TVA/WR/WQ--90/4

DE91 005453

TENNESSEE VALLEY AUTHORITY

Resource Development
River Basin Operations
Water Resources

WATER QUALITY INVESTIGATION OF KINGSTON
FOSSIL PLANT DRY ASH STACKING

by

Charles E. Bohac
Water Quality Department

TVA/WR/WQ--90/4

Chattanooga, Tennessee

April 1990

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ps

CONTENTS

	Page
Tables	iv
Figures	v
Introduction	1
Predicted Changes in Ash Pond	3
Introduction	3
Theoretical Considerations	3
Ash Effects	5
Historical Alkalinity and pH	5
1988 Data Collection	5
1988 Data Analysis and Projected Impacts	8
Bottom Ash and Flow Considerations	17
Effect of Metal Loading	19
Coal Pile Drainage Effects	20
Settling Effects	26
Chemical Speciation	27
Summary	34
Impacts Resulting from Collected Leachate and Runoff	37
Introduction	37
Leachate Characteristics	37
Disposal of Collected Leachate and Runoff	47
Soil Attenuation Capability	51
Introduction	51
Kingston Soil Composition	51
Metal Attenuation	53
Impact on Domestic Users and Proposed Site Groundwater Quality . .	63
Domestic Users	63
Site Groundwater Quality	66
Conclusions and Recommendations	69
Conclusions	69
Recommendations	71
References	73
Appendixes	
A. Ash Pond Effluent Data	75
B. Settling Test Data	81
C. Bull Run Ash Pond Flow and pH	85

TABLES

Number	Page
1. Ash Pond Influent-Fly Ash	9
2. Pond River Data	11
3. Bottom Ash Sluice and River Intake	13
4. Ash and Sluice Water Volumes	14
5. Comparison of Fly and Bottom Ash Supernatants to River Water	21
6. Results for Minimum and Maximum pH-- Kingston Steam Plant	28
7. Kingston Fly Ash--Elemental Mass and Leachable Fractions	38
8. Kingston Rainwater Quality	40
9. Kingston Assumed Dry Ash Stack Characteristics	41
10. Comparison of Leachate Quality Estimates	42
11. Estimated Leach Time	45
12. Fowl Leachate Predictions Compared to Extraction Concentrations	46
13. Kingston Ash Pond Effluent Coal Pile Drainage and Predicted Leachate Composition Compared to Drinking Water Standards	48
14. Mineral Composition of Soils	52
15. Adsorption of Metals on Soil Minerals	55
16. Leachate Speciation	59
17. Comparison of Offsite and Site Groundwater Quality	65
18. Dry Fly Ash Disposal and Site Groundwater Quality	67

FIGURES

Number	Page
1. River and Ash Pond Alkalinity and pH	6
2. Titration Curves for Neutral Fly Ash Slurry with Coal Pile Drainage	23
3. Kingston Fossil Fuel Plant Well Sites	64

WATER QUALITY INVESTIGATION OF KINGSTON
FOSSIL PLANT DRY ASH STACKING

INTRODUCTION

Changing to a dry ash disposal system at Kingston Fossil Plant (KFP) raises several water quality issues. The first is that removing the fly ash from the ash pond could alter the characteristics of the ash pond discharge to the river. The second concerns proper disposal of the runoff and possibly leachate from the dry ash stack. The third is that dry ash stacking might change the potential for groundwater contamination at the KFP. This report addresses each of these issues. The effects on the ash pond and its discharge are described first.

The report is intended to provide reference material to TVA staff in preparation of environmental review documents for new ash disposal areas at Kingston. Although the investigation was directed toward analysis of dry stacking, considerations for other disposal options are also discussed.

This report was reviewed in draft form under the title "Assessment of Kingston Fossil Plant Dry Ash Stacking on the Ash Pond and Groundwater Quality."

PREDICTED CHANGES IN ASH POND

Introduction

Removal of the fly ash from the Kingston ash pond could change the discharge pH from its historical levels. Metals which were leached from the fly ash in the ash pond will no longer be present in the ash pond discharge. Changes in the ash pond pH will also change the form in which the metals leached from the bottom ash will be discharged to the river.

Because the other plant wastewater discharges are routed through the ash pond, their effect on the ash pond will be altered without the presence of the fly ash in the pond.

Alteration of the ash pond chemistry by removal of the fly ash might also produce different settling properties of the pond's suspended solids. This might result in a change in the suspended solids concentrations being discharged to the river.

Theoretical Considerations

Chu, et al. (1980) in studying the leaching of trace metals from power plant ash found the pH of the ash sluice water depended upon the relative amounts of alkaline metal oxides and sulfur oxides which dissolved in the water. The alkaline metal oxides of calcium, magnesium, potassium, and sodium produce a basic reaction with water as follows:

On the other hand, sulfur compounds react with water to produce acid. Using sulfur trioxide as a typical sulfur compound, the reaction with water is: $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{-2} + 2 \text{H}^+$

If the ash contains more equivalent leachable sulfur compounds than alkaline metal oxides, the ash sluice water will tend to have a depressed pH compared to the intake water prior to the ash addition. If the alkaline metal oxides predominate, the sluice water will tend to have an elevated pH.

The alkalinity and acidity of the intake river water will tend to buffer the effects of the ash. The alkalinity is defined as the capacity of the water to react with an acid while acidity is the capacity of the water to react with a base. The chemical species important to alkalinity are HCO_3^- , CO_3^{2-} , OH^- , and H^+ . The chemical species important to acidity are H_2CO_2 (CO_2 dissolved in water), HCO_3^- , H^+ , and OH^- . The pH is a function of the concentrations at which all these species equilibrate.

It is important to note that the total carbonate concentration composed of the sum of the H_2CO_3 , HCO_3^- , and CO_3^{2-} concentrations is theoretically not directly affected by the reactions involving the dissolution of sulfur and alkaline metal oxide species. In other words, because no carbonate is added or lost in the sulfur and metal oxide reactions, its concentration should remain constant even though the alkalinity and acidity would be changed. There are some indirect effects on total carbonate concentration, however, and they will be pointed out where they are important.

Ash Effects

Historical Alkalinity and pH

In 1974 and 1975 raw intake river water and ash pond effluent samples were collected on a weekly basis. Alkalinity and pH were measured and these data are shown in figure 1.¹ As figure 1 indicates the ash reduced both the alkalinity and the pH of the river water. Ash pond pH and raw river water were correlated using a linear regression model. The regression coefficient (R^2) was 0.69.

1988 Data Collection

In order to determine the effect of removing the fly ash from the ash pond, the change in alkalinity of the sluice water for the fly ash and the bottom ash were measured. This was determined over a three-day period in which samples were collected from the fly ash discharge channel a few feet below the discharge pipes. Samples were also collected from the bottom ash sluice pipes once every hour for eight hours each day. The bottom ash samples from the various operating pipes were composited each hour on an equal volume basis.

After holding two to three hours,² the conductivity, pH, temperature, alkalinity, and CO_2 acidity³ of the bottom ash and fly ash samples were measured. At the end of the eight-hour collection period each day, equal volumes from each of the eight fly ash and eight

1. The data for figure 1 are presented in table A-1.

2. Chu, et al. (1980) in working with Kingston fly ash found that alkalinity stabilized after holding two to three hours.

3. Titration to a pH = 8.3 end point.

FIGURE 1
RIVER AND ASH POND

bottom ash samples were composited. The conductivity, pH, temperature, alkalinity, and CO₂ acidity of the composite samples were then determined. Samples from each of the individual samples and the composites were then sent to the Environmental Chemistry Laboratory for total suspended solids (TSS) analyses. Samples of the composites were also sent to the Water Quality Department Unit Operations Laboratory where settling tests were run and the samples were decanted for mineral and metals analyses.

After visual observation of the samples and review of the field data, it was felt that the bottom ash samples did not contain enough bottom ash to be representative. Although at least one of the fly ash sluice lines operated almost continuously, the bottom ash hoppers were sluiced at most only once per shift. Because sluicing of the bottom ash hoppers only took 15-20 minutes per hopper, little bottom ash was collected.

Bottom ash sample collection was therefore repeated. This time arrangements were made with the Kingston personnel to start at one end of the plant and sluice the bottom ash hoppers one at a time. Sample collection personnel were notified by radio each time a new hopper was sluiced so that a sample could be obtained from that hopper. Seven samples were collected over an eight-hour period. Analyses were conducted for the previously described field parameters for the individual samples and for a composite made up of equal volumes of the individual samples. The chemical analyses and the settling tests were also repeated.

1988 Data Analysis and Projected Impacts

Fly ash data are shown in table 1. Table 2 shows the composition of the river water. Means for alkalinity, CO_2 acidity and pH for the individual samples for each day are also shown in table 1. Also shown in table 1 are two total carbonate concentrations as calculated from the alkalinity and pH plus CO_2 acidity (see Stumm and Morgan, 1981, for procedure).

Although the mean pH of the daily individual samples and the mean CO_2 acidity do not match the pH and the CO_2 acidity of the composites, there is fairly close agreement between the mean of the individual alkalinities and the alkalinity for the composite on that day. The reason the individual sample CO_2 acidities and total carbonate concentrations differ markedly from the composite values can be explained by the additional amount of CO_2 that the individual samples contained. When the individual samples, which were supersaturated with CO_2 , were mixed to make the composites, the CO_2 came out of solution and the pH rose about 0.5 units on two out of three of the composites. Because the CO_2 acidity is a function of the CO_2 concentration, the acidities for the individual samples were consistently higher than in the composites. Alkalinity is not a function of CO_2 and was used to estimate the change in ash pond pH rather than the observed change in sample pH which is a function of CO_2 concentration as discussed above. The CO_2 is likely dissolved in the sluice water when the sluice water picks up the ash. The pore volume of the fly ash in the hoppers is filled with CO_2 and it appears to go into the sluice water along with the ash.

