

EFFECTS OF pH, ORP, AND CONDUCTIVITY ON LEACHING OF TRACE METALS FROM FLY ASH

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ABSTRACT

Leaching of metals from coal utilization by-products (CUB) is being studied to assess the potential for environmental damage. Samples contained in fixed-bed columns were leached with five lixiviants. The lixiviants simulated environmental liquids and varied from acidic to alkaline (pH 1 to pH 11). The leachates were analyzed for major and trace metals. Trace metals that formed cations were leached by acidic lixiviants although, in most cases, the total amount leached was small. The concentrations of metals were low initially, increased rapidly after the alkalinity of the CUB was depleted, then dropped rapidly after a maximum was reached. For normal Class F fly ash samples, the maximum concentrations of acid soluble trace metals in the leachate were typically less than 10 mg/L. A Class F fly ash produced during an SCR test produced leachates with much higher concentrations of metals. ORP appeared to be as good an indicator of leaching progress as pH while conductivity was a less indicative but possibly adequate monitor.

INTRODUCTION

Approximately one billion tons of coal is burned each year for the generation of electrical power in the United States. Between 10% and 15% of the weight of coal burned by utilities is recovered as coal utilization by-product (CUB). About 40 million short tons of CUB was produced in 1970, 66 million in 1980, 87 million in 1990, and 108 million tons in 2000 (ACAA, 2003). Only about 1/3 of CUB is currently being utilized (primarily for concrete and land fill); consequently, about 70 million tons per year is now accumulating. Fill material and materials in stockpiles will be exposed to naturally occurring liquids, possibly releasing contained metals. Leaching of metals from CUB is being studied at the National Energy Technology Laboratory (NETL). In order to understand the reactions of CUB in various situations, the U.S. Department of Energy (DOE) has been conducting leaching tests with acidic, neutral, and alkaline leachants that simulate liquids found in the environment (Kim, et al., 2003). This research estimates the amount of metals leached from various types of CUB while in storage and in anticipated beneficial uses.

EXPERIMENTAL

The CUB leaching columns were constructed of 1 meter sections of clear PVC pipe. The pipe had a 5 cm inside diameter and a volume of approximately 2 liters. PVC pipe caps closed each end of the column and had 1/4 inch NPT fittings tapped into them for lixiviant inflow or leachate outflow. Each column was loaded by putting ten grams of glass wool into an empty column and pushing it against the bottom cap. The CUB sample was then poured into the column and another 10 grams of glass wool was inserted. The top cap was attached and the sealed column was hung vertically. The column was then connected to the lixiviant delivery system. A peristaltic pump fed liquid from a reservoir containing 20 L of lixiviant to multiple leaching columns containing different CUB samples. A typical leaching test consisted of 4 samples with 5 different lixiviants for a total of 20 columns. Average flow rates with the peristaltic pumps were approximately 230 mL/day/column.

The lixiviants are described in Table 1. The deionized water ($>18.2 \text{ M}\Omega\text{-cm}$ warranty, $<10\mu\text{S}$ conductivity measured) was produced by a Millipore Corporation RO60 Milli-Q Reverse Osmosis (RO) Unit using building RO water as feed. All other solutions used this doubly RO treated water and Trace Metal Grade acids or certified A.C.S. grade anhydrous sodium carbonate to make the lixiviant.

Table 1. Lixiviants for Column Leaching Tests.

Lixiviant	ID	pH
Sulfuric Acid ¹	H ₂ SO ₄	1.2
Acetic Acid ¹	HAc	2.9
Synthetic Precipitation ²	SP	4.2
Deionized Water	H ₂ O	6.0
Sodium Carbonate ¹	Na ₂ CO ₃	11.1

¹Concentration = 0.1 N

² Deionized water adjusted to pH 4.2 with a 60/40 mixture of H₂SO₄/HNO₃

Class F fly ash samples were typically leached from 60 to 120 days until the acetic acid leachates were pH 4 or less. Leachate samples were collected at 2 to 3 day intervals. Samples were analyzed for pH, acidity or alkalinity, aluminum, calcium, iron, magnesium, manganese, potassium, sodium, sulfur and the toxic metals: antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc. Analyses of the leachates were done by ICP-OES.

