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

PART 1: DEVELOPMENT AND EXAMPLES OF STUDY METHODS

by

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SUMMARY

A study has been started concerning the variables involved in the weathering process of tailings ponds in relation to water pollution.

The daily variation of the pH of water percolating through a tailings sample from the Hudson Bay Mining Company was measured, when the design of percolators required for the experiments was tested. The pH reached a stable value at approximately 8.25, whether acid or neutral water had been used initially.

The daily variations of the pH, redox potential, and conductivity of waters percolating through various samples of the tailings from the Heath Steele Mine in New Brunswick were measured when the performance of a group of twelve percolators was being checked.

A preliminary indication of the combined results was that, apparently, the stable pH of the waters depended on the exposed grain surface area of the tailings. The more the tailings sample was diluted with sand, the more acid the percolating water became and the more the Eh-pH value represented the oxidation of ferrous ions. However, it is very probable that variables other than the exposed grain surface area are involved in this phenomenon; therefore, the results have to be considered as examples of the type of information that may be obtained in future experiments on samples that contain fewer variables than do the tailings.

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1. INTRODUCTION

In early 1971, a study was started with the objective of contributing basic knowledge to the attempts being made in the mining community to correct ecologically undesirable effects from the weathering of such wastes of ore processing plants, as tailings ponds and slag dumps.

The efforts to reduce pollution that originates in tailings ponds and dumps are, in general, focussed on the elimination of air pollution caused by fine particles being blown about by the wind and on the elimination of water pollution caused by drainage of substances being dissolved out of the tailings during the weathering process.

This study is particularly concerned with the action of, and the interaction between, variable factors in the physical, and chemical properties of the tailings, including the microbial population, that affect the weathering process chemically. This study deals with the nature and quantity of substances dissolved in the water that percolates, through the tailings and that finally drains off into creeks, rivers and lakes.

The study is, therefore, not concerned at this stage with the treatment and the development of preventive measures that have to be taken in connection with water pollution, but with attempts to indicate the nature of the processes as they occur naturally in tailings ponds.

Any study of a weathering process requires relatively long-term experiments. When, in addition, the study is confronted with the extreme complexity of multi-component systems subject to many variables, accurate and scientifically meaningful results cannot be expected to be available for several years. Because of the urgency to acquire knowledge on these weathering processes, it was decided to describe the results of the experiments in a series of reports as the study progresses.

In the preliminary experiments needed to develop the most suitable instrumentation and methods, actual tailings were used so that some indication as to the relative importance of a few variables might be obtained. The purposes of this report are (a), to describe the apparatus and methods that will be used in future experiments and (b), to demonstrate, by a few examples with different experimental conditions, that subsequent variations in electrochemical properties of the water can be measured.

The reason for this course of action is that, although various physical and chemical aspects in the weathering process may already be realized, the ultimate problem in the study is to determine the relationships and proportions between various aspects of the process. Although assumptions about certain parts of the process may be right, by themselves, much of the significance of the assumed equilibria or mechanisms may be lost, when they appear to be dominated by other aspects of the process. The results of the observations in these preliminary experiments are intended, therefore, to outline the nature of future experiments. Along with results of observations of experiments on the tailings, they will also be used to compare the polluting effects of tailings that have different mineralogical compositions. Consequently, any conclusions drawn by the reader of this report that do not take into account the preliminary nature and the limitations of the experiments, will have a great risk of being invalid. It is emphasized that, according to the experience obtained during the work on this subject, it is important to realize that what is valid for one particular type of tailings may not be valid for another.

2. EXPERIMENTAL METHODS

The objective of the experiments was to study the action of, and the interaction between, several variables on the nature and quantity of inorganic substances dissolving out of tailings during the weathering process.

Four aspects of this process were considered in the initial approach to the problem. The purely chemical (abiotic) action and microbial (biotic) action on the tailings might simulate, respectively, conditions in freshly dumped materials and conditions in old tailings ponds. Each of these types of action could be studied in both closed and open systems. The closed system, in which water is recirculated without treatment, might simulate the conditions of stagnant water. The conditions of an open system, simulating free-flowing water, could be obtained by inserting an ion-exchange column in the water-flow circuit of the percolator so that mostly fresh water would act on the tailings.

For this purpose, an apparatus had to be designed that would permit a tailings sample to be subjected to the action of percolating water under a variety of conditions and for long periods of time.

After experimenting with the air-lift(1) as well as with the suction(2) principle, which has been used in the design of existing percolators, a type of percolator was constructed that was basically a modification of the air-lift apparatus.

2.1 Percolator

The design of the apparatus was based on the following requirements of the experimental procedure.

a) The apparatus should be made out of chemically inert material, preferably all glass.

b) It should be possible to percolate and recycle one to five litres of solution through a tailings sample for several months if necessary.

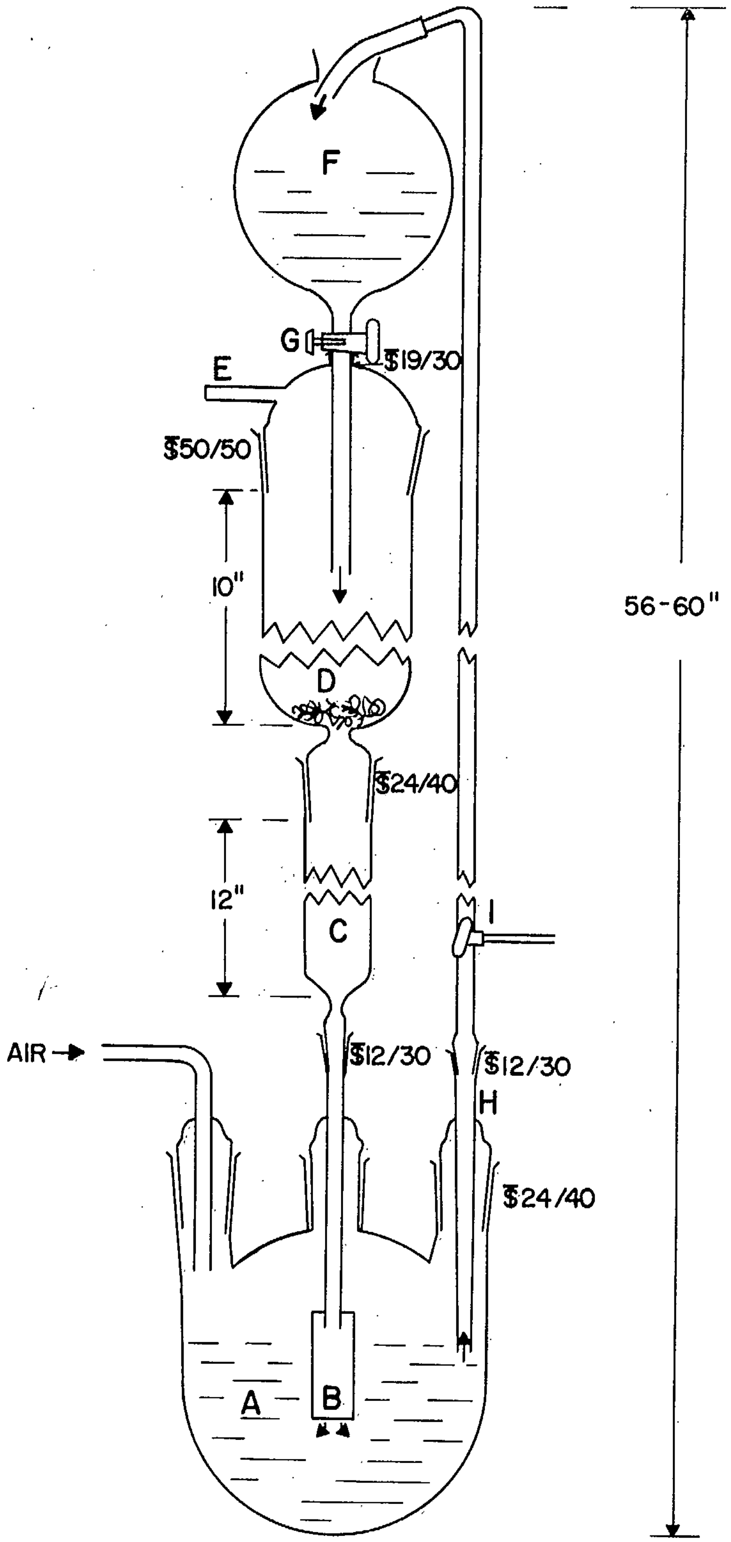

Figure 1. The percolator used in the weathering experiments.

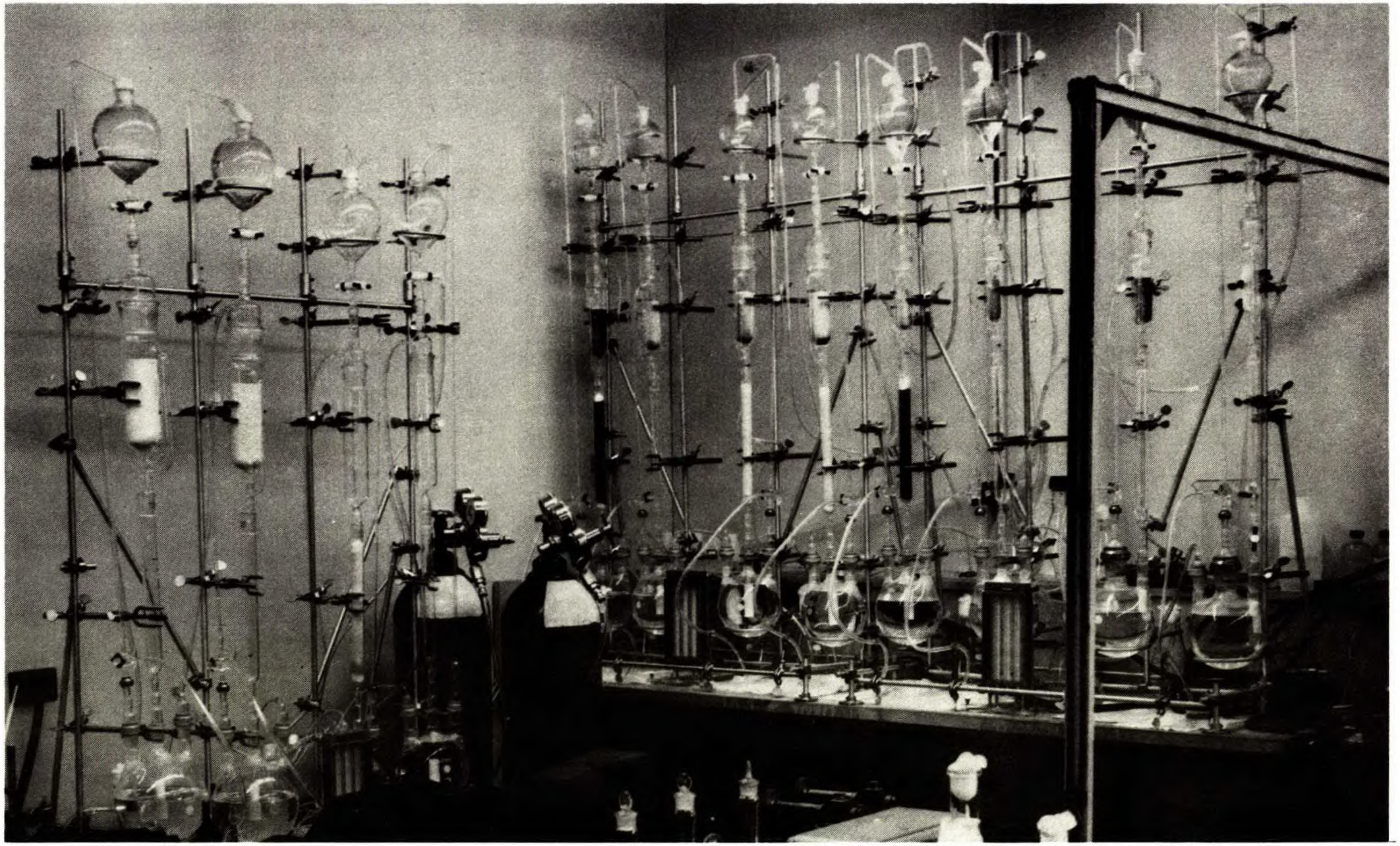

Figure 2. A series of percolators such as is being used in the weathering experiments.

c) The apparatus should be closed off from the air as much as possible in order to reduce evaporation of the water.

d) It should be possible to sterilize the apparatus and to prevent micro-organisms from entering.

e) It should be possible to vary the amount of sample, possibly from 10 to 500 grams.

f) It should be possible to introduce substances other than the tailings or mineral mixture, for example, an ion-exchange resin to act on the water as a variable not included in the tailings.

g) It should be possible to control, vary, and measure the flow of water through the sample.

h) It should be possible to tap off small water samples for analysis and to return unused portions to the system without disturbing the conditions.

i) It should be possible to vary the oxygen partial pressure in the water to a certain extent.

