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Leaching Kinetics of As, Mo, and Se from Acidic Coal Fly Ash Samples

Ghanashyam Neupane[1,2]*, Rona J. Donahoe[3], Siddhartha Bhattacharyya[3], Prakash Dhakal[4]

[1]Idaho National Laboratory, Idaho Falls, Idaho, USA
[2]Center for Advanced Energy Studies, Idaho Falls, Idaho, USA
[3]Department of Geological Sciences, University of Alabama, Tuscaloosa, Alabama, USA
[4]Department of Soil, Water and Environmental Sciences, University of Arizona, Tucson, Arizona, USA
Email: *ghanashyam.neupane@inl.gov, rdonahoe@ua.edu, sidhartha@ua.edu, dhakal@email.arizona.edu

Abstract

Annually, coal-fired electric power plants produce large volumes of potentially hazardous coal combustion products (CCPs) including fly ash. Since majority of the coal fly ash and other CCPs deposited in dry land fills or wet lagoons, they pose risk of contamination to local environment. In this study, we present results of leaching kinetics for As, Mo, and Se from three acidic fly ash samples collected from coal-fired power plants in the southeastern United States. This study shows that the leachate concentrations of As, Mo, and Se increase over time. Three kinetics equations, pseudo-second order, Elovich, and power-function, are able to adequately describe the experimental leaching kinetics data. Experimental leaching data and modeling results indicate that the rate limiting leaching of As, Mo, and Se is controlled by the diffusional process responsible for transferring these elements from interior to the surface of the particles as well as the dissolution of the fly ash particles. Therefore, it is important to adopt effective containment/treatment schemes to avoid potential and persistent dispersion of trace elements from ash disposal facilities to surrounding environment for a long time.

Keywords

Coal Fly Ash, Arsenic, Molybdenum, Selenium, Kinetics, Leaching

1. Introduction

Coal-fired electric power plants generate large volumes of coal combustion products (CCPs) such as fly ash, bottom ash, boiler slag, flue gas desulfurization (FGD) materials, and various gases. Fly ash is the most voluminous fraction, accounting almost 53.0% (in 2013) and projected to increase to 55.0% (2022) of the

total of CCPs produced in the United Sates [1]. While recycling of fly ash for beneficial use in the United States alone has increased from 30% in 2000 [2] to nearly 54% in 2015 [3], the majority of the ash is impounded in lagoons and landfills located throughout the country [1] [4]. Fly ash contains large quantities of major element constituents as oxides, hydroxides and sulfates. It also contains environmentally significant quantities of hazardous leachable trace elements such as As, Mo, and Se [5] [6]. During combustion, the organic matter in coal is destroyed and, as a result, the concentrations of trace elements in fly ash are enhanced relative to the source coal [7].

The release of trace elements to the environment is of concern because of their potential toxicity. Several studies show that coal fly ash with elevated concentration of trace elements can readily release these elements into the environment [5] [6] [7]. The leaching behavior of major and trace elements in fly ash varies with the properties of the ash, such as pH, composition, and the leachant. Owing to the production and deposition of large volumes of fly ash in landfills each year, the risk associated with potential release of fly ash into local environment is real. For example, an incident that was occurred on December 22, 2008 with the rupture of a containment structure spilled over 3.7 million cubic meters of wet coal ash at the Kingston coal-fired power plant of Tennessee Valley Authority (TVA) in Tennessee [8]. Additionally, seepage and leakage of toxic elements such as As, Mo, Se etc. from coal ash ponds have been recently reported, and, in some cases, contaminating nearby water sources and creating health hazard risk to numerous parts of the southern US [9].

Total leachable amount as well as overall leaching behavior of hazardous trace elements from fly ash samples is important for determining the environmental consequences of potential release of fly ash into local environment. A large number of studies on dissolution kinetics have been conducted in the past for several minerals [10]; however, there have been very few studies on leaching kinetics of trace elements from contaminated geomedia [11] [12]. Even there is no uniformity among several regulatory leaching protocols for leachant-solid material interaction period [13]. Similarly, most of the laboratory leaching schemes also use a leaching period in the range of 3 to 168 h [14]. In this situation, leaching kinetics, particularly, leaching behavior over time and factors controlling the rate limiting leaching of trace elements are very important for understanding the leaching persistency of trace elements from coal fly ash. In this study, we present results evaluating the leaching kinetics of As, Mo, and Se from three acidic fly ash samples derived from the Eastern Bituminous coals in the United States.

2. Materials and Methods

2.1. Fly Ash Samples and Characterization

Fresh acidic fly ash samples (HA, HB and MA) were collected from three electric power plants located in the southeastern USA. These fly ash samples were the combustion products of the Eastern Bituminous coals. All three fly ash samples were collected dry and were homogenized in the laboratory before using them

for kinetics experiments.

The pH of the acidic fly ash samples are reported in the range of slightly acidic to neutral. Details on physical and chemical properties of these fly ash were described elsewhere [6]. In general, these fly samples are more acidic at the surface than their bulk composition. The specific surface area of these fly ash samples measured with single-point Brunauer-Emmet-Teller (BET) method was reported to be 3.18, 2.11, and 3.46 m^2/g for HA, HB, and MA, respectively. Similarly, the carbon contents in these fly ash samples are reported to be 6.74%, 6.37%, and 14.7% for HA, HB, and MA, respectively. Concentrations of As, Mo, and Se along with some major elements determined with microwave assisted acid digestion [15] are presented in Table 1. The concentrations of several other trace elements and their leachabilities have been reported elsewhere [6] [16] [17] [18] [19].

2.2. Kinetics Experiments

Leaching kinetics of As, Mo, and Se from acidic fly ash samples were conducted using jar leaching and batch leaching experiments. For both schemes of experiments, Barnstead nanopure water (18.2 MΩ) was used as leachant.