Table 1. Ash Pond Influent—Fly Ash

March 1 to 3, 1988											
Date	Time of analysis	Temperature (°C)	Conductivity (µS)	pH s.u.	Alkalinity ^a (ppm)	Acidity ^a (ppm)	Total suspended solids (ppm)	CAL. C _T ^b (mM/l)			CHA-ALK/TSS ^d
								A+A	C _T	C _T	
March 1	0730	18.0	266	6.0	45	67	4800	2.70	2.24	2.24	0.0022
	0830	18.5	278	5.6	27	100	4800	3.26	2.54	2.54	0.0060
	0930	18.0	272	5.9	36	89		2.53	2.50	2.50	
	1030	18.0	252	5.8	36	81	4400	3.00	2.34	2.34	0.0045
	1130	18.0	280	5.8	33	73	5600	2.75	2.12	2.12	0.0041
	1230	18.0	250	5.8	29	98	3300	2.42	2.54	2.54	0.0081
	1330	18.0	273	5.6	20	80		2.42	2.00	2.00	
	1430	18.0	255	6.2	37	57	6200	1.67	1.88	1.88	0.0030
	Mean							2.59	2.27	2.27	0.0047
	Composite	1640	275	6.6	38	17	6500	1.14	1.10	1.10	0.0027
March 2	0730	11.0	32	5.9	43	67	4900	3.02	2.20	2.20	0.0029
	0830	11.3	310	6.4	49	45	6400	1.76	1.88	1.88	0.0013
	0930	16.5	290	6.3	42	52	5000	1.68	1.88	1.88	0.0031
	1030	16.2	300	6.2	45	34	7700	2.03	1.58	1.58	0.0016
	1130	16.2	280	6.2	45	37	4600	2.03	1.64	1.64	0.0027
	1230	16.8	300	6.4	46	38	6200	1.65	1.68	1.68	0.0018
	1330	18.0	255	6.5	54	42	4100	1.76	1.92	1.92	0.0008
	1430	19.0	260	6.3	46	58	5200	1.84	2.08	2.08	0.0022
	Mean							1.97	1.86	1.86	0.0021
	Composite	1650	260	6.3	46	58	6500	1.84	2.08	2.08	0.0017

Table 1 (Continued))

March 1 to 3, 1988											
Date	Time of analysis	Temperature (°C)	Conductivity (μS)	pH s.u.	Alkalinity ^a (ppm)	Acidity ^a (ppm)	Total suspended solids (ppm)	CAL. C _T ^b (mM/l)	A+A C _T ^c (mM/l)	CHA-ALK/TSS ^d	
March 3	0730	18.0	260	6.1	36	62	6400	1.86	1.96	0.0038	
	0830	18.0	250	6.1	37	64	4300	1.92	2.02	0.0054	
	0930	18.0	250	6.0	42	78	3700	2.52	2.40	0.0050	
	1030	18.2	297	6.1	46	62	5300	2.38	2.16	0.0027	
	1130	17.8	330	6.2	46	58	6700	2.08	2.08	0.0021	
	1230	18.0	305	5.9	38	79	6100	2.67	2.34	0.0031	
	1330	18.0	240	6.2	40	77	4600	1.81	2.34	0.0044	
	1430	18.0	240	6.0	30	68	4500	1.80	1.96	0.0067	
Mean											
Composite	1725	18.0	280	6.6	43	22	8300	2.13	2.16	0.0042	
								1.29	1.30	0.0021	

a. As CaCO₃

b. Total carbonate concentration in millimoles/l, calculated from pH and alkalinity

c. Total carbonate concentration in millimoles/l, calculated from sum of alkalinity and CO₂ acidity

d. Change in alkalinity per mg of fly ash; river water alkalinity minus ash sluice alkalinity divided by TSS

Table 2. Pond River Data

March 1 to 3, 1988								
Date	Time	Temperature (°C)	Conductivity (μS)	pH s.u.	Alkalinity ^a (ppm)	Acidity ^a (ppm)	CAL. C _T ^b (mM/l)	A+A C _T ^c (mM/l)
March 1	0821	8.0	205	7.0	58	4	1.39	1.24
	1215	9.0	170	7.7	53	4	1.10	1.14
	1530	9.0	195	7.8	56	3	1.15	1.18
	Mean			7.5	56.7		1.19	1.19
March 2	0715	9.0	170	7.8	61	3	1.25	1.28
	1300	9.0	190	7.8	56	2	1.15	1.16
	1600	9.0	195	7.8	55	3	1.13	1.16
	Mean			7.8	57.3		1.18	1.20
March 3	0710	9.0	180	7.9	50	2	1.02	1.04
	1240	10.0	205	8.0	59	2	1.20	1.22
	1625	10.0	230	7.9	72	4	1.47	1.52
	Mean				60.3		1.23	1.26

b. Total carbonate concentration in millimoles/l, calculated from pH and alkalinity

c. Total carbonate concentration in millimoles/l, calculated from sum of alkalinity and CO₂ acidity

a. As CaCO₃

Table 3 shows the bottom ash and river data collected during the second bottom ash sampling effort. As seen in table 3, neither the alkalinity nor the pH of the river water was decreased by the bottom ash. In fact, the pH of the river water and possibly the alkalinity appear to have been raised. In addition, there was no CO_2 effect as the CO_2 acidity remained constant.

Table 4 shows ash and sluice water volumes for the past two years of operation and the values assumed for future operation of KFP. Based on the volumes shown in table 4, the present fly ash sluice concentration is about 7500 mg/l and the bottom ash sluice concentration is 16,700 mg/l. The mean alkalinity decrease per mg of TSS of fly ash, as shown in table 1, was 0.0034 mg/l as CaCO_3 /mg of fly ash. Using the mean of all the samples shown in table 1 for the changes in alkalinity per unit of ash, the expected alkalinity change is 24 mg/l for the fly ash. Therefore, removal of the fly ash from the ash pond would suggest that the alkalinity in the ash pond would be higher than it historically has been.

Although the data in table 3 indicate that the alkalinity of the river water might have been increased by the bottom ash, the increase is probably less than the mean value of 0.0039 mg/l/mg of bottom ash as shown in table 3. The difference between the sluice water alkalinity and the river water alkalinity is small. With only one river water sample it is not possible to say if such a small difference in alkalinity is a real difference or not. However, the pH difference is of interest and does suggest that the alkalinity has indeed increased. The pH increase probably is a real increase because the pH values are higher than the high

Table 3. Bottom Ash Sluice and River Intake

March 14, 1988									
Collection Time	Analyze Time	Unit sampled	Temperature (°C)	Conductivity (μS)	pH s.u.	Alkalinity ^a (ppm)	Acidity ^a (ppm)	Total suspended solids (ppm)	CAL. C _T ^b (mM/l)
0735	0935	1	17.5	96	7.8	18	1	130	0.369
0740	0940	6	17.4	102	8.1	20	1	12000	0.402
0925	1125	3	18.0	108	8.8	22	0	21000	0.421
0950	1150	7	18.3	108	9.0	23	0	2100	0.428
1040	1240	8	17.3	108	9.2	23	0	20000	0.411
1045	1245	4	16.5	102	9.5	23	0	110000	0.372
1205	1405	9	17.0	92	8.1	15	1	1500	0.301
Mean									0.386
Composite		-	17.5	110	9.1	23	0	2700	0.420

River Sample--Intake

March 14, 1988							
Collection Time	Temperature (°C)	Conductivity (μS)	pH s.u.	Alkalinity ^a (ppm)	Acidity ^a (ppm)	CAL. C _T ^c (mM/l)	
1235	11.0	87	7.4	15	1	0.323	

a. As CaCO₃

b. Total carbonate concentration in millimoles/l, calculated from pH and alkalinity

Table 4. Ash and Sluice Water Volumes

	1985	1986	1987	Mean
Bottom ash (tons)	90,527	95,145	84,684	90,119
Fly ash (tons)	362,107	380,580	338,736	360,474
Bottom ash sluice (gpm)		2,455		
Fly ash (gpm)				
New ESP		11,140		
Old ESP		4,140		
Mechanical		6,750		
Ash pond discharge (gpd)		34,000,000		
Fly ash concentration (mg/l) (both fly and bottom ash volumes included)		7,500		
Bottom ash concentration (mg/l) (bottom ash sluice volume only)		16,700		

range of the river water pHs shown in figure 1. Another argument for the bottom ash giving rise to only a small increase in alkalinity is that the river water was so poorly buffered that an increase in alkalinity of only 3 mg/l with a total carbonate concentration of 0.323 millimoles/l (the observed river total carbonate concentration, C_T , in table 3) would give a pH equal to the composite value pH of 9.1. Also if the total carbonate concentration of the river water were really 0.42 millimoles/l, which is the value of the composite carbonate concentration, then the alkalinity would really be about 20 mg/l. A pH of 9.1 would then result if the alkalinity rose only 3 mg/l to 23 mg/l, which is the composite alkalinity in table 3. The variability in the river water alkalinity observed in table 2 certainly suggests that the alkalinity of the river water might have been closer to the mean of the individual samples of 20.6 mg/l rather than 15 mg/l as observed in the sole river sample on March 14.

Ash pond pH is a function of ash/sludge water ratio, the initial pH of the sludge water, and the alkalinity of the sludge water. Because insufficient data were obtained to calculate the ash/sludge water ratio on a daily or weekly basis, the ash/sludge water ratios corresponding to the alkalinity and pH data shown in figure 1 cannot be calculated. However, it is useful to calculate the expected ash pond pH without fly ash by using the assumed ash/sludge water ratio shown in table 4 and the alkalinity and pH of the sludge water for several extreme cases of low ash pond pH as shown in figure 1. The calculations were performed assuming the total carbonate concentration (C_T) is constant. This assumption is consistent with the reaction theory and is appropriate

after the CO_2 scrubbed by the fly ash is allowed to degas as the composite samples shown in table 1 have done.

Assuming that the bottom ash has little effect on the alkalinity of the sluice water, removing the fly ash from the ash pond should significantly raise the pH of the ash pond. For example, for the data shown in figure 1, the lowest ash pond pHs are found when the river water alkalinity is low. On March 26, 1975 the alkalinity of the river was 5 mg/l as CaCO_3 and the pH was 6.9. Using the change in alkalinity (acidity) for the fly ash at the assumed ash/sluice ratio shown in table 4 and assuming the total carbonate concentration is unchanged, the calculated ash pond pH is about 3.5 compared with the observed pH of 3.4. For this example, which is typical, all the pH change in the low alkalinity range can be explained based solely on the presence of the fly ash. Therefore, if all other inputs to the ash pond are ignored except the bottom ash, removing the fly ash from the pond when the river water alkalinity is low should result in pHs similar to the river water pHs.

When the river water alkalinity is high, river pH tends also to be in the high range. Although the fly ash has historically lowered the alkalinity of the ash pond, the pH of the sluice water has often remained high when high alkalinity was present in the intake water. For example on August 6, 1975 the alkalinity of the river water was 83 mg/l as CaCO_3 and the pH was 8.4. Using the same fly ash reduction of 24 mg/l as before, the resulting alkalinity in the ash pond should have been 59 mg/l. Assuming total carbonate to remain constant, the corresponding new pH should have been about 6.7. Although the ash pond alkalinity did

indeed decrease even more than predicted to about 50 mg/l, the pH remained relatively constant at about 8.

Although the bottom ash could hold the pH up through the dissolution of magnesium and calcium oxides, such dissolution that would be reflected by a smaller decrease in the alkalinity. Because the alkalinity did decrease as expected but the pH stayed high, the total carbonate concentration must have decreased. This could have occurred because the additional aluminum, calcium, magnesium, and iron from the ash precipitated with the carbonate (the water softening effect). Lowering the total carbonate concentration would enable the pH to remain high even though the alkalinity were lowered. This hypothesis was verified using the chemical equilibrium code MINTEQ to conduct a chemical simulation of the potential reactions. Concentrations of metals and minerals observed in the ash pond discharge over the years 1974-75 were used (Chu, et al., 1976) in conjunction with the August 6, 1975 intake water alkalinity and pH conditions. MINTEQ predicted that the total carbonate concentration would indeed decrease by the precipitation of calcite which allowed the pH to remain constant at 8.4 as observed in the ash pond data. Although MINTEQ predicted the precipitation of aluminum and iron as well as calcium, the aluminum and iron precipitated as oxides and hydroxides and not carbonates. In addition, the loss of carbonate was larger than the loss of hydroxide.

