Characterization of Arsenic Emissions from a Coal-Fired Power Plant

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An emissions study for arsenic was conducted at a 300-MW coal-fired plant that was equipped with an electrostatic precipitator (ESP). The input and output streams, such as coal, slag, ESP ash, and flue gas that contained the post-ESP particulates, were collected. Gaseous arsenic was sampled using United States Environmental Protection Agency (USEPA) Method 29, and the arsenic concentrations in the samples were measured using inductively coupled plasma−atomic emission spectrometry. The mass balance recovery of arsenic estimated in this study was 87.2%. The arsenic concentration in the stack gas was 2.5 μg/Nm^3. Approximately 0.53% of the coal-derived arsenic was incorporated into slag, 84.6% of the arsenic was found on the fly ash that was collected by the ESPs, and 2.16% was found in the vapor phase. The relationship between arsenic concentration and ash particle size was also assessed, and arsenic was significantly concentrated in the small-sized particles. The modes of occurrence of arsenic in ash samples were studied using a modified sequential chemical extraction method. The extractable fraction was 13.78%−25.27% of the total arsenic in the fly ash particles, from the four ESP hopper samples. The arsenic concentrations found in the different extraction fractions were as follows: 74.73%−86.22% in the residue; 11%−19% in carbonate-bound, surface oxide-bound ions; 2.7%−6.0% in readily extractable ions; and 0.076−0.27% in water-extractable form. There were no appreciable differences in the arsenic solubility fractions between the different particle sizes of fly ash.

1. Introduction

Arsenic has become an increasingly important environmental concern, because of its potential carcinogenic properties.[1] Both natural and anthropogenic arsenic sources pose threats to human health and global, agricultural, and social sustainability.[2] Although arsenic is present in low concentrations in coal (on the level of parts per million (ppm))—the geometric mean of arsenic in China is 4.26 ppm[3]—the large volume of coal consumed makes coal combustion one major anthropogenic source of arsenic in the environment. Coal combustion has been suggested to account for 2%−5% of the total arsenic emissions from anthropogenic sources globally.[4]

Arsenic in coal occurs in two different forms, which vary depending upon the rank of the coal. In bituminous coals, arsenic occurs in the mineral pyrite, where it substitutes for sulfur in the pyrite structure. In lower-rank coals, arsenic occurs as part of an oxygenated complex.[5] Under coal combustion flame conditions, both forms of arsenic can vaporize in the hot portions of the combustor.[6,7] It then may undergo several additional transformation processes as the post-combustion gases cool. These processes include persistence as a vapor throughout the combustor and the air pollution control device, heterogeneous condensation on the surface of existing fly ash particles, dissolution in the alumino-silicate ash particles to form highly nonideal solution, heterogeneous chemical reaction with compounds on the surface of existing fly ash particles,[8] and, ultimately, partition between the vapor phase and particulate fly ash. Many bench studies have reported that this partitioning process leads to the enrichment of arsenic in the smallest particles.[9] Particles with diameters of ∼0.5 μm are collected with the least efficiency in particulate collection devices such as electrostatic precipitators (ESPs) and baghouses,[10] which may increase the deposition of submicrometer-sized particles in the downwind environment and subsequent migration into the water table.[11]

To understand the fate of this element in modern coal combustion, investigations have been conducted and are

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**Table 1. Proximate and Ultimate Analysis of Coal Sample**

Proximate Analysis (wt %, as received)				Ultimate Analysis (wt %, daf)				
moisture	volatile matter, VM	ash	fixed carbon, FC	C	H	N	S	O
0.28	12.97	29.75	56	57.30	3.679	0.737	1.969	6.585

now underway in China. In this study, we investigated the characterization of arsenic emissions in a 300-MW coal-fired plant that was equipped with ESPs. The objectives of this study were (i) to examine the arsenic concentration in stack emissions, (ii) to calculate the arsenic overall mass balances and relative distribution in the power plant, and (iii) to gain insight into the environmental mobility of fly ash particle deposition.