This paper focuses on two fly ash samples. Sample A was produced in a commercial PC power plant burning an eastern coal and is a typical Class F fly ash. Sample B is also a Class F fly ash but was produced during selective catalytic reduction (SCR) operation.

Table 2. Chemical Composition of fly ash samples¹.

Trace Metal	Fly Ash A	Fly Ash B	Major Oxide, %	Fly Ash A	Fly Ash B
Antimony	NA	<6	Aluminum	23.32	25.31
Arsenic	<100	<8	Calcium	2.72	3.67
Barium	456	593	Iron	13.22	15.73
Beryllium	12	12.7	Magnesium	0.71	0.16
Cadmium	<15	7.5	Manganese	0.03	0.03
Chromium	184	125	Moisture	0.25	.21
Cobalt	40	40.4	Phosphorus	0.58	NA
Copper	93	58.6	Potassium	1.62	0.88
Lead	71	61.5	Sodium	0.47	0.80
Nickel	124	86.9	Silicon	46.55	NA
Selenium	7.6	13.3	Sulfur	1.00	1.18
Zinc	175	154	Titanium	1.06	0.85

¹ Trace Metal values are in mg/kg of fly ash and Major Oxide figures are in percent.

NA = Not Analyzed.

Mercury is absent from the above list because its reactions are more complex than the acid-base neutralizations that control the formation of other cations. Mercury will be discussed in several papers that are currently being prepared at NETL (NETL, 2003) to address new EPA regulations for Hg release from power plants (EPA, 2000).

Although a specific silica analysis was not done for sample B, it is about 49% silicon dioxide (calculated by difference). Most Class F fly ash samples are about ½ silica.

Generally, these two samples are chemically very similar with major oxides being within a few percent of each other and many trace metals being within 10 mg/kg of the other sample.

As is often the case with fly ash, the results of leaching these 2 samples were very different. Because the chemical analyses were similar (ie. 93 and 59 ppm copper for samples A and B), this indicates that the mineralogy of the samples were different (probably because of differing conditions during the ash formation). More information will be provided about sample B in a poster being presented at this conference (Cardone, et al.,2005).

