

## LEACHING CHARACTERISTICS OF FLUORIDE FROM COAL FLY ASH

R Piekos and S Paslawska  
Gdansk, Poland

**SUMMARY:** Leaching of fluoride from fly ash has been studied at different ash/water ratios and temperatures and also over a broad range of pH. The efficiency of leaching was only slightly dependent on the ash/water ratio, thus revealing a solubility-controlled mechanism of the process. The efficiency was also independent of the temperature over the range 20 - 90°C.

Key words: Coal burning; Fluoride leaching; Fly ash.

### INTRODUCTION

More than 150 million tons of fly ash are produced annually worldwide from the combustion of coal in power plants. At least a half of this amount is disposed of by landfill, thus contributing to environmental pollution due to leaching of its toxic constituents. One of the critical constituents is fluoride which may be toxic at elevated levels in water.

Disposal of huge amounts of fly ash in landfills and surface impoundments or its re-use in construction materials is of environmental concern. While much effort has been devoted to the problem of leaching of heavy metals from disposed fly ash,<sup>1-8</sup> the release of non-metals has attracted considerably less attention. Of these, arsenic,<sup>9,10</sup> selenium,<sup>9,10</sup> and boron<sup>11</sup> stand out as potentially harmful to both vegetation and animals.

The fluoride levels of coal fly ash vary within broad limits of 0.4 - 610  $\mu\text{g/g}$ <sup>12</sup> and depend on the type of coal being burnt, the particle size of the ash, and the efficiency of electrostatic precipitators. Under natural leaching conditions, the fluoride levels may exceed legal standards for drinking water (1.4 - 2.4 mg/L)<sup>7</sup> attaining a level of 5.8,<sup>13</sup> or even as high as 18 mg/L.<sup>14</sup>

As the knowledge of the amount of leachable constituents of fly ash is important to estimate their availability for the biological systems, the primary objective of the present study was to investigate the release of fluoride from fly ash to water under a variety of conditions.

### MATERIALS AND METHODS

Fly ash was collected directly at the electrostatic precipitators installed in two power-generating units of the Gdansk Thermolectric Power Plant. One of the precipitators has three successive hoppers for collecting the ash and the other has four. The fluoride contents in the leachates obtained from the ash taken from the three successive hoppers were 0.37, 0.55 and 0.60 mg/L, whereas those from the ash taken from the 4-hopper precipitator were 0.56, 0.69, 0.72 and 0.75 mg/L after 3-hr leachings.

Further experiments were conducted with fly ash taken from the second hopper of the first-named precipitator. The sample represented dry materials collected at the station. The grain size of the ash ranged between 1 - 90  $\mu\text{m}$  with a mean diameter of 20 - 30  $\mu\text{m}$ . The results of its chemical analysis (main constituents) are as follows:  $\text{SiO}_2$  52.7%;  $\text{Al}_2\text{O}_3$  21.9%,  $\text{Fe}_2\text{O}_3$  8.4%, and CaO 7.2% (a class F fly ash according to ASTM standards).

All chemicals were of analytical reagent grade quality, and distilled water was used throughout.

Polyethylene labware was used for handling fluoride-containing solutions.

#### ANALYTICAL PROCEDURE

The total fluoride level in the leachates was determined potentiometrically by using a fluoride ion-selective electrode. As the electrode does not measure fluoride complexed with silicon, iron, aluminium and other polyvalent cations, the complexes had to be destroyed by adding a total ionic strength adjustment buffer (TISAB).<sup>15</sup> Further, an optimum pH of 5.2-5.5 was adjusted to prevent the formation of the  $\text{HF}_2^-$  ion emerging at a pH less than 5.

The buffer was prepared by dissolving 57 mL of glacial acetic acid, 58 g of NaCl, and 0.3 g of sodium citrate in distilled water and making the volume up to 500 mL in a volumetric flask. The pH of this solution was then adjusted to 5.2 with a 5 M NaOH solution.

