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U.S. Atomic Energy Commission

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SUBJECT: Environmental Effects of the Secondary Discharges from Fly Ash Ponds

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ABSTRACT

Secondary water flow from ash ponds at the Bull Run Steam Plant has been characterized. A mechanism for the formation of materials found in the discharge was developed. A literature review was compiled on the effluent formation processes. The effects of the stream on representative samples of the fish population in the Clinch River have been observed. The major constituent of the precipitate present in this secondary water flow was found by x-ray diffraction to be ferric oxide hydroxide (FeOOH) produced in the transformation of ferric hydroxide [$Fe(OH)_3$]. Significant ferrous iron oxidation occurs in the drainage ditch containing the secondary water flow resulting in the precipitation of ferric hydroxide. Catfish cannot survive in environments that are either too acidic or contain a large amount of suspended solids such as ferric hydroxide. The large amount of iron deposits suspended in the discharge cove waters results from the sudden mixing of the acidic secondary discharge with the slightly alkaline cove waters.

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Contents

1. SUMMARY

A study was conducted to characterize the secondary water flow at the Bull Run Steam Plant's ash pond system. This water flow originates from water seepage through the settled ash material and ash pond embankment, collects in a drainage ditch running along the embankment, and then flows through a culvert into the Clinch River.

Water samples were collected at various points in the ash pond area. These samples were then sent to the Analytical Chemistry Division for analysis. Flow rates in the drainage ditch were measured at its beginning and at the culvert. Samples of fish were placed in cages at various points of interest and observed on a regular basis.

A laboratory simulation of the seepage through the pond wall was conducted using batches of sterilized and unsterilized samples of ash material taken at locations where aerobic and anaerobic bacteria might exist. Aerobic and anaerobic bacteria cultures were grown in petri dishes.

The major constituent of the precipitate found at the bottom of the drainage ditch and in the discharge cove was identified by x-ray diffraction as ferric oxide hydroxide (FeOOH). Total soluble iron and soluble sulfate present in the drainage ditch both decrease with distance down the ditch. In addition, the pH and the ratio of ferrous to ferric ions in solution decrease with distance down the ditch.

Fish placed directly in the ditch at the entrance to the culvert died within 24 hr from excess mucous secretion. Fish placed in the discharge cove, directly opposite the culvert, died within 3 days due to iron deposits found on the gills.

After 6 days all four batch simulations (aerobic and anaerobic) contained only trace amounts of soluble iron, and the solution was found to be alkaline. Distinction between the results for the sterilized and unsterilized batches could not be made.

After a 10-day period, bacterial colonies of iron bacteria were not observed. Significant ferrous iron oxidation occurs in the drainage ditch waters, resulting in the precipitation of ferric hydroxide. This oxidation is probably catalyzed by the bacteria Ferrobacillus ferrooxidans. Catfish cannot survive in environments that are too acidic or that contain a high degree of suspended solids such as ferric hydroxide. The large amount of iron deposits suspended in solution in the cove waters results from the sudden mixing of the acidic secondary discharge with the slightly alkaline cove waters.

Additional bacteria cultures prepared from ash samples should be made at a pH of 3.5. Batch simulations should be run for at least 30 days at an initial pH of 3.5 using percolation with nitrogen or air to simulate anaerobic or aerobic conditions. Additional fish experiments should be run with much longer exposure times (greater than 2 weeks). Additional flow rate measurements should be performed on the drainage ditch.

2. INTRODUCTION

2.1 Background

2.1.1 History of Problem

The disposal of ash materials produced at coal-fired electric utility plants can be accomplished by two methods depending upon the availability of land near the plant and the cost of purchasing that land. In cases where land is not readily available or where it is too expensive to be purchased, the ash material can be contracted to companies for further handling or disposal. Where land is cheap and plentiful, the fly ash can be used as landfill. The Bull Run Steam Plant disposes of the ash material by creating a slurry with water which is pumped from the plant to a series of three ash ponds. There, the ash material settles to the bottom and the water flows over a surface skimming weir into the Clinch River at the end of the third pond at about 7200 gpm (20). The water quality of the ash pond effluent is checked periodically by TVA at the discharge weir. These data are available for the period from October 1967 to December 1973 (20).

In addition to the main flow through the ash ponds, there is a secondary water flow which is not well characterized. Water seeps through the settled ash material and ash pond embankment and collects in a drainage ditch which runs parallel to the embankment for a distance of the first two ash ponds, at which point it flows through a culvert into the Clinch River. The water in this ditch is reddish in color and the ditch bottom is covered with a fine reddish powder. A recent MIT Practice School project (9) determined the concentration of mercury in this ditch, but did not examine the extent to which any other constituents were present.

2.1.2 Previous Work

Research has been conducted in the area of catalytic oxidation of water containing ferrous iron (13). The effect of bacterial catalysis of iron oxidation in streams associated with coal and copper mines has been studied by several other investigators (2, 11, 12, 14).

2.2 Objectives

The immediate objective was to determine the cause of the precipitate and the water color by characterizing the secondary flow with respect to flow rate, temperature, pH, turbidity, and chemical concentration, and to develop a mechanism for the formation of such chemicals. The effects of the stream on samples of the fish population near the discharge point in the Clinch River were studied.

2.3 Method of Attack

1. A literature search was conducted to obtain information on the processes occurring during the seepage through the pond wall and the subsequent flow down the drainage ditch.

2. Water samples were collected at various points along the path of the secondary stream, from the initial seepage point to a point downstream of the culvert discharge where the discharge plume was no longer visible. These samples were analyzed for chemical composition.

3. Catfish nurtured at the fish ponds of the aquatic ecology laboratory were caged and placed at various points in the river in the general vicinity of the discharge point (including one cage within the ditch) for a period of two weeks. The condition of the fish was checked on a daily basis.

4. A laboratory simulation of the water seepage through the ash pond wall was performed to observe whether bacteria that extract iron via a metabolic process play a role in the possible release of ferrous and/or ferric compounds.

5. Cultures were prepared (under aerobic and anaerobic conditions) from fly ash samples to enable identification of bacteria present in the ash material.

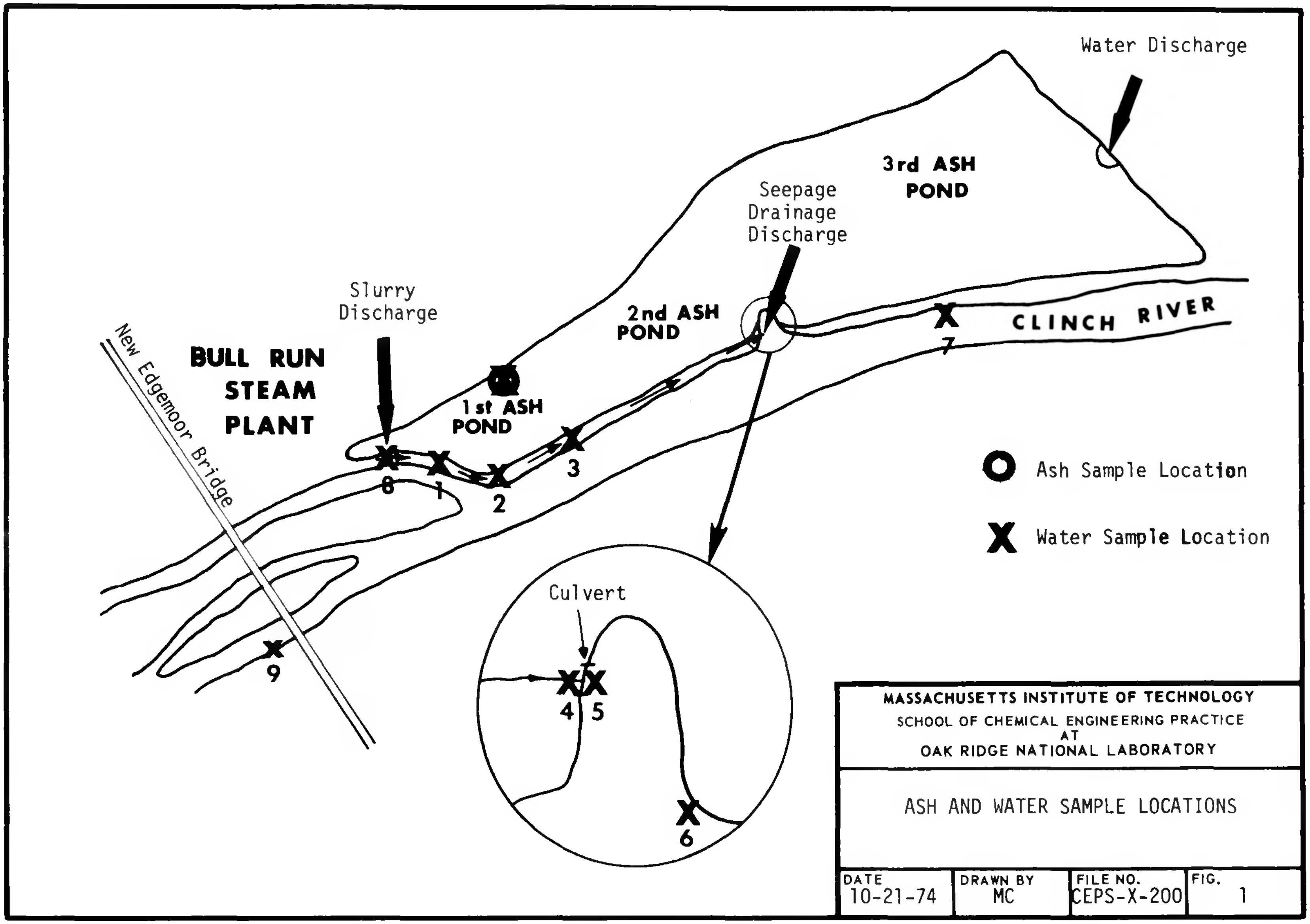
3. PROCEDURE

3.1 Field Work

Water samples were collected at various locations (see Figs. 1-3) and were then analyzed by the Analytical Chemistry Division of ORNL for the concentration of dissolved iron, aluminum, silicon, calcium, magnesium, zinc, manganese, sulfate and bicarbonate anions, ferrous and ferric iron, total dissolved solids, dissolved oxygen, absorbance, pH, and composition of the precipitate. Caged fish samples were placed at various positions (see Fig. 4) and their conditions were observed on a daily basis. Fish killed during the experiment were returned to the laboratory for dissection. Samples of the surviving fish were also returned for dissection.

3.2 Laboratory Work

Seepage through the ash pond wall was simulated under anaerobic and aerobic conditions using fly ash samples from the pond. Continuous (dynamic) and batchwise simulation was attempted.