2. Experimental Section

2.1. Sampling. This study was performed in a 300-MW pulverized-coal-fired power station, which has a tangentially fired boiler and a WR direct-flow burner (manufactured by CE Company). The power plant does not use staged combustion to control the nitrogen oxides (NO_x). Normal coal consumption is ~136 tons/h during full load operation of the power plant. During the course of experiment, coal consumption was ~78 tons/h at a load of 180 MW. The fraction of coal particles >88 μm in size was 11%−15%. The same type of coal was burned for 5−6 days, including the pre-sampling and sampling to provide a stable environment. The coal data are shown in Table 1. The ash produced by the boilers is comprised of ~12% slag and ~88% fly ash. The cleaning equipment used for the flue gases include electrostatic precipitators (ESPs), which have an average removal efficiency of ~99.6%. Four electrically separated zones are installed in the direction of the flue gas flow; each zone has its own hopper. Coal samples were composites from grab samples taken at 15-min intervals during the flue gas sampling. Grab samples of slag were synchronized with hopper fly ash sampling. Fly ash and flue gas sampling sites are shown in Figure 1. The flue gas streams were sampled at the exit of the ESP, using United States Environmental Protection Agency (USEPA) Method 29. EF-1 is indicated for ash collected in hopper 1, EF-2 for ash collected in hopper 2, etc. The ash carried away with the flue gases out of the ESP will be termed particulate fly ash (PFA) in this paper. Figure 2 shows the arrangement of the sampling system used. The flue gas was sampled isokinetically, using a heated probe. Particulate matter was collected on a quartz fiber filter, and the vapor-phase samples were absorbed in an impinger train. Four chilled impingers were connected in series with leak-free ground glass fittings. The first was empty and was used as a moisture trap. The second and third impingers, which contained 100 mL of 5% HNO_3/10% H_2O_2, absorbed and retained elemental arsenic in the gaseous phase. The fourth impinger contained ~200−300 g of preweighed silica gel, to determine the moisture gain and prevent moisture condensation in the pump and the metering device. The flue gas temperature at this point was ~150 °C. Because of the very low concentration of arsenic in the flue gas, the sampling times were 1.5 h.

2.2. Analytical Methods. The concentration of major elements in the coal and fly ash were determined by inductively coupled plasma−atomic emission spectroscopy (ICP−AES). The analyses of arsenic in the coal, coal fly ash, slag, absorbent solution, and leachates were performed using hydride generation inductively coupled plasma−atomic emission spectrometry (HG−ICP−AES). The validity of the determination of the coal ash, slag, absorbent solution, and leachates contents was ensured by triplicate analyses and standard
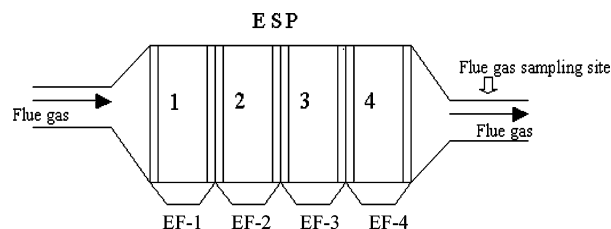
Figure 1. Schematic diagram of the sampling sites.
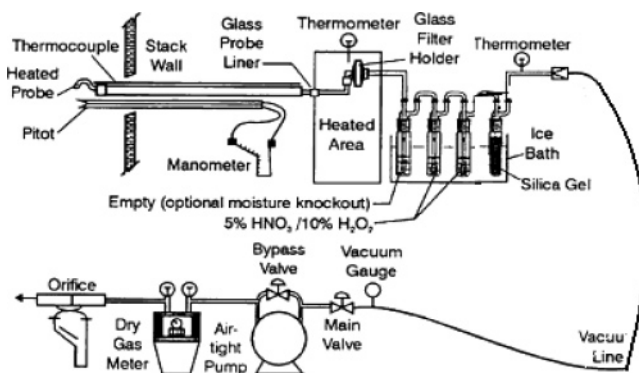
Figure 2. Arrangement of USEPA Method 29 for stack sampling.

additions methods. Certified reference materials GBW08401 fly ash (from the Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences) were also analyzed, as an independent check.

2.2.1. Sample Recovery of Particulate Fly Ash. At the end of a sampling period, the probe should be allowed to cool prior to sample recovery. Carefully remove the filter from the filter holder and place it in its labeled Petri dish container. Particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder should be quantitatively recovered by washing these components with a total of 100 mL of acetone, desiccating the filter and filter catch without added heat, and weighing to a constant weight.