RESULTS AND DISCUSSION

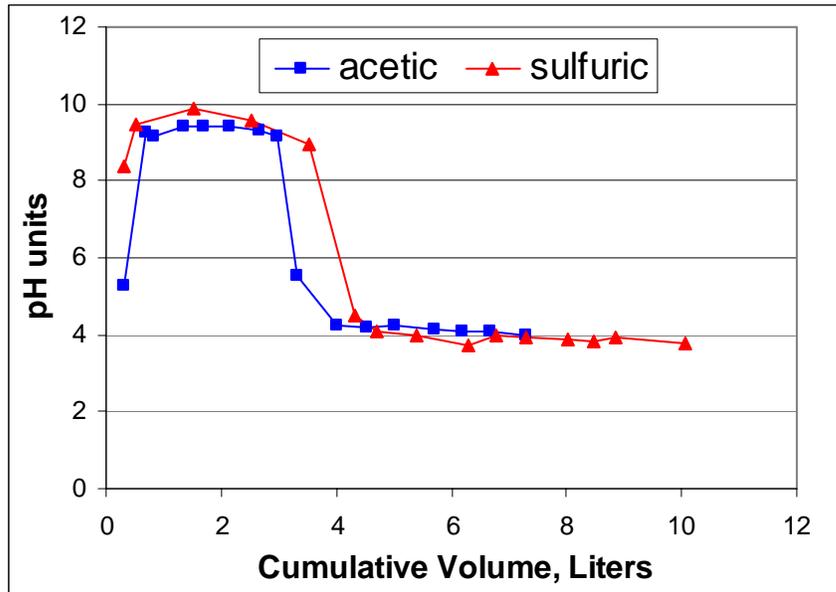


Figure 1, pH of Leachates for Acid Leaches of Sample A

Plots of pH vs liters of leachate recovered from the columns of sample A are shown in figure 1 for acetic and sulfuric acids. The acetic acid lixiviant acidified sample A with slightly less volume than the sulfuric even though the sulfuric solution was slightly stronger (0.101N versus 0.0994N). This may be caused by elements such as barium and calcium in the ash which removed sulfate from the lixiviant (precipitation of insoluble BaSO_4 and/or gypsum). High concentrations of calcium in the initial acetic leachates (~2000 mg/l) indicated rapid dissolution of individual alkaline particles or surface coatings on the fly ash particles (Figure 1 looks much like an alkalinity titration). If alkaline compounds had been inside the predominantly silica and alumina particles, a shallower pH decline curve would have occurred. Time was not an important factor in the acidification of sample A because the two acids produced similar curves in Figure 1 even though the acetic acid took 54% more time than the sulfuric acid (20 days versus 13 days because of different flowrates). Time might have affected the leaching if acid feed rates were higher; however, these tests were designed to keep the lixiviant and ash in equilibrium (saturated liquid) during the test. Figure 1 also shows that the kind of acid was not very important because (again) the two different acids have similar plots. Figure 1 shows that 3 liters of solution or about 300 milliequivalents (meq's) of acid were needed to overcome the initial alkalinity of A and make the pH start to fall. Until this much acid was added, the pH stayed high and the concentration of cation producing trace metals in the leachates stayed below the ICP-OES detection limit. Consequently, about 300 meq's of alkalinity would be available from each kilogram of this fly ash for beneficial uses such as the neutralization of acid mine drainage or animal wastes, before any release of metals to the environment would occur. Figure 1 shows that 4 liters of acid were needed to drop the pH to 4 in both the sulfuric and acetic acid leaches. The pH 4 figure was significant because most cations began leaching out of the fly ash at that level.

Neither water nor acid rain were able to drop the pH below 9 during these leaching tests because of the small amount of H^+ in those solutions (only 0.44 meq's of acid was added during the acid rain leaching test and even less H^+ was supplied in the deionized water and Na_2CO_3 tests). Consequently, cation forming trace metals were leached only by the acetic and sulfuric lixivants and the results of only those lixivants will be discussed further.

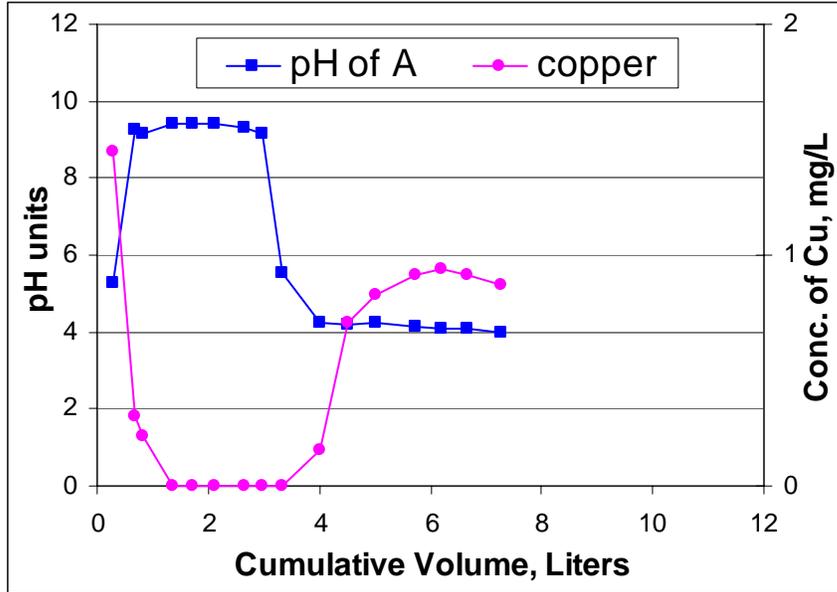


Figure 2, Concentration versus pH for Acetic Acid Leach of Sample A.

