
CENTER FOR TRANSPORTATION INFRASTRUCTURE AND SAFETY

# Use of Absorption Mechanisms to Decrease Heavy Metal Mobility

by

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16. Abstract

The objective of this project is to reduce the toxic heavy metal leaching from coal fly ash so that the fly ash may be used for road surface or related applications. Trona (trisodium hydrogendicarbonate dihydrate, Na3HCO3CO3·2H2O) is injected into a flue gas duct to control SOx emission in field tests at coal-fired power plants. While SOx decreased from emitting to air, our recent research result showed significant increased leaching of heavy metal elements from produced fly ash to environment (water) [Yongbo Dan, Casey Zimmerman, Kun Liu, Honglan Shi, and Jianmin Wang, Increased Leaching of As, Se, Mo, and V from High Calcium Coal Ash Containing Trona Reaction Products, *Energy & Fuels*, 2013, 27:1531-1537]. In this project, we investigated the heavy metal leaching control by replace Trona with hydrated lime. Then the collected fly ashes were leached by following EPA standard method 1312. Nine metal elements, V, Cr, As, Se, Ag, Mo, Cd, Pb, and Ba concentrations were detected by inductively coupled plasma-mass spectrometry (ICP-MS).

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Feb 21, 2014

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## Methods

### ***Moisture content***

The moisture content was measured using gravimetric method briefly described below:
(1) Place a crucible to a muffle furnace at 110 $^0$C for 1 h. Transfer the crucible to a desiccator and allow it to cool, then weigh the crucible.
(2) Add 2 – 3 g fly ash sample to the crucible and record the total weight (crucible + raw ash). Dry the sample at 110 $^o$C until constant weight, and then move it to a desiccator to allow it to cool. Record the total weight of the crucible with the sample again (crucible + dried ash).
Total moisture content was calculated:
Moisture content = [(crucible + raw ash) - (crucible + dried ash)]/[(crucible + raw ash) - (crucible)]

### ***pH of the leached solutions***

The pH of each leaching solution was measured with a pH meter right after finishing leaching.

### ***Total dissolved solid (TDS) detection***

The TDSs were measured by a TDS meter.

### ***Leaching***

The fly ash samples were leached using Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312 with slight modification) with 20:1 liquid/solid (L/S) ratio and 4:1 L/S ratio (Modified SPLP). The procedures are listed below.

1) Prepare sulfuric acid/nitric acid mixture: Add 6 g concentrated sulfuric acid and 4 g nitric acid into ~90 ml MQ water slowly with stirring, then bring to 100 mL with MQ water.
2) Prepare leaching fluid at pH 4.2: Transfer MQ water into a large plastic container (1 L or larger), adjust pH to 4.2 with the acid mixture prepared in step 1.
3) For L/S = 4:1 leaching, weigh 20 g fly ash and add 80 mL leaching fluid to a 125-ml plastic leaching bottle. For L/S = 20:1, weight 4 g fly ash and add 80 mL leaching fluid to the leaching bottle. Seal all leaching bottles.
4) Shake all bottles at 180 rpm for 24 hours, measure pH, then allow the bottles settle for 2 hours.
5) Filter the supernatant through a 0.22 µm pore size nylon membrane filter.
6) Take small aliquot to measure TDS.
7) Acidify the filtrate with trace metal grade nitric acid to a pH < 2 and analyze the samples by ICP-MS (and ICP-OES analysis for double check to confirm Ba concentrations in high Ba samples).

**Quality Assurance/Quality Control**

To ensure the high quality data, most of the recommended QA/QC by the EPA methods were followed. For analysis by ICP-MS and ICP-OES, US EPA methods 200.8 and 200.7 QC guidelines were followed. ICP-MS and ICP-OES instrument responses were calibrated with standard solutions diluted from a calibration standard mixture containing all the elements (purchased from PerkinElmer). For ICP-OES detection of Ba, another standard purchased from High Purity was used. The linear ranges of the calibration were determined and used for the quantitative analysis of the samples. Laboratory reagent blank (BLK) test was conducted for checking procedural error. These sources of error or contamination potentially can be introduced from the laboratory environment, the reagents used in the analysis, the analytical instruments, and the analyst. BLK was prepared and measured using the same procedures as for the samples except no fly ash. The method detection limit (MDL) for this study was determined by instrumentation detection limits (IDLs) based on the signal to noise ratios of 3 to 5, and got the MDLs at 5 to 10 times of IDLs. To make sure the good reproducibility, duplicated samples were performed for all the samples. The precision of the duplication is expressed as the relative percent difference (RPD) and is calculated using the equation below.

$$RPD\ (\%) = 100 \times (C_h - C_l)/C_{av}$$

where
$C_h$ is detected high concentration of duplicated sample,
$C_l$ is detected low concentration of duplicated sample, and
$C_{av}$ is the average of the $C_h$ and $C_l$

Sample spike (spk) was tested for each fly ash by adding known concentration standard into the leached sample solution and performed ICP-MS analysis. The spike recovery (%) was calculated by the following equation:

$$\text{Spike recovery (\%)} = \frac{100 \times (\text{detected conc. of spiked sample} - \text{detected conc. of unspiked samples})}{\text{Spiked concentration}}$$

## Results and discussions

The fly ash sample information and moisture content are listed in Table 1.

