

Leaching of Selected Constituents from Ammoniated Fly Ash from a Coal-Fired Power Plant

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KEYWORDS: ammoniated ash, batch leaching, fly ash

ABSTRACT

A laboratory effort was undertaken to obtain quantitative data on leaching of ammonia, nitrite and nitrate, and select trace elements from ammoniated fly ashes. A single sample of power plant fly ash was first ammoniated in the laboratory to generate three different samples containing low, moderate, and high concentrations of ammonia. These three ammoniated ash samples were subjected to batch equilibrium tests in the laboratory. In the laboratory experiments, the three ammoniated ash samples were extracted in duplicate at four liquid-to-solid ratios. Leaching was carried out with end-over-end agitation for 24 hours. The leachates were analyzed for pH, nitrite, nitrate, ammonia, sulfate, mercury, fluoride, chloride, bromide, aluminum, barium, chromium, copper, molybdenum, nickel, zinc, boron, arsenic, cadmium, selenium, and vanadium.

Preliminary leaching results clearly demonstrate that ammonia is a highly soluble and easily leached constituent from fly ash. Leaching of ammonia appears to be linearly related both to ammonia concentration in the ash and leaching ratios. Nitrite and nitrate were not detected in the leachates because ammonia in the ash is not readily converted to nitrate and nitrite. The presence of ammonia in fly ash did not change leaching characteristics of aluminum, barium, boron, chromium, copper, sulfate, chloride, and bromide contained in fly ash. Ammonia in ash resulted in decreased leaching of cadmium, nickel, and zinc contained in fly ash. However, the increasing levels of ammonia in fly ash increased leaching of arsenic, molybdenum, selenium, fluoride, and vanadium. Arsenic and selenium leaching chemistry appears to change the most because of the presence of ammonia in fly ash.

INTRODUCTION

The use of NO_x control technologies at coal-fired power plants is increasing in the United States, with a corresponding increase in the generation of ammoniated fly ash at these power plants. The disposal and use of ammoniated ash require that we develop

the necessary technical understanding of the potential environmental impacts of ammonium that may be released from the ammoniated ash. The objectives of this research were to 1) design and conduct laboratory experiments to develop quantitative results on leaching characteristics of ammonia from ammoniated ash samples; 2) examine the effects of ammonium on leaching of selected trace constituents contained in the fly ash samples; and 3) design and conduct a limited set of experiments to determine transformation rates for ammonium to nitrite and nitrate by the microbial populations in subsurface soils and in aged ash retrieved from the Armstrong Plant ash landfill. Allegheny Energy and EPRI contracted with Ish Inc. to design and conduct laboratory research to answer questions regarding leaching, transformation, and fate of ammonia and other selected constituents contained in acidic and alkaline coal fly ashes generated at power plants with NO_x control equipment. Allegheny Energy supplied one near-neutral and one alkaline fly ash sample for this study. Ish Inc. subcontracted with the University of North Dakota Energy & Environmental Research Center (EERC) to carry out the laboratory components of this research. The acidic fly ash sample received from Allegheny Energy was ammoniated in the laboratory to generate three different samples with three different concentrations of ammonia. This manuscript examines only the batch leaching results for the laboratory ammoniated acidic ash samples and the unammoniated acidic ash.

Assumptions can be made for the ammonia levels expected in coal-fired power plant fly ash:

- Flue gas is assumed to be at 500°C and 2 atm pressure.
- Flue gas behaves as an ideal gas.
- 90% of the ammonia in flue gas partitions to the fly ash particles.
- 10 lb of fly ash particles is present in 1 million L of flue gas.
- Most of the gaseous ammonia adsorbs onto the fly ash particles.
- Ammonium ion does not convert to nitrate in the flue gas.

The ideal gas law states that:

$$(PV)/(P_s V_s) = (NT)/(N_s T_s)$$

where the subscript "s" indicates standard conditions of $P_s = 1$ atm, $T_s = 273$ K, $N_s = 1$ mol, and $V_s = 22.4$ L.

