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**DEPARTMENT OF ENERGY, MINES AND RESOURCES**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 73-55**

*Mines Branch Program  
on Environmental Improvement*

**AN EXPERIMENTAL STUDY OF THE  
WEATHERING OF MILL TAILINGS IN  
CONNECTION WITH WATER POLLUTION**

**Part 4:**

**THE EFFECT OF TAILINGS SAMPLES FROM  
VARIOUS CANADIAN MINING COMPANIES  
ON THE COMPOSITION OF WATER**

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**MINERAL SCIENCES DIVISION**

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by

A. Jongejan\*

SUMMARY

Tailings samples from eighteen companies mining sulphide orebodies in Canada were subjected to percolation tests. The experimental results indicated that a sulphide: carbonate ratio in the bulk mineral composition greater than 6.5:1 produced acid waters. The calcium contents of the waters were not correlated to the carbonate content of the tailings but to its grain-surface area exposed to water.

The weight surplus of sulphides over carbonates required to produce acid water is partly due to the difference between the specific gravities of these minerals. The ratio between the grain-surface areas, along which dissolution taken place, is smaller than the ratio between the weights of the relevant minerals. However, the surface-area properties of the tailings minerals exposed to water and the relevant ratios between the minerals-grain surfaces can be expected to change as tailings weather.

A reaction between the solutes formed by the dissolution of pyrite and calcite is considered. Calcium sulphate is produced and, in the carbonate equilibria, ferric hydroxide is present as a precipitate. It is possible that an intermediate type of iron carbonate is formed before all iron ions are hydrolyzed.

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CONTENTS

	<u>Page</u>
Summary .....	i
1. Introduction .....	1
2. Experimental Methods .....	3
3. Experimental Results .....	4
3.1. The Effect of the Tailings Sample Supplied by Mining Company No. 1 on the Composition of Water .....	5
3.2. do. for Mining Company No. 2 .....	7
3.3. do. for Mining Company No. 3 .....	8
3.4. do. for Mining Company No. 4 .....	10
3.5. do. for Mining Company No. 5 .....	12
3.6. do. for Mining Company No. 6 .....	14
3.7. do. for Mining Company No. 7 .....	18
3.8. do. for Mining Company No. 8 .....	19
3.9. do. for Mining Company No. 9 .....	21
3.10. do. for Mining Company No. 10 .....	23
3.11. do. for Mining Company No. 11 .....	25
3.12. do. for Mining Company No. 12 .....	30
3.13. do. for Mining Company No. 13 .....	34
3.14. do. for Mining Company No. 14 .....	36
3.15. do. for Mining Company No. 15 .....	37
3.16. do. for Mining Company No. 16 .....	44
3.17. Information on the Weathering Process Obtained from Field Samples Collected from Tailings Ponds of Mining Companies No. 17 and No. 18 .....	46
4. Discussion .....	53
5. Acknowledgements .....	64
6. References .....	65

## 1. INTRODUCTION

The differences between the mineral compositions of tailings from sixteen companies mining sulphide ores in Canada have been described in Part 3 of this series of reports<sup>(1)</sup>. Part 4 (i. e., this part) indicates to what extent the predictions made in Part 3 on the effect of these differences on the composition of water percolating through tailings in laboratory experiments were valid.

Although concepts have been developed concerning the nature of some of the reactions that possibly take place in the weathering process, the conclusions and assumptions made in the discussion of this report will be restricted primarily to phenomena indicated by the results of the laboratory experiments involving the effects of various tailings compositions on water. All tailings samples were subjected to tests of the type described in the first two parts of this series of reports<sup>(2, 3)</sup>.

The experiments described in the first four parts of the study were aimed at providing information on the subject from a practical point of view. It is emphasized that only a few aspects of the problem could be discussed. The experiments on these aspects were very limited because of the large number of variables inherent in the weathering process. The experiments, for instance, have been done on sterilized samples only, because the effect of the microbiological action on tailings has to be separated completely from the other variables in order to limit the observed effects to the action of purely chemical and physical factors. Parts of the microbiological aspects are being studied separately until concepts about the chemical and physical variables have been developed<sup>(4)</sup>. The influence of the microbiological action on the latter can then be studied in the last phase of this project.

Statements in this report concerning a possible acid reaction of a mineral composition in water or about a mineral composition having a pollutant potential do not necessarily imply that they will be valid in field conditions. The results of the experiments involving tailings samples are aimed solely at providing information from an experimental point of view. Whether or not, or how, this information could be applied technically to reduce acid drainage is beyond the scope of this study. In order to avoid invalid interpretations of the information supplied by this study, the names of the mining companies have been withheld. Any reference to observations made in the field apply to conditions where a minimum of tailings pond management had been practised. Elimination of as many variables not inherent in the natural weathering process as can be expected from management was important. The term tailings pond, used in these reports, refers to tailings deposited in various locations. These ponds are, therefore, not embanked. They are partly dry, depending on the geomorphological aspects of the location, the rainfall and the drainage pattern.

The percolation experiments on the tailings samples supplied by the various mining companies, as described in this report, simulate the results of temporary water accumulation and stagnancy in order to eliminate the drainage factor. A difference between drainage and stagnant conditions, involving the chemical reactions that take place in the process, has been described in Part 2 of this series of reports<sup>(3)</sup>. Although the difference in the effects appeared to be very significant, it will vary for each tailings pond (pile) and, probably also, within each tailings pond, depending on the geomorphology of the location.

It is thus emphasized that, even though certain relationships between the mineral compositions of tailings and the compositions of the waters percolating through these tailings could be demonstrated, no definite conclusions should be made as to the composition of the drainage water in the field and as to the pollutant potential of an actual tailings pond.

If the volume of a tailings pond is compared with that of the drainage water, the flow of water draining away may be so slow as to suggest stagnancy. However, it can be expected that the water flow is layered

and that the flow affecting the water composition depends on the depth (age) to which a tailings pond is weathered.

The conclusions or remarks made in the descriptions of the percolation runs refer, thus, only to conditions which seem to be indicated by particular experimental conditions. Although concepts about possible reactions, the effect of drainage, etc., have been developed, they require further experiments, involving simplified mineral compositions, for verification. Consequently, any reference to existing systems, dealing with the reduction of water pollution, which are known to be practised by various companies, have not been taken into account because they have no bearing on the experiments described in this report. If, in the future, the results of these experiments appear to represent a majority of field conditions, a survey of the polluting potential of small, active or abandoned, tailings ponds in Canada where no abatement is practised, could be facilitated by using percolation or flow experiments as a rough screening method.

## 2. EXPERIMENTAL METHODS

The percolators that were used in the experiments have been described in detail in Part 1 of this series of reports, as were the procedures followed in preparing the samples and in the measuring of the electrical conductivity, the pH, and the redox potential (Eh).

The Ca, Cu, and Zn contents of the percolating water have been determined by means of the tantalum-strip atomic-absorption method\*. The Ca contents were measured approximately twice per week and the Cu

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\*Note: All atomic-absorption spectrophotometric analyses were done by Mrs. V.H.E. Rolko, Chemist, Analytical Chemistry Section, Mineral Sciences Division, Mines Branch, who was seconded to perform this service in connection with this project.

and Zn contents once per week. The compositions of the waters at the end of the experiment were analyzed by conventional flame atomic-absorption methods.

Fifty-gram sterilized tailings samples were used and the percolating capacity of the water, having an initial pH = 7, was 2000 ml.

Although the decision to use the particular quantity of 50-g tailings samples is based primarily on practical considerations, it originates in the length of time required to reach a certain stage in the weathering process. Observations and measurements concerning variables in the process that have been and will be made in tailings ponds in the field, provide information concerning the conditions in this process at a certain point in time. This applies to most geological field studies. The time periods that are involved in weathering, however, are long. Twenty-year-old tailings ponds, covering only a few acres, have been observed still to contain a considerable acid-producing capacity. The period during which acid is produced is thus far longer than twenty years. Consequently, as small a sample as possible should be used ideally in the laboratory experiments, in order to reduce the capacity of the "tailings pond" (i. e., the sample) and, thus, to facilitate the observation of weathering phenomena.

However, not only the possibility that reactions might proceed too rapidly to be measured, but also the limit of chemical detectability of traces of such metals as copper and zinc in the water regulated the lower limit of the sample size. Preliminary experiments indicated that 10-g samples were too small and that 100-g samples probably represented the upper limit in the foregoing considerations.

The duration of the experiments, in which the samples were subjected to the percolating waters, was approximately 55 days. Although some waters may have reached equilibrium conditions, the compositions of other waters were still changing at the end of the experiments. One hundred days had been considered to be a standard period for the percolation experiments but, in view of the limited information that could be expected to be gleaned from the experiments at this stage of the study, the duration was halved.

The principal results of the mineral analysis of each tailings sample have been summarized in the description of the results of the percolation experiments on tailings from each company. For details on the mineralogical analysis, one is referred to Part 3<sup>(1)</sup> of this series of reports.

### 3. EXPERIMENTAL RESULTS

#### 3. 1. The Effect of the Tailings Sample Supplied by Mining Company No. 1\* on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water that percolated through the tailings sample from Mining Company No. 1 are plotted in Figure 1.

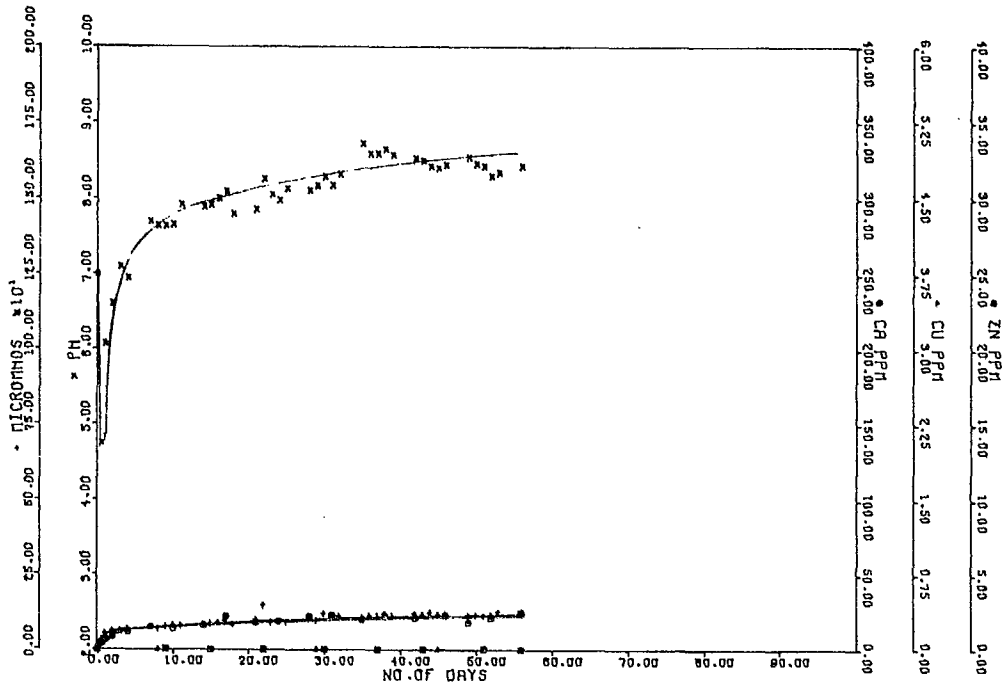


Figure 1. Variables in the water percolating through a tailings sample from Mining Company No. 1.

\*The mining companies are numbered the same as in Part 3 of this series of reports.



The water became alkaline after the first couple of days. The alkalinity was higher than that of the water percolating through a tailings sample from Company No. 2, possibly because of a more favourable carbonate: sulphide ratio (see page 8 ).

The conductivities followed the comparatively small amounts of calcium that dissolved. The amounts of Zn and Cu in the water were not detectable.

The principal results of the mineralogical analysis of this tailings are listed in Table 1.

TABLE 1

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 1

Composition	Wt%	Physical Properties*	
Sulphides	0.5	Specific Gravity	3.07
Iron (hydro)oxides	15	Particle-Size Code	3.3.4.
Carbonates	8	Surface Area	68
Silicates	56.5		
Quartz	15		

At the end of the run, the water contained 4.0 ppm Na, 2.4 ppm K, 25 ppm Ca, 1.3 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu and < 0.01 ppm Zn.

Although it seems unlikely, the effect of drainage may even be indicated during the first couple of days, while the waters are acid. The grain-surface area of this tailings sample exposed to water is small

\*Note: The particle-size code "a. b. c." used in this and all the subsequent tables listing the principal results of the mineralogical analyses, stands for +100 mesh 10a%, -100 +325 mesh 10b%, and -325 mesh 10c%. The surface area exposed to water is expressed in  $\text{cm}^2 / \text{cm}^3$  and an asterisk indicates variability in its measurement for that particular sample.

and it can be expected to produce a drainage rate significantly different from near-stagnant conditions. A system that would contain the water for a sufficient period of time to reach saturation equilibrium would be beneficial.

### 3.2. The Effect of the Tailings Sample Supplied by Mining Company No. 2 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu and Zn contents of the water that percolated through the tailings sample from Mining Company No. 2 are plotted in Figure 2.

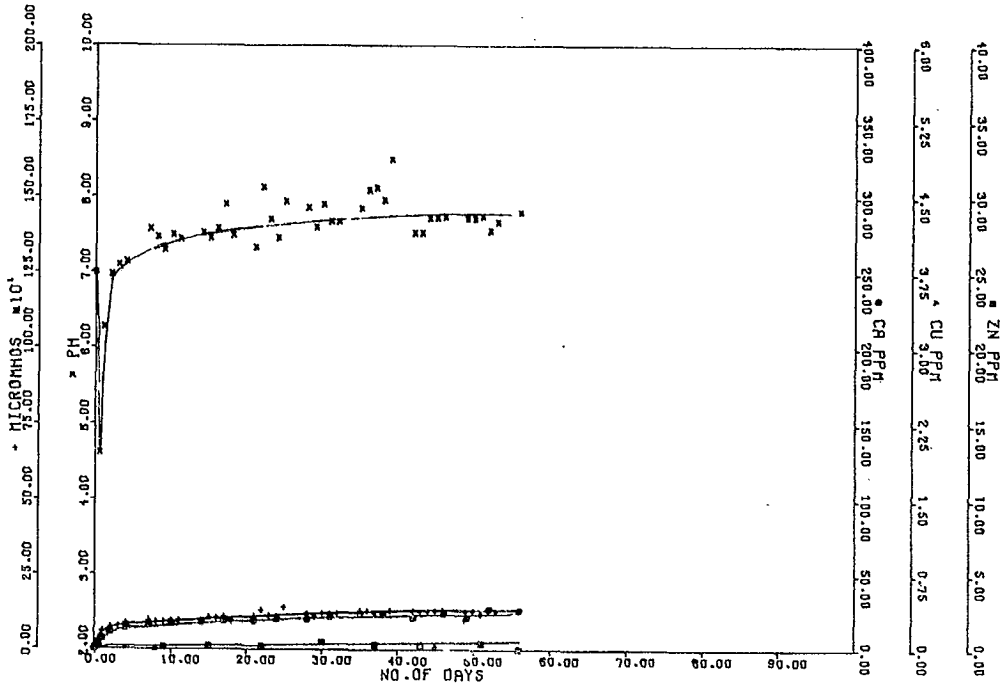


Figure 2. Variables in the water percolating through the tailings sample from Mining Company No. 2.