Table 1. Fly ash sample information and moisture content.

| Sample ID | Disreption | Moisture (%) |
|---|---|---|
| BLK | Reagent blank | |
| 434052 | Trona based ash (Trona injected ash) | 2.12 |
| 478159 | Sodium based ash (sodium bicarbonate injected) | 0.13 |
| 434566 | Baseline control ash (normal fly ash without any injection) | 1.46 |
| 434567 | Hydrated lime ash (hydrate lime injected) | 2.01 |

Fly ash leaching results at 20:1 L/S ratio are shown in Table 2 and 4:1 ratio are shown in Table 3. The Ba concentration in sample 434566 and 434567 are high. To confirm these results, these samples were also analyzed by ICP-OES with calibration standard purchased from different supplier, and the data from both ICP-MS and ICP-OES are very close, indicating the analytical data are trustable.

Table 2. Fly ash SPLP leaching results at 20:1 L/S ratio.

| Sample ID | PH | TDS(ppm) | V (ppb) | Cr (ppb) | As (ppb) | Se (ppb) | Mo (ppb) | Ag (ppb) | Cd (ppb) | Ba (ppb) | Pb (ppb) | Ba (ppm) by ICP-OES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BLK | | 197 | <MDL | <MDL | <MDL | <MDL | 4.83 | <MDL | <MDL | 4.58 | <MDL | |
| 434052-20 | 11.98 | 3990 | 225.48 | 203.55 | 5.27 | 228.84 | 191.39 | <MDL | 0.71 | 697.10 | <MDL | |
| 434052-20D | 12.07 | 4460 | 249.59 | 220.63 | 6.36 | 317.44 | 220.14 | <MDL | 0.80 | 753.52 | <MDL | |
| 478159-20 | 11.31 | 960 | 121.17 | 58.32 | 57.67 | 136.73 | 1066.36 | <MDL | 4.41 | 137.82 | <MDL | |
| 478159-20D | 11.30 | 990 | 110.54 | 60.02 | 54.26 | 142.55 | 1104.12 | <MDL | 4.37 | 134.51 | <MDL | |
| 434566-20 | 11.93 | 1190 | 20.66 | 84.53 | <MDL | 49.01 | 144.67 | <MDL | 0.55 | 1909.95 | <MDL | 1.74 |
| 434566-20D | 11.95 | 1240 | 19.57 | 84.04 | <MDL | 47.17 | 132.87 | <MDL | 0.50 | 2063.67 | <MDL | 1.88 |
| 434567-20 | 12.32 | 2870 | 1.85 | <MDL | <MDL | 11.45 | 33.31 | <MDL | <MDL | 15216.60 | 1.49 | 16.12 |
| 434567-20D | 12.36 | 2760 | 1.60 | <MDL | <MDL | 9.53 | 24.19 | <MDL | <MDL | 15848.70 | 1.53 | 17.06 |
| | | | | | | | | | | | | |
| 434052-20D spk recovery (%) | | | 87.15 | 83.98 | 101.05 | 88.95 | 100.43 | 84.41 | 95.78 | 99.80 | 88.08 | |
| 478159-20 spk recovery (%) | | | 101.70 | 99.73 | 101.40 | 101.07 | 98.47 | 99.80 | 100.80 | 101.52 | 98.01 | |
| 434566-20 spk recovery (%) | | | 96.23 | 96.53 | 95.39 | 95.23 | 96.32 | 91.24 | 95.27 | 104.51 | 92.94 | |
| 434567-20 spk recovery (%) | | | 97.90 | 98.06 | 95.41 | 90.65 | 97.44 | 88.67 | 95.63 | 89.91 | 96.47 | |
| | | | | | | | | | | | | |
| 434052-20 RPD (%) | 0.75 | 11.12 | 10.15 | 8.05 | 18.77 | 32.44 | 13.97 | 0.00 | 11.11 | 7.78 | 0.00 | |
| 478159-20 RPD (%) | 6.50 | 3.08 | 9.17 | 2.87 | 6.08 | 4.17 | 3.48 | 0.00 | 0.96 | 2.44 | 0.00 | |
| 434566-20 RPD (%) | 0.09 | 4.12 | 5.43 | 0.57 | 0.00 | 3.84 | 8.50 | 0.00 | 8.00 | 7.74 | 0.00 | 7.88 |
| 434567-20 RPD (%) | 5.42 | 3.91 | 14.63 | 0.00 | 0.00 | 18.22 | 31.70 | 0.00 | 0.00 | 4.07 | 2.78 | 5.70 |
| **MDL** | | | **1** | **5** | **0.6** | **10** | **1** | **1** | **0.4** | **1** | **0.6** | **0.08** |

