In Situ Leaching of Trace Elements in a Coal Ash Dump and Time Dependence Laboratory Evaluation†

4 AUTHORS, INCLUDING:

Xun Gong
Huazhong University of Science and Technol…
10 PUBLICATIONS **42** CITATIONS

SEE PROFILE

Yu Qiao
Huazhong University of Science and Technol…
32 PUBLICATIONS **462** CITATIONS

SEE PROFILE

In Situ Leaching of Trace Elements in a Coal Ash Dump and Time Dependence Laboratory Evaluation[†]

Xun Gong, Tao Wu, Yu Qiao, and Minghou Xu*

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

This paper investigates the leaching behavior of trace elements in a typical ash dump in the Guizhou province of western China. The ash samples obtained from a power plant were sieved into three sizes: < 45, 45−71, and > 71 μm. Column leaching tests were performed for the size-classified fly ash samples. The HCl solution of pH 4.5 was used to simulate local precipitation. The flow rate was chosen as 1 mL/min. Leaching time intervals were selected in a range from 15 min to 40 days. The results show that the surrounding soil is strongly affected by the ash dump, and the concentrations of some harmful elements in soil are much higher than the background values. The maximal single element pollution index of the soil sample is 134.81 for Cd. In comparison to the concentrations of trace elements in the upstream water, Cr, Cd, Pb, Zn, and Co are greatly enriched in the downstream water. The pollution of the underground water is mitigated by the use of leakproof film. The column leaching test results show that the concentrations of Pb and Cd fluctuate in short-time column leaching. The concentrations of Cd are kept stable after 16 days in three size-classified fly ash samples. However, the concentrations of Pb increase from 1 day to 40 days in the fly ash with a small particle size but are kept stable after 16 days for large particle size fly ash. In comparison to Cd and Pb, the concentrations of Zn in short-time column leaching increase significantly with relatively small fluctuations.

Introduction

Coal is a major resource in the western region of China. There are nearly 600 billion tons of coal reserves in this area, and 90% of the total high-quality coal in China is distributed in the northwest region. The total annual coal production is 230 million tons in four western provinces, including Inner Mongolia and Guizhou.[1] A large amount of fly ash is generated because of the use of coal. The production of fly ash is approximately 20 million tons every year in the Guizhou province, which lead to the dumping of 14 million tons after comprehensive use.[2] The dumping of ash leads to some environmental problems, e.g., the leaching of heavy metals from the fly ash. Enrichment associated with combustion may concentrate elements, and enriched elements, such as Cd, Cr, Pb, and Zn, are most likely to be leached out from the solid phase. When the fly ash interacts with water, the principal processes affecting the leaching process are dissolution of primary solids and precipitation of secondary solids, redox, sorption, and hydrolysis reactions. The alkaline-earth elements present on particle surfaces will be initially dissolved rapidly and pass into solution but, later, with the increasing pH and element concentration, may reprecipitated to form the

secondary solids that are more stable during the fly ash−water interaction.[3−6] If leached, the trace elements can cause contamination of soil, surface water, and especially, the groundwater, mainly because of their changing form and not easily breaking down into harmless substances. Possible toxic contamination could lead to problems of health, environment, using the land.[7−11]

For a long time, the western region of China has been seriously short of water, which has become a restricting factor to the economic development of this region. At present, the use rate of surface water in western China has reached 70%, which has limited the further development of this region. The total amount of recoverable groundwater reserves reaches 43 billion cubic meters per year. However, the current use rate is only 28%. Many of the western cities gradually increase the exploitation of groundwater resources. However, because many ash dumps are present in those areas, the groundwater resources might be contaminated because of the migration of trace elements. Therefore, it is necessary to investigate the environmental risk impacts of the ash dumps.

Dreesen et al.[7] studied the concentrations of the trace element in the effluent waters at a plant compared to the intake waters. Djinovic et al.[8] studied the *in situ* pollution of

[†] Presented at the 2009 Sino−Australian Symposium on Advanced Coal and Biomass Utilisation Technologies.

*To whom correspondence should be addressed. Telephone: 86-27-87546631. Fax: 86-27-87545526. E-mail: mhxu@hust.edu.cn.

(1) Li, X. Y.; Jing, X. L.; Li, G. H. *Coal Geol. China* **2005**, *17*, 5–8.

(2) Jianming, L.; Haitao, L.; Yuan, L.; Zhijian, S. *Fly Ash Compr. Util.* **2008**, *3*, 44–46.

(3) Eary, L. E.; Rai, D.; Mattigod, S. V.; Ainsworth, C. C. *J. Environ. Qual.* **1990**, *19*, 202–216.

(4) Mattigod, S. V.; Rai, D.; Eary, L. E.; Ainsworth, C. C. *J. Environ. Qual.* **1990**, *19*, 188–201.

(5) Roy, W. R.; Griffin, R. A.; Dickerson, D. R.; Schuller, R. M. *Environ. Sci. Technol.* **1984**, *18*, 734–743.

(6) Jankowski, J.; Ward, C. R.; French, D.; Groves, S. *Fuel* **2006**, *85*, 243–256.