Jar leaching experiments for kinetic study were performed using 2 L high density polyethylene (HDPE) bottles at a 1:30 solid:liquid ratio. For these experiments, 60 g of each fly ash was mixed with 1.8 L of nanopure water and agitated on an orbital platform shaker at 200 rpm. About 20 mL of the leachate solution was withdrawn at each sampling event from each experimental bottle at 1, 4, 8, 12, 24, 36, 48, 72, 96, and 120 h. The leachate supernatants were separated by centrifugation at 8500 rpm for 10 minutes and filtration through 0.2 μm syringe filters. After the separation, leachate solutions were acidified to 2% with ultrapure OPTIMA nitric acid and stored in refrigerator until chemical analysis with a Perkin Elmer Optima 3000DV inductively coupled plasma optical emission spectrometer (ICP-OES).

In compliment to the Jar leaching experiment, a separate experimental scheme

Table 1. Environmentally available concentrations (mg/kg) of major elements, As, Mo, and Se in fly ash samples.

Elements	HA	HB	MA	LOD[a]
Al	21,800	14,010	9310	0.001
As	82	167	158	0.009
Ca	4860	7580	5730	0.015
Fe	19,590	18,310	12,110	0.003
K	3160	1690	1570	0.077
Mg	1890	1300	1130	0.001
Mo	13	20	12	0.002
Na	722	460	616	0.009
Se	7.7	23	14	0.004
Si	7290	2180	3880	0.015

[a]ICP-OES limit of detection (LOD) values are given in mg/L.

was also employed to evaluate the leaching kinetics of As, Mo, and Se from acidic fly ash samples with a long-period leaching. A different (1:15) solid: liquid ratio was selected for this series of experiments to investigate whether the initial loading scheme has any effect on leaching kinetics. For each fly ash sample, multiple batch leaching sets were prepared by mixing 3 g fly ash and 45 mL of nanopure water in 50 mL centrifuge tubes. The fly ash-water mixtures were continuously agitated until sample collection. At each sampling time, duplicate aliquots of each fly ash leachate solution were collected for chemical analysis by sacrificing two tubes. The last samples for this series of experiments were collected after a leaching period of 30 weeks. Concentration of As, Mo, Se, and pH from leaching experiment is presented in Supplementary Table S1 & Table S2.

2.3. Kinetic Modeling of Leaching

Leaching of trace elements from fly ash could be explained by assuming that this process is similar to desorption/dissolution of elements from solid surface/materials (Ash *et al.*, 2013). Desorption kinetics of different sorbates from several sorbents including soils, metal oxides, and others have been previously described using zero order, first order, second order, and their derivative equations [20] [21] [22]. An additional suite of kinetic models such as Elovich equation [23], power function equation [24] [25], and parabolic diffusion equation [20] were also used previously for modeling desorption kinetics. The selection of kinetic models could depend on several factors such as simplicity to determine fitting parameters and its ability to describe the experimental data. For example, Evans and Jurinak (1976) used multiple simultaneous first order reactions while Chien and Clayton (1980) used Elovich equation to adequately describe the release and sorption kinetics of phosphate in soils [26] [27].

In this study, leaching kinetics of As, Mo, and Se are analyzed using three kinetic equations: pseudo-second order, Elovich, and power-function equations. The attempt of using other kinetic models failed because of their inability to adequately describe the experimental data. Kinetic equations with their linear forms and fitting parameters are presented in Table 2. Kinetic parameters for pseudo-second order equation were obtained by plotting t versus t/q_t. The q_e was the reciprocal of the slope while k and h were obtained from intercept. If

Table 2. Kinetic equations, their linear forms, and model fitting parameters.

Kinetic equations		linear form	Kinetic parameters
Pseudo-second order[a]	$\dfrac{\mathrm{d}q_t}{\mathrm{d}t} = k\left(q_e - q_t\right)^2$	$\dfrac{t}{q_t} = \dfrac{1}{kq_e^2} + \dfrac{1}{q_e}t$	$k, \ h = kq_e^2$
Elovich[b]	$\dfrac{\mathrm{d}q_t}{\mathrm{d}t} = \alpha \exp\left(-\beta q_t\right)$	$q_t = \dfrac{1}{\beta}\ln\left(\alpha\beta\right) + \dfrac{1}{\beta}\ln\left(t\right)$	α, β
Power function[c]	$q_t = at^n$	$\log q_t = \log a + n\log t$	a, n

[a]Ho and McKay (1999) [21]; [b]Low (1960) [23]; [c]Aharoni and Sparks (1991) [25]; q_e is equilibrium concentration of leaching element, q_t is concentration of leaching element at any time t. The units of various model parameters (e.g., k, h, α, β, a, and n) are given in Tables 3-5.

leaching kinetics of As were to obey the Elovich equation, the plot of q_t vs. $\ln(t)$ should yield a linear relation with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ $\ln(\alpha\beta)$. Similarly, if log transformed kinetic data plotted as $\log(q_t)$ vs. $\log(t)$ result in a linear line, then the leaching kinetic was said to be in compliance with power function equation. Power function rate constant and its order were then obtained from slope (n) and intercept ($\log\alpha$) of the fit. The coefficient of determination (R^2) for each model was obtained by using experimental and model derived data. The goodness of model fit was also evaluated by calculating two additional parameters, normalized deviation (ND) and normalized standard deviation (NSD) using Equations (1) and (2), respectively [28].

$$ND = 100/n \sum \left| \left(q_{t(\exp)} - q_{t(\text{model})} \right) \middle/ q_{t(\exp)} \right| \tag{1}$$

$$ND = 100 \sqrt{\sum \left(\left(q_{t(\exp)} - q_{t(\text{model})} \right) \middle/ q_{t(\exp)} \right)^2 \middle/ n} \tag{2}$$

where n is number of experimental measurements, $q_{t(\exp)}$ is the experimental concentration of element at time t, and $q_{t(\text{model})}$ is the model predicted concentration of element at time t. The smaller the values of ND and NSD, the better is the fit of experimental data for the kinetic model.