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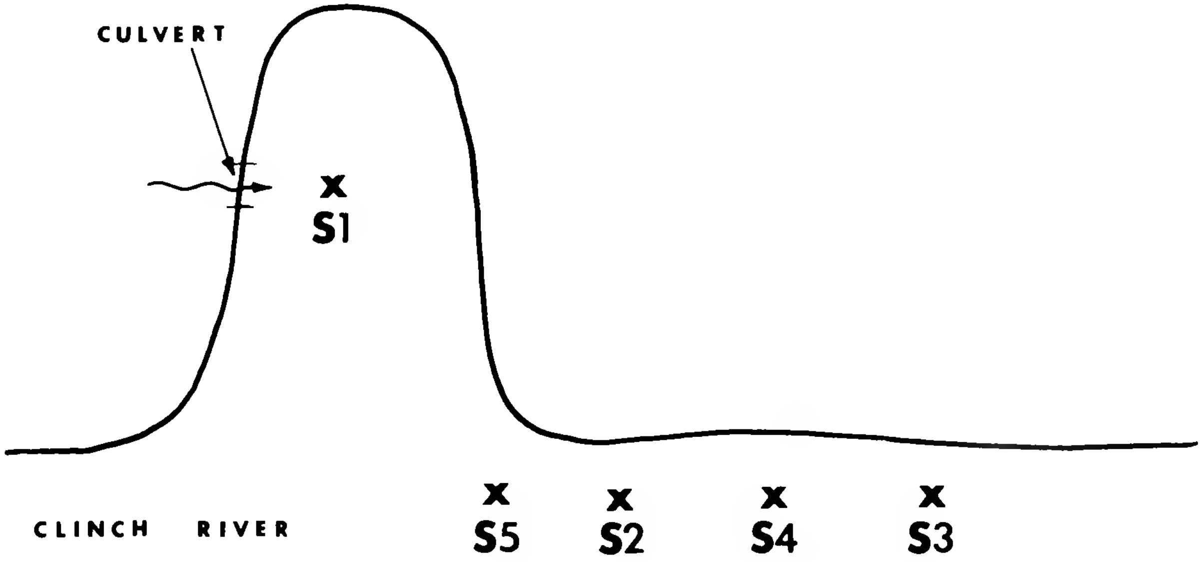
ASH AND WATER SAMPLE LOCATIONS

DATE	DRAWN BY	FILE NO.	FIG.
10-21-74	MC	CEPS-X-200	1



X - denotes water sample locations

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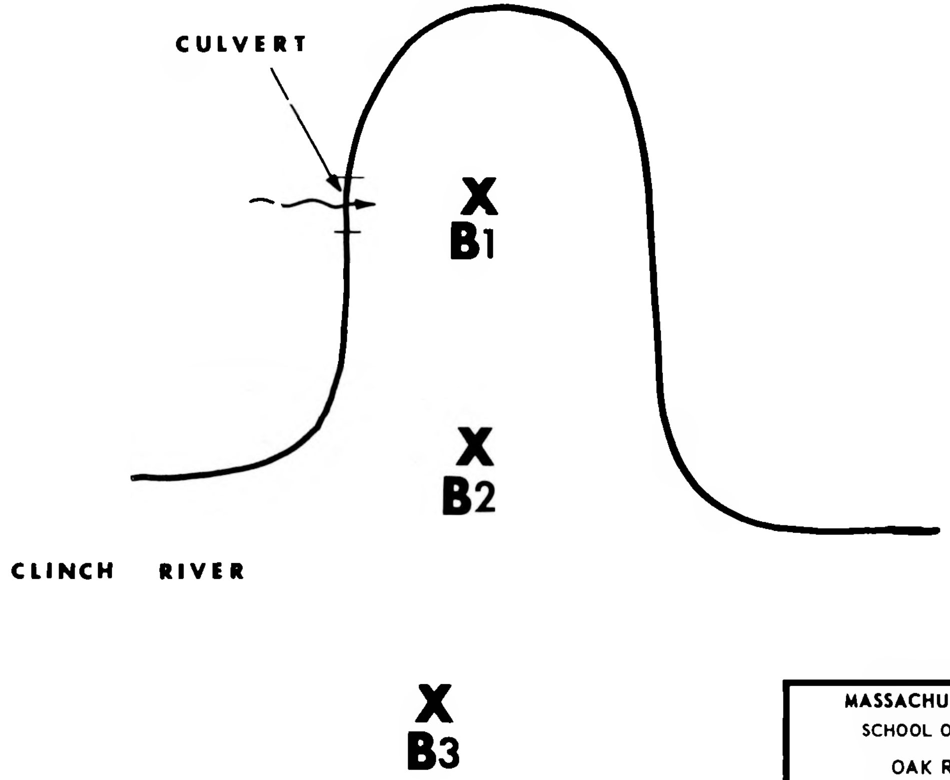
PLUME SAMPLE LOCATIONS

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	MC	CEPS-X-200	2



X - denotes water sample locations

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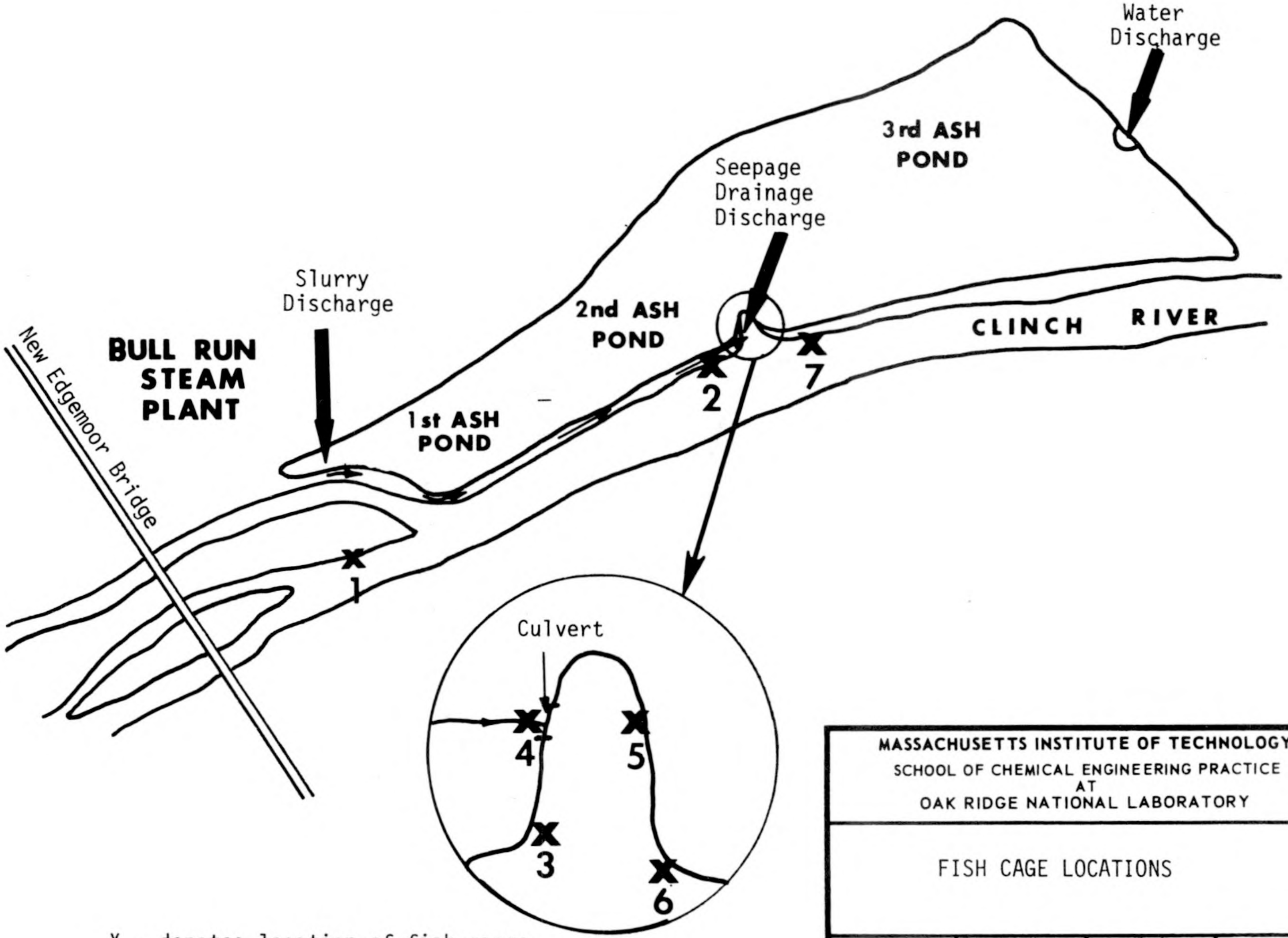
LOCATIONS WHERE SAMPLES
WERE TAKEN BELOW WATER SURFACE

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	MC	CEPS-X-20	3



X - denotes location of fish cages

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FISH CAGE LOCATIONS

DATE	DRAWN BY	FILE NO.	FIG.
10-21-74	MC	CEPS-X-200	4

An attempt was made to grow bacteria cultures from fly ash samples under aerobic and anaerobic conditions. Nutrient agar was prepared from fly ash samples so as to obtain an agar specific for bacteria that might exist in the fly ash. Mixtures of the ash and nutrient agar in the ratio of 1 part ash to 10^4, 10^5, 10^6, and 10^7 parts agar and water mixture respectively were used, five from each sample dilution.

4. RESULTS

4.1 Chemical Analysis of Precipitate

The suspended solids and the deposits on the floor of the drainage ditch were found to contain 40% of iron by weight (see Table 1 and Appendix 9.5.1 for details). Other metallic elements were present in trace amounts. Aluminum and calcium, two important inorganic elements in the slurry (see Appendix 9.2) were present in the precipitate at 0.7 and 0.4 wt %, respectively. Although the precipitate was thought to be ferric hydroxide, x-ray diffraction revealed that greater than 70% of the amorphous precipitate was FeOOH.

A test was performed to determine whether the precipitate was ferric hydroxide. Ferric hydroxide readily dissolves in $FeCl_3$ and in $CrCl_3$, but not in $AlCl_3$ (7). It was found that the precipitate samples would not dissolve in either $AlCl_3$ or $FeCl_3$. ($CrCl_3$ was not available for the test.)

4.2 Chemical Analysis of Dissolved Solids in Water Samples

Table 2 presents averaged results of the chemical analysis of water samples taken in the slurry discharge, ditch, cove, and in the Clinch River (see Appendix 9.1 for a complete listing of the results). The results show that iron and sulfate levels were much higher in the secondary discharge from the ash pond than in the river water upstream. Calcium and aluminum levels were also much higher. Analysis for Mn, Mg, and Zn indicated that concentration of these species were extremely low in comparison to the major chemical species, Fe and SO_4^{-2}.