(7) Dreesen, D. R.; Gladney, E. S.; Owens, J. W.; Perkins, B. L.; Wienke, C. L. *Environ. Sci. Technol.* **1977**, *11*, 1017–1019.

(8) Djinovic, J. M.; Popovic, A. R. *Fuel* **2007**, *86*, 218–226.

(9) Baba, A. *Global NEST* **2000**, *2*, 51–58.

(10) Baba, A. *Water, Air, Soil Pollut.* **2003**, *144*, 3–21.

(11) Moufti, A.; Mountadar, M. *Water Qual. Res. J. Can.* **2004**, *39*, 113–121.

trace elements from ash dumps in Serbia. However, they ignored the influence of the trace elements on the surrounding soil, which is the main intermediate medium. Previous studies[8,12,13] have focused on the influence of trace elements on water bodies. Laboratory evaluation studies on trace metal mobility in fly ash were usually performed by leaching experiments, e.g., batch leaching and column leaching experiments. Batch leaching[6,14−18] was commonly used in previous studies, but few studies on column leaching[19−23] were reported, although column leaching is closer to simulate a real landfill situation. The actual final leachability data can be obtained by a long-term leaching experiment in the laboratory,[24] but it is difficult to study the process of equilibrium for the leaching of trace elements during this time. More importantly, no work has been reported on relating column leaching and *in situ* leaching for trace elements.

This study aims to understand the leaching characteristics of trace elements in an ash dump. The *in situ* influence of the coal ash dump on the surrounding soil and water was first studied in a typical landfill of a coal-fired power plant in the Guizhou province. Then, laboratory experiments were performed to investigate the leachability of trace elements in the fly ash using a column leaching system. When the *in situ* leaching and column leaching were related, the influence of the ash dump on its neighboring environment could be better understood.

Sampling and Testing Process

Sampling in the Power Plant. The site of the sampling plant is in the northwest of the Guizhou province. There are four 300 MW units of burning local anthracite coal in the plant. Pneumatic conveying is taken for dry storage of the fly ash. All ash and slag are transported to the ash dump near the power plant, shown in Figure 1. The ash dump covers an area of 41.20 ha and is located at the southeast of the plant. The dump was designed for landfill after 7 years of service and has been used for 2 years. The geomorphic form of the site is gully erosion landform.

The schematic diagram of sampling is shown in Figure 1. The sampling points A1−A5 are in the ash dump. Each sampling point is a mixture of five samples distributed around the center of the sampling point (1 m radius). The depth of sampling is 15 cm under the surface. The points A6 and A7 are in the ash storehouse for storing the fly ash before transported to the ash dump by trucks. About 10 kg of fly ash was collected in the ash storehouse for the leaching test. The points A8 and A9 were
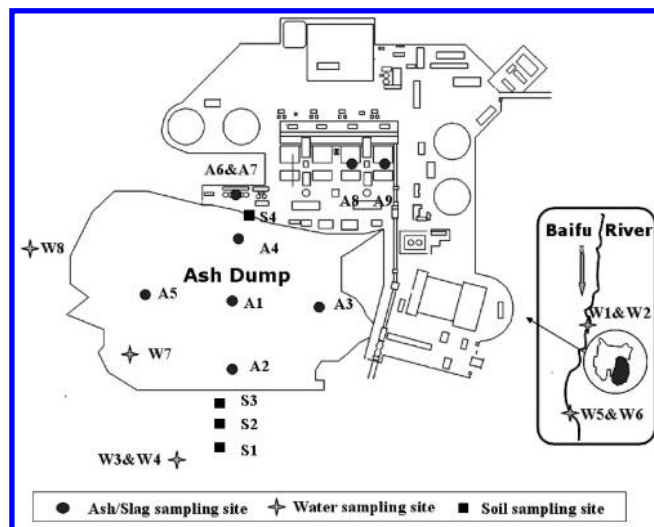
(12) Kanungo, S. B.; Mohapatra, R. *J. Environ. Qual.* **2000**, *29*, 188–196.

(13) Azzaoui, S.; Hanbali, E.; Leblanc, M. *Water Qual. Res. J. Can.* **2002**, *37*, 773–784.

(14) Seferinoglu, M.; Paul, M.; Sandstrom, A.; Koker, A.; Toprak, S.; Paul, J. *Fuel* **2003**, *82*, 1721–1734.

(15) Kim, A. G.; Hesbach, P. *Fuel* **2009**, *88*, 926–937.

(16) Ward, C. R.; French, D.; Jankowski, J. 21st Annual International Pittsburgh Coal Conference, Osaka, Japan, 2004; p 326.

(17) Theis, T. L.; Wirth, J. L. *Environ. Sci. Technol.* **1977**, *11*, 1096–1100.

(18) Talbot, R. W.; Anderson, M. A.; Andren, A. W. *Environ. Sci. Technol.* **1978**, *12*, 1056–1062.

(19) Mahmoudkhani, M.; Wilewska-Bien, M.; Steenari, B.; Theliander, H. *Waste Manage.* **2008**, *28*, 133–141.

