

Characterization of Hg, As and Se in Lime Spray Dryer Ash

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KEYWORDS: Lime Spray Dryer, Hg, As, Se, Unburned Carbon

ABSTRACT

Current research is investigating the feasibility of utilizing lime spray dryer by-product in different engineering applications. However, concerns about the release of trace elements, in particular Hg, As and Se, from lime spray dryer by-product potentially limit re-use applications. In this study, lime spray dryer samples as well as feed coal and lime were collected from the McCracken Power Plant located on the Ohio State University main campus. Concentrations and leaching properties of Hg, As and Se were monitored over two years and compared to a previous study performed in 1991-1992. Distributions of Hg, As and Se in unburned carbon (>140 mesh, <1.87 g/cm³), fly ash-rich (>140 mesh, >1.87 g/cm³), and calcium-rich (<140 mesh) fractions were also investigated. Results indicated that the levels of Hg, As and Se in lime spray dryer by-product were constant within a factor of two; and the leaching properties were constant within an order of magnitude over the 11-year time period of the study. Fractionation of the lime spray dryer by-product indicated that the As concentration was highest in the calcium-rich fraction, accounting for 94% of the total As. The Se concentration was highest in the unburned carbon fraction, accounting for 32% of total Se. More Se (42%) on a mass basis, however, was found in calcium-rich fraction due to greater mass fraction of residual lime. The concentration of Hg was found to be similar in both unburned carbon and calcium-rich fractions; however, approximately 78% of the Hg mass was present in the calcium-rich fraction.

INTRODUCTION

Approximately 26 million metric tons of flue gas desulfurization (FGD) by-product is produced in the United States every year (1,2,3). The majority of this material (more than 18 million metric tons) is sent to landfills. As a result, a number of studies have been conducted examining the utilization of FGD by-product, such as in construction, agriculture or mine reclamation (4,5,6,7,8,9,10).

The lime spray dryer (LSD) system is one of the most popular dry FGD techniques (11) and utilizes a fine spray of slaked lime ($\text{Ca}(\text{OH})_2$) to absorb sulfur dioxide in the scrubber resulting in the formation of calcium sulfate or calcium sulfite. Moisture in the reacted lime is lost due to the heat from the flue gas. The resulting calcium sulfite/sulfate is then removed, along with fly ash, in a baghouse or electrostatic precipitator.

In a 1999 Report to Congress, it was established that LSD ash be regulated under Subtitle D of the Resource Conservation and Recovery Act (RCRA). This allows these materials to be exempt from physical and chemical tests for hazardous material if utilized in a few specific applications (1). However, there are still environmental concerns about the release of trace elements during utilization of this material, and of particular concern is the release of Hg, As and Se. In addition, potential changes in physical and/or chemical properties of LSD ash over time hinder development of long-term applications.

This study characterized Hg, As, and Se in LSD ash from the McCracken Power Plant in Columbus, Ohio. Elemental composition and leaching analyses of Hg, As, and Se in LSD ash were carried out. Coal and lime were also collected for elemental composition analyses. Data were compared with a previous study conducted in 1991-1992 to determine long-term variability. LSD by-product samples were fractionated into carbon-rich, fly ash-rich and calcium-rich fractions to examine the fate of Hg, As, and Se in LSD by-product.

MATERIAL AND METHODS

LSD by-product, coal, and lime (unslaked) were collected from the McCracken Power Plant located on the Ohio State University, main campus. LSD ash, coal, and lime samples were collected May 2001 to January 2002 at the McCracken Power Plant. LSD ash was collected in hopper F in the fabric filter baghouse. Lime samples were taken from a falling stream immediately prior to slaking. Coal samples were obtained from the release point of the feed into the combustion chamber.

Fractionation of unburned carbon in LSD ash samples was accomplished by using a 140-mesh sieve made of stainless steel net to separate large particles that were experimentally found to contain unburned carbon. The material passing through sieve was found to be calcium-rich. Sieved particles were then transferred into prepared lithium metatungstate (LST) solution, which has density of 1.87 g/cm^3 , and centrifuged at a rotation speed of 15,000 rpm for 1 hour. The floating portion ($<1.87 \text{ g/cm}^3$) which contain mostly unburned carbon was removed, filtered, rinsed by deionized water on a filter paper, and then dried in a desiccator at $60 \text{ }^\circ\text{C}$ for 24 hours. The non-floating portion ($>1.87 \text{ g/cm}^3$) was also washed with deionized water and dried. This fraction consisted significantly of fly ash.