The water became alkaline after the first couple of days; the conductivities followed the comparatively small amounts of calcium that dissolved, and the Zn and Cu contents also remained low.

The principal results of the mineralogical analysis of this tailings sample are listed in Table 2.

TABLE 2

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 2

Composition	Wt%	Physical Properties	
Sulphides	1	Specific Gravity	2.73
Iron (hydr)oxides	3	Particle-Size Code	2.3.5.
Carbonates	3	Surface Area	99
Silicates	58		
Quartz	31		

At the end of the experiment, the water contained 5 ppm Na, 5.4 ppm K, 26 ppm Ca, 1.5 ppm Mg, .06 ppm Fe, < .01 ppm Cu, < .01 ppm Zn.

The tailings composition and its effect on water are very similar to those of the foregoing tailings sample. The effect of drainage may be indicated during the first couple of days, when the water was acid. The grain-surface area exposed to water can again be expected to produce a drainage rate significantly higher than corresponds to near-stagnant conditions.

3.3. The Effect of the Tailings Sample Supplied by Mining Company No. 3 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu and Zn contents of the water that percolated through a tailings sample from Mining Company No. 3 are plotted in Figure 3.

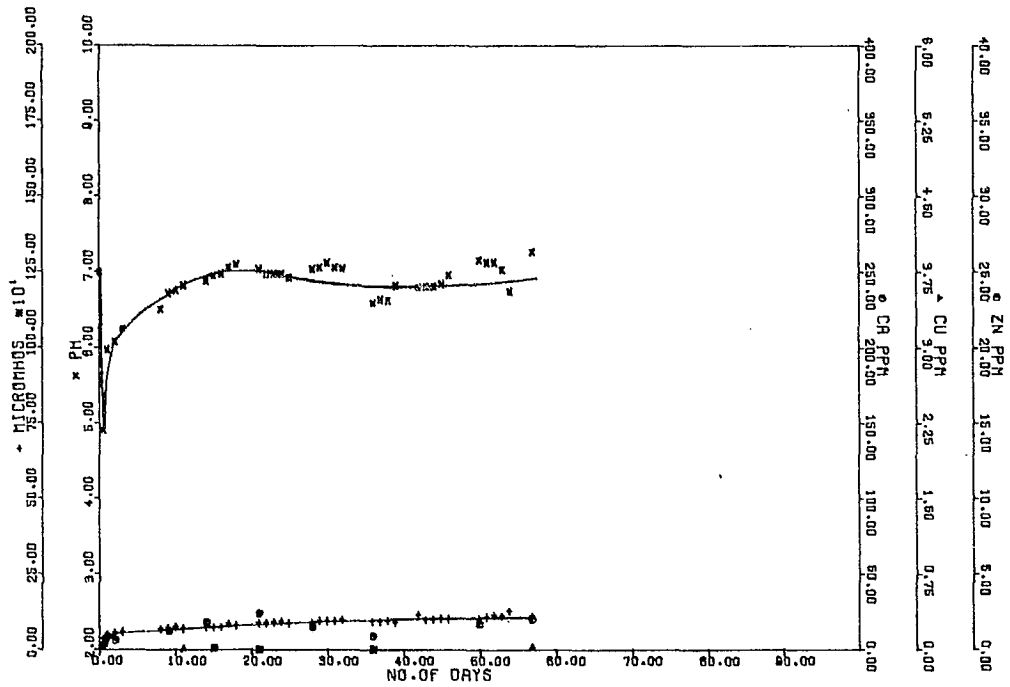


Figure 3. Variables in the water percolating through a tailings sample from Mining Company No. 3.

The pH increased after the first couple of days and appeared to reach an equilibrium at a near-neutral level. The conductivities followed the comparatively small amounts of calcium that dissolved. The amounts of Cu and Zn in the water were low.

The principal results of the mineralogical analysis of this tailings are listed in Table 3.

TABLE 3  
Mineralogical Analysis of a Tailings Sample Supplied by  
by Mining Company No. 3

Composition	Wt%	Physical Properties	
Sulphides	1	Specific Gravity	2.72
Iron (hydr)oxides	4	Particle-Size Code	2.3.5.
Carbonates	3	Surface Area	135
Silicates	60		
Quartz	29		

At the end of the experiment, the water contained 4.5 ppm Na, 2.3 ppm K, 20 ppm Ca, 14 ppm Mg, 0.52 ppm Fe, 0.02 ppm Cu and < 0.01 ppm Zn.

The principal ore minerals were arsenides but, unfortunately, a chemical analysis for the As content of the percolating water was not available. The results shown in Figure 3 indicate, however, that this is not an acid tailings and that any pollutant action may be due more to the toxic nature of the arsenic present in the water than to its acidity.

3.4. The Effect of the Tailings Sample Supplied by Mining  
Company No. 4 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water that percolated through a tailings sample from Mining Company No. 4 are plotted in Figure 4.

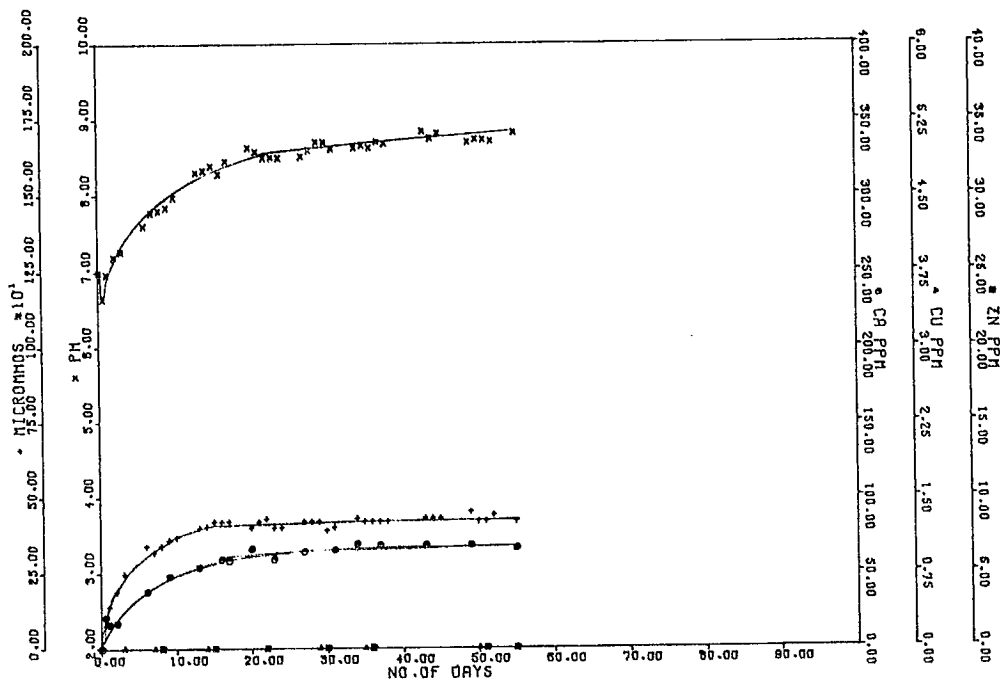


Figure 4. Variables in the water percolating through a tailings sample from Mining Company No. 4.

Although the Cu and Zn contents were below the limits of detection, more ions dissolved out of this tailings sample than out of the foregoing ones. Also, the water reached an alkalinity that was possibly slightly higher, despite the fact that the sulphide: carbonate ratio was much lower than in the foregoing samples according to the principal results of the mineralogical analysis of this tailings listed in Table 4.

TABLE 4

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 4

Composition	Wt%	Physical Properties	
Sulphides	3	Specific Gravity	2.83
Iron (hydr)oxides	6	Particle-Size Code	0.3.7.
Carbonates	4	Surface Area	327*
Silicates	63		
Quartz	20		

At the end of the run, the water contained 6 ppm Na, 1.2 ppm K, 148 ppm Ca, 42 ppm Mg, .08 ppm Fe, and < .01 ppm Cu and Zn.

The duration of the temporary acidity at the beginning of the run was shorter than for the foregoing samples. This phenomenon may originate in the effect of drainage. This effect shows up before equilibrium has been reached, and is connected with the grain-surface area exposed to water and the water flow along it. It should be noted that the grain-surface area and the fine particle size of this tailings sample are much larger than those of the foregoing tailings and that the drainage is not as rapid.

3.5. The Effect of the Tailings Sample Supplied by Mining Company No. 5 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Cu and Zn content of the water that percolated through a tailings sample from Mining Company No. 5 are drawn in Figure 5.

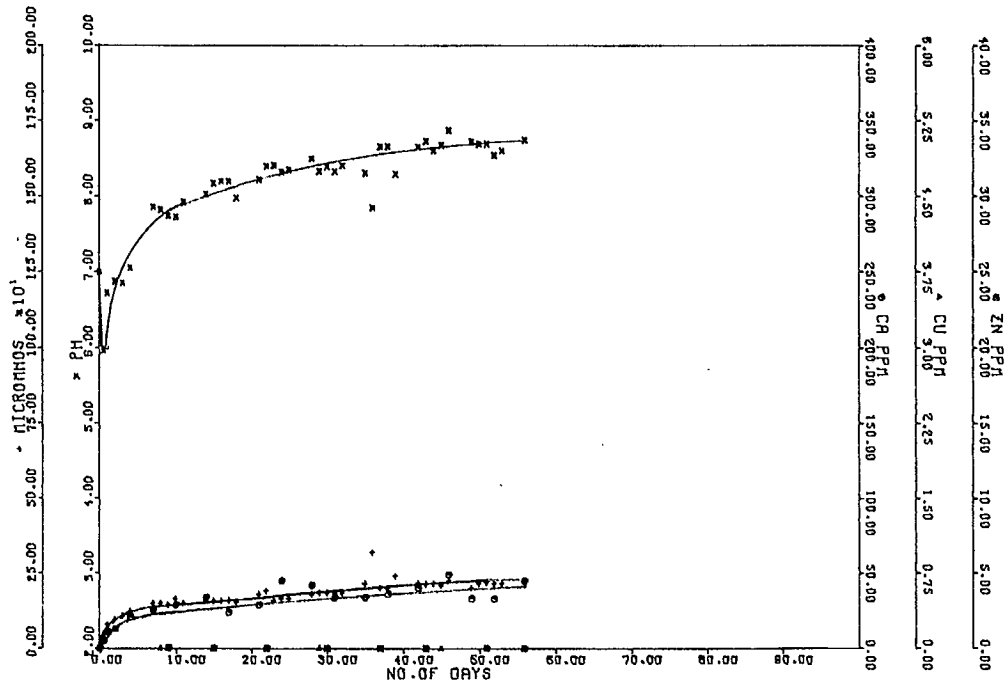


Figure 5. Variables in the water percolating through a tailings sample from Mining Company No. 5.

The results were very similar to those of the foregoing tailings. The water became alkaline. The low conductivity and the amount of calcium that dissolved appeared to be related. The Cu and Zn contents were low.

The principal results of the mineralogical analysis are listed in Table 5.



TABLE 5  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 5

Composition	Wt%	Physical Properties	
Sulphides	4	Specific Gravity	2.95
Iron (hydr)oxides	10	Particle-Size Code	3, 3, 4.
Carbonates	5	Surface Area	102
Silicates	63		
Quartz	14		

At the end of the run, the water contained 7 ppm Na, 10 ppm K, 45 ppm Ca, 0.9 ppm Mg, 0.2 ppm Fe, < 0.01 ppm Cu, and 0.01 ppm Zn.

The results are not significantly different from those of the foregoing runs.

3.6. The Effect of the Tailings Sample Supplied by Mining Company No. 6 on the Composition of Water

The results of the measurements of the pH, conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water that percolated through a tailings sample from Mining Company No. 6 are plotted in Figure 6.

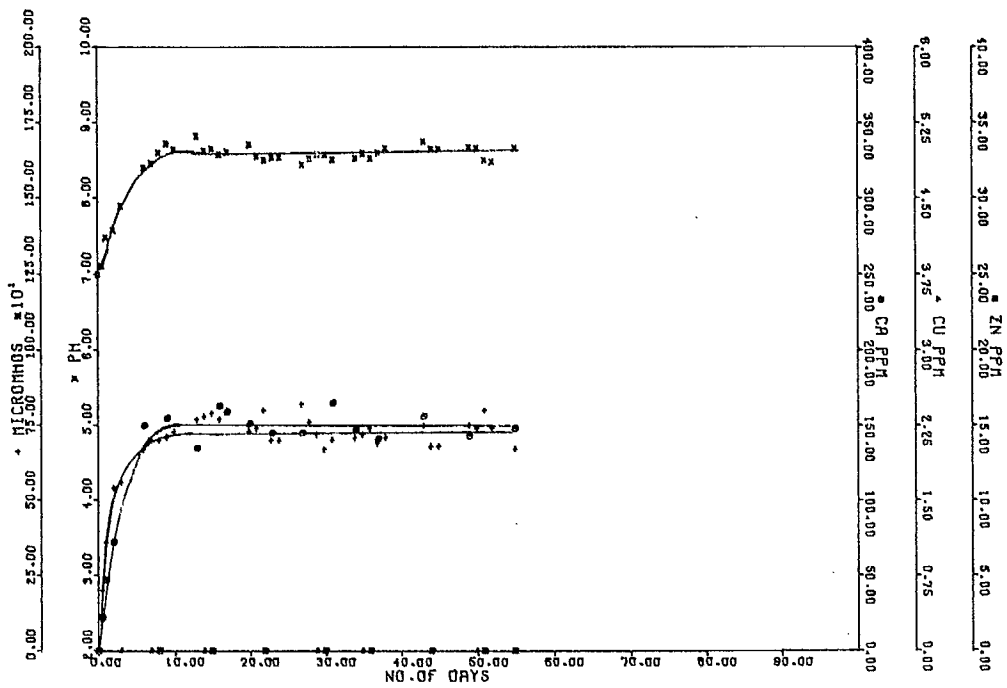


Figure 6. Variables in the water percolating through a tailings sample from Mining Company No. 6.

Although the water became alkaline, as in the foregoing samples, and the Cu and Zn contents remained low, the Ca content and the conductivity of the water had increased.

The principal results of the mineralogical analysis of this tailings sample are listed in Table 6.

