

Trace Metals Analysis of Fly Ash by  
Inductively Coupled Plasma Atomic Emission Spectrometry

Bassam S. Attili  
Dr. Kenneth E. Daugherty\*  
University of North Texas  
Denton, Texas

A binding agent has been developed for pelletized densified refuse derived fuel (dRDF). Initial studies showed that calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is effective in reducing the rate of biological and chemical degradation of dRDF pellets. A commercial test of dRDF, with  $\text{Ca}(\text{OH})_2$  as a binder, was conducted at Jacksonville, Florida Naval Air Station in the summer of 1985.

In June/July of 1987 a full-scale cofiring of a binder densified refuse derived fuel (bd-RDF) and high sulfur content coal was conducted at Argonne National Laboratories (ANL). About 567 tons of bd-RDF pellets was cofired with coal, at 0, 10, 20, 30, 50 percent d-RDF Btu content and 0, 4, 8 percent calcium hydroxide binder. Results indicated that some trace elements decreased in fly ash with the increase in dRDF percentage while others increased.

The most toxic elements of concern are As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V and Zn. A microwave oven dissolution method was used to dissolve the ash in a mixture of aqua-regia and hydrofluoric acid using a Parr bomb. The solution was then analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy after approximate dilution.

Introduction

Incineration of municipal solid waste is an attractive solution to landfills<sup>1,4</sup>. However the physical and chemical characteristics of ash are becoming more and more important for safe disposal<sup>5</sup>. Some trace metals are important in the ash because of their potential toxicity, which plays a role in characterizing the ash as hazardous, and how and where to dispose of it.

Mass burn incineration produces ash residues amounting to 15 to 25 percent by weight and 5 to 10 percent by volume of the incoming Municipal Solid Waste (MSW)<sup>3,6</sup>. Ash comes in two forms. Fly ash the fine particles in the flue gas collected by electrostatic precipitators or bag house, and bottom ash the material dropped from the grate in the furnace. The ashes during the 1987 study at ANL were collected three times a day for six weeks from both the bag house and the grate.

Trace element concentrations in ash are of great interest because of their relationship to regulatory criteria under the Resource Conservation and Recovery Act (RCRA) regarding toxicity. Trace metals in fly ash were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Several investigators have examined the feasibility of ICP-AES for the rapid, precise, and accurate multi-element analysis<sup>7-13</sup>. ICP-AES permits the determination of a large number of elements with high sensitivity and precision and with relative freedom from chemical interferences<sup>14-17</sup>.

### Methodology

#### Fuel Preparation

The binder enhanced d-RDF pellets for the 1987 ANL study were supplied by two facilities, one located at Thief River Falls, (Future Fuel Inc.) Minnesota, and the other at Eden Prairie, Minnesota (Reuter Inc.). The dRDF was made with 0, 4, 8 percent Ca(OH)<sub>2</sub> binder. High-sulfur Kentucky coal is normally burned in the power plant of Argonne National Laboratory at the rate of nine tons per hour.

Before each test run, d-RDF pellets and coal were blended together using a front-end loader until the material looked roughly homogenous. Three volumes of coal and one volume of d-RDF produces a blend close to 10 percent d-RDF by Btu content. Then the blend was moved by front-end loader to the coal pit and transported by conveyor to coal bunker prior to use in the ANL stoker fired boiler.

#### Sampling Plan

A total of 567 tons of d-RDF pellets were cofired with 2,041 tons of sulfur-rich coal in 12 test runs. The runs were classified according to the different Btu contents of d-RDF in the fuel and different binder content of d-RDF. Runs 1 and 12 used coal alone in order to establish base line data. In between the different runs and to avoid cross-contamination, coal runs were performed to cleanout the d-RDF from the previous run. Details of the test plan and sampling locations have already been published<sup>3,18,19,20</sup>.

#### Sample Collection

During the test runs, samples were collected from various plant locations that were of interest in the study. Economizer, multicyclone fly ash and bottom ash samples were collected in aluminum containers and then transferred to plastic zip-lock bags for subsequent analysis at the University of North Texas.

## Equipment

### Parr Bombs

Parr Teflon acid bombs were obtained from Parr Instrument Company. The bomb is made of a microwave transparent polymer. A compressible relief disc is built into the closure to release excessive pressure. Over 1500 psi the relief disc will be compressed to a point where support for the O-ring will be lost and it will blow out. In most cases all parts of the bomb were reusable except for the O-ring.

### Microwave Oven.

A Kenmore commercial microwave oven was used in this work. The oven has a variable timing cycle from 1 second to 100 minutes and a variable heating cycle based on power setting from 10% through 100% full power (700 w).

### Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES

A Perkin-Elmer ICP-5500 Atomic Emission Spectrometer with a 27.12-MH, RF generator was used in this analysis. A Perkin-Elmer Model-10 data station was used with a Pr-100 printer.

### Sample Analysis

After the samples were returned to the laboratory, they were arranged on the shelves according to the dates and times they were collected. About 10 grams of a homogenous sample was ground to pass at least a 75 mesh sieve. A 400 mg sample was placed in a polyteflon container and treated with 1 mL of hydrofluoric acid and 3 mL of aqua regia. The teflon container was then placed in the bomb and the bomb was tightly capped. The bomb was placed in the microwave oven and heated for 4 minutes and left for several hours to cool. After cooling, the PTFE container was uncapped and 2 mL of saturated boric acid was added quickly. The container was then recapped, returned to the microwave oven and reheated for 1 more minute, then cooled again.

At this stage some uncombusted carbon remained, so the solution with the residue was filtered, washed with deionized water and the filtrate was diluted to 50 mL in a polyethylene volumetric flask.

The microwave heating procedure has been used to determine minor and major constituent in the past. The solution was finally analyzed by ICP-AES using a blank and a standard solution containing the same amounts of acids. Standards with varied concentrations of As, Hg, Pb, Sb, Se, Tl, Ba, Be, Cd, Cr, Cu, Ni, V, Zn, were used for the analysis.

## Results and Discussion

The chemical composition of coal/dRDF ash depends on geological and geographic factors related to the coal deposits, the combustion conditions and the efficiency of air pollution control devices. The fly ash samples which were investigated by ICP-AES were the Economizer fly ash samples. The results are summarized in Table 2. Thirteen elements were investigated; As, Cd, Hg, Pb, Sb, Se, Te, Ba, Be, Cr, Cu, Ni, V, and Zn. The metals As, Cd, Hg, Pb, Sb, Se and Tl are not included in the table because their concentrations were too low to be detected by ICP. Table 3 shows the ICP detection limits of all elements studied.

### Effect of d-RDF content on trace metals:

Processing of MSW to RDF removes much of the unwanted trace metals. The metal content of coal/RDF blend ash is expected to be affected by the different percentages of RDF.

The trace metal concentration in economizer fly ash are listed in Table 2. Elements such as Cd, Cr, Cu, Hg, Pb and Zn are known to be enriched in RDF related to coal.

Table 2 and the graphs show the percent bd-RDF versus concentration (ug/g) for each element alone at a constant level of binder. The top graph shows 0, 10, 20, 30 percent bd-RDF versus element concentration at 0 percent binder. The middle graph shows the 10, 20, 30, 50 percent bd-RDF versus element concentration at 4 percent binder. The bottom graph shows the concentrations at 8 percent binder. The graphs show how the elements are increasing or decreasing in concentration with the increase in bd-RDF.

From Table 2 and the graphs, the most prominent increase in concentration resulting from cofiring coal/RDF mixtures were Cu and Zn. Ba and Cr were increased slightly in economizer fly ash. This increase is due to these elements being more enriched in RDF ash than in coal ash, while Be, Ni and V content were lower or close to those in coal ash.

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Table 2. Summary of Toxic Metals Concentration  
in Economizer Fly Ash (ug/g).\*

Run#	Ba	Be	Cr	Cu	Ni	V	Zn	Btu%DRDF	Binder%
1.	158.2	25.3	105.2	152.7	130.0	223.4	324.8	0	-
2.	240.1	27.7	111.3	199.5	135.3	234.1	338.5	10	0
3.	202.2	19.6	100.3	151.8	122.2	177.9	293.7	10	4
4.	144.4	14.7	94.9	143.7	100.8	160.7	390.8	10	8
5.	227.7	20.2	143.8	243.4	137.4	231.0	404.6	20	0
7.	155.7	11.3	108.3	208.5	149.0	187.1	478.2	20	4
8.	182.8	13.3	127.6	243.6	121.3	193.4	466.7	20	8
9.	160.1	11.4	114.4	360.6	92.7	181.3	443.6	30	0
10.	158.3	10.5	115.9	207.9	75.6	149.6	455.9	30	4
6.	190.2	10.5	112.2	227.6	130.5	161.3	470.8	30	8
11.	228.5	14.9	126.1	353.5	97.7	179.8	372.1	50	4
12.	177.4	16.6	93.5	217.1	97.8	171.6	240.3	0	-

\* Average of Three Replicates.

Table 3. Detection Limits of ICP (ug/g).

As (ug/g)	62.5
Ba	12.5
Be	0.63
Cd	6.25
Cr	6.25
Cu	6.25
Hg	125.0
Ni	12.5
Pb	125.0
Sb	125.0
Se	62.5
Tl	125.0
Zn	6.25