Sample preparation for elemental composition analyses in LSD ash and lime were accomplished by digesting approximate 300 mg of LSD ash by a microwave heating method with a combination of 10-mL deionized water, 6-mL nitric acid, 2-mL hydrochloric acid, and 2-mL hydrofluoric acid. A second microwave heating with 20-mL boric acid was followed (EPA method 3052). Leachate analyses were conducted by using the toxicity characteristic leaching procedure (TCLP) test (EPA method 1311).

Elemental compositions except As, Se, and Hg in sample solutions were examined by a Vista Pro simultaneous inductively coupled plasma optical emission spectrometer system (Varian, Walnut Creek, CA) (EPA method 6010B). As and Se were analyzed by a SpectrAA 880Z Zeeman graphite furnace atomic absorption (AA) spectrometer (Varian, Walnut Creek, CA), and Hg was determined by AA with a vapor generation accessory (EPA method 7060A, EPA method 7740 and EPA method 7470A). Anions were determined by using a DX-500 ion chromatography system (Dionex, Sunnyvale, CA) (EPA method 300.0). All analyses included controls (duplicate, blank, and check standards) for every fifteen samples or less.

Coal samples were sent to commercial laboratories for elemental analyses. Proton Induced X-ray Emission or "PIXE" was used for determining Al, As, Ca, Fe, S, Se and Si. Hg was analyzed by cold vapor atomic fluorescence spectrometry following acid digestion by microwave heating.

Scanning electron microscopic (SEM) images were taken by using a Philips XL-30 ESEM. Mineralogical analysis of LSD ash samples were accomplished by using a Philips X-Ray Diffraction (XRD) instrument (Philips Analytical, Natick, MA). The specific surface area of LSD ash samples were measured by BET surface area analysis.

RESULTS AND DISCUSSION

The levels of Hg, As, and Se in LSD ash may be influenced by changes in lime and coal properties, plant operation conditions, and feed rates. To investigate the impacts of feed coal and lime on the levels of As, Hg, and Se in LSD ash, the elemental composition of feed coal and lime were examined. Data in Table 1 show that variability (as relative standard deviation or RSD) of As in lime was 25% while Se and Hg were undetected. The RSDs of As, Se, and Hg in coal were 74%, 12% and 9%, respectively. The variability of Hg, As and Se in coal were greater than in LSD ash suggesting insignificant impacts from variability of coal on the variability of LSD ash. The higher variability in coal compared to LSD ash may, however, be due to limitations in analysis of trace elements near detection levels.

Changes in plant operations and sources of coal may result in large long-term variability. Data in 1991-1992 were used to examine the variation over long term

periods. Se had a greater average concentration of 10.9 mg/kg in 1991-1992 compared to 30.1 mg/kg in 2001-2002. However, As changed only slightly from an average concentration of 36.7 mg/kg in 1991-1992 to 35.2 mg/kg in 2001-2002. No Hg data were collected in the 1991-1992 period.

Figure 1 shows the concentrations of Hg, As, and Se in LSD ash samples collected from May 2001 to January 2002. Data from the previous study in January 1991 to January 1992 were also included. From the results, the upper range of 99% confidence t-test interval was 0.47 mg/kg which is below the limit of 17 mg/kg for land application. For As, the limit is 41 mg/kg and the upper range of 99% confidence t-test was slight below at 39.7 mg/kg. The upper bound of the 99% confidence t-test interval of Se was 30.6 mg/kg which is below the limit at 36 mg/kg (12). There was no Hg, As, and Se data violating the ceiling limits of 75, 100, and 57 mg/kg, respectively (12).

To examine whether the LSD ash is considered a hazardous material, TCLP tests were carried out on all samples. Table 2 shows the mean concentrations and standard deviations of TCLP elements of the samples collected in 2001-2002 and in 1991. RSDs of elements measured in leachates were greater than RSDs found for elemental composition. Comparing the data in 1991 to the 2001-2002 data, concentrations of elements in leachates were similar. Variations were within a factor of three for Hg, As, and Se.

