(0.5)</td>
<td>18.1(9.5)</td>
<td>14.6(7.7)</td>
<td>16.5(8.7)</td>
<td>140(73.6)</td>
<td>177/(107)</td>
</tr>
<tr>
<td>20~45</td>
<td>0.9(0.5)</td>
<td>19.8(11.0)</td>
<td>12.0(6.7)</td>
<td>9.6(5.3)</td>
<td>138(76.5)</td>
<td>180/(100)</td>
</tr>
<tr>
<td>45~75</td>
<td>1.0(0.6)</td>
<td>13.2(8.4)</td>
<td>9.2(5.8)</td>
<td>3.9(2.5)</td>
<td>131(82.7)</td>
<td>173/(91)</td>
</tr>
<tr>
<td>75~106</td>
<td>1.0(0.7)</td>
<td>13.4(9.2)</td>
<td>9.4(6.5)</td>
<td>4.4(3.0)</td>
<td>117(80.6)</td>
<td>177/(82)</td>
</tr>
<tr>
<td>106~150</td>
<td>1.2(0.8)</td>
<td>14.4(9.1)</td>
<td>11.3(7.1)</td>
<td>6.6(4.2)</td>
<td>124(78.8)</td>
<td>164/(96)</td>
</tr>
<tr>
<td>&gt;150</td>
<td>1.4(1.0)</td>
<td>13.4(9.9)</td>
<td>15.9(11.7)</td>
<td>14.7(10.8)</td>
<td>90(66.5)</td>
<td>170/(80)</td>
</tr>
</tbody>
</table>

Concentrations are in mg/kg outside of bracket and in %wt inside of bracket.

### Table 4.5: Elemental concentration measured with TCLP method at pH=5.

<table>
<thead>
<tr>
<th>PS (μm)</th>
<th>As</th>
<th>Al</th>
<th>Ba</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>5</td>
<td>n/a</td>
<td>100</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>&lt;20</td>
<td>0.42</td>
<td>17.24</td>
<td>0.24</td>
<td>105.85</td>
<td>14.67</td>
<td>4.85</td>
<td>0.27</td>
<td>0.71</td>
</tr>
<tr>
<td>20~45</td>
<td>0.34</td>
<td>15.31</td>
<td>0.22</td>
<td>82.73</td>
<td>3.34</td>
<td>3.10</td>
<td>0.18</td>
<td>0.63</td>
</tr>
<tr>
<td>45~75</td>
<td>0.07</td>
<td>9.54</td>
<td>0.29</td>
<td>67.78</td>
<td>0.71</td>
<td>0.82</td>
<td>0.11</td>
<td>0.25</td>
</tr>
<tr>
<td>75~106</td>
<td>0.04</td>
<td>8.94</td>
<td>0.32</td>
<td>56.62</td>
<td>0.72</td>
<td>0.45</td>
<td>0.09</td>
<td>0.32</td>
</tr>
<tr>
<td>106~150</td>
<td>0.04</td>
<td>12.78</td>
<td>0.23</td>
<td>53.37</td>
<td>1.01</td>
<td>0.45</td>
<td>0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>&gt;150</td>
<td>0.04</td>
<td>26.99</td>
<td>0.12</td>
<td>47.50</td>
<td>0.44</td>
<td>1.09</td>
<td>0.15</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Unit: in mg/l.

### Table 4.6: Theoretical concentration for leachable elements at pH=5.

<table>
<thead>
<tr>
<th>PS (μm)</th>
<th>As</th>
<th>Al</th>
<th>Ba</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>0.89</td>
<td>34.04</td>
<td>0.58</td>
<td>155.24</td>
<td>10.12</td>
<td>12.09</td>
<td>0.27</td>
<td>0.71</td>
</tr>
<tr>
<td>20~45</td>
<td>1.03</td>
<td>25.57</td>
<td>0.47</td>
<td>136.31</td>
<td>3.14</td>
<td>9.34</td>
<td>0.18</td>
<td>0.64</td>
</tr>
<tr>
<td>45~75</td>
<td>0.78</td>
<td>18.90</td>
<td>0.40</td>
<td>105.74</td>
<td>1.21</td>
<td>5.72</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>75~106</td>
<td>0.88</td>
<td>19.55</td>
<td>0.27</td>
<td>104.05</td>
<td>0.84</td>
<td>5.29</td>
<td>0.09</td>
<td>0.28</td>
</tr>
<tr>
<td>106~150</td>
<td>0.81</td>
<td>19.04</td>
<td>0.25</td>
<td>92.99</td>
<td>0.47</td>
<td>4.50</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>&gt;150</td>
<td>0.93</td>
<td>35.75</td>
<td>0.31</td>
<td>84.92</td>
<td>0.48</td>
<td>6.28</td>
<td>0.11</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Unit: in mg/l.
4.3.3. Chemical sequential extraction in size-fractionated fly ashes

The analysis of sequential extraction analysis for As, Fe and Ca are summarized in Table 4.4, 4.5 and 4.6 accordingly. Arsenic hardly dissolved into aqueous phase because sequential extraction indicated that more than 80% of total As in coal ash are either in difficult reducible or in indissolvable form. This finding is applicable for all fractionated coal ash particles. Sequential extraction shows that the majority of Iron element is in the residue which is indissolvable form. It means element iron is incorporated into glass phase of coal fly ash particle which can survive from hard acid condition. Only HF acid can destruct the glass phase to dissolve iron into aqueous phase. However, calcium is more easily extractible in coal fly ash particle, only less than 25% of calcium was intact in the residue after experiencing hard acid condition at pH=2, which means calcium hardly be integrated into glass phase. Calcium is most likely in crystalline form so most of calcium can be dissolved through sequential extraction.

4.3.4. Mobility of arsenic in size-fractionated fly ashes

The mobility of arsenic can be evaluated based on the results from sequential extraction. In general, mobile fractions of trace elements are treated as the potentially leachable in environmental conditions [33]. The sum of extractable arsenic from water-soluble and acids-soluble fractions was used to assess the mobility of arsenic under typical environmental conditions. The mobility of arsenic in size-fractionated fly ash varies from 9.0 to 11.5%, which is consistent with the findings by Jegadeesam et al [102]. As seen in Table 4.4, finer particle contains more acid soluble fraction of arsenic while coarse particle has higher water-soluble fraction of arsenic. The main reason is coarse particle contains carbon which absorb
much more arsenic which can be leachable in neutral condition while the finer particle has higher surface area which arsenic was condensed on it and higher surface area also means higher surface reaction so higher dissolution occurs on finer particle.

4.3.5. Effect of mineral equilibrium on Arsenic leaching from size-fractionated fly ashes

TCLP is used to evaluate leaching potential of toxic elements in environmental conditions which has two extraction liquids of pH 4.93 and 2.88, simulating mild and extreme acid conditions. The theoretically leachable fraction is defined in 3.4, which sums up the water-soluble and acids-soluble extracted fractions. The extraction liquid used in acids-soluble extraction step has pH 5.0. Therefore, the calculated elemental concentration from theoretical leachable fraction for each element should be comparable to the measured concentration at pH 4.93 in TCLP test. The comparisons of leaching concentrations for As, Ca and Fe between TCLP and theoretical calculation are summarized in Table 4.7. Arsenic concentrations for particle sizes less than 20 micrometers are consistent between theoretical value and TCLP measurements. While arsenic concentrations for larger particles in TCLP vary from 0.04 to 0.42mg.L, they are significantly lower than the concentrations in those fractions with particle size of 20 micrometers or smaller. By comparison of measured arsenic concentrations at pH 2.88 and pH 4.93, it shows that there was no difference for fly ash particles larger than 45 micrometers. However, the arsenic concentrations at pH 2.88 are significantly lower than the one at pH 4.93 for fly ash particles with size of more than 45 micrometers.
4.4. Conclusions

Unburned carbon in size-fractionated fly ashes has a direct impact on arsenic distribution among size-fractionated fly ashes. Unburned carbon is concentrated in coarse fractions of pulverized fly ash and adsorbs more gaseous arsenic on the particle surface due to high surface area compared with fly ash particle.

Sequential extraction on size-fractionated fly ashes concluded that about 60 to 80% of total arsenic in pulverized CFA is present in inert form which is categorized as residual in sequential extraction experiment. Only about 10% of arsenic is present in mobile phase which can be known as water-soluble and acid-soluble fractions defined in sequential extraction. Iron is mainly incorporated into glass phase so it hardly dissolves into acid solution while most of calcium in crystalline phase is easily leached out through sequential extraction.

As observed in TCLP, arsenic concentrations in leachate from particles with size of less than 45 microns are obviously lower at pH 2.88 than the one than at pH 4.95. On the contrary, the arsenic concentrations in leachate from other size-fractionated fly ashes gave a positive correlation that the more acidity of leaching liquid, the more elements leached out in aqueous phase. Based on theories as defined in other literature, arsenic is precipitated out as ferric arsenate and calcium arsenate in the leachate which caused the lower arsenic concentration in extreme acid condition. The median acid extraction at pH 4.95 cannot even completely extract out the exchangeable fraction of arsenic in particle with size of more than 150 microns. In this fraction, the carbon adsorption of arsenic has strong effect on the leachable
capacity of arsenic. Therefore, TCLP maybe underestimate the leachability of mobile fraction of arsenic in pulverized coal fly ash.
CHAPTER 5  KINETIC STUDY AND MODELING OF DISSOLUTION OF FOUR ELEMENTS FROM COAL FLY ASH PARTICLE IN AQUEOUS PHASE

5.1. Introduction

Coal fly ash is the byproduct of coal combustion for energy generation. As the coal is composed of different mineral compounds which contain major and rare elements, even trace toxic elements, the coal combustion process somehow acts like a concentrator for toxic elements which are enriched on the secondary mineral products, coal fly ash and bottom ash. Since the coal fly ash production takes up 70% of total coal combustion byproduct, the disposal of coal fly ash containing toxic elements poses a great risk on surrounding environment, especially in wet condition. There are many studies until now about the environmental hazard or potential risk of coal fly ash. Traditionally, US EPA suggests the Toxicity Characteristic Leaching Procedure (TCLP) could be used to characterize solid waste whether it is hazardous waste [103]. TCLP method artificially chooses two extraction liquids at pH 4.93 and 2.88 and suggest the extraction test lasts for 18 ± 2 hours, then the concentration of interested element in the extraction liquid would be defined their hazard in environmental condition. This test could not be applicable for kinetic leaching or dissolution analysis for interested elements but only for regulation guidance. Therefore, it is critical information to understand the kinetic behavior of leaching or dissolution for interested elements in fly ash. The knowledge of kinetic characterization for elements will be further utilized in environmental risk assessment and prediction.