The concentrations of copper found in the acetic acid leachates of A are shown in figure 2. Copper is presented as an indicator of cation forming metals because it can be accurately analyzed down to very low levels and there is usually about 100 ppm of copper in most fly ash samples. Fly ash A had 93 ppm of copper. Because copper is soluble in acid solutions, it usually shows up in the leachates if it is present in the solid ash. Note that the beginning of the increase in Cu concentration in the leachates of A coincides with the fall in pH.

The graph of the sulfuric acid leach (not shown) looks very much like figure 2 with the pH dropping at about 3 liters of leachate recovered and all cation forming metals remaining below the detection limits until the pH falls to about 5.

Plots of pH versus liters of leachate for sample B are shown in figure 3 for acetic and sulfuric acid leaches. This sample is more alkaline than sample A and requires about twice as much acidic lixiviant or about 8 liters (800 meq's) to acidify the fly ash. The rapid fall from pH 9 to pH 4 also occurred in sample B as alkaline materials were depleted. The plots again show that slightly less acetic acid was needed to acidify the sample than sulfuric acid (probably for the reasons explained in the text below Figure 1). Interestingly, there was no initial low pH region as seen in Figure 1. The initial low pH readings of Figure 1 were apparently real because the initial metal concentrations reflected the low pH conditions (high metal concentrations).

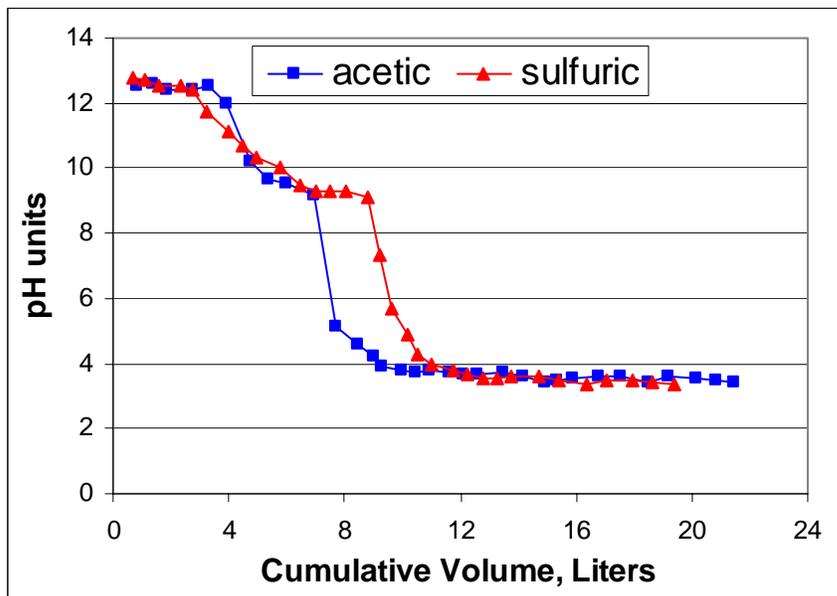


Figure 3, pH for Acid Leaches of Sample B

Sample B also appears to be a typical class F ash. It contains a few percent more aluminum, calcium, and iron than sample A but most trace metal analyses were similar (Table2). The maximum concentrations of metals in the acetic acid leachates of B were considerably higher than those of sample A. In the example of copper, this difference was more than 2 orders of magnitude (1 versus 300 mg/L). Since the chemical analyses of these samples would not explain such a great difference, other factors must be responsible (SCR gas treatment?).