Bottom Ash and Flow Considerations

Up to this point the discussion has assumed that the water flow rates through the ash pond will remain at its current level of about 34 mgd. This assumption is appropriate if a water inductor system is

used to provide the vacuum required for the ash collection system. Presently the water used for this purpose is also used to sluice the collected ash to the pond.

One possible dry ash system would be to use water to provide the necessary system vacuum but not mix the ash in the inductor water. In this case, large amounts of water would still be diverted to the ash pond. Bull Run uses such a system. The discharge flow rate from the Bull Run ash pond has changed little since the dry ash stack went into operation in 1984-85 (see appendix C).

Another type of system would use something other than water eductors such as vacuum pumps to provide the system vacuum. In this case, all the water presently used to evacuate the ash from the ash collection systems and sluice it to the ash pond would no longer be present in the ash pond. The bottom ash sluice water would then become the major contributor of water to the ash pond.

If the fly ash sluice water were removed from the ash pond as well as the fly ash, then the bottom ashes influence on the pond would significantly increase. The question concerning dissolution of the alkaline metal oxides is more important without the fly ash sluice water present than with it, especially for the high alkalinity, high pH condition for the river water. It is important because it implies that if significant dissolution of calcium and manganese oxides does come from the bottom ash, the pH would go up more than just that attributable to the increase in alkalinity. The pH would also rise because of the precipitation of the carbonate. Therefore, even though the limited data collected and analyzed for this assessment suggest that the bottom

ash should have little effect on alkalinity, this suspicion should be verified because of the potential for increases in pH even greater than the alkalinity effect alone if it does. For example, if the alkalinity of the river water were 83 with a pH of 8.4 and total carbonate concentration of 0.00165 moles/l (same data as the August 6, 1975, example), and the bottom ash increased the alkalinity to 100 (17 mg/l increase)¹ and the total carbonate concentration remained unchanged, the resulting pH would be about 9.5. If the alkalinity were to rise to 100 and the total carbonate were to drop an amount equivalent to the calcium carbonate which would precipitate, the pH would rise higher than 10.

A modest increase in alkalinity when the river water alkalinities were low and poorly buffered also shows the potential for driving the pH above 9. For example, on November 20, 1974 the alkalinity of the river was 7 and the river pH was 7.4. A 10 mg/l increase in alkalinity would increase the pH to about 10 and possibly higher if the carbonate precipitation were also considered.

Effect of Metal Loading

The literature suggests (Ainsworth and Rai, 1987) that arsenic, boron, chloride, fluoride, sulfur, and selenium are concentrated on the

1. With the fly ash sluice water present, the effects of the bottom ash are diluted by about 10 to 1 and, therefore, the alkalinity change induced by the bottom ash would likely be insignificant. The average alkalinity increase in table 3 and the bottom ash concentration of table 4 combine for a predicted alkalinity increase of over 60 mg/l although an increase of this magnitude has been discounted by earlier arguments.

surface of fly ash at significantly higher levels than in bottom ash. Thus these elements are expected to be at higher concentrations in leachates from fly ash than bottom ash. Aluminum, calcium, iron, and silicon are found at about the same percentage in both fly and bottom ash and thus the concentrations of these elements in the leachates are expected to be about the same.

Table 5 is based on only two samples but shows the elemental composition of supernatant from settled fly and bottom ash obtained in the Unit Operations Laboratory settling tests. The data in table 5 generally follow the literature prediction discussed above. In addition, table 5 shows that the calcium concentration in the fly ash was elevated from that of the river.

Using the assumed ash/sludge water ratios for bottom and fly ash discussed above and conservatively assuming that the elemental contribution to the ash pond is the same per unit weight of both fly and bottom ash, the mass loading of metals to the pond will be only 20 percent of the present loading. Therefore, dry stacking the ash might significantly reduce the mass of metals discharged to the river.

Coal Pile Drainage Effects

Other waste streams are routed into the ash pond before discharge to the river. The metal cleaning waste discharge could be of high pH, but low in metal content (iron ≤ 1 mg/l) due to the treatment in the metal cleaning pond. The coal pile drainage is not treated and can contain high concentrations of metals and can be very acidic.

Table 5. Comparison of Fly and Bottom Ash Supernatants to River Water

	River water <u>March 3, 1988</u>	Fly ash supernatant composite <u>March 3, 1988</u>	Bottom ash supernatant composite ^a March 16, 1988
	Total	Dissolved	
Sulfate, mg/l	26	62	22/20
Cadmium, µg/l		1.1	0.3/<0.1
Zinc, µg/l	<10	10	30/30
Iron, µg/l	340	2.0	2500/60
Manganese, µg/l	84	32	61/22
Magnesium, mg/l	7.9	7.8	3.1/2.9
Calcium, mg/l	25	38	15/14
Copper, µg/l	<10	<10	<10/<10
Aluminum, µg/l	110	<50	2200/<50
Selenium, µg/l		14	<1/<1
Chromium, µg/l		10	3/<1
Arsenic, µg/l		130	28/22
Boron, µg/l		170	<50/<50
Sodium, mg/l	5	5.6	3.2/3.1
Lead, µg/l		<1	5/1
Lithium, µg/l		<10	<10/<10
Barium, µg/l		410	160/100
Chloride, mg/l	4	4.5	3.5/3.5
Silica, µg/l			2200/1700
TDS, mg/l			72/
SS, mg/l			160/

a. Total concentration/dissolved concentration

Cox, et al. (1979), found pH values typically below 3 and acidities¹ ranging up to 6000 mg/l as CaCO_3 . Historically, the ash pond has diluted and helped neutralize the coal pile drainage.

Although the Kingston fly ash reduces the alkalinity of the ash pond, there is, on average, still residual alkalinity left in the sluice water to neutralize the coal pile drainage acidity. Removing the fly ash sluice water from the ash pond and assuming that the bottom ash has no effect on alkalinity, the alkalinity available to neutralize the coal pile drainage on a yearly average basis will be reduced by 80 percent. The coal pile drainage would be 4 percent of the sluice water volume without the fly ash sluice water as compared to about 0.4 percent with the fly ash sluice water.

Figure 2 shows the titration of a Kingston fly ash slurry with coal pile drainage containing an initial acidity of about 9100 mg/l as CaCO_3 .

The acidity of the coal pile drainage will react with the residual alkalinity in the ash sluice water. For the 1.09 percent slurry curve shown in figure 2, the residual alkalinity at the start of the titration has been backcalculated to be about 30 mg/l. However, because the slurries all start at the same initial pH, they must have the same residual alkalinity. If the coal pile drainage were then to react only

1. The acidity described by Cox, et al. (1979) was determined by titrating to a pH of 7.0. This is not consistent with the classical definition of either CO_2 acidity (pH=8.3 endpoint) or total acidity (pH=10.2). For this discussion it is assumed that most of the acidity is mineral acidity with very little CO_2 acidity by comparison. Therefore, the acidity determined by Cox, et al., is assumed to be total acidity.

FIGURE 2

FIGURE 2. TITRATION CURVES FOR NEUTRAL FLY ASH SLURRY WITH COAL PILE DRAINAGE

with the residual alkalinity, the titration curves for each slurry should be the same. The curves are not the same, however.

Because the different slurry concentrations should consume different amounts of alkalinity, the initial pH of each slurry concentration would be expected to be different. Because all the curves start at the same pH it is suspected that the initial dissolution of sulfur and alkaline species has already taken place and the pH was adjusted to the same initial value. If this were so, then the coal pile drainage would be reacting with the alkaline metal oxides on the fly ash solids as the coal pile drainage is titrated. The 2.5 percent slurry shows more neutralizing capacity indicating that more alkaline species were dissolved under this assumption compared to the lower concentration slurries. Under this assumption, subsequent titration with the acidic coal pile drainage is a reaction with the alkaline metal oxides which dissolve as the pH is lowered and help buffer the pH upward.

Because the fly ash sluice water is about 90 percent of the total sluice water flow for the bottom ash and fly ash combined, it supplies most of the alkalinity to neutralize the acidic coal pile drainage. Using average river alkalinity and an assumed alkalinity decrease of 24 mg/l with fly ash addition, the fly ash sluice water still supplies over 80 percent of the alkalinity in the ash pond on an average annual basis. If the fly ash were removed but the fly ash sluice water remained, the alkalinity in the ash pond would increase by almost 90 percent from its existing levels on an average yearly basis. This assumes no additional dissolution of alkaline species from the fly ash due to the presence of the coal pile drainage.

Based on mean concentrations presented by Cox, et al. (1979), the Kingston coal pile drainage accounts for about 16 percent of the ash pond acidity on an annual average basis. This amount of acidity might decrease the pH of the ash pond as it is presently operated by about 0.5 units under average river alkalinity and pH conditions. The coal pile drainage influence would, of course, be greater under extreme conditions of high rainfall with low river alkalinity. If the fly ash were removed from the ash pond but the fly ash sluice water remained, the acidity of the ash pond would drop and the alkalinity would increase. The result would be that the coal pile drainage would have less than an 0.5 unit impact on pH and hence be less of an impact than at present.

If the fly ash sluice water were no longer in the ash pond, the coal pile drainage would account for 72 percent of the ash pond acidity. Based strictly on carbonate equilibrium, the ash pond pH would be less than 4 with average river alkalinity conditions and assuming that the bottom ash does not actually add alkalinity (this assumption was justified and used earlier). However, the second scenario discussed above is that the acidity of the coal pile drainage causes more alkaline oxides (calcium oxide, etc.) in the ash to dissolve than would dissolve under more neutral conditions. This in effect would add alkalinity to the ash pond and help neutralize the coal pile drainage at a pH higher than that predicted by carbonate equilibria. Although FOWL¹ does not support this hypothesis (FOWL indicates that about the same total amount of calcium would leach at pH 7 as pH 4), it still bears investigation

1. See next section for a discussion on FOWL.

because of the experimental condition of FOWL. Also Cox, et al. (1979), suggest that the reactions involving the acidity of the coal pile drainage in the ash pond are complex and carbonate equilibria might not be entirely applicable.

If the fly ash and its sluice water were removed from the ash pond, the coal pile drainage might contribute as much as 70 percent of the ash pond acidity which could potentially affect the discharge pH to a much greater extent than at the present. Because of the lack of data, especially concerning the additional dissolution of alkaline metal oxides in the bottom ash as the pH is lowered which could neutralize the coal pile drainage, a prediction of the precise impact is not possible at the present.

The effects of other waste streams such as the demineralizer waste are unknown but should be investigated when additional data on the bottom ash are collected.

Settling Effects

Settling tests were conducted on the fly ash and the bottom ash in the Unit Operations Laboratory in an attempt to determine the effect of removing the fly ash stream. Zone settling rates were determined using 1000 ml graduated cylinders. Fly ash slurries of the composite samples in table 1 settled at rates ranging between 0.03 and 0.11 ft/hr with poor reproducibility.

The bottom ash slurry of the composite sample in table 3 settled at rates ranging between 0.37 and 140 ft/hr. The lower value, which is believed to be more representative sample, was calculated from the slope

of a line with an R-squared value of 0.995. Settling of the ash in the pond would, therefore, be much more rapid if the fly ash is removed.

Data from fly ash and bottom ash slurry settling tests appear in the figures in appendix B.