3. Results and Discussion

3.1. Results of Jar Leaching Kinetic Experiments

Figure 1 shows solution pH trends and concentrations of As, Mo, and Se released during jar leaching tests of the fly ash samples. Leachate pH slightly increased until 20 hours and stabilized thereafter for HB and MA fly ash samples. The leachate pH for HA fly ash decreased slightly during the early stage of leaching and increased to about 7 after 30 hours. For all fly ash samples, leaching of As, Mo, and Se was relatively faster at the early stage; however, their leaching trend became slightly sluggish or plateaued in the later part of the experiment (Figure 1).

3.2. Results of Batch Leaching Kinetic Experiments

The leachate pH and concentrations of As, Mo, and Se mobilized during long-term leaching kinetic experiments are presented in Figure 2. All fly ash samples showed increasing leachate pH until 10 weeks and it remained near-neutral over time. Although the trend is visible in results after Jar leaching tests (Figure 1), the results of long-term leaching experiments clearly illustrate the early rapid release followed by a slow but persistent increase in leachate concentration of these elements until 18 weeks (Figure 2). At the latter part of the experiment (after 18 week, leaching trend became slightly sluggish, and or plateaued.

The early relatively rapid leaching of As, Mo, and Se from these acidic fly ash samples are potentially related to their mobility from fly ash particles' surface enrichment or association of these elements in the finest fraction of the fly ash. It has been well established in literature that such early rapid mobility of elements
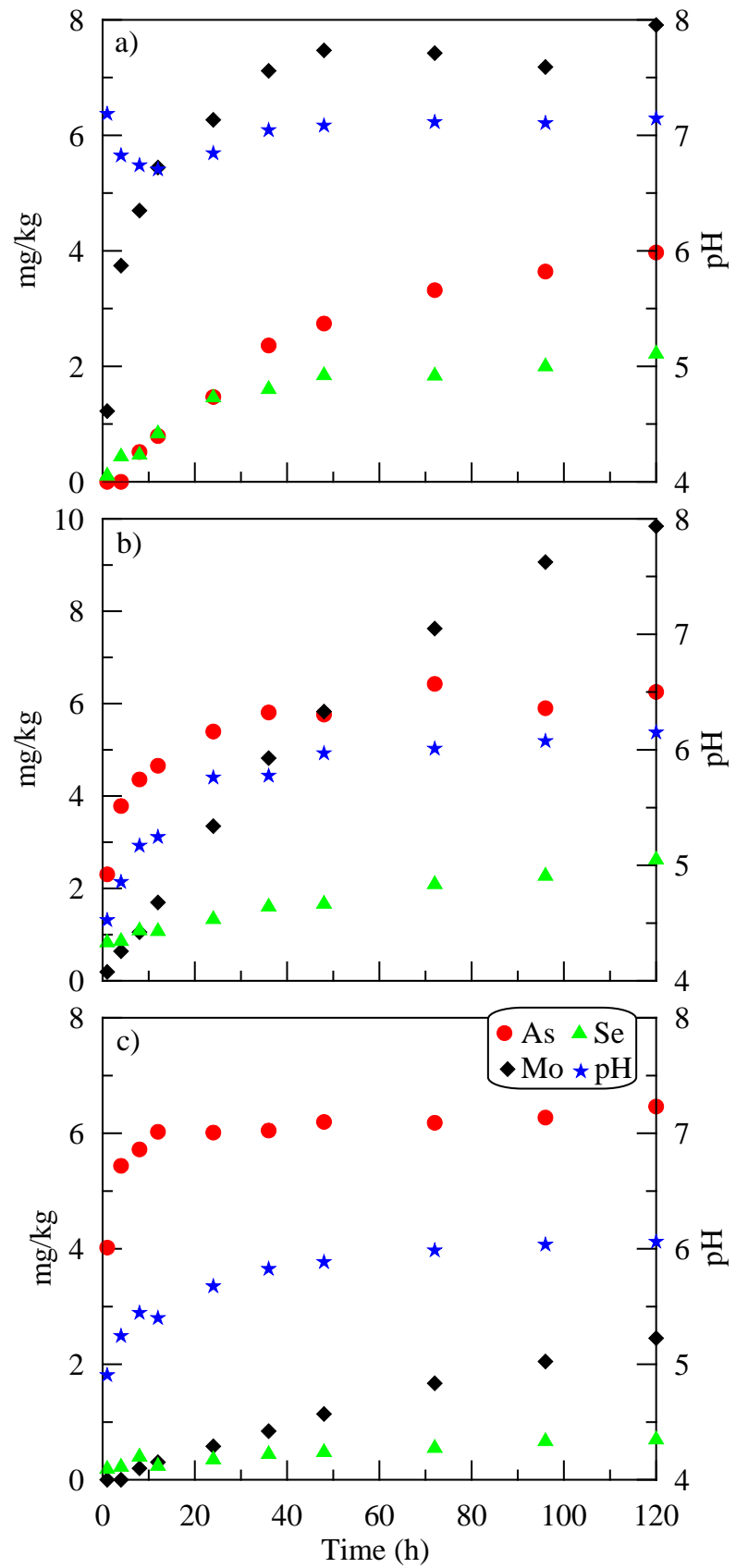
Figure 1. Leachate pH trends and concentrations of As, Mo, and Se elements mobilized during fly ash jar leaching tests: a) HA fly ash, b) HB fly ash, and c) MA fly ash.
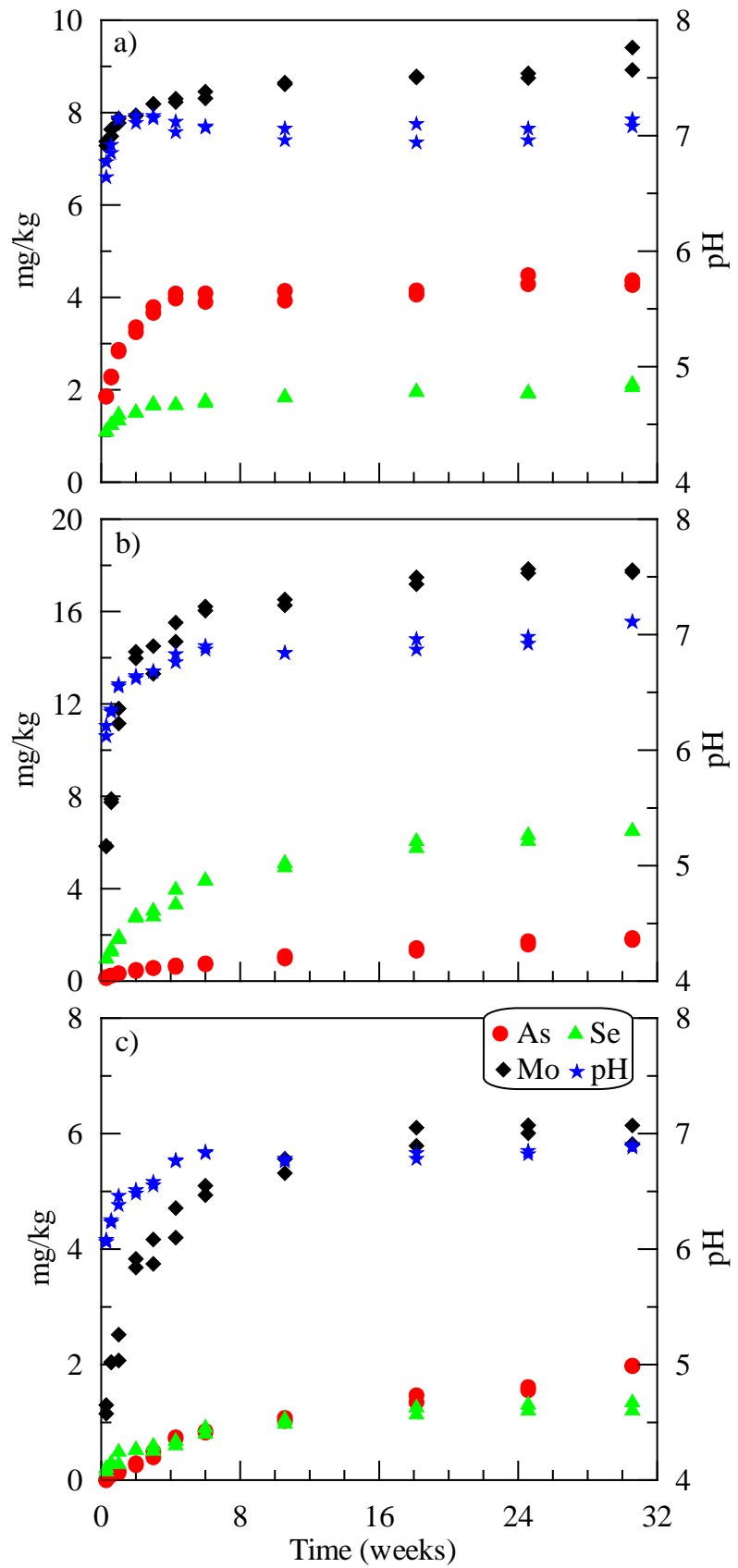
Figure 2. Leachate pH trends and concentrations of As, Mo, and Se mobilized from (a) HA, (b)HB, and (c) MA fly ash samples over a period of 30 weeks.