4.2.1 Slurry

The slurry discharge contained only trace amounts of iron and aluminum (<3 mg/liter). The level of calcium (32 mg/liter) was similar to upstream control levels. The sulfate concentration (69.2 mg/liter) was significantly higher than that of the control (14.9 mg/liter), presumably because the slurry contains some dissolved SO_2 and SO_3 gases which originate from the sluiced bottom ash from the Bull Run Steam Plant furnace.

Table 1. Results of Analysis of Precipitate

Date	PPT Sample	Fe wt %	Al wt %	Si wt %	Ca wt %	ID (x-ray diffraction)	Test for $Fe(OH)_3$		
							$AlCl_3$	$FeCl_3$	$CrCl_3$
10-14-74	P-3*	39.9	0.7	2.0	0.4	FeOOH (>70%)	insoluble	insoluble	not done
10-8-74	P-4*	39.8	0.2	1.0	0.03	FeOOH (>70%)	insoluble	insoluble	not done
10-8-74	P-5*	42.5	0.1	0.1	0.03	FeOOH (>70%)	insoluble	insoluble	not done

*P-3: deposit on floor of ditch.

P-4: ppt filtered from water sample, 42.2 mg/liter

P-5: ppt filtered from water sample, 30.9 mg/liter

Table 2. Averaged Results of Chemical Analysis of Water Samples

Sample Number and Location	Concentrations in mg/liter											
	Total Fe	Fe^{+2}	Fe^{+3}	Al	Ca	SO_4^{-2}	HCO_3^{-1}	pH	Si	Mg	Zn	Mn
Slurry (#8)	<0.05	-	-	<2.5	32	69.2	60	7.21	2.0	8.83	<0.004	0.05
Start of Ditch (#1)	927	920	43	80	148	2777	-	3.20	36	19.3	0.19	0.63
Middle of Ditch (#3)	571	575	75	57	133	2054	-	3.01	28	15.9	0.16	0.67
End of Ditch (Before Culvert Discharge)(#4)	320	225	146	57	126	1554	-	2.89	24	15.7	0.16	0.55
Cove (#6)	0.09	-	-	<3.5	29	15.3	112	7.93	1.8	8.5	0.097	0.02
Downstream (#7)	0.10	-	-	<2	29	15.1	114	7.69	1.7	8.43	0.006	0.01
Upstream (Control)(#9)	0.10	-	-	<3.5	32	14.9	115	7.90	2.2	8.30	0.004	0.02

4.2.2 Ditch

Total dissolved iron concentration fell 65% along the ditch, from 927 mg/liter at the beginning of the ditch to 320 mg/liter at the culvert entrance. On the average, ferrous iron levels started at 920 mg/liter and dropped to 225 mg/liter, while ferric levels rose to 146 mg/liter from 43 mg/liter at the ditch origin. Correspondingly, the ferrous to ferric iron ratio began at about 21 and fell to 1.5 at the culvert entrance.

The major anion, SO_4^{-2}, ranged from 2777 mg/liter at the ditch origin to 1554 mg/liter at the culvert, a 44% decrease. Other elements of interest, Al and Ca, maintained steadier levels in the ditch. Calcium concentrations dropped 15% from 148 to 126 mg/liter. Aluminum decreased 29% from 80 to 57 mg/liter. The pH of the ditch water (3.2) was quite acidic, becoming even more acidic near the culvert discharge (2.89).

4.2.3 Clinch River

Dissolved iron concentrations were much lower in the cove (0.09 mg/liter) where culvert discharge water had time to mix, which explained the slightly alkaline pH of 7.93. Samples taken close to the culvert exit (Point 5 in Fig. 1) maintained high dissolved Fe concentration (288 mg/liter average). Concentrations of other chemical species (Al, Ca, SO_4^{-2}) were close to their reported values in the control upstream.

4.3 Fish Experiments

All the fish in Cage 4 placed in the entrance of the culvert survived at least one hour but died within 24 hr. In Cage 5, placed directly opposite the culvert discharge, six fish died within 24 hr, three died within 36 hr, and the last one died within 72 hr.

The skin of the fish from Cage 4 was discolored and badly damaged. The fish from Cage 5 showed no damage to their gills and external features (see Fig. 5). The bodies, mouths, and gills of the fish from Cage 4 were covered with mucous. No particulate deposit was observed on the gills. Iron precipitates clogged the gill filaments and the linings of the mouth of the fish from Cage 5 (see Fig. 6). The fish in the remaining cages were alive and active in the river. No solid precipitate was observed on their gills and in their mouths and digestive systems. Small amounts of mucous were found on the skin and gills.

4.4 Determination of Flow Rates

Volumetric flow rates at the beginning of the ditch and in the culvert were found to be 84 and 360 gpm, respectively.

Fig. 5. Comparison of the Effects of the Seepage Drainage on Fish Before and After Discharge (External Appearance)

Fig. 6. Comparison of the Effects of the Seepage Drainage on Fish Before and After Discharge (Gills)

4.5 Comparison Between Compositions of the Weir and Culvert Discharges

The environmental effects of the culvert discharge stream on the Clinch River relative to the weir discharge can be determined from the flow rates and the compositions of the two streams. More total dissolved solids were found flowing to the Clinch River at the weir (5450 gm/min) than at the culvert (3563 gm/min). The ditch discharged about 44 times more total dissolved iron (437 gm/min) into the river than at the weir (10.6 gm/min). Total dissolved sulfate levels were almost identical in both cases (2289 gm/min at the weir versus 2121 gm/min at the culvert). Total dissolved calcium leaving the weir was much greater (1008 gm/min) than that leaving the culvert.

4.6 Batch Experiment

The batch experiment ran for six days. Table 3 summarizes the results. All four batches contained only trace amounts of dissolved iron (<0.05 mg/ℓ). Calcium levels were significantly higher in the aerobic batches (55 vs 29 mg/liter) as were sulfate levels (115 vs 35 mg/liter). All four batches were found to be alkaline. The pH of the anaerobic batches was higher than the aerobic batches (9.6 vs 8.3). Distinction between the results for the sterilized and unsterilized batches could not be made.

Table 3. Chemical Analysis of Water Sample from Batch Experiments

	Concentrations in mg/liter				
Water Sample Batch	Fe	Ca	Mg	SO_4^{-2}	pH
Aerobic	<0.05	56.1	18	111.36	8.14
Aerobic, Presterilized	<0.05	54.2	11.1	119.52	8.49
Anaerobic	<0.05	25.7	10.7	33.33	9.52
Anaerobic, Presterilized	<0.05	31.4	5.9	37.32	9.65

4.7 Bacteria Cultures

After a ten-day incubation period, bacterial colonies of iron bacteria were not observed on the Petri dishes. A few commonly observed bacterial colonies and fungal growths were present in the dishes.

5. DISCUSSION OF RESULTS

5.1 Chemical Analysis of the Red Precipitate

Although x-ray diffraction analysis identified the precipitate to be FeOOH, there is strong evidence that its original state was ferric hydroxide [$Fe(OH)_3$]. The pattern projected by the x-ray diffraction was not very distinct, possibly due to the fact that the sample was not a pure crystalline structure (partially amorphous). Purely amorphous materials do not give diffraction patterns since there is no crystal lattice. Pure ferric hydroxide is amorphous and would not give any pattern. Krause (5) and Lengweiler (6) present evidence of certain situations where ferric hydroxide will incompletely transform to crystalline α-FeOOH through an "aging process."

The laboratory test which indicated that the precipitate would not dissolve in $FeCl_3$ or $AlCl_3$ is not conclusive enough to rule out the presence of ferric hydroxide. For these reasons the precipitate will be treated as ferric hydroxide in the following sections.

5.2 Chemical Analysis of Dissolved Solids and Oxygen in Water Samples

5.2.1 Chemistry of Ditch Waters

5.2.1.1 Dissolved Solids. The 44% decrease in sulfate levels along the ditch cannot be attributed to the deposition of sulfate containing precipitates for two reasons. First, the solubilities of ferrous and ferric sulfate in water are too large for precipitation to occur. Solubilities of ferrous and ferric sulfates are 156 and 4400 gm/liter, respectively (17). Secondly, x-ray diffraction of the precipitate does not indicate the presence of sulfate compounds. (See Sect. 4.1 for results of the analysis of precipitate composition.)

If sulfate is not precipitated, then lower sulfate levels can only be explained in terms of a dilution effect; i.e., dilution of ditch waters with seepage water of lower sulfate concentration downstream. Since the major source of the sulfate is from iron pyrite degradation (see Appendix 9.3 for description of pyrite degradation), then it follows that iron pyrite degradation must be proceeding at much lower levels in ash material which downstream waters seep through. Iron bacteria which increase iron pyrite degradation rates may not be present in the newer ash deposits downstream from the slurry discharge, thus explaining the reduced sulfate production rates in the downstream direction. More than likely, however, the heavier pyrite material in the slurry discharge may be settling out before lighter fly ash, producing the situation where ash deposits downstream have a lower pyrite content, thus accounting for the lower potential for pyrite degradation there.

The fact that calcium and aluminum levels in the ditch do not decrease as much as sulfate is consistent with the arguments presented above. The large amounts of $CaCO_3$ (calcite), the main source of calcium in the ditch water, present in fly ash and in the minerals of the pond wall, are presumably present in all sections of the ash material downstream. This carbonate rock can readily dissolve in the drainage water, thus keeping ditch calcium levels relatively constant. (See Appendix 9.2 for composition of fly ash.)

The major source of aluminum in the drainage is presumed to come from the decomposition of $AlSiO_5(OH)_4$ (kaolinite) and $3Al_2O_3 \cdot 2SiO_2$ (mullite). The fact that aluminum levels decrease only 29% cannot readily be explained; however, since decomposition of these aluminum compounds is not linked to iron pyrite degradation, the explanations presented for dilution of the sulfate are not refuted.

The larger decrease in dissolved iron levels, 21% more than the drop in sulfate levels, is attributed to the added precipitation of ferric hydroxide along the ditch. Examination of the solubility product, $[Fe^{+3}][OH^-]^3$, reveals that the ditch waters were supersaturated with ferric ion (see sample calculations in Appendix 9.7) indicating a high potential for precipitation of ferric hydroxide. The decrease in pH along the ditch waters can be accounted for by the ferric hydroxide precipitation reaction which yields three moles of hydrogen ion per ferric ion precipitated out of solution. [This reaction is shown on Table 11, Eq. (4), in Appendix 9.3.]