Chemical Speciation

The results of metal speciation calculations on the Kingston ash pond at both high and low pH values are shown in table 6. During periods of low ash pond pH, the highest concentrations of soluble iron, copper, cadmium, zinc, nickel, lead, aluminum, manganese, arsenic, and selenium are expected. pH adjustment before discharge would help reduce these levels, but the precipitation kinetics have not been examined so it is not possible to say whether the present pH adjustment system provides sufficient time for such metal removals. Removal of the fly ash from the ash pond might reduce the levels of some trace elements, but much of the iron and manganese in the ash pond comes from the coal pile drainage and pyrite in the coal crusher and pulverizer rejects. The coal pile drainage also contains arsenic and selenium. These metals would be very soluble if the acidity of the coal pile drainage prevailed in the ash pond. All four of these elements sometimes exceed the Drinking Water Standard (DWS) in the ash pond effluent.

Possible excursions into the high pH range will help precipitate most metals. However, copper, beryllium, selenium, and potentially arsenic, will possibly remain as soluble complexes. Of these four elements, only arsenic and selenium are potentially important in relation to Kingston. Selenium appears to just shift oxidation states

Table 6. Results for Minimum and Maximum pH--Kingston Steam Plant

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
Ca	Ca^{+2}	7.5×10^{-4}	99.3	
	CaSO_4			
	$\text{CaCO}_3(2)$			98.8
Mg	Mg^{+2}	2.9×10^{-4}	99.1	27.4
	MgSO_4			
	MgCO_3			66.7
	MgCO_3^+			5.3
K	K^+	2.2×10^{-5}	99.8	99.8
Na	Na^+	9.7×10^{-5}	99.9	90.6
	NaCO_3^-			9.4
Fe	Fe^{+3}	2.1×10^{-5}	5.0	
	FeOH^{+2}		47.3	
	Fe(OH)_2^+		45.8	
	$\text{Fe(OH)}_3(s)$			100.0
	Fe(OH)_4^-			

Table 6 (Continued)

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
Cu		6.9×10^{-7}		
	Cu^{2+}		99.2	
	CuSO_4			
	CuSO_3			2.2
	$\text{Cu}(\text{CO}_3)_2^{-2}$		-	97.8
Ba		1.5×10^{-6}		
	Ba^{+2}		11.4	4.3
	$\text{Ba}_3(\text{AsO}_4)_2(\text{s})$			53.0
	$\text{BaCO}_3(\text{s})$			42.7
	$\text{BaSO}_4(\text{s})$		88.6	
Cd		5.1×10^{-9}		
	Cd^{+2}		98.8	18.6
	CdCO_3			45.1
	CdSO_4			
	CdOH^+			28.5
	$\text{Cd}(\text{OH})_2$			7.2
	$\text{Cd}(\text{OH})_3^-$			
	$\text{CdCO}_3(\text{s})$			
Zn		4.7×10^{-7}		
	Zn^{+2}		99.3	
	ZnSO_4			
	$\text{Zn}(\text{OH})_3^-$			
	$\text{Zn}(\text{OH})_4^{-2}$			
	$\text{ZnSiO}_3(\text{s})$			99.2

Table 6 (Continued)

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
Ni		5.4×10^{-7}		
	Ni ⁺²		99.3	
	NiSO ₄			
	Ni(CN) ₄ ⁻²			2.9
	NiOH ⁺			1.5
	Ni(OH) ₂ (s)			95.1
Hg		1.2×10^{-9}		
	Hg(CN) ₂		95.3	100.0
	Hg(OH) ₂			
	HgBr ₂		4.7	
Pb		3.4×10^{-8}		
	Pb ⁺²		98.0	
	PbSO ₄		1.8	
	Pb(OH) ⁺			
	PbCO ₃			1.4
	Pb(CO ₃) ₂ ⁻²			98.6
Ag		4.6×10^{-8}		
	Ag ⁺		52.3	
	Ag(CN) ₂ ⁻			100.0
	AgCl		4.5	
	AgBr		21.7	
	AgBr(s)		18.7	

Table 6 (Continued)

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
Al		4.8×10^{-5}		
	Al^{+3}		78.9	
	AlSO_4^+		1.1	
	AlF^{+2}		17.6	
	AlF_2^+		1.3	
	AlOH^{+2}		1.2	
	$\text{Al}(\text{OH})_3(\text{s})$			97.3
	$\text{Al}(\text{OH})_4^-$			2.7
	$\text{Al}_2(\text{OH})_2(\text{SiO}_3)_2(\text{s})$			
Be		5.5×10^{-7}		
	Be		97.3	
	BeF^+		2.2	
	BeF_2			
	BeOH^+			99.7
NH_3		9.8×10^{-6}		
	NH_3			76.0
	NH_4^+		100.0	24.0
NO_3^-		-		
	NO_3^-			

Table 6 (Continued)

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
CO_3^{-2}		2.5×10^{-5}		
	CO_3^{-2}			45.2
	HCO_3^-			53.2
	H_2CO_3		99.8	
	CaCO_3^+			
	$\text{CaCO}_3(\text{s})$			1.2
SO_4^{-2}		6.9×10^{-4}		
	SO_4^{-2}		96.7	99.9
	HSO_4^-		1.8	
	CaSO_4			
Cl		1.4×10^{-4}		
	Cl^-		100.0	100.0
Br		4.3×10^{-5}		
	Br^-		100.0	100.0
F		1.0×10^{-5}		
	F^-		2.5	99.9
	AlF^{+2}		84.2	
	AlF_2^+		12.2	
SiO_3		5.6×10^{-5}		
	HSiO_3^-			61.5
	H_2SiO_3		99.7	37.6

Table 6 (Continued)

Species	Form	Total analytical concentration	Low pH (3.3) percent of each form	High pH (9.5) percent of each form
CN		1.9×10^{-7}		
	CN^-			13.3
	HCN		98.8	4.1
	$\text{Ni}(\text{CN})_4^{-2}$			33.0
	$\text{Hg}(\text{CN})_2$		1.2	1.3
	$\text{Ag}(\text{CN})_2^-$			48.4
As		5.3×10^{-7}		
	H_2AsO_4^-		99.9	
	$\text{Ba}_3(\text{AsO}_4)_2(\text{s})^a$			100.0
Se		8.0×10^{-8}		
	SeO_3^-			97.7
	HSeO_3^-		89.1	2.3
	H_2SeO_3		10.9	

a. Could oversaturate and not form.

(s) = Solid (precipitate)

Source: Bailey, 1987

as a function of pH and remain soluble. A barium solid could precipitate arsenic as indicated by studies at high pH which have shown a tendency for supersaturation of the solids (Turner, 1981). Although possibly existing as soluble complexes at the high pH, there is evidence that arsenic and selenium are readily adsorbed by precipitated iron oxides and hydroxides (Rai and Zachara, 1984).

Summary

The fly ash appears to be largely responsible for depressing the pH of the river water used for sluicing, especially during times of low river alkalinity. Removal of the fly ash then would seemingly significantly raise the pH of the ash pond during periods of the year when it historically has been low.

Limited data and analysis suggest that the pH of the river water is not significantly affected by the bottom ash. However, under several conditions such as when the ash pond pH has historically been high (high river pH usually associated with high river alkalinity), a small increase in alkalinity coupled with carbonate precipitation might drive the pH above 9. A modest increase in alkalinity when the river water alkalinity was low and poorly buffered also shows the potential for driving the pH above 9.

Because of the potential sensitivity of the ash pond pH to the dissolution of alkaline metal hydroxides, their effect warrants further investigation. If it is found that bottom ash does indeed raise the pH

significantly, a pH adjustment system might be required to lower the pH during the same periods of the year.

Presently the fly ash sluice water significantly masks the effect of the coal pile drainage. Removal of the fly ash sluice water could change the ash pond behavior dramatically. Therefore, the above conclusions might only be appropriate during dry weather when little coal pile drainage would be present.

Although enough data do not presently exist to determine the extent of the impact, the available data do suggest that the coal pile drainage might be more difficult to neutralize in an ash pond without the fly ash sluice water. Therefore, even though the removal of the fly ash would help raise the pH during times of low river alkalinity as discussed above, the coal pile drainage could potentially overwhelm the bottom ash sluice neutralizing capability not only during times of low river alkalinity, but under conditions of average alkalinity as well. The coal pile drainage and bottom ash sluice combination needs further investigation.

IMPACTS RESULTING FROM COLLECTED LEACHATE AND RUNOFF

Introduction

The estimation of leachate quality is important for two reasons. Leachate from a dry stack might be collected and its need for treatment prior to disposal needs to be assessed. The leachate might also reach the groundwater. The next section will discuss how leachate and runoff quality were estimated. The following sections will discuss the implications if the leachate were to be collected and the possibility of the leachate reaching the groundwater will be discussed last.

Leachate Characteristics

Fly ash leachate quality was estimated in several ways. The first was to use Kingston fly ash elemental analyses supplemented with literature values to determine the mass of elements present in the fly ash and the amount which might be leached from the fly ash. Table 7 lists the results of this compilation. The first elemental analysis of Kingston fly ash corresponds closely with the means of nine fly ash samples based on bituminous coal fired in a tangential boiler. These data were reported by Rai (1987a). Because the first Kingston fly ash analysis shown in table 7 was not complete, literature values were used for the missing elements. Because of the close agreement on the composition of major elements as discussed above to those in the literature, the literature values for other elements missing in the Kingston analysis were considered appropriate.

A second and more complete Kingston fly ash elemental analysis was conducted. The second analysis was based on 60 percent mechanical fly

Table 7. Kingston Fly Ash—Elemental Mass and Leachable Fractions

Element	Mass (mg/kg) ^a	Mass (mg/kg) ^a	Mass (mg/kg) ^b	HOT H ₂ O	Leachable Fraction ^{a(3)}	
					Acid	Best estimate
Al	147,000 (1)	133,200 (2)	90,100	0.0012	0.167	0.17
As	111 (2)		12	0.03	1.9	1
B	525	12	12	0.32	0.79	0.8
Ba	1,013 (2)	156	156	0.008	0.77	0.8
Ca	19,000 (1)	21,000 (2)	8,520	0.0587	0.714	0.5
Cd	12 (3)		1	0.0029	0.297	0.3
Cr	150 (2)		44	0.0192	0.427	0.4
Cu	122 (2)		65	0.0044	0.393	0.4
Fe	40,000 (1)	72,600 (2)	25,000	5×10 ⁻⁶	0.393	0.4
Mg	8,000 (1)	7,460 (2)	9,960	0.0059	0.371	0.4
Mo	28 (2)		38	0.432	0.871	0.9
Na	3,000 (1)	4,000 (2)	880	0.0186	0.157	0.16
Ni	139 (2)		45	0.0016	0.330	0.3
S	3,000 (1)	4,200 (2)	1,452	0.214	—	1
Se	11 (2)		0.1	1	1	1
Si	220,000 (1)	230,880 (2)	325,700	0.00048	0.0008	0.008
Sr	709 (2)		5,398	0.0283	0.46	0.46
Zn	347 (2)		58	0.0024	0.357	0.36
K	25,000 (1)	19,500 (2)	9,840	0.00735	0.135	0.14
Ti	7,000 (1)	6,500 (2)	1,878	7×10 ⁻⁶	0.107	0.11
P	4,400 (1)	1,410 (1)	—	0.001	0.565	0.57
Mn	267 (2)		67	0.0042	0.602	0.6

a. Source Key:

- (1) Kingston fly ash sample 87-5250—"first Kingston analysis"
- (2) Mean from 9 samples (EA-5321, Ainsworth and Rai, 1987)
- (3) Mean from table 4-1 (EA-5321, Ainsworth and Rai, 1987)

- b. Kingston fly ash sample 88192-9124; 60 percent mechanical and 40 percent ESP—"second Kingston analysis"

ash and 40 percent electrostatic precipitator fly ash. This is the composition assumed for the dry stack. The first Kingston fly ash sample contained no mechanical ash. As table 7 shows, the elemental composition of the fly ash in the second sample is lower for all elements except magnesium, molybdenum, silica, and strontium.