(20) Li, L. Y.; Ohtsubo, M.; Higashi, T.; Yamaoka, S.; Morishita, T. *Waste Manage.* **2007**, *27*, 932–945.

(21) Benito, Y.; Ruiz, M.; Cosmen, P.; Merino, J. L. *Chem. Eng. J.* **2001**, *84*, 167–171.

(22) Querol, X.; Umana, J. C.; Alastuey, A.; Ayora, C.; Lopez-Soler, A.; Plana, F. *Fuel* **2001**, *80*, 801–813.

(23) Kim, A. G.; Kazonich, G.; Dahlberg, M. *Environ. Sci. Technol.* **2003**, *37*, 4507–4511.

(24) Dudas, M. J. *Environ. Sci. Technol.* **1981**, *15*, 840–843.

Figure 1. Schematic map and sampling points in the studied area.

generated by sampling the slag at the bottom of the boiler. The sampling points W1 and W2 are in the water from the Baifu River upstream from the ash dump. The distance between the sampling points of upstream water and the ash dump is approximately 2 km. The location of upstream water sampling is just at the recycled water intake of the sampling power plant on the river. The points W5 and W6 are in the downstream of the Baifu River. The location of downstream water sampling is approximately 15 km away from the ash dump subject to the limitation of landform in the downstream area. There are no other inflows flowing into the river between the sampling points and the ash dump. The sampling points are near the center of the river, 20−30 cm below the water surface. W3 and W4 were sampled in the water wells in the village nearby the ash dump. The point W7 was sampled at the seeper of the ash dump. W8 is the sampling point at the outlet of the drainage. Each sampling point represents a mixture of three samples taking in different times during 20 working days. The volume of each liquid sample is 500 mL. The points S1, S2, and S3 were sampled between the ash dump and the village, with a space of 50 m. The point S4 is at the edge the ash dump. About 500 g of soil was collected in each sampling location. Particularly, the soil and ash samples have been dried by an oven under 105 °C for at least 24 h and then treated with the standard reduction process and sealed in the desiccators before performing analysis and experiment. Liquid samples were immediately acidified using 1 mL of nitrate after the determination of their pH values and electrical conductivity (EC). All glass containers and equipment have been soaked with 6 M HNO_3 for at least 24 h before experiment.

The U.S. EDAX's EAGLE III highlights scanning X-ray fluorescence (XRF) probe instrument and the U.S. Thermoelectric's Tracescan Advantage inductively coupled plasma−atomic emission spectrometer (ICP−AES) were used for elemental analysis. The Italy Milestone's ETHOS E microwave chemical reaction system was used in the digestion process. The SartoriusPB-10 pH meter was used for determination of the pH values of the liquid samples.

Column Leaching Process. The column leaching system is shown in Figure 2. It contains a column for loading the fly ash, a 2 L vitreous container for leachate, a peristaltic pump, and a pHstat apparatus, which can control the pH value of the leaching solution. The ash samples was mechanically sieved into three sizes, i.e., < 45, 45−71, and > 71 μm, and marked as FA1, FA2 and FA3. Column leaching tests were performed for the three fly ash samples, and 66.6 g of each fly ash sample was used in this study. The HCl solution of pH 4.5 is used to simulate the local precipitation. The leaching time is chosen from 15 min to 40 days. A microporous membrane was used to separate the
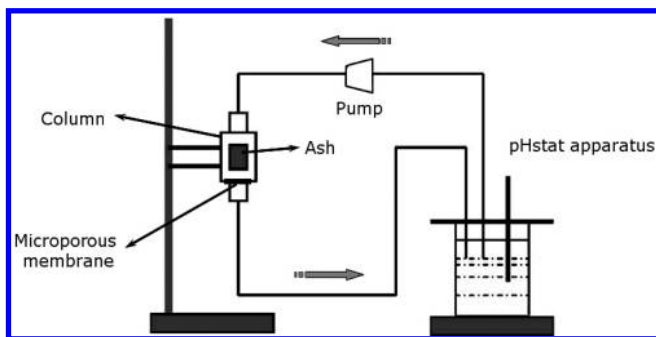
Figure 2. Plan of the column leaching system.

leachate from the fly ash. The flow rate of the pump was controlled at 1 mL/min. The system has operated continuously for 40 days. At each sampling time, 50 mL of leachate was taken out from the container for the ICP−AES analysis and then 50 mL of HCl (pH 4.5) was added into the container. A synchronous leaching blank was used to remove the leachate and other factors in each leaching time. The concentrations of total trace elements in the deionized water used in solutions preparation were less than 1 μg/L. These concentrations were much lower than those in the samples obtained from the leaching test and, therefore, will not affect the results from the leaching tests.