Elemental leaching from CFA is a quit complex process which involves dissolution, advection, diffusion, adsorption and mineral precipitation. Leaching of ash takes place
through dissolution of constituents inside or on the surface of ash and transport through the pore structure to the surrounding pore waters [104]. These processes have been summarized by Cote et al., as chemical or physical (transport) phenomena. The most common progression for leaching many different waste materials is a large initial leachate plug, known as “initial washoff”, which decreases rapidly to a much lower steady state value, controlled by a diffusive leaching flux. Known from a morphological study by SEM, there are two types of fly ash particles, solid and hollow ash particle. CFA is mostly in spherical. Dudas and Warren [105] proposed that fly ash has a glassy core and vesicles are most likely present inside, as seen in Fig.6.1. Other oxides or salts are accumulated on the exterior glass hull. This surface and subsurface layers are prone to dissolve in aqueous solution therefore elements are leached out from coal ash particle easily. As we already know elemental dissolution or leaching is very complex process, could the process be expressed in a simplified mathematic model so it facilitates the application of environmental risk assessment and impact prediction for coal ash disposal practice?

The elemental dissolution from solid particle can be controlled either by mineral solubility which need chemical equilibrium models to predict leachate concentration of elements or by reaction kinetics and transport properties which require more complex predictive models [106]. In our case, we try to find the predictive models to explain the dissolution or leaching process for trace or minor elements in coal fly ashes.
5.2. Theory and method

Elemental dissolution in the fly ash particle strongly depends on the elemental speciation. According to various studies [33, 34, 107], the elemental speciation in the fly ash can be divided into five fractions: water-soluble, acid-soluble, oxide, difficult reducible and residual. The elements in water soluble and acid soluble fractions are thought to be leachable parts in the fly ash which is the determining factors on leaching characteristic in environmental conditions [33]. The dissolution of elemental speciation can be treated as the dissolution of minerals or dissolution of a solid substance. This process occurs on the boundary between two phases, solid and liquid, which is called the phase interface. In this process, there are five major steps involved as follows:

- Diffusion of interfacing substance to the surface
- Adsorption on the surface
- Reaction on the surface
- Desorption from the surface
• Diffusion of products from the surface.

The total reaction rate of heterogeneous processes is controlled by the rate of slowest step. If the overall diffusion mentioned above is neglected, the limiting step will be the dissolution of solid particle. In this case, let us assume that the solid depletion rate equation in the batch reactor can be written as either first order or multi-order which depends on the complexity of the mineral. If the solid dissolved in a first order, it can be written as follows:

\[
\frac{dS_s}{dt} = -kS_s \quad \text{Eq. 1.}
\]

\[
S_{s(t)} = S_{s\text{max}} \cdot e^{-kt} \quad \text{Eq. 2.}
\]

Consider mass conservation in batch reactor, so

\[
m = S_{s\text{max}} \cdot w = C_{b\text{max}} \cdot V = S_{s(t)} \cdot w + C_{b(t)} \cdot V \quad \text{Eq. 3.}
\]

\[
S_{s\text{max}} \cdot w - C_{b(t)} \cdot V = S_{s(t)} \cdot w \quad \text{Eq. 4.}
\]

\[
C_{b(t)} \cdot V = S_{s\text{max}} \cdot w \cdot (1 - e^{-kt}) \quad \text{Eq. 5.}
\]

\[
C_{b(t)} = C_{b\text{max}} (1 - e^{-kt}) \quad \text{Eq. 6.}
\]

Transform Eq.6. into Eq.7,

\[
1 - \frac{C_{b(t)}}{C_{b\text{max}}} = e^{-kt} \quad \text{Eq. 7.}
\]

Resolving differential equation in terms to time, then Eq. 6 can be transformed to

\[
\frac{dC_b}{dt} = C_{b\text{max}} \cdot k \cdot e^{-kt} \quad \text{Eq. 8.}
\]

Assuming \( k' = C_{b\text{max}} \cdot k \)

\[
\frac{dC_b}{dt} = k' \cdot (1 - C_{b(t)}/C_{b\text{max}}) \quad \text{Eq. 10.}
\]

\[
\log\left(\frac{dC_b}{dt}\right) = \log(1 - C_{b(t)}/C_{b\text{max}}) + \log k' \quad \text{Eq. 11.}
\]

If the elemental dissolving process fell into multi-order dissolution equation, the mathematic equation could be written as follows:

\[
\frac{dS_s}{dt} = -kS_s^n \quad \text{Eq. 12.}
\]

\[
\frac{1}{S_{s\text{max}}^{n-1}} = \frac{1}{S_{s(t)}^{n-1}} + k \cdot t \cdot (n-1) \quad \text{Eq. 13.}
\]
\[
S_{s(t)} = \frac{S_{s_{\text{max}}}}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot S_{s_{\text{max}}}]^{n-1}} \quad \text{Eq. 14.}
\]

Replace \(S_{s(t)}\) in the Eq. 3 with Eq. 14 so it can be written as
\[
\left(C_{b_{\text{max}}} - C_{b(t)}\right) \cdot V = \frac{S_{s_{\text{max}}}}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot S_{s_{\text{max}}}]^{n-1}} \cdot W \quad \text{Eq. 15.}
\]

Replace \(S_{s_{\text{max}}}\) with Eq. 3, Eq. 15 can be converted into Eq. 19,
\[
C_{b_{\text{max}}} - C_{b(t)} = \frac{C_{b_{\text{max}}}}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{C_{b_{\text{max}}} \cdot V}{W}\right)]^{n-1}}
\]
\[
C_{b(t)} = C_{b_{\text{max}}} \left(1 - \frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{C_{b_{\text{max}}} \cdot V}{W}\right)]^{n-1}}\right) \quad \text{Eq. 16.}
\]
\[
C_{b(t)} = C_{b_{\text{max}}} \left(1 - \frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{k_n}{C_{b_{\text{max}}} V}\right)]^{n-1}}\right) \quad \text{Eq. 17.}
\]

Assuming \(k_n = k \cdot C_{b_{\text{max}}} \cdot \left(\frac{C_{b_{\text{max}}} \cdot V}{W}\right)^{n-1}\)
\[
C_{b(t)} = C_{b_{\text{max}}} \left(1 - \frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{k_n}{C_{b_{\text{max}}} V}\right)]^{n-1}}\right) \quad \text{Eq. 18.}
\]
\[
C_{b(t)} = C_{b_{\text{max}}} \left(1 - \frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{k_n}{C_{b_{\text{max}}} V}\right)]^{n-1}}\right) \quad \text{Eq. 19.}
\]
\[
\frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{k_n}{C_{b_{\text{max}}} V}\right)]^{n-1}} = \frac{1}{n^{-\frac{1}{2}}[1 + k \cdot t \cdot (n-1) \cdot \left(\frac{k_n}{C_{b_{\text{max}}} V}\right)]^{n-1}} \quad \text{Eq. 20.}
\]
\[
1 - \frac{C_b}{C_{b_{\text{max}}}} = 1 + t \cdot (n-1) \cdot \left\{\frac{k_n}{C_{b_{\text{max}}} V}\right\} \quad \text{Eq. 21.}
\]
\[
\frac{C_{b_{\text{max}}}}{n-1} \cdot \left\{1 - \frac{C_b}{C_{b_{\text{max}}}}\right\}^{n-1} = k_n \cdot t \quad \text{Eq. 22.}
\]
\[
\int_0^t \frac{dC_b}{1 - \frac{C_b}{C_{b_{\text{max}}}}} = \int_0^t k_n dt \quad \text{Eq. 23.}
\]
\[
\frac{dC_b}{dt} = k_n \left[1 - \frac{C_{b(t)}}{C_{b_{\text{max}}}}\right]^n \quad \text{Eq. 24.}
\]
\[
\log\left(\frac{dC_b}{dt}\right) = n \log\left[1 - \frac{C_{b(t)}}{C_{b_{\text{max}}}}\right] + \log(k_n) \quad \text{Eq. 25.}
\]
As seen from the above derivation, both solid dissolution equations could be converted to linear equations with variables of \( \log\left(\frac{dC_b}{dt}\right) \) versus \( \log\left[1 - \frac{C_{b(t)}}{C_{b,max}}\right] \). The differences between them are the slope and intercept. The slope would determine whether dissolution process is first order or multi-order, while the intercept is the logarithmic value of dissolution coefficient. Through monitoring the element concentration in the aqueous phase of batch reactor, the dissolution of element from solid phase would be obtained and furthermore maximum bulk concentration or equilibrium concentration of dissolved elements, rate constant and empirical reaction order during particle dissolution can be determined by using Jeschke and Dreybrodt’ method.

Jeschke and Dreybrodt also summarized the empirical dissolution rate equation for minerals which is commonly written as

\[
dC = k(1 - \frac{C}{C_{max}})^n
\]

[108]. Some minerals, like rocksalt [109], have a linear dissolution rate as \( n = 1 \) while other minerals involves a more complex process where the interplay of transport and chemical processes such as dissolution at the surface of mineral occurs as \( n \neq 1 \). Therefore, the \( n \) is purely empirical reaction order to explain the dissolution of substance in aqueous phase.

To find the rate constants \( k \) and \( n \), experimentally determined rates, one must use a fitting procedure. When applying a logarithm to both sides of empirical dissolution rate equation, it can be written as

\[
\log\left(\frac{dC}{dt}\right) = n \log\left(1 - \frac{C}{C_{max}}\right) + \log k
\]

Eq. 26.
To plot $\log\left(\frac{dC}{dt}\right)$ versus $\log(1 - \frac{C}{C_{\text{max}}})$, a straight line can be obtained with the slope of $n$ and intercept of $\log k$. According to method by Jeschke and Dreybrodt [108], the $C_{\text{max}}$ can be obtained by varying its value to fit the measured data. When the maximum $R^2$ for the linear equation is achieved, the value of $C_{\text{max}}$ would be the optimum equilibrium concentration or maximum concentration for this specific element. Then the rate constants $k$ and $n$ can be estimated from the best-fitting equation for the measured data. By following this approach, it enables to calculate the unknown constants for dissolution rate equation if the saturated or maximum concentration of dissolved substance is known through experiment.