generally associates with fast dissolution of sub-micron sized particles in the sample during mineral-water interaction [29]. However, slow but persistent increases in the concentrations of these elements with increasing contact time could be related to slow dissolution of or solid-medium diffusion from the particle interior. In coal fly ash, As, Mo, and Se are reported to be present as surface enrichment and remain within solid particles either as impurities in crystalline phases or as heterogeneous/homogeneous mixture in glassy phases [5] [30]. Glassy aluminosilicate particles in fly ash are less stable phases in aqueous environment than mullite and quartz [31] [32]. Such amorphous particles in fly ash samples could gradually dissolved during leaching experiments releasing trace elements over time. In our previous study, we observed that fly ash leachates produced with comparable interaction period are undersaturated with respect to quartz, mullite, and amorphous silica [6]. Therefore, the increasing leachate concentrations of As, Mo, and Se with time measured in this study is likely a result from the slow dissolution of fly ash particles.

3.3. Modeling Results

The pseudo-second order, Elovich, and power-function kinetic models were used to describe the leaching behavior of As, Mo, and Se from acidic fly ash samples. Linear plots for these kinetic models for both leaching schemes are shown in Figure 3 and Figure 4. Similarly, the kinetic parameters for these models are presented in Tables 3-5 along with coefficient of determination (R^2), ND, and NSD. Results suggest that all three models were able to describe the general behavior of As, Mo, and Se from acidic fly ash samples.

Table 3. Leaching kinetic parameters for pseudo-second order model.