TABLE 6

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 6

Composition	Wt%	Physical Properties	
Sulphides	5	Specific Gravity	2.88
Iron (hydr)oxides	5	Particle-Size Code	0.0.10.
Carbonates	30	Surface Area	114
Silicates	43		
Quartz	12		

At the end of the run, the water contained 6 ppm Na, 1.2 ppm K, 141 ppm Ca, 42 ppm Mg, 0.08 ppm Fe, < 0.01 ppm Cu, and < 0.01 ppm Zn.

The trend towards acidity during the beginning of the run was not present. This is possibly due to a complete suppression of acid (from the sulphides) by the large amount of carbonate present in this tailings sample.

A sample of this tailings collected in the field had also been run in a percolator. The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through that sample are plotted in Figure 7.

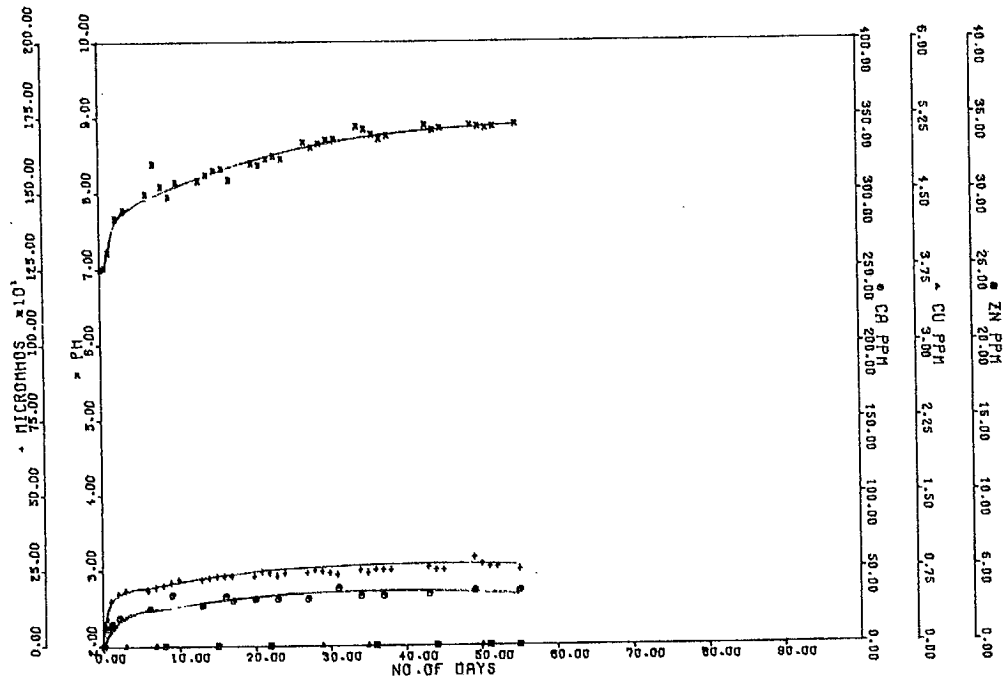


Figure 7. Variables in the water percolating through a sample of tailings collected in the field from Mining Company No. 6.

An estimate of the mineralogical composition, based on the results of a chemical analysis and the composition of the fresh tailings, is shown in Table 7.

TABLE 7  
Mineralogical Analysis of a Sample Collected from the Tailings  
Pond of Mining Company No. 6

Composition	Wt%	Physical Properties	
Sulphides	1	Specific Gravity	) ) ) ) ) Not determined
Iron (hydr)oxides	-	Particle-Size Code	
Carbonates	27		
Silicates	28		
Quartz	36		

At the end of the run, the water contained 4 ppm Na, 0.5 ppm K, 34 ppm Ca, 15 ppm Mg, 0.08 ppm Fe, < 0.01 ppm Cu and < 0.01 ppm Zn. These results indicate that the dissolution of Ca and Mg ions possibly decreased with time and that a certain amount drained away. Although it would be surprising if the drainage water from this tailings pond was found to be pollutant in field conditions, the phenomena of the drainage of Ca and Mg, and the absence of initial acidity, will contribute significantly to the development of concepts about the reactions involved in the weathering process.

### 3.7. The Effect of the Tailings Sample Supplied by Mining Company No. 7 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water that percolated through the tailings sample from Mining Company No. 7 are plotted in Figure 8.

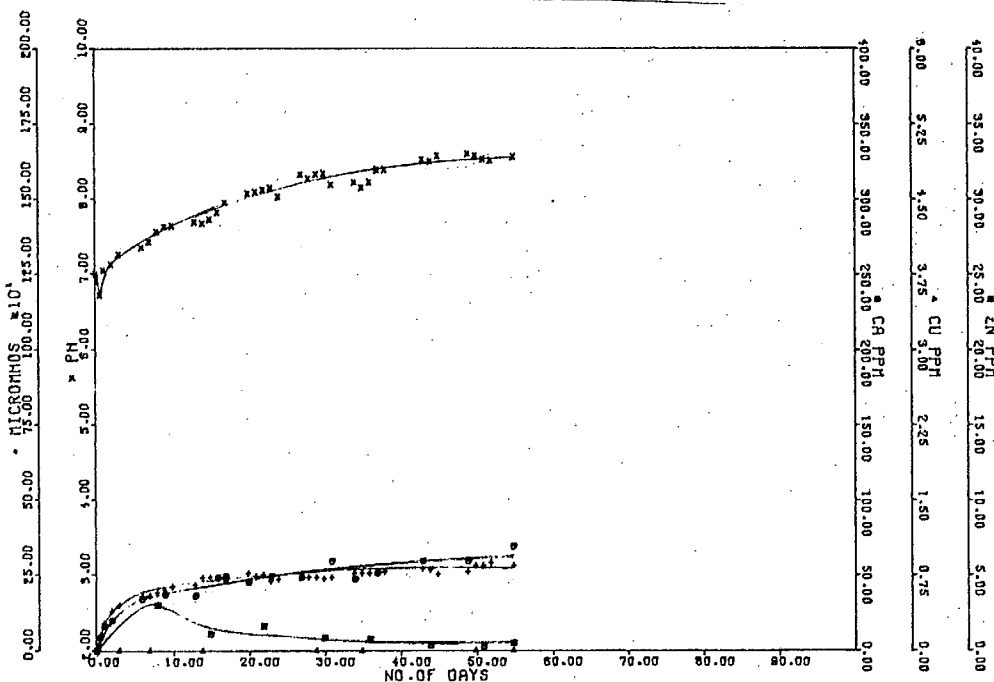


Figure 8. Variables in the water percolating through a tailings sample from Mining Company No. 7.

The results were very similar to those of the foregoing tailings samples in that the water became alkaline, the calcium content and conductivity remained low, and the Cu content was not detectable. The trend to become acid at the beginning of the run was very small. Because the tailings contained a significant amount of sphalerite, the zinc content could be expected to be higher than in the foregoing runs. At the beginning of the run, this zinc content was higher than after the system had reached equilibrium

The principal results of the mineralogical analysis of this sample are listed in Table 8.

TABLE 8  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 7

Composition	Wt%	Physical Properties	
Sulphides	6	Specific Gravity	3.30
Iron (hydr)oxides	2	Particle-Size Code	1.3.6.
Carbonates	2.5	Surface Area	180
Silicates	29		
Quartz	23.5		
Barite	34.5		

At the end of the run, the water contained 3 ppm Na, 2 ppm K, 60 ppm Ca, < 0.01 ppm Fe, < 0.01 Cu, and 1 ppm Zn. The large amount of barite in this sample could be expected to produce no significant effects, so that the action of this tailings sample on water was very similar to those of the first five samples.

3.8. The Effect of the Tailings Sample Supplied by Mining Company No. 8 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu and Zn contents of the water that

percolated through the tailings sample from Mining Company No. 8 are plotted in Figure 9.

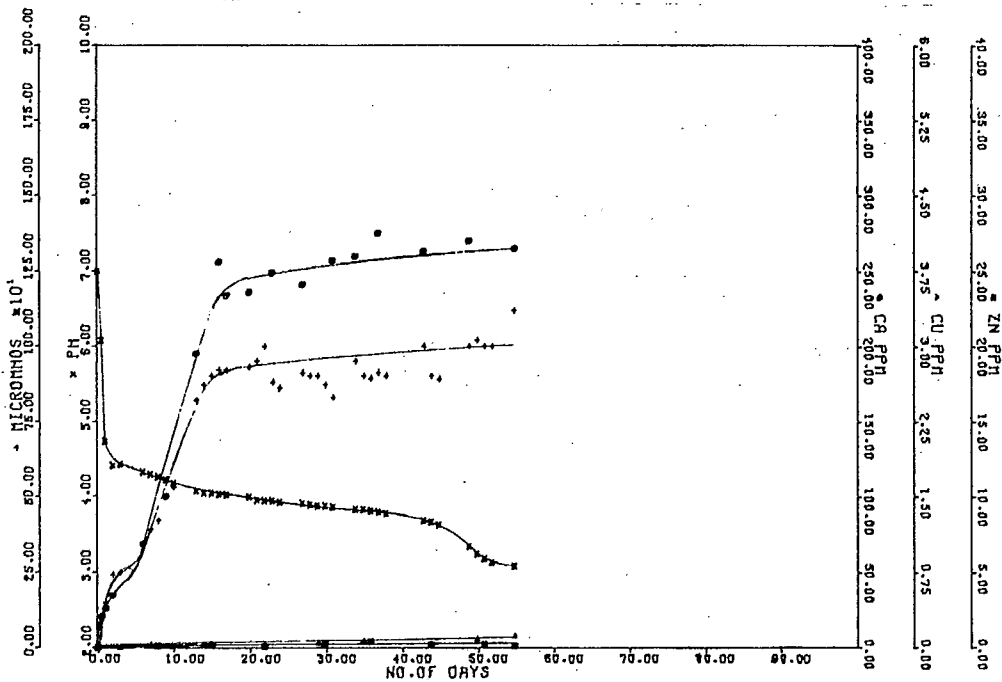


Figure 9. Variables in the water percolating through a tailings sample from Mining Company No. 8.

The results are quite different from those of the foregoing tailings. Not only did the pH rise gradually after its initial drop to about 4.5, but the calcium content and the conductivity values were significantly higher than those in the foregoing runs. Also, the low Cu and Zn contents increased gradually.

The principal results of the mineralogical analysis of this tailings sample are listed in Table 9.

TABLE 9  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 8

Composition	Wt%	Physical Properties	
Sulphides	5	Specific Gravity	2.81
Iron (hydr)oxides	-	Particle-Size Code	1.3.6.
Carbonates	0.5	Surface Area	149
Silicates	28		
Quartz	60.5		

At the end of the run, the water contained 3 ppm Na, 1.2 ppm K, 265 ppm Ca, 0.6 ppm Mg, 5.2 ppm Fe, 0.1 ppm Cu and 0.1 ppm Zn. Although the sulphide content in this tailings is comparatively low, the amount of carbonates is apparently too small to offset the acid effect of the sulphides.

3.9. The Effect of the Tailings Sample Supplied by Mining Company No. 9 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water that percolated through the tailings sample from Mining Company No. 9 are plotted in Figure 10.



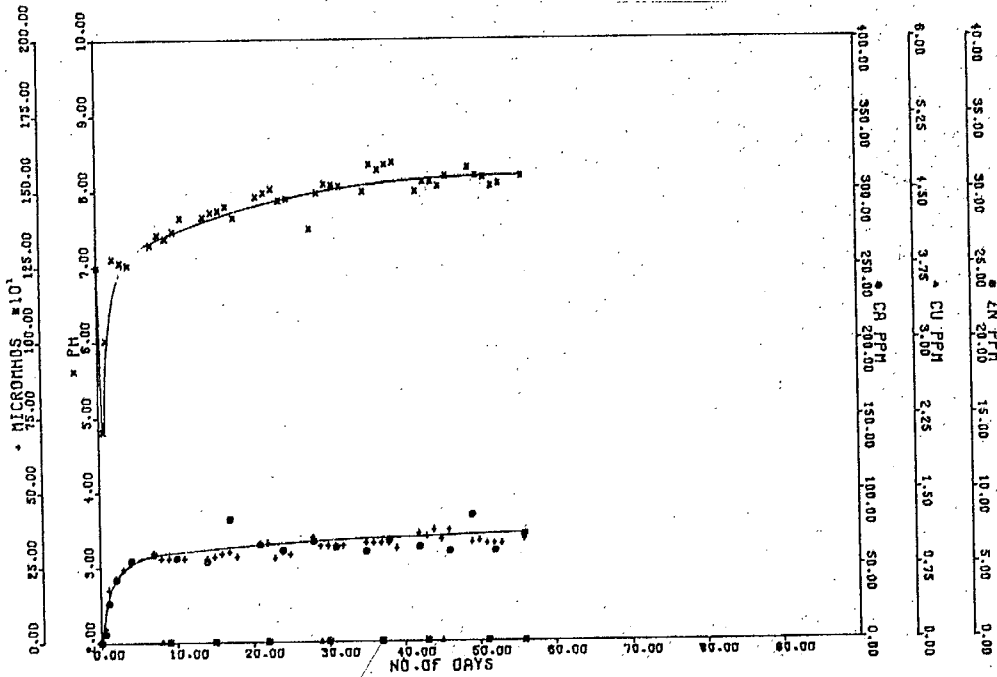


Figure 10. Variables in the water percolating through a tailings sample from Mining Company No. 9.

The results are very similar to those for the tailings from the first three companies. The water became alkaline, and the dissolution of calcium appeared to be related to the conductivities. The amount of Cu that dissolved was below the limit of detection and that of Zn remained low during the greatest part of the run.

The principal results of the mineralogical analysis of this sample are listed in Table 10.

TABLE 10  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 9

Composition	Wt%	Physical Properties	
Sulphides	8	Specific Gravity	3.02
Iron (hydr)oxides	10	Particle-Size Code	3.3.4.
Carbonates	11	Surface Area	133
Silicates	40		
Quartz	26		

At the end of the run, the water contained 2.1 ppm Na, 0.6 ppm K, 82 ppm Ca, 9.4 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu and 0.01 ppm Zn.

3.10. The Effect of the Tailings Sample Supplied by Mining Company No. 10 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu and Zn contents of the water that percolated through the tailings sample are plotted in Figure 11.