For assessing the potential of elemental mobility in environmental conditions, the maximum leachable fraction of elements will give more specific information which can be realized though sequential extraction analysis. Furthermore, elemental mobility is also affected by the leaching kinetics which is missing in conventional leaching method. By taking mathematic model into account, the kinetic constant can be obtained in the batch study and further taken into prediction model.

5.3. Batch reactor modeling with AQUASIM

AQUASIM is a computer program for the identification and simulation of aquatic systems, which includes several models for various environmental systems like lakes, rivers, soil column, Biofilm, completely mixed and advective-diffusive reactors [46]. The simulation of fly ash batch leaching can be realized in a completely mixed reactor with fixed volume and no flow in or out. The temporal change of the concentration of substance dissolved or suspended in the water is given as
\[
\frac{dC_i}{dt} = r_{C_i} = r_{S_i}
\]

Eq. 27.

\[
S_{seq} = K_p \cdot C_i \cdot \frac{\theta}{(1-\theta) \cdot \rho}
\]

Eq. 28.

Where \(C_i\) is the substance concentration represented by a dynamic volume state variable, \(C_{\text{seq}}\) is the partition equilibrium for interested element in dominant chemical form, and \(\theta\) is the porosity of solid and liquid mixture, \(\rho\) is the density of fly ash particle, \(K_p\) is considered the linear coefficient for interested elements at solid and liquid partition equilibrium.

The temporal change of substances attached to a surface is given by

\[
r_{S_i} = \frac{dC_s}{dt} = k_d \cdot (C_s - C_{seq})^n
\]

Eq. 29.

Where \(r_{S_i}\) is the transformation rate of the substance described by \(S_{si}\), and \(S_{si}\) is the concentration, surface density or mass of the attached substance represented by a dynamic surface state variable, and \(S_{\text{seq}}\) is the partition equilibrium for interested element in dominant chemical form, \(k_d\) and \(n\) are the fly ash particle dissolution constants. This transformation rate is calculated analogously to the transformation rate \(r_{C_i}\) described above. The dimension of \(S_{si}\) can be chosen by the program user who is responsible to make consistent process definitions: if a substance is converted from attached \((S_{si})\) to dissolved \((C_i\); e.g. by a dissolution process\) the stoichiometric coefficients must be chosen in order to convert the units of \(S_{si}\) correctly of those of \(C_i\). For equilibrium state variables algebraic equations specified as equilibrium processes are solved in the compartment.
5.4. Experimental design

Two fly ashes, labeled as BR and CO, collected in a dry state from two fossil fuel plants in Tennessee, United States where pulverized coal combustion technology are used and flue gas emission control facilities, like Electrostatic Precipitator, Selective Catalytic Reduction system, are equipped. The raw coal fly ashes were ignited at 750°C for 4 hours to remove any carbon residual in the fly ash samples and then cool down to room temperature in a desiccator.

The leaching solutions used in the study were buffer solutions at pH = 7. The pH = 7 buffer solution used in the study was prepared with 12.8 g of KH₂PO₄ and 15.8 g of K₂HPO₄ dissolved in a liter of deionized water.

Three masses of 10, 20 and 40 g treated fly ash samples were added into 200ml leaching solution in 250 ml VWR® Polycarbonate Erlenmeyer Flasks with solid caps and then stirring rods were put in flasks. Finally the flask is sealed up with the cap to avoid any evaporation.
loss during leaching process. Therefore the ratio of solid and liquid is maintained the same 1:10 for all treatments. There are totally four treatments for each fly ash sample with different mixing speeds at 60, 125, 350 and 700 RPM. The prepared Erlenmeyer flashes were then put on the stirring plate with mixing speed control. Once the experiment starts, a 5ml of liquid sample was taken each time from the supernatant and filtrated through a syringe filter with filter size of 0.7 micrometer. There were totally 10 time points chosen in about 60 to 70 hours.

The filtrates were acidified with concentrated nitric acid to be ready for metal analysis. Inductively Coupled Plasma – Atomic Emission Spectrometry was used to analysis interested metals – Arsenic, Cadmium, Magnesium and Selenium.

5.5. Results and Discussion

5.5.1. Determination of rate-limiting steps for particle dissolution

The fly ash particle dissolution can be consisted of two major processes: diffusive mass transfer and surface reaction. To determine which steps is rate-limiting step for particle dissolution, it is critical to characterize the dissolution kinetics. The surface reaction may involve more complex processes, for example, precipitation, adsorption and phase partition, etc. On the contrary, the mass diffusion in a fluid solid interface is much easily manipulated and estimated by properly designed laboratory approach. Hypothetically, by varying the mixing speeds for fly ash liquid mixture in batch reactors, the mass diffusive coefficient will be alternated accordingly to the mixing intensity. At high mixing speed, the mass diffusive control will be completely eliminated so the surface reaction will be the limiting factor. If mass diffusion between fluid and solid phase was the limiting step, it would be shown that at
the minimal mixing speed, the mass diffusive coefficient will be significantly smaller than the ones at other mixing speeds.

The results, seen in Fig.5.3 and Fig.5.4, showed that the elements of As, Cd, Mg and Se dissolved into aqueous phase in a similar pattern that the dissolution rate was maximized in the beginning and dramatically decreased as time continued. At certain time, it would reach an equilibrium condition in batch reactor as there was no tendency of continuous increase of dissolved elements in fluid. In all four mixing scenarios at mixing speeds, 60, 125, 350 and 700 RPM, there was no significant difference in the concentration profile for four elements in two coal fly ashes, BR and CT. Therefore, it will be positive that diffusive mass transfer between fluid-solid interfaces was not rate-limiting step during fly ash dissolution process. In other words, surface reaction process determined the fly ash dissolution kinetics.

In the batch experiment, the increased aqueous concentration of interested elements could become rate-limiting factor, too, as theoretically, the surface diffusion from solid surface to bulk water is one of the processes involved as element dissolved into aqueous phase. Considering the ratio between liquid and solid is 10 times and the interested elements are minor or trace in coal fly ash, the dissolved elemental concentration would be minimal not enough to hindrance the surface diffusion process in the batch reactor. However, in other situation, like coal ash slurry in the retention pond or in landfill compartment, the ratio between liquid and solid will be significant small, the fluid concentration in the pore space could be critically higher enough to diminish particle dissolution from solid phase to liquid phase. Therefore, surface diffusivity should be taken into consideration for those two scenarios.
Figure 5.3: Concentration profile of dissolution of As, Cd, Mg and Se in batch reactors for BR fly ash.
Figure 5.4: Concentration profile of dissolution of As (a) and Se (b) in batch reactors for CO coal fly ash at four mixing speed of 60, 125, 350 and 700 RPM.
5.5.2. Partition effect on particle dissolution

As interested elements released into fluid, it simultaneously experienced surface complexation/surface precipitation, even competitive sorption in a complex system. To determine whether surface complexation/precipitation occurred in the fluid phase, it is critical to justify the validity of proposed mathematic equation for dissolution modeling. Mineral dissolution, solution speciation and sorption modelling was performed with the hydrogeochemical computer model PHREEQC for Windows. The thermodynamic database of the geochemical speciation code MINTEQA2 was used for all calculations. The main objective of using PHREEQC is to do speciation and saturation-index calculations in fly ash and extraction fluid mixture system. Saturation indices were calculated using the measured concentrations of the elements listed in Table 5.1 as input in the model. The pH was fixed to the measured value and solid precipitation was suppressed. Based on the output, there was no precipitation related to elements, As, Cb, Mg and Se at the given concentration, shown in Table 5.1. Therefore, the elemental dissolution equation could be simplified whole based on the solid concentration of each element.

Table 5.1: Bulk chemical characteristics of the coal fly ash samples used in this study.

| Temp.(°C) | Ca  | Mg  | Mn  | Se  | pH | Cd  | Co  | Mn  | Se  | Al  | Cr  | V   | As  | Fe  | Zn  | Ba  | P   |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 20        | 0.4 | 1.78| 0.0031 | 0.005 | 0.0117 | 0.0492 | 0.005 | 0.024 | 0.0537 | 0.01 | 185 |
| 4         |     |     |     |     | 0.0012 |       |     |     |       |     |     | 0.0031 |     |     |     |     |
| 0.01      |     |     |     |     |       |       |     |     |       |     |     |       |     |     |     |     |
| 0.389     |     |     |     |     |       |       |     |     |       |     |     |       |     |     |     |     |
| 0.0008    |     |     |     |     |       |       |     |     |       |     |     |       |     |     |     |     |

Unit for elements: mmol/l.
5.5.3. Numerical solution for elemental dissolution with multi-order dissolution model

First of all, set up a reasonable estimation for $S_{\text{max}}$ according to the estimated $C_{b_{\text{max}}}$ known from Jeschke and Dreybrodt’s method [108]. Based on mass conservation, it will be easily estimated for the solid concentration $S_{s(t)}$ from the measured bulk concentration for each elements. As shown in Eq.35, the constant $n$ and $k$ could be calculated by plotting $\log(-\frac{dS}{dt})$ vs. $\log S_s$ in a coordinate. By varying the $C_{\text{max}}$ in a proper step size, a group of $C_{b_{\text{max}}}$, $k$ and $n$ can be found, as shown in Table 5.2. Furthermore, by using Eq.36, we can predict the bulk concentration of interest elements from different group of $C_{b_{\text{max}}}$, $k$ and $n$, seen in Table 5.3. Finally, Comparing each predicted $C_{b(i)}$ with measured $C_{b(i)}$ and using least square regression, seen in Fig.5.5, as criteria to choose best fit parameter combination for $S_{\text{max}}$, $n$, $k$, and $C_{b_{\text{max}}}$, marked as green color in Table 5.2.