All the foregoing requirements were met by the apparatus shown in Figure 1. A photograph of the actual arrangement of a group of twelve units being used in the laboratory is shown in Figure 2. The apparatus consists of a distilling flask (A) having three parallel necks with 24/40 S.T. (Standard Taper) glass joints. The group of twelve percolators was equipped with distilling flasks of both 2000 ml and 3000 ml capacities.

One of the outside necks* is connected via a flowmeter to a compressed-air cylinder. The central neck carries a column consisting of the following parts:

a) A part that is fitted with a valve (B) at the bottom, dips into the water and has a 12/30 S.T. glass joint on top.

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*All the glass-blowing work on the apparatus was done by P. Hernandez, Glass-blower, Physical Metallurgy Division, and all the machining by J.F. Tippins, Technician, Physical Chemistry Group, Mineral Sciences Division.

b) A 12-inch-high column (C), into which ion-exchange resin or other material required by the experiment may be placed, fits into the 12/30 S. T. glass joint of the part described in (a). It has a width of the 24/40 S. T. glass joint fitted on top. (see requirement f, page 6).

c) Either a Soxhlet extractor or a column (D) that is constricted just above the 24/40 S. T. glass joint and has a width of the 50/50 S. T. glass joint on top, fitted into the column (C) below.

d) Each extractor column is closed with a suitable size S. T. glass joint connected to a 19/38 S. T. joint and provided with an overflow outlet (E).

e) Globe-shaped 500- and 1000-ml separatory funnels (F) were fitted with 19/38 S. T. glass joints and long stems to reach down into the extractors. The Teflon stopcocks of the funnels were fitted with a "screw-in" type of metering valve (G) to improve the control of the rate of water flow, which was unsatisfactory in Experiments Nos. 1 and 2. The funnels were closed at the top with a plug of non-absorbent cotton.

The second outside neck carries a part (H) with a tube that extends down into the distilling flask. When air pressure is supplied, the depth of this tube regulates the water level in the flask. A length of 8-mm tubing fitted with a three-way stopcock (J), is connected by a 12/30 S. T. glass joint in part (H). This glass tubing is bent at the top and is fitted with a piece of Teflon tubing to direct the water flow into the separatory funnel (F) on top of the extractor. The three-way stopcock is used for tapping off water samples and for measuring the water flow through the system.

The valve (B) at the bottom of the extractor column closes when the air pressure in the distilling flask forces the water up the 8-mm tubing into the separatory funnel. This valve was machined from a Teflon cylinder and encloses a polyethylene float. The depth at which the valve is suspended depends on the depth of the stem of the 8-mm upright (H) in the distilling flask. The end of the latter is fitted with a small piece of Teflon tubing, so that it is possible to adjust the water level to the capacity of the separatory funnel.

Both 24/40 S.T. glass joints of the outside necks of the distilling flask and the 12/30 S.T. joint in the 8-mm upright were fitted with glass joint clamps in order to prevent the pressure inside the flask from opening them.

The percolators were arranged in units of four in Flexaframe stands, and each unit was connected, via a bench-mounted, four-60-tube flowmeter unit, model 640 BV from Matheson of Canada Ltd.*, to a compressed-air or other gas cylinder. The cylinder was fitted with a two-stage regulator and filter. A manifold was machined to fit the four inlets of the flowmeter; Tygon tubing and Swagelock connectors were used throughout.

In between the flowmeter outlet and the air inlet of the distilling flask, which also contains a small plug of non-absorbent cotton, a pressure-relief valve was inserted. This valve was constructed of a metal cylinder containing a ball-bearing and a spring with adjustable tension, and was designed to reduce the chance of a sample overflowing. An overflow could happen only when either the three-way stopcock (J) in the 8-mm upright or the sample in the column type of extractor (D) clogs up unexpectedly. The overflow outlet (E) was covered with a piece of Tygon tubing that hung into a large-capacity Erlenmeyer flask closed with a non-absorbent cotton plug.

It is evident that, in addition to the funnels and distilling flasks, which all have the same size glass joints (19/38 S.T. and 24/40 S.T., respectively), the other parts in the apparatus can be made interchangeable by having several parts in stock.

The diameter of the column (C) depends on the size of the glass joint of part (D); for example, when a large-size Soxhlet extractor is used, the upper S.T. glass joint is 71/60 and the lower is 29/42, so that the diameter of column (C) is that of 29/42 S.T.

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*The brand names mentioned in this report are not an endorsement but merely examples of the types of products used in the experiments.

Although it is possible to disassemble the apparatus and autoclave the parts (except perhaps for the 8-mm upright) in a suitable verticle sterilizer, the apparatus for the second experiment was sterilized by percolating and washing each part in a solution of 2.5% formaldehyde/HCl (95/5) solution and then rinsing the parts in sterile water.

By using a compressed-gas cylinder, it is possible to vary the nature of the gas (see requirement i, page 6) and it is possible to aerate the water by inserting in the top of the separatory funnel a glass tube, possibly outfitted with a gas-dispersion disc.

2.2. Procedures

The appropriate amount of sample or sample-mixture was weighed out and then sterilized (in its extraction thimble) by heating it to 140°C for 48 hours in a drying oven. Non-sterilized samples were used when the effect of bacterial action of the sample itself had to be included in the experiment.

The apparatus was sterilized as described on page 9 and the distilling flasks were filled with double-distilled water, possibly pre-adjusted to a certain pH or inoculated with a sample of specific bacteria.

Each morning the electrical conductivity, the hydrogen-ion activity and the redox potential (Eh) were measured in micromhos, in pH units, and in volts respectively, on 50- to 100-ml samples of the water.

These samples were obtained by changing the flow in the three-way stopcock (J, Figure 1), and directing it through a piece of Tygon tubing into a 150-ml sterilized beaker. The beakers were covered with watch glasses most of the time. During the measurement of the electrochemical properties, a watch glass was used in which two holes had been drilled to provide space for the electrodes.

Except for Experiment No. 1, in which only the pH was measured with a Beckman Expandomatic pH meter, a Corning Model 110 Expanded Scale pH meter was used for the measurement of pH and Eh. The pH determinations were standardized daily by using buffer solutions of pH = 4 and pH = 7. The Eh determinations were standardized by using a potassium ferro-ferric cyanide solution as described by ZoBell(3). A Model 31 Y.S.I. Conductivity Bridge, fitted with a No. 3403 (K = 1.0) Y.S.I. cell, was used for the conductivity measurements. The value of the constant was checked periodically according to A.S.T.M. Procedure No. D 1125, using a 0.01 N KCℓ solution. After each determination, the conductivity of the distilled water used in rinsing the electrode was checked to be below 2 micromhos. After approximately 50 determinations, the electrode was cleaned in a solution of 100 ml isopropyl alcohol, 100 ml diethyl ether and 50 ml HCl (1:1).

The water flow-rate through the percolators was about 100 ml/hr, while the air flow-rate was 35 ml/min.

2.2.1. Microbiological Methods

The microbiological work was initially concerned with attempts to establish standard procedures that could be used during the experiments. They were focussed on the selection of the most suitable nutrient media and methods for the determination of iron and sulphur bacteria.

Conventional tests were done using the microscope and many nutrient media, as described by Parker, Postgate, Wieringa(4), etc., were tried out. The result was that several liquids, as well as solidified media, were used covering the possible presence of aciduric and non-aciduric thiobacilli, ferro-oxidizing and facultative heterotrophic iron and sulphur bacteria. For the routine check on the presence of thiobacilli, a slight modification of London's solution(5) was used. Erlenmeyer flasks containing 100 ml of the solution were inoculated with a 5- or 10-ml sample of solution, or as much as a 100-ml sample was filtered through a type HA Millipore filter, and the bacteria on the filter were cultured. This method appeared to be preferable to concentration by centrifuging.

Thiosulphate and polythionates, if present in the water, were determined iodometrically using the methods described by Starkey(6).

Although ferrobacilli were still detectable in inoculated water in the percolators after 24 days, the amount seemed to have been reduced drastically at the end of the second experiment. It is possible, however, that the bacteria were concentrated in one or more particular layers of the samples. Although it is not very probable, these layers may have had a filtering effect. However, no tests were done on the tailings samples in the percolators.

The examination of waters from different tailings ponds, collected during field investigations, resulted in the isolation of bacteria such as those of the genera Pseudomonas, Achromobacter, Brevibacterium, and Streptomyces. They did not belong to the typical iron and sulphur group of bacteria; therefore their presence was attributed to contamination of the samples. Later in the study, however, it appeared that such bacteria were consistently present in the media inoculated with water samples taken in the field and not in the blanks. At present, it would appear preferable to consider the possibility that the composition of the microbial population of a tailings pond and of the water percolating through it may vary significantly from one tailings pond to another and within a single pond.

This course of the investigation will not affect the planning of the percolator experiments in the beginning because, after the preliminary experiments in which tailings samples are used, the actual study will start with the investigation of mineral mixtures that simulate generally simplified tailings' compositions.

3. EXPERIMENTAL RESULTS

3.1. Experiment No. 1

In order to test the performance of the percolator and to get an impression about the order of magnitude of the quantities of elements dissolved at the end of a certain period, tailings from the Hudson Bay Mining Company were selected for the first experiment. According to its X-ray diffraction powder pattern, the sample consisted principally of pyrite and quartz, while pyrrhotite and possibly enstatite were present as minor constituents.

3.1.1. Composition of the Tailings Sample

The results of the chemical analyses* are listed in Table 1.

TABLE 1

Chemical Analysis of Tailings from the Hudson Bay Mining Company

Composition in Wt %	
Element	%
Na (calculated as Na_2O)	0.39
K (calculated as K_2O)	0.47
Ca (calculated as CaO)	2.60
Mg (calculated as MgO)	2.87
Al (calculated as Al_2O_3)	8.22
Si (calculated as SiO_2)	28.87
S	24.10
CO_2	2.38
Fe	26.88
Pb	0.18
Zn	0.60
Cu	0.18
Total	97.74

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*Chemical analyses by R.R. Craig, Chemist, Analytical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

Several of the elements listed in the analytical results are known to occur as oxides in the tailings. The converted values are listed in the table. Although Fe may be present in silicates or in ankerite, it was assumed to occur as an iron sulphide. The results indicated that calcite, pyroxene, and feldspar could possibly be present as minor constituents. A problem is created by a possible surplus of Al_2O_3 that can be combined only with SiO_2, any SiO_2 "surplus" being present as quartz. Because of the suspicion that a type of clay mineral might be present, some attempts were made to determine this possibility by differential thermal analysis and X-ray diffraction methods. However, no specific type of clay mineral could be detected and it is possible that Al_2O_3 is present as a partly altered feldspar. A detailed mineralogical analysis using separation techniques is needed to establish the mineralogical composition of the tailings. In order to "typify" tailings it should be possible to convert the results of their chemical analyses into their mineralogical composition quantitatively.