Experiments/fly ash/elements			Model parameters			Goodness of fit		
			k (kg·mg^{-1}·h^{-1})	h (mg·kg^{-1}·h^{-1})	q_e (mg·kg^{-1})	R^2	ND	NSD
Jar leaching	HA	As	0.0015	0.080	7.25	0.9384	6.7	7.9
		Mo	0.0229	1.470	8.01	0.9965	3.3	4.1
		Se	0.0178	0.119	2.58	0.9829	10.9	15.2
	HB	As	0.0479	1.928	6.34	0.9972	7.1	12.2
		Mo	0.0004	0.165	20.55	0.9326	5.3	7.9
		Se	0.0241	0.178	2.72	0.9548	21.6	30.8
	MA	As	0.1210	4.984	6.42	0.9994	5.7	10.3
		Mo	0.0001	0.052	13.31	0.9230	1.7	1.9
		Se	0.0881	0.052	0.77	0.9561	25.2	32.6
Long-term leaching	HA	As	0.392	7.55	4.39	0.9986	4.58	7.37
		Mo	0.358	29.42	9.06	0.9986	8.04	14.47
		Se	0.662	2.93	2.10	0.9970	10.47	17.48
	HB	As	0.0657	0.291	2.11	0.9534	19.02	23.28
		Mo	0.0727	23.96	18.2	0.9996	4.14	6.32
		Se	0.0459	2.30	7.08	0.9931	11.43	16.72
	MA	As	0.0201	0.168	2.89	0.9283	10.10	12.05
		Mo	0.1029	4.145	6.35	0.9978	6.55	13.28
		Se	0.2181	0.447	1.43	0.9850	15.19	21.06

Table 4. Leaching kinetic parameters for Elovich model.

Experiments/fly ash/elements			Model parameters		Goodness of fit		
			α (mg·kg^{-1}·h^{-1})	β kg·kg^{-1}	R^2	ND	NSD
Jar leaching	HA	As	0.21	0.75	0.9873	9.3	16.0
		Mo	5.0	0.74	0.9593	8.8	14.9
		Se	0.37	2.09	0.9425	32.1	64.2
	HB	As	18.3	1.21	0.9620	4.1	5.2
		Mo	0.81	0.46	0.8531	155.4	381.8
		Se	1.34	2.71	0.8285	15.5	19.3
	MA	As	2.4×10^4	2.40	0.8334	4.1	5.6
		Mo	0.09	1.22	0.9163	35.4	56.3
		Se	0.40	9.48	0.8129	17.4	22.0
Long-term leaching	HA	As	111	1.90	0.9003	6.86	8.21
		Mo	8.3×10^8	2.78	0.8589	0.86	1.24
		Se	252	5.04	0.9756	2.02	2.75
	HB	As	0.92	2.78	0.9777	35.01	58.39
		Mo	175	0.40	0.9120	8.90	11.69
		Se	6.81	0.79	0.9777	9.30	16.33
	MA	As	0.57	2.17	0.9357	44.42	89.69
		Mo	12.9	0.92	0.9686	6.47	9.06
		Se	1.38	3.96	0.9487	14.29	20.02

Table 5. Leaching kinetic parameters for power function model

| Experiments/fly ash/elements			Model parameters		Goodness of fit		
			α (mg·kg^{-1})	n (mg·kg^{-1}·h^{-1})	R^2	ND	NSD
Jar leaching	HA	As	0.12	0.76	0.9649	11.4	13.1
		Mo	1.89	0.34	0.8467	19.3	23.2
		Se	0.18	0.57	0.9505	18.2	19.0
	HB	As	2.69	0.20	0.9209	7.4	8.7
		Mo	0.20	0.85	0.9943	7.7	9.4
		Se	0.71	0.24	0.9092	9.7	11.0
	MA	As	4.55	0.08	0.7916	4.8	6.0
		Mo	0.03	0.94	0.9985	2.8	3.3
		Se	0.20	0.25	0.8608	11.7	15.4
Long-term leaching	HA	As	2.71	0.17	0.8581	9.30	10.28
		Mo	7.76	0.04	0.9654	0.89	1.22
		Se	1.40	0.12	0.9604	2.87	3.71
	HB	As	0.30	0.54	0.9756	6.76	8.01
		Mo	9.88	0.21	0.8348	12.54	14.44
		Se	1.92	0.40	0.9756	7.91	9.20
	MA	As	0.17	0.76	0.9624	15.44	18.75
		Mo	2.41	0.33	0.9052	13.28	16.25
		Se	0.39	0.39	0.9553	9.72	12.69
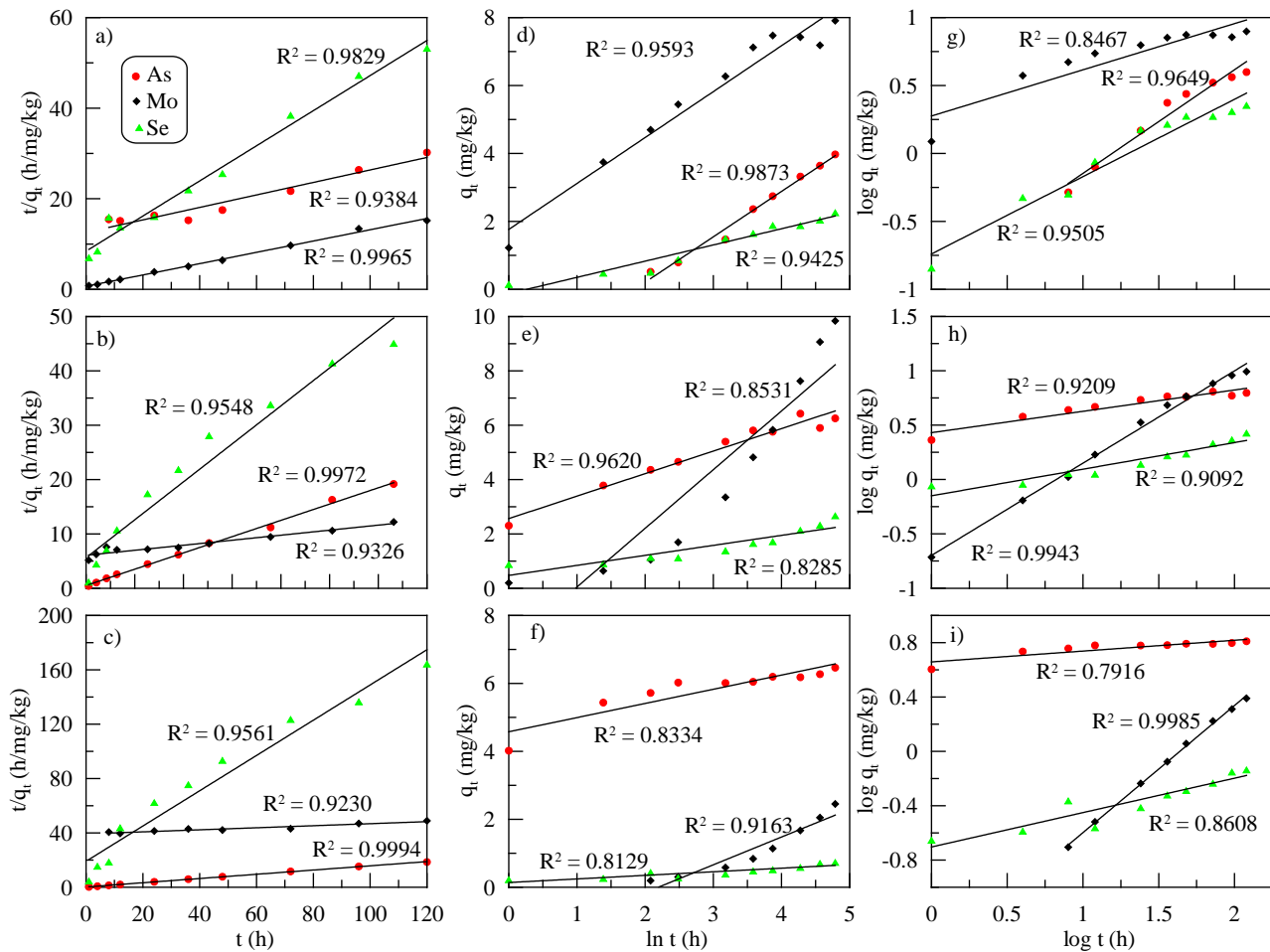
Figure 3. Kinetic leaching modeling using pseudo-second order (a. HA, b. HB, and c. MA), Elovich (d. HA, e. HB, and f. MA), and power function (g. HA, h. HB, and i. MA) models for jar leaching of As, Mo, and Se from acidic fly ash samples.