Results and Discussion

***In Situ* Mobility of Trace Elements in the Ash Dump.** The fly ash sampled from the ash dump is used for the study of the mobility of trace elements in the actual condition. The contents of trace elements in the ash samples from the ash dump are showed in Table 1. In comparison to the average contents of the trace elements in the ash from the dump, the contents in the storehouse samples and the slag are showed in Figure 3. The inhomogeneity of the ash from the ash dump is more significant than the ash in the storehouse because of its long-term dumping. These trace elements are typically harmful to the environment. Standard samples were used to ensure the accuracy of the analysis for these trace elements. The results show that the trace metal elements, except for Co, in the slag are significantly smaller than those in other samples. Those data indicate that all of the trace metal elements are mobile in the process of dumping compared to the original contents in the fly ash samples in the storehouse. Generally, the trace metal elements in the slag are relatively stable and much smaller than those in the fly ash. Therefore, this study focuses on the fly ash in the storehouse. To study the *in situ* mobility of different elements, the mobility index is defined as follows:

$$M_i = \frac{C_{i0} - C_{i1}}{C_{i0}} \tag{1}$$

where C_{i0} is the content of the element *i* in the ash sample from the storehouse and C_{i1} is the content in the ash sample from the ash dump. The mobility indexes of some trace elements are shown in Table 2. The results show that the mobility of Cd is higher than that of the other elements, although the absolute amount of Cd is small in these samples. The order of the mobility for those elements is Cd > Zn > Cu > Pb > Cr > Co.

Soil Pollution Index of Trace Elements. The soil pollution index P_i and comprehensive pollution index P_c (Nemerow index) are defined as follows:

$$P_i = \frac{C_i}{S_i} \tag{2}$$

$$P_c = \sqrt{\frac{P_{max}^2 + (\overline{P_i})^2}{2}} \tag{3}$$

In eq 2, C_i is the concentration of the element *i* in the soil sample and S_i is the background concentration of the element *i* in the Guizhou province.[25,26] In eq 3, P_{max} and $\overline{P_i}$ are the maximal and average values of P_i, respectively. The pollution index was divided into five levels by Sutherland et al.:[27] nonpollution ($P < 1$), the first class or slight pollution ($1 < P < 2$), the secondary class or pollution ($2 < P < 5$), the third class or moderate to significant pollution ($5 < P < 20$), the fourth class or strong pollution ($20 < P < 40$), and the fifth class or high pollution ($P > 40$). The results are shown in Table 3. The single pollution indexes of Cd in soils 1−4 are 93.78, 86.57, 105.60, and 134.81, respectively. The single element index of Cd is significantly higher than those for other elements, which is similar to the results of the *in situ* mobility index. This means that the ash dump could improve the enrichment of Cd in the circumambient soil. The concentrations of Cd and Pb in soil 4 are relatively higher because the sampling site of soil 4 is closer to the ash dump. The concentrations of other elements are relatively higher in soil 1 because of the competition functions within the trace elements to the matrix of the soil. Different methods of index calculation lead to different results of evaluation. The average pollution indexes show that the contamination of soils 4 and 1 is more serious. However, the Nemerow indexes show that soils 4 and 3 are polluted more seriously. The Nemerow index takes into account the average and maximal values of the single pollution index and, therefore, is better than the common average index for pollution evaluation.

Water Pollution Analysis. Guizhou is a province that is seriously affected by acid rain. The pH value of precipitation is 4.53, and the sampling sites are in the residential area and the ash dump of the power plant. In the open ash dump, the alkaline matrix and trace elements will be dissolved partially by precipitation. The liquidity of precipitation will lead to the migration of the trace elements to the surrounding water environment. When the shallow level of the water environment is shallower than the depth of the ash dump, the carrying function of interstitial fluid generated by the precipitation will be improved and the harmful elements in the fly ash easily contaminate the underground water and surface water. In the ash dump, a water layer is always found on the surface of the ash unless there is no rain for a long time. The leachate of the precipitation and the fly ash will gradually infiltrate into the surrounding soil or rock and diffuse along with the bottom of the deeper fissures of underground. Although some measures have been taken to prevent the leachate pollution, such as the leakproof film on the bottom of the ash dump, the same process will occur at the side of the ash dump and drainage. Table 4 shows the concentrations of the trace elements in the water circumstance. The fly ash in

(25) Ministry of Environmental Protection (MEP), People's Republic of China. *Background Value of Soil Elements in China*; Environmental Science Press of China: Beijing, People's Republic of China, 1990.
(26) Zhang, J. J.; Yang, S. Y.; Wang, L. *Guizhou Geol.* **2008**, *25*, 292–296.
(27) Sutherland, R. A.; Tack, F. M.; Verloo, G. M. G. *Arch. Environ. Contam. Toxicol.* **2000**, *38*, 428–438.