3.1.2. Experimental Conditions and Procedures

The following runs were done using the tailings sample from the Hudson Bay Mining Company.

a) A blank run (a_1) was made using 2000 ml distilled water whose pH was adjusted to 4 with H_2SO_4 and an empty 33 x 80-mm cellulose Whatman extraction thimble, plugged on top with glass wool. Another run, designated (a_2), will be detailed later.

b) The conditions in this percolator run were the same as those under (a), except that the extraction thimble contained 60 g of non-sterilized tailings from the Hudson Bay Mining Company. Two runs were performed, designated (b_1) and (b_2).

c) In a percolator of the design described by Audus(2), 450 g of purified sea sand (Baker and Adamson, Code 2161) was used with 1000 ml of distilled water whose pH was adjusted to 4.

The results of the pH measurements of these runs are shown in Figure 3.

The blank (a_1), of which the pH variation is indicated as (ı) in Figure 3, was run from 14 January to 2 February, 1971. Another blank (a_2) was run from 3 February to 25 May, 1971, of which the pH variation is indicated also as (ı). In the blank (a_2), the column below the separatory funnel had been filled with Dowex 50W-X8 ion-exchange resin. This resin had been washed with 2.33 M H_2SO_4 and then rinsed with distilled water until the pH was 3.5.

The run (b_1), of which the pH is indicated as (+) in Figure 3, lasted from 14 January to 22 February, 1971. The water was then changed to distilled water whose pH was 7 and the run (b_2), using the same sample, continued to 25 May, 1971. The pH variation of this run is shown in Figure 3, as line (x).

The run (c) containing sand, of which the variation in pH is shown in Figure 2 as (o), lasted from 25 January to 25 May. Although the pH values are compared with each other in Figure 3, they were not measured on the same day. The daily measurements were discontinued approximately 6 weeks before the runs were stopped. Water samples from the blank run (a_1) and from the tailings run (b_1) were retained and stored in glass bottles after the termination of these runs. The pH values of the retained water samples, and of those obtained on 25 May, the termination date of the runs, were all measured on that date and are plotted arbitrarily at the 75th day in Figure 3.

3.1.3. Results of Experiment No. 1

3.1.3.1. pH Determinations

The pH of neither blank varied markedly, as is shown in Figure 3. However, the Dowex resin had started to deteriorate slowly after approximately one month, judging by the discoloration of the water, so that another type of resin would have to be tested in this respect.

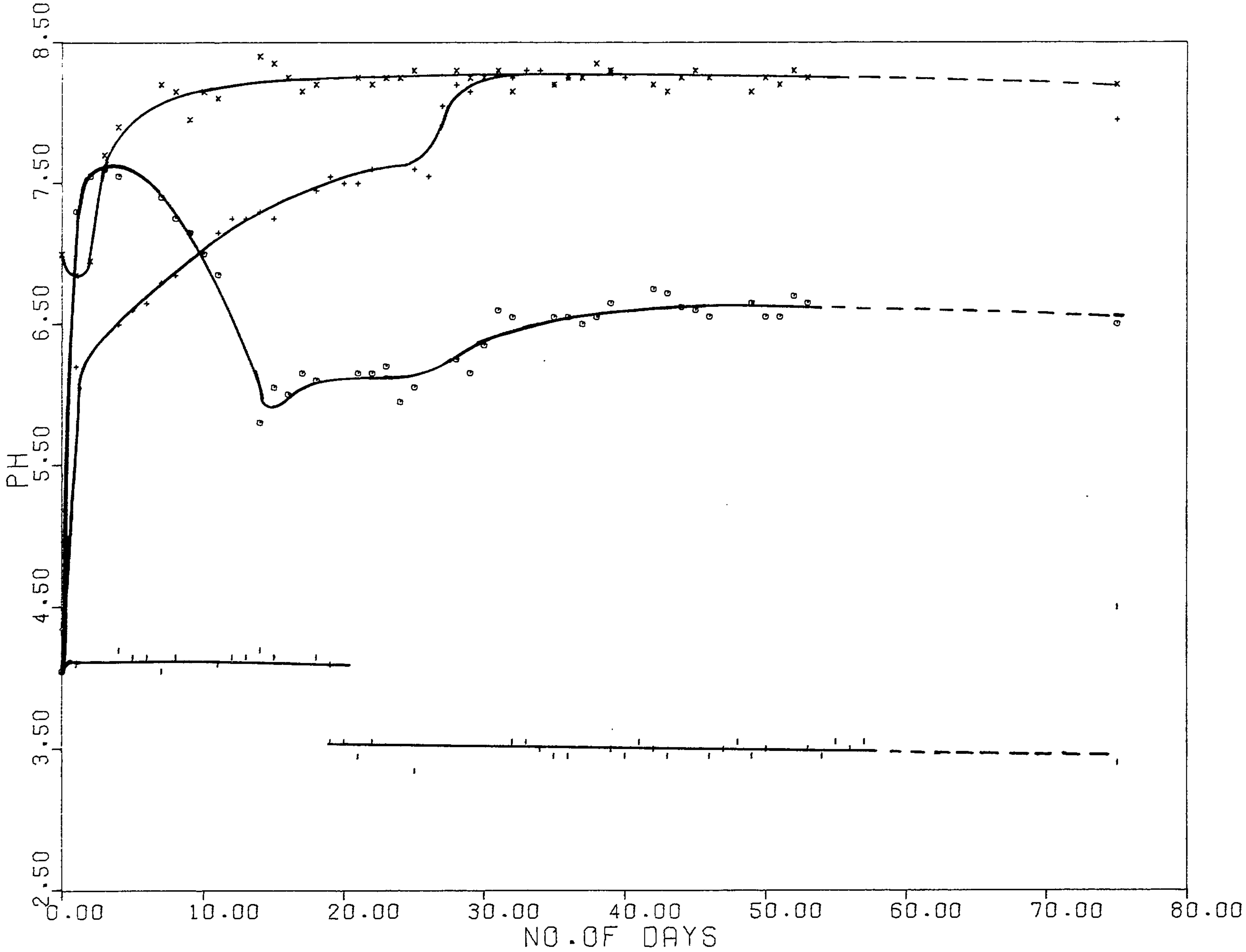

Figure 3. The variation of pH during the experiments using a tailing sample from the Hudson Bay Mining Company.

ı pH of blank runs, (a_1) and (a_2). + pH of water percolating through a tailing sample, starting pH 4 (b_1).

⊚ pH of water percolating through sea sand (c). x pH of water percolating through same, starting pH 7 (b_2).

Both run (b_1) and run (b_2), using the tailings sample from the Hudson Bay Mining Company, reached the same pH of approximately 8.25; the initial pH of the water apparently does not affect the final pH.

The initial acid reaction in the run starting from pH 7 disappeared after the first two days. This may indicate an overlapping of reactions in which the basic reaction superseded the acid reaction.

The pH of the water in the run (c), using sand, varied during the first 14 days, but reached an equilibrium of 6.65. The initial alkalinity may originate in some ion-exchange properties of the purified silica.

3.1.3.2 Chemical Analyses

After the runs had been finished, water samples were submitted for chemical analyses. The results of the analyses are listed in Table 2.

TABLE 2

Chemical Composition of Waters Obtained During Experiment No. 1*

	Composition in ppm								
	Na	K	Ca	Mg	Al	Si	Fe	Cu	Zn
Blank (a_1)	1.4	1.3	0.7	0.07	N	0.54	N	0.3	0.07
Blank (a_2)	0.6	3.0	0.1	0.01	N	0.59	N	N	N
Dowex Concentrate **	1.3	0.4	1.0	0.20	0.2	0.29	0.28	0.26	0.08
Hudson Bay (b_1)	8.8	6.8	150	13	N	33	N	N	N
Hudson Bay (b_2)	1.9	3.3	85	13	N	2.7	N	N	N
Sand (c)	4.2	5.7	3.9	0.59	N	8.0	N	N	0.04

*Chemical analyses by Mrs. V.H.E. Rolko, Chemist, Analytical Chemistry Group, Mineral Sciences Division, Mines Branch.

**NOTE: a) The Dowex resin from the blank run (a_2) was eluted with 250 ml 2.33 M H_2SO_4, then washed with distilled water until the sample was 1000 ml. For comparison with the 2000 ml water in the percolators, the analytical results were divided by a factor 2.

b) N = not detectable.

The composition of the water sample (a_1) can be only partly compared with that of the runs (b_1), (b_2), and (c) because of the differences in conditions during the runs. The enrichment of the elements in the water flowing through the Hudson Bay Company tailings and the sand sample, however, is obvious.

Significant concentrations of Na, Ca, Mg, Al, Fe, Cu, and Zn in the ion-exchange resin are also indicated, but K and Si were barely, if at all, retained. In view of the contents of the blank run (a_1), it is probable that several elements were dissolved out of the resin because the totals of the blank (a_2) and the Dowex concentrate are higher than the levels of the elements in the blank (a_1).

The higher concentration of silica in the water flowing through the tailings samples than that in the water from the longer run through pure sand may be caused by the presence,in the tailings, of silicates, that are more soluble than quartz.

3.2. Experiment No. 2

This experiment was concerned with the performance of a dozen percolator units. A tailings sample from the Heath Steele Mines in New Brunswick was used to obtain some preliminary information on the weathering process. It was supplied on 10 September, 1971, by the Montreal Engineering Co. Ltd., Montreal, co-ordinator of the North Eastern New Brunswick Mine Water Quality Program, initiated by the Canada-New Brunswick Joint Consultative Committee. According to discussions at the meeting between the Program Co-ordinators and Mines Branch Personnel held on 17 May, 1971, it was decided that it would be informative to use the Heath Steele tailings in the preliminary experiments.

The sample represented fresh tailings filtered from the process effluent before discharge to the tailings pond.

3.2.1. Composition of the Tailings Sample

The tailings from the Heath Steele Mine consisted, according to the X-ray diffraction powder pattern, principally of pyrite with small amounts of quartz and sphalerite.

The chemical analyses of the sample are listed in Table 3

TABLE 3

Chemical Composition of the Heath Steele Mine Tailings*

Composition in Wt %	
Element	%
Na (calculated as Na_2O)	0.04
K (calculated as K_2O)	0.36
Ca (calculated as CaO)	1.72
Mg (calculated as MgO)	2.10
Al (calculated as Al_2O_3)	5.05
Si (calculated as SiO_2)	12.63
Fe	35.63
S	33.60
CO_2	1.61
Zn	0.47
Cu	trace
SO_4	1.44
Total	94.65

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*Chemical analysis by R.R. Craig, Chemist, Analytical Chemistry Section, Mineral Sciences Division, Mines Branch, Ottawa.

The results of the analyses indicate that the ratio of iron sulphide to silica, present either in silicates or as free quartz, in the Heath Steele tailings, is definitely larger than that in the tailings of the Hudson Bay Mining Company. The alkali and magnesia contents appear to be of the same order of magnitude so that any other significant difference might be caused by the alumina and the lime contents in the Heath Steele tailings being lower than those of the tailings from the Hudson Bay Mining Company.

It is possible that more CO_2 is present in the tailings from Heath Steele Mine than is reported in the analysis. No pyrrhotite was detected in the X-ray diffraction powder pattern, therefore, the Fe not present as pyrite may occur as a carbonate. The weight loss indicated by a thermogravimetric analysis of a tailings sample heated to 600°C accounted for about half the sulphur content, the amount that pyrite would lose by converting to pyrrhotite, plus approximately 7%, which might be attributed to a CO_2 content higher than is reported in Table 3.

3.2.2. Experimental Conditions and Procedures

An amount of the sample, sufficient for the charges of eight percolators was dried at 85°C for 48 hr, i.e., low enough to prevent the water in the sample from boiling. Samples were then weighed and sterilized in their extraction thimbles at 140°C for another 48 hr. The samples that had to be placed in the "column" extractors were sterilized in beakers covered with watch glasses.