The pseudo-second order kinetic model appears to fit the leaching data for both leaching schemes for all fly ash samples (Table 3). For the adsorption phenomenon, the good compliance of kinetic data with pseudo-second order equation is attributed to a sorption phenomenon in which the rate-limiting step is associated with chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [21]. Conversely, in the case of leaching, the excellent fitting of kinetic data could be attributed to a bond breaking mechanism such as dissolution of amorphous fly ash particles. Fly ash samples contain glassy materials such as amorphous aluminosilicates particles [33], and as mentioned earlier, these glassy particles in fly ash are least stable in aqueous environment [32].

It is important to note that the leaching of any solute (e.g. trace elements) from a solid phase (e.g., fly ash) involves displacement of former from the latter into the leachant. This process is assumed to be consisted of multiple steps including chemical interactions such as dissociation of chemical bonds and transport of slackened trace elements from solid phase to the leachant. Once the ions of the trace elements reach to the particle surface from interior or become loose
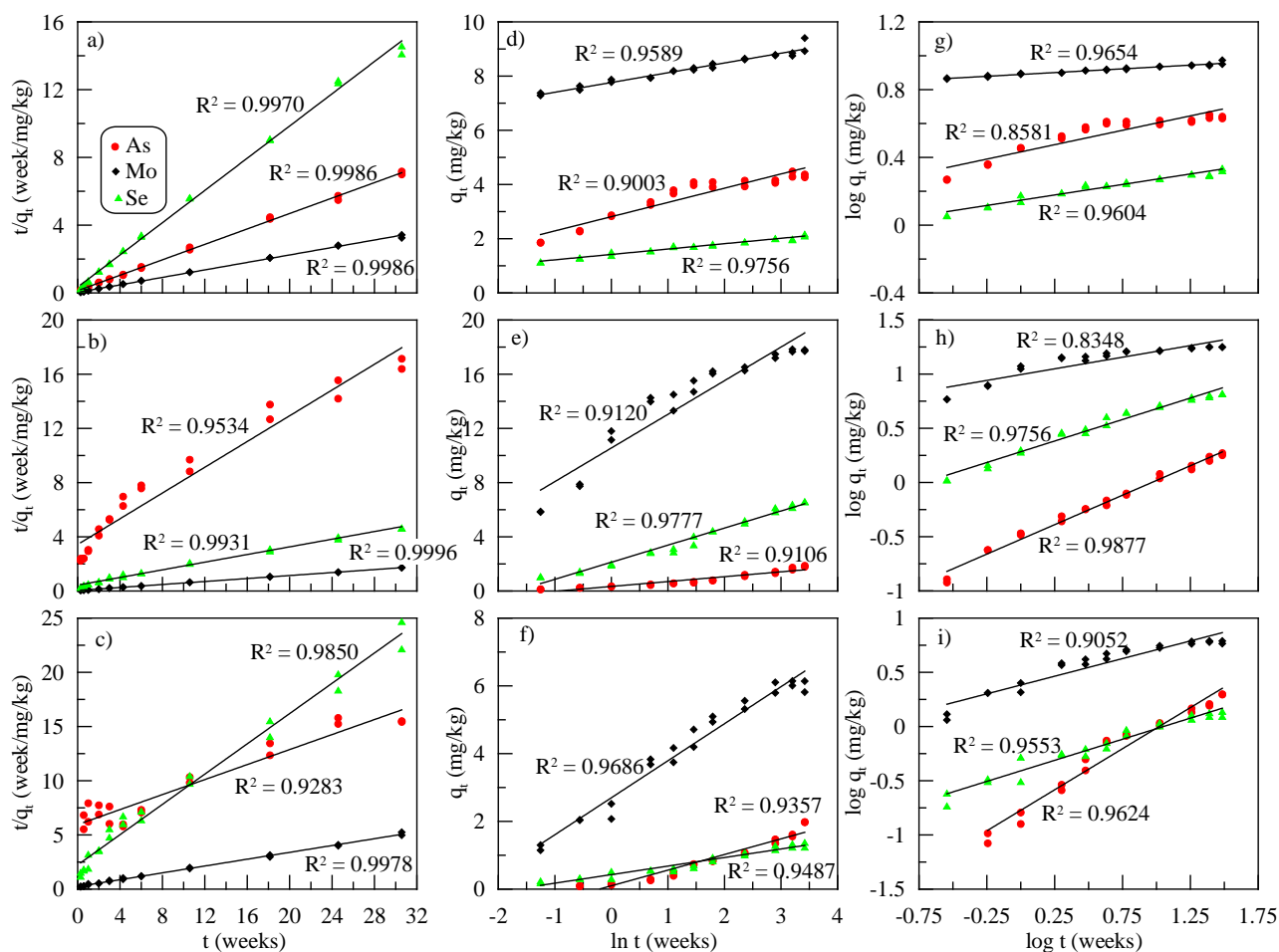
Figure 4. Kinetic leaching modeling using pseudo-second order (a. HA, b. HB, and c. MA), Elovich (d. HA, e. HB, and f. MA), and power function (g. HA, h. HB, and i. MA) models for batch leaching of As, Mo, and Se from acidic fly ash samples.