A case example is shown as follows to introduce procedure for parameter estimation of $C_{\text{max}}$, $n$, $k$ and $C_{b_{\text{max}}}$ for interested elements.

\[
S_{\text{max}} = \frac{C_{b_{\text{max}}} \cdot V}{w} \quad \text{Eq. 30.}
\]

\[
m = S_{s(t)} \cdot w + C_{b(t)} \cdot V \quad \text{Eq. 31.}
\]

\[-\frac{dS}{dt} = kS_s^n \quad \text{Eq. 32.}\]

\[
\log(-\frac{dS}{dt}) = n \log S_s + \log k \quad \text{Eq. 33.}
\]

\[
C_{b(i)} = C_{b_{\text{max}}}(1 - \frac{1}{n \cdot \left[1 + k \cdot (n - 1) \cdot \left(\frac{C_{b_{\text{max}}} \cdot V \cdot n}{a}\right)^{-1}\right]}) \quad \text{Eq. 34.}
\]

\[
S = \sum_{i=1}^{n} (C_i - f(t_i))^2 \quad \text{Eq. 35.}
\]
Non-linear Least Square fit is chosen to be the criteria in determining the best parameter estimation. The objective consists of adjusting the parameters of a model function to best fit a data set. A simple data set consists of n points (data pairs) \((x_i, y_i), i = 1, ..., n\), where \(x_i\) is an independent variable and \(y_i\) is a dependent variable whose value is found by observation. The model function has the form \(f(x)\). The goal is to find the parameter values for the model which "best" fits the data. The least squares method finds its optimum when the sum, \(S\), of squared residuals

\[
S = \sum_{i=1}^{n} r_i^2
\]

Eq. 36.

is a minimum. A residual is defined as the difference between the actual value of the dependent variable and the value predicted by the model.

\[
r_i = y_i - f(x_i)
\]

Eq. 37.

<table>
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<tr>
<th>Trial test No.</th>
<th>S_{\text{max}}</th>
<th>n</th>
<th>\log k</th>
<th>k</th>
<th>C_{\text{bmax}}</th>
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<td>1.7384</td>
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<tr>
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<td>5.1699</td>
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<td>4.5889</td>
<td>5.1741</td>
<td>149298.8</td>
<td>1.7395</td>
</tr>
<tr>
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<td>4.5919</td>
<td>5.1782</td>
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</tr>
<tr>
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</tr>
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<td>5.1866</td>
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<td>4.6042</td>
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Table 5.3: Summary of measured and predicted $C_b$s based on estimated parameters.

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<th>Time(hr)</th>
<th>Measured</th>
<th>T-1</th>
<th>T-2</th>
<th>T-3</th>
<th>T-4</th>
<th>T-5</th>
<th>T-6</th>
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<td>0.3619</td>
<td>0.3619</td>
<td>0.3620</td>
<td>0.3621</td>
</tr>
<tr>
<td>1.00</td>
<td>0.48</td>
<td>0.5236</td>
<td>0.5237</td>
<td>0.5237</td>
<td>0.5238</td>
<td>0.5239</td>
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</tr>
<tr>
<td>2.00</td>
<td>0.63</td>
<td>0.6948</td>
<td>0.6948</td>
<td>0.6949</td>
<td>0.6949</td>
<td>0.6949</td>
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<td>0.6950</td>
<td>0.6950</td>
</tr>
<tr>
<td>4.00</td>
<td>0.78</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
<td>0.8580</td>
</tr>
<tr>
<td>7.42</td>
<td>0.91</td>
<td>0.9888</td>
<td>0.9888</td>
<td>0.9888</td>
<td>0.9888</td>
<td>0.9888</td>
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<td>48.58</td>
<td>1.25</td>
<td>1.2895</td>
<td>1.2895</td>
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<td>1.2896</td>
<td>1.2896</td>
<td>1.2896</td>
<td>1.2896</td>
</tr>
</tbody>
</table>

Figure 5.5: Plot of Least square results versus trial test numbers.

Table 5.4: Parameter summary of $C_{max}$, $k$, $n$ and $C_{bmax}$ for As, Cd, Mg and Se for BR fly ash dissolution modeling.

<table>
<thead>
<tr>
<th>Elements at pH =7</th>
<th>$C_{max}$ (mg/g)</th>
<th>$k$ (h-1)</th>
<th>n</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.0331</td>
<td>1.51E05</td>
<td>4.59</td>
<td>0.0004</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>1.43E-04</td>
<td>1.76E12</td>
<td>4.14</td>
<td>0</td>
</tr>
<tr>
<td>Magnesium(Mg)</td>
<td>0.2018</td>
<td>17.30</td>
<td>3.06</td>
<td>0.002</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.0011</td>
<td>11.90</td>
<td>1.53</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

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Table 5.5: Parameter summary of $C_{s\text{max}}$, $k$, $n$ and $K_p$ for As, Cd, Mg and Se for CT fly ash dissolution modeling.

<table>
<thead>
<tr>
<th>Elements at pH =7</th>
<th>$C_{s\text{max}}$ (mg/g)</th>
<th>$k$ (h$^{-1}$)</th>
<th>$n$</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.0168</td>
<td>2.45E07</td>
<td>4.27</td>
<td>0</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>1.11E-04</td>
<td>4.43E07</td>
<td>2.72</td>
<td>0.0016</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>2.4585</td>
<td>1.2901</td>
<td>2.94</td>
<td>0.001</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.0055</td>
<td>2116</td>
<td>2.23</td>
<td>0</td>
</tr>
</tbody>
</table>

We chose data set in batch dissolution test for sample with solid and liquid ratio (S:L) = 0.05 to estimate the kinetic parameters, $C_{s\text{max}}$, $k$ and $n$, which are summarized in the Tables 5.4 and 5.5. By using those parameters, it has been successfully implemented in AQUASIM TO predict the concentration of As, Cd, Mg and Se at another scenario with solid and liquid ratio = 0.2. To get even better curve fitting, we took the partition equilibrium effect into consideration and introduce the parameter, $K_p$. Through parameter estimation function in AQUASIM software, we were able to estimate the constant $K_p$. Once again using the three obtained kinetic parameters, we tested the model with scenarios of S:L = 0.05 and 0.2, the measured bulk concentrations for As, Cd, Mg and Se are shown in circles and the predicted one in solid lines in Fig.5.6 and Fig.5.7. For trace elements, As, Cd and Se, the dissolution equation has demonstrated the effectiveness of capturing the dissolution process and successfully predicting the elemental concentration in aqueous phase of batch reactors. However, for Magnesium, at low concentration below 100 mg/l, the model can be used to describe the elemental dissolution process in both experiments. As magnesium concentration increased in aqueous phase, complexation or precipitation played a major role in determining the aqueous concentration of magnesium. As shown in Fig.5.7, magnesium concentration did
not exceed 250 mg/l in the scenario of S:L = 0.2. The main reason is magnesium in the aqueous phase is in saturation state so it won’t dissolve more than the need to reach saturation. The simplified dissolution equation did not consider the factor of saturation so it failed to predict the final concentration for the scenario of S:L = 0.2.

Another interesting finding which is also consistent with the logical judgment is the higher the bulk concentration of dissolved elements in batch reactor, the larger the partition equilibrium $K_p$ value. As mentioned in 5.5.1, the surface diffusion could be a rate-limiting factor in elemental dissolution process. Therefore, a linear phase partition equilibrium constant, $K_p$, was introduced into the dissolution equation. Just like the equation itself says that the larger the difference between solid concentration and the partition equilibrium concentration would result in faster elemental dissolution. This process can be treated as surface diffusion-control step. At low concentration, $K_p$ did not play the role of controlling dissolution. The predicted concentration is always higher than measured one in both cases which is true for all elements, As, Cd, Mg and Se.
Figure 5.6: Model predicted (line) and Measured (circle) As, Cd, Mg and Se concentration profiles during dissolution in BR batch reactors.
Figure 5.7: Model predicted (line) and Measured (circle) As, Cd, Mg and Se concentration profile during dissolution in CT batch reactors.
5.6. Conclusions

The Jeschke and Dreybrodt’s method was effectively applied to estimate the maximum liquid concentration, maximum solid concentration of interested elements (As, Cd, Mg and Se). This method provided good tools for interpreting experimental data and estimating initial value of kinetic parameters.

Trace and minor elemental dissolution from coal fly ash involves much more complex processes that cannot be described by linear kinetics. The introduction of multi-order dissolution equation successfully described the dissolution process of As, Cd, Mg and Se, and has been used for concentration prediction in batch reactor below the ratio of solid and liquid of 0.2.

In the batch dissolution process, at solid and liquid ratio equal to 0.1, there were no diffusive mass transport limitation were observed by varying series of mixing intensity at 60, 125, 350 and 700 rpm. For trace elements, As, Cd, and Se, even at solid and liquid ratio of 0.2, the model simulation indicated that diffusive mass transport did not play major role in elemental batch dissolution process. While, for minor element of Mg, the comparison between measured and predicted concentration indicated that diffusive mass transport were rate-limiting factor during elemental dissolution. The main cause for diffusive mass transfer limitation could be surface complexation or precipitation from over saturation of dissolved magnesium in aqueous phase.
CHAPTER 6 MODELING OF METAL RELEASE AND TRANSPORT WITHIN PACKED COAL FLY ASH COLUMN

6.1. Introduction

Metal leaching from coal fly ash is one piece of critical information in performing environmental risk assessment for coal fly ash disposal, especially for toxic constituents like heavy metal, Cd, Zn, and other toxic elements, As and Se. In the practice of coal fly ash management, coal fly ash either stores in settling ponds (wet disposal) or buries at landfills (dry disposal) [110]. Wet disposal will gradually phase out according to EPA regulation after the catastrophically breakdown of coal ash slurry pond occurred in 2008 at Kingston in one of TVA fossil plants which caused environmental hazard and potential ecological disaster [111]. Therefore, the alternative practice for coal fly ash disposal, landfills or storage silos starts to draw more attention as far as potential environmental impact is concerned. Although engineered landfill provides effective protection from metal or toxic constituents leaching out from coal fly ash, there are still chances that rainfall infiltration into landfill results in metal dissolution into aqueous phase. Researchers have been using column leaching to test the leaching behavior and contaminant transport in fly ash landfills [112]. Since column leaching experiment gives the flexibility of manipulating flow condition, particle size selection and pore structure and easily obtaining flow rate and transport kinetics factor, the result column leaching experiment produces can be used to predict the actual leaching characteristics [40]. Furthermore, column leaching experiment could quantify the relative leached mass and give element behavior in function of time[113]. Therefore, column leaching test has been used commonly for characterization of coal fly ash.
To better understand the mechanism of elemental leaching and transport in a column setting, researchers have attempted to develop mathematical models to interpret the leaching behavior, even to predict the potential impact from different leaching scenarios [40]. The elemental leaching and transport in a column include many processes, including elemental dissolution from coal ash particle, mass transfer from particle surface to bulk phase in pore space in the column, then convective mass transfer from inlet to outlet of the column. In addition, adsorption and precipitation may also occur during the leaching period. Furthermore, the leachate from fly ash column contains both major elements and trace elements which will show different leaching and transport fashion. For major elements, calcium and magnesium, they are the most likely solubility controlling mineral phase in the fly ash while other trace elements, such as As, Se, their leaching may also involve adsorption and co-precipitation controls [114]. As coal fly ash are so diverse, it is very important to study the characterization of fly ash properties and perform column leaching and modeling simultaneously in order to generate useful information for further application, especially for environmental risk assessment.