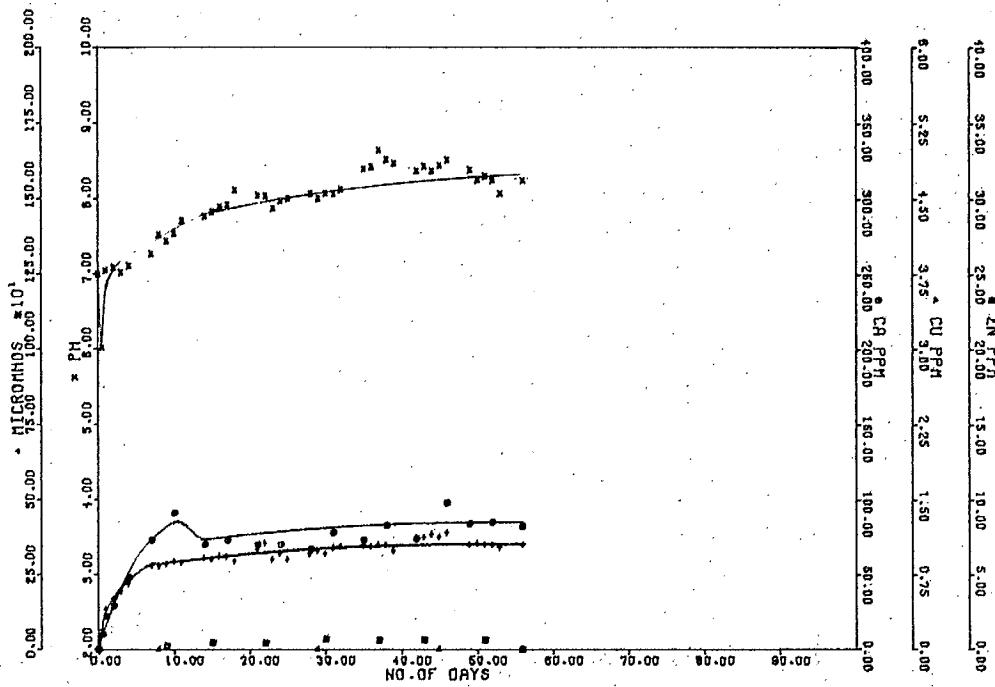


Figure 11. Variables in the water percolating through a tailings sample from Mining Company No. 10.

The results are very similar to those of the first tailings. The water became alkaline, the calcium contents and the conductivity were comparatively low, and the Cu and Zn contents were also very low. The acidity during the first couple of days should again be noted.

The principal results of the mineralogical analysis of this tailings sample are listed in Table 11.

TABLE 11  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 10

Composition	Wt%	Physical Properties	
Sulphides	15	Specific Gravity	3.21
Iron (hydr)oxides	5	Particle-Size Code	1, 4, 5.
Carbonates	2.5	Surface Area	85
Silicates	60		
Quartz	12		

At the end of the run, the water contained 5 ppm Na, 13 ppm K, 71 ppm Ca, 6 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu and 0.01 ppm Zn.

The phenomenon of the water becoming alkaline under equilibrium conditions, despite the apparent surplus of sulphide over carbonate in the tailings, indicated that factors other than stoichiometric proportions of the various minerals, control the pH. Because the dissolution of a mineral grain in water takes place at the surface of that grain, it is very probable that the grain-surface area exposed to water is one of these factors.

3. 11. The Effect of the Tailings Sample Supplied by Mining Company No. 11 on the Composition of Water

The results of the measurements of the pH, the conductivity and of the determinations of the Ca, Cu and Zn contents of the water that percolated through the tailings sample from Mining Company No. 11 are plotted in Figure 11.

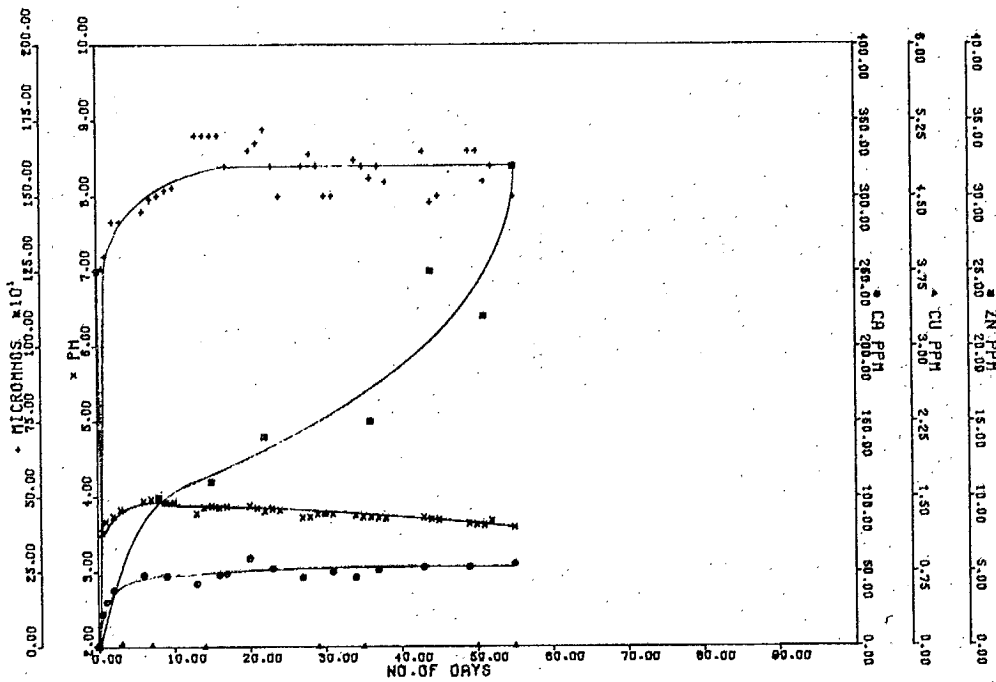


Figure 12. Variables in the water percolating through a tailings sample from Mining Company No. 11.

Although the calcium content remained comparatively low, the conductivity was high and the water became acid. The solution of the Zn indicated that equilibrium conditions had not been reached. The trend in the curves indicates that the acidity may progressively increase.

The principal results of the mineralogical analysis of this tailings are listed in Table 12.

TABLE 12  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 11

Composition	Wt%	Physical Properties	
Sulphides	36	Specific Gravity	3.39
Iron (hydr)oxides	15	Particle-Size Code	1.4.5.
Carbonates	2	Surface Area	105
Silicates	18		
Quartz	24		

At the end of the run, the water contained 23 ppm Na, 5 ppm K, 52 ppm Ca, 22 ppm Mg, 700 ppm Fe, < 0.01 ppm Cu, and 24 ppm Zn.

The dip in the pH curve during the first week of the run, which probably originates in the difference in reaction rates between two components of the final equilibrium, should be noted. The acidity of the water can be attributed to the large sulphide : carbonate ratio. The high conductivity is due to the large amount of iron in the water. The iron very probably did not dissolve only out of the sulphides, but possibly partly out of the iron hydroxides. A large precipitate of secondary iron hydroxides had formed in all parts of the percolator. The total amount of iron that dissolved could, therefore, not be determined nor could the proportionation between the portion that precipitated and the portion that dissolved be determined. The Zn content increased with the acidity.

A tailings sample collected in the field was also run and the results of the measurements of the pH, the conductivity and of the determinations of the Ca, Cu, and Zn contents of the water percolating through that sample are drawn in Figure 13.

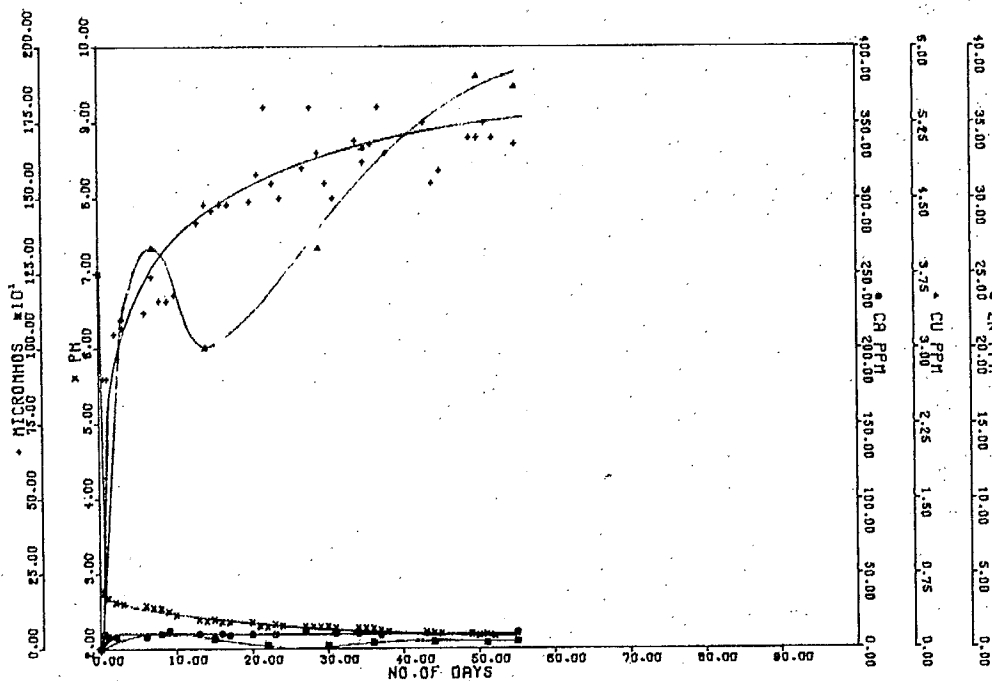


Figure 13. Variables in the water percolating through a sample of tailings collected on the field from Mining Company No. 11.

The mineral composition, listed in Table 13, was estimated from the results of a chemical analysis and from the mineral composition of the fresh tailings. The iron hydroxide content is probably higher than that given in the table. This is reflected in the chemical analysis, which totalled 62%.

TABLE 13

Mineralogical Analysis of a Sample Collected from the Tailings  
Pond of Mining Company No. 11

Composition	Wt%	Physical Properties
Sulphides	2	Specific Gravity )
Iron (hydr)oxides	25	Particle-Size Code )
Carbonates	0.5	Surface Area )
Silicates	11	
Quartz	35	
Sulphates	19	

At the end of the run, the water contained 3 ppm Na, 0.1 ppm K, 10 ppm Ca, 2.3 ppm Mg, 35 ppm Fe, 5.6 ppm Cu and 0.3 ppm Zn. It is quite possible that the field sample did not originally have the composition of the fresh sample supplied by the company. This possibility may be indicated by the fact that the dissolution of Cu had not reached equilibrium conditions at the end of the run. Although the conductivity of the water percolating through the field sample was of the same order of magnitude as that of the water percolating through the fresh tailings, the Ca, Mg, Fe, and Zn contents were all lower and the acidity appeared to be higher.

The results of the experiment indicated, again, that reaction rates of components of the final equilibrium under stagnant water conditions are of importance in the weathering process. If water drains away, it cannot reach the equilibrium condition in which the ions dissolving out of the tailings can interact with those already dissolved. The experimental results produced by the field samples in percolators may be indicative of a late phase in the drainage experiments.



### 3. 12. The Effect of the Tailings Sample Supplied by Mining Company No. 12 on the Composition of Water

A tailings sample containing a large amount of sulphides and another containing a small amount of sulphides were supplied by Mining Company No. 12.

The results of the measurements of the pH, the conductivity and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the sulphide-poor tailings sample from Mining Company No. 12 are plotted in Figure 14.

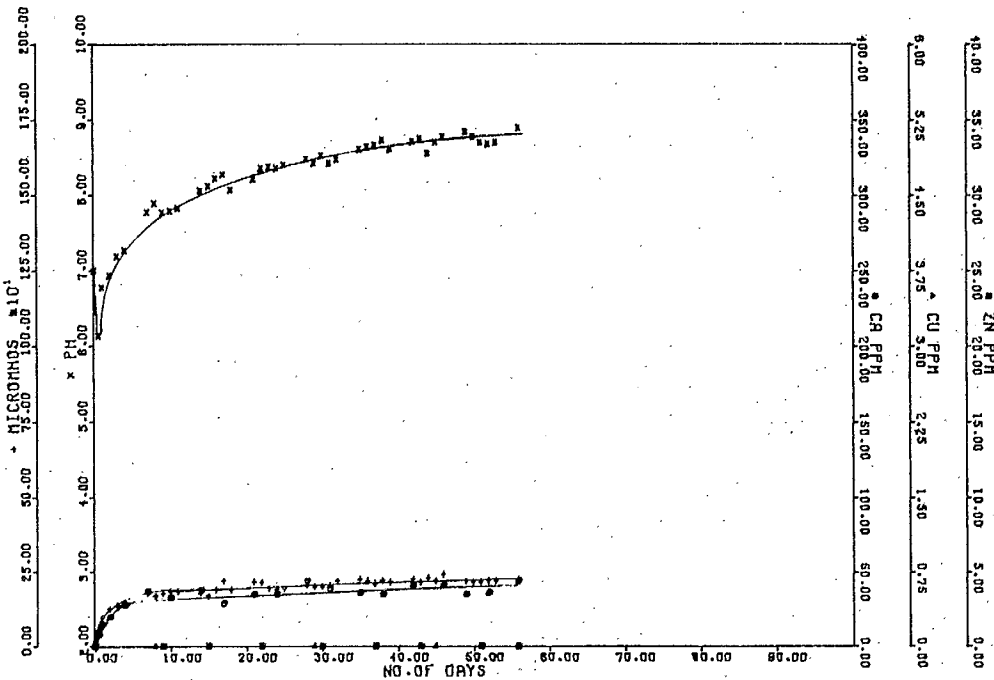


Figure 14. Variables in the water percolating through a sulphide-poor tailings sample from Mining Company No. 12.

The results were very similar to those of the percolation test on low-sulphide tailings from the first few companies. After exhibiting initial acidity, the water became alkaline, the conductivity and the calcium content were low, and the Cu and Zn contents were not detectable.

The principal results of the mineralogical examination of this sample are listed in Table 14.

TABLE 14  
Mineralogical Analysis of a Sulphide-Poor Tailings Sample  
Supplied by Mining Company No. 12

Composition	Wt%	Physical Properties	
Sulphides	1	Specific Gravity	2.85
Iron (hydr)oxides	2	Particle-Size Code	2.3.5.
Carbonates	15	Surface Area	128
Silicates	49		
Quartz	31		

At the end of the run, the water contained 3 ppm Na, 1.3 ppm K, 44 ppm Ca, 7 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu, and < 0.01 ppm Zn.

The results of measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the sulphide-rich tailings sample from Company No. 12 are plotted in Figure 15.