Table 1. Contents of Trace Elements in the Ash Samples from the Ash Dump (mg/kg)[a]

element	Cr	Cu	Cd	Pb	Zn	Co
ash 1	214.0 ± 3.9	252.0 ± 5.8	22.8 ± 0.6	453.1 ± 21.1	140.4 ± 3.5	136.2 ± 5.7
ash 2	210.0 ± 7.6	208.6 ± 6.9	29.4 ± 0.8	485.2 ± 15.6	125.2 ± 4.7	141.1 ± 5.0
ash 3	204.0 ± 2.6	171.2 ± 8.2	10.2 ± 1.4	427.9 ± 22.8	87.5 ± 3.7	108.9 ± 3.1
ash 4	218.2 ± 5.6	214.2 ± 10.0	49.6 ± 1.4	551.3 ± 14.7	155.3 ± 2.0	117.1 ± 0.5
ash 5	216.4 ± 3.3	135.6 ± 13.4	20.0 ± 1.0	484.6 ± 9.7	121.3 ± 1.3	127.5 ± 3.0

[a] The contents of trace elements in the ash samples are analyzed 3 times. The average values and the standard deviations are showed in the table.
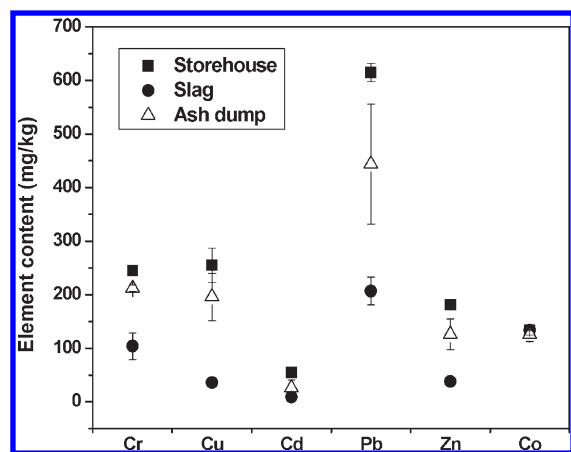

Figure 3. Contents of trace elements in storehouse, slag, and ash dump samples. The contents of the trace elements in the ash dump are the average values of ashes 1−5. The error bars indicate 1 standard deviation.

Table 2. Mobility Index of Trace Elements

element	Cr	Cu	Cd	Pb	Zn	Co
mobility index	0.13	0.23	0.52	0.22	0.30	0.06

this ash dump is alkaline because of the alkaline components in the ash matrix. The alkalescence of the fly ash causes the alkalization of the seeper and drainage. In comparison to the upstream sample, the pH value of the downstream water is higher. The EC value represents the total ionic concentration of the liquid sample. The high EC value of the drainage and seeper shows the function of the alkaline matrix dissolving in the fly ash. From the concentration data of the trace elements in the up- and downstream samples, all trace elements, except for Cu, are enriched in the downstream samples. Zn and Co, which cannot be detected in the upstream samples, exist in the downstream samples. It is noteworthy that the concentration of Cd, Cr, and Pb in the downstream samples is beyond grade III of the Quality Standards for Surface Water Resources. The pollution of the underground water has been mitigated using the leakproof film. Only the concentration of Pb is beyond grade III of the Quality Standards for Ground Water.

Column Leaching Test. Generally, the size of ash particles has an important impact on the ash leaching characteristics, because it can affect the leaching characteristics of the trace element in the surface of the particles. Generally, the ash particles in smaller size have a larger surface. In the process of coal combustion, the trace elements that are gasified at a high temperature coagulate on the surface of the fly ash when the temperature decreases. In the leaching of the fly ash, the trace elements on the surface of the ash particles, which are often combined with the alkaline matrix in ion exchange and acid-soluble state, are easy to leach out. In this study, the fly ash was divided into three fractions to investigate the effects

of the size of ash particles on the leaching characteristics of the trace elements. Actually, the range of the ash size by sieving is inaccurate because of the penetrability and quality of the sieves. To solve the problem, the size analysis has been performed by the British Malvern's MAM5004 laser particle size analyzer. The accumulative particle size distributions of the three ash samples FA1, FA2, and FA3 are shown in Figure 4. The average particle diameters of FA1, FA2, and FA3 are 9.67, 17.38, and 40.99 μm, respectively. The element analysis of the three size-classified original fly ash samples is showed in Table 5. These data show that Si and Al are the dominant elements in these samples. The content of Fe is comparatively high with ordinary fly ash. When the particle size is decreased, the contents of Cd, Co, Cr, Cu, Ni, V, and Zn increase significantly, probably because of their easy enrichments on the surface of the small particles.

The column leaching test has been conducted to understand the leaching characteristics of the trace elements in the fly ash. The results of Cd, Pb, and Zn are shown in this paper because they demonstrate different features when using the *in situ* mobility index. The concentrations of Cd in the short-time (from 15 min to 1 day) and long-time (from 1 to 40 days) column leaching tests are shown in panels a and b of Figure 5, respectively. The short-time column leaching data show that the concentrations of Cd fluctuate in a range of 6.5−8.0 μg/L rather than increase with the leaching time. As shown by Brunori et al.,[30] matrix composition can influence the leachability of Cd. The leachability of Cd is high at low pH levels if Cd is present as cadmium chloride in the chemical matrix of the material. However, cadmium can be present in the compounds with Ca, such as $Ca_xCd-xCO_3$, which has lower solubility. In the column leaching test, the alkalinity of the leachate will fluctuate with the solution and reprecipitation of the Ca compound on the surface of the fly ash. The concentration of Cd in the leachate is influenced by the secondary precipitation, such as $Ca_xCd-xCO_3$.[19] In the long-time column leaching test, the concentrations of Cd increase significantly from 1 to 16 days and are kept stable after 16 days. It is also found that the leaching of Cd decreases with the increase of the particle size, because Cd is more enriched in the smaller ash particles. The final concentration of Cd in FA1 is 10.9 μg/L, which is higher than FA3 (10.0 μg/L) and FA2 (9.3 μg/L).