The fact that ferric concentration levels actually increase down the ditch is thought to be due from the ferrous to ferric ion conversion. This conversion is attributed to the presence of ferrooxidans bacteria in the ditch waters. Walsh (16) and Singer and Stumm (12) have experimentally determined a kinetic rate expression for abiotic ferrous ion oxidation at pH's less than 3.5. Calculations show that the maximum abiotic, non-catalytic, ferrous ion oxidation rate in the ditch is 0.0264 mg/liter/day, a very slow rate (see Appendix 9.7 for details of calculations). The rate of oxidation with the bacteria would be 10^6 times greater (12) or 30 gm/liter/day, a rate sufficient to account for the increase of ferric ions in the ditch.

5.2.1.2 Dissolved Oxygen. The results of the dissolved oxygen analyses are presented in Appendix 9.1, Table 8. The two methods used [Alsterberg (Azide) and Rideal-Stewart (Permanganate)] determined the amount of dissolved oxygen in industrial waste water in the presence of certain interfering substances.

The Alsterberg (Azide) method is intended for use where more than 0.1 ppm of nitrate nitrogen and less than 0.1 ppm of ferrous iron are present (18). The method is applicable in the presence of 100 to 200 ppm ferric iron if one milliliter of fluoride solution is added before final acidification and the titration is carried out immediately (18). Due to the presence of ferrous iron in great excess of the 0.1 ppm limit in the ditch, it is obvious that there was a great deal of interference as indicated by the results.

The Rideal-Stewart (Permanganate) procedure is intended for use only on samples containing ferrous iron (18). To overcome high ferric iron concentration (up to hundreds of ppm), one milliliter of KF solution was added and the solution was titrated immediately upon acidification. The presence of one ppm of ferrous iron results in the apparent loss of 0.14 ppm dissolved oxygen (18). The precision and accuracy of this method cannot be stated since they will vary according to the interfering compounds present and their concentrations(18). In addition, this procedure was used in the General Analysis Laboratory for the first time, the Alsterberg (Azide) method being the standard procedure.

5.2.2 Chemistry Downstream from Culvert

The results presented in Sect 4.2, Appendix 9.1, and Tables 2 and 5 indicate that dissolved iron concentration decreases quickly to low levels at the exit of the culvert. The large amounts of suspended solids in the cove are probably due to precipitation of ferric hydroxide when the low pH drainage initially mixes with the alkaline waters in the cove. By examining solubility product for $Fe(OH)_3$, one can readily see that ferric ion solubility decreases by a factor of 10^{12} when exposed to neutral or slightly alkaline water (see Appendix 9.7 for sample calculation of ferric ion solubility). Most of precipitate settles to the bottom of the cove although some is transported into the Clinch River.

5.3 Fish Experiments

The fish in Cage 4 secreted protective mucous in the acidic medium, pH = 2.9 (see Table 2). Continuous secretion caused the observed accumulation of mucous on the gills, mouth, and skin. The iron precipitate suspended in solution clogged the gills and the gill filaments of the fish in Cage 5. In both cases, the aeration of the blood with its accompanying gas exchanges was prevented, and death followed from a combination of anoxemia and carbon dioxide retention. Kolff (1908) found that movement of the gills is important in maintaining the gill capillary circulation (4). Immobilization of the gill filaments due to the large mass of iron deposit on them caused circulatory failure and death. Although acids below pH = 4.0 are considered lethal (4), the major cause of death in Cage 4 was respiratory and circulatory failure, and gill injury caused by the acidity.

No immediate effects on the internal organs of the fish were observed. Nonetheless,the swallowing of the water allows toxic substances access to the gastrointestinal tract and internal vital organs. Accumulation of toxic material can result after long exposure to low concentrations. A small amount of mucous on the fish from Cages 1, 2, 3, and 6 was secreted during examination of the fish out of water.

5.4 Batch Experiments

Several reasons can be cited to explain why dissolved iron levels remained at trace amounts after six days. Walsh (16) indicates that abiotic, aerobic, iron pyrite degradation rates are high at pH's over 5.5; therefore, one would expect a significant production of iron [Fe^{+2}, $Fe(OH)_3$] in the aerobic batches. The fact that iron was not present can be explained by the fact that aerobic fly ash samples were taken from the top of the ash surface where very light fly ash particles containing oxides of iron are present. Iron oxides, Fe_2O_3, Fe_3O_4, are very stable at neutral or alkaline pH(s) (17). (See Appendix 9.2 for composition of fly ash and Appendix 9.4 for location of ash samples.)

The anaerobic samples were made up of heavier, large particles, indicating that they do contain iron pyrite; however, significant iron production was not anticipated in the anaerobic batches because iron pyrite degradation requires oxygen (see Appendix 9.3).

If iron bacteria were present in the unsterilized batches, one would not expect significant bacterial enhancement of iron pyrite degradation at alkaline pH(s). Iron bacteria responsible for pyrite degradation, Metallogenium and T. Ferrooxidans, function best in acid environments (see Appendix 9.3 for description of iron pyrite degradation).

5.5 Culture Experiments

When the cultures were made, it was anticipated that the anaerobic bacteria might be responsible for iron pyrite degradation; hence, anaerobic cultures were prepared. Walsh (16), Bryner (1, 2), and Sutton (14) cite evidence indicating that the iron bacteria are aerobic. Since the anaerobic cultures were placed in an evacuated dessicator, the anaerobic cultures can be considered to have been subjected to reduced oxygen partial pressures, a condition that exists below the ash surface.

Iron bacteria were not observed in our cultures because the growth medium may not have been acidic enough for growth. Samples were taken too close to the primary flow from the slurry discharge where the pH is slightly alkaline. It is suspected that iron bacteria were not present in our samples because the bacteria only thrive in very acidic areas.

The utility of using a clear fly ash extract has not been verified. Although the clear extract may be very specific for iron bacteria in the ash ponds, it has not been verified that the extract contains the vital nutrients for iron bacterial growth. The extract, prepared by autoclaving an ash in water mixture, probably contains the vital organic nutrients for growth, but may lack the vital inorganic nutrients.

5.6 Flow Rate Estimates

The cross-sectional area for flow through the culvert pipe was estimated as a circular segment bounded by the water level. Since the bottom of the pipe was encrusted with deposits, this cross-sectional area for flow may be an upper limit. Measurements of the culvert characteristics (length, inner diameter, maximum depth of water, and distance across the water layer) were subject to error.

The manner of estimating the flow rate at the beginning of the drainage ditch was so affected by wind sweeping across the surface of the water that it should not be used in any flow rate calculations.

6. CONCLUSIONS

1. The red deposits have been analyzed by x-ray diffraction as FeOOH. The precipitate is believed to be composed of ferric hydroxide (an amorphous compound which cannot be analyzed by x-ray diffraction) and α-FeOOH, a crystalline substance believed to be a transformation product resulting from aging of ferric hydroxide.

2. The total amount of dissolved solids leaving the culvert, specifically iron, aluminum, calcium, and sulfate, is a very significant amount when compared to total dissolved solids leaving the weir.

3. If iron pyrite degradation is occurring, then it is occurring at very reduced levels at points downstream from the slurry discharge.

4. There must be significant ferrous iron oxidation to the ferric state occurring in the ditch waters, resulting in the precipitation of ferric hydroxide. The oxidation is probably catalyzed by Ferrobacillus ferrooxidans bacteria. The decreasing pH along the ditch is due to ferric hydroxide precipitation, resulting in the net production of hydrogen ions.

5. Catfish cannot live in environments that are too acidic or that contain a large amount of suspended solids such as ferric hydroxide.

6. The large amount of iron deposits suspended in solution in the cove waters results from the mixing of the very acidic secondary discharge with the slightly alkaline cove waters.

7. RECOMMENDATIONS

1. More cultures should be prepared under high and low oxygen partial pressures using ash material taken from several locations and at various depths. A phthalate buffer should be added to maintain the pH of the cultures at 3.5, an environment more conducive to the growth of iron bacteria.

2. The batches should be run with the above ash samples for a period of at least 30 days. The ash mixtures should be percolated so that there is uniform contact with the surrounding environment. Sulfuric acid should be added, if necessary, to keep the pH below 3.5.

3. More experiments to test the tolerance of catfish to low iron concentrations at longer exposure times should be run.

4. The effluent from the drainage ditch should be pumped back into the last ash pond. Then, the iron hydroxide would precipitate and settle in the ash pond rather than in the Clinch River and the discharge to the Clinch River would be neutral rather than acidic.

8. ACKNOWLEDGEMENTS

We are grateful to our consultant, C.C. Coutant, for his valuable help and suggestions throughout the project. Our special thanks go to G.H. Wheaton of the Bull Run Steam Plant for his permission to perform our studies on the plant property and S. Draggan for his assistance in the area of bacterial growth. In addition, we would like to thank L.J. Brady and W.R. Laing of the General Analysis Laboratory, N.M. Ferguson of the Environmental Analysis Laboratory, H.W. Dunn of the Physics Methods Laboratory, the staff of the Analytical Chemistry Division, and J.W. Jones of the staff of the Photography Department for their cooperation.

9. APPENDIX

9.1 Results of the Chemical Analysis of Dissolved Solids

See Figs. 1 through 3 for the location of sample collection points. A description and accuracy of the tests are discussed in Appendix 9.5. Results of all samples are shown in Tables 4 through 9.