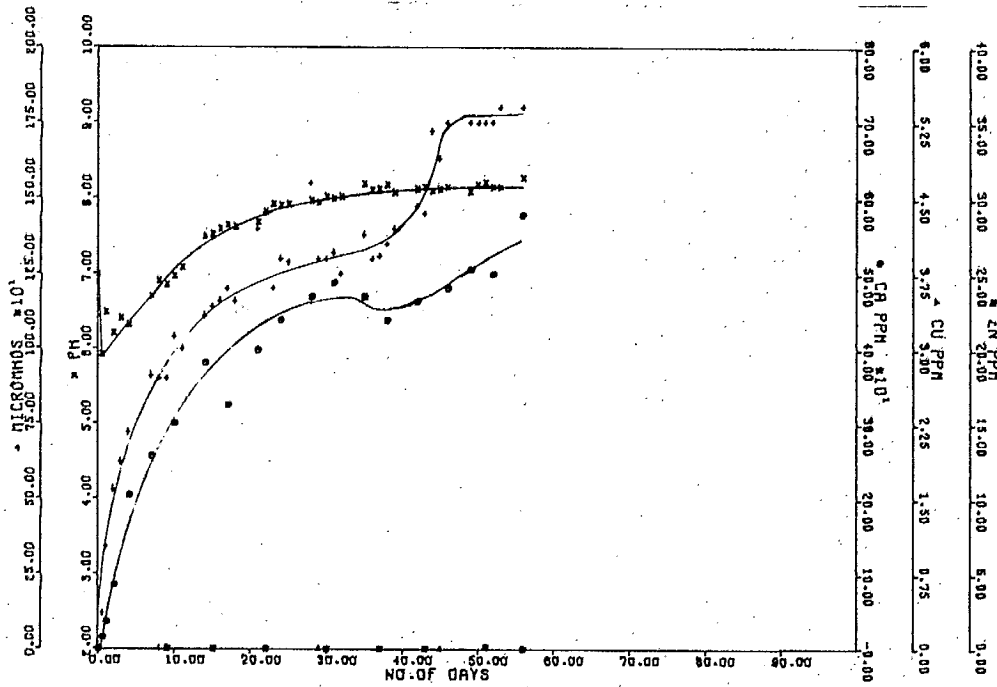


Figure 15. Variables in the water percolating through a sulphide-rich tailings sample from Mining Company No. 12.

In spite of the higher sulphide content, the water reached an alkaline pH that was lower than that developed in the water from the silica-rich sample. The Cu and Zn contents were again beyond the limit of detection. The significant difference, however, was in the calcium content, which was still increasing at the end of the run.

The principal results of the mineralogical analysis of this sample are listed in Table 15.

TABLE 15

Mineralogical Analysis of a Sulphide-Rich Tailings Sample  
Supplied by Mining Company No. 12

Composition	Wt %	Physical Properties	
Sulphides	37	Specific Gravity	3.45
Iron (hydr)oxides	6	Particle-Size Code	1.2.7.
Carbonates	10	Surface Area	216*
Silicates	33		
Quartz	9		

At the end of the run, the water contained 8 ppm Na, 1.3 ppm K, 578 ppm Ca, 45 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu and < 0.01 ppm Zn.

Although the sulphide-rich tailings contained less carbonates than did the sulphide-poor sample, far more calcium and magnesium were dissolved into the water percolating through the sulphide-rich tailings. The pH of both waters was alkaline.

The results of the experiments on the tailings samples from this company were considered to be very good examples of the interaction between sulphides and carbonates that traditionally controls the pH of the water. The combination of the large amount of dissolved calcium with the comparatively large amount of sulphides, present in the tailings, is probably significant for this interaction. However, no definite conclusions on the nature of this interaction will be made before experiments containing mixtures of these minerals, simulating simplified tailings compositions, have been completed.

3.13. The Effect of the Tailings Sample Supplied by Mining Company No. 13 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the Ca, Cu and Zn contents of the water percolating through the tailings sample from Mining Company No. 13 are plotted in Figure 16.

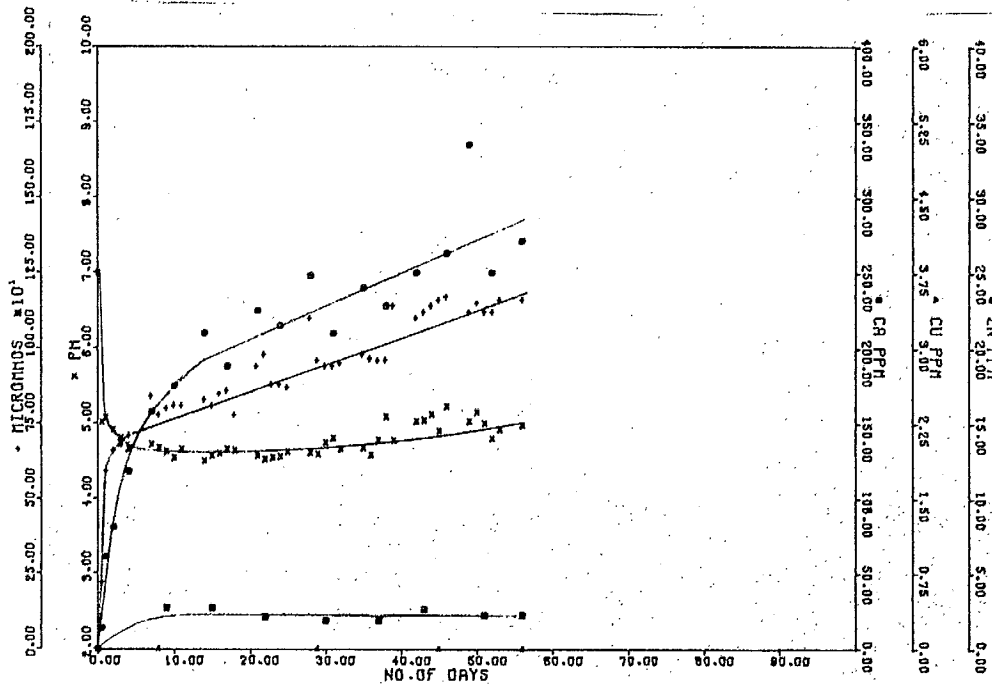


Figure 16. Variables in the water percolating through a tailings sample from Mining Company No. 13

Although experimental results involving the variation of various factors affecting the composition of water percolating through tailings samples from this company have been described in an earlier report<sup>(3)</sup>, the experiments were actually done and selected according to the results of the experiment described in this report. The results indicate that the system had not reached equilibrium at the end of the run. The calcium content and the conductivity were still increasing, as was the pH to a slight extent. The pH was significantly higher than that of acid waters described previously. It has been pointed out in Part 2 of this series of reports that

several factors can produce these differences and that the experiments described in the first stage of the study are aimed solely at indicating the possible effects of various factors that will have to be studied in greater detail before definite conclusions can be made.

The composition of samples can be expected to vary with changes in the composition of the ore that is mined, so that samples supplied at different times could vary in composition. The composition of samples have been observed to change on standing. It is also possible that particular tailings compositions have a sensitivity to variations in experimental conditions.

The principal results of the mineralogical analysis of this sample are listed in Table 16.

TABLE 16  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 13

Composition	Wt%	Physical Properties	
Sulphides	34	Specific Gravity	3.27
Iron (hydr)oxides	5	Particle-Size Code	1.5.4.
Carbonates	5	Surface Area	78*
Silicates	25		
Quartz	26		

At the end of the run, the water contained 3.3 ppm Na, 16 ppm K, 271 ppm Ca, 39 ppm Mg, 16 ppm Fe, 0.01 ppm Cu, and 2.2 ppm Zn.

Because the system in the percolator had not reached equilibrium, a further comparison with the results of other tests, done on tailings samples from this company, is not valid, particularly because the samples were not treated and obtained from the head sample at the same time.

3. 14. The Effect of the Tailings Sample Supplied by Mining Company No. 14 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the tailings sample from Mining Company No. 14 are plotted in Figure 17.

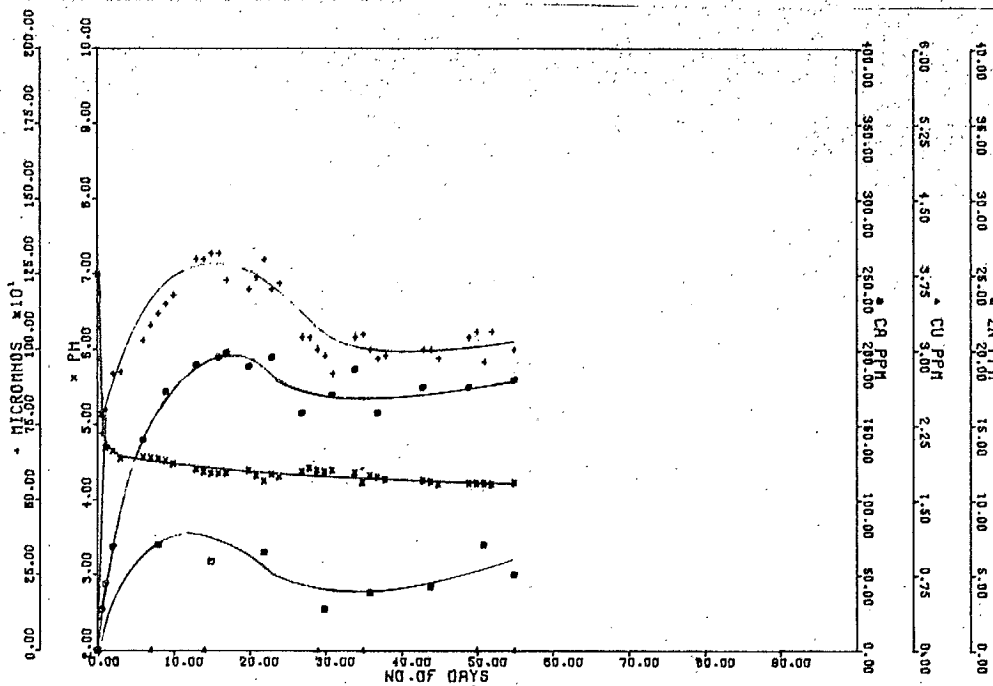


Figure 17. Variables in the water percolating through a tailings sample from Mining Company No. 14.

The results again indicate that the system had not reached equilibrium at the end of the run. The calcium and zinc contents were still increasing. It is, therefore, uncertain as to whether the pH might have decreased beyond what is shown in Figure 17.

The principal results of the mineralogical analysis of this sample are listed in Table 17.

TABLE 17  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 14

Composition	Wt%	Physical Properties	
Sulphides	55	Specific Gravity	3.70
Iron (hydr)oxides	1	Particle-Size Code	1.3.6.
Carbonates	2	Surface Area	106*
Silicates	30		
Quartz	10		

At the end of the experiment, the water contained 3 ppm Na, 7 ppm K, 171 ppm Ca, 33 ppm Mg, 140 ppm Fe, < 0.01 ppm Cu and 3 ppm Zn.

Acid water could be expected to be produced from the large amount of sulphides, as compared with that of the carbonates. The large variations in the conductivity, and in the Ca and Zn contents are probably controlled by the dissolution of sulphides. Although a precipitation of iron hydroxides was visible, the amount was small, so that a greater portion of the dissolved iron remained in solution than, for instance, in the water percolating through the tailings sample from Mining Company No. 11.

3. 15. The Effect of the Tailings Samples Supplied by Mining Company No. 15 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the tailings sample from Mining Company No. 15 are plotted in Figure 18.



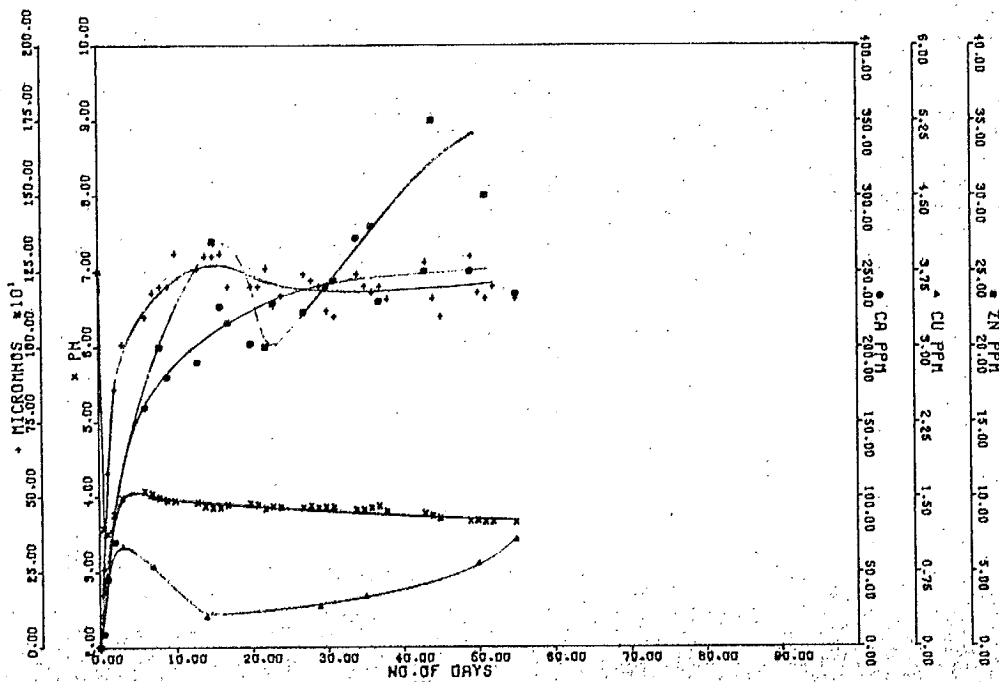


Figure 18. Variables in the water percolating through a tailings sample from Mining Company No. 15.

This tailings sample had also been used in experiments described in earlier reports. Because analytical chemical methods had been developed for the determination of several elements not reported previously, the results of a few runs, using the tailings from this company, have been included in this report.

Figure 18 obviously shows that the system had not reached equilibrium at the end of the experiment. The water was decidedly acid and showed the dip in pH during the first week. The amount of calcium that dissolved was high.

The principal results of the mineralogical analysis of this sample are listed in Table 18.

TABLE 18  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 15

Composition	Wt%	Physical Properties	
Sulphides	64	Specific Gravity	4.55
Iron (hydr)oxides	3	Particle-Size Code	0.3.7.
Carbonates	6.5	Surface Area	183*
Silicates	11		
Quartz	9		

At the end of the run, the water contained 2.7 ppm Na, 1.3 ppm K, 242 ppm Ca, 74 ppm Mg, 24 ppm Fe, 1.05 ppm Cu, and 36 ppm Zn.

A sulphide-poor and a sulphide-rich fraction from this tailings, similar to the two types of tailings supplied by Mining Company No. 12, were also run in the percolators.

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the sulphide-poor and the sulphide-rich fractions are plotted in Figures 19 and 20, respectively.