The concentrations of Pb in the short- and long-time column leaching are shown in panels a and b of Figure 6, respectively. The results show the similar trends as those of Cd. The short-time column leaching data show that the concentrations of Pb are remarkably higher than Cd in the leachate, because the concentration of Pb in the fly ash is

(28) Ministry of Water Resources (MWR), People's Republic of China, 1994; SL 63-94.

(29) Guobiao (GB), National Standards of the People's Republic of China, 1993; GB/T 14848-93.

(30) Brunori, C.; Balzamo, S.; Morabito, R. *J. Anal. Chem.* **2001**, *6*, 843–848.

Table 3. Pollution Index of Trace Elements and Nemerow Comprehensive Pollution Index

| sample number | element pollution index | | | | | | $\overline{P_i}$ | P_c |
	Cr	Cu	Cd	Pb	Zn	Co		
soil 1	6.27 ± 0.12	3.24 ± 0.10	93.78 ± 2.12	7.63 ± 0.25	4.61 ± 0.55	3.27 ± 0.12	20	96
soil 2	1.29 ± 0.03	3.19 ± 0.08	86.57 ± 4.04	8.85 ± 0.21	0.66 ± 0.02	3.84 ± 0.10	17	88
soil 3	0.61 ± 0.03	1.23 ± 0.02	105.60 ± 1.94	6.46 ± 0.27	0.30 ± 0.02	2.60 ± 0.10	19	107
soil 4	1.09 ± 0.03	1.75 ± 0.05	134.81 ± 4.47	7.77 ± 0.22	0.56 ± 0.02	2.97 ± 0.30	25	137

Table 4. Trace Elements Concentration in the Water Circumstance (μg/L)

	pH	EC	Cr	Cu	Cd	Pb	Zn	Co
upstream	7.66	405.5	42.7 ± 0.4	43.1 ± 0.9	3.1 ± 0.2	55.1 ± 4.9	nd	nd
downstream	8.39	274.5	70.1 ± 0.3	18.5 ± 5.0	5.9 ± 0.1	81.1 ± 2.1	20.7 ± 0.6	6.1 ± 1.2
underground	7.49	168.1	41.3 ± 0.6	25.6 ± 3.6	5.3 ± 0.3	72.5 ± 5.4	3.7 ± 0.9	nd
seeper	8.30	410.0	77.8 ± 0.7	48.2 ± 0.4	6.0 ± 0.3	82.0 ± 4.8	29.4 ± 0.2	6.5 ± 0.8
drainage	8.04	761.0	84.8 ± 4.2	55.9 ± 3.0	56.0 ± 4.1	629.8 ± 51.5	95.4 ± 3.5	19.7 ± 2.9
precipitation	4.53	33.2						
QS1[a]			50	100	5	50		
QS2[b]			50	1000	10	50	1000	50

[a] QS1 = grade in Quality Standards for Surface Water Resources (SL 63-94).[28] [b] QS2 = grade in Quality Standards for Ground Water (GB/T 14848-93).[29]
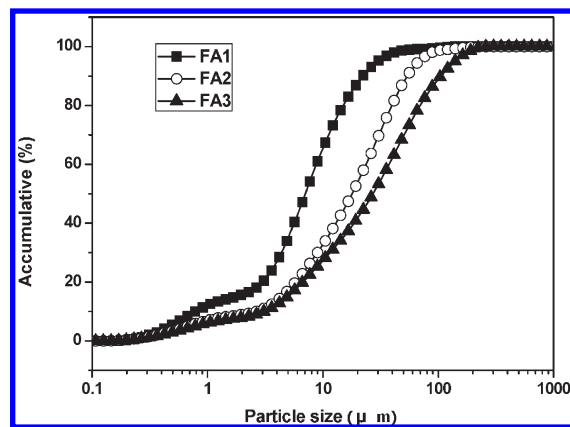

Figure 4. Particle size accumulative distribution. Note that the scale of the *x* axis is not linear.