Analyses of rainwater collected at Kingston and shown in table 8 and physical parameters shown in table 9 were then used with a pre-release version of FOWL to generate an estimate of leachate quality. The assumptions shown in table 9 were based upon preliminary results of the Bull Run dry ash stack investigations (Young, 1988). FOWL is the Electric Power Research Institute's computer code which calculates the quantities, aqueous concentrations, and release durations of selected inorganic elements leached from fossil fuel wastes (Hostetler, et al., 1988).

Two steady-state concentrations were predicted by FOWL based on a pH of 3 and another of 4. The predictions are shown in table 10. Also shown in table 10 are data from other sources which can be used to determine whether the FOWL predictions are reasonable. The first estimate is the range of two samples taken from eleven groundwater wells in and around the Kingston ash pond during 1976 and 1977. The second data set is the 1977 well sample which most closely matched the predicted pH of the leachate and as supplied as input to FOWL Run 1. The third data set is from well samples obtained in March of 1988 from the same well in the ash pond dike as sampled in 1977 and the fourth is from another well in close proximity. Two borings were made through the Bull Run dry ash

Table 8. Kingston Rainwater Quality

01/13/81 to 07/14/81					
Parameter	Total rain sampled (liters)	Minimum concentration to date (mg/l)	Maximum concentration to date (mg/l)	Weighted mean to date (mg/l)	Total milligrams to date
Acid acidity	16.63	0.05	0.54	0.15	2.53
SO ₄	16.63	1.20	5.60	2.57	42.78
NO ₃	16.63	0.04	3.70	1.09	18.12
PO ₄	16.63	0.04	0.24	0.06	1.05
F	16.63	0.02	0.07	0.03	0.49
Cl	16.63	0.23	0.70	0.42	7.02
NH ₄	16.63	0.01	0.54	0.19	3.19
K	16.63	0.02	0.30	0.08	1.29
Na	16.63	0.01	0.48	0.16	2.63
Ca	16.63	0.11	0.97	0.19	3.11
Mg	16.63	0.01	0.10	0.02	0.33
H+	16.65	7.94E-03	1.26E-01	5.66E-02	9.43E-01

ANALYSIS OF pH TO DATE

<u>Total rain sampled (liters)</u>	<u>Minimum</u>	<u>Maximum</u>
16.65	3.90	5.10

Table 9. Kingston Assumed Dry Ash Stack Characteristics

Area	50 acres
Average depth	20 feet
Bulk density	1.2 gm/cm ³
Initial volumetric moisture content	20 percent
Net infiltration	19 cm/yr
Saturation moisture content (porosity)	45 percent
Field capacity	38 percent

stack and the water near the bottom of the stack was collected and analyzed (Young, 1988). These data are shown as the fifth and sixth data sets. The next reference data set is that of the analysis of one sample of the runoff from the Bull Run dry ash stack. The last data set shows the range of concentrations observed in the Kingston ash pond discharge over the period 1973-1974 as measured with quarterly grab samples.

The concentrations predicted by FOWL at pH 4 (Run 2) are shown in table 10. All appear to be the same order of magnitude as a range defined by the other measured concentrations in table 10. However, the concentrations of some elements increase substantially at pH 3 (Run 1). In particular, chromium, molybdenum, cadmium, copper, iron, zinc, and arsenic all increase by an order of magnitude compared to the prediction of pH 4. It is expected that the initial pH of leachate at the stack bottom could well be about 3 or less. Because of the low pH and alkalinity of the rainwater and because approximately 4.4 feet of fresh ash over a 50-acre site would be applied for every 0.66 feet of net infiltration, there will be very little buffering of the pH.¹ Therefore, an initial leachate pH of 3 to 4 appears likely.

The estimate for arsenic from FOWL appears high compared to all other reference concentrations except the maximum concentration observed in the ash pond is the same order of magnitude. If the concentrations

1. For example, the rainfall pH and acidity were used to estimate the pH of a solution with 7600 mg/l of ash (10^{-5} more dilute than 4.5 feet of ash in 0.6 feet of water). The result was pH = 3.4.

1
predicted by FOWL at pH 3 for arsenic,¹ chromium, copper, iron, zinc, and cadmium are appropriate, they will exceed the Drinking Water Standards (DWS).

pH is the variable FOWL uses to predict leachate concentration. The importance of the ash matrix composition, which is also supplied as input to FOWL, is in the estimate of the leaching time. The estimated times to leach the various elements from the ash, based on the ash samples of table 7, are shown in table 11.

Table 12 compares the FOWL leachate predictions to the results of EP toxicity and TCLP extraction tests. The EP toxicity test is conducted at pH 5 with the pH adjusted during the course of the extraction. The TCLP extraction starts at pH 5 but the extraction is allowed to seek its own pH as the extraction proceeds. Often a pH higher than 5 is observed at the end of the extraction. Runs 1 and 2 of FOWL are for pHs below 5. FOWL predicts increased leachate concentrations for most elements with decreasing pH. Because the FOWL leachate estimates are for lower pHs than used in the extractions, the leachate concentrations are lower. FOWL was run again at pH 5. The predicted leachate concentrations at this pH are closer to those of the extractions shown in table 12.

1. Exploration into the inner workings of FOWL revealed that the minimum concentration for arsenic predicted will be about 100 µg/l. Therefore, FOWL's arsenic prediction for this case might not be very accurate.

Table 11. Estimated Leach Time

Element	Leach Time (Years)		
	Matrix 1 ^a		Matrix 2 ^b
	pH=3	pH=4	pH=3
Aluminum	2.4×10^4	2.4×10^5	1.4×10^4
Barium	1.2×10^5	1.2×10^5	1.8×10^4
Calcium	900	930	400
Chromium	550	5600	160
Molybdenum	67	520	91
Silica	250	250	380
Strontium	7400	7700	5.1×10^4
Sulfur	310	360	150
Arsenic	4100	3.9×10^4	450
Boron	6600	5600	150
Cadmium	1000	4060	90
Copper	760	7700	400
Iron	2.5×10^5	1.2×10^6	1.6×10^5
Magnesium	7500	1.4×10^4	9400
Sodium	2500	2200	740
Nickel	2100	8200	680
Selenium	4.4×10^5	4.4×10^5	4000
Zinc	736	6400	120

a. Matrix 1 = "first Kingston analysis"

b. Matrix 2 = "second Kingston analysis"

NOTE: A higher pH will reduce the leachate concentration for most elements but increase the leach time.

Table 12. FOWL Leachate Predictions Compared to Extraction Concentrations

Parameter	FOWL			EP toxicity	TCLP
	pH=3	pH=4	pH=5		
Aluminum, mg/l	4.1	4.0	0.5		
Barium, mg/l	0.3	0.2	0.2	<0.1	<0.1
Calcium, mg/l	394	394	396		
Chromium, mg/l	4.2	0.05	0.002	<0.05	<0.003-0.10
Molybdenum, mg/l	14.5	1.9	0.75		
Silica, mg/l	26	27	27		
Strontium, mg/l	1.7	1.6	1.6		
Sulfate, mg/l	1114	960	950		160-340
Boron, mg/l	2.4	2.9	3.3		
Cadmium, mg/l	0.2	0.03	0.009	<0.005-0.02	<0.002
Copper, mg/l	2.4	0.2	0.02		
Iron, mg/l	2.5	0.5	0.1		<0.005
Magnesium, mg/l	16.1	8.8	4.8		
Sodium, mg/l	7.4	8.5	9.7		
Selenium, mg/l	0.0001	0.001	0.001	<0.002	<0.002
Zinc, mg/l	6.5	0.7	0.3		
Arsenic, mg/l	1.0	0.1	0.1	<0.002	<0.002
Manganese, mg/l					0.29-0.44
Nickel, mg/l	0.8	0.2	0.5		0.1-0.15
Mercury, mg/l				<0.0002	<0.0002
Lead, mg/l				<0.05	<0.01
Silver, mg/l				<0.01	<0.002
Thallium, mg/l					<0.05-0.1
Beryllium, mg/l					<0.002
Antimony, mg/l					<0.04

The extraction test data shown in table 12 indicates the fly ash to be a nonhazardous waste and suitable for disposal in landfills.

Disposal of Collected Leachate and Runoff

The collection of leachate at the new dry ash disposal facility at Kingston might be undertaken to reduce the flux of leachate into the groundwater. This would likely be done with an underdrain system installed beneath the stack during its construction. Regardless of whether or not leachate is collected, runoff from the stack will be collected. The implications of its disposal will be discussed as well.

Although an underdrain system might be used to collect leachate from the dry stack, leachate might still be collected even if an underdrain system is not used. The subbase might be constructed to be highly impermeable. Leachate encountering the low permeability of the subbase might then follow the natural slope of the site from the hillside toward the river. Near the river at the toe of the stack, a ditch might be provided to prevent site runoff from flowing directly to the river. Substantial volumes of leachate might also find their way to such a ditch even if no underdrain system were provided.

The FOWL concentrations at pH 3 (Run 1) exceed those observed in the one sample of the Bull Run runoff. Therefore, the estimates from FOWL (Run 1) will be used as a conservative estimate of the runoff from the Kingston dry ash stack.

Table 13 compares the yearly mean trace metal concentrations of Kingston ash pond effluents to DWS. Table 13 also shows trace metal and

Table 13. Kingston Ash Pond Effluent Coal Pile Drainage and Predicted Leachate Composition Compared to Drinking Water Standards

Plant	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Se	Zn	Ba	SO ₄
Coal pile runoff ^a	3	B	B	B	3143	B	562	B	B	1.3	B	38
FOWL ^a	10	20	84	2.4	8.3	-	-	-	1.3	B	B	4.4
Ash pond ^b	2/1.5	0/-	0/-	0/-	4/3.5	0/-	5/4.2	0/-	3/1	0/-	-	-

a. Entries are coal pile drainage or predicted leachate concentration divided by drinking water standard; B denotes the ratio is below 1.0.

b. Entries are: Above slash--number of years during period 1976-1980 ash pond effluent concentrations exceeded drinking water standards. Below slash--average concentrations for those years divided by drinking water standards.