In this study, the laboratory tests for coal fly ash in batch leaching and column leaching were performed in order to collect kinetic information of fly ash leaching process. Furthermore, mathematical models that can be used to study the elemental mobility in land fill pile were built based on the knowledge obtained from laboratory tests. With aid of AQUASIM 2.0 software, a dynamic modeling can be established to estimate kinetic parameters which describe the mobility of elements of CFA in either batch or laboratory packed column reactors.
6.2. Theory and methods

To model the kinetic reaction and transport for leached interested elements from packed coal fly ashes column, a computer program called AQUASIM was used to accomplish this task. In AQUASIM program, the saturated soil column compartment can be used to describe advective-dispersive transport of dissolved substances in a saturated soil column, exchange process with immobile regions consisting of serially connected mixed zones, and transformations of dissolved and solid substances. With the soil column, fast sorption process can be used to describe equilibrium sorption and slow sorption processes to model the effects of sorption kinetics. The use of any linear or nonlinear sorption isotherm is possible. The inlet and outlet of the soil column compartment can be advectively linked to other AQUASIM compartments.

In the column system, water flow through the soil column is described by

$$\frac{\partial Q}{\partial x} = q$$

Eq. 38.

The spatial gradient of the discharge, $Q$, is determined by the lateral inflow, $q$. Positive values of $q$ (inflow) increase the downstream discharge, negative values (outflow) decrease the downstream discharge.

The behavior of dissolved substances in the mobile zone of the column can be described as the following equation:

$$\frac{\partial C_i}{\partial t} = -\frac{1}{A\theta} \frac{\partial}{\partial x} (QC_i) + \frac{\partial}{\partial x} (D \frac{\partial C_i}{\partial x}) + r_c$$

Eq. 39.

The concentration is affected by advection with the water flow (first term), dispersion (second term), transformation processes (third term).
The first row of this equation describes the behavior of a dissolved substance within the first mixed zone of an immobile region, the second row the behavior in an inner zone, and the third row that in an end zone of the immobile region.

Figure 6.1: Schematic setup of column leaching and particle mass transport process.
The behavior of solid substance in the mobile zone and the immobile zones can be described respectively:

\[
\frac{\partial S_{s,i}}{\partial t} = r_{s,j} \tag{Eq. 40}
\]

The concentrations are only influenced by transformation processes. Note that dissolution must also be formulated as a transformation process transforming the dissolved species, \( C_i \), to the solid species, \( S_j \). When describing solid substances, the conventional notation of \( C \) is mass of a substance per unit liquid volume and of \( S \) is mass of a substance per unit mass of the solid phase. If the concentrations are expressed as mass per unit of total column volume, \( C \) in zone \( zo \) must be converted to \( \theta C \) (multiplication of \( C \) with the porosity of the zone), and \( S \) must be converted to \( S \rho_{\text{solid}} (1 - \theta) \) (multiplication with the density of the solid phase and with the volume fraction of the solid phase). Considering these conversion factors, dissolution can be described by a dynamic dissolving process with a process rate of

\[
r_{c_i} = r_{S_j} = k_d (C_{\text{eq},i}(C_i) - C_{s,i})^q \tag{Eq. 41}
\]

and with stoichiometric coefficient of

\[
C_i : -\rho_s \frac{1 - \theta}{\theta} \tag{Eq. 42}
\]

for the dissolved concentration \( C_i \), and

\[
S_{s,i} : 1 \tag{Eq. 43}
\]

for the solid concentration, \( S_j \). In these equations, \( \rho_{\text{solid}} \) is the density of the solid material in the soil column, \( S_{\text{eq},i}(C_i) \) is the equilibrium isotherm and the process describes relaxation of the actually solid concentration to the equilibrium concentration with a rate constant \( k_i \). If
$k$ is set to a sufficiently large value, this model is a good approximation to equilibrium sorption.

In order to make the solution to the above system of differential equations unique, one boundary condition for the ordinary differential equation Eq.(8) and two boundary conditions for the partial differential equation Eq.(9) are required. The ordinary differential equation Eq.(11) to Eq.(12) that do not contain spatial derivatives does not require boundary conditions.

The boundary condition for equation Eq.(8) that describes discharge through the compartment is given by

$$Q(x_s) = Q_{in} \quad \text{Eq. 44.}$$

at the start point, $x_s$, of the column. According to equation Eq.(8), due to the lateral inflow, $q$, this results in a discharge of

$$Q(x_e) = Q(x_s) + \int_{x_s}^{x_e} q \, dx \quad \text{Eq. 45.}$$

at the column outlet.

The boundary conditions for equation Eq.(9) are given by the continuity of the substance loading entering the compartment and by a ‘transmission boundary conditions’ at the end of the compartment:

$$QC_i(x_s) - A\theta D \frac{\partial C_i}{\partial x} = I_{in,i} \quad \text{Eq. 46.}$$

$$\frac{\partial^2 C_{mob,i}}{\partial x^2} = 0 \quad \text{Eq. 47.}$$

where $I_{in,i}$ is the total mass input of the substance $i$ per unit of time. The second of these boundary conditions Eq.(15b) is omitted for dispersion-free transport.
6.3. Materials and Methods

6.3.1. Estimation of fly ash density and porosity in column

The porosity of both sediment and column tests were estimated by using the same method as described below.

Weight an empty glass graduated cylinder, \( M_0 \), and then fill with a volume of \( V_s \) ml of fly ash and weight it again as \( M_1 \). Add a certain volume \( V_1 \) of water into the cylinder and mix thoroughly and put the mixture still for an hour to settle down the suspended particle, then record the final volume \( V_2 \).

\[
\text{Bulk density } \rho_b = \frac{M_1 - M_0}{V_s} \quad \text{Eq. 48.}
\]

\[
\text{Specific density } \rho_s = \frac{M_1 - M_0}{V_2 - V_1} \quad \text{Eq. 49.}
\]

To estimate the porosity of fly ash, pack a certain amount of fly ash in a graduated cylinder and measure the length of the column or depth for the sediment as \( L_0 \) and then pure water into column or container and thoroughly mix with fly ash to fill any void in the column or sediment with water, after leave the suspended fly ash settle for at least 1 hour and record the final length or depth of the settled fly ash layer, \( L_1 \). It would be easy to calculate the porosity, \( \theta \), of fly ash by applying the following equation.

\[
\theta = \frac{L_1 - L_0}{L_0} \cdot \frac{\rho_b}{\rho_s} \times 100\% \quad \text{Eq. 50.}
\]

6.3.2. Column dispersivity test

After completing the column leaching test, column dispersion test were performed. Decant any residue extraction solution on the top of fly ash column and put a glass wool layer on the top of fly ash column avoiding any disturbance from pouring tracer solution. The tracer solution was chosen to be 50g/l of NaCl solution. As conductivity is strongly
proportional to the concentration of the sum of cations and anions, the change of conductivity in leachate will reflect the pattern of dispersion of elements leached from fly ash in the column. Here it is assumed that there is no adsorption effect for leached elements during their downward transport. During the test, the effluent was collected periodically to measure the average conductivity during the collection period. The test lasted until the effluent had the same concentration of NaCl as the influent. The correlation between conductivity and concentration of NaCl is given as bellows.

The sodium chloride transport in a compacted fly ash column can be described with the general advection-reaction-dispersion equation [115]:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A\theta} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} = \frac{\partial q}{\partial t}$$

where $C$ is the concentration of NaCl in water (mg/l), $t$ is time (hour), $Q$ is flow rate (m^3/hour) and $A$ is cross-sectional area (m^2), $\theta$ is the porosity of column, $x$ is column length (m). $D$ is the hydrodynamic dispersion coefficient (m^2/hour). $q$ is the concentration of NaCl in the solid phase (expressed as mg/l). For a conservative element, like Na and Cl, $\frac{\partial q}{\partial t} = 0$. The usual assumption for elemental leaching in column setup will be that $Q$ and $D$ are equal for all solute species.

Appelo and Postma also provided an analytical solution of Eq. 51. [115] that is

$$C(x,t) - C_i = \frac{A}{C_0 - C_i}$$

where $x$ is the column length (m), $C_i$ is the initial concentration in the column, $C_0$ is the concentration in the injected solution and $C(x,t)$ is the effluent concentration from the column:

$$A = erfc\left(\frac{x - Qt/A\theta}{\sqrt{4Dt}}\right) + \exp\left(\frac{xQ/A\theta}{D}\right)erfc\left(\frac{x + Qt/A\theta}{\sqrt{4Dt}}\right)$$
The dispersivity of the column was calculated by a least square fit of Eq.52 on the breakthrough curves.

The dispersion coefficient can be also estimated by AQUASIM model software with numerical method. Since other parameters, like flow rate, column porosity, particle density, column cross-sectional area are known in the Eq.39, and there is no transformation process as sodium chloride solution pass through packed fly ash column, the only unknown will be the dispersion coefficient. It is easily to be calculated by AQUASIM with the function of parameter estimation.

6.3.3. Batch leaching test

Two fly ashes, labeled as BR and CT, collected in a dry state from two fossil fuel plants in Tennessee, United States where pulverized coal combustion technology are used and flue gas emission control facilities, like Electrostatic Precipitator, Selective Catalytic Reduction system, are equipped. The raw coal fly ashes were ignited at 750°C for 4 hours to remove any carbon residual in the fly ash samples and then cool down to room temperature in a desiccator.