Calibration graphs were constructed immediately before carrying out the measurements of the fluoride levels in the leachates for each series of measurements. The standard solution of fluoride was prepared by dissolving 0.2210 g of NaF (previously dried at 120°C), in 1 L of water. Its concentration was 100 mg  $\text{F}^-/\text{L}$  ( $5.2 \cdot 10^{-3}$  M). Solutions for constructing the calibration graphs containing 0.5, 1.0, 2.0, 5.0 and 10.0  $\mu\text{g F}^-/8$  mL were prepared by pipetting out 0.05, 0.10, 0.20, 0.50 and 1.00 mL of the standard solution, addition of 3.95, 3.90, 3.80, 3.50 and 3.00 mL of distilled water, respectively, and of 4 mL of the TISAB buffering system to each. During the measurements the solutions were stirred with a magnetic stirrer. Potential readings were recorded after fixed time intervals.

The calibration plot constructed in this way was linear for the concentration range 0.5 - 10.0  $\mu\text{g F}^-/\text{mL}$ .

In a similar way, the fluoride concentration was measured in the fly ash leachates. Samples of the leachates (up to 4 mL, depending on the expected  $\text{F}^-$  concentration) were mixed with 4 mL of TISAB to ensure optimum pH of 5.2 for fluoride measurement. The results were taken from the calibration graph.

#### PREPARATION OF THE LEACHATES

During preliminary tests, the fly ash/water ratios used were 1g/100 mL water, 1 g/50 mL water, and 10 g/100 mL water. The slurries were placed on a mechanical shaker and shaken for 0.5, 1, 2, 3, 24, and 48 hrs, at 25°C. The results of the fluoride determinations in these slurries are shown in the Table.

TABLE. The kinetics of fluoride leaching at various fly ash/water ratios at 25°C ( $\text{F}^-$  concentration in mg/L)

Fly ash/water ratio	0.5 hr	1 hr	2 hrs	3 hrs	24 hrs	48 hrs
A: 1.0 g/100 mL	0.45	0.50	0.52	0.54	0.61	0.71
B: 1.0 g/50 mL	0.50	0.54	0.56	0.58	0.84	-
B/A ratio	1.11	1.08	1.08	1.07	1.38	-

Because the 1.0 g/50 mL slurry was too dense and difficult to handle, further experiments were conducted with the 1.0 g/100 mL water slurry only.

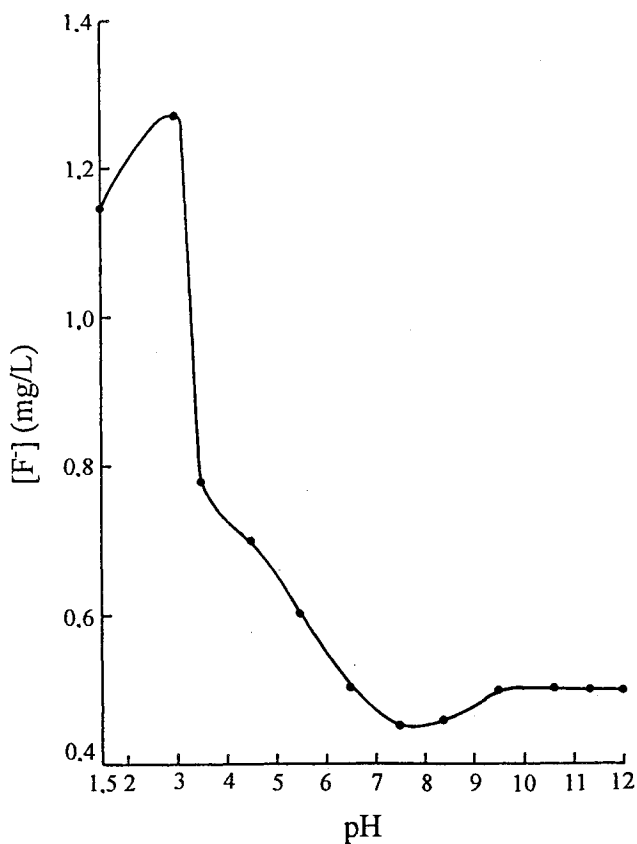
### EFFECT OF TEMPERATURE

To check the influence of the temperature on the fluoride extraction, a series of measurements were run for 3 hrs at 20, 30, 50 and 90°C using the 1.0 g/100 mL water slurry. The concentrations of the fluoride released at these temperatures were 0.54, 0.58, 0.55 and 0.58 mg/L.