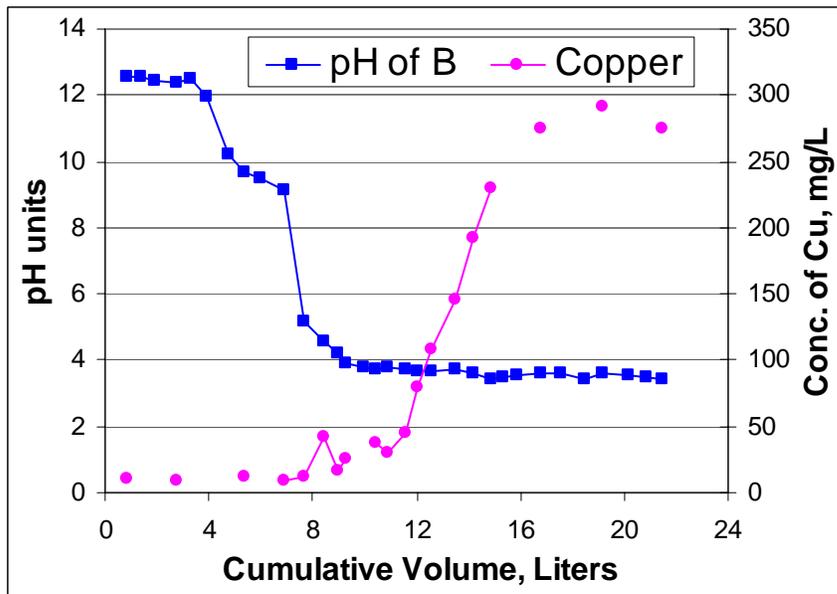


Figure 4, Concentrations versus pH for Acetic Acid Leach of Sample B.

The coincidence of the increase in copper concentration and the decrease in pH is also evident in Figure 4. Clearly, dissolution of cation trace metals is strongly related to pH.

Other factors that might affect metals release from fly ash include oxidation-reduction potential (ORP) and conductivity. The ORP and conductivity were taken for the period of interest during the acetic leaching of Sample B. The ORP results are shown in Figure 5.

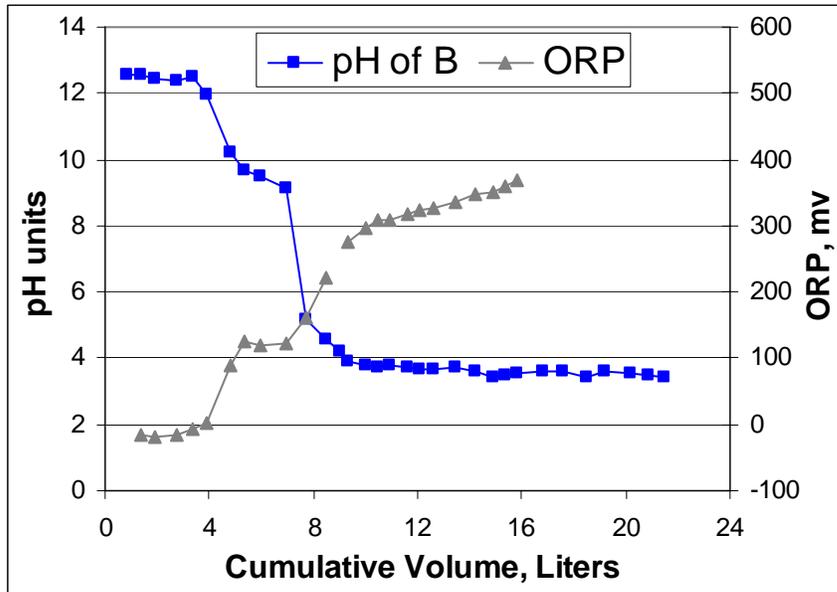


Figure 5, pH versus ORP for Acetic Acid Leaching of B

It can be easily seen that the pH and ORP responses are nearly mirror images of each other.