Table 5. Element Analysis of Size-Classified Original Fly Ash (mg/kg)

element	FA1	FA2	FA3	element	FA1	FA2	FA3
Al	274450	246800	268400	Mg	12300	14000	7550
Ca	48300	39500	55450	Na	21150	17350	17200
Cd	15	12	11	Ni	1305	1193	1006
Co	142	130	111	Pb	270	206	254
Cr	148	137	135	S	8800	8500	14750
Cu	159	149	136	Si	453102	476238	435413
Fe	150350	166900	171950	V	1027	779	637
K	28250	27900	26850	Zn	232	206	147

higher than that of Cd. The concentrations of Pb also fluctuate in a range of 65−85 μg/L in the short-time column leaching test. With the dissolution of the alkaline matrix in the surface of the ash particles, some primary dissolved trace elements can generate secondary precipitation. The formation of the secondary minerals will lead to the temporary decrease of the concentration of Pb before the further dissolving reaction with the acid leachate. While in the long-time column leaching, the concentrations of Pb increase from 1 to 40 days in FA1 and FA2 but are kept relative stable after 16 days in FA3. The final concentration of Pb in the leachate of FA1 is 121.8 μg/L, which is higher than that in FA2 (117.0 μg/L) and FA3 (110.0 μg/L).

The concentrations of Zn in the short- and long-time column leaching are shown in Figure 7. In comparison to Cd and Pb, the concentrations of Zn in the short-time column leaching increase significantly with relatively small fluctuations. Few secondary precipitations are generated for Zn. In the long-time column leaching, the concentrations of Zn increase rapidly from 1 to 6 days and the rate of the concentrations slows down gradually after 6 days. In comparison to the fly ash samples of different sizes, the final concentration of Zn in FA3 is 114.6 μg/L, which is higher than that for FA1 (106.5 μg/L) and FA2 (108.5 μg/L). Although the element analysis shows that Zn is enriched in smaller particles, the concentrations of the leachate are affected by the existing species of Zn. The results of Zn are different from Cd because more Zn exists as spinel (such as $ZnFe_2O_4$ and $ZnAl_2O_4$), which is a stable phase in the FA1, and more Zn exists as sphalerite, which is formed by oxidation of organic matrices during combustion in FA3.[31,32]

To compare the column leaching with the *in situ* leaching, L_i is defined as the leachability of elements in the column leaching test

$$L_i = \frac{VC_i 10^{-6}}{mw_i} \qquad (4)$$

where *V* is the volume of leachate in milliliters, C_i is the concentration in mg/L of element *i* in the leachate, *m* is the quality of the original fly ash in grams, and w_i is the mass concentration of element *i* in the original fly ash. The final leachabilities of Cd are 21.8, 23.3, and 27.3 mg/g for FA1, FA2, and FA3, respectively. The final leachabilities of Zn are 13.8, 15.8, and 23.4 mg/g for FA1, FA2, and FA3, respectively. The final leachabilities of Pb are 13.6, 17.6, and 13.0 mg/g for FA1, FA2, and FA3, respectively. L_i is significantly smaller than M_i because the *in situ* leaching time is longer and the leaching process is not carried on within a system of circulation. Although the concentrations of Pb and