2.2.2. Sample Recovery of Arsenic in Impingers. The liquid in the first three impingers was measured to within 0.5 mL using a graduated cylinder, and then the volume was recorded. Each of the impingers, the filter support, the back half of the filter housing, and the connecting glassware were all cleaned by rinsing with 100 mL of 0.1 N HNO_3 thoroughly. The pH of the sample solution was verified to be 2 or lower. Water was used to rinse the sample solution into a beaker, and then the beaker was covered with a ribbed watchglass. The volume of sample solution was reduced to ~20 mL by heating the solution on a hot plate at temperatures just below boiling. Thirty milliliters of 50% HNO_3 then were added, and the sample was heated for 30 min on a hot plate to just below boiling. Ten milliliters of 3% H_2O_2 were added, and the sample was heated for 10 more minutes. Hot water (50 mL) was added, and the sample was then heated for an additional 20 min. The sample was then cooled, filtered, and diluted to 100 mL with water, to determine the arsenic concentration, using HG−ICP−AES.

The particle size distribution of the as-received ash was determined to be in the range of 0.05−900 μm, using laser diffraction (MNM5004, Malvern, U.K.). Because of the low particulate loadings, it is difficult to sample enough particulate fly ash (PFA) that is carried away with the flue gases out of the ESP for analysis; only four hopper fly ashes were assessed.

2.3. Sequential Extraction Experiment. To gain insight into the environmental impact of fly ash deposition in soil downwind of coal-fired combustors or fly ash disposal sites, the leaching sequence used in this study was a modification

Table 2. Concentration of Major Components and Loss on Ignition (LOI) of Fly Ash

	Concentration (wt %)								LOI (wt %)
	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	K$_2$O	MgO	Na$_2$O	TiO$_2$	
coal	54.92	26.15	8.64	6.44	1.08	0.82	0.08	1.07	
EF-1	57.91	26.79	5.74	5.37	1.23	1.02	0.063	1.17	2.79
EF-2	51.56	31.03	8.42	5.84	1.24	0.99	0.076	1.33	3.57
EF-3	56.81	28.47	5.02	5.31	1.37	1.09	0.062	1.47	3.28
EF-4	58.52	26.01	5.87	5.39	1.12	0.78	0.063	1.44	3.85
PFA[a]	59.31	25.7	4.17	5.27	1.77	1.46	0.058	1.39	2.01

[a] Particulate fly ash.

Table 3. Particle Size Analysis of Fly Ash

sampling site	Content (%)				D(4,3)[a] (μm)
	10−30 μm	<10 μm	<2.5 μm	<1.0 μm	
EF-1	38.6	17.3	2.0	0.8	35.49
EF-2	33.8	58.7	12.6	4.0	11.97
EF-3	6.2	93.8	38.8	11.2	4.30
EF-4	3.2	96.9	41.7	11.7	3.84

[a] D(4,3) represents the bulk particle size obtained using the volume average method.

of the leaching sequence used by Tessler.[12] The leaching sequence consisted of four main extraction steps:

(1) Water-solubles. Samples (1 ± 0.001 g) were accurately weighed and mixed with 15 mL of deionized water in 50-mL polyethylene bottles. The bottles were shaken for 15 h in an auto-shaking apparatus at room temperature. The supernatants were decanted and analyzed for arsenic.

(2) Exchangeable ions. The remaining solid was mixed with 15 mL of ammonium acetate (NH$_4$AC) and shaken for 15 h. Buffer solution was added to bring the pH to 7. The pH was checked every hour until two consecutive pH readings were essentially the same. The supernatants were decanted and analyzed for arsenic.

(3) Carbonate-bound, surface oxide-bound ions. The remaining solid was mixed with 15 mL NH$_4$AC and shaken for 15 h. Buffer solution was added to bring the pH to 5. The pH was checked every hour until two consecutive pH readings were essentially the same. The supernatants were decanted and analyzed for arsenic.