An amount of sample, sufficient for the charge of two percolators, that would be inoculated with bacteria was dried at 45°C for 66 hr. A problem in the study of the effect of microbial action is the possibility that a slight change in the composition of the tailings, after being heated to 140°C, may alter the living conditions for the micro-organisms in the tailings drastically, while the nature of the purely chemical action might be less affected by this heat treatment. The comparatively low temperature of 45°C, however, might be too low for sterilization.

The percolators were filled with double-distilled water adjusted to pH 4 with H_2SO_4. The percolators were then charged as follows:

Percolator No. 1 - Blank, no ion-exchange resin; 2000 ml water, pH 4.00.

Percolator No. 2 - Blank, ion-exchange column filled with Amberlite IR 120, 2000 ml water, pH 4.00.

Percolator No. 3 - 100 g Heath Steele tailings (dried at 45°C); 2000 ml water, pH 4.00.

Percolator No. 4 - 100 g Heath Steele tailings (dried at 45°C); 2000 ml water, pH 4.00, containing 25 ml water from the tailings creek of a gold mine in N. W. Quebec*.

Soxhlet extractors containing 33 x 95-mm cellulose Whatman extraction thimbles were used in percolators No. 1 to No. 4.

Percolator No. 5 - 200 g Heath Steele tailings; 2000 ml water, pH 4.00.

Percolator No. 6 - 100 g Heath Steele tailings mixed with 100 g Baker and Adamson's sea sand; 2000 ml water, pH 4.00.

Percolator No. 7 - 75 g Heath Steele tailings mixed with 75 g Fisher's laboratory-grade kaolin; 2000 ml water, pH 4.00.

Percolator No. 8 - 100 g Heath Steele tailings mixed with 50 g sea sand and 50 g kaolin; 2000 ml water, pH 4.00.

The samples in percolators No. 5 to No. 8 were contained in 43 x 123-mm cellulose Whatman extraction thimbles.

Percolator No. 9 - 10 g Heath Steele tailings mixed with 450 g sea sand; 3000 ml water, pH 4.00.

Percolator No.10 - 100 g Heath Steele tailings mixed with 350 g sand; 3000 ml water, pH 4.00.

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*Water of the creek draining from the tailings pond of a gold mine in N. W. Quebec was used for inoculation. It was selected randomly out of a number of similar waters collected from tailings ponds of fourteen different mining companies in N.E. Ontario and N. W. Quebec during the summer of 1971. Because the water had a pH 3.00, it was assumed that it would contain thiobacilli. Microbiological tests after the runs had been started indicated that this assumption was incorrect, because the principal species in the inoculum had been ferrobacillus ferro-oxidans. This organism does not decompose sulphur compounds but grows on the energy involved in the oxidation of iron.

Percolator No. 11 - 10 g FeS* mixed with 450 g sea sand; 3000 ml water, pH 4.00.

Percolator No. 12 - 10 g FeS mixed with 450 g sea sand; 3000 ml water, pH 4.00 containing 25 ml water from the tailings creek of a gold mine in N. W. Quebec.

The purpose of the series of experiments was to obtain the following preliminary information about the effects of the foregoing sets of conditions on the three variables pH, Eh, and conductivity (see footnote).

a) The effect of differences in the exposed surface area of the minerals in the tailings due to solution with sand.

Sample No. 3 - 100 g tailings, i.e., 100 % tailings.

Sample No. 6 - 100 g tailings plus 100 g sand, i.e., 50% tailings.

Sample No. 10 - 100 g tailings plus 350 g sand, i.e., 22% tailings.

Sample No. 9 - 10 g tailings plus 450 g sand, i.e., 2.2% tailings.

The average grain size of the sand was approximately 200 µm. A microscope examination of the tailings indicated that its grain size varied considerably, from approximately 15 µm down to very fine grains. There is thus a considerable difference in grain size between the tailings and the sand. It could, therefore, be expected that dilution with sand would increase the surface area of the tailings available for dissolution. Furthermore, the grain sizes in the tailings may be preferentially distributed among the various minerals, because quartz, opaque minerals (sulphides), and some calcite

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*The FeS was produced by heating a mixture of the appropriate amounts of iron powder and sulphur in a glass tube. An X-ray diffraction powder pattern of this material indicated that it consisted principally of pyrrhotite ($Fe_{1-x}S$), and that it contained only a very small amount of pyrite and possibly magnetite.

NOTE: In the following part of this report the word "sample" refers to the mineral mixture in a percolator, and the word "water sample" to a sample of water taken out of a percolator. The word "run" is a general term that refers to the conditions and processes taking place in a particular percolator. The numbers of the (water) samples and runs are indicative for the relevant percolators.

were present in large-size grains and other minerals appeared to be confined to small-size grains. However, a detailed examination of the mineralogical composition and the grain-size distribution of the major mineral components in the tailings has been started. It will supply the information required to assess the effect of grain-size distribution and the interaction between the principal minerals. The dilution of the sample No. 9 is not directly comparable to the dilution of the other samples because the tailings content in the mixture was decreased by 90%.

b) The effect of the difference in exposed surface area due to the total quantity of sample.

Sample No. 3 - 100 g tailings.

Sample No. 5 - 200 g tailings.

The comparison of these two charges could be only partly valid because of the difference in the drying procedure used during the sample preparation, as mentioned earlier (see pages 19-20).

c) The possible effect of the presence of kaolin. The kaolin was introduced because of the possibility that a significant amount of clay minerals might be present in the tailings (see page 13).

Sample No. 6 - 100 g tailings, 100 g sand, i.e., additive of 100% sand.

Sample No. 8 - 100 g tailings, 50 g sand, 50 g kaolin, i.e., additive 50% sand, 50% kaolin.

Sample No. 7 - 75 g tailings, 75 g kaolin, i.e., additive of 100% kaolin.

The dilution of the sample No. 7 is not directly comparable with the dilution of the other two samples because the total quantity of tailings was different.

d) The effect of the difference between the tailings sample, consisting of iron sulphide (pyrite) and gangue, and synthetic iron sulphide only.

Sample No. 9 - 10 g tailings in 450 g sand.

Sample No. 11 - 10 g FeS in 450 g sand.

In this comparison, it was assumed that differences in the exposed surface areas of the samples would be of about the same magnitude because of the great dilution with sand. However, a significant difference may exist between the solubility of pyrite and pyrrhotite ($Fe_{1-x}S$) in the tailings; therefore the comparison may not indicate the action of the gangue minerals in the tailings.

e) The effect of microbial action on the tailings.

Sample No. 3 - 100 g tailings.
Sample No. 4 - 100 g tailings; "inoculated" with bacteria.

The tailings themselves might contain bacteria after treatment at 45°C; therefore only the difference due to the added inoculum would be indicated. The problem of a possible change in the composition of the tailings during heating has been mentioned previously.

f) The effect of microbial action on synthetic iron sulphide.

Sample No. 11 - 10 g FeS in 450 g sand.
Sample No. 12 - 10 g FeS in 450 g sand; "inoculated" with bacteria.

3.2.3. Results of Experiment No. 2

3.2.3.1. Conductivity Measurements

Since the conductivity of a water sample would be indicative of the total ionic concentration in the sample, the results of the measurements could be considered to represent the total amount of ionic matter that had dissolved out of the tailings. Although the foregoing is not strictly valid because of the differences between the mobilities of the various ions, a comparison would serve a useful purpose at this stage of the study and would certainly indicate when matter had stopped dissolving.

In this section, a comparison will be made between the conductivities of samples tapped from the percolators during the run, as outlined in Section 3.2.2.

a) In Figure 4* the conductivities of water samples Nos. 3, 6, 10 and 9 are compared. The results indicate the effect of the available surface area, and show that it is impossible to ignore the differences between the total amounts of sample present. Sample No. 9 contained only one tenth of the amount of tailings that was present in the other percolators, and the conductivity of the water sample from that run was clearly an order of magnitude less than the conductivities of the water samples from the other runs. The curves drawn in Figure 4 indicate, however, that the increasing effective surface area in the samples Nos. 3, 6, and 10, due to dilution with sand, also increased the amount of material that dissolved during the first few days. Later in the run, however, the effect of this variable changed. The indication that sample No. 6 dissolved less than No. 3 might originate in the difference in the sample preparation. A test for the possible presence of bacteria that might cause the difference was negative.

The deviations in the daily determinations from the lines do have meaning and will be discussed later. They should not be attributed only to instrumental errors.

The conductivities of the water samples from the blank runs Nos. 1 (-) and 2 (I), as shown in Figure 4, indicate that the introduction of the ion-exchange resin increased the conductivity slightly but sufficiently that a very small amount of material appears to dissolve out of the resin.

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*NOTE: In Figure 4, as well as in all the following figures, the lines were drawn on the plots for each sample separately in order to get the best "fit". The lines were then superimposed. The figures were plotted by W.S. Bowman, Technical Officer, Physical Chemistry Group, Mineral Sciences Division, using the Mines Branch computer.

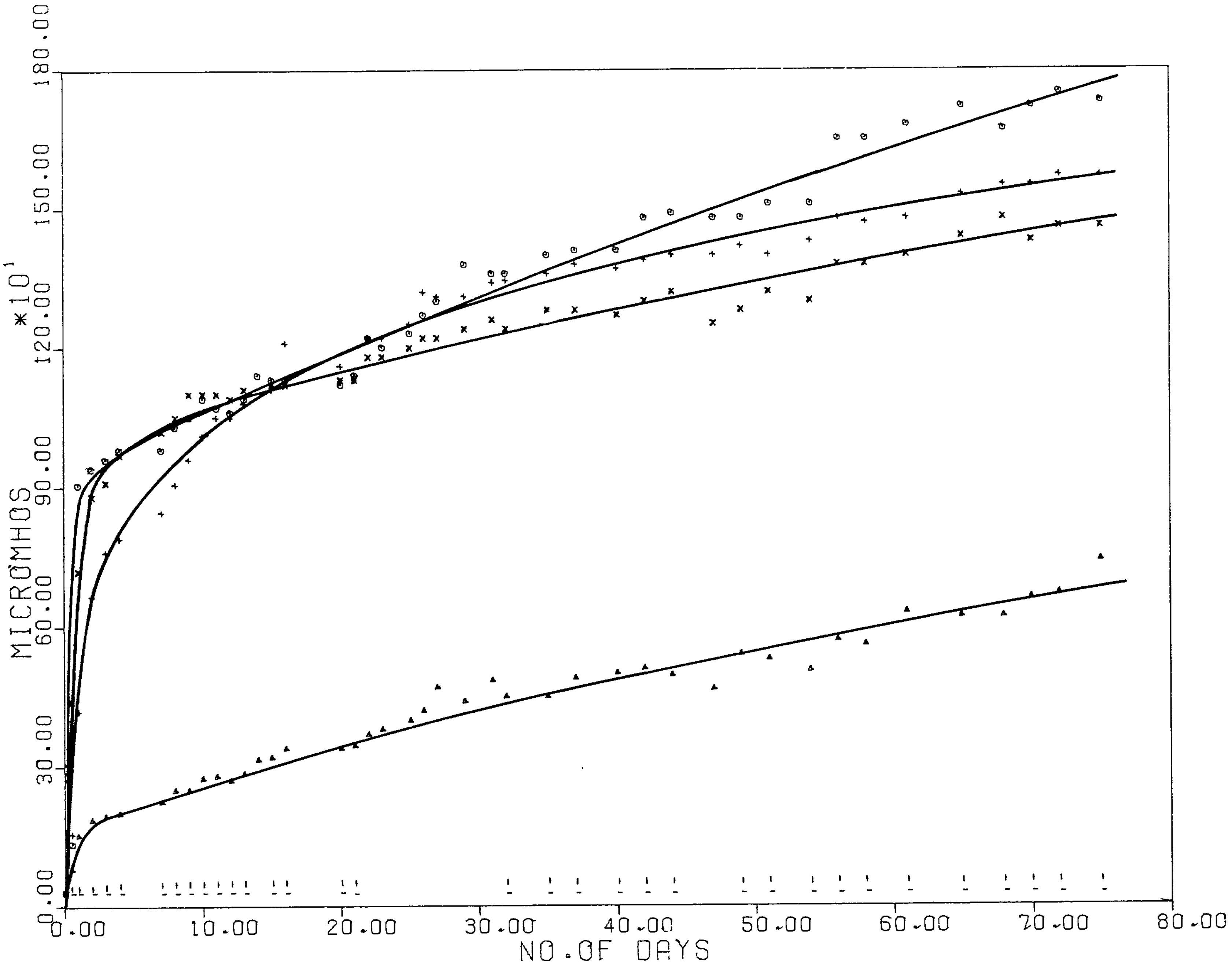


Figure 4. Conductivities of water samples from runs in which the tailings were increasingly diluted with sand.
+ Run No. 3, 100 g tailings. o Run No. 10, 100 g tailings + 350 g sand. - Run No. 1, blank.
x Run No. 6, 100 g tailings + 100 g sand. Δ Run No. 9, 10 g tailings + 450 g sand. ╵ Run No. 2, blank + Amberlite.