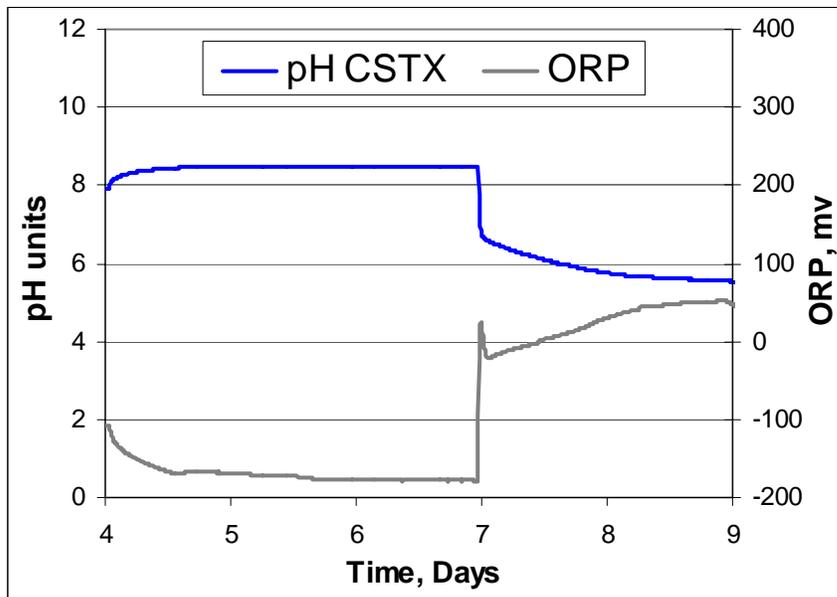


Figure 6, pH versus ORP for CSTX Leaching Test

Figure 6 is an even better example of the relationship of ORP and pH. This strong acid leach of a high calcium CUB was done by other NETL scientists (Kairies et al.2005). The X axis is plotted as time; but because the acid addition rate is constant, it could also be plotted in

volume as are the figures for samples A and B. Obviously, pH and ORP are interchangeable indicators of the depletion of alkalinity in the leaching of this CUB sample.

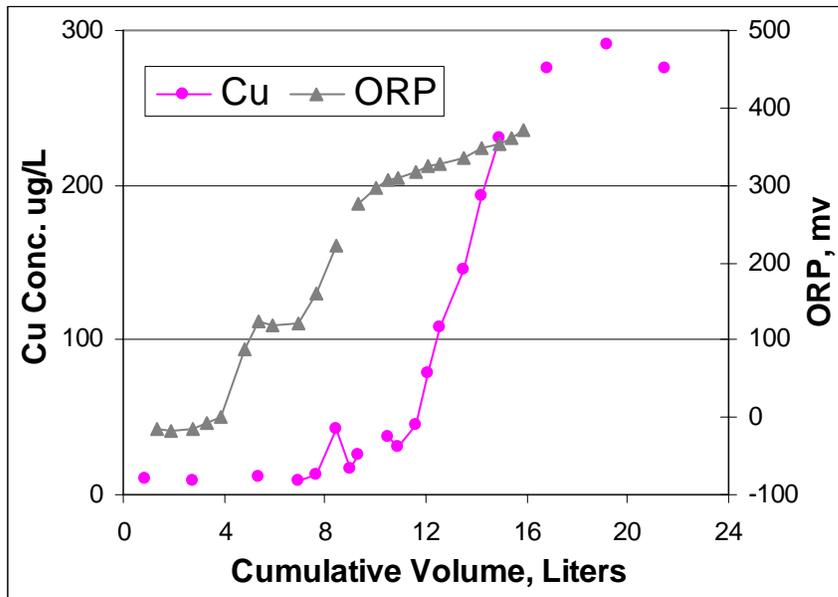


Figure 7, ORP versus Copper Concentration for Acetic Leaching of Sample B.

Although the relationship of ORP to metals release would be a direct or positive one (rather than the inverse or negative one of pH versus metals release); essentially, there would be little or no benefit to utilize ORP instead of pH to analyze the leaching operation. In theory, ORP should be a better indicator than pH but acid additions are the only significant factor influencing ORP so the two are equivalent. In practice, manual ORP readings take much longer to obtain than pH reading. Also, the ORP buffer solutions are more expensive and much more toxic than pH buffers. Consequently, there is no advantage to using ORP instead of pH for correlations of laboratory column leaching test data.