Source: The coal pile runoff and ash pond entries are from Betson and Bohac (1987).

sulfate concentrations of Kingston coal pile drainage compared to DWS. This comparison is presented to show that the constituent concentrations in the coal pile drainage are generally higher for iron and sulfate than those predicted by FOWL. FOWL predicts arsenic, cadmium, chromium, and copper to be higher than the coal pile drainage.

At the present, the coal pile drainage is impounded and then pumped to the ash pond. Cox, et al. (1979) found that 73 percent of the total rainfall resulted as direct runoff from the approximately 50-acre coal pile at Kingston. Data from the Bull Run dry ash stacking study presently underway suggests a runoff volume from the exposed part of the stack of only up to 5 percent of the rainfall. Leachate generation is expected to only be up to 15 percent of the rainfall for a combined total of 20 percent of rainfall (Young, 1988). This would assume that all leachate is collected as previously described. Assume that, at a maximum, 50 acres of the fly ash in the dry ash stack would be rained upon at one time.¹ Using this assumption, the leachate/runoff collected from a 50-acre dry ash stacking facility should, therefore, be only 28 percent of the volume of the coal pile drainage.

The coal pile drainage is treated by pumping it to the ash pond. If the dry ash stack leachate/runoff were disposed of in a similar fashion, impounding prior to pumping to the ash pond would be recommended to equalize the flow to the ash pond during large storm events.

1. It is expected that eventually a low permeability cap would be applied to the dry ash stack and that no more than 50 acres of ash would be exposed at any one time.

Should the arsenic, cadmium, and chromium estimates made by FOWL turn out to be appropriate, dilution of these elements with the bottom ash sluice water would, on a yearly average, be about 100 to 1. If little storage were provided for the leachate/runoff such that the dilution by the bottom ash sluice water were only 10 to 1 during heavy rains, cadmium and chromium might still be 2 to 8 times the DWS. Although a higher pH in the ash pond than assumed for the leachate/runoff might reduce these concentrations, these concentrations would appear to increase the concentrations above what has historically been observed in the ash pond discharge. If water volumes equivalent to those presently used for fly ash disposal were maintained, the cadmium and chromium concentrations should be less than the DWS. Under this scenario, the leachate/runoff effects on the ash pond would probably be insignificant.

If treatment prior to pumping to the ash pond were needed, the arsenic could be precipitated with barium. Providing a pH between approximately 7 to 11 would theoretically reduce the solubility of chromium to less than the DWS (Rai, et al., 1986). Theoretically, the solubility of cadmium could be reduced to the DWS by providing a pH of 8 or greater (Rai, et al., 1987). Raising the pH out of the acidic range would reduce the iron concentrations and sulfate and zinc could be diluted by the bottom ash flow.

SOIL ATTENUATION CAPABILITY

Introduction

There are two processes by which the migration of dissolved metals can be attenuated by soils. The first is precipitation and the second is adsorption. The solubility of some metals is controlled by the presence of the same metal in a mineral phase of the soil. High concentrations of a particular metal might, therefore, be precipitated because the pore water is already in equilibrium with a particular metal found in a soil mineral. Precipitates might also form as the pH or oxidation-reduction potential of this leachate changes as it moves through the soil. Soil minerals can also adsorb ionic species and remove them from further migration.

Kingston Soil Composition

X-ray powder diffraction and polarized-light microscopy were used to determine the soil minerals and to estimate their relative abundance in two Kingston soil samples. The soil samples were obtained during the soil core drilling activity and were selected by the soils engineer onsite as being representative of the soil at the proposed dry ash stacking facility. The soils at this site were primarily classified as clay or chert or mixtures of both. Therefore, one sample (4) which was typical of the material logged as clay and another sample (3W) typical of the material logged as chert were submitted for analysis. The estimated composition of the two samples is as shown in table 14.

Table 14. Mineral Composition of Soils

Mineral	Percent Composition	
	Sample 3W	Sample 4
Quartz	70-80	50-60
Kaolinite (primary) and Halloysite (secondary)	20-30	40-50
Goethite	5-10	5-10

Quartz, which predominates in both samples is a silicon oxide. It often controls no precipitation/dissolution reactions of importance to the trace metals. It can adsorb some metals, however.

Two clay minerals are present, kaolinite and halloysite. Kaolinite is comprised of silica, aluminum, and water. Halloysite is an aluminum silicate as is kaolinite except halloysite contains more water than kaolinite and is amorphous. Chemically, these clay minerals can be important to precipitation or dissolution reactions of aluminum. The clays are very important adsorbents.

The last mineral of importance in the soils is goethite, which is a hydrous iron oxide. This mineral is important to the solubility of iron and may also be an important adsorbent.

Metal Attenuation

The potential attenuation of selected metal migration due to precipitation and adsorption will now be discussed. The discussion is based upon Rai and Zachara (1984) and Rai, et al. (1987).

Arsenic is adsorbed by iron oxides and, therefore, the goethite could be a help in retarding arsenic migration. Barium is also adsorbable on hydrous iron oxide and clays. Boron, although adsorbable on iron oxide, shows its maximum adsorption on clays between pH 7.5 and 10. This pH is probably much higher than will be experienced at Kingston.

At the concentration of cadmium predicted by FOWL, hydrous iron oxides are effective specific adsorbents for cadmium. Clay can also adsorb cadmium although high calcium concentrations compete for adsorption sites and reduce the adsorption on both clays and iron

oxides. The calcium concentrations predicted by FOWL might, therefore, be a negative factor for cadmium adsorption. Studies of goethite and clays have also shown this is true for copper which will adsorb on these minerals.

Chromium species are adsorbed by iron oxides and clay under acidic conditions. The adsorption capacity of chromium on kaolinite is a function of pH and is greatest at low pH expected at Kingston.

Most often iron is controlled by solubility reactions and not adsorbed especially in the expected acidic pH range of the Kingston leachate.

Manganese can be adsorbed by clay minerals and iron oxides but few data exist. At the expected pH of the leachate, most manganese will be soluble so any attenuation would have to be through sorption.

Molybdenum is predicted to be adsorbed by hydrous iron oxides and amorphous alumino-silicates. Goethite has been studied and found to be an important adsorbent for nickel. Clay minerals, especially between pH 5.5 and 8.5 are important adsorbents for nickel. Selenium has been found to be removed by specific adsorption in the acidic pH range by hydrous iron oxides and amorphous alumino-silicates. Selenium is not, however, predicted to appear in the leachate in significant concentrations.

Zinc would likely be specifically adsorbed by iron oxide. The adsorption is pH dependent, however.

Table 15 shows the estimated capacity of a cubic foot of soil beneath the dry ash stack to absorb selected metals. The adsorption data used in the calculations are from Rai and Zachara (1984). The capacity

Table 15. Adsorption of Metals on Soil Minerals

Element	pH	Concentration at which data obtained M	Assumed concentration M (mg/l)	Adsorbent	Capacity (years)
Chromium	3	10^{-4} - $10^{-2.2}$	$10^{-4.1}$ (4)	Kaolinite	2.5
	7	10^{-4} - $10^{-2.2}$	$10^{-4.1}$ (4)	Kaolinite	3.6
Manganese	4.9	0 - $10^{-2.9}$	$10^{-4.1}$ (4.5)	Kaolinite	20
Arsenic (V)	6	10^{-4} - 10^{-2}	$10^{-4.9}$ (1)	Kaolinite	18
Cadmium	5-6	$10^{-2.3}$ - $10^{-1.3}$	$10^{-5.7}$ (6.2)	Kaolinite	0.6^a -7.6
Copper	-	10^{-4}	$10^{-4.4}$ (2.4)	Goethite	20
	5.5	$10^{-5.8}$ - $10^{-3.8}$	$10^{-4.4}$ (2.4)	Kaolinite	20
Iron	3	$10^{-5.5}$ - 10^{-5}	$10^{-4.5}$ (2.5)	Goethite	68
Molybdenum	4	10^{-7} - 10^{-5}	$10^{-3.8}$ (4.5)	Kaolinite	157
Nickel	-	$10^{-3.7}$ - $10^{-4.8}$	$10^{-4.9}$ (0.8)	Kaolinite	43
	6	$10^{-4.4}$	$10^{-4.4}$ (2.4)	Goethite	94
Selenium (V)	3-11	10^{-3} - 10^{-5}	$10^{-5.4}$ (0.34)	Goethite	7.6
	3	10^{-3} - 10^{-4}	$10^{-5.4}$ (0.34)	Kaolinite	5

Table 15 (Continued)

Element	pH	Concentration at which data obtained M	Assumed concentration M (mg/l)	Adsorbent	Capacity (years)
Zinc	5	$10^{-4.3}$ - $10^{-2.9}$	10^{-4} (6.5)	Goethite	5
	6	$10^{-4.3}$ - $10^{-2.9}$	10^{-4} (6.5)	Goethite	25

Soil density = 100 lb/ft³, 30% kaolinite, 5% Goethite

Net infiltration = 19 cm/ft² (15% of precipitation)

a. Clay saturated with calcium.

shown in table 15 is expressed in terms of the years required for the leachate infiltrating at $19/\text{cm}/\text{ft}^2/\text{year}$ to supply enough of a particular metal to exhaust the adsorption sites. The concentrations used for the metals were generally the maximum concentrations found in FOWL Run 1 of table 10. The adsorption capacity is a function of concentration. The higher the concentration, the more mass of the metal will be adsorbed onto the soil.

The "breakthrough" time might be significantly different than the time indicated in the table 15 capacity column, however. The breakthrough time is the time at which the concentration of metals leaving the bottom of a soil column approaches the concentration of metals entering the soil column. The breakthrough time will be less than the capacity times shown in table 15. Adsorption studies would be needed to estimate actual breakthrough times. Because the anticipated infiltration rate is small, the leachate flow through each foot of soil might exchange itself about two times each year. Because of the relatively small leachate flow rate, the breakthrough times might also be on the order of years as are the capacity times in table 15. If this were true, breakthrough time where the soil was several feet thick would not be expected for many years for some metals.

If the infiltration rate were significantly changed, the time required to saturate the adsorption sites would also change directly. Another important variable is the pH. The leachate near the bottom of the stack is expected initially to be of low pH (3 to 4). For this reason adsorption constants obtained under acidic conditions were selected.

Table 15 indicates the potential capacity to adsorb all the manganese, nickel, molybdenum, copper, and possibly zinc and chromium produced by the stack in 20 years in the first foot of soil beneath the stack. Although table 15 indicates that each cubic foot of clay beneath the stack has the capacity to hold at least 60 to 70 years' worth of iron produced by the stack, solubility calculations indicate that the goethite in the soil has the potential to dissolve in the presence of the acidic leachate thus releasing iron into solution. Therefore, iron is probably not attenuated at very low pH and reducing conditions. The capacity for selenium adsorption appears relatively low but most estimates indicate it will be of low concentration in the leachate.

Table 16 shows the speciation of the leachate at two combinations of pH and oxidation-reduction potential. MINTEQ was used for the speciation. The initial concentration of leachate used was the FOWL estimate of pH 3 from table 10 although the lowest pH used in the speciation calculations was pH 4.