b) The comparison between the conductivities of water samples Nos. 3 and 5, as shown in Figure 5, indicates clearly that the amount of material dissolving out of the tailings depends on the total quantity of tailings available. The curve of the conductivity of sample No. 5 is in two parts because approximately 350 ml of the water was lost after 30 days due to an experiment with the apparatus. After diluting the water to its original 2000-ml volume, the final conductivity was still higher than in any of the other runs. If a portion of the water had not been lost, the upward trend of the original curve would probably have continued.

c) The comparison between the conductivities of water samples Nos. 6, 8, and 7, indicating the effect of kaolin on the solution, is shown in Figure 6. This figure indicates that the presence of kaolin decreased the amount of material going into solution during the first 10 to 15 days. It is probable that the initial effect is due to the ion-exchange properties of kaolin.

Later in the run, this trend changed. When the tailings sample had been diluted with kaolin, the rate of solution started to overtake that of the run on tailings that had been diluted with sand. In addition, only 75 g tailings is present in sample No. 7 as compared with 100 g tailings in sample No. 6. It is possible that the kaolin itself started to dissolve slightly. This effect was increased in sample No. 8, which with its kaolin had been diluted with sand - kaolin having a grain size an order **of** magnitude smaller than that of the tailings.

d) The comparison between the conductivities of water samples Nos. 9 and 11, concerning the difference between the dissolution of the tailings and that of the artificial FeS, is presented in Figure 7. It can be seen that the tailings initially dissolved to a greater extent than did the FeS. This difference decreased gradually after 25 days, when the commencement of a faint yellow colour of the water in run No. 11 could be observed.

In the beginning of the run, gangue minerals in the tailings might have dissolved quickly, but later in the run, the iron compounds might have dissolved more quickly because the curve of the conductivities of the

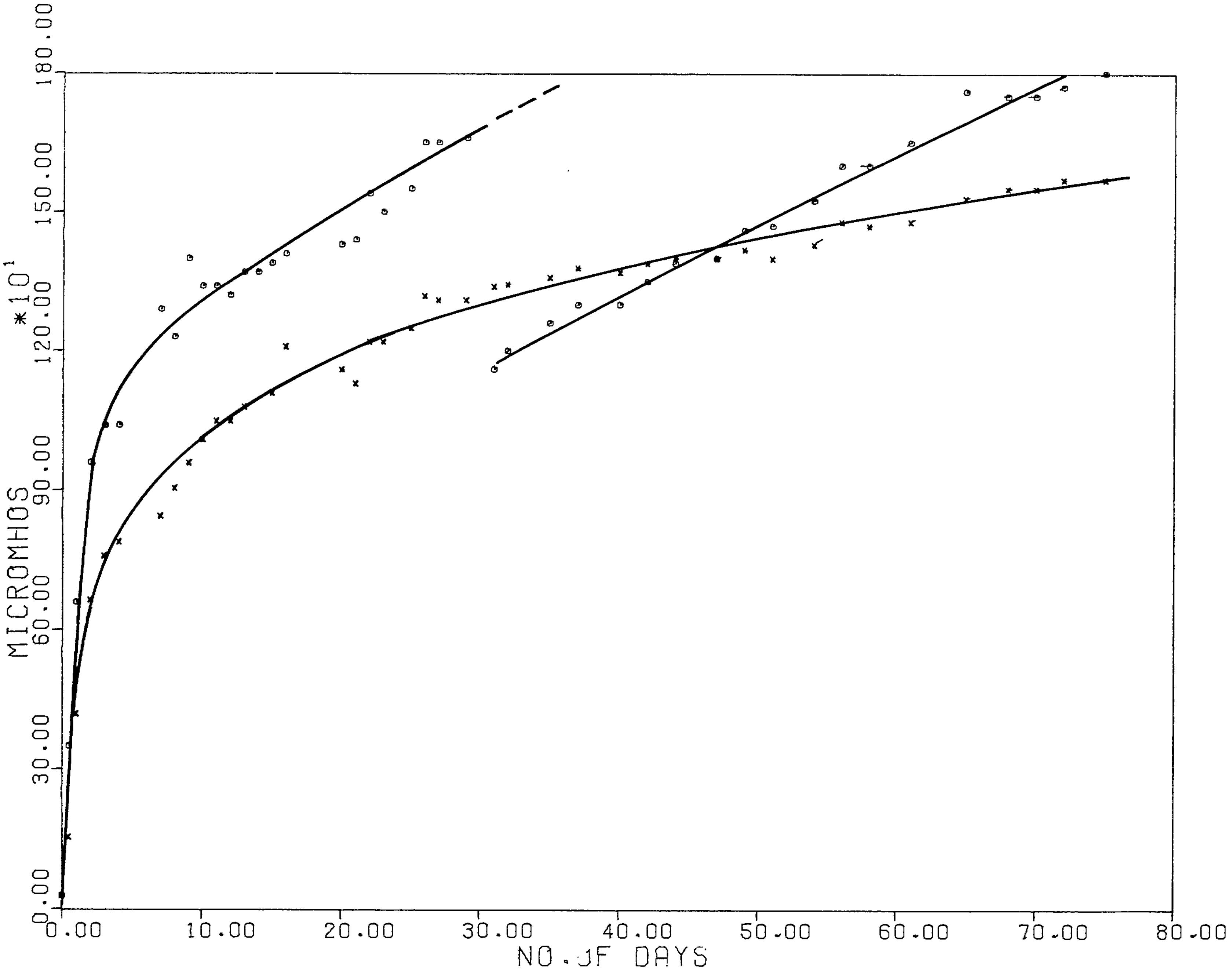


Figure 5. Conductivities of water samples from runs containing different quantities of tailings.
x Run No. 3, 100 g tailings.
o Run No. 5, 200 g tailings.

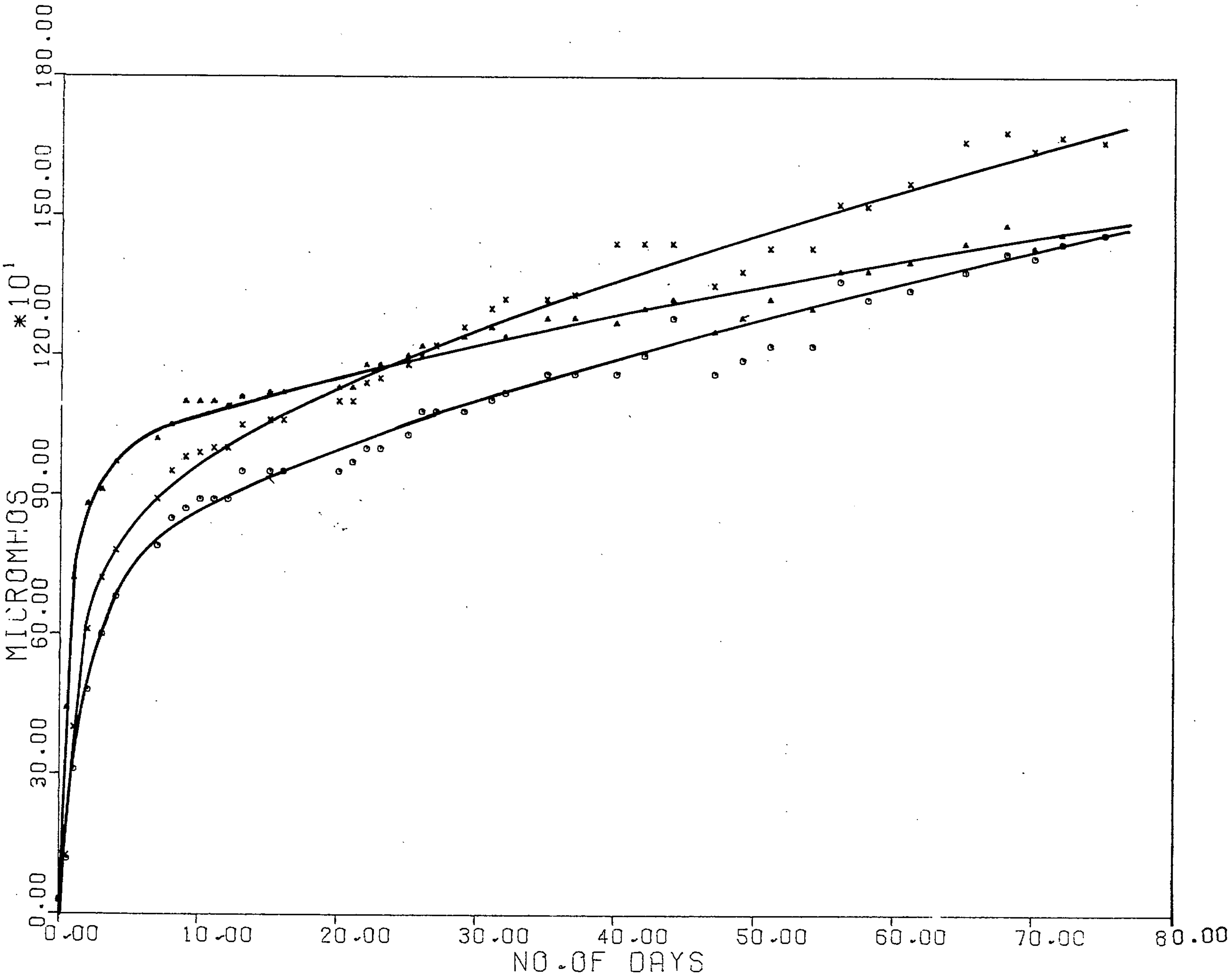


Figure 6. Conductivities of water samples from runs in which kaolin was increased by substituting it for quartz.
Δ Run No. 6, 100 g tailings + 100 g sand.
o Run No. 7, 75 g tailings + 75 g kaolin.
x Run No. 8, 100 g tailings + 50 g sand + 50 g kaolin.