For a 5-ppmv slipstream, there is 5 L of NH₄ in 10⁶ L of flue gas. Therefore, we can solve for moles of ammonium (i.e., N) in flue gas by using the ideal gas equation and rearranging for N by the following equation:

$$N = (PVN_s T_s)/(P_s V_s T)$$

Substituting the appropriate values, we get:

$$\begin{aligned}
N &= (2)(5)(273)/(22.4)(773) \\
&= 0.1577 \text{ mol of NH}_4 \text{ in } 10^6 \text{ L of flue gas} \\
&= 2.838 \text{ g NH}_4/10^6 \text{ L of flue gas}
\end{aligned}$$

Applying the 90% partition factor and the 10 lb of ash particles in 106 L of flue gas, we get:

$$[(2.838) (0.9)/10]/454 = 5.62 \times 10^{-4} \text{ g of ammonia per gram of fly ash}$$

These calculations are linear in nature and, therefore, Table 1 provides a range of slipstream ammonia levels and the corresponding ammonium concentrations in fly ash.

Table 1. Slipstream Ammonia Levels and Fly Ash Ammonium Concentrations

Slipstream Ammonia, ppmv	Ammonium Concentrations in Fly Ash, mg NH ₄ /kg ash
2	225
3	337.5
4	450
5	562.5
6	675
7	787.5
8	900

These calculations suggest that a significant amount of ammonia can be present in fly ash, depending on the ammonia levels in the slipstream. These calculated ammonia concentrations need to be verified with actual concentration data from ashes when generated by operating power plants with NO_x control technologies.

EXPERIMENTAL

The acidic fly ash was ammoniated to three levels in the laboratory. The laboratory ammoniation of the ash was carried out using the following procedure. Approximately 2 kg of fly ash was placed in a 1-gal small-mouth bottle. The amount of ash was chosen so that when the bottle was laid on its side, a large flat surface area of ash was presented that did not physically contact the cap. At the beginning of this ammoniation procedure the bottle was laid on its side and any dust was allowed to settle. Filter paper pads were cut to fit snugly into the cap of the bottle. Three to four of the filter paper circles were inserted into the cap. Using a microliter pipette, 100 μ L of ammonium hydroxide was deposited onto the filter paper, and the cap was immediately screwed onto the bottle. During the next half-hour, the bottle was gently rolled several times to present fresh ash to the headspace of the bottle. After approximately 1/2 hour, the odor of ammonia disappeared. This procedure was repeated several times, and after several additions had been made, the bottle was shaken vigorously. After the dust settled, the cap was removed, one or more of the paper disks was removed to present a fresh surface, and the disks removed were replaced with fresh disks. This was necessary to avoid directly exposing ash particles to ammonium hydroxide. The disks should be replaced at any time that ash particles are noticed on the filter paper. Analyses of the

ammonia concentration on the ash were performed at regular intervals, and the process was repeated until the desired concentration was achieved. The ammonia concentrations in the acidic fly ash solids were 77.4 mg/kg for low, 157 mg/kg for medium, and 262 mg/kg for high.

This entire process could be modified to suit individual needs. Diluted ammonium hydroxide could be used, and 100- μ L additions are only a suggestion. For instance, if very low ammoniation levels were desired, amounts and concentrations of ammonium hydroxide could be decreased as needed. It should be noted that this procedure does add water to the ash.

Batch leaching tests of the three ammoniated acidic ash samples and the unammoniated ash were extracted in duplicate at four liquid-to-solid ratios: 3:1, 9:1, 27:1, and 100:1. Distilled deionized water was used to conduct all leaching tests in this study. The extraction or equilibration period was 24 hours of continuous end-over-end agitation at 30 rpm for all leaching tests.

The leachates were analyzed for pH, aluminum, ammonia, arsenic, barium, bromide, boron, cadmium, chloride, chromium, copper, fluoride, mercury, molybdenum, nickel, nitrite, nitrate, selenium, sulfate, vanadium, and zinc. The measured concentrations of the selected constituents in the leachates were evaluated for trends and correlations, and the results are presented in tables and graphs in this report.

RESULTS AND DISCUSSION

Tables 2 and 3 report averaged concentrations for the batch dilution leachates generated in duplicate for the four liquid-to-solid leaching ratios for each of the three ammonia levels in the acidic fly ash and the unammoniated acidic ash. The resulting data were analyzed to identify some of the notable trends and correlations between ammonia levels in the fly ash and leaching characteristics of the selected ash constituents as determined by the batch leaching tests.