The leaching solutions used in the study were buffer solutions at pH = 7. The pH = 7 buffer solution used in the study was prepared with 12.8 g of KH$_2$PO$_4$ and 15.8 g of K$_2$HPO$_4$ dissolved in a liter of deionized water and the pH = 5 buffer solution was prepared by mixing 5.7ml glacial acetic acid and 64.3 ml of 1N NaOH, diluted with deionized water to 1 liter of a volume.

Mass of 10 and 40g of treated fly ash samples were added into 250 ml VWR® Polycarbonate Erlenmeyer Flasks with solid caps and then another 200ml of leaching
solution and a stirring rod were put in the flask. Finally the flask is sealed up with the cap to avoid any evaporation loss during leaching process. There are totally four treatments for each fly ash sample with different mixing speeds at 60, 125, 350 and 700 RPM. The prepared Erlenmeyer flashes were then put on the stirring plate with mixing speed control. Once the experiment starts, a 5ml of liquid sample was taken each time from the supernatant and filtrated through a syringe filter with filter size of 0.7 micrometer. There were totally 10 time points chosen in about 60 to 70 hours.

The filtrates were acidified with concentrated nitric acid to be ready for metal analysis. Inductively Coupled Plasma – Atomic Emission Spectrometry was used to analysis interested metals – Arsenic, Cadmium, Magnesium and Selenium.

![Figure 6.2: The standard curve for the correlation between NaCl concentration and Conductivity for standard solutions.](image)

6.3.4. Column leaching test
The column leaching system was designed to simulate fluid exposure that fly ash pile most likely encounters in the open field and landfill or in the fly ash impoundment pond without impermeable layer at bottom, such as precipitation, groundwater. The columns were constructed of acrylic pipe with inner diameter of 2.54 cm and length of 46 cm. A layer of glass wool was placed at the bottom of the column. Threaded PVC pipe caps ¼" NPT fitting were tapped into the ends for leachate inflow, pressure control, and leachate outflow. Parallel column leaching systems were set up for each CFA sample. Each column held a representative 150g sample. The leaching solution is laboratory deionized water which has a pH = 5.0 and zero alkalinity. Fresh DI water is delivered thought peristaltic pump to the column and leaching solution transport downward to collector at the bottom of column. A water cap formed on the top of fly ash which will maintain fly ash completer immerse in water. The flow rate was usually between 2.27 to 4.2 mL/h, although it varied, especially with the gravity system.

Leachate was collected daily and taken to measure the pH and leachate volume. The metal concentration including aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium [116], chromium (Cr), cobalt (Co), and other metals, in the leachate were determined by inductively coupled plasma-atomic emission spectroscopy [117].
6.3.5. Calculation of saturation states

Precipitation of solid mineral phases is the most important chemical process influencing on the mobility of both major and trace elements from coal fly ashes. Activities of aqueous species and mineral saturation indices of selected mineral phases were calculated using PHREEQC software [93] and the MINTEQ.V4 database. Saturation index (SI) is used when large deviations from equilibrium are observed. For SI = 0, there is equilibrium between mineral and the solution; SI > 0 indicates super-saturation, and SI < 0 sub-saturation. For a state of supersaturating, precipitation of the solid mineral may be possible and sub-saturation suggests dissolution of mineral is expected.
6.4. Results and discussions

6.4.1. Batch reactor experiment

The trace element leaching from fly ash particle is a complex process which involves surface reaction and diffusive transport. The batch reactor tests were designed to study the dissolution process and attempt to interpret the process in a mathematic approach. The detailed data analysis is given in Chapter 5. As observed from chapter 5, experimental multi-order equation can explain the complexity of elemental leaching from fly ash particle but the mechanism of leaching interested elements is still vague. As the leaching time prolonged, it seems internal mass transfer has strong effect on trace elemental dissolution. This phenomenon has been known that trace elements in coal fly ash have very long leaching vibrancy. However, compared to the contribution from facial dissolution into the total leaching potential, the internal mass transfer has less significant impact on environmental hazard. The acute environmental risk most likely accompany with the quick dissolution of facial elemental dissolution in aqueous phase. To column leaching, as the leachate pass through the packed fly ash particle, the elemental leaching behaves the same way as elemental dissolution in aqueous phase. Therefore, the mathematical equation that is used to describe the elemental dissolution from solid particle in fluid is still valid for column leaching modeling.
Figure 6.4: NaCl concentration profile for BR columns leaching setups from both measured (circle with red line) and predicted outputs with AQUASIM method (black line).

Figure 6.5: NaCl concentration profile for BR columns leaching setups from both measured (circle with red line) and predicted outputs with Analytical method (black line).

Table 6.1: Summary of parameters and estimated column dispersion coefficients.

<table>
<thead>
<tr>
<th>Column name</th>
<th>Coal ash filled (g)</th>
<th>Flow rate (m³/hr)</th>
<th>Porosity (%)</th>
<th>Dispersion coefficient (m²/hr) Analytical</th>
<th>Dispersion coefficient (m²/hr) Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR-A</td>
<td>151.3</td>
<td>3.75E-06</td>
<td>44.3</td>
<td>1.00E-04</td>
<td>9.45E-05</td>
</tr>
<tr>
<td>BR-B</td>
<td>151.5</td>
<td>3.70E-06</td>
<td>43.7</td>
<td>1.11E-04</td>
<td>9.13E-05</td>
</tr>
</tbody>
</table>
6.4.2. Dispersion coefficients in column leaching

Two approaches have been used to estimate the dispersivity of packed coal fly ash columns. The column dispersion coefficients for two parallel column setups are summarized in Table 6.1. The difference of estimated dispersion coefficients for same column from both approaches is less than 5%, therefore, it is positive that both approaches are equally reliable. Since AQUASIM software will be used for batch and column leaching, the estimated value obtained from AQUASIM simulation will be chosen to be used for afterwards modeling.

In addition, the estimated dispersion coefficients for both identical columns are very close, which indicated that the result for same type of coal fly ash column leaching is replicable.

6.4.3. Comparison of model output and measurement for column leaching test

The two parallel columns were continuously monitored over 2000 hours and the flow rate and pH value for leaching effluent were plotted in Fig. 6.17. As it shows that flow rate varied from 3.6 to 4.0 ml/hour. The variance for flow rate mainly came from measurement approach as the average flow rate was calculated based on the volume accumulation of effluent in certain time. This approach had congenital defect in measuring continuous flow. The effluent shows a rather stable pH throughout the whole leaching period, which was just barely above neutral condition. This steady pH created the same elemental dissolution environment in the column as the one in batch dissolution experiment. Therefore, the elemental dissolution equation obtained from batch test would be valid for column leaching simulation.

By implementing simulation in AQUASIM software, arsenic, cadmium, magnesium and selenium were simulated in a column leaching setup, the measured and simulated effluent
concentration were separately plotted in Fig. 19, 20, 21, 22, accordingly. By comparing the results from two approaches, it shows that cadmium and magnesium concentrations in simulation output were quite well matched the concentration measurement from column leaching experiment. The mass balance calculation for Cd and Mg, shown in Table 6.3, also indicated that the model simulation successfully captured the leaching characteristics in column environment. As to arsenic and selenium, the simulation output did not match the measured result for effluent concentration. The batch analysis for As in both raw fly ash (with carbon content) and treated fly ash (without carbon), plotted in Fig. 6.18, indicated that carbon in coal fly ash had great adsorption effect on arsenic. In the mixture of ash and liquid, the arsenic concentration increased over time as arsenic dissolved into extraction liquid and finally reach the maximum concentration in a batch setup. While in the other group of setup that the raw coal ash contains carbon residue in the ash-liquid mixture, arsenic concentration had a very low concentration in the beginning and continuously decreased over time and finally reach a minimal level. The results indicated that arsenic adsorption could be so quick that the dissolution process did not outpace the adsorption process. Therefore, there was no apparent arsenic accumulation in aqueous phase. At the same time, the column leaching result, shown in Fig. 6.19, also pointed out that carbon residue in coal fly ash have adsorption effect on arsenic. There is an apparent retardation effect on Arsenic indicated in the concentration profile for arsenic during the leaching period. The mass balance for Arsenic, in Table 6.3, shows that only half of the total amount of As has been leached out in 2000 hours. The carbon residue in coal fly ash had significantly slowed down the leaching process of arsenic in this case. For Selenium, there is also obviously gap in total captured mass between
leached and simulated results. The reasonable explanation is that selenium loosed into gas phase during carbon removal process (at 750°C) as selenium has a boiling point of 685°C. Diaz-Somoano et al. [118] reported that selenium was lost at least 50% at 750°C during coal gasification. Their finding completely supported the explanation of selenium imbalance between laboratory leaching and model simulation.

![Figure 6.6: pH and effluent flow rate profiles during leaching period for BR coal fly columns.](image)

**Figure 6.6:** pH and effluent flow rate profiles during leaching period for BR coal fly columns.
Table 6.2: Mass balance for As, Cd and Mg in column settings and modeling output.

<table>
<thead>
<tr>
<th>Mass</th>
<th>As (mg)</th>
<th>Cd (mg)</th>
<th>Mg (mg)</th>
<th>Se (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available in each column</td>
<td>4.0073</td>
<td>0.0216</td>
<td>24.4313</td>
<td>N/A</td>
</tr>
<tr>
<td>In the leachate from BR-A</td>
<td>1.9837</td>
<td>0.0166</td>
<td>20.5877</td>
<td>0.9609</td>
</tr>
<tr>
<td>In the leachate from BR-B</td>
<td>1.9069</td>
<td>0.0238</td>
<td>20.4062</td>
<td>1.0232</td>
</tr>
<tr>
<td>Recovered by modeling</td>
<td>3.4378</td>
<td>0.0198</td>
<td>23.0380</td>
<td>0.1614</td>
</tr>
</tbody>
</table>

Figure 6.7: Arsenic concentration in batch reactor with raw BR fly ash (with carbon) and treated BR fly ashes (without carbon).
Figure 6.8: Arsenic concentration in leachate from BR- columns A and B and output from AQUASIM model.

Figure 6.9: Cadmium concentration in leachate from BR- columns A and B and output from AQUASIM model.
Figure 6.10: Magnesium concentration in leachate from BR-columns A and B and output from AQUASIM model.