Results from leaching analyses were compared with RCRA limits. As and Se concentrations are shown in Figure 2. Using 99% confidence t-tests, the maximum mean concentrations of As and Se were calculated to be 2.7 and 13.4 $\mu\text{g/L}$, and therefore LSD ash does not violate the RCRA limits for As and Se at 5000 and 1000 $\mu\text{g/L}$, respectively. The 99% confidence interval was also used to calculate other regulated elements such as Ag, Ba, Cd, Cr, and Pb, which were consistently below the RCRA limit. These 11-year period data showed that the concentration of contaminants in leachate produced were consistently lower than RCRA limits, indicating a consistently non-hazardous material.

To examine the fate of inorganic constituents in different fractions of LSD material, the ash was fractionated by size and density. Three different fractions were separated. (1) The fraction passing a 140-mesh sieve was calcium-rich residue (i.e. hannebachite and portlandite), accounted for 76% of total mass, and had specific surface area of 7.1 m^2/g . This portion contained 4.9% of the organic carbon. (2) The fraction retained on the 140-mesh sieve and with high density ($>1.87 \text{ g/m}^3$) accounted for 11% of the total mass of LSD ash and had a specific surface area of 10.2 m^2/g . This portion was considered to be fly ash - rich particles due to the greater proportion of Al (4.9%) and Si (9.7%) over Ca (15.2%) than in the calcium-rich fraction. (3) The fraction passing the 140-mesh sieve and having low density ($<1.87 \text{ g/m}^3$) was 10% of the total mass and had a specific surface area of 3.1 m^2/g . This fraction contained 88.7% of the organic

carbon. Table 3 summarizes the physical and chemical characteristics of the calcium-rich, the fly ash-rich and the carbon-rich fractions.

From Table 3, the largest constituents in the calcium-rich fraction were Ca and S which suggested that portlandite and hannerbachite predominated in this fraction. For the fly ash-rich fraction, Ca, Fe, Si, S and Al were the largest inorganic constituents. A large amount of Ca and S in this fraction indicated significant amount of portlandite and hannerbachite. However, a larger portion of fly ash constituents, Fe, Si, and Al, also indicated greater proportion of fly ash than in the calcium-rich and the carbon rich fractions. There was only a small contribution of inorganic constituents (10%) to the carbon-rich fraction.

Hg levels were similar at around 550 $\mu\text{g}/\text{kg}$ in the three fractions. Previous researchers found that $\text{Ca}(\text{OH})_2(\text{s})$ can effectively capture $\text{HgCl}_2(\text{g})$ by physical adsorption (13,14). Hg is also captured by unburned carbon via chemi-sorption of $\text{Hg}^0(\text{g})$ and $\text{HgCl}_2(\text{g})$ on the surface of the unburned carbon (15,16). The Hg concentration in the carbon-rich fraction was higher than the Hg concentration in the coal collected on the same day. However, based on the mass fraction, 78% of the total Hg in LSD ash was captured by the calcium-rich fraction.

As was found to be captured in the calcium-rich fraction at a concentration of 46.4 mg/kg. For the fly ash-rich and unburned carbon fractions, As concentrations were 13.9 mg/kg and <6.7 mg/kg, respectively. These results indicated that arsenic oxide, which is condensed at around 600°C, is effectively adsorbed by $\text{Ca}(\text{OH})_2(\text{s})$ (17). As was captured by the fly ash-rich fraction, however, this fraction also contained a significant amount of Ca (15.2%). It was unclear whether $\text{Ca}(\text{OH})_2(\text{s})$ or fly ash constituents were responsible for As capture. For the carbon-rich fraction, As was poorly captured in this fraction.

From the results in Table 3, Se was captured in the unburned carbon fraction at 176.7 mg/kg. Se in fly ash-rich and in the calcium-rich fraction were 136.1 mg/kg 31.9 mg/kg, respectively. Previous research indicated that Se is completely vaporized during combustion and removed in ash as oxides and sulfates (18). Se was also found to be captured by $\text{Ca}(\text{OH})_2$ at 400 to 600°C forming calcium selenite (19). However, the Se concentration in the calcium-rich fraction was much lower than in the fly ash-rich and the carbon-rich fractions suggesting that Se can be re-adsorbed by unburned carbon and fly ash-rich particles during post combustion processes.