Table 2. Anionic Constituent Concentrations in Batch Leachates

Ammonia Level in Ash	Liquid-to-Solid Ratio	pH, s.u.	NO ₂ , mg/L	NO ₃ , mg/L	NH ₃ , mg/L	SO ₄ , mg/L	Hg, µg/L	F, mg/L	Cl, mg/L	Br, mg/L
None	100:1	6.01	< 0.5	< 0.5	0.37	< 5	< 0.01	< 0.5	1.1	< 0.5
Low	100:1	6.81	< 0.5	< 0.5	0.90	48.4	< 0.01	< 0.5	<1	< 0.5
Medium	100:1	7.09	< 0.5	< 0.5	1.47	47.0	< 0.01	0.26	0.85	< 0.5
High	100:1	7.80	< 0.5	< 0.5	3.31	52.0	< 0.01	0.34	0.95	< 0.5
None	27:1	6.00	< 0.5	< 0.5	0.40	167	< 0.01	1.3	2.8	0.6
Low	27:1	6.58	< 0.1	< 0.1	2.29	169	0.015	0.47	2.54	0.71
Medium	27:1	6.90	< 0.1	< 0.1	6.99	170	0.010	0.45	2.57	0.75
High	27:1	7.78	< 0.1	< 0.1	9.74	171	< 0.01	0.84	2.63	0.83
None	9:1	5.97	< 0.5	< 0.5	0.65	516	< 0.01	0.54	7.60	2.22
Low	9:1	6.52	< 0.1	< 0.1	8.71	532	< 0.01	0.61	7.42	2.04
Medium	9:1	6.66	< 0.1	< 0.1	18.0	535	< 0.01	0.98	6.83	1.87
High	9:1	7.73	< 0.1	< 0.1	29.5	553	< 0.01	1.78	6.95	1.88
None	3:1	5.92	< 0.5	< 0.5	1.45	1563	< 0.01	0.77	21.6	5.68
Low	3:1	6.56	< 0.5	< 0.5	24.4	1560	< 0.01	0.66	21.7	6.32
Medium	3:1	6.64	< 0.5	< 0.5	50.8	1571	< 0.01	0.82	19.1	5.71
High	3:1	7.64	< 0.5	< 0.5	85.4	1601	< 0.01	2.71	20.3	6.25

Table 3. Metal Concentrations in Batch Leachates

Ammonia Level in Ash	Liquid-to-Solid Ratio	Al, mg/L	Ba, mg/L	Cr, mg/L	Cu, mg/L	Mo, mg/L	Ni, mg/L	Zn, mg/L	B, mg/L	As, mg/L	Cd, mg/L	Se, mg/L	V, mg/L
None	100:1	< 0.1	0.21	< 0.05	< 0.05	0.16	< 0.04	0.05	0.27	0.128	0.0008	0.050	0.0335
Low	100:1	< 0.1	0.17	< 0.05	< 0.05	0.16	< 0.04	< 0.05	0.31	0.086	0.0004	0.048	0.0226
Medium	100:1	< 0.1	0.12	< 0.05	< 0.05	0.17	< 0.04	< 0.05	0.30	0.172	0.0003	0.060	0.0308
High	100:1	0.21	0.12	< 0.05	< 0.05	0.19	< 0.04	< 0.05	0.29	0.452	< 0.0002	0.079	0.0423
None	27:1	0.10	0.10	< 0.05	< 0.05	0.35	0.06	0.18	1.05	0.164	0.0033	0.075	0.0403
Low	27:1	< 0.1	< 0.1	< 0.05	< 0.05	0.50	< 0.04	< 0.05	1.26	0.116	0.0013	0.089	0.0335
Medium	27:1	< 0.1	0.1	< 0.05	< 0.05	0.59	< 0.04	< 0.05	1.19	0.128	0.0012	0.119	0.0262
High	27:1	0.16	0.15	< 0.05	< 0.05	0.70	< 0.04	< 0.05	1.22	0.560	0.0002	0.192	0.0677
None	9:1	0.22	< 0.1	< 0.05	< 0.05	0.62	0.17	0.45	3.10	0.229	0.0089	0.095	0.0486
Low	9:1	< 0.1	< 0.1	< 0.05	< 0.05	1.22	0.11	0.10	3.38	0.175	0.0035	0.133	0.0461
Medium	9:1	< 0.1	< 0.1	< 0.05	< 0.05	1.51	0.09	0.07	3.18	0.261	0.0026	0.176	0.0623
High	9:1	0.13	< 0.1	< 0.05	< 0.05	2.06	< 0.04	< 0.05	3.20	0.613	0.0006	0.329	0.0887
None	3:1	0.31	< 0.1	< 0.05	< 0.05	1.05	0.46	1.05	9.50	0.202	0.0218	0.115	0.0557
Low	3:1	< 0.1	< 0.1	< 0.05	< 0.05	2.64	0.28	0.21	8.91	0.263	0.0083	0.179	0.0635
Medium	3:1	< 0.1	< 0.1	< 0.05	< 0.05	3.33	0.23	0.10	7.89	0.328	0.0058	0.230	0.0756
High	3:1	< 0.1	< 0.1	< 0.05	< 0.05	5.45	< 0.04	< 0.05	7.92	0.601	0.0015	0.434	0.0907