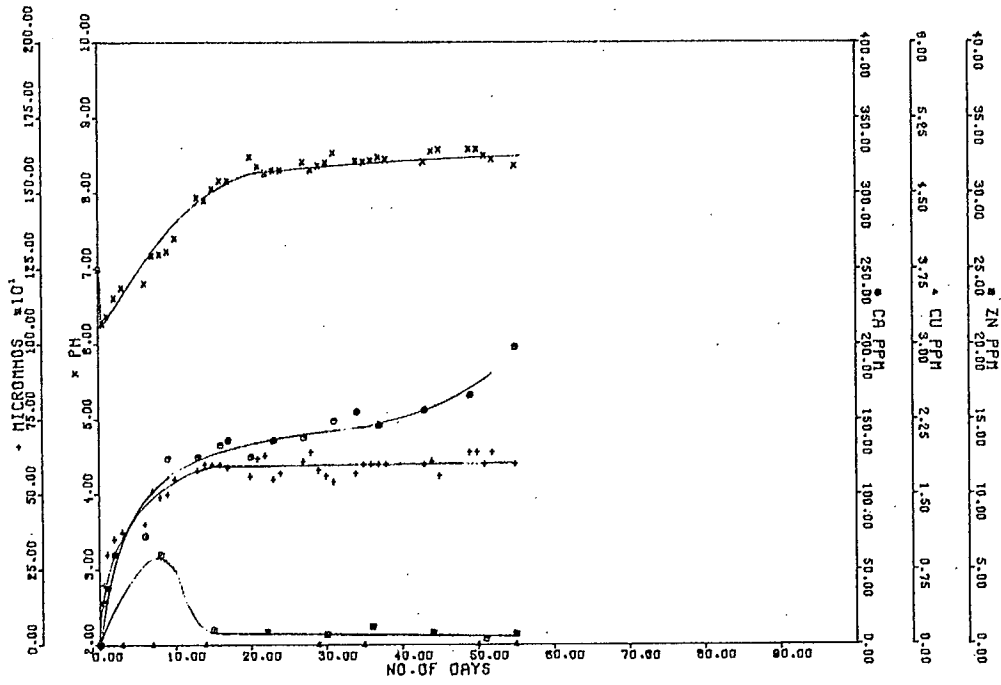


Figure 19. Variables in the water percolating through a sulphide-poor fraction of the tailings from Mining Company No. 15.

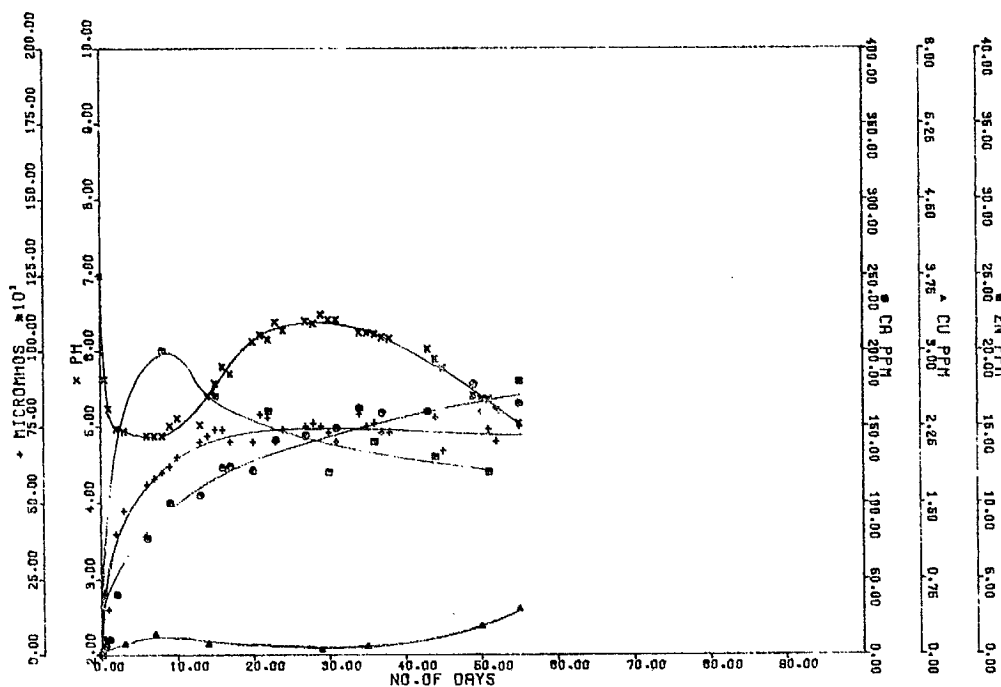


Figure 20. Variables in the water percolating through a sulphide-rich fraction of the tailings from Mining Company No. 15.

It is again obvious that both systems had not reached equilibrium conditions at the end of the experiment. However, several of the results were similar to those observed in runs of other tailings samples.

The water percolating through the sulphide-poor fraction was acid for a few days at the beginning of the run before it became alkaline. The same trend could be observed in the run containing the sulphide-rich fraction. However, before an alkaline pH could be reached in the latter, it decreased again, presumably to reach a low value under equilibrium conditions.

The conductivities and the calcium contents were not significantly different. The amount of Cu that dissolved in the run containing the sulphide-rich fraction was appreciable. Although the Zn content was higher in the run containing the sulphide-rich fraction than in the other, both Zn curves indicated a temporary increase at the beginning of the experiment.

The estimates of the mineral composition of these fractions, based on the results of the chemical analyses of these fractions and on the mineral composition of the head sample, are listed in Tables 19 and 20.

TABLE 19

Mineralogical Analysis of a Sulphide-Poor Fraction of a Tailings  
Sample Supplied by Mining Company No. 15

Composition	Wt%	Physical Properties
Sulphides	5	Specific Gravity )
Iron (hydr)oxides	1	Particle-Size Code )
Carbonates	12	Surface Area )
Silicates	15	
Quartz	60	
Sulphates	1	

TABLE 20

Mineralogical Analysis of a Sulphide-Rich Fraction of a Tailings  
Sample Supplied by Mining Company No. 15

Composition	Wt%	Physical Properties
Sulphides	70	Specific Gravity )
Iron (hydr)oxides	2	Particle-Size Code )
Carbonates	5	Surface Area )
Silicates	7	
Quartz	6	
Sulphates	2	

The sulphide content of the sulphide-rich fraction is probably higher than the figure given in the table. The value, however, reflects the low chemical analysis, which totalled 92.8%.

At the end of the experiment the water percolating through the sulphide-poor fraction contained 3 ppm Na, 0.7 ppm K, 154 ppm Ca, 10 ppm Mg, < 0.01 ppm Fe, < 0.01 ppm Cu and 0.1 ppm Zn. The water percolating through the sulphide-rich fraction contained 3 ppm Na, 1.3 ppm K, 242 ppm Ca, 74 ppm Mg, 24 ppm Fe, 1.05 ppm Cu, and 36 ppm Zn.

3.16. The Effect of the Tailings Sample Supplied by Mining Company No. 16 on the Composition of Water

The results of the measurements of the pH, the conductivity, and of the determinations of the Ca, Cu, and Zn contents of the water percolating through the tailings sample from Mining Company No. 16 are plotted in Figure 21.

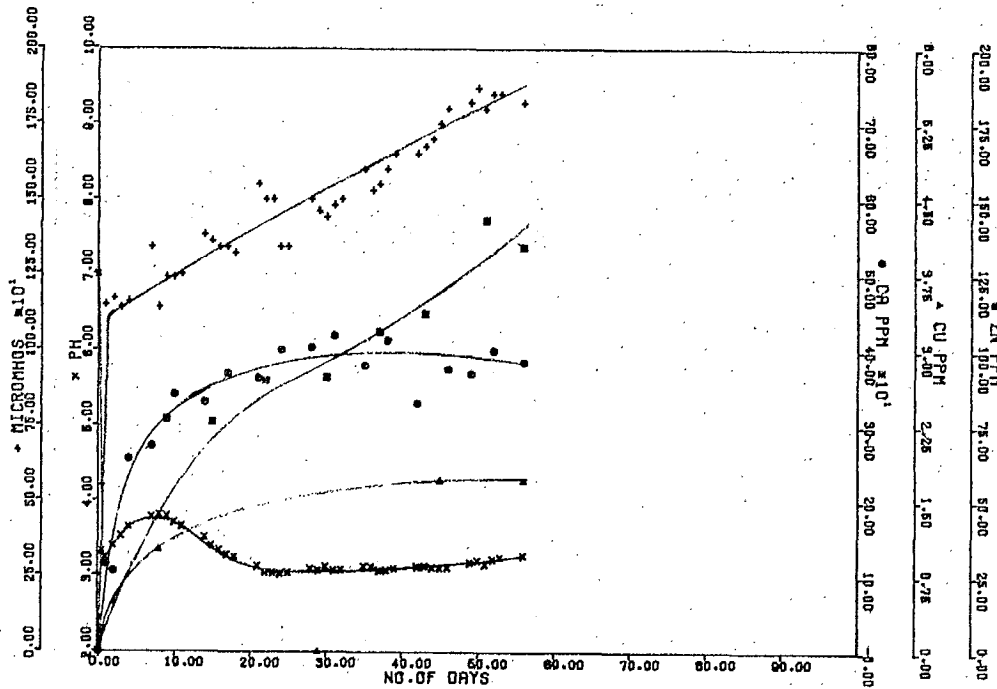


Figure 21. Variables in water percolating through a tailings sample from Mining Company No. 16.

It is again obvious that the system had not reached equilibrium conditions at the end of the experiment, since the conductivity, the Zn and, possibly, the Ca contents were still increasing. The pH curve showed a shape similar to that for the acid fraction of the tailings from Company No. 15. It reached a low pH that appeared to increase slightly.

The principal results of the mineralogical analysis of this sample are listed in Table 21.

TABLE 21  
Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 16

Composition	Wt%	Physical Properties	
Sulphides	75	Specific	3.57
Iron (hydr)oxides	5	Particle-Size Code	0.2.8.
Carbonates	5	Surface Area	127*
Silicates	3		
Quartz	9		

At the end of the experiment, the water contained 3 ppm Na, 0.4 ppm K, 385 ppm Ca, 49 ppm Mg, 5.4 ppm Fe, 1.7 ppm Cu, and 134 ppm Zn.

Although the general pattern, shown in Figure 21, is typical for the variations in acid waters produced by a tailings sample containing much sulphides, the variations of the individual elements within this general pattern have apparently increased in magnitude.



3.17 Information on the Weathering Process Obtained from Field Samples Collected from Tailings Ponds of Mining Companies No. 17 and No. 18

The results of the measurements of the pH values and of the conductivities of waters percolating through tailings samples, collected in the field from tailings ponds of Mining Companies No. 17 and 18, are shown, in Figures 23 and 24\*, respectively.

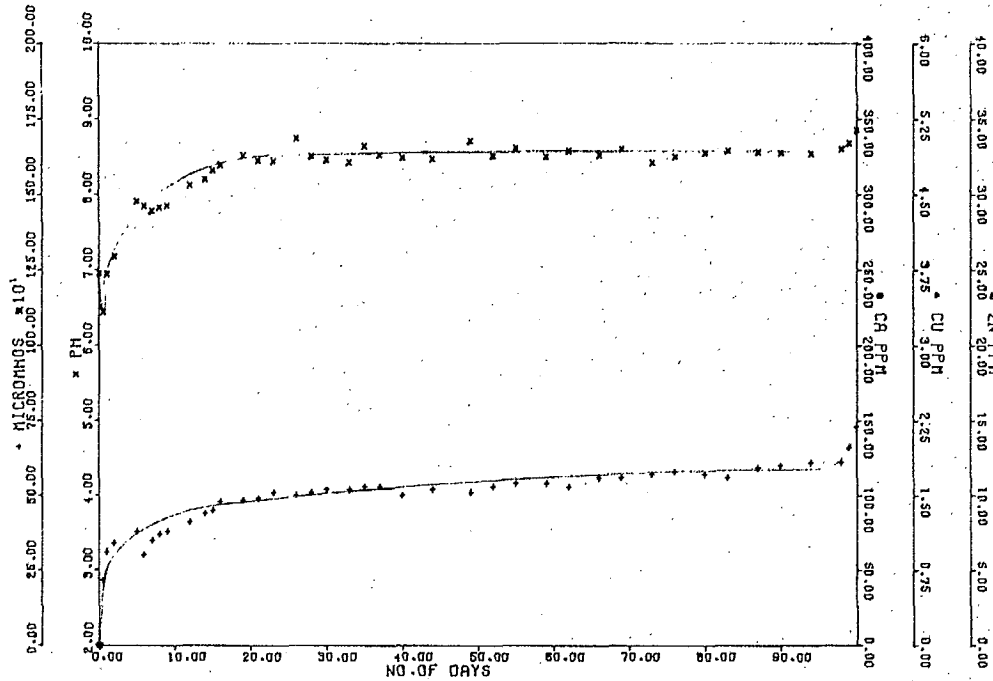


Figure 23. Variations in the pH and conductivity of water percolating through a field sample collected from the tailings pond of Company No. 17.

\*The values for the last two days represent those measured after 124 and 145 days. The tailings samples were mixed with sand in order to decrease the amount of agglomeration.

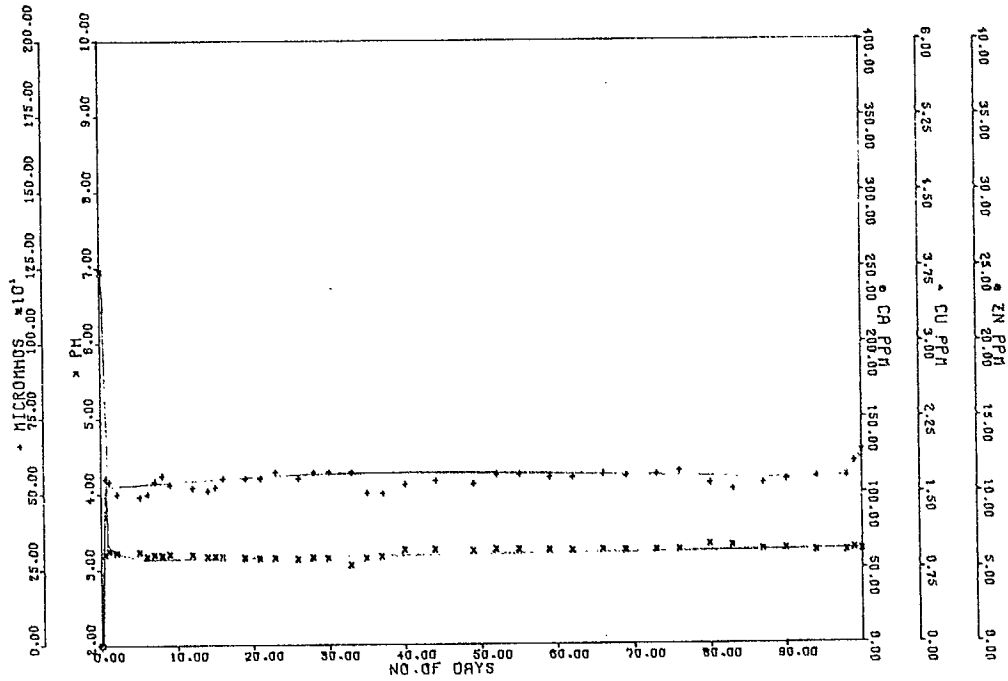


Figure 24. Variations in the pH and conductivity of water percolating through a field sample collected from the tailings pond of Company No. 18.