CONCLUSION

Both elemental composition and leachate analysis of LSD ash over 11-year time period indicated this material was consistently below regulatory limits for re-use. LSD ash can be fractionated into carbon-rich, fly ash-rich and calcium-rich fractions. The calcium-rich fraction had greatest distributions of every element due to the largest mass fraction in LSD ash. Hg concentrations were similar in all

fractions, but the mass fraction was the highest in the calcium-rich fraction. The As concentration and mass distribution were high in the calcium-rich fraction. Se concentrations were high in the fly ash-rich and the carbon-rich fraction. However, larger mass fraction of the calcium-rich had a higher Se mass fraction than the other fractions.

ACKNOWLEDGMENT

This research was supported by the Ohio State Carbon Ash Reactivation (OSCAR) Demonstration Project. Funding from the Ohio Coal Development Office (OCDO) and the Ohio State University is gratefully acknowledged. We also thank staffs at McCracken power plant for their assistance during the sampling phase of this research.

REFERENCES

- [1] U.S. Environmental Protection Agency. Wastes from the Combustion of Fossil Fuels, Volume 1 and 2- Methods, Findings, and Recommendations, Report to Congress, EPA 530-S-99-010, March 1999.
- [2] Kalyoncu RS. Coal combustion products, U.S. Geological Survey Minerals Yearbook-1999, U.S. Geological Survey, Reston, VA., 1999.
- [3] U.S. Geological Survey, 1997-2002, Minerals YearBook: Vol I Metals and Mineral, 1996-2001.
- [4] Walker, H.W., Taerakul, P., Butalia, T.S., Wolfe, W.E., Dick, W.A., Minimization and Use of Coal Combustion By-Products: Concepts and Applications. In: The Handbook of Pollution Control and Waste Minimization, (Eds A. Ghassemi) Marcel Dekker, New York, 2002.
- [5] Butalia, T.S., Dyer, P., Stowell, R., Wolfe, W.E., Construction of Livestock Feeding and Hay Bale Storage Pads Using FGD Material, The Ohio State Extension Fact Sheet, AEX-332-99, Columbus, Ohio: The Ohio State University, 1999.
- [6] Butalia, T.S., Wolfe, W.E., Re-Use of Clean Coal Technology By-Products in the Construction of Impervious Liners. 1997 Ash Utilization Symposium, Lexington, Kentucky, 1997.
- [7] Lamminen, M., Wood, J., Walker, H., Chin, Y.-P., He, Y., Traina, S. J., J Env Quality, 2001, 30, pp. 1371-1381.
- [8] Butalia, T.S., Wolfe, W.E., Lee, J.W., Fuel, 2001, 80, pp. 845-850.
- [9] Clark, R.B., Ritchey, K.D., Baligar, V.C., Fuel, 2001, 80, pp. 821-828.
- [10] Kelly, T.D., Kalyoncu, R.S., Coal Combustion Products Statistics; USGS Open-File Report 01-006; May 21, 2002.
- [11] U.S. Environmental Protection Agency. Wastes from the Combustion of Coal by Electric Utility Power Plants, Report to Congress, EPA 530-SW-88-002, February, 1988.
- [12] U.S. Environmental Protection Agency. Standards for the use of or disposal of sewage sludge: Final rule. Fed. Reg. 58:032., 1993.

- [13] Galbreath, K.C., Zygarlicke, C.J., Fuel Proc.Tech., 2000, 65-66, pp. 289-310.
- [14] Senior, C.L., Helble, J.J. and Srofim, A.F., Fuel Proc.Tech., 2000, 65-66, pp.263-288.
- [15] Ghorishi, S.B., Keeney, R.M., Serre, S.D., Gullett, B.K. and Jozewicz, W.S., Environ. Sci. Tech., 2002, 36, pp. 4454-4459.
- [16] Huggins, F.E., Huffman, G.P., Energy& Fuel, 1999, 13, pp. 114-121.
- [17] Mahuli, S., Agnihotri, R., Chauk, S., Ghosh-Dastidar, A. and Fan, L.S., Environ. Sci. Tech., 1997, 31, pp.3226-3231.
- [18] Querol, X., Fernández-Turiel, J.L., López-Soler, A., Fuel, 1995, 74, pp. 331-343.
- [19] Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R. and Fan, L-S., Environ Sci. Tech., 1996, 30, pp. 447-452.