At least three groups of leaching behaviors involving the different constituents that were included in this study have been noted. The first group of constituents shows a leaching behavior where leachate concentrations increase as a function of increasing amounts of ammonia in the acidic fly ash. Ammonia, arsenic, fluoride, molybdenum, pH, selenium, and vanadium are included in this leaching behavior group. The second group of constituents shows that their leaching characteristics are not changed/alterd by the elevated levels of ammonia in the acidic fly ash. Boron, bromide, chloride, and sulfate are included in this group of constituents. It should be noted that these four constituents are present as anions in the ash. The third group of constituents shows a leaching

behavior where leachate concentrations decrease as a function of increasing levels of ammonia in the ash. Cadmium, nickel, and zinc are included in this group.

In addition to these three groups of leaching behaviors, there is a fourth group of constituents that either showed no leaching or leached at very low levels. This group of constituents contains aluminum, nitrite, nitrate, chromium, copper, and mercury.

Constituents Showing Increased Leaching

The batch leaching results obtained for the constituents showing generally increasing leachability trends with increased ammonium levels on the fly ash are represented graphically in Figure 1 at the 3:1 leaching ratio.

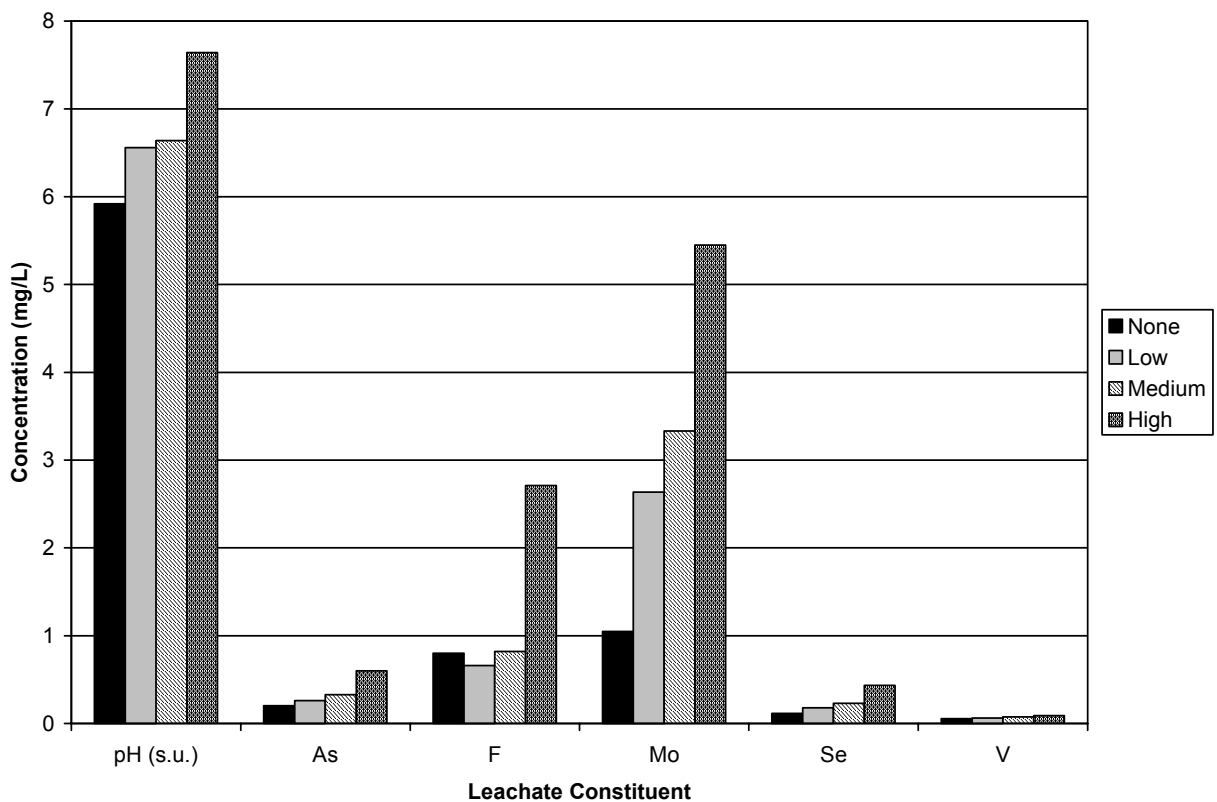


Figure 1. Constituents showing increasing leaching with increased ash ammoniation levels at the 3:1 leaching ratio.

Ammonia in Leachates: The ammonia concentrations in batch dilution leachates generated in this study were examined. As expected, ammonia concentrations in the leachates increase linearly because of an increase of ammonia levels in the acidic fly ash and because the increasing liquid-to-solid leaching ratios dilute the resulting concentrations of ammonia in the leachates. This set of results, therefore, indicates that ammonia in fly ash is quite soluble and easily leached. The highest ammonia concentration of about 85.5 mg/L in the ash leachate occurred when the acidic fly ash

containing 262 mg/kg ammonia was leached by the 3:1 water-to-ash extraction ratio. The lowest ammonia concentration of about 0.9 mg/L in the ash leachate occurred when the fly ash containing 77.4 mg/kg ammonia was leached by the 100:1 water-to-ash ratio. The unammoniated acidic fly ash sample leachate contained a relatively small amount of ammonia under all leaching conditions.