### EFFECT OF pH

In order to estimate the influence of pH on leaching of the fluoride ion, a set of 3 M HCl, 6 M HCl and ammonia buffer solutions was prepared covering a pH range of 1 - 12. The fly ash/buffer solution ratio was 1g/100mL, and the temperature was held constant at 25°C. Three hours after preparation of the slurries, 4 mL aliquots were taken, filtered, 4 mL of TISAB buffer was added to the aliquot and the F<sup>-</sup> level was determined potentiometrically. Following the addition of the TISAB, the pH of all aliquots fell within the range 4 - 5. The results are recorded in the Figure.

**FIGURE.** The effect of pH on leachability of fluoride from fly ash (for details, see text)



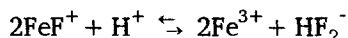
## DISCUSSION

Fluoride in coal is typically associated with organic matter and with minerals of the apatite group, fluorite, clay minerals and phosphates.<sup>16,17</sup> Upon combustion, coal releases fluoride partly into the atmosphere and partly in the form of fly ash and bottom ash as well as in an organic phase adsorbed on unburnt coal particles.<sup>13</sup> According to Meij,<sup>18</sup> the mean fluorine concentration in coal combusted in the Netherlands is 80 ppm.

During combustion in dry-bottom boilers,  $81 \pm 31\%$  of F is vapourised, and its concentration in flue gases is  $7000 \mu\text{g}/\text{m}_0^3$ . The relative enrichment factor in collected fly ash is 0.2 having an F concentration of 129 ppm, whereas, in emitted fly ash, respective values are 1.5 and 1089 ppm.<sup>18</sup>

Successive hoppers of the electrostatic precipitator collect fly ash particles of gradually decreasing grain size.<sup>18</sup> The accompanying surface area enlargement favours the leaching of fluoride as demonstrated by the results presented in the section Materials and Methods.

As far as the influence of the pH on the leaching of fluoride is concerned, there is a remarkable increase in the  $\text{F}^-$  level in strongly acidic medium below pH 2.5 (*cf* Figure). Additional thiocyanate tests carried out with the slurries revealed a striking red colour of a slurry with pH 1.5 and a fainter one of a slurry with pH 3.0, while at higher pH values the thiocyanate reaction was negative. Since it has long been known that the  $\text{FeF}^{2+}$  complex is destroyed at pH below 3.2, it is likely that in strongly acidic slurries the fluoride associated with iron(III) is released by the reaction:



As shown recently by Reardon *et al*<sup>6</sup> by conducting fly ash leaching tests at two different water/ash ratios, it is possible to determine whether or not the concentration of an element in the leachate is controlled by mineral solubility.

If a mineral solubility control exists, the concentration of an elemental ion can be readily predicted with chemical equilibrium models.<sup>6</sup>

Our results presented in the Table show that the fluoride concentration is fairly constant with time, and that doubling the mass of solid relative to the mass of water does not double the  $\text{F}^-$  concentration in solution ( $\text{B}/\text{A} = 1.07$  to  $1.38$ ; Table). Bearing Reardon's rule in mind, these findings indicate that F in ash occurs in the form of sparingly soluble salts embedded in surfaces of glass particles formed at low temperatures in the stack. This conclusion appears to be supported by the weak temperature response of  $\text{F}^-$  leaching over the range 20 - 90°C (see section on Effect of Temperature).

In this context it is interesting to note that, unlike fluoride, the chloride in ash occurs in the form of readily soluble salts as indicated by doubling its concentration upon doubling the fly ash/water ratio.<sup>6</sup>

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