(4) Residue. The remaining solid was added to 10 mL of aqua regia, covered with a watchglass, and heated at 95−98 °C for a half hour, uncovered. The sample then was vaporized to ~2 mL and heated for 5−10 min; 6 mL of hydrochloric acid (1:1) was added, and the sample was cooled and diluted to a volume of 50 mL with reagent water. Duplicate samples were processed using the aforementioned sequence.

3. Results and Discussion

3.1. Arsenic Distribution in the Combustion Product. The concentration of major elements and the loss on ignition (LOI) of fly ash is shown in Table 2. The particle size distribution analysis of the fly ash from four ESP fields is shown in Table 3 and Figure 3. The particle size distribution at sites EF-1, EF-2, EF-3, and EF-4 is 0.31−140.58 μm, 0.09−56.23 μm, 0.09−22.49 μm, and 0.09−14.22 μm, respectively. When going from EF-1 to EF-4, the <10-μm size fraction (the "respirable" particles) increases from 17.26% to 96.85%, the <2.5-μm size fraction increases from 2.0% to 41.7%, and the bulk particle size D(4,3) decreases from 35.49 μm to 3.84 μm. Therefore, when going from hopper 1 to hopper 4, the particle size decreases. It could also be supposed

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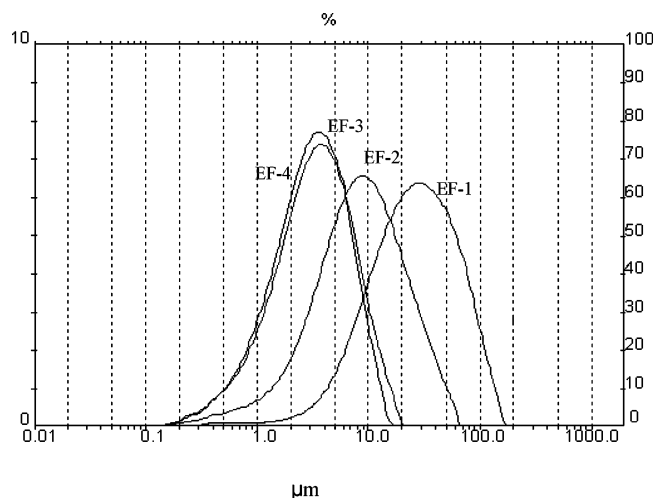
Figure 3. Size distribution of fly ash.

Table 4. Concentration and Relative Enrichment Factor (RE) of Arsenic in Coal and Coal Ashes (for *n* = 3)

	concentration (μg/g)	RE
coal	3.60	
EF-1	6.03	0.50
EF-2	25.6	2.12
EF-3	37.7	3.11
EF-4	45.6	3.79
PFA	66.9	5.53
slag	0.54	0.045

that the particle size of the PFA is finer than that of the ash collected in hopper 4, in which all the total sample particles are <10 μm in size.

The relationship between arsenic concentration and ash particle size is an important factor in regard to determining component behavior. The term "relative enrichments" was introduced to describe the observed behavior properly.[13] The relative enrichment factor (RE) is defined as

$$RE = \left(\frac{\text{element concentration in ash}}{\text{element concentration in coal}}\right) \times \left(\frac{\text{ash content in coal (\%)}}{100}\right)$$

Table 4 shows the concentration and RE of arsenic in the coal and coal ashes. Arsenic is significantly concentrated in the smaller particles.

In the finest particles (PFA), RE = 5.53, and for the coarsest particles, RE = 0.5. The preferential concentration on finer fly ash particles has been frequently observed.[14,15] There are two views that explain these phenomena. Quann and Sarofim[14] suggested that the volatilization of arsenic was followed by condensation on the total available surface area, which is larger in the small particles. Seams et al.[15] reported that the calcium present in fly ash was the probable cause of a solid−gas surface reaction transformation mechanism

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(15) Seams, W. S.; Wendt, J. O. L. *Fuel Process. Technol.* **2000**, *63*, 179−196.