at the surface by dissolution of host material, it is assumed that they instantaneously mix with the leachant owing to the consistent agitating environment during experiment. Therefore, the rate limiting leaching kinetics during the experiment is related only to the either gradual dissolution of fly ash particles or diffusional transport from particle interior to the surface. However, in natural environments where a comparable agitating condition is absent, the transport related processes active in the exterior milieu of the particles are also important for rate limiting leaching of trace elements from fly ash. In general, diffusive transport within the solid particles and/or dissolution of particles at the surface, transfer of elements from solid-leachant interface to leachant, and dispersive as well as diffusive transport in the leachant are important rate limiting processes in natural environment.

Similarly, Elovich equation also shows a strong ability to describe the leaching behavior of these trace elements from fly ash samples during batch leaching (**Figure 4**). However, the fits of jar leaching data with Elovich equation for Mo and Se from HB and As and Se from MA are relatively weak (**Table 4**). Nevertheless, this kinetic model fits the jar leaching data for Mo and Se from HB and

As and Se from MA far better than other kinetic equations (e.g., first order and second order kinetic equations). The Elovich equation, which is based on assumption that the adsorption energy increases with surface coverage [23], has been previously also used to describe the kinetics of desorption of oxyanions from soils and soil constituents [27]. In their study, Chein and Clayton (1980) suggested that an increase in α with or without change in β would indicate a relatively rapid reaction [27]. In this perspective, the α values are relatively larger for the same elements during long-term leaching experiments, and could indicate a relatively faster leaching than during jar leaching experiments [27]. However, these two experiments were conducted at different solid: liquid ratio and different time scales, and could not be directly comparable. Furthermore, such inference drawn from nature of α and β variation could be questionable at different situations [22].

The power-function equation is also able to describe most of the leaching data for both leaching schemes with few exceptions (Figure 3 and Figure 4; Table 5). Particularly, the model fits for Mo (from HA) and As and Se (from MA) are relatively poor for jar leaching data. Similarly, this model resulted in weak fits for As leached from HA and Se leached from HB (Table 5).

The good agreement of experimental data with the model equations indicate the presence of one or multiple rate limiting mechanisms controlling the release of trace elements from fly ash samples [21] [25]. As indicated above, one of such potential mechanism could be dissolution of glassy fly ash particles where these trace elements are disseminated. Similarly, another likely mechanism for rate-limiting process is migration of these elements from particle interior to the surface. A similar diffusion controlled rate limiting kinetics has been previously reported for late-stage sorption/desorption of phosphate and arsenate to/from ferric hydroxide particles [34] [35] [36]. However, because these fly ash samples are rich in glassy constituents and our previous observation of increasing $SiO_2(aq)$ concentration over time [6], we propose that long-term kinetics of As, Mo, and Se release from these fly ash samples occur largely via dissolution of fly ash particles. During both (jar and long-term) experiments, the leachate pH shows, in general, an increasing trend with time. The proton consumption during dissolution of aluminosilicates is a well-documented phenomena in water-rock interactions [29] [37]. Therefore, the increasing pH with increasing duration of fly ash-leachant interaction is a manifestation of ongoing dissolution of aluminosilicate fly ash particles, and such dissolution is attributed to be the major factor for slow but persistent increase in leachate concentrations of As, Mo, and Se over time.

4. Summary and Conclusions

The leaching tests of three acidic fly ash samples collected from coal-fired power plants in the southeastern United States show the increasing leachate concentrations of As, Mo, and Se with time. The jar leaching experiments show that the leachate concentrations of these elements are relatively low during the early

phase of leaching; however, their concentrations increase with increasing time. Similar leaching trends are observed during long-term leaching experiments.

Kinetic leaching of As, Mo, and Se from acidic fly ash samples can be described by pseudo-second order, Elovich, and power function kinetic equations. Although all three kinetic equations are able to fit experimental data, relatively, pseudo-second order model represents the experimental data strongly than the other two models. The experimental as well as modeling results indicate that the rate limiting release of As, Mo, and Se from fly ash samples is largely controlled by dissolution of fly ash particles. Such leaching behavior could make fly ash a persistent source of contaminates in the environment should a catastrophic event akin the TVA fly ash spill occur either from operational or old fly ash disposal facility. Therefore, it is desirable to adopt containment as well as treatment plans for fly ash deposited in present/past fly ash disposal facilities.