Table 3. Fly ash leaching results at 4:1 L/S ratio.

| Sample ID | PH | TDS(ppm) | V (ppb) | Cr (ppb) | As (ppb) | Se (ppb) | Mo (ppb) | Ag (ppb) | Cd (ppb) | Ba (ppb) | Pb (ppb) | Ba (ppm) by ICP-OES |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BLK | | 197 | <MDL | <MDL | <MDL | <MDL | 4.83 | <MDL | <MDL | 4.58 | <MDL | |
| 434052-4 | 12.53 | 13080 | 1194.44 | 941.98 | 140.45 | 1933.93 | 1124.40 | <MDL | 4.45 | 243.47 | 1.05 | |
| 434052-4D | 12.52 | 13090 | 1197.67 | 955.12 | 134.06 | 1945.92 | 1160.31 | <MDL | 4.58 | 204.77 | 0.95 | |
| 478159-4 | 11.05 | 2030 | 258.07 | 218.53 | 136.79 | 215.42 | 5433.56 | 1.07 | 20.98 | 255.38 | 0.67 | |
| 478159-4D | 11.06 | 2130 | 268.55 | 210.55 | 144.42 | 204.48 | 5500.45 | <MDL | 21.80 | 269.81 | <MDL | |
| 434566-4 | 12.38 | 3780 | 49.18 | 295.89 | 1.72 | 196.39 | 625.25 | <MDL | 2.29 | 1971.17 | 0.67 | 1.82 |
| 434566-4D | 12.37 | 3870 | 50.23 | 307.13 | 1.28 | 205.93 | 599.61 | <MDL | 2.18 | 2036.27 | <MDL | 1.79 |
| 434567-4 | 12.58 | 5030 | 2.48 | 11.19 | <MDL | 14.70 | 65.46 | <MDL | <MDL | 37227.75 | 2.10 | 40.11 |
| 434567-4D | 12.55 | 4920 | 3.34 | 11.72 | <MDL | 15.56 | 56.20 | <MDL | <MDL | 35086.80 | 2.06 | 37.70 |
| | | | | | | | | | | | | |
| 434052-4 spk recovery (%) | | | 93.60 | 84.95 | 108.03 | 112.39 | 103.08 | 67.79 | 92.31 | 98.94 | 90.83 | |
| 478159-4 spk recovery (%) | | | 96.54 | 92.57 | 99.79 | 101.22 | 66.36 | 95.58 | 99.06 | 93.89 | 92.78 | |
| 434566-4 spk recovery (%) | | | 95.75 | 93.60 | 97.89 | 99.93 | 103.48 | 77.35 | 94.10 | 93.57 | 86.98 | |
| 434567-4 spk recovery (%) | | | 96.43 | 92.81 | 97.57 | 99.28 | 100.51 | 78.83 | 94.78 | 87.15 | 91.57 | 97.20 |
| | | | | | | | | | | | | |
| 434052-4 RPD (%) | 0.08 | 0.08 | 0.27 | 1.39 | 4.65 | 0.62 | 3.14 | 0.00 | 2.79 | 17.27 | 10.53 | |
| 478159-4 RPD (%) | 0.09 | 4.81 | 3.98 | 3.72 | 5.42 | 5.21 | 1.22 | 0.00 | 3.83 | 5.49 | | |
| 434566-4 RPD (%) | 0.08 | 2.35 | 2.11 | 3.73 | 29.37 | 4.74 | 4.19 | 0.00 | 4.69 | 3.25 | | 1.40 |
| 434567-4 RPD (%) | 0.24 | 2.21 | 29.60 | 4.58 | 0.00 | 5.69 | 15.23 | 0.00 | 0.00 | 5.92 | 2.02 | 6.21 |
| **MDL** | | | **1** | **5** | **0.6** | **10** | **1** | **1** | **0.4** | **1** | **0.6** | **0.08** |

The results indicate that the toxic heavy metal in hydrate lime ash leaching decreased drastically not only than the Trona ash, it also much less than the normal control ash without any injection. However, Ba leached concentration was increased significantly in the hydrate lime ash. The Ba concentrations were further confirmed by different methods and standards. These preliminary tests results are very promising because **the hydrate lime injection was not only controlled the toxic gas emission from coal burning, it also controlled the fly ash pollution to the environment**. The data are limited to only one fly ash sample at this time from each type for this study. More detailed studies with different hydrate lime injection time, more other elements leaching, and other conditions are desirable and important. If the detailed study confirm our current test results, the hydrate lime may not only be routinely used for fly ash pollution control, **it may also been used as material for road surface and other construction works.**