As a result of all of the leaching tests performed on the fly ash samples, it is clear that ammonia from ammoniated fly ash samples is readily dissolved by water. The potential leachate concentrations of ammonia in leachates are determined by the amount of ammonia in the ash. In this study, over 85 mg/L of ammonia concentration was measured in the leachate generated from an ammoniated acidic ash containing 262 mg/kg of ammonia extracted by a 3:1 liquid-to-solid ratio. This study suggests that acidic fly ash has the potential to retain quite high levels of ammonia likely due to the formation of ammonium sulfate.

pH of the Leachate: Figure 1 clearly indicates that the pH of the leachates increases with an increase in ammonia in the fly ash. This occurs regardless of the leaching ratio used. The pH of the ash leachate from unammoniated acidic ash was between 5.75 and 6.10, which increased to about 7.9 for the leachate from acidic fly ash containing 262 mg/kg ammonia. An increase in leachate pH can have some effect on leaching of ash constituents. But the actual effect of pH on leaching of ash constituents is not easily discernible from this dataset because of the confounding effect of ammonia concentrations in the ash.

Arsenic in Leachates: The arsenic concentration data show a couple of interesting trends. First, more arsenic from fly ash is leached when the ammonia concentration in ash increases. The highest arsenic concentration of about 0.6 mg/L is reached when the ammonia concentration in the ash is 262 mg/kg and the ash is leached using the batch dilution method. These results suggest that the arsenic present in the fly ash neither dissolves nor desorbs completely and is a source of sustained leaching from the fly ash.

Fluoride in Leachates: Figure 1 shows concentrations of fluoride in leachates from ammoniated ash at the 3:1 liquid-to-solid ratio. These results indicate that leaching of fluoride from fly ash increases in response to the higher concentration of ammonia in the fly ash. The fluoride concentrations in leachates from all ammoniated ashes become nearly the same at the 100:1 liquid-to-solid ratio.

Molybdenum in Leachates: Figure 1 shows concentrations of molybdenum in leachates from the three ammoniated ash samples. These results indicate that an increase in ammonia in fly ash results in a corresponding linear increase in leaching of molybdenum. However, the intensity of the linear correlation decreases as the leaching ratio increases.