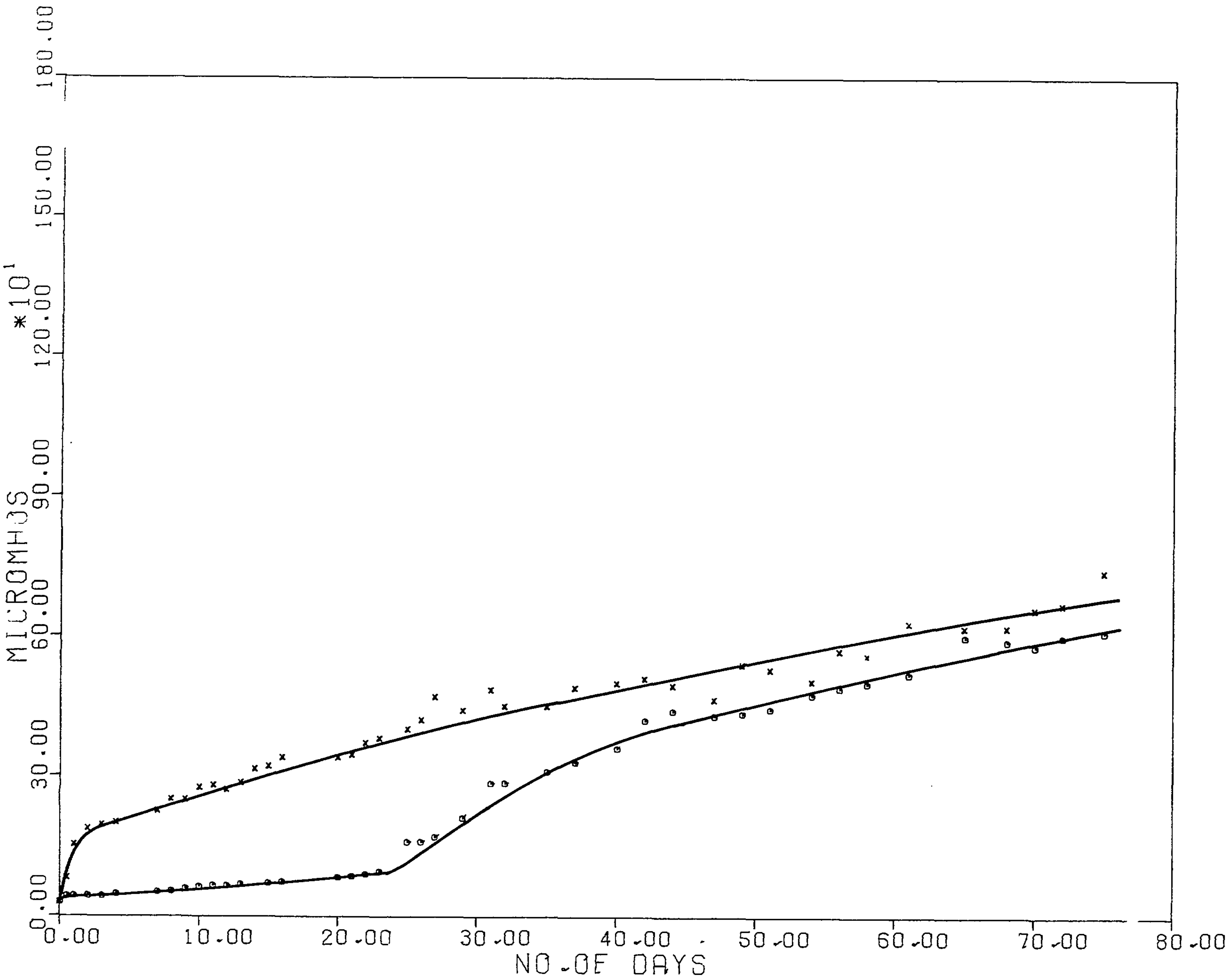


Figure 7. Conductivities of water samples from runs that compared the dissolution of iron sulphide with that of the tailings.
x Run No. 9, 10 g tailings + 450 g sand.
o Run No. 11, 10 g FeS + 450 g sand.

water samples from run No. 11 approached that of run No. 9 in which only iron sulphide was present.

Because several interacting variables are involved in the experiments, any explanation of the observations during these preliminary observations is tentative, and no attempt is made to offer a hypothesis for the presence of the discontinuity in the conductivity curve of run No. 11. A few examples of variables will be given later in the report.

e)-f) The effect of bacterial activity is indicated to a certain extent in the comparison between the conductivities of water samples Nos. 11 and 12, as is shown in Figure 8. In the same figure, the conductivities of water samples Nos. 3 and 4 are compared. In this latter case there is not much difference.

Although periodic tests on the activities of the bacteria were not done, the results of a few tests indicated that bacteria were still present after the first three days. Later during the run, bacteria still could be detected in run No. 12 but not in No. 4. Finally, at the end of the run, the bacterial population had decreased to the extent that tests remained negative.

If the microbial population be typical for various types of tailings ponds and creeks, it is possible that the bacteria in the inoculum acted initially on ferrous ions in run No. 12 and that the process producing the discontinuities in the curves of runs Nos. 11 and 12 was unfavourable to these bacteria. For instance, when the alkaline reaction of the gangue minerals in run No. 4 supersedes the acid reaction, an environment may be produced that is unfavourable for the bacterial activity of the inoculum, as indicated by the results of run No. 4. Because the process in run No. 12 is similar to that in run No. 11, no possible explanation can be given.

The foregoing assumptions about the changes in the living conditions of bacteria are described because they influenced the course of the studies. Although the evidence to support these assumptions is slight at the present stage, they do represent situations that could be expected to occur from

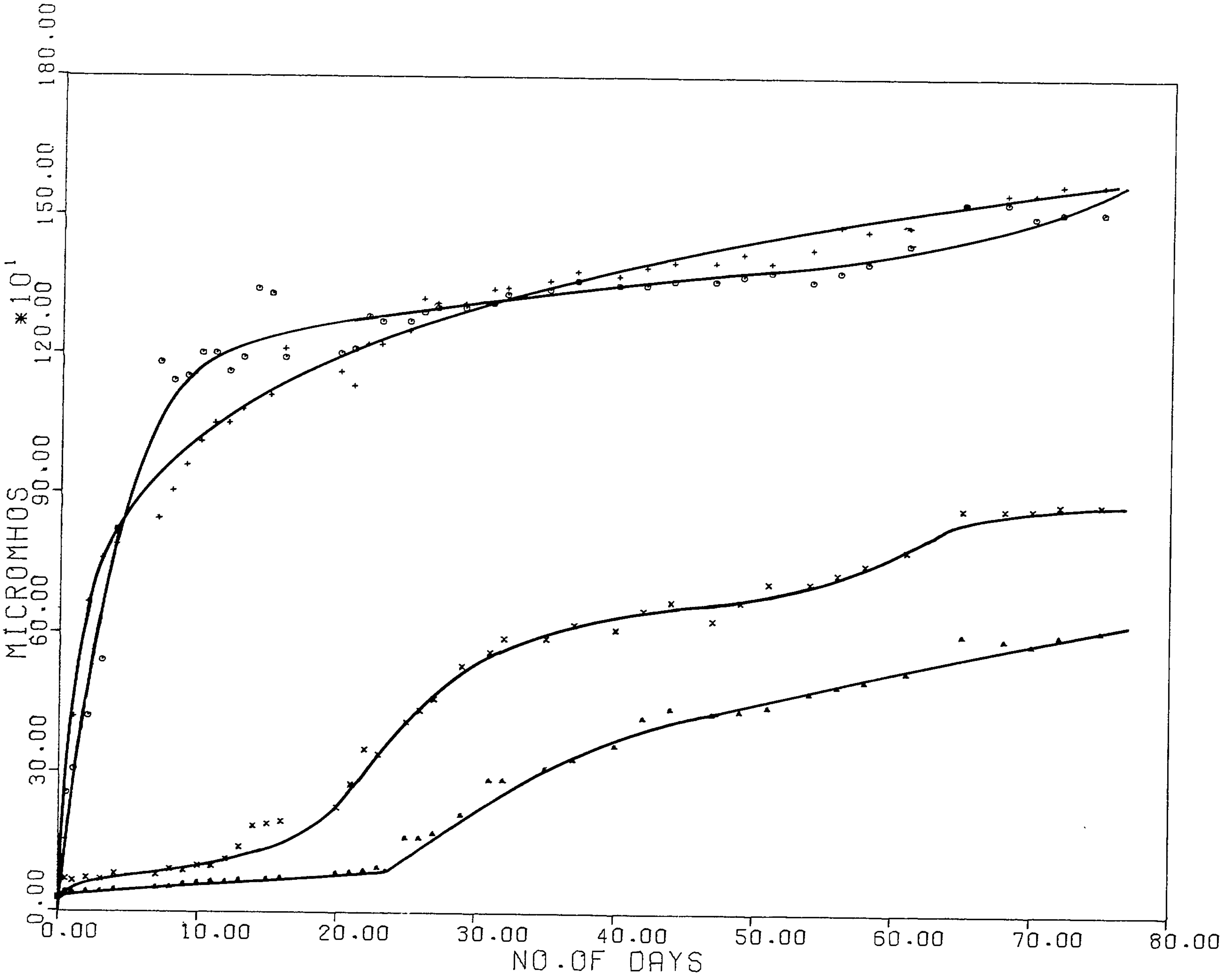


Figure 8. Conductivities of water samples from two pairs of runs that attempted to compare the effect of bacterial activity.
+ Run No. 3, 100 g tailings.
o Run No. 4, 100 g tailings + bacteria.
Δ Run No. 11, 10 g FeS + 450 g sand.
x Run No. 12, 10 g FeS + 450 g sand + bacteria.

a biological point of view; the consequences of adapting these assumptions affected the planning of future experiments favourably and possibly led to a more economical acquisition of information.

3.2.3.2. pH Measurements

Because of the practice of considering the possible effects of tailings effluents in terms of pH, in the sense that acidity should be avoided, comparisons among the pH's of the water samples will be made. In the following section, the same information will be combined with the results of the redox-potential measurements.

Figure 9 shows the variation of the pH of water samples Nos. 3, 6, 10, and 9. The pH in all of the runs tends to become alkaline during the first few days. After this reaction, another gradually renders the solution acid. This phenomenon is very markedly shown by the results of run No. 9; it is probable that the solution from run No. 10 would reach the same acidity after a period longer than the run. The pH's of the water samples Nos. 3 and 6, however, do not show this tendency, and it is possible that the plateau formed during the first 30 days in run No. 3 is prolonged in run No. 6.

A comparison involving sample No. 5, which remained basic, is not valid due to the partial loss of the solution after 30 days. Apart from the effect of the exposed surface area due to dilution of the sample with sand and its total quantity, the influence of sand itself should not be disregarded completely. Those factors, however, will be studied separately in future runs.

A comparison of the pH's of samples Nos. 6, 8, and 7, in which kaolin was substituted increasingly for sand, is shown in Figure 10. It is indicated that kaolin had a very marked influence on the pH, and the ion-exchange properties of the clay have been mentioned. As in all runs, it is unfortunate that no information is available on the daily variation of the chemical composition of the solutions, which might have supplied more details on the results shown in Figure 10.