Because of the limited amount and the weathered state of these samples, no results could be expected from a mineralogical analysis within a reasonable amount of time. However, the results of X-ray diffraction analyses indicated the presence of quartz, chlorite, pyrite, feldspar, mica, and calcite in the sample from Company No. 17 and that of quartz, mica, chlorite, and feldspar in the sample from Company No. 18.

The results of the chemical analyses of these samples are listed in Table 22.

TABLE 22

Results of Chemical Analyses of Tailings Samples from Mining  
Companies No. 17 and No. 18\*

	Composition in Wt%	
	Mining Company	
	No. 17	No. 18
Na <sub>2</sub> O	0.85	1.91
K <sub>2</sub> O	1.36	1.99
CaO	2.25	0.90
MgO	2.19	1.59
Al <sub>2</sub> O <sub>3</sub>	9.62	7.91
SiO <sub>2</sub>	48.37	58.86
Fe	15.1	8.72
Zn	0.06	0.27
Cu	0.062	0.055
S	9.90	5.08
CO <sub>2</sub>	0.68	1.30
SO <sub>4</sub> <sup>=</sup>	<u>1.85</u>	<u>4.94</u>
Total	92.29	93.52

\*Chemical analyses by R. Craig, Chemist, Mineral Sciences Division,  
Mines Branch.

Using the foregoing information, a tentative estimate of the mineral composition was made, so that the composition would be comparable with those described in Part 3 of this series of reports. The results of these estimates are listed in Tables 23 and 24, respectively.

TABLE 23

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 17

Composition	Wt%	Physical Properties
Sulphides	18	Specific Gravity )
Iron (hydr)oxides	12	Particle-Size Code )
Carbonates	1.5	Surface Area )
Silicates	30	
Quartz	34	
Sulphates	3.5	

TABLE 24

Mineralogical Analysis of a Tailings Sample Supplied  
by Mining Company No. 18

Composition	Wt%	Physical Properties
Sulphides	7	Specific Gravity )
Iron (hydr)oxides	8	Particle-Size Code )
Carbonates	4	Surface Area )
Silicates	31	
Quartz	40	
Sulphates	10	

The results of the chemical analyses of the composition of the waters, percolating through these samples after 8, 35, and 145 days, are listed in Table 25.

TABLE 25

Composition of Waters through Tailings Samples from  
Mining Companies No. 17 and No. 18\*

Company No.	Composition in ppm							
	Na	K	Ca	Mg	Si	Fe	Cu	Zn
17	2.25	1.04	66	12	2	-	-	0.03
	3.00	1.10	110	17	5	-	-	-
	20.00	2.7	130	28	3	-	-	-
18	1.31	0.33	11.3	13	2	37.4	0.67	13.7
	1.90	0.23	12.0	14	6	47.0	0.70	14.0
	3.1	0.04	11.0	13	14	47.0	0.86	14.0

\*The values obtained after 8, 35 and 145 days of the run are listed from top to bottom.

The foregoing results can be compared with the analyses of the waters collected in the field from the tailings pond of Company No. 17 and from the ditch draining the tailings pond of Company No. 18. The chemical analyses are listed in Table 26.

TABLE 26

Company No.	Composition in ppm							
	Na	K	Ca	Mg	Si	Fe	Cu	Zn
17	37	7.7	243	58	7	0.1	0.4	1.5
18	46	3.3	170	64	18	4	0.5	32

The results indicate that calcium and magnesium were leached out of the tailings of Mining Company No. 18, but not out of that from Company No. 17 to the same extent. The iron contents were low in both waters, so that this situation probably represents the results of the drainage experiments<sup>(3)</sup>, after the initial dissolution of the sulphides. No suggestions can yet be made as to the patterns followed by the alkalies, copper, or zinc. However, it is obvious that copper, zinc, and iron dissolved in the acid water from Tailings 18, and that the iron content of the drainage water was smaller than in the percolators, due to precipitation.

Experimental results, obtained from a weathered tailings, can represent conditions at different times during the process. Section 3. 17 has been included, particularly to show that coherent information on field conditions depends on more factors than are included in the percolation experiments. One of these factors is time. Another is the variation in the rate of weathering of various parts of a tailings pond; this factor can only be studied locally.

However, the following seems to be indicated:

- (a) Although Tailings 17 contained little carbonate, this carbonate was still present as calcite; in Tailings 18, most of the carbonate content could not be present as calcite; it is even questionable whether any CaO, above that required for some basic silicates, is available for calcite; the significant amount of calcite in Tailings 17, as compared with that of Tailings 18, is supported by the results of X-ray diffraction analysis,
- (b) The sulphide: carbonate ratios in both tailings could be expected to produce acid and alkaline waters, respectively, in the percolation runs on Tailings 17 and 18; however, the reverse was experienced.
- (c) The drainage water, collected in the field from Tailings 17, was acid (pH 3.33), and that from Tailings 18 had a pH of 3.00; the water from Tailings 17 possibly did not represent the drainage water from the whole tailings pond, as well as Tailings 18 (the last was collected from

the drainage ditch and the first was collected from a small basin in the pond); Tailings Pond 17 covers several square miles and Tailings Pond 18 covers less than one square mile.

- (d) The pH and conductivity values were generally less subject to large or sudden variations than those measured in waters percolating through fresh tailings samples.

Some of the most important phenomena, observed in the field relating to approximately twenty different tailings ponds and in the drainage experiments, were the agglomeration of the tailings minerals, the layered structures, and the formation of high-sulphide lenses. The type of weathering that takes place in a tailings pond, consequently, depends, not only on the composition, but also on the structure of its mineral aggregates and on the geomorphology of the tailings pond area. The results of chemical analyses of two other samples, collected in the field from Tailings 18 at significant locations, indicate, for instance, that the  $\text{CO}_2$  content can range between 1.30% and 3.72%. The basin in Tailings 17 may have been connected with a high-sulphide lens.

The purpose of mixing sand with the tailings had been to increase the exposure of the mineral-grain surfaces to water in the hope that the effect of the agglomeration factor would be eliminated to a great extent. Experience in experiments involving the variations in surface areas of minerals exposed to water, however, indicated the difficulties inherent in reducing agglomerates of tailings minerals to original grains<sup>(5)</sup>. The agglomeration was probably still present in the samples used in the percolator experiments; thus, the agglomeration and the weathered stage of the minerals seemed to be the only factors that could produce the foregoing results. Further, an as-yet unknown intermediate type of iron carbonate, which might be formed during the dissolution of pyrite and whose presence might be indicated by the experimental result that calcium drains out of the tailings while the  $\text{CO}_2$  content is retained, can contribute to the complexity of the process.

#### 4. DISCUSSION

The following, possibly significant, information concerning the weathering process was obtained from the foregoing results of experiments dealing with the action of water on a variety of tailings compositions.

- (1) The traditional sulphide: carbonate ratio in the composition of tailings indicated whether the waters percolating through these samples became acid or alkaline. The relation is shown in Figure 27.

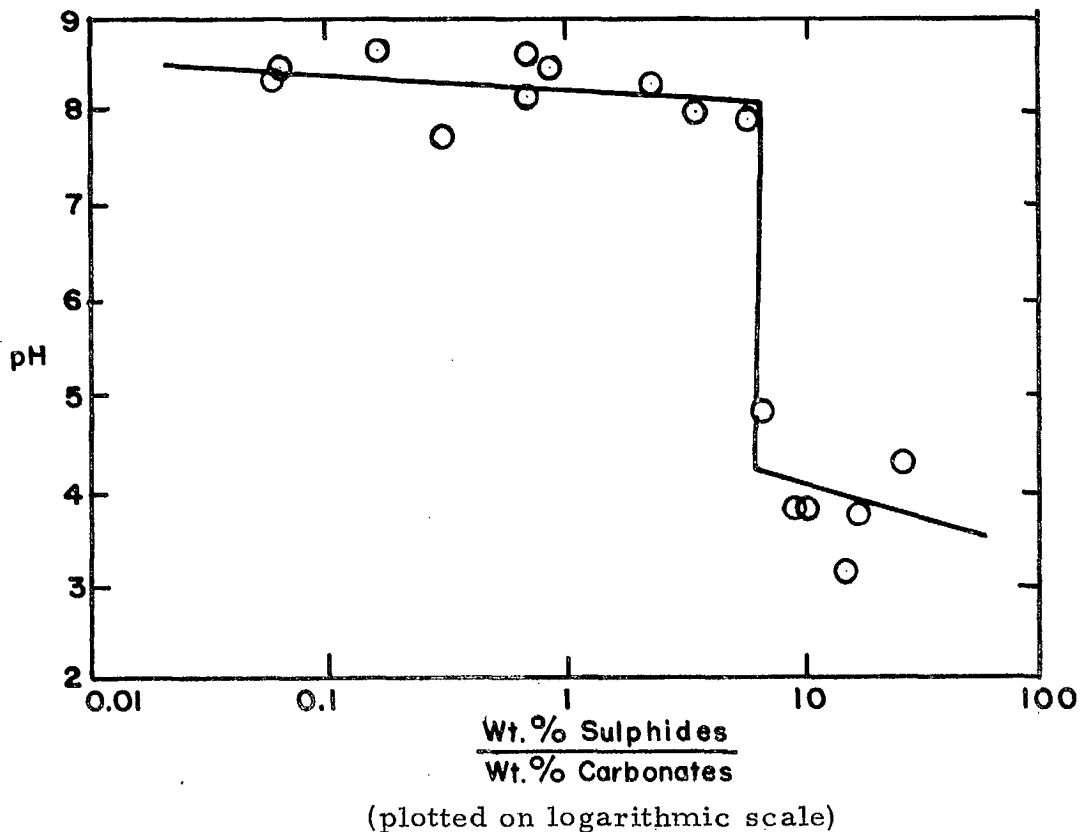


Figure 27. The relation between  $\left[ \frac{\text{wt}\% \text{ sulphides}}{\text{wt}\% \text{ carbonates}} \right]$  (plotted on logarithmic scale) in various tailings compositions and the pH of the water percolating through the tailings.



The slope of the lines at the two pH levels is not significant because of the magnitude of the daily variations in the pH. The water percolating through tailings, having a sulphide: carbonate ratio less than 6.5:1, reached approximately the same pH, viz., 8.2. When this ratio was greater than 6.5:1, the waters suddenly became acid. Although the value of the ratio (6.5:1) has to be analyzed by experiments on mixtures containing pyrite and calcite only, it appears that the amount of sulphides should be several times larger than the amount of carbonate in tailings to produce acid waters, at least in percolation experiments.

(2) The amount of calcium that dissolved in the waters percolating through the various tailings samples could not be correlated with the carbonate contents in the fresh tailings samples. However, they appeared to be related to the surface areas of the mineral grains exposed to water. The correlation was calculated statistically to be significant. However, it was not highly significant, because the correlation appeared to be also affected by the pH to a lesser extent. Obviously, the dissolution of carbonates does not produce calcium ions only, nor do calcium ions originate solely from the dissolution of carbonates.

Since the solution of mineral grains takes place along the surfaces of these grains, the surface area exposed to water could be expected to be of importance in the weathering process. The ratio between the surface areas of the sulphides and those of the carbonate minerals exposed to water, together with the rates of dissolution of these minerals, probably contributes to the greatest extent to the production of either acid or basic conditions in the water. Both factors include the resultant chemical reactions. The above-mentioned ratios for relevant minerals could not be measured, but can be expected to vary in different tailings compositions.

The carbonates appeared to be coarser-grained than the sulphides in several, but not in all, tailings samples. Although the determination of the particle-size distributions of mineral groups, such as sulphides and carbonates, can be conceived to be possible, the relation

between the particle-size distribution and the surface area exposed to water appeared to be very complex<sup>(5)</sup>. These factors, as well as the pH dependency, may cause the calcium contents to be not highly significantly related to the grain-surface areas exposed to water.

Intricate chemical procedures can possibly be conceived to estimate the ratios between the surface areas of the relevant mineral groups exposed to water, but they cannot be expected to be of much practical use. Any progress in this aspect, therefore, will probably depend on the results of percolation experiments on mixtures of pure minerals, of which the particle sizes and surface areas have been measured before and after mixing.

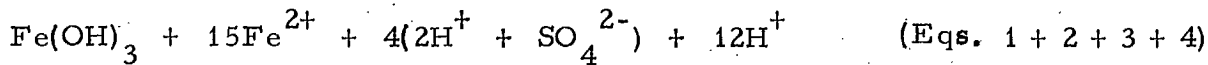
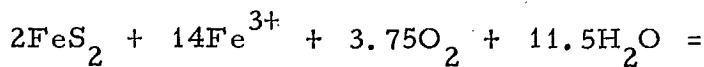
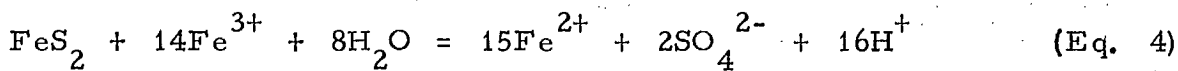
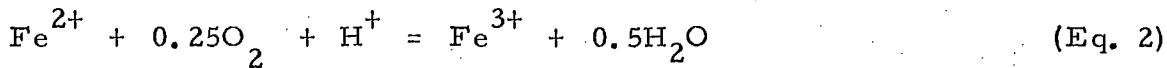
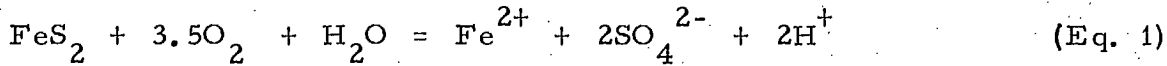
(3) During the beginning of various runs, before the percolation systems had reached equilibrium, at least two reactions were indicated, one reaction moving the equilibrium towards an acid pH and the other moving it towards an alkaline pH.

Results from drainage experiments indicated that, at the beginning of the runs, calcium and, to a far lesser extent, iron are flushed out of the tailings in acid water<sup>(3)</sup>. This acidity may originate in the dissolution of very-fine-grained sulphides, which promotes the dissolution of carbonates.

However, the opposite was indicated in experiments described in Part 1 of this series of reports. In those experiments, the initial acidity of the water may have dissolved the carbonates more rapidly than the acidity was being produced by the fine-grained fraction of the sulphides, so that the effect of dissolving carbonates suppressed that of the sulphides for a certain period to time.

Without considering the effect of the surface area, it seems possible that the large amount of sulphides, required to offset the alkalinity produced by carbonates, indicates that the rate of acid production from sulphides is slower than the dissolution of carbonates. The difference between these two processes can lie in the fact that the base production from mineral carbonates is chemically a simpler process than the acid production from sulphides, which partly depends on available oxygen.

The traditional concepts of the production of acid in the oxidation process of pyrite use chemical equations that are valid stoichiometrically.