Table 1. Elemental Composition of Lime Spray Dryer By-Product, Quick Lime, and Coal Collected from McCracken Power Plant

| Elemental Compositions | Units | Spray Dryer By-Product | | | | Quick Lime (2001) (n=14) | Coal Feed (2001) (n=14) |
|------------------------|-------|------------------------|--------|----------------------|--------|-----------------------------|----------------------------|
| | | (2001- 2002) (n=14) | | (1991-1992) (n=5) | | | |
| | | | | | | | |
| Ca | % | 32.7 | ± 1.58 | 31.4 | ± 3.89 | 69.3 ± 0.9 | 0.1 ± 0.02 |
| S | % | 12.7 | ± 0.77 | 8.4 | ± 2.29 | 0.038 ± 0.004 | 2.3 ± 0.2 |
| Si | % | 3.5 | ± 0.58 | 2.9 | ± 0.78 | 0.5 ± 0.03 | 0.8 ± 0.1 |
| Fe | % | 2.5 | ± 0.41 | 2.8 | ± 1.03 | 0.2 ± 0.01 | 1.1 ± 0.2 |
| Al | % | 1.3 | ± 0.12 | 1.9 | ± 0.52 | 0.1 ± 0.01 | 0.6 ± 0.1 |
| As | mg/kg | 35.2 | ± 6.8 | 36.7 | ± 8.0 | 0.4 ± 0.1 | 6.5 ± 4.8 |
| Se | mg/kg | 30.1 | ± 2.8 | 10.9 | ± 5.0 | UDL | 1.6 ± 0.2 |
| Hg | µg/kg | 428 | ± 57 | N/A | | UDL | 199 ± 35 |

UDL – Under detection limit, N/A - No data available

Table 2. Results of TCLP test of Spray Dryer By-Product from McCracken Power Plant

| Leachate Constituents | Units | 2001-2002 | 1991 | RCRA Limits |
|------------------------------|--------------|------------------|-------------|--------------------|
| Ba | µg/L | 225 ± 39% | 348 | 100000 |
| Pb | µg/L | 53.5 ± 17% | 17 | 5000 |
| Se | µg/L | 11.3 ± 34% | 4 | 1000 |
| Ag | µg/L | 8.8 ± 6% | <24 | 5000 |
| As | µg/L | 2.3 ± 35% | <5 | 5000 |
| Cr | µg/L | 1.8 ± 36% | 9 | 5000 |
| Cd | µg/L | <1 | <3 | 1000 |
| Hg | µg/L | <0.2 | <0.2 | 200 |

Table 3. Physical and Chemical Characteristics of Fractions in LSD Material Collected from McCracken Power Plant on June 14, 2001

| Fractions | | Calcium-Rich | Fly Ash-Rich | Carbon-Rich |
|------------------------------|-------------------|--------------|--------------|-------------|
| Org. Carbon | % | 4.9 | N/A | 88.7 |
| Specific Surface Area | m ² /g | 7.09 | 10.24 | 3.08 |
| Total Mass | % | 76 | 11 | 10 |
| Inorg. Elements | | | | |
| Ca | % | 34.1 | 15.2 | 0.4 |
| S | % | 13.9 | 6.0 | 0.2 |
| Si | % | 5.8 | 9.7 | 6.8 |
| Fe | % | 2.2 | 10.5 | 1.2 |
| Al | % | 1.5 | 4.9 | 2.4 |
| As | mg/kg | 46.4 | 13.9 | 0.0 |
| Se | mg/kg | 31.9 | 136.1 | 176.7 |
| Hg | μg/kg | 551.82 | 549.85 | 540.18 |

N/A – No data available.