Table 4. Water Sample Analyses (10-2-74)

Water Sample	mg/liter					
	Fe	Ca	Zn	Mn	SO_4	pH
1	985	142	0.2	0.64	3190	3.21
2	620	124	0.162	0.65	2347	3.00
3	595	127	0.168	0.69	2301	2.96
4	370	126	0.134	0.56	1966	2.82
5	0.36	32.2	0.008	0.01	13.3	7.50
6	0.05	31.4	0.007	0.02	14.9	7.73
7	0.08	32.5	0.006	0.01	14.6	7.73
8	<0.05	33.4	0.007	0.07	47.9	7.29
9	0.08	31.6	0.005	0.03	15.3	7.73

Table 5. Plume Water Sample Analyses (10-7-74)

Water Sample	mg/liter					
	Fe	Ca	Zn	Mn	SO_4	pH
S1	0.61	31.4	0.018	0.08	44.8	7.73
S2	0.10	29.9	0.006	<0.01	15.75	7.89
S3	0.10	30.3	0.003	<0.01	15.09	7.84
S4	0.10	29.9	0.002	<0.01	15.15	7.89
S5	0.13	30.2	<0.001	<0.01	16.14	8.13

Table 6. Water Sample Analyses (10-8-74)

Water Sample	mg/liter											pH	Total Dissolved Solids	Absorbance vs Dist. H_2O 450 nm
	Fe	Fe^{+2}	Fe^{+3}	Al	Si	Ca	Mg	Zn	Mn	SO_4	HCO_3			
1	965	990	80	85	39	148	18.6	0.191	0.62	2778	-	3.14	3857	0.041
2	610	610	73	60	31	118	14.4	0.181	0.62	2001	-	2.98	-	0.065
3	630	580	84	62	33	125.4	14.8	0.164	0.65	2010	-	3.08	-	0.056
4	370	200	217	68	28	119.8	15.6	0.196	0.55	1644	-	2.74	2610	0.038
5	360	-	-	61	27	120	15.8	0.238	0.55	1575	-	2.73	2749	0.037
6	∿0.05	-	-	5	2	-	-	-	-	-	112.2	8.37	49	0.002
7	0.09	-	-	2	1.9	29.3	8.3	0.006	0.02	15	115.9	7.83	-	0.002
8	<0.05	-	-	3	2.4	37.9	9.0	<0.001	0.03	101.76	51.2	6.68	31	0.014
9	0.11	-	-	5	2.4	29.6	8.3	0.004	0.01	14.61	117.1	7.70	-	0.001
Ash	<0.05	-	-	3	2.1	37.6	9.1	0.004	0.07	84.64	53.7	7.27	219	0.012

Table 7. Water Sample Analyses (10-14-74)

Water Sample	mg/liter									pH	Absorbance vs Dist. H_2O 450 nm
	Fe	Fe^{+2}	Fe^{+3}	Al	Si	Ca	Mg	SO_4	HCO_3		
1	850	851	6	75	33	141.6	17.3	2220	-	3.41	0.032
2	575	597	40	48	25	115	14.0	1767	-	3.23	0.056
3	550	571	66	52	23	126.4	14.9	1797	-	3.19	0.065
4	270	250	75	46	21	120.6	15.0	1212	-	3.20	0.066
5	200	-	-	44	21	206	14.3	1029	-	3.19	0.061
6	0.08	-	-	<2	1.6	28.4	8.5	14.22	111.02	7.74	0.011
7	0.07	-	-	<2	1.5	28.2	8.6	14.25	112.24	7.89	0.010
8	<0.05	-	-	<2	1.7	31.3	8.7	62.72	68.32	6.92	0.028
9	0.07	-	-	<2	2.1	27.9	8.2	14.34	112.24	8.04	0.012
10	26.8	-	-	4	3.0	42.4	9.4	163.1	29.28	6.14	0.065

Table 8. Water Sample Analyses (10-16-74)

Water Sample	mg/liter Fe	Ca	Mg	SO_4^{-2}	pH	Dissolved O_2
1	910	159.2	22.1	2922	3.05	$<0.05^*$
2	580	132.6	17.3	2229	2.89	$<0.05^*$
3	510	153.6	17.9	2109	2.83	$<0.05^*$
4	270	138.4	16.5	1395	2.80	$<0.05^*$
5	123	86.5	12.8	747	2.93	$<0.05^*$
6	0.16	28.2	8.5	16.68	7.88	6.72
7	0.14	29.0	8.4	16.83	7.32	-
8	<0.05	28.2	8.8	64.32	7.97	-
9	0.12	27.3	8.4	15.57	8.14	-

*Possible interference from high Fe concentration - unreliable.

Table 9. Cove Water Sample Analyses (10-16-74)

Water Sample	Depth (m)	mg/liter Fe	Ca	Mg	SO_4^{-2}	pH
B1	1	220	47.9	10.4	664.5	3.19
B2	2	7.4	33.4	8.9	133.0	6.13
B3	2.5	0.40	28.4	8.5	17.97	7.62

9.2 Composition of Slurry Deposited in Ash Ponds

Coal contains minerals which are oxidized during combustion in a furnace (see Table 10). Average compositions of fly ashes are shown in Fig. 7. The ash material present in the slurry discharge consists of chunks of pyrite separated from the coal before combustion, bottom ash from the furnaces (including unburned carbon), and fly ash (Table 10) (15).

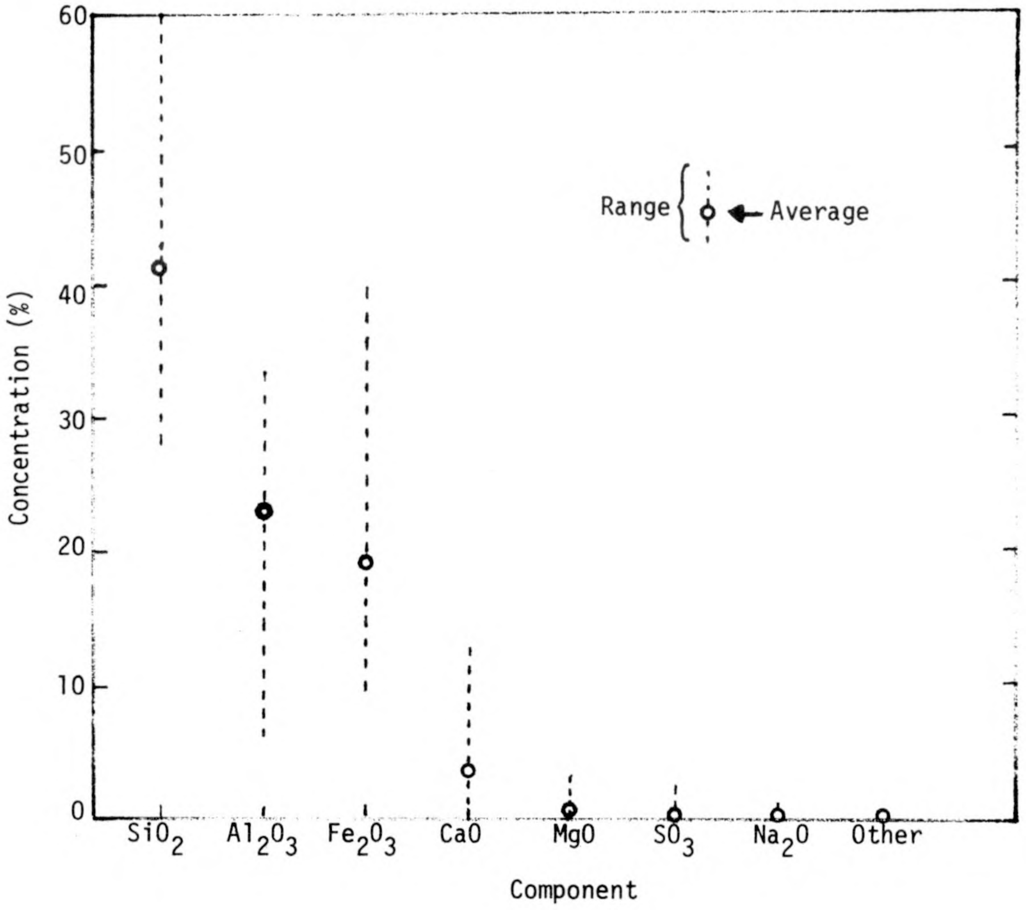
Table 10. Solid Components in the Slurry Discharge (3)

95% Minerals in Coal	FeS_2 $AlSiO_5(OH)_4$ $CaCO_3$
Ash	FeS_2 $3Al_2O_3 \cdot 2SiO_2$ Fe_2O_3, Fe_3O CaO, MgO, $CaSO_4$ C

9.3 Oxygenation of Ferrous Iron and the Role of Iron Bacteria in Its Catalysis

Dissolved iron in water is often removed by oxidizing the ferrous iron with dissolved oxygen and then removing the resulting ferric oxide floc by sedimentation or filtration. Ferrous iron in natural waters not only disturbs the oxygen balance but reduces the pH and forms suspended matter as ferric oxide - $Fe_2O_3 \cdot XH_2O$, where X may vary (13).

It has been found that bacteria can cause the dissolution of iron-bearing minerals such as pyrite (11, 14). Strains of bacteria identified with pyrite degradation are Ferrobacillus ferrooxidans (11, 14), Thiobacillus ferrooxidans (11, 14, 16), and Metallogenium (16). Referring to Table 11, these bacteria do not attack pyrite directly in Reaction 1, but increase the rate of aerobic oxidation of ferrous ions to the ferric state in Reaction 2. The ferric ions can oxidize additional pyrite (Reaction 3) producing ferrous ions, so that a cycle between Reactions 2 and 3 occur. In addition, ferric hydroxide can precipitate out by Reaction 4. Walsh and Mitchell found that acid-tolerant Metallogenium catalyzed ferrous iron oxidation in the pH 3.5-5.0 range with an optimum at pH 4.1. They found that growth of T. ferrooxidans, also acid-tolerant, was dependent on the growth of Metallogenium to lower solution pH through acid production from the ferric iron reaction following catalysis of ferrous iron oxidation. Its optimal activity is at pH 3.5 (16).



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RANGE AND AVERAGE OF COMPOSITION
ANALYSIS OF U.S. FLY ASHES
(% concentration by weight) (3)

DATE	DRAWN BY	FILE NO.	FIG.
10-14-74	MC	CEPS-X-200	7

Table 11. Chemical Reactions in Iron Pyrite Degradation (16)

1. Pyrite Oxidation

$$FeS_2(s) + \frac{7}{2} O_2 + H_2O \longrightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+$$

2. Pyrite Degradation Cycle

$$Fe^{+2} + \frac{1}{4} O_2 + H^+ \longrightarrow Fe^{+3} + \frac{1}{2} H_2O$$

3. $FeS_2(s) + 14Fe^{+3} + 8H_2O \longrightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+$

4. Ferric Iron Deposition

$$Fe^{+3} + 3H_2O \rightleftarrows Fe(OH)_3(s) + 3H^+$$

It has been shown (12) that oxidation of iron pyrite occurs much faster by Reaction 3 than by Reaction 1. Thus, only ferrous iron oxidation is a significant source of ferric iron. The rate of abiotic ferrous iron oxidation is directly related to solution pH (12) with the relationship above pH 4.5 being:

$$-\frac{d[Fe^{+2}]}{dt} = k[Fe^{+2}]\ [O_2][OH^-]^2$$

where:

$$k = 8.0 \times 10^{13} \text{ liter}^2\text{-mole}^{-2}\text{-atm}^{-1}\text{-min}^{-1}$$

at 25°C. Only above pH 4.5 is abiotic ferrous iron oxidation significantly rapid since at pH < 4.5 the cycle is rate-limited by the ferrous iron oxidation rate (12). At pH between 4.5 and 3.5, chemical ferrous iron oxidation proceeds at a rate indirectly pH dependent (12). The oxidation rate at pH less than 3.5 is independent of pH by the following rate expression:

$$-\frac{d[Fe^{+2}]}{dt} = k'[Fe^{+2}]\ [O_2]$$

where:

$$k' = 1.0 \times 10^{-7} \text{ atm}^{-1}\text{min}^{-1} \text{ at } 25°\text{C } (12)$$

9.4 Procedure

9.4.1 Field Work

9.4.1.1 Water Samples. Four sets, consisting of 9 sample points each, were collected in 500-ml plastic bottles at the points shown on Fig. 1. The results of the analytical tests performed on these samples are presented in Tables 4, 6, 7, and 8. On October 14, in addition to the above nine samples, one sample was collected at the location of fish cage 5 (see Fig. 4).