The production of  $\text{H}^+$  ions, that has to be balanced by the dissociation of carbonates, is so large that the ratio of sulphides to carbonates could be expected to be the opposite of that indicated by the experimental results. The observation that the grain sizes of the sulphide minerals were generally smaller, and definitely not larger, than those of the carbonate minerals, could also have an effect opposite to that indicated by the experimental results.

(4) The foregoing contradictions, however, may possibly be caused by the under-estimation of the experimental result that the Ca contents of the waters were related to the surface areas of the mineral grains and that general dissolution takes place along surface areas. Weight percentages are validly considered after all solids have gone into solution.

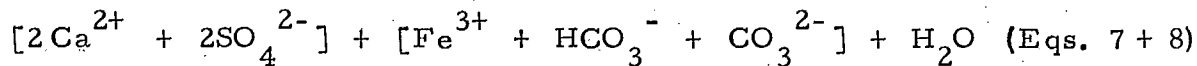
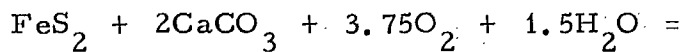
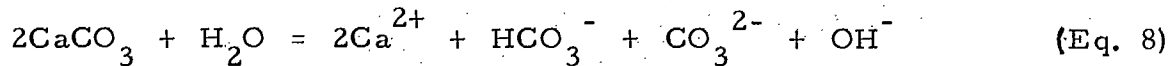
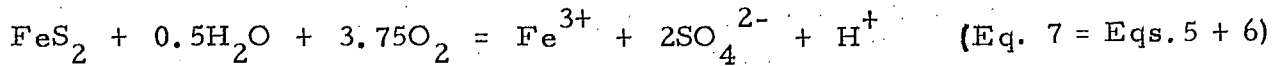
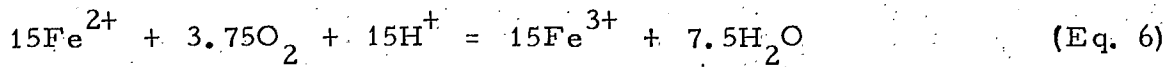
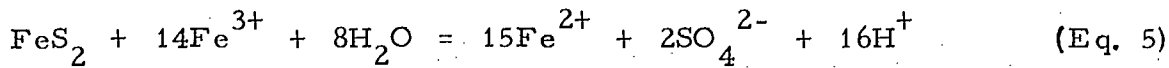
The results described under "1" (pp. 52-53) had been expressed as  $W(\text{eight})_{\text{pyrite}} = 6.5 W(\text{eight})_{\text{calcite}}$ . The ratio 6.5:1 can be reduced to approximately 3:1 or even less when the difference between the specific gravities of the relevant minerals - pyrite, 5.1, and calcite, 2.7, - is considered in combination with the relation that the surface of a spherical particle ( $4\pi r^2$ ) equals  $3\left(\frac{4}{3}\pi r^3\right)^{2/3}$ , and the volume is represented by  $\frac{4}{3}\pi r^3$ .

The principal difficulty in making assumptions required to arrive at a numerical value for this reduction originates in the conditions under which the individual grains contribute to the magnitude of the surface area.

The mineral grain-surface area exposed to water is much smaller than the actual surface area of the grains. Many particles that contribute to the bulk weight are completely enclosed or have only a small part of their surface exposed to the water, due to packing, agglomeration, cementing action of iron (hydr)oxides that form during the weathering, and other possibilities that will be mentioned later. Although these particles contribute to the bulk weight, they do not contribute correspondingly to the magnitude of the surface area.

It is not known to what extent factors such as agglomeration cement the relevant minerals together into lumps. Consequently, the size of the actual surface area to be considered in connection with the bulk weight can be expected to be between that valid for a condition in which all particles are individually dispersed, and that valid for a condition in which all grains are lumped together.

However, the only important result of the foregoing approach that emphasizes the effect of the surface area of minerals exposed to water rather than their weight, is in the direction of the proportions that could be expected chemically. The following chemical reactions can be conceived concerning the resultant interaction between the solutes formed by the dissolution of the relevant minerals in water.



The last equation indicates that 1 mole of pyrite would be balanced by 2 moles of calcite, so that acid conditions would be produced according to Equation (7), or even possibly according to the more extensive oxidation process of pyrite (page 55), when the ratio is greater than about 1:2. Although the numbers of molecules per specific surface areas of the relevant minerals cannot be compared, it seems probable that the conditions indicated by the experimental results require a pyrite surface area that is much larger than that indicated by the reaction (7 + 8), to balance the alkalinity produced by the calcite surface.

However, the following factors will then have to be taken into account in this respect:

- a) Equations (5 to 8) indicate the importance of carbonate ions in water because of the presence of iron carbonate equilibria. The  $\{[\text{Fe}^{3+} + \text{HCO}_3^- + \text{CO}_3^{2-}] + \text{H}_2\text{O}\}$  part of the final equation, (7 + 8), is obviously dependent on dissolved  $\text{CO}_2$ , as can be expressed by the equation

$\text{Fe}^{3+} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{CO}_2$ . As part of the surplus of the required sulphide surface may not only be to neutralize the alkalinity of the  $\text{CO}_2$  equilibria, but to produce permanent acidity in the water.

The production of  $\text{CO}_2$  is probably supported by the observation of the formation of gas bubbles in flow-rate experiments<sup>(5)</sup>.

Crystalline deposits that had formed on the side of the percolator after the run, due to evaporation, were determined by X-ray diffraction analysis to be calcium sulphate. This observation supports the foregoing views on the complexity in the interaction between the solutes formed by the dissolution of pyrite and calcite, in that it decreases the importance of the roles of calcium and sulphate ions in nearly-balanced equilibrium conditions.

b) The experimental results generally indicated that the pH dependency of the Ca contents in the waters was linked with the sulphide: carbonate ratio. If this ratio favoured the production of acid waters, the acid dissolved a large amount of calcium out of calcite.

The results described in Section 17 indicate the possibility that, after dissolution, the cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , of the mineral carbonates seep away in drainage water, whereas the anions ( $\text{CO}_3^{2-}$ ) may be retained to a certain extent. The results of the drainage experiments show that alkalinity in the water continues to exist for a period during which hardly any calcite dissolves. Although these and other results may all originate under particular pH conditions, in that iron ions precipitate and remain in the tailings as iron (hydr)oxides, while the calcium and sulphate ions remain in solution and drain away, the possibility that carbonate ions are retained temporarily remains a factor to be considered in connection with the microbial activity.

c) When the surface of a sulphide grain becomes temporarily "masked" by the formation of a type of (hydr)ous iron carbonate, further acid

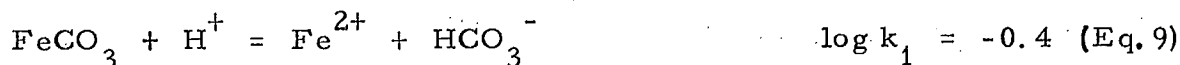
reaction of that grain is prevented for a certain period of time. The masking of mineral-grain surfaces is a common petrological phenomenon ("Tarnung"). The increased rate of solution of sulphides when bacteria are present, as has been observed by others in percolation experiments, may be caused by the bacteria acting on the combination of carbonate and sulphide ions, present in the surface layers of the "masked" grains.

However, various possibilities in this respect will not be discussed before further evidence has been obtained in the second part of the study. The following considerations seem worthwhile mentioning from a purely chemical point of view.

No specific information is available concerning the possibility that a type of iron carbonate may be formed as a metastable intermediate phase before complete hydrolysis of the iron ions has taken place. This suggestion is based solely on field observations, which may be unreliable because of the difficulties inherent in the determination of  $\text{CO}_2$  in the presence of S, and the great spread in the results of that determination.

However, the following consideration contributes to the possibility that, upon dissolution of calcium carbonate, the carbonate is temporarily retained by the iron ions dissolving out of the pyrite.

The solubility of  $\text{FeCO}_3$  in combination with that of  $\text{CaCO}_3$  was considered as follows:



All ions are present in one solution, so that both reactions share the  $H^+$  and  $HCO_3^-$  concentrations.

$$-0.4 = \log \frac{[Fe^{2+}][HCO_3^-]}{[H^+]} \quad \text{and} \quad 2.0 = \log \frac{[Ca^{2+}][HCO_3^-]}{[H^+]}$$

$$\text{or } -0.4 - \log [Fe^{2+}] = \text{pH} + \log [HCO_3^-]$$

$$2.0 - \log [Ca^{2+}] = \text{pH} + \log [HCO_3^-] \quad \text{so that}$$

$$2.0 - \log [Ca^{2+}] = -0.4 - \log [Fe^{2+}]$$

$$\text{or } \log [Ca^{2+}] - \log [Fe^{2+}] = 2.4.$$

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This comparison between calcium and ferrous carbonates would indicate that the concentration of Ca ions is higher in the water than that of ferrous ions, when the pH and  $HCO_3^-$  concentrations favour the presence of carbonate. Although the equation concerning the interaction between  $FeS_2$  and  $CaCO_3$  (Equations 5 to 8, page 57) showed ferric rather than ferrous ions in combination with carbonate ions, the problems appear to be mostly concentrated on a complex interaction between carbonates (not only from mineral carbonates but also from the air-) and the ions dissolving out of pyrite.

c) Generally, however, the complexity of the weathering process is considered to be, for a large part, of a physical nature. The cementing action of precipitated iron hydroxides may contribute to the masking of pyrite grains to a greater extent than the possible formation of an intermediate type of (hydrous) iron carbonate.



The largest effect, however, is very probably in the difference between the particular dissolution processes of pyrite and calcite. Although a difference in solution rate has already been mentioned (page 54), because the pyrite oxidation depends on available oxygen, pyrite usually forms a crust of iron (hydr)oxides around its grains in the weathering process, whereas the calcite surface remains more readily available to the action of water. Diffusion through this crust is slow, and the effect is very similar to that of masking. When the pyrite surface area exposed to water exceeds the 3:1 factor, Equation (7) (page 57) will cause the pH of the water to be acid. When this surface area is smaller than approximately the 3:1 ratio, Equation (8) will cause the pH of the water to be alkaline. The factor 3:1 will very probably vary, because it will depend, not only on the bulk surface phenomena, but also on surface area distribution between minerals, temporary imperviousness, local concentration of solutes, irregular water flow, channeling, initial pH etc., <sup>(3, 5)</sup> which emphasize the importance of the structural conditions. The cementing action of precipitated iron hydroxides and the possibility that the grain-size distribution of sulphides and carbonates are essentially different in particular tailings compositions (e. g., Tailings 15<sup>(1)</sup>) should be considered in this respect. Consequently, just as the mineral surface-area of a tailings sample exposed to water appeared to have more effect on the composition of water percolating through it than its weight; so has the structure of the mineral aggregates in a tailings pond (pile) more effect on the composition of drainage water than the weight percentages in a customary "representative" sample. Field observations indicate the possibility that the pH of the drainage water changes with time, as parts of the layers consisting of coarse particles are leached out, leaving lenses of fine-grained material. All field observations involved old, weathered tailings ponds that had not been embanked and built according to modern disposal practices. In some tailings, the mineral components were not all equally distributed over the grain sizes, so that layers produced by sedimentation segregation can be expected to have different compositions and, hence, to affect the water composition differently.

The foregoing is merely stated to emphasize that the principal focus of the present, and of any interdisciplinary, study is in the correlation between the relevant areas of study and, in this case, particularly between the most significant results of laboratory experiments and those of field studies. In laboratory experiments, such as have been described in this series of reports, the effect of one or more variables can be discovered, demonstrated, and partly interpreted. However, their effect in the over-all weathering process can be evaluated only by field studies; therefore, in the interpretation of the laboratory experiments, the field observations have to be kept in mind. These experiments attempt to outline the effects of the principal factors shared by the chemical, physical and microbiological aspects of the weathering process. The first two aspects appear to be connected in the surface properties of the mineral grains exposed to water. Although the effect of a particular ratio between the surface areas of sulphides and carbonates was indicated, the factors constituting this ratio should be analyzed before it can be put into practical use.

(5) It is emphasized that, although the weathering process in a tailings pond might be conceived to be a result of many chemical reactions, it is essentially a geological process. And, although much experimental work has been done over the years to simulate geological processes, the highly important factor, time, cannot be duplicated. This factor is possibly decisive in explaining the differences that might be established between the results of laboratory experiments and those of field observations. If the effects of individual variables are studied in laboratory experiments, the time factor becomes less decisive. The latitude in the uncertainty in the results of these experiments, however, increases when interactions between several factors are studied. This increase is usually magnified by the time factor. An indication in this respect has already been obtained in studying the chemical aspects of the process when they had to be combined with those of the physical aspects<sup>(3, 5)</sup>.

Another indication was obtained from results of redox-potential measurements. The possible significance of the measurements that have

been made on the waters that percolated through various tailings samples, will not be discussed in detail in this report because of the uncertainties inherent in the measurements themselves. Generally however, when the Eh-pH values of all the waters are plotted in a diagram, and when they are compared with those measured in waters collected in the field on or near tailings ponds, it appears that they follow different directions. The direction of the values obtained from waters percolating through fresh tailings samples indicated the possible presence of aqueous ferrous ions. The direction of the values obtained from the field samples does not show this possibility and indicates the presence of only hydrolyzed states of iron containing ions. This difference very probably originates in the time factor. Recent field observations suggest possibilities, however, that are considered to be due to local conditions, indigenous to particular tailings ponds. To what extent these conditions are local or are due to the weathering of particular tailings compositions over time, is not known.

Consequently, all the reservations, made in this series of reports concerning the extrapolation of the experimental results to field conditions, are based, not only on the wide latitude in the results of experiments dealing with a great number of variables, but, even more, on the unknown effect of variables not included in the experiments. One of the most important of these factors, other than the microbiological action, is time.

## 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

1. A. Jongejan, An Experimental Study of the Weathering of Mill Tailings in Connection with Water Pollution. Part 3: Mineralogical Analyses of Tailings Samples from Various Mining Companies in Canada. Mines Branch Investigation Report IR 73-14, 4 May 1973.
2. id. Part 1: Development and Examples of Study Methods, Mines Branch Investigation Report IR 72-4, 8 March 1972.
3. id. Part 2: Preliminary Experiments, Mines Branch Investigation Report IR 73-54, 18 September 1973.
4. A. Jongejan, Progress Report on Project No. E-PC 71-02. The Effects of Slag Heaps and Tailings Ponds on the Pollution of Water. A summary of the Progress in the Study of the Microbiological Aspects of the Project, Mineral Sciences Internal Report MS 73-25, 18 September 1973.
5. A. Jongejan and A. L. Wilkins, An Experimental Study of the Weathering of Mill Tailings in Connection with Water Pollution, Physical Aspects of the Weathering Process of Tailings Ponds, Mines Branch Investigation Report IR 73-56, 18 September 1973.