Table 5. Comparison of Arsenic Concentration after Desorption

	Arsenic Concentration (μg/g)	
sample	before desorption	after desorption
EF-1	6.03	4.81
EF-2	25.6	18.3
EF-3	37.7	36.6
EF-4	45.6	44.9
PFA	66.9	65.5

Table 6. Mass Balance of Arsenic between the Output and Input Streams in a Coal-Fired Power Plant

stream	result
input	
coal	280.8 g/h
output	
slag	1.5 g/h
EP-1	92.4 g/h
EP-2	98.0 g/h
EP-3	36.1 g/h
EP-4	11.2 g/h
particulate fly ash, PFA	4.4 g/h
flue gas after ESP	1.7 g/h
mass balance	
(input/output)/100	87.3%

that occurred under post-combustion conditions. It is this interaction of fly ash particles with arsenic vapor that contributes to the final partitioning of arsenic. Although it is well-established that fly ash particles do capture arsenic species, the nature of interaction between fly ash particles and arsenic is not well understood.[16,17] To elucidate the mechanism of arsenic and fly ash interaction, Table 5 shows the results of fly ashes vacuumized at 150 °C for 10 h and then absorbed with arsenic-free nitrogen gas, after which point the arsenic concentration in the fly ashes is reanalyzed. As can be observed, the concentration of arsenic decreases for the EF-1 and EF-2 fly ashes after desorption, suggesting that physical adsorption has happened, in some sense. A negligible loss of arsenic is observed for EF-3, EF-4, and the PFA. This irreversible process indicates that physical adsorption is not the mechanism between the fly ash and the arsenic at the post-combustion zone of 150 °C. Further experimentation is needed to study the mechanism of arsenic-fly-ash reaction; later research will address this issue.

3.2. Mass Balance Results. Mass balances for arsenic have been calculated, assuming that the only input is the arsenic content of the combusted coal. Process outputs are hopper fly ash, slag, and in-stack arsenic in the form of particulate and gas species. The quantities of the coal burned during the tests are known, and, from the proximate and ultimate analyses, the total volume of gas produced during the test has been calculated. The quantity of PFA collected on the filter and the total volume of flue gas sampled are known from the sampling experiments. Through determination of the arsenic content in the absorbent solution, the concentration of arsenic in the flue gas is also determined. Manual determination of the total amount of ash deposited in the four electric fields and slag throughout the experiment would be practically impossible. The quantities of fly ash and slag have been estimated mathematically, using the assumption that the ash produced by the boilers is comprised of ~12% slag and ~88% fly ash. The total mass efficiency of the ESP is 99.6%, and each ESP row captures 75% of the ash entering that row (based on the annual figures of the power station). The mass efficiency, from the first electric field to the fourth electric field, for total fly ash is 75% (first electric field), 18.75% (second electric field), 4.68% (third electric field), and 1.17% (fourth electric field). The mass balance results are shown in Table 6. The sampling and analytical techniques are very complex, and the results include the uncertainties. The recovery of arsenic is 87.2%, which is within the accepted boundary of 70%–130%. Although we must

consider the use of range values and standard deviations, we focused on the overall contributions of the flue gas cleaning system in the coal-fired plant to the stack emissions and to the characteristics of the coal residues. Therefore, for arsenic recovery of <100%, an unknown percentage remains. Based on this modification, the percentage of arsenic in the slag, in the fly ash, and in the stack emissions is 0.53%, 84.6%, and 2.16%, respectively. This means that fly ash is effective in capturing arsenic, which is consistent with the results of other researchers.[18] The experimental data show that the arsenic concentration of the flue gas is 2.5 μg/Nm^3, which is below the China Pollution control standard for hazardous waste incineration ([As] + [Ni] = 1 mg/Nm^3). The particulate loading after the ESP is 98 mg/Nm^3. Attention must be given to the enrichment of arsenic in these particulates, which may increase the risk of pollution after emission into the atmosphere.

3.3. Leaching Behavior of Fly Ash. According to the experimental results, most of the arsenic is captured on the fly ashes; therefore, concern should be given to the leaching behavior and possible contamination. Leaching test results are shown in Table 7. Only data from EF-1 to EF-4 were assessed, because there was an insufficient mass of PFA. The "total" values are derived by summing the arsenic mass recovered from water-extractables, readily exchangeable ions, carbonate-bound, surface oxide-bound ions, and residue. The values reported for the "bulk" are derived from microwave digestion fly ash and determination by HG–ICP–AES. According to the experiment results, the "total" value is almost equal to the "bulk" value, which indicates validation of the leaching protocol.