Figure 6.11: Selenium concentration in leachate from BR-columns A and B and output from AQUASIM model.
6.5. Conclusions

This study demonstrated that trace and minor elemental leaching in a controlled environment-packed column leaching can be modeled by AQUASIM with knowing of empirical dissolution equation and other critical kinetic parameters, porosity, dispersion coefficient and so on. The multi-order empirical equation has effectively represented the complex processes involved during elemental dissolution, especially for trace elements as their dissolution is controlled by reaction kinetics and transport processes.

Adsorption should be taken into consideration for certain elements in column leaching environment. The carbon residue adsorbed the dissolved arsenic in the fluid and had retardation effect in column leaching environment. Therefore, it greatly prolongs the arsenic leaching time in column environment.

pH is very critical factor that determine dissolution for all dissolved element. A properly developed dissolution equation should always be used with caution and proved the validity at certain pH condition.
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The present work aimed at characterizing both physical and chemical properties of CFA, investigating elemental distribution and dissolution behavior at different pH conditions, and developing mathematical dissolution equation for elemental leaching. In addition, the equation simulates elemental leaching characteristics in both and column environment.

A systematic analysis of fly ash particle size fractions established linkages between particle size, particle morphology, unburned carbon content, surface area, and sorption capacity. Unburned carbon was enriched in fly ash fraction with size of more than 150 microns. Further, the majority of surface area and sorption capacity of fly ash was attributed to the presence of unburned carbon. More importantly, unburned carbon content, specific surface area, and methylene blue sorption capacity were strongly correlated to each other as revealed by regression analysis, providing a quantitative basis for understanding the surface properties of fly ash and developing more effective practices for the beneficial use of fly ash.

Most elements were relative inert in the environment because a major part of the element resides in the inert form. Only less than 40% of total amount of elements might be mobilized under certain conditions by ion exchange, acid dissolution.

Unburned carbon in size-fractionated fly ash has an impact on arsenic distribution among size-fractionated fly ashes. Sequential extraction on size-fractionated fly ashes concluded that about 60 to 80% of total arsenic in pulverized CFA is present in inert form which is categorized as residual in sequential extraction experiment. Only about 10% of arsenic is
present in mobile phase which can be known as water-soluble and acid-soluble fractions defined in sequential extraction.

As observed from TCLP, the arsenic concentration in leachate from size-fractionated fly ashes was lower than the theoretical concentration for all fractionated fly ashes, calculated from sequential extraction test. Mineral phase analysis with PHREEQC indicated that no surface precipitation occurred among the dissolved elements in acetic-based buffer solution at pH=5. Therefore, it leads to the conclusion that it is carbon content that adsorbed dissolved arsenic in solution resulting arsenic concentration decreased in the TCLP test. Therefore, TCLP analysis for coal fly ash with carbon presence definitely underestimates the leachability of mobile fraction of arsenic in pulverized coal fly ash.

The Jeschke and Dreybrodt’s method has been effectively applied into initial estimation of maximum liquid concentration, maximum solid concentration of interested elements, like As, Cd, Mg and Se. This method provides good tools for interpreting experimental data and estimating initial value of kinetic parameters. Trace and minor elemental dissolution from coal fly ash involves much more complex processes that cannot be described by linear kinetics. The introduction of multi-order dissolution equation successfully described the dissolution process of As, Cd, Mg and Se, and has been used for concentration prediction in batch reactor below the ratio of solid and liquid of 0.2.

In the batch dissolution process, there were no diffusive mass transport limitation were observed at the ratio of S/L = 0.1 and a series of mixing intensity. For trace elements, As, Cd, and Se, even at of the ratio of S/L = 0.2, the model simulation indicated that diffusive mass transport did not play major role in elemental batch dissolution process. While, for minor
element of Mg, the comparison between measured and predicted concentration indicated that diffusive mass transport were rate-limiting factor during elemental dissolution. The main cause for diffusive mass transfer limitation could be surface complexation or precipitation from over saturation of dissolved magnesium in aqueous phase.

This study has demonstrated that trace and minor elemental leaching process from a packed coal fly ash column can be modeled by AQUASIM giving empirical dissolution equation and other critical kinetic parameters, porosity, dispersion coefficient are properly estimated. The multi-order empirical equation has effectively represented the complex processes involved during elemental dissolution, especially for trace elements as their dissolution are controlled by reaction kinetics and mass transport processes.

Adsorption should be taken into consideration for certain elements in column leaching environment. To coal fly ash, the carbon residue adsorbed the dissolved arsenic in the fluid and had retardation effect in column leaching environment. Therefore, it greatly prolongs the arsenic leaching time in column environment.

Validation of the elemental dissolution equation was conducted by performing a comparison with an experimental study at two different solid-liquid mixtures. The comparison was focused on the prediction of leached elemental concentration in the batch environment. Furthermore, the dissolution equation was also successfully applied in the column leaching simulation. Both batch and column leaching simulations proved this model is valid for elemental leaching simulation under controlled environment.
7.2. Recommendations

As discovered in this study, trace element dissolution from coal fly ash is complicated by several factors, surface reaction, diffusive mass transport and phase equilibrium and so on. The challenging task would be to establish a mathematic equation which can describe those factors in a meaning fashion. If it could be realized, it would make simulation of elemental dissolution from coal fly ash particle more universal and more flexible for application purpose.

The pH condition in both extraction solution and aqueous phase in solid and liquid mixture plays a critical role in determining elemental dissolution and dissolving rate therefore a neutral condition was chosen in this study. Further research can be put onto the kinetic study of fly ash leaching at other pH conditions which often be observed in natural environment. A case in point would be to simulate acid rain precipitation on elemental leaching from coal fly ash pills. This scenario could provide valuable information on predicting environmental impact of surface runoff from coal fly ash pills after storm events.

The approach used in this study for trace elemental dissolution and column leaching simulation were strictly limited to controllable laboratory setting. It has been approved that it is very useful as references to model special conditions, like neutral pH and only dissolution-control for mass transfer in a homogeneous packed fly ash column, but the complication for laboratory analysis and parameter estimation makes engineering or consultant companies very reluctant to take advantage of this approach for coal fly ash risk assessment and environmental predication. The upcoming study could focus on how to streamline the approach to make it more universally acceptable for field application.
LIST OF REFERENCES


3. Thomas, L., Coal Geology. 2002: John Wiley & Sons Ltd.


APPENDIX

A. Dissolving solution preparation

1. Reagent solution (100mL) preparation:

<table>
<thead>
<tr>
<th>Chemical name (form)</th>
<th>Molar Concentration (M)</th>
<th>Molar weight (g/mol)</th>
<th>Purity</th>
<th>Density (g/mL)</th>
<th>Reagent Vol.</th>
<th>Chemials (g or mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCL (S)</td>
<td>0.2</td>
<td>74.551</td>
<td>1</td>
<td>n/a</td>
<td>100</td>
<td>1.4910</td>
</tr>
<tr>
<td>KHP (S)</td>
<td>0.1</td>
<td>204.221</td>
<td>0.999</td>
<td>n/a</td>
<td>100</td>
<td>2.0443</td>
</tr>
<tr>
<td>KH2PO4 (S)</td>
<td>0.1</td>
<td>136.086</td>
<td>0.997</td>
<td>n/a</td>
<td>100</td>
<td>1.3650</td>
</tr>
<tr>
<td>NaOH (S)</td>
<td>0.1</td>
<td>39.997</td>
<td>0.986</td>
<td>n/a</td>
<td>100</td>
<td>0.4057</td>
</tr>
<tr>
<td>Na2B4O7.10H2O (S)</td>
<td>0.025</td>
<td>381.372</td>
<td>1</td>
<td>n/a</td>
<td>100</td>
<td>0.9534</td>
</tr>
<tr>
<td>NaHCO3 (S)</td>
<td>0.05</td>
<td>84.010</td>
<td>1</td>
<td>n/a</td>
<td>100</td>
<td>0.4201</td>
</tr>
<tr>
<td>Na2HPO4 (S)</td>
<td>0.05</td>
<td>141.959</td>
<td>1</td>
<td>n/a</td>
<td>100</td>
<td>0.7098</td>
</tr>
<tr>
<td>HCL (L)</td>
<td>0.2</td>
<td>36.500</td>
<td>0.374</td>
<td>1.18</td>
<td>100</td>
<td>1.6541</td>
</tr>
</tbody>
</table>

Note: All reagent solutions were prepared with high-purity grade chemical and reagent grade water from MP Biomedicals, Inc.

2. Fly ash dissolving solution preparation procedure:

<table>
<thead>
<tr>
<th>Fly ash dissolving solution pH</th>
<th>Reagents mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>50mL 0.2M KCl + 13.0 mL 0.2M HCl</td>
</tr>
<tr>
<td>4</td>
<td>100mL 0.1M potassium hydrogen phthalate (KHP) + 0.2mL 0.1M HCl</td>
</tr>
<tr>
<td>6</td>
<td>100mL 0.1M KH2PO4 + 11.2mL 0.1M NaOH</td>
</tr>
<tr>
<td>7</td>
<td>100mL 0.1M KH2PO4 + 58.2mL 0.1M NaOH</td>
</tr>
<tr>
<td>8</td>
<td>100mL 0.025M Na2B4O7.10H2O (borax) + 41mL0.1M HC1</td>
</tr>
<tr>
<td>10</td>
<td>100mL 0.05M NaHCO3+21.4 mL 0.1M NaOH</td>
</tr>
<tr>
<td>12</td>
<td>100mL 0.05M Na2HPO4+53.8mL0.1M NaOH</td>
</tr>
</tbody>
</table>
B. Microwave assisted acid digestion procedure

1. Reagents:
   Hydrochloric acid (37% m:V)
   Nitric acid (69.6% m:V)
   Aqua regia, prepared by mixing nitric acid and hydrochloric acid in a volumetric ratio of 1:3, respectively.
   Hydrofluoric acid
   Boric acid saturated solution

2. Acid digestion procedure
   A 0.4 gram of ash sample, either raw or after combustion (750°C), was placed in a PFA liner and treated with 3mL of HF and 9mL of HCl and 3mL of HNO3. After vigorous reaction stops, the container was tightly capped and stabilized in the frame and then placed the digestion module into the microwave oven. The microwave heating program was set up as follows:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Power</th>
<th>Level</th>
<th>% Ramp</th>
<th>Pressure (psi - limit)</th>
<th>Temp °C</th>
<th>Stir</th>
<th>Hold Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400W</td>
<td>100</td>
<td>15:00</td>
<td>800</td>
<td>180</td>
<td>Off</td>
<td>30:00</td>
</tr>
</tbody>
</table>

After cooling, the container was uncapped and 10mL of boric acid neutralization solution was quickly added. The container was then re-capped, returned to the oven and changed to another heating program as follows:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Power</th>
<th>Level</th>
<th>% Ramp</th>
<th>Pressure (psi - limit)</th>
<th>Temp °C</th>
<th>Stir</th>
<th>Hold Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400W</td>
<td>100</td>
<td>15:00</td>
<td>800</td>
<td>170</td>
<td>Off</td>
<td>20:00</td>
</tr>
</tbody>
</table>

The solution was finally analyzed by ICP-AES using a blank solution containing the same amount of aqua regia, HF and boric acid.
C. AQUASIM model setup for batch reactor

The kinetic model was implemented in the software AQUASIM 2.1 [46] by using both complete mixed reactor to estimate batch leaching kinetic constant. The detailed procedure is explained using Arsenic as an example.