(31) Seferinoglu, M.; Paul, M.; Sandstrom, A.; Koker, A.; Toprak, S.; Paul, J. *Fuel* **2003**, *82*, 1721–1734.
(32) Yang, Y.; Xiao, Y.; Wilson, N.; Voncken, J. H. L. *J. Hazard. Mater.* **2009**, *166*, 567–575.
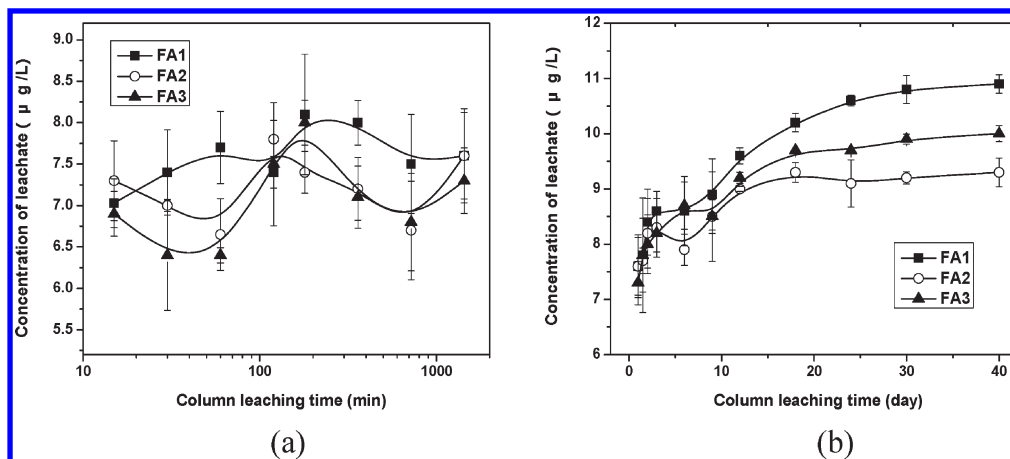
Figure 5. Concentration of Cd in (a) short- and (b) long-time column leaching. The concentrations in the leachate at each time point are the average values by analyzing 3 times. The error bars indicate 1 standard deviation.
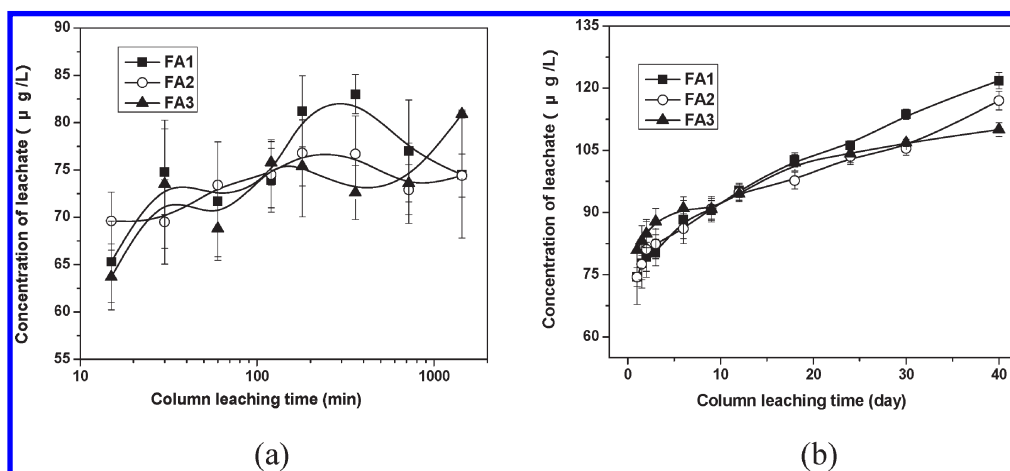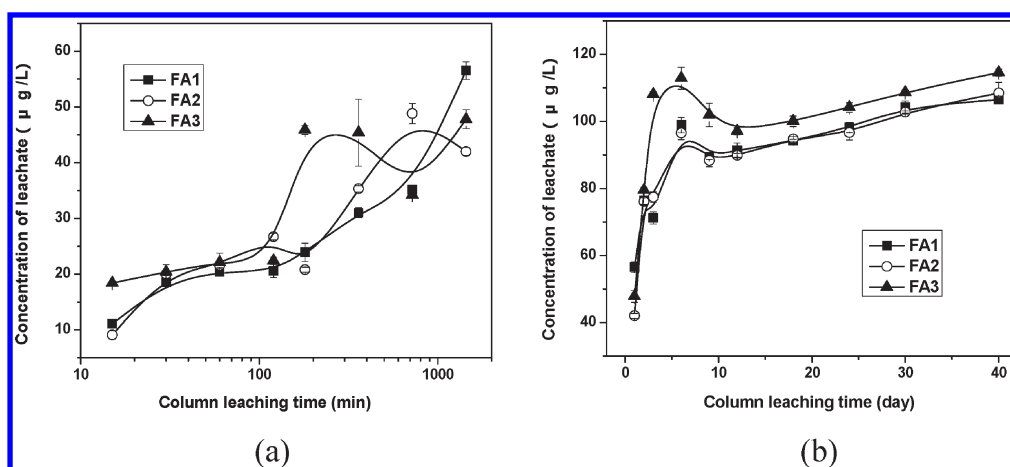

Figure 6. Concentration of Pb in (a) short- and (b) long-time column leaching. The concentrations in the leachate at each time point are the average values by analyzing 3 times. The error bars indicate 1 standard deviation.

Figure 7. Concentration of Zn in (a) short- and (b) long-time column leaching. The concentrations in the leachate at each time points are the average values by analyzing 3 times. The error bars indicate 1 standard deviation.

Zn are remarkably higher than Cd in the leachate, their leachabilities are relatively small. The results agree with those obtained using the *in situ* mobility index. The order of the *in situ* mobility for these elements is Cd > Zn > Pb. From the column leaching test, the dynamic leachabilities of different elements can be obtained. The pHstat apparatus, which controls the pH value of the leachate at 4.5, makes the leaching process similar to the function of the local acid precipitation. In comparison to the static batch leaching, the column leaching of the fly ash is more similar to the situation of the ash dump. Especially, the secondary precipitation reaction will occur in the column leaching. The risk of different trace elements in the ash dump can be forecasted by the column leaching test.

Conclusions

In this study, the *in situ* influences of an ash dump on surrounding soil, surface, and groundwater have been investigated. The column leaching tests on the size-classified fly ash samples have been performed to evaluate the dynamic leachabilities of the trace elements. The following conclusions can be drawn from this study: (1) On the basis of the calculation of the mobility index of the trace elements in the storehouse samples and ash dump samples in this study, the order of the *in situ* trace elements mobility in the ash dump is Cd > Zn > Cu > Pb > Cr > Co. (2) The ash dump has a significant influence on the surrounding soil. The closer soil samples have higher comprehensive pollution indexes. The single pollution index of Cd in some soil samples is even larger than 100. (3)

The concentrations of Pb and Cd fluctuate in the short-time column leaching. The concentrations of Cd are kept stable after 16 days for all three size-classified fly ash samples. However, the concentrations of Pb increase from 1 to 40 days for FA1 and FA2 but are kept stable after 16 days for FA3. In comparison to Cd and Pb, the concentrations of Zn in the short-time column leaching increase significantly with relatively small fluctuations because of few secondary precipitations of Zn.