Selenium in Leachates: Selenium shows a nonlinear increase in leaching in response to increases in the amount of ammonia in the fly ash. However, selenium concentrations in the leachates show a dilution effect when the leaching ratio increases.

Vanadium in Leachates: The data show an increasing pattern in leaching of vanadium when ammonia in the fly ash increases.

Constituents with No Effect on Leaching

Boron in Leachates: While there is some variability in the boron concentrations measured in the leachates, there is essentially no change in leaching of boron that can be ascribed to the presence of ammonia in the ash. Therefore, the presence of ammonia does not affect leaching of boron from the acidic fly ash.

Bromide in Leachates: The batch dilution extractions do not show any significant difference or trends in measured bromide concentrations in the leachates as a result of different ammonia levels in the acidic fly ash. Therefore, bromide leaching from fly ash is not affected by the amount of ammonia in the fly ash. Bromide shows dilution response as a function of increasing leaching ratio.

Chloride in Leachates: Table 2 shows concentrations of chloride in leachates from ammoniated acidic ash. These results show that leaching of chloride from the acidic ash does not increase or decrease by the levels of ammonia in fly ash. Chloride shows dilution response as a function of increasing leaching ratio.

Sulfate in Leachates: Coal ash contains sulfate in significant quantities. Therefore, concentrations of sulfate in the leachates from ammoniated ash were measured as part of this research. The amount of ammonia in ash does not increase or decrease (i.e., no change) sulfate concentrations in the leachates as depicted by these results. However, increases in leaching ratios do dilute and, therefore, decrease the sulfate concentrations found in leachates. From these test results, it can be concluded that leaching of sulfate from acidic fly ash is not affected by the presence or absence of ammonia in the fly ash.

Constituents Showing Decreased Leaching

The batch leaching results obtained for the constituents showing generally decreasing leachability trends with increased ammonium levels on the fly ash are represented graphically in Figure 2 at the 3:1 leaching ratio.