In addition, on October 8 and 14, two samples each were taken in 125-ml ground-glass stoppered bottles at sample points 1 through 4 for ferrous/ferric analysis. Each bottle was filled to the top and then stoppered so that no air bubbles could be present to cause any oxidation of the sample. On October 8, samples were collected at positions 4 and 5 for precipitate analysis. On October 14, a sample of precipitate was taken from the bank of the ditch at position 3. Also on the 8th, a sample (labeled "ASH" in Table 6) of the main water flow was taken in the ash ponds at a position near the point where ash samples were taken for subsequent batch simulations.

On October 16, samples were collected in stoppered ground-glass bottles for dissolved oxygen content at positions 1 through 6. Additional samples were collected on October 18 at positions 1, 2, and 4. The technique used to fill the ferrous/ferric bottles was again used.

On October 7, "plume" samples were taken from the side of an ORNL boat at the surface of the river at the locations indicated on Fig. 2. "Cove" samples were taken at several depths on October 15 (see Fig. 3 for relative locations).

9.4.1.2 Sample Fish Observations. On October 3, seventy baby catfish, nurtured at the Aquatic Ecology Laboratory fish ponds, were placed in seven wire cages, ten fish per cage, at position 1 (Fig. 4) to become acclimated to the waters of the Clinch River. On October 7, six of the cages were moved to positions 2 through 6. It was discovered on October 9 that the cage at position 5 had opened part way, allowing all 10 fish to escape. A new batch of 10 fish was placed at position 5 on October 10.

The conditions of the fish were observed on a daily basis. When it was discovered that fish in a particular cage (either 4 or 5) had died, they were immediately transferred to the laboratory for examination. On October 18, three surviving fish from positions 1, 2, 3, 6, and 7 were returned to the laboratory to determine the effects of the two-week immersion in the river. The remaining seven fish from each cage were released into the river.

9.4.1.3 Flow Rate in Drainage Ditch Culvert. Two small plastic bottles partially filled with water were released at the entrance of the culvert. The time required to travel to the exit of the culvert was measured. Three runs were made. The length of the culvert, its inner diameter, the depth of water at its vertical centerline, and the chord formed by the water line in the culvert were all measured.

An attempt was made to measure the flow rate at the point marked position 1 on Fig. 4 using the same procedure followed in the culvert. The velocity of the plastic bottles was observed to vary with any changes in wind velocity. An attempt was then made to follow the flow pattern of oil drops observed on the surface of the stream. Again, it was found that the velocity of an oil drop would vary with any changes in wind velocity.

9.4.2 Water Seepage Simulation

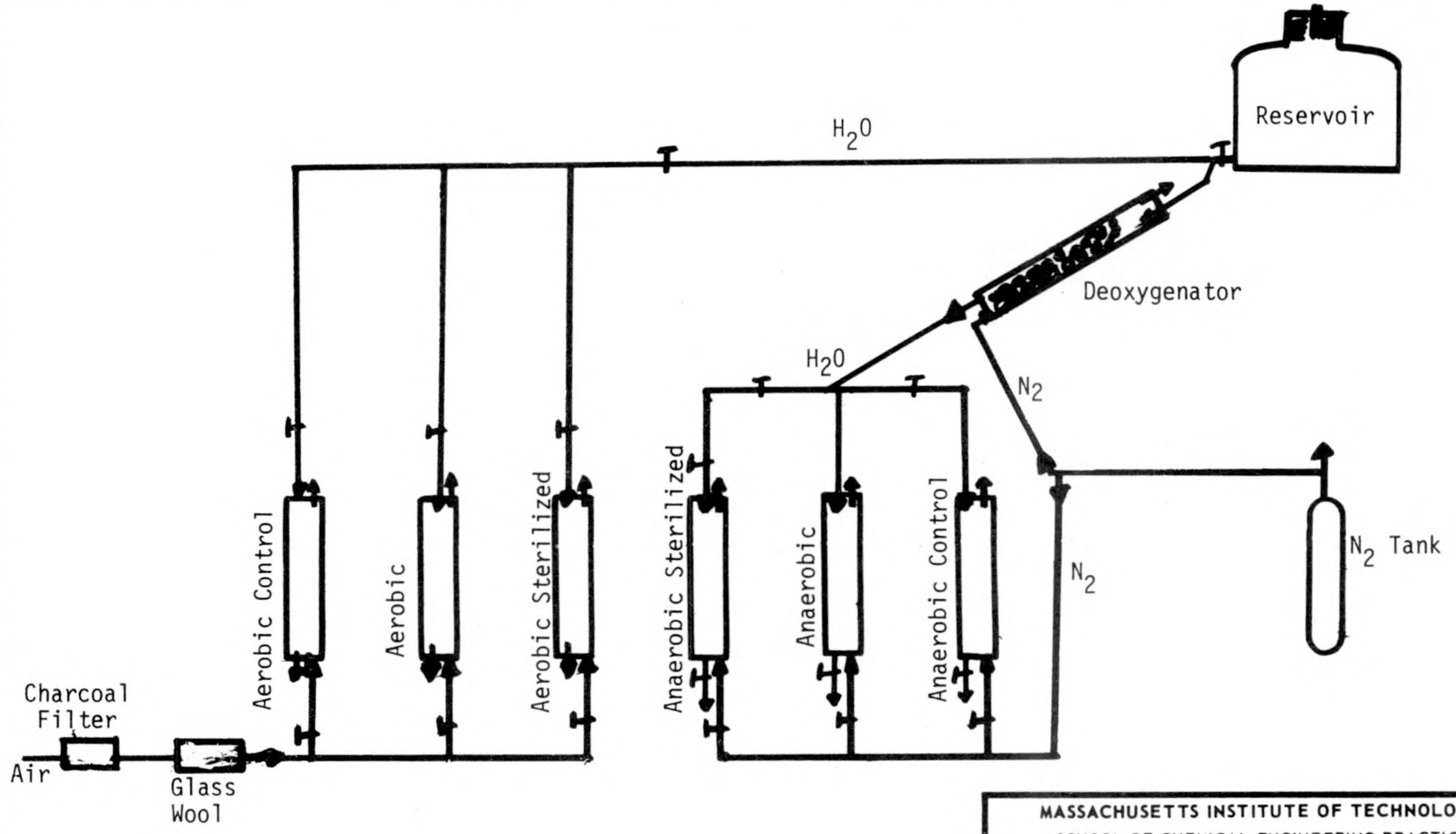
Experiments were set up to simulate four water seepage environments: aerobic, sterilized aerobic, anaerobic, and sterilized anaerobic. Sterilized fly ash required was prepared by placing fly ash in a 250°F, saturated steam environment (autoclave) for 20 min. Anaerobic conditions were maintained by bubbling a nitrogen stream through the mixtures, aerobic conditions by constant aeration of mixture. Anaerobic environments employed a fly ash mixture obtained from a point midway from the slurry discharge to the weir just below ground water levels. Aerobic environments used ash samples taken from the same location but sampling at the surface instead.

The first experiment was set up to simulate steady state drainage conditions present in fly ash (see Fig. 8). Four glass columns (1.75-in.-diam x 3-ft long) were packed with the appropriate fly ash mixture and glass wool at the bottom for support. The two control glass columns were packed with chunks of styrofoam. Spring water from a tap in Bldg. 2001 was used for the reservoir after sterilization in an autoclave. Water used for the anaerobic column was run through a deoxygenator column (PVC) countercurrently with nitrogen. Air supply was purified by running it through two small columns, one packed with charcoal and the other with glass wool. The experiment was abandoned in the later stages of preparation because of leaks around the rubber stoppers. However, it is felt that this experiment should be performed at some future date with sturdier, more water-tight columns.

The second experiment was a batch process (see Fig. 9). Four one-liter flasks were fitted with two-hole rubber stoppers. Approximately 300-400 ml of the appropriate wet fly ash was placed in each flask along with 300-400 ml of sterilized water. The air supply was again purified by running it through charcoal and glass wool. The mixtures were stirred, capped, and allowed to stand for six days, at which time the spring water was sampled for chemical analysis.

9.4.3 Bacterial Cultures

A clear fly ash extract was prepared from which a nutrient agar was made that should be very specific for any bacteria that might be present in fly ash material. Forty petri dishes were coated with this agar mixture. The petri dishes were then plated in batches of five with a particular water dilution of ash material. Four batches were prepared, each of a different dilution, for a total of twenty plates. (Dilution of $1:10^7$, $1:10^6$, $1:10^5$, and $1:10^4$ were chosen because the dilution that grows the purest cultures with the least interference of ash material was not known.)



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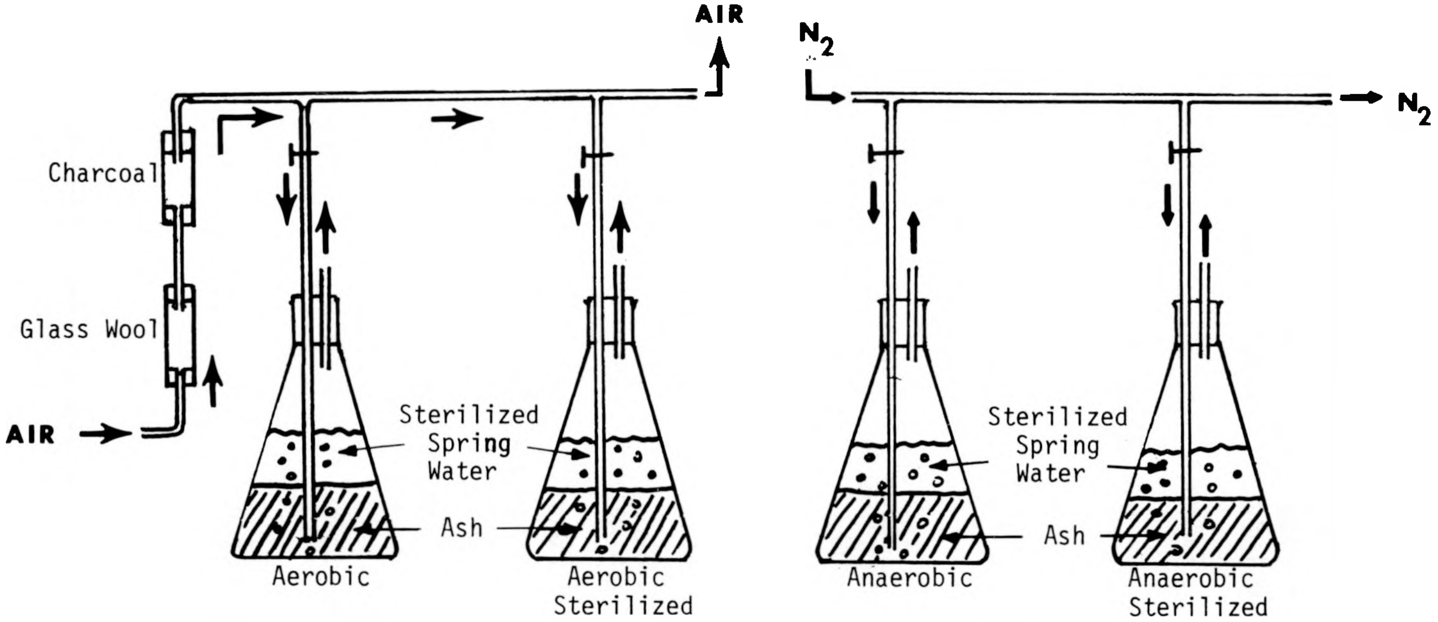
SCHEMATIC DIAGRAM OF COLUMN APPARATUS