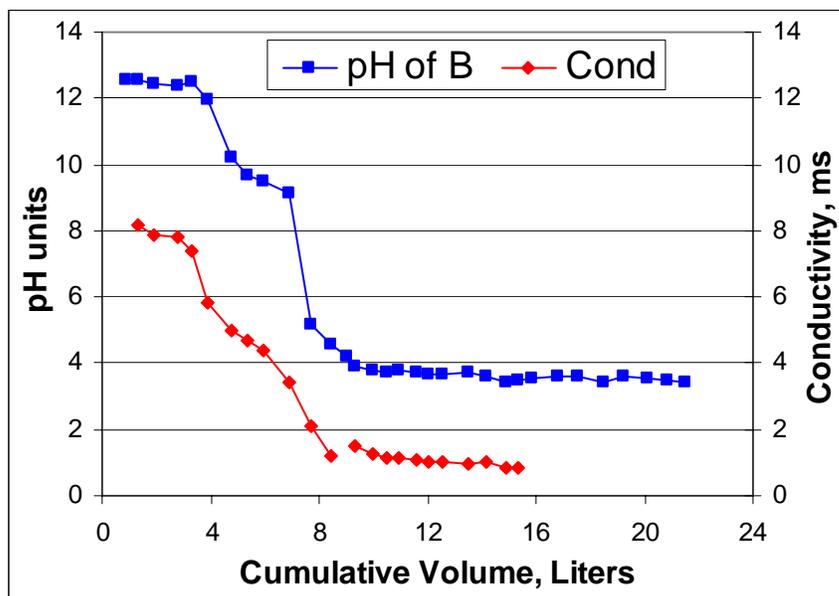


Figure 8, pH versus Conductivity for Acetic Leaching of Sample B.

The addition of acetic acid to the columns made the conductivity of the leachates decrease in roughly the same fashion as pH. This appears counterintuitive because adding ions (through acid additions and release of trace metals from ash) would normally increase the conductivity of solutions. However, the initial dissolution of calcium into the acetic acid lixiviant is very high (~2000mg/L) and continues at that (equilibrium) level until calcium is depleted. The concentration of calcium in the leachates then falls rapidly. This fall coincides with the drop in pH (plot not shown). The release of trace metals which follows the drop in pH adds only a few hundred mg/L of cations (at maximum) which is much less than the calcium lost. Consequently, the conductivity falls.

In some cases conductivity may be an easier way to monitor the release of metals from fly ash and therefore make a better field or industrial technique to detect the release of metals from fly ash. For laboratory work by experienced personnel, however, pH appears to be a better indicator of the depletion of alkalinity and therefore a better predictor of the imminent release of metals.

The plots for the sulfuric acid leaching of sample B look similar to Figures 4 through 8. Consequently, they are not presented for that lixiviant.

CONCLUSIONS

From Figures 1 and 3, it can be seen that the leachates of Class F fly ash samples undergo a sharp drop in pH when the alkalinity of the ash is depleted. Figures 2 and 4 show that release of metal begins right after the drop in pH occurs. Consequently, predicting (or preventing)

the release of metals from fly ash depends on knowing when the fall in pH occurs. Figures 5 and 6 show that pH and ORP are linked during acid leaching of CUB samples and that either one could be used to predict the release of metals. Figure 8 shows that conductivity roughly parallels pH during leaching. The change in conductivity is not as dramatic as that of pH; however, so it is not as clear an indicator of the release of metals.

Because plots of pH and ORP are nearly mirror images of each other, either one could be used equally well to predict the beginning of metal release from fly ash. Because of considerations such as time, cost, and toxicity of generated wastes, pH will continue to be used for monitoring the progress of acid leaching tests at NETL. Other operations may find ORP to be a better indicator for their purposes. Although conductivity is not as decisive an indicator as pH for predicting metals release, it may be more convenient for some installations (especially if conductivity is already being monitored). The final decision of which system should be used to monitor leaching progress will depend upon the nature of the operation and the experience of the personnel involved.

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