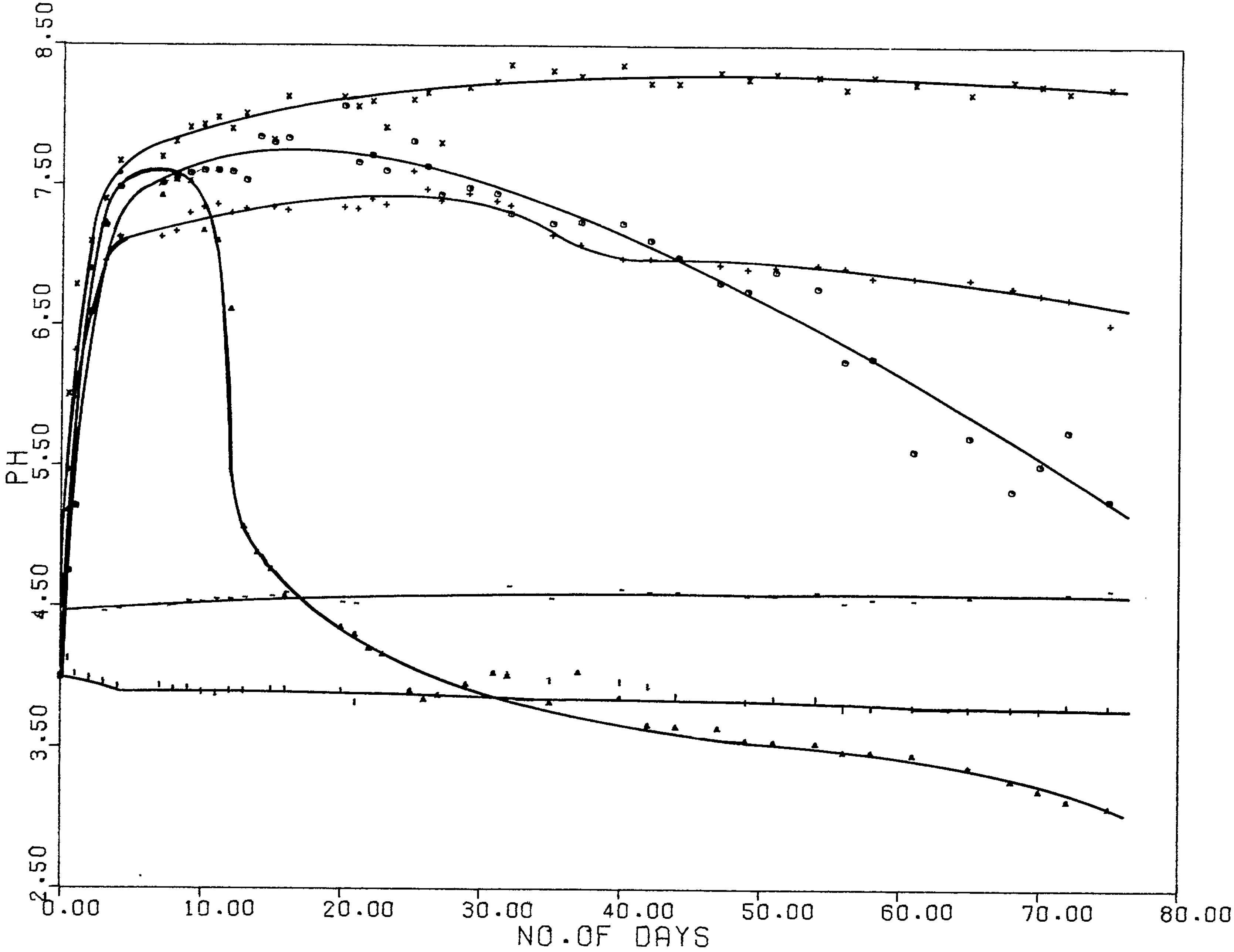


Figure 9. The pH of water samples from runs in which the tailings were increasingly diluted with sand.
+ Run No. 3, 100 g tailings. o Run No. 10, 100 g tailings + 350 g sand. - Run No. 1, blank.
x Run No. 6, 100 g tailings + 100 sand. Δ Run No. 9, 10 g tailings + 450 g sand. ǀ Run No. 2, blank + Amberlite.

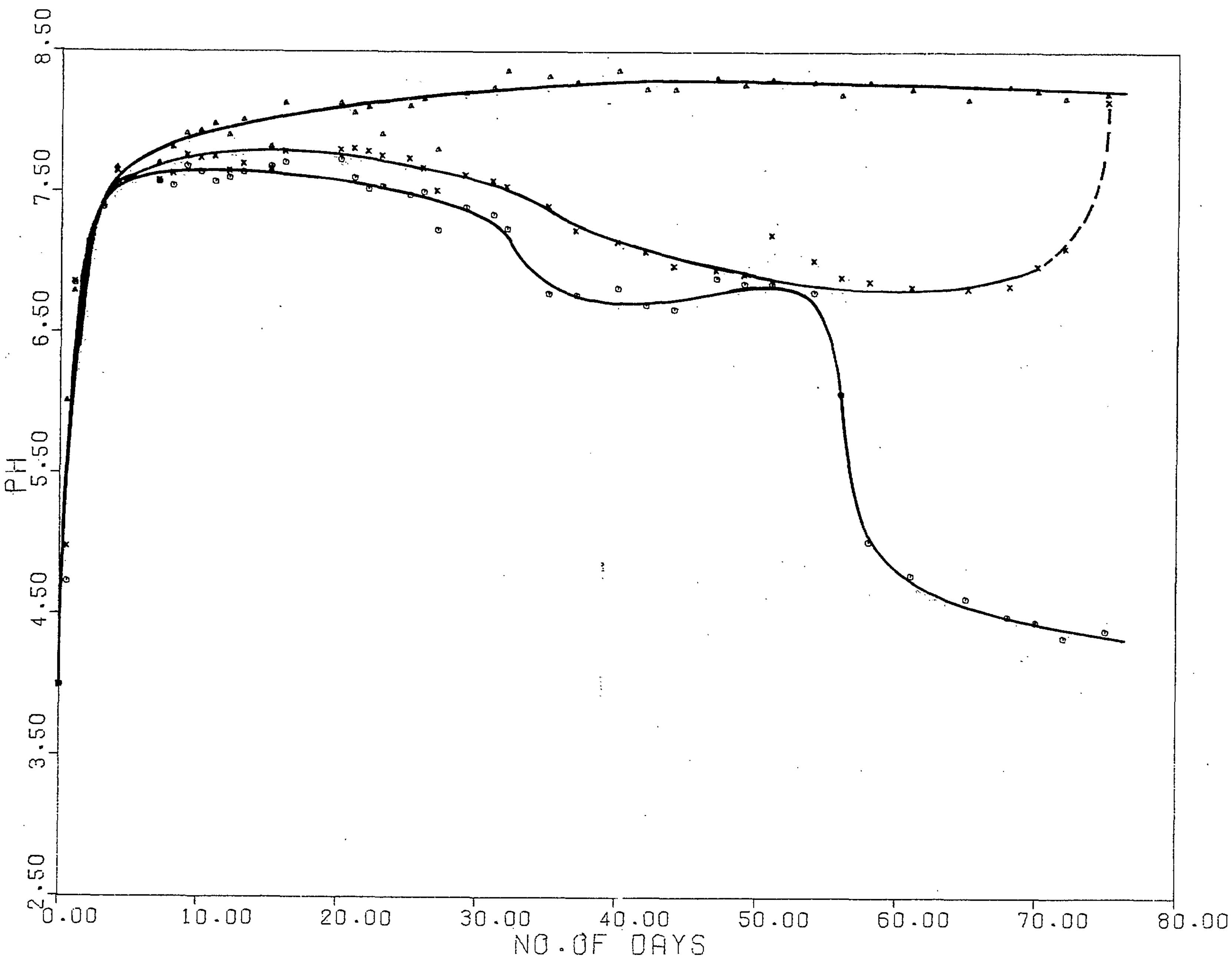


Figure 10. The pH of the water samples from runs in which kaolin was increasingly substituted for quartz.
Δ Run No. 6, 100 g tailings + 100 g sand. o Run No. 7, 75 g Tailings + 75 g kaolin.
x Run No. 8, 100 g tailings + 50 g sand + 50 g kaolin.

A comparison between the pH of the water samples Nos. 9 (tailings) and 11 (FeS) is shown in Figure 11. It indicates that the basic reaction, as observed in all samples containing tailings, is probably due to constituents other than iron sulphide and quartz because the difference in the shape of these curves can hardly be expected to originate in the difference between pyrite and pyrrhotite. However, in view of the difference observed in the conductivity curve of the same samples, shown in Figure 7, which indicated a discontinuity in the solution of iron sulphide, other variables than pH appear to be involved. These particular variables, among others, will form the subject of future experiments.

The influence of the bacterial action indicated in the runs Nos. 11 (FeS) and 12 (FeS + bacteria), is apparently not very marked, as is shown in Figure 12. The initial trend in the curve of run No. 12 to become more acid than run No. 11 may be significant.

The observation that water sample No. 3 became comparatively more acid than sample No. 4, inoculated with bacteria, is probably indicative of the possibility that alkalinity of the water prevented bacterial action. However, the apparent contradictions that, in addition, no bacteria could be detected in water sample No. 12, is one of the reasons why little indicative information on bacterial action was obtained during this experiment.

3.2.3.3. Eh-pH Relationships

The variation of the redox potential of the solutions is considered most conveniently in its relation to the pH of the solution. Notwithstanding that the Eh (redox potential) of a solution is a measure of the oxidizing or reducing tendency of the solution, it is fundamentally a factor in an electrical process with which the pH is intimately connected. The equilibrium concepts concerning the solution of minerals have been explained in detail by, among others, Garrels and Christ(7).

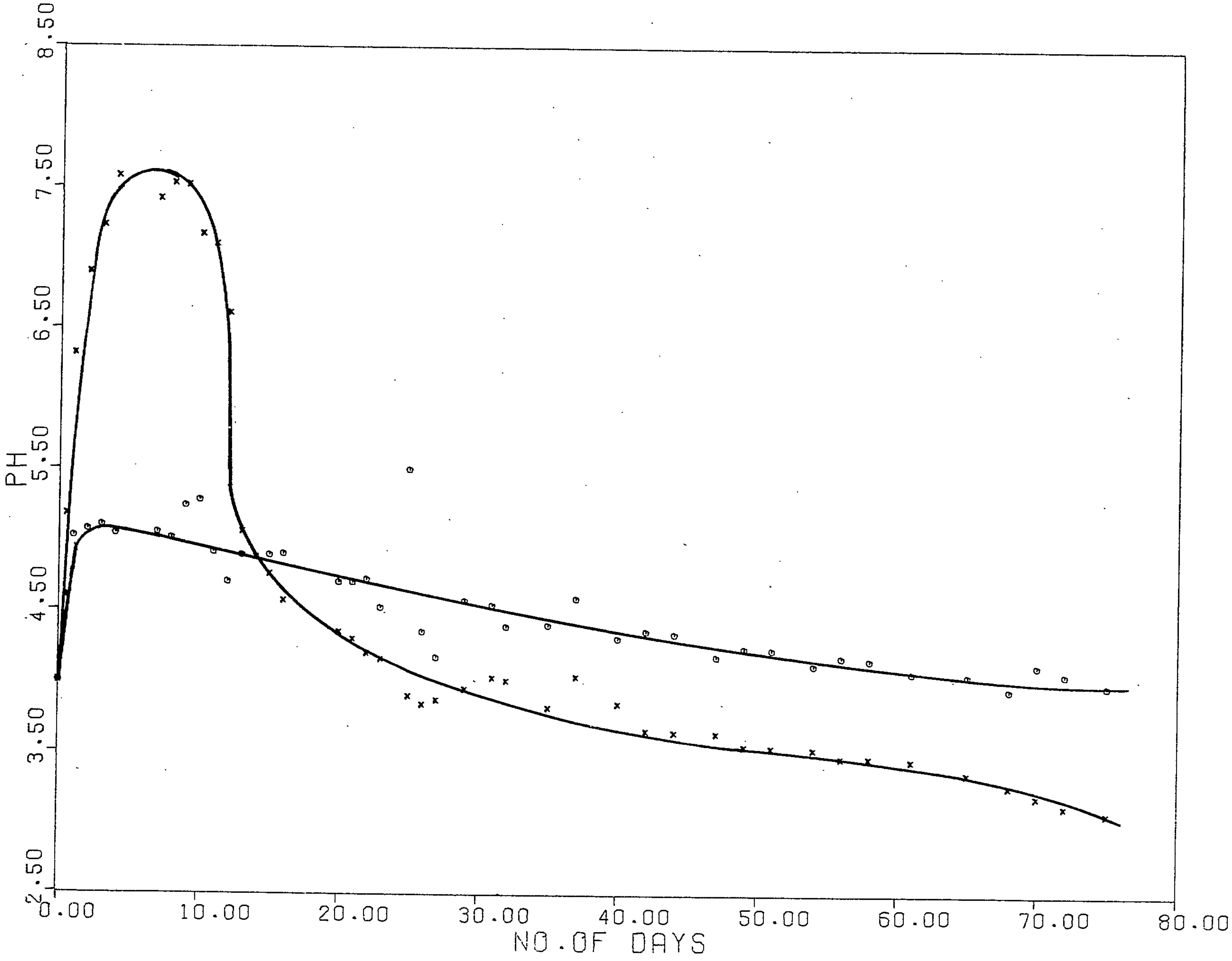


Figure 11. The pH of water samples from runs that compared the dissolution of iron sulphide with that of the tailings.
x Run No. 9, 10 g tailings + 450 g sand.
o Run No. 11, 10 g FeS + 450 g sand.