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	CW	CEPS-X-200	8



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SCHEMATIC DIAGRAM OF BATCH PROCESS

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	MC	CEPS-X-200	9

The plates of the remaining twenty petri dishes were carried out in the same manner, only a mixture of fly ash was used that was thought to be more conducive to growing anaerobic bacteria. The fly ash for these anaerobic cultures was taken from a point just below ground water levels at a point midway down the ditch and close to the primary flow in the ash ponds. The fly ash for the other samples was taken from the same location but at the surface. Aerobic cultures were incubated at 25°C; anaerobic cultures were placed in an evacuated dessicator. Preparation of fly ash extract agar and the dilution method are summarized below:

Preparation of Nutrient Fly Ash Extract Agar:

1. One kg of fly ash aerobic blend was placed in a 4-liter flask with 1000 ml of H_2O.

2. Flask was autoclaved for 20 min at 250°F and 2 atm steam pressure. Then, 1/4 teaspoon of Celite filteraid was added; the contents were swirled and filtered.

3. Filtrate was autoclaved for 20 min.

4. In a two-liter flask, 100 ml of clear ash extract, 15 gm bacto agar, 1 gm dextrose, 0.5 gm K_2HPO_4, and 900 ml distilled water was added. The solution was autoclaved for 15 min and allowed to cool, then transferred to 500-ml flasks, and autoclaved again for 20 min.

Preparation of Culture:

1. Ten grams of aerobic ash material was subjected to a series of dilutions down to $1:10^5$.

2. Five petri dishes were prepared at any one time. Four batches were prepared in all:

$1:10^7$ prepared by pipetting 0.1 ml from a test tube containing a 10^5 dilution into each dish.

$1:10^6$ prepared by pipetting 1.0 ml from a test tube containing a 10^5 dilution into each dish.

$1:10^5$ prepared by pipetting 0.1 ml from a test tube containing a 10^3 dilution into each dish.

$1:10^4$ prepared by pipetting 1.0 ml from a test tube containing a 10^3 dilution into each dish.

Plates were transferred to a 25° incubator.

3. The procedure in Step (2) was repeated using 10 grams of anaerobic ash. Twenty plates were stored in an evacuated dessicator.

4. Cultures were checked daily. Smears of observable bacterial colonies were prepared on microscope slides and observed under a microscope.

9.5 Evaluation of Results of Chemical Analysis

9.5.1 Methods and Accuracies of Chemical Analyses (19)

The procedures for the analyses of the samples are presented in detail in the ORNL laboratory manuals or user's manuals of the equipment used for measurements. The analytical method and their accuracies are summarized below:

	Method	Accuracy
Fe (total)	Atomic absorption (measured in Bldg. 2024, ORNL)	From 5% for >100 ppm to 10% for >0.1 ppm. Lower limit: 0.05 ppm
Fe^{+2}	Determined spectrophotometrically as orange-red, O-phenathroline-ferrous complex in a solution buffered at pH 3.5. The absorbance was determined at 515 mμ.	2-3%
Fe^{+3}	$[Fe^{+3}] = [Fe^{total}] - [Fe^{+2}]$. $[Fe^{total}]$ was determined by reducing Fe^{+3} ions to Fe^{+2} ions and then measuring Fe^{+2} concentration as described above.	5%
Al	pH of the solution was adjusted to ∿11 with NaOH to precipitate $Fe(OH)_2$. After centrifuging, the absorbance of Al in the supernatant was measured at 520 nm wavelength versus a reagent blank.	From 5-10% for >50 ppm to 50% for <5 ppm
Si	Reacted with molybdate ion reagent in acid medium to form silicomolybdate. This complex was reduced to silicoheteropoly-blue. The absorbance was measured at 690 nm against a reagent blank.	From 5-10% for >20 ppm to 50% for <5 ppm
Ca, Mg	Atomic absorption	5%
Zn, Mn	Atomic absorption	5-10%. Lower Limit: 0.01 ppm
SO_4^{-2}	Using methylthymolblue as color agent and measuring the absorbance with colorimeter.	2-5%

	Method	Accuracy
CO_3^{-2}	In samples with pH <4.5, 99% of CO_2 is present in the form of H_2CO_3 which decomposes readily to H_2O and CO_2 and cannot be traced (18)	
HCO_3^-	98% of CO_2 is present in solutions of $4.5 < pH < 8.5$ as HCO_3^- (18). The concentration of HCO_3^- was determined by titration with HCl to pH 4.6, with methylorange as indicator.	2%
pH	pH meter	2%
total dissolved solids	Filtered and then evaporated to dryness at 110°C. The residue was weighed.	From 5% for >2000 ppm to 100% for 31 ppm
Absorbance	Determined at 450 nm against distilled water.	5%
Precipitate	Spectrographic analysis	50%
wt % of Fe in ppt	Weighed and dissolved to known volume, reduced all Fe^{+3} to Fe^{+2}, spectrophotometric methods for total Fe^{+2} described above, mg/liter $\text{wt }\% = \frac{[Fe^{+2}]\text{mg/liter x sample volume}}{\text{wt of ppt used to prepare sample}}(100\%)$	5%
dissolved O_2	1. Alsterberg procedure (18) 2. Rideal-Stewart (permanganate) procedure (18)	result unreliable result unreliable

9.5.2 Completeness of Chemical Analysis

A material balance of a water sample gives

$$\begin{array}{l}\text{concentration of}\\\text{total dissolved}\\\text{solids}\end{array} - \sum_{i=1}^{n} \begin{array}{l}\text{concentration}\\\text{of species i}\\\text{tested}\end{array} = \begin{array}{l}\text{concentration of}\\\text{species not analyzed}\end{array}$$

Material balances were made for five water samples (see Appendix 9.7). The results are presented in Table 12.

Table 12. Amount of Dissolved Solid Unaccounted for in Chemical Analyses and Their Accuracies

Sample (10-8-74)	Concentration of Species Not Analyzed (mg/liter)	Total Dissolved Solids Unaccounted For (%)	Accuracy (%)
1	-177	-4.6	± 35 - 90
4	364	14	± 10 - 46
5	589	21.4	± 6 - 28
8	-174	-562	± 1 - 7
Ash	29	13.1	± 8 - 51

Assuming maximum inaccuracy in the chemical analyses, the minimum amount of species in the solution unaccounted for were calculated (see Appendix 9.7). The results are tabulated in Table 13.

Table 13. Minimum Amount of Dissolved Solid Unaccounted for in Chemical Analyses

Sample	Concentration of Species Not Analyzed (Maximum Inaccuracy) (mg/liter)	Total Dissolved Solids Unaccounted for (minimum) (%)
1	-17.7	-0.45
4	197	7.5
5	424	15.4
8	-162	-522
Ash	14.2	6.5

The chemical analyses of the water samples were not complete, but accounted for the majority of the dissolved solids. The negative values obtained for the concentration of species not analyzed in samples 1 and 8 (see Tables 12 and 13) indicate that the total dissolved solids in these samples were less than the amounts analyzed which is impossible. The actual amount of total dissolved solids must be larger than those obtained by the analytical methods. The water samples were evaporated to dryness at 110°C. The weight of the residue was reported as amount of total dissolved solids. Assuming 51.8 mg/liter of bicarbonates in sample 8 (see Table 8) decomposed to carbon dioxide and water during evaporation, the total dissolved solids in the sample were 110.8 mg/liter less than the total species analyzed. This discrepancy cannot be accounted for.

9.6 Location of Original Data

The original data are located in ORNL Databook A-7220-G, pp. 1-73, on file at the MIT School of Chemical Engineering Practice, Bldg. 3001, ORNL.

9.7 Sample Calculations

Discharge Rate at Culvert

From measurements (see Fig. 10),

culvert diameter = 57 cm

depth of water in the center of culvert = 7.5 cm

distance across water surface in culvert = 47 cm

$$\text{velocity of water} = \frac{28.23 \text{ m}}{30 \text{ sec}} = 94.1 \text{ cm/sec}$$

It was observed that the bottom of the culvert was covered with iron deposits. The cross-section of flow was approximated to be a circular segment.