The results from the leaching experiments on the fly ashes help to assess the potential for arsenic that is contained in fly ash particles to migrate into the water supply after ground deposition downwind of the power plant.[19] Among the previously mentioned four modes of occurrence, the water-extractable arsenic could migrate to water during the early stage of fly ash when in contact with water. The readily exchangeable As ions could be released under neutral conditions. These two are expected to influence the groundwater and soil environment. The arsenic in carbonate-bound, surface oxide-bound ions is sensitive to pH and has a tendency to dissolve into acid solution. The pH values of the leachate from fly ash were alkaline, in the range of

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(18) Sakulpitakphon, T.; Hower, J. C.; Trimble, A. S. *Energy Fuels* **2003**, *17*, 1028–1033.
(19) Querol, X.; Juan, R.; Lopez-Soler, A. *Fuel* **1996**, *75* (7), 821–838.

Table 7. Analysis of the Leachates Obtained from Fly Ash of the Different Hoppers (for $n = 2$)

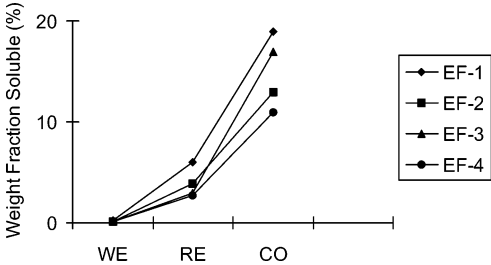|	Concentration (μg/g)					
sample	water-extractables	readily exchangeable ions	carbonate-bound, surface oxide-bound ions	residue	total	bulk
EF-1	0.021	0.46	1.44	5.66	7.58	6.03
EF-2	0.028	1.13	3.69	23.6	28.5	25.6
EF-3	0.058	1.08	6.16	20.5	36.3	37.7
EF-4	0.036	1.32	5.19	40.7	47.2	45.6

Figure 4. Extractables rate of arsenic in fly ash collected in different electric fields. Legend is as follows: WE, water-extractables; RE, readily exchangeable ions; and CO, carbonate-bound, surface oxide-bound ions.

10.45−12.02, using distilled water in this experiment, in agreement with previous studies,[20] which prevents it from dissolving into the environment. However, in China, the problem of acid rain is serious; thus, the fraction of carbonate-bound, surface oxide-bound ions might continue to be released into solution over long periods. The residue fraction is stable in the environment. As the extraction results suggest, in every case that has been examined, arsenic is partially soluble and some arsenic is expected to leach out of ash particles. When going from hopper 1 to hopper 4, the arsenic contents of the extracts are 1.92 (hopper 1), 4.84 (hopper 2), 7.29 (hopper 3), and 6.5 μg/g (hopper 4), which means that finer fly ash would release more arsenic into the environment, under the same conditions. However, Figure 4 shows that there are no appreciable differences in the arsenic-extractable rate results for different-sized

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particles. The content of arsenic bound in different forms of occurrences in the fly ash studied increases in the following order: residue > carbonate-bound, surface oxide-bound ions > readily exchangeable ions > water-extractables (74.73%−86.22% arsenic in residue; 11%−19% arsenic in carbonate-bound, surface oxide-bound ions; 2.7%−6.0% arsenic in readily exchangeable ions; and 0.076%−0.27% arsenic in water-extractables). The extractables rate of arsenic (carbonate-bound, surface oxide-bound ions + readily exchangeable ions + water-extractables) is 25.27% in EF-1, 17% in EF-2, 20.06% in EF-3, and 13.78% in EF-4. The leaching behavior of fly ash indicates that the arsenic in the ash particles is partially associated with the surface, but most of it is incorporated within the glass matrix as well.

4. Conclusion

To study the behavior of arsenic after coal combustion in a power station, a synchronized sampling of pulverized coal, slag, fly ash, and flue gas was conducted over a limited period. The leaching behavior and possible contamination of fly ash were also assessed. The research has shown that arsenic was preferentially concentrated on finer fly ash particles and most of the arsenic was captured on the fly ash. The arsenic extractables rate was 13.78%−25.27% in different fly ashes.