At pH 4, and under reducing conditions ($E_h < 0$), most elements are quite soluble although copper is expected to precipitate over the range of the oxidation-reduction potentials examined. Also at pH 4, and under reducing conditions, goethite is expected to be soluble.¹ Iron concentrations might, therefore, initially increase as the iron in the soil is dissolved. Iron concentrations shown in table 16 might exceed the amount of goethite initially present in the soil and thus might be

1. The soil minerals determinations did not indicate significant amounts of calcite in the soil. Recent soils data collected at other TVA plants for the application of FASTCHEM suggests that soils often do contain calcite or other carbonates in sufficient quantities to help neutralize acidic leachates.

Table 16. Leathate Speciation (Note that values are in mg/l unless otherwise indicated)

Parameter	Species	Initial Aqueous Concentration	pH=4 Eh=-0.05	pH=6 Eh=0.05
Aluminum	Al ⁺³	4	14.1	1.5x10 ⁻⁴
Barium	Ba ⁺²	0.3	0.3	0.006
Calcium	Ca ⁺²	394	394	364
	Cr(OH) ₂ , Cr ⁺²			
Chromium	CrO ₄	4.2	0.81	0.0035
Strontium	SR ⁺²	1.7	1.7	1.7
Sulfate	SO ₄ ⁻²	1114	1114	1038
Iron	Fe ⁺² , Fe ⁺³	2.0	4-5x10 ⁻⁴ ^a	1.2 ^b
Cadmium	Cd ⁺²	0.2	0.2	0.2 ^c
Copper	Cu ⁺ , Cu ⁺²	2.4	3.8x10 ⁻⁴	2.2x10 ⁻⁵
Magnesium	Mg ⁺²	16.1	16.1	16.1
Chloride	Cl ⁻	10.0	10.0	10.0
Zinc	Zn ⁺²	6.5	6.5	5.9
Arsenic	H ₃ ASO ₃ ,	1.0	1.0	0.89
	H ₃ ASO ₄			
Nickel	Ni ⁺²	0.8	0.8	0.8
Manganese	Mn ⁺² , Mn ⁺³	2.0	2.0	2.0
Carbonate	CO ₃ ⁻²	353	353	353

Table 16 (Continued)

Parameter	Species	Initial Aqueous Concentration	pH=4 Eh=-0.05	pH=6 Eh=0.05
Initial solids			Goethite Kaolinite Quartz	Goethite Kaolinite Quartz
Precipitates			Cu metal Cr ₃ O	Cuprite Cr ₃ O FeCr ₂ O ₄ Be(ASO) 4 2 Gypsum ZnSi ₂ O

- Some siderite could form.
- Iron-hydroxide-chloride precipitate might reduce this concentration.
- Could precipitate as Otavite.

artificially high. Dissolution of the iron requires protons and, therefore, the pH should tend to rise as the leachate moves downward. Aluminum concentrations also increase with the dissolution of the clay minerals. It is important to note that even under low pH and reducing conditions, chromium is expected to precipitate.

At pH 6, and with oxidizing conditions, arsenic, aluminum, barium, chromium, iron, and copper precipitate. In addition, a cadmium precipitate was supersaturated and could possibly precipitate. The pH 6 case shows that although the metals might be quite soluble when initially leached from the stack, many will precipitate to below the DWS if the pH will rise. Dissolution of the goethite will consume protons and cause the pH to rise. Mixing of the leachate with groundwater would also cause an increase in pH.

The leach time estimates shown in table 11 indicate that the stack will continue to leach for many years. Once the depth of soil beneath the stack is determined in the design phase, the estimates of table 15 could be used to determine the number of years the metals would be retarded before they would reach the groundwater. The combination of tables 11 and 16 indicate that eventually some metals will reach the groundwater. Adsorption will only slow their arrival. However, several feet of soil between the stack and the groundwater and holding the net infiltration to 15 percent of precipitation has the potential to retard the metals for many years. The combination of adsorption, dispersion, and precipitation with increasing pH might combine to make the time longer than that predicted by adsorption alone. Certainly chromium and copper are not expected to be very soluble at all. The FASTCHEM

package, which is currently being evaluated for use at TVA facilities, appears to be capable of evaluating the relative importance of these factors simultaneously.

IMPACT ON DOMESTIC USERS AND PROPOSED
SITE GROUNDWATER QUALITY

Domestic Users

During the week of March 21, 1988, a survey was conducted along Swan Pond Road to determine the number and location of domestic wells. Twenty private wells used for potable water supply were identified. The wells are shown in figure 3. All the domestic wells were determined to lie within the Conasauga formation. Plant monitoring well number 1, which was thought to represent background conditions, is also shown in figure 3. The plant well sampled water from a shale aquifer and, therefore, probably sampled from the Conasauga formation as well.

An analysis of a sample obtained from the plant well in March of 1977 is shown in table 17. Also shown in table 17 is an analysis of a sample taken from a USGS well located southwest of the plant site which also samples from the Conasauga formation. The primary anion for the USGS well is bicarbonate which comprises 91 percent of the negative charge balance in the sample. Sulfate accounts for 5 percent of the total. The primary anion for the Kingston plant well No. 1 is still bicarbonate accounting for 73 percent of the total with sulfate accounting for remaining 27 percent. Chloride was not measured in Kingston well No. 1, which would have reduced the sulfate percentage somewhat. However, sulfate is elevated as is TDS in the plant well compared to the USGS well. Although the sulfate and TDS could indicate the potential for some effect of the ash disposal activities or perhaps the coal pile on the nearby domestic wells, the iron and manganese

FIGURE 3

KINGSTON
FOSSIL FUEL PLANT

- Residential Wells
- Sampling Wells

Table 17. Comparison of Offsite and Site Groundwater Quality

Parameter	USGS well May 24, 1977	Kingston Well No. 1 March 9, 1977
Temperature, °C	16	-
Color, PCU	0	-
Conductance, μ S/cm	400	470
pH, std. units	7.2	7.5
Alkalinity (CaCO_3), mg/l	190	192
Bicarbonate, mg/l	230	234
N- NO_2+NO_3 , mg/l	0.24	-
P, mg/l	<0.01	-
TOC, mg/l	2.8	-
Hardness, mg/l	140	-
Ca, mg/l	43	62
Mg, mg/l	7.9	17
Na, mg/l	29	-
SAR	1	-
K, mg/l	2.7	-
Cl, mg/l	7.9	-
SO_4 , mg/l	6.3	68
F, mg/l	0.1	-
Si, mg/l	16	-
Fe, mg/l	<0.01	<0.05
Mn, mg/l	<0.01	0.13
TDS, mg/l	211	410
Well depth, feet	293	28
% Difference in anions and cations	1.1	7.6
Calculated conductivity	404	501
Aquifer	Probably Conasauga	

concentrations in Kingston well No. 1 remain low. The low levels of these parameters indicate no effect from the ash disposal activities in 1977.

If there is a potential for contamination of the domestic wells, it is more likely to occur from the existing disposal facilities than from the new dry stacking facility. It will be important to determine the potential effect of the existing ash disposal areas on the existing domestic wells in order to prove such a distinction, however. Discontinuing the sluicing of fly ash to the ash pond will likely not have a significant immediate effect on the domestic wells if the existing ash pond is affecting them.

Site Groundwater Quality

Table 18 shows groundwater quality from two of the soil investigation's boreholes. The wells were uncased and undeveloped. As a result, the samples were turbid and filtration was necessary. The data of table 18, therefore, represents dissolved species. Because of the turbidity, which might have adsorbed metals, the metal concentrations are probably low. The mineral components (e.g., Ca, Mg, Cl) are more reliable and might be compared to the values in table 17.

Table 18. Dry Fly Ash Disposal and Site Groundwater Quality

Parameter	Bore Hole 2 April 12, 1988	Bore Hole 10 April 12, 1988
Temperature, °C	16	-
Conductance, $\mu\text{S}/\text{cm}$	400	470
pH, std. units	7.2	7.5
Alkalinity (CaCO_3), mg/l	190	192
Hardness, mg/l	71	238
Ca, mg/l	14	49
Mg, mg/l	8.8	28
Na, mg/l	1.2	2.4
K, mg/l	1.1	1.7
Cl, mg/l	8	6.3
SO_4 , mg/l	2	3
Fe, $\mu\text{g}/\text{l}$	20	50
Mn, $\mu\text{g}/\text{l}$	340	42
TDS, mg/l	80	220
Se, $\mu\text{g}/\text{l}$	<1	<1
Pb, $\mu\text{g}/\text{l}$	1	2
Cd, $\mu\text{g}/\text{l}$	1.4	0.3
As, $\mu\text{g}/\text{l}$	<1	<1
Cr, $\mu\text{g}/\text{l}$	<1	<1
Zn, $\mu\text{g}/\text{l}$	60	20
Cu, $\mu\text{g}/\text{l}$	10	20
Al, $\mu\text{g}/\text{l}$	<50	<50
B, $\mu\text{g}/\text{l}$	<50	<50
Mo, $\mu\text{g}/\text{l}$	<20	<20
Ba, $\mu\text{g}/\text{l}$	100	140
Sr, $\mu\text{g}/\text{l}$	<5	<5
Ni, $\mu\text{g}/\text{l}$	7	1

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The fly ash reacts with the alkalinity of the sluice water and tends to lower the pH of the sluice water. Limited data suggest that the bottom ash will have little effect on sluice water alkalinity or pH. However, there is the possibility that the bottom ash could add some alkalinity to the sluice water, thereby acting to raise the pH. These factors taken together suggest that in the absence of other ash pond inputs, removing the fly ash from the ash pond could raise the pH from the low levels commonly observed during a portion of the year.

However, even though the fly ash consumes alkalinity and acts to depress pH, the fly ash sluice water at the present often contains residual alkalinity to help buffer the acidic coal pile drainage. In addition, the fly ash matrix itself might help neutralize the coal pile drainage. The acidity of the coal pile drainage appears to possibly react with the alkaline oxides in the fly ash which might not dissolve unless the pH is depressed. Removal of both the fly ash and its sluice water will, therefore, allow the coal pile drainage to become significantly more important to the ash pond pH than it presently is. The result might be an exacerbation of the pH swings which are presently observed in the ash pond. During periods of high coal pile drainage flow into the ash pond when the river water alkalinity and pH were low, the ash pond pH might be pushed even lower than at the present. If only the fly ash were removed from the ash pond but the fly ash sluice water (in this case used only for ash system collection vacuum and would carry no

ash) remained flowing through the pond, the impact of the coal pile drainage would be less than at the present. During dry periods, when there was no coal pile drainage and the fly ash and its sluice water were removed, the pH might also become very high should it be found that the bottom ash does indeed add alkalinity to the sluice water. If only the fly ash is removed and the sluice water remains, this effect would be insignificant.

If the low end of the ash pond pH range without the fly ash is higher than the historical low pHs, the metal species now in the ash pond shown in table 6 should be shifted toward species which tend to be less soluble. As the pH is raised from acid conditions to alkaline conditions, many of the metals move from the free ion state to soluble complexes and might even form precipitates (Bailey, 1987). Although selenium's solubility increases with pH, selenium is associated more with fly ash than bottom ash. Therefore, its total concentration should be less if the fly ash were removed from the ash pond. If the coal pile drainage holds the pH low, most of the metals discharged to the river will be in their more soluble forms. However, as discussed previously, the total mass of metals discharged will be reduced if the fly ash is removed from the ash pond.