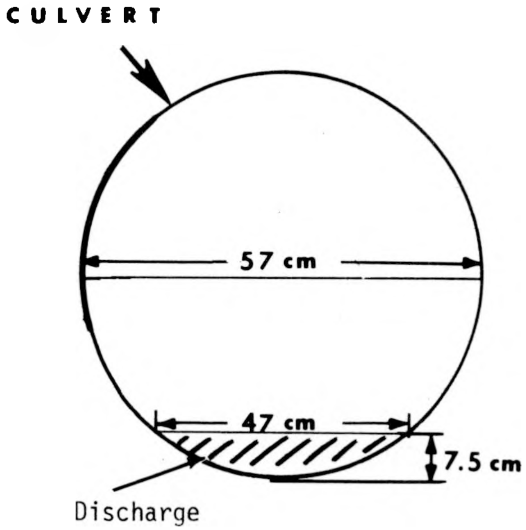
$$\frac{\text{height}}{\text{radius}} = \frac{7.5 \text{ cm}}{(57 \times 0.5)\text{cm}} = 0.263$$

The corresponding central angle is 85° (10).

$$\frac{\text{area}}{(\text{radius})^2} = 0.244 \ (\underline{10})$$

Therefore,

$$\text{cross-sectional area} = (0.244)(28.5)^2 = 198.2 \text{ cm}^2$$



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CROSS SECTION OF CULVERT

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	mc	CEPS-X-200	10

$$\frac{\text{chord}}{\text{radius}} = \frac{47\text{ cm}}{(57 \times 0.5)\text{cm}} = 1.65$$

The corresponding central angle is 111° (10).

$$\frac{\text{area}}{(\text{radius})^2} = 0.502\ (\underline{10})$$

Therefore,

$$\text{cross-sectional area} = (0.502)(28.5)^2 = 407.7\text{ cm}^2$$

$$\frac{\text{height}}{\text{chord}} = \frac{7.5\text{ cm}}{47\text{ cm}} = 0.160$$

The corresponding central angle is 71° (10).

$$\frac{\text{area}}{(\text{radius})^2} = 0.147\ (\underline{10})$$

Therefore,

$$\text{cross-sectional area} = (0.147)(28.5)^2 = 119.4\text{ cm}^2$$

The above areas were averaged to obtain the cross-sectional area of the flow in the culvert:

$$\text{cross-sectional area of flow in culvert} = \frac{198.2 + 407.7 + 119.4}{3}$$

$$= 241.8\text{ cm}^2$$

$$\text{flow rate} = \text{velocity, cm/sec, x cross-sectional area of flow, cm}^2$$

$$= (241.8)(94.1)\text{ cm}^3/\text{sec} \times 10^{-3}\text{ liter/cm}^3$$

$$= 22.75\text{ liter/sec} \times 60\text{ sec/min} \times 1/3.785\text{ gal/liter}$$

$$= 360\text{ gpm}$$

Flow Rate at Beginning of Drainage Ditch

width of ditch = 121 cm

depth of the stream = 15 cm

average velocity of the stream = 1 m/37 sec = 2.7 cm/sec

maximum cross-sectional area (rectangular) = (121)(15) cm^2
= 1815 cm^2

flow rate = velocity (cm/sec) x cross-sectional area of flow (cm^2)
= 1815 cm^2 x 2.7 cm/sec x 10^{-3} liter/cm^3
= 4.9 liter/sec

Estimation of Maximum Abiotic Ferrous Oxidation Rate (at beginning of the drainage ditch where $[Fe^{+2}]$ is highest)

pH = 3.2 (Table 2)

oxidation rate = $-\frac{d[Fe^{+3}]}{dt} = k'[Fe^{+2}][O_2] \neq f(pH)$ (12)

$k' = 10^{-7}\ \text{atm}^{-1}\ \text{min}^{-1}$ at 25°C (12)

$[Fe^{+2}]$ = 920 mg/liter (see Table 2)

maximum dissolved $[O_2]$ = 0.2 atm

oxidation rate = (920 mg/liter)(0.2 atm x $10^{-7}\ \text{atm}^{-1}\text{min}^{-1}$)
x (60 min/hr)(24 hr/day)
= 0.0264 mg/liter/day

Walsh and Mitchell (12) considered 0.007 mg/liter/day an extremely slow oxidation rate and 5.76 mg/liter/day a rapid one.

Equilibrium Constants for $Fe(OH)_2$ and $Fe(OH)_3$

$$Fe(OH)_2(s) \rightleftarrows Fe^{+2} + 2OH^-$$

$$K_{ferrous} = [Fe^{+2}][OH^-]^2 = 8 \times 10^{-16}$$ (8)

At point 1 (beginning of the drainage ditch),

$$pH = 3.2$$

$$[H^+] = 10^{-3.2}$$

but,

$$[H^+][OH^-] = 10^{-14}$$

Therefore,

$$[OH^-] = (10^{-14})/(10^{-3.2}) = 10^{-10.8} \text{ moles/liter}$$

$$[Fe^{+2}] = 920 \text{ mg/liter (Table 2)}$$

$$= (920 \text{ mg/liter}) \times (1/56 \text{ moles/gm})(10^{-3} \text{gm/mg})$$

$$= 1.6 \times 10^{-2} \text{ moles/liter}$$

$$K_{ferrous} = (1.6 \times 10^{-2})(10^{-10.8})^2 = 1.6 \times 10^{-23.6} (\text{moles/liter})^3$$

$$Fe(OH)_3(s) \rightleftarrows Fe^{+3} + 3OH^-$$

$$K_{ferric} = [Fe^{+3}][OH^-]^3 = 4 \times 10^{-38}$$ (8)

At point 1 (beginning of the ditch),

$$[OH^-] = 10^{-10.8} \text{ moles/liter as calculated above}$$

$$[Fe^{+3}] = 43 \text{ mg/liter (Table 2)}$$

$$= (43 \text{ mg/liter})(1/56 \text{ moles/gm})(10^{-3} \text{ gm/mg})$$

$$= 7.7 \times 10^{-4} \text{ moles/liter}$$

$$K_{ferric} = (7.7 \times 10^{-4})(10^{-10.8})^3 = 7.7 \times 10^{-36.4} (\text{moles/liter})^4$$

Dissolved Solids Leaving the Weir and Culvert

amount of dissolved solid in flow = concentration x flow rate

concentration of iron in culvert = 320 mg/liter (Table 2)

flow rate of drainage ditch at culvert = 22.75 liter/sec

total iron leaving culvert = 320 mg/liter x 22.75 liter/sec x 10^{-3} gm/mg x 60 sec/min

= 437 gm/min

Mass Balance of Dissolved Solids in a Water Sample

From the results of chemical analysis of a water sample taken at point 4 on 10-8-74 (Table 6),

concentration of total dissolved solids = 2610 mg/liter

total concentration of dissolved Fe, Al, Si, Ca, Mg, Zn, Mn, and SO_4 = 2246 mg/liter

concentration of species not analyzed = 2610 - 2246 = 364 mg/liter

total dissolved solids unaccounted for = $\frac{364}{2610}(100)$ = 14%

The accuracy of the analytical result for each species ranges from 0 to ±10%. These errors summed to 1.7 to 5.2% of the total concentrations of the species tested. The amount of total dissolved solids was determined with 2% accuracy. The accumulated errors range from 10.4 to 46.5%. If maximum inaccuracy in the analyses is assumed, the minimum amount of dissolved solids unaccounted for can be estimated.

minimum amount of species unaccounted for, mg/liter = amount of species unaccounted for, mg/liter, x (1 - maximum inaccuracy)

= (364)(1 - 0.46) = 196.6 mg/liter

maximum % of dissolved solids unaccounted for = $(\frac{196.6}{2610})(100)$

= 7.5%

9.8 Nomenclature

B#	water sample taken below water surface (see Fig. 3 for location)
$[Fe^{+2}]$,$[Fe^{+3}]$	ferrous (ferric) ion concentration in solution, moles/liter
$[H^+]$	hydrogen ion concentration, moles/liter
k	ferrous ion oxidation rate constant for pH > 3.5, $k = 8 \times 10^{13}$ $liter^{2}$-$mole^{-2}$-atm^{-1}-min^{-1} at 25°C
k'	ferrous ion oxidation rate constant for pH < 3.5, $k' = 10^{-7}$ atm^{-1}-min^{-1} at 25°C
K	solubility product
$[O_2]$	concentration of dissolved oxygen, atm^{-1}
$[OH^-]$	concentration of hydroxyl ion in solution, moles/liter
P#	precipitate samples, # is the number indicating the location where the samples were collected
S#	plume water samples, # is the number indicating the location where the samples were collected (see Fig. 2)

9.9 Literature References

1. Bryner, L.C., J.V. Beck, D.B. Davis, and D.G. Wilson, "Microorganisms in Leaching Sulfide Minerals," Ind. Eng. Chem., 46, 2587 (1954).

2. Bryner, L.C., and R. Anderson, "Microorganisms in Leaching Sulfide Minerals," Ind. Eng. Chem., 49(10), 1721 (1957).

3. Cavin, D.C., "A Study of Iron and Aluminum Recovery from Power Plant Fly Ash," IS-T-611, Ph.D. Thesis, Ames Laboratory, Iowa State Univ., Ames (1973).

4. Ellis, M.M., "Detection and Measurement of Stream Pollution," in "Biology of Water Pollution," L.E. Keup, W.M. Ingram, and K.M. Mackenthun, pp. 129-182, Federal Water Pollution Control Administration (1967).

5. Krause, A., and J. Lezuchowska, "Aging of Iron (III) Hydroxide Dry Gel that are Amorphous to X-ray," Kolloid-Z, 181, 69 (1962) Abstract in Chemical Abstracts, 57, 1588(c) (1957).

6. Lengweiler, H., W. Buser, and W.F. Feitknecht, "Determination of the Solubility of Iron (III) Hydroxide with Ion," Helv. Chem. Acta, 44, 796 (1961) abstract in Chem. Abs., 55, 26628 (e.f.) (1961).

7. McAlpine, R.K., and B.A. Soule, "Qualitative Chemical Analysis," 4th ed., D. Van Nostrand, New York (1933).

8. Meites, L., "Handbook of Analytical Chemistry," 1st ed., McGraw-Hill, New York (1963).

9. Montgomery, T.L., R.A. Casper, A.I. El-Twaty, and L.M. Rosenbaum, "The Importance of Temperature in the Transport of Mercury in a Living Ecosystem - Transport to Daphnia Magna," ORNL-MIT-188, MIT School of Chemical Engineering Practice, ORNL, Oak Ridge (March 25, 1974).

10. Perry, J.H., C.H. Chilton, and S.D. Kirkpatrick, "Chemical Engineers' Handbook," 4th ed., McGraw-Hill, New York (1963).

11. Silverman, M.P., M.H. Rogoff, and I. Wender, "Removal of Pyritic Sulphur from Coal by Bacterial Action," Fuel, 42, 113 (1963).

12. Singer, P.C., and W. Stumm, "Acidic Mine Drainage: The Rate-Determining Step," Science, 167, 1121 (1970).

13. Stumm, W., and G.F. Lee, "Oxygenation of Ferrous Iron," Ind. Eng. Chem., 53, 143 (1961).

14. Sutton, J.A., and J.C. Corrick, "Microbial Leaching of Copper Minerals," Mining Eng., 37 (June 1963).

15. Tennessee Valley Authority, "The Bull Run Steam Plant," Technical Report #38, Knoxville (1967).

16. Walsh, F., and R. Mitchell, "A pH-Dependent Succession of Iron Bacteria," Env. Sci. Tech., 6, 809 (1972).

17. Weast, R.C., "Handbook of Chemistry and Physics," 54th ed., CRC Press (1973).

18. "Annual Book of ASTM Standards," Part 23, Am. Soc. for Testing and Materials, Philadelphia (1972).

19. Chemical Analysis Laboratory Manual, ORNL, Oak Ridge.

20. Letter dated March 8, 1974, from A.H. Smalley, TVA, Chattanooga, to C.C. Coutant, ORNL.

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