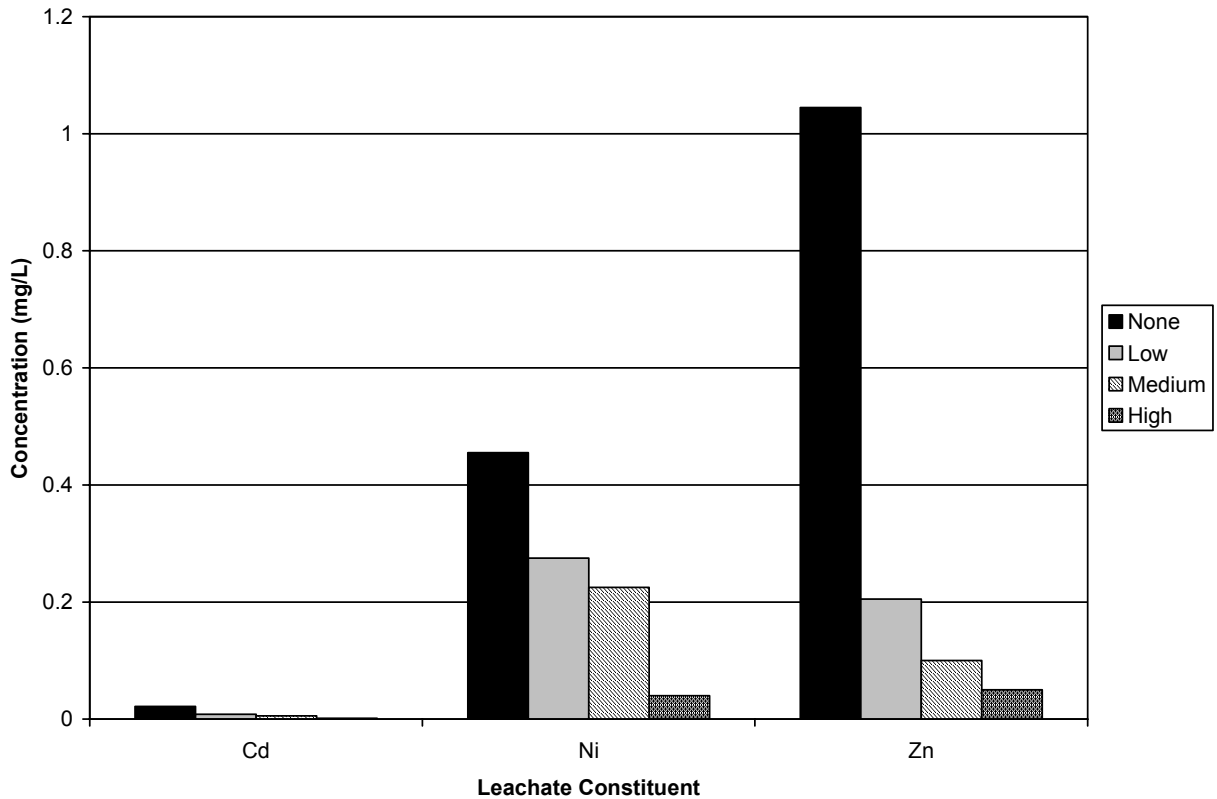


Figure 2. Constituents showing decreasing leaching with increased ash ammoniation levels at the 3:1 leaching ratio.

Cadmium in Leachates: Table 3 shows the measured concentrations of cadmium in leachates from the three ammoniated and one unammoniated acidic ash samples. These data suggest that the increasing levels of ammonia in the fly ash decreased leaching of cadmium from the fly ash. This trend is best noted for results from the 3:1 leaching ratio where the leachate from the unammoniated acidic ash contained about 22 $\mu\text{g/L}$ of cadmium and decreased to about 1.4 $\mu\text{g/L}$ in the leachate from the ash with 262 mg/kg ammonia. These results suggest that cadmium leaching is decreased by the addition of ammonia in fly ash, which is contrary to what would be expected with the potential for the formation of $[\text{Cd}(\text{NH}_3)_6]^{2+}$ and $[\text{Cd}(\text{NH}_3)_4]^{2+}$.

Nickel and Zinc in Leachates: Both nickel and zinc were below detection limits for leachates generated with the 27:1 and 100:1 leaching ratios. However, for the 9:1 and 3:1 leaching ratios, it appears that increasing levels of ammonia in the fly ash may be reducing the leaching of nickel and zinc contained in the acidic fly ash. This would not be expected for nickel or zinc, which form complexes with ammonia $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Zn}(\text{NH}_3)_6]^{2+}$.

Constituents Showing No or Low Leaching

Aluminum, Barium, Chromium, and Copper in Leachates: Table 3 presents measured concentration data for aluminum, barium, chromium, and copper in leachates from the three ammoniated ashes. Again, chromium and copper form highly soluble ammonia complexes $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Because of this, one would expect to see increasing concentrations for these two elements. It is likely the low concentrations limit the possibility of increased solubility, at least for this particular ash. Except for some variability in the leachate concentrations, these four constituents either do not leach at all or are near their detection limits and show no change in leaching characteristics as a result of the presence of ammonia in the acidic fly ash.

CONCLUSIONS

These leaching data/results for ammoniated fly ash samples clearly demonstrate that ammonia as ammonium ion is a highly soluble and easily leached constituent when present in acidic fly ash. Leaching of ammonium ion appears to be linearly related to the ammonia concentration in the ash. Acidic ash has a potential for retaining large amounts of ammonia from flue gas.

The presence of ammonia in fly ash does not appear to change the leaching characteristics of aluminum, barium, boron, chromium, copper, sulfate, chloride, and bromide contained in fly ash. Ammonia in the ash is not readily converted to nitrate and nitrite; therefore, nitrite and nitrate are absent from the leachates altogether. This is somewhat contrary to what might be expected, however, especially with copper which forms a highly soluble ammonium complex. Low concentrations of some of these trace elements along with an uncertain phase location are likely the cause for their low leachability.

Ammonia in ash results in decreased leaching of cadmium, nickel, and zinc contained in fly ash. However, the increasing levels of ammonia in fly ash increase leaching of arsenic, fluoride, molybdenum, selenium, and vanadium. Arsenic and selenium leaching chemistry appears to change the most because of the presence of ammonia in fly ash.

ACKNOWLEDGMENTS

This paper was prepared with the support of U.S. Department of Energy (DOE) under Cooperative Agreement No. DE-FC26-98FT40321. EPRI and Allegheny Energy also provided funding through Ish Inc. for this project. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of the DOE, EPRI, or Allegheny Energy.