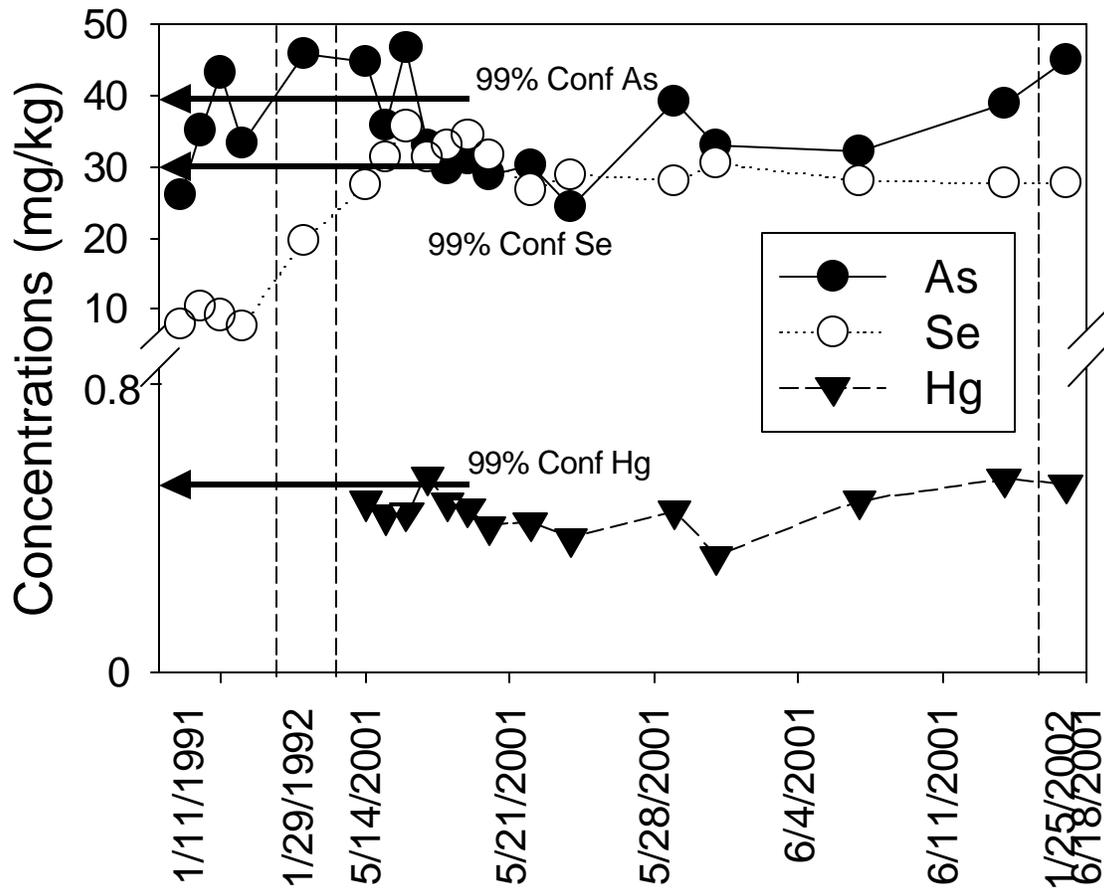


Figure 1. As, Se, and Hg in LSD Ash from 1991 - 2002

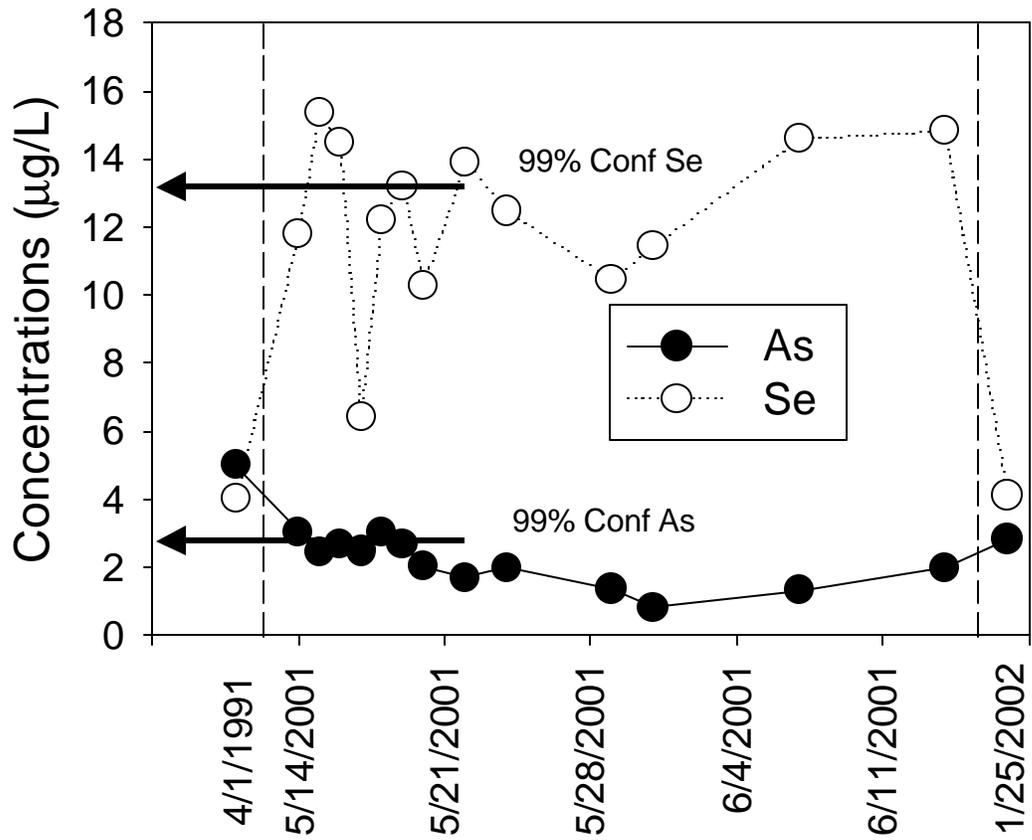