The runoff and any leachate collected from a 50-acre active dry ash stack might be a maximum of 20 to 30 percent of the runoff from the coal pile drainage. The predicted metals concentrations at this point are so preliminary that further study of the actual leachate is recommended should it be desired to discharge the runoff and leachate directly

to the river. Evidence does exist for the possibility of elevated concentrations of arsenic, cadmium, and chromium. These metals could be diluted by the bottom ash sluice water to reduce their concentrations to the same order of magnitude as the DWS if adequate storage were provided. If water volumes on the order of those presently used for fly ash sluicing are still diverted to the ash pond, the metals from the collected leachate/runoff should be diluted to concentrations below the DWS. However, pretreatment options are available if storage prior to pumping to the ash pond is desired or if it is found that the coal pile drainage needs pretreatment before being sent to the ash pond.

Although the dry ash stack might eventually have some effect on the groundwater quality beneath the stack, the existing soils appear to have the ability to attenuate many of the metals for many years. Some metals, such as copper and chromium are expected to reach the groundwater only in very low concentrations. Once leachate reaches the groundwater, the pH will be raised from the assumptions used in the leaching analysis. This will precipitate additional metals and provide additional adsorption sites on the precipitates for metals breaking through.

Curtailment of fly ash disposal in the existing ash pond should have little effect on any offsite migration of leachate from the existing ash pond for many years.

Recommendations

An additional study on the effect of sluice water alkalinity by the bottom ash is recommended. If the sluice water is withdrawn from the ash pond along with the fly ash, the following two additional studies are recommended.

1. Data are needed to verify the assumptions concerning the characteristics of the dry ash stack leachate and runoff. There is uncertainty surrounding their characterization. Therefore, disposal through the ash pond or with pretreatment of the coal pile drainage should the coal pile drainage be proven to be a real problem, should be explored. Estimates used in this analysis are thought to be conservative; therefore, data on the collected leachate and runoff might indicate that discharge to the river would be appropriate.
2. A study concerning how the bottom ash will react with the coal pile drainage is also needed. Such data would be useful to determine whether additional alkaline oxides in the bottom ash matrix will react with the acidity in the coal pile drainage.

Alternative designs in which leachate would be retarded or possibly collected at the toe of the hill should be examined. Adsorption and precipitation have the potential to significantly retard the movement of metals in the leachate for many years. If some of the leachate can be directed to a surface collector, more detailed chemical and hydrogeologic analysis might show that any effect on groundwater would be minimal. In any event, monitoring of wells around the dry ash disposal site is recommended.

REFERENCES

- Ainsworth, C. C. and D. Rai. 1987. Chemical Characterization of Fossil Fuel Combustion Wastes, EA-5321, Electric Power Research Institute, Palo Alto, California.
- Bailey, E. M. 1987. Chemical Speciation in Ash Pond Effluents and River Waters, in Toxics in Power Plant Coal Ash Sluice Systems, H. Olem (ed), Tennessee Valley Authority, Chattanooga, Tennessee.
- Betson, R. P. and C. E. Bohac. 1987. TVA Power Plant Groundwater Assessment Plan Phase I, TVA/ONRED/AWR 87/23, Tennessee Valley Authority, Norris and Chattanooga, Tennessee.
- Chu, T.-Y. J., B. R. Kim, and R. J. Ruane. 1980. Behavior of Coal Ash Particles in Water: Trace Metal Leaching and Ash Settling, EPA-600/7-80-067, Tennessee Valley Authority, Chattanooga, Tennessee.
- Cox, D. B., T.-Y. J. Chu, and R. J. Ruane. 1979. Characterization of Coal Pile Drainage, EPA-600/7-79-051, Tennessee Valley Authority, Chattanooga, Tennessee.
- Chu, T.-Y. J., R. J. Ruane, and G. R. Steiner. 1976. "Characteristics of Wastewater Discharges from Coal-Fired Power Plants," In: 31st Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, Indiana.
- Hostetler, C. J., R. L. Erikson, D. Rai. 1988. The Fossil Fuel Combustion Waste Leaching (FOWL™) Code: Version 1. EA-5742-CCM. Research Project 2485-8, Electric Power Research Institute, Palo Alto, California.
- Rai, D., C. C. Ainsworth, L. E. Eary, S. V. Mattigob, and D. R. Jackson. 1987. Inorganic and Organic Constituents in Fossil Fuel Combustion Residues, vol. 1, EA-5176, Electric Power Research Institute, Palo Alto, California.
- Rai, D., J. M. Zachara, et al. 1986. Geochemical Behavior of Chromium Species, EA-4544, Electric Power Research Institute, Palo Alto, California.
- Rai, D., J. M. Zachara, et al. 1984. Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, EA-3356, Electric Power Research Institute, Palo Alto, California.
- Stumm, W. and J. J. Morgan. 1981. Aquatic Chemistry, John Wiley and Sons, New York, New York.

APPENDIX A

ASH POND EFFLUENT DATA

Table A-1. Kingston Steam Plant (1974-1975)

Date	Raw Water Intake		Ash Pond Discharge			
	pH	Total CaCO ₃ (mg/l) ³	pH	Meth.O acidity (mg/l)	Total alkalinity (mg/l)	CO ₂ acidity (mg/l)
01/30/74	6.7	14	3.7	11	0	41
02/06/74	6.7	9	3.5	11	0	87
02/13/74	6.5	14	3.5	14	0	69
02/20/74	6.8	10	3.3	35	0	100
02/27/74	6.9	12	3.5	23	0	67
03/06/74	7.8	35	4.5	0	0	0
03/13/74	7.2	18	3.8	8	0	45
03/20/74	7.0	15	4.1	7	0	28
03/27/74	7.2	12	5.0	0	4	
04/03/74	7.0	8	4.5	0	0	
04/10/74	7.5	8	4.7	0	3	
04/17/74	7.1	73	6.7	0	15	
04/24/74	7.9	55	7.4	0	34	
05/01/74	8.0	84	7.9	0	54	
05/08/74	7.8	70	7.3	0	32	
05/15/74	7.3	10	6.0	0	6	
05/22/74	7.9	55	7.5	0	35	
05/29/74	7.5	36	7.1	0	15	
06/05/74	7.3	73	7.1	0	29	
06/12/74	7.8	75	7.1	0	38	
06/26/74	8.1	43	7.5	0	60	
07/03/74	8.2	66	8.1	0	54	
07/10/74	8.1	63	7.9	0	79	
07/17/74	8.1	52	8.0	0	73	
07/24/74	7.9	67	7.5	0	69	
07/31/74	8.2	65	7.9	0	72	
08/07/74	7.9	83	8.7	0	96	
08/14/74	8.3	78	8.5	0	83	
08/21/74	8.3	82	8.8	0	91	
08/28/74	8.0	80	7.8	0	85	
09/04/74	7.9	74	7.7	0	50	
09/11/74	8.2	86	8.4	0	72	
09/18/74	7.8	46	7.1	0	50	
09/25/74	7.9	67	7.9	0	72	
10/02/74	7.9	108	7.3	0	62	
10/16/74	7.9	95	7.8	0	74	
10/23/74	8.0	95	7.7	0	56	
10/30/74	8.2	100	8.1	0	62	
11/06/74	8.1	108	7.8	0	62	
11/13/74	7.8	92	7.8	0	61	
11/20/74	7.5	7	7.4	0	39	
11/27/74	7.5	61	6.8	0	16	
12/04/74	7.3	14	6.6	0	12	

Table A-1 (Continued)

Date	Raw Water Intake		Ash Pond Discharge			
	pH	Total CaCO ₃ (mg/l) ³	pH	Meth.O acidity (mg/l)	Total alkalinity (mg/l)	CO ₂ acidity (mg/l)
12/11/74	7.0	7	5.4	0	3	
12/18/74	6.6	15	5.7	0	14	
12/26/74	7.0	8	6.6	0	5	
01/02/75	6.6	7	4.1	2	0	74
01/08/75	6.4	8	4.0	8	0	85
01/15/75	7.4	4	3.9	16	0	135
01/22/75	6.0	15	3.9	13	0	140
01/29/75	7.0	6	3.7	6	0	146
02/05/75	6.9	13	4.1	11	0	103
02/12/75	6.6	6	3.9	18	0	137
02/19/75	6.5	6	3.7	15	0	148
02/26/75	6.8	11	3.6	17	0	175
03/12/75	7.0	5	5.0	0	2	
03/19/75	6.3	3	3.7	9	0	119
03/26/75	6.9	5	3.4	25	0	183
04/02/75	6.7	7	4.0	13	0	85
04/09/75	7.0	28	3.7	13	0	54
04/16/75	7.2	44	6.7	0	15	
04/23/75	7.2	13	6.9	0	16	
04/30/75	7.7	40	7.2	0	19	
05/07/75	7.7	57	7.7	0	32	
05/14/75	8.1	77	7.9	0	39	
05/21/75	7.2	17	6.7	0	9	
06/18/75	7.8	58	7.6	0	38	
06/25/75	7.8	78	7.4	0	37	
07/02/75	8.0	75	7.6	0	42	
07/09/75	7.9	78	7.4	0	44	
07/16/75	8.0	93	9.1	0	57	
07/23/75	8.1	78	8.2	0	81	
07/30/75	8.4	82	8.4	0	48	
08/06/75	8.4	83	8.4	0	47	
08/13/75	8.2	85	7.9	0	53	
08/20/75	8.2	87	8.4	0	60	
08/27/75	7.9	90	8.7	0	62	
09/03/75	8.0	96	8.2	0	65	
09/17/75	8.1	92	8.1	0	60	
09/24/75	7.6	33	6.2	0	9	
10/02/75	8.0	80	7.6	0	42	
10/09/75	7.7	42	7.5	0	40	
10/15/75	7.9	77	7.5	0	24	
10/22/75	7.3	28	4.3	0	0	6
10/29/75	7.6	43	4.9	0	4	
11/05/75	7.9	78	7.1	0	25	

Table A-1 (Continued)

Date	<u>Raw Water Intake</u>		<u>Ash Pond Discharge</u>			
	pH	Total CaCO ₃ (mg/l)	pH	Meth.O acidity (mg/l)	Total alkalinity (mg/l)	CO ₂ acidity (mg/l)
11/13/75	7.0	9	5.4	0	3	
11/19/75	7.5	38	4.1	0	0	45
11/26/75	7.7	50	4.9	0	4	
12/03/75	7.2	14	6.4	0	5	
12/10/75	6.9	14	4.5	0	0	
12/17/75	7.0	8	5.3	0	3	
12/23/75	7.6	32	7.2	0	24	
12/31/75	6.6	9	4.5	0	0	

APPENDIX B
SETTLING TEST DATA

Ash Pond Influent Settling Tests

Kingston Steam Plant 3/3/88 Samples

Ash Pond Influent Settling Tests

Kingston Steam Plant 3/14/88 Samples

APPENDIX C

BULL RUN ASH POND FLOW
AND pH

Bull Run Steam Plant

Flow from Ash Pond

Bull Run Steam Plant

pH of Ash Pond Discharge

pH (s.u.)

END

DATE FILMED

01 / 31 / 91