Acknowledgements

Conflicts of Interest

The authors declare no competing financial interest.

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Supplementary

Table S1. Concentrations of As, Mo, and Se during Jar leaching tests.

ID	Time (hours)	pH	Concentrations (mg/kg)		
			As	Mo	Se
HA	1	7.19	0.00	1.22	0.14
	4	6.83	0.00	3.74	0.47
	8	6.74	0.52	4.70	0.50
	12	6.71	0.79	5.44	0.87
	24	6.85	1.47	6.27	1.49
	36	7.05	2.36	7.12	1.64
	48	7.09	2.74	7.47	1.88
	72	7.12	3.32	7.42	1.87
	96	7.11	3.64	7.18	2.03
	120	7.15	3.97	7.91	2.25
HB	1	4.53	2.30	0.19	0.87
	4	4.86	3.78	0.64	0.90
	8	5.17	4.36	1.05	1.13
	12	5.25	4.65	1.70	1.12
	24	5.76	5.40	3.35	1.38
	36	5.78	5.81	4.82	1.65
	48	5.97	5.76	5.83	1.71
	72	6.01	6.43	7.62	2.13
	96	6.08	5.90	9.07	2.32
	120	6.15	6.25	9.84	2.66
MA	1	4.91	4.02	0.00	0.22
	4	5.25	5.44	0.00	0.26
	8	5.45	5.72	0.20	0.43
	12	5.40	6.02	0.30	0.27
	24	5.68	6.01	0.58	0.39
	36	5.83	6.05	0.84	0.48
	48	5.89	6.20	1.14	0.51
	72	5.99	6.18	1.67	0.58
	96	6.04	6.27	2.05	0.70
	120	6.06	6.46	2.45	0.73

Table S2. Concentrations of As, Mo, and Se during long-term batch leaching tests.

ID	Time (week)	pH	Concentrations (mg/kg)		
			As	Mo	Se
HA	0.29	6.64	1.86	7.38	1.13
	0.29	6.77	1.85	7.28	1.14
	0.57	6.85	2.27	7.49	1.29
	0.57	6.92	2.29	7.63	1.28
	1.00	7.14	2.86	7.87	1.51
	1.00	7.15	2.83	7.78	1.38
	2.00	7.11	3.25	7.93	1.56
	2.00	7.17	3.36	7.94	1.55
	3.00	7.15	3.66	8.19	1.70
	3.00	7.17	3.79	8.18	1.74
	4.29	7.03	3.97	8.30	1.72
	4.29	7.12	4.08	8.23	1.71
	6.00	7.07	4.09	8.45	1.80
	6.00	7.08	3.90	8.31	1.76
	10.57	6.96	4.14	8.61	1.88
	10.57	7.06	3.93	8.65	1.89
	18.14	6.94	4.15	8.76	2.01
	18.14	7.10	4.06	8.78	2.00
	24.57	6.96	4.48	8.75	1.98
	24.57	7.06	4.28	8.85	1.96
	30.57	7.08	4.37	9.41	2.17
	30.57	7.14	4.27	8.93	2.10

ID	Time (week)	pH	Concentrations (mg/kg)		
			As	Mo	Se
HB	0.29	6.21	0.13	5.83	1.06
	0.29	6.12	0.17	5.86	1.06
	0.57	6.35	0.24	7.88	1.46
	0.57	6.33	0.24	7.74	1.36
	1.00	6.57	0.33	11.15	1.90
	1.00	6.55	0.34	11.80	2.00
	2.00	6.62	0.44	13.98	2.84
	2.00	6.64	0.49	14.26	2.91
	3.00	6.68	0.56	13.31	2.88
	3.00	6.68	0.57	14.50	3.13
	4.29	6.76	0.62	14.70	3.40

Continued

4.29	6.83	0.68	15.52	4.05
6.00	6.87	0.72	16.04	4.45
6.00	6.90	0.77	16.22	4.44
10.57	6.84	0.98	16.27	5.01
10.57	6.84	1.09	16.52	5.20
18.14	6.87	1.32	17.19	5.84
18.14	6.96	1.43	17.48	6.15
24.57	6.92	1.73	17.84	6.40
24.57	6.98	1.58	17.66	6.16
30.57	7.11	1.87	17.80	6.59
30.57	7.11	1.78	17.70	6.58

ID	Time (week)	pH	Concentrations (mg/kg)		
			As	Mo	Se
	0.29	6.08	0.00	1.15	0.18
	0.29	6.06	0.00	1.30	0.24
	0.57	6.25	0.08	2.04	0.33
	0.57	6.23	0.10	2.04	0.31
	1.00	6.46	0.13	2.52	0.52
	1.00	6.38	0.16	2.07	0.31
	2.00	6.51	0.29	3.83	0.55
	2.00	6.48	0.26	3.68	0.56
	3.00	6.58	0.39	4.17	0.63
	3.00	6.55	0.50	3.75	0.54
MA	4.29	6.76	0.72	4.71	0.71
	4.29	6.77	0.74	4.20	0.63
	6.00	6.84	0.85	4.93	0.83
	6.00	6.83	0.82	5.10	0.94
	10.57	6.78	1.02	5.31	1.01
	10.57	6.76	1.08	5.56	1.08
	18.14	6.83	1.47	6.10	1.29
	18.14	6.78	1.35	5.79	1.17
	24.57	6.85	1.56	6.01	1.24
	24.57	6.82	1.61	6.14	1.34
	30.57	6.90	1.97	6.14	1.38
	30.57	6.88	1.98	5.82	1.24

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