1. Define a dynamic volume state variable C_b10 for the dissolved concentration of As and a dynamic surface state variable S_s10 for the mass of As per unit of solid mass as shown Fig.8.1.
2. Define a program variable for time, as shown in Fig.8.2.
3. Define formula variable for general model parameters, as given in Table 8.1, are shown in Fig. 8.3 ~ 8.5.
4. To compare the model output with the laboratory measurement, a real list variable for measured leachate concentration is defined in the model as given in Fig.8.6.
5. Define a dissolution process as shown in Fig.8.7. Note that the rate describes the arsenic dissolving process from solid particles and that stoichiometric coefficients are used to convert the units from C_b10 to S_s10 as described in the theory section.
6. Define a completely mixed reactor compartment as shown in Fig.8.8. Activate the state variable C_b10 and S_10 as Fig.8.9, and the process dissolution as Fig.8.10. Then define the initial conditions for the state variable C_b10 and S_s10 as Fig.8.11.
7. Define the simulation with 700 steps of size 0.1 hour for the calculation number 0, as shown in Fig.8.12.
8. Define a plot with abscissa Time and the variables C and Measure C at the outlet location, as shown in Fig.8.13. Save the system definitions by clicking the command File \(\rightarrow\) save from the main bar.
9. Activate all simulations and click the button Start/Continue of the dialog box Simulation. Then plot the curves defined above. Fig.5.19 and 5.20 show the results.
Table 0.1: Summary of formula variables for elemental dissolution in batch reactor.

<table>
<thead>
<tr>
<th>Meaning</th>
<th>Name</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of batch reactor</td>
<td>V</td>
<td>L</td>
<td>0.2</td>
</tr>
<tr>
<td>Porosity for BR batch</td>
<td>θ</td>
<td></td>
<td>(1-mass_fa/ρ_s)/(mass_fa/ρ_s+V)</td>
</tr>
<tr>
<td>Porosity for CT batch</td>
<td>θ</td>
<td></td>
<td>(1-mass_fa/ρ_s)/(mass_fa/ρ_s+V)</td>
</tr>
<tr>
<td>Solid density for BR</td>
<td>ρ_s</td>
<td>kg/m³</td>
<td>2020</td>
</tr>
<tr>
<td>Solid density for CT</td>
<td>ρ_s</td>
<td>kg/m³</td>
<td>1880</td>
</tr>
<tr>
<td>Initial concentration of elements</td>
<td>Cin</td>
<td>g/m³</td>
<td>0</td>
</tr>
<tr>
<td>Mass of coal fly ash for BR</td>
<td>mass_fa</td>
<td>g</td>
<td>10.5037/40.0224</td>
</tr>
<tr>
<td>Mass of coal fly ash for CT</td>
<td>mass_fa</td>
<td>g</td>
<td>10.0873/40.0343</td>
</tr>
<tr>
<td>Dissolution coefficient</td>
<td>k_d</td>
<td></td>
<td>Shown in Tables 5.4 &amp; 5.5.</td>
</tr>
<tr>
<td>Dissolution constant</td>
<td>n</td>
<td></td>
<td>Shown in Tables 5.4 &amp; 5.5.</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>k_p</td>
<td></td>
<td>Shown in Tables 5.4 &amp; 5.5.</td>
</tr>
</tbody>
</table>
Figure 0.1: Definition of the dynamic volume variable C and surface variable S.

Figure 0.2: Definition of program variable t.
Figure 0.3: Definition of the linear partition of As between liquid and solid phases.

Figure 0.4: Definition of the mass of coal fly ash added into batch reactor.

Figure 0.5: Definition of porosity of coal ash and liquid mixture.
Figure 0.6: Definition of the time-dependent leachate concentration.

Figure 0.7: Definition of the dissolution process.
Figure 0.8: Definition of the mixed reactor compartment.

Figure 0.9: Activate the variables of As in liquid and solid.
Figure 0.10: Activate the dissolution process for As.

Figure 0.11: Set up initial concentration for variables.
Figure 0.12: Definition of model simulation

Figure 0.13: Definition of model output for plots.
D. AQUASIM model setup for fly ash packed column leaching

The kinetic model was implemented in the software AQUASIM 2.1 [46] by using both complete mixed reactor and the saturated soil column compartment to estimate batch leaching kinetic constant and column leaching constant.

The column leaching model was created with AQUASIM 2.0 software and the detailed procedure is explained using Arsenic as an example.

1. Define a dynamic volume state variable C for the dissolved concentration of As and a dynamic surface state variable S for the mass of As per unit of solid mass as shown Fig.8.14.
2. Define a program variable for time, as shown in Fig.8.15.
3. Define formula variable for general model parameters, as given in Table 8.2. The last parameter is required to describe the equilibrium for arsenic between liquid and solid phases, defined as formula variable, S_eqAs, shown in Fig.8.16.
4. To compare the model output with the laboratory measurement, a real list variable for measured leachate concentration is defined in the model as given in Fig.8.17.
5. Define a dissolution process as shown in Fig.8.18. Note that the rate describes the arsenic dissolving process from solid particles and that stoichiometric coefficients are used to convert the units from C to S as described in the theory section.
6. Define a saturated soil column compartment and give the column coordinate from 0 to L, cross-sectional area A, porosity and choose the button of “with dispersion” and give dispersion coefficients. Finally, give number of grits and choose resolution, as shown in Fig.8.19. Activate the state variable C and S as Fig.8.20, and the process dissolution as Fig.8.21. Then define the initial conditions for the state variable C and S as Fig.8.22. Define the Input as an Inlet Input with a Water Inflow of Qin and a loading of Qin*Cin for the variable C, as seen in Fig.8.23.
7. Define the simulation with 2100 steps of size 1 hour for the calculation number 0, seen in Fig.8.24.
8. Define a plot with abscissa Time and the variables C at the outlet location and measured Cs as well in the same plot, as shown in Fig.8.25. Save the system definitions by clicking the command File → save from the main bar.
9. Activate all simulations and click the button **Start/Continue** of the dialog box **Simulation**. Then plot the curves defined above. Fig.6.18 ~ 6.20 shows the results.

<table>
<thead>
<tr>
<th>Meaning</th>
<th>Name</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-sectional area</td>
<td>A</td>
<td>m²</td>
<td>5.06E-4</td>
</tr>
<tr>
<td>Column length</td>
<td>L</td>
<td>m</td>
<td>0.25</td>
</tr>
<tr>
<td>Porosity</td>
<td>( \theta )</td>
<td></td>
<td>0.441</td>
</tr>
<tr>
<td>Solid density</td>
<td>( \rho_s )</td>
<td>kg/m³</td>
<td>2020</td>
</tr>
<tr>
<td>Water flow rate into column</td>
<td>Qin</td>
<td>m³/h</td>
<td>3.76E-6</td>
</tr>
<tr>
<td>Water concentration into column</td>
<td>Cin</td>
<td>g/m³</td>
<td></td>
</tr>
<tr>
<td>Dissolution coefficient</td>
<td>( k_d )</td>
<td></td>
<td>1.51E5</td>
</tr>
<tr>
<td>Dissolution constant</td>
<td>n</td>
<td></td>
<td>4.59</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>( k_p )</td>
<td></td>
<td>0.0004</td>
</tr>
<tr>
<td>Solid concentration</td>
<td>( C_{\text{max}} )</td>
<td>g/kg</td>
<td>0.0331</td>
</tr>
<tr>
<td>Dispersion coefficient</td>
<td>D</td>
<td>m²/hour</td>
<td>9.3e-5</td>
</tr>
</tbody>
</table>
Figure 0.14: Definition of the dynamic volume variable C and surface variable S.

Figure 0.15: Definition of program variable t.
Figure 0.16: Definition of the linear partition of As between liquid and solid phases.

Figure 0.17: Definition of the time-dependent leachate concentration.
Figure 0.18: Definition of the dissolution process.

Figure 0.19: Definition of the saturated column compartment.
Figure 0.20: Activate both volume and surface variable for As.

Figure 0.21: Activate the dissolution process for As.
Figure 0.22: Set up initial concentration for variables.

Figure 0.23: Set up the inflow condition.
Figure 0.24: Definition of model simulation.

Figure 0.25: Definition of model output for plots.
VITA

Zhenwei Zhu was born in Anshan, Liaoning, China on October 30, 1977, who received his undergraduate education in Liaoning University and obtained bachelor degree on analytical chemistry in July 2000. After graduation, he ever worked as a laboratory technician in Anshan Environmental Monitoring Center, Anshan whose main responsibilities were to perform routine administered regional rivers’ water quality monitor, to assist on industrial wastewater discharge control, to develop and test new analytical techniques improving working efficiency. After four-year full-time work there, he left to pursue his study on the direction of environmental engineering in Europe. He was enrolled on the Master program on environmental engineering at Technical University of Denmark in the fall of 2004. In 2006, he successfully graduated with Master degree of environmental engineering. Then he first came to study at South Dakota School of Mines & Technologies in January, 2007 at the direction of environmental engineering. After one semester, he transferred to the University of Tennessee, Knoxville in August. He continued his PhD study in Civil Engineering under Department of Civil & Environmental Engineering, concentrated on Environmental Engineering. In the summer of 2011, he finishes his academic requirement for doctoral degree and will defense the dissertation on July 18, 2011.