Figure 2. As, Se, and Hg in Leachates of LSD Ash from 1991 - 2002

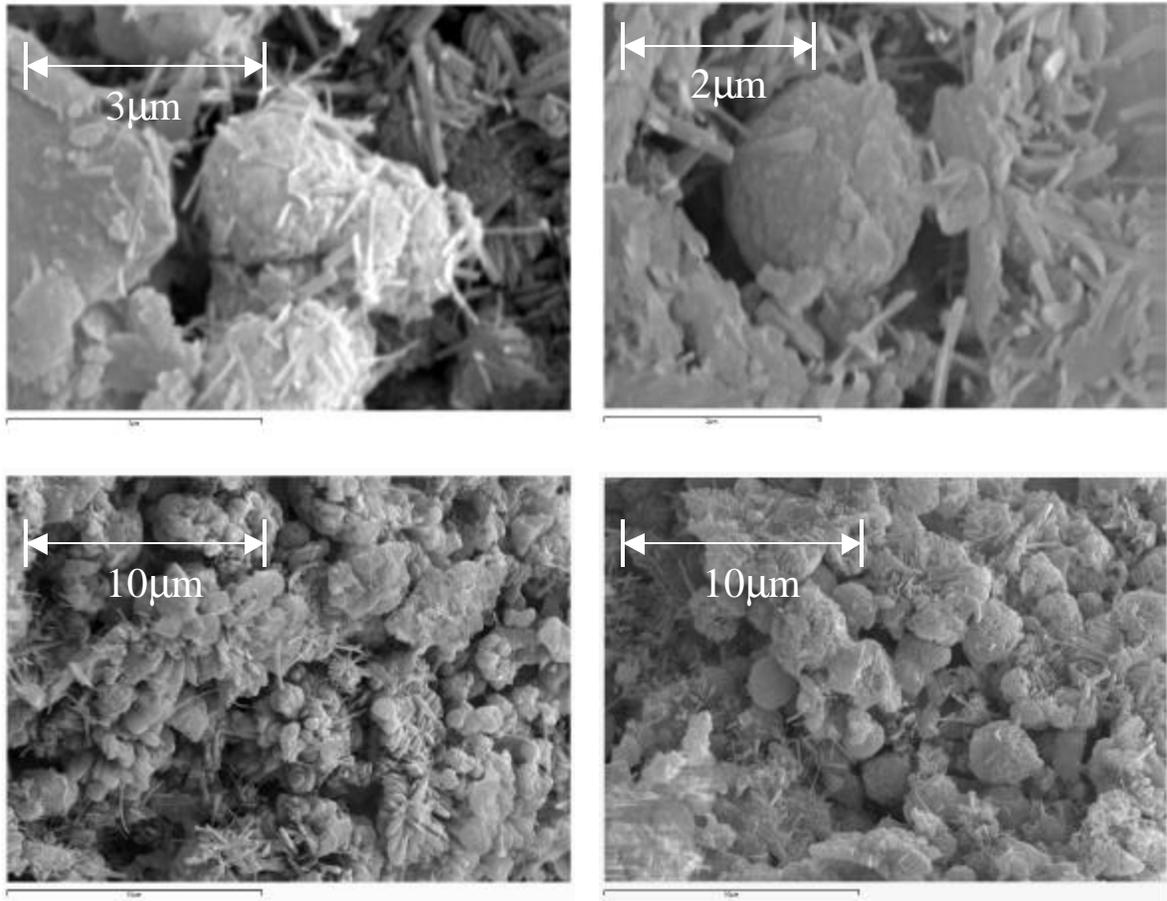


Figure 3. SEM Images of LSD Material from McCracken Power Plant