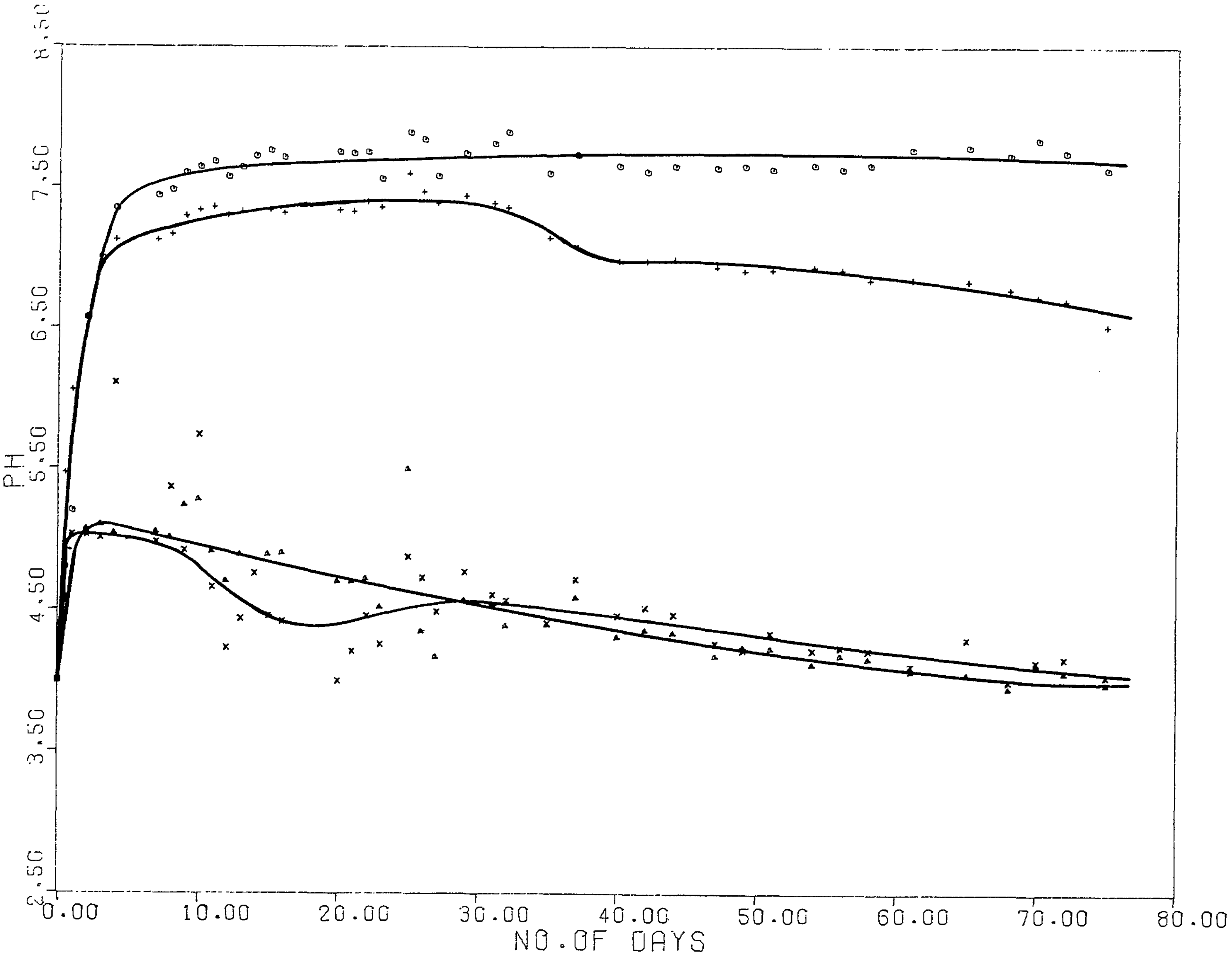


Figure 12. The pH of water samples from two pairs of runs that attempted to compare the effects of bacterial activity.

+ Run No. 3, 100 g tailings.	Δ Run No. 11, 10 g FeS + 450 g sand.
o Run No. 4, 100 g tailings + bacteria	x Run No. 12, 10 g FeS + 450 g sand + bacteria.

In Figure 13 several lines are drawn in an Eh-pH equilibrium diagram which may be relevant to some of the processes taking place in the solutions in the percolators. The line No. 1 is the theoretical limit of the existence of water, above which water starts to dissociate.

Iron sulphides are among the major constituents of the tailings, and the oxidation of iron sulphides is one of the processes taking place in tailings ponds. To illustrate trends in the Eh-pH values during the runs, the Eh-pH diagram was selected that indicates the stability relations between aqueous ferrous and ferric ions and ferric oxide and water. The limits of the stability field of a solid are, for geological purposes, drawn where the sum of the activities of the ions in equilibrium with the solids equals 10^{-6} mol/ℓ. This is done on the premise that a solid will behave as an inert immobile constituent in the environment when the above sum is less than 10^{-6}. This premise is based largely on experience.

Although ferrous and ferric hydroxides are formed as initial phases of the oxidation process in the experimental runs, they can be considered as metastable phases in a tailings pond where, above the waterline, the formation of ferric oxide can eventually be expected. Other factors in this arbitrary selection of ferric oxide are the uncertainty about (a), the presence, composition, and stability of the hydrated oxides intermediate between ferric hydroxide and ferric oxide, (b), their concentrations, and (c), principally the preference to adhere to the keynote of this report described in the introduction that assumptions should be avoided, that may be premature in view of the fact that the stability relations of a multi-component system cannot be represented by those of one type of compound — the iron (hydro-) oxides.

Line 2 in Figure 13 represents the Eh-pH conditions for the transition of aqueous ferrous ions to ferric oxide and vice versa, and line 3 limits the field of existence of aqueous ferric ions. The stability field of Fe_2O_3 is thus on the right side of that of aqueous ferrous ions and is limited by lines 1, 2, and 3 (in part). It is not labelled because of the presence of the lines 4-8.

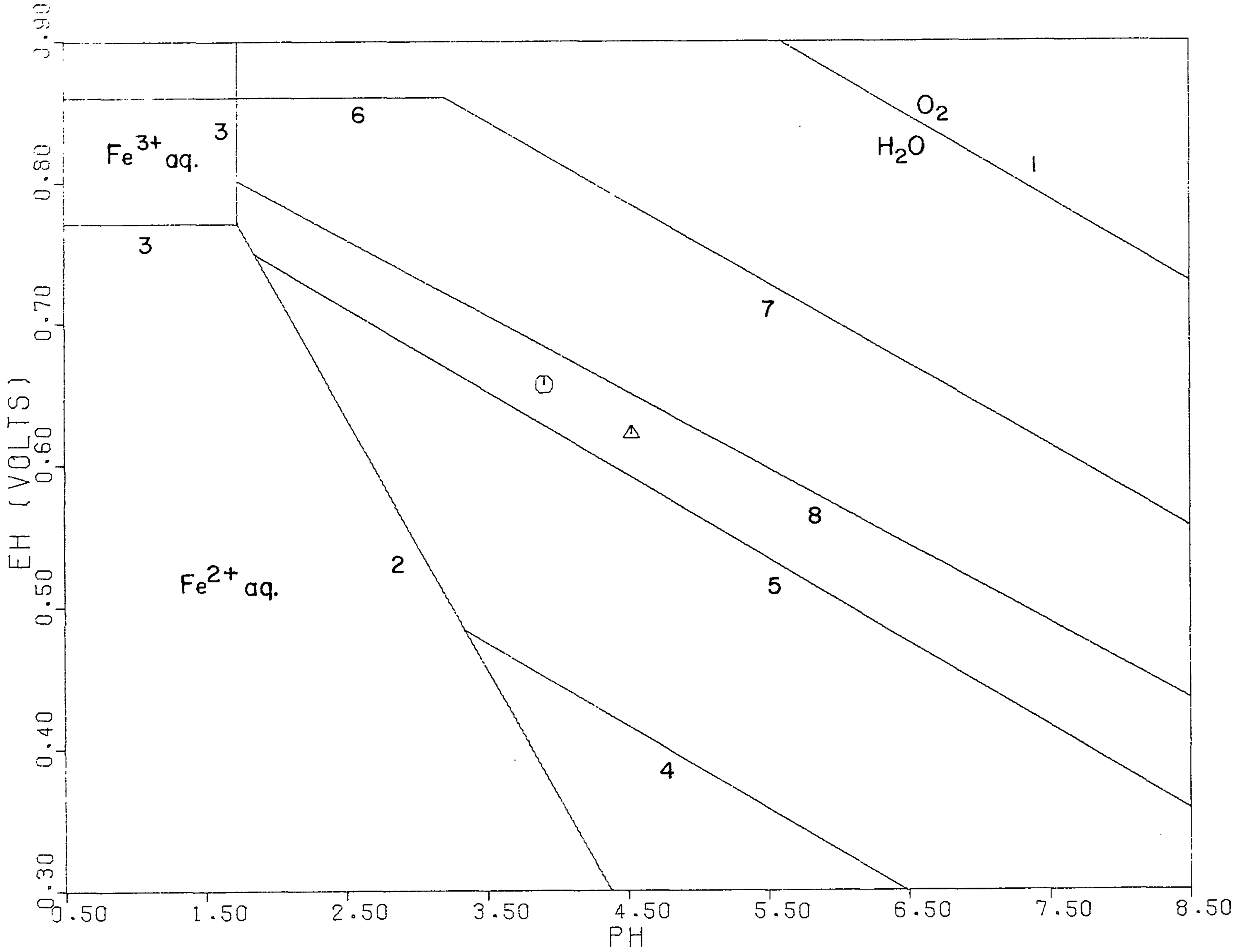


Figure 13. Boundaries of Eh-pH equilibria that may be relevant, to a certain extent, to some of the weathering processes of tailings. For reference numbers, see text.

Since Eh-pH values measured in natural waters apparently never reach the theoretical limit of the existence of water (line 1), two lines, No. 4 and No. 5, are drawn in Figure 13 which are a result of discussions by Sato(8) concerning the processes occurring in the natural waters of various mining districts. The Eh-pH values for an oxygenated water environment lie, according to his findings, in a relatively narrow zone above the potential of a gas couple in which hydrogen peroxide may be involved as a transient phase. This zone lies between lines No. 4 and No. 5.

Baas Becking et al(9) collected the Eh-pH values of a great number of natural waters and outlined the limits of the natural environment in these terms. Lines No. 6 and No. 7 are a part of the boundaries of the natural environment relevant to the values obtained in the present study.

Finally, line No. 8 represents the regression of Eh-pH values of natural waters collected during the summer of 1971 on and near a number of tailings ponds in N. E. Ontario and N. W. Quebec. The individual values of the measurements are shown in Figure 14. Because these values are scattered along a line higher than the upper limit given by Sato, it is assumed that the oxygen partial pressure in these waters increased in the direction from the actual weathering conditions at the bottom towards the air-water interface of the creek or pool.

In addition to the lines, two points are drawn in Figures 13 and 14, which represent the average of the Eh-pH values of both blank runs in the Experiment No. 2. It has already been shown that the variation in the pH of the blank water samples was much less than in that of the others. Similarly, the variation in Eh of the blanks, although greater than that of the pH, was considerably smaller than the variation in the runs containing the samples. The average Eh-pH value of water sample No. 1 is indicated as Δ and that of water sample No. 2 as o.

The Eh-pH values of the water samples Nos. 3, 6, 10, and 9 are shown in Figure 15. In these figures, the lines and the two points of Figure 13 are superimposed on the Eh-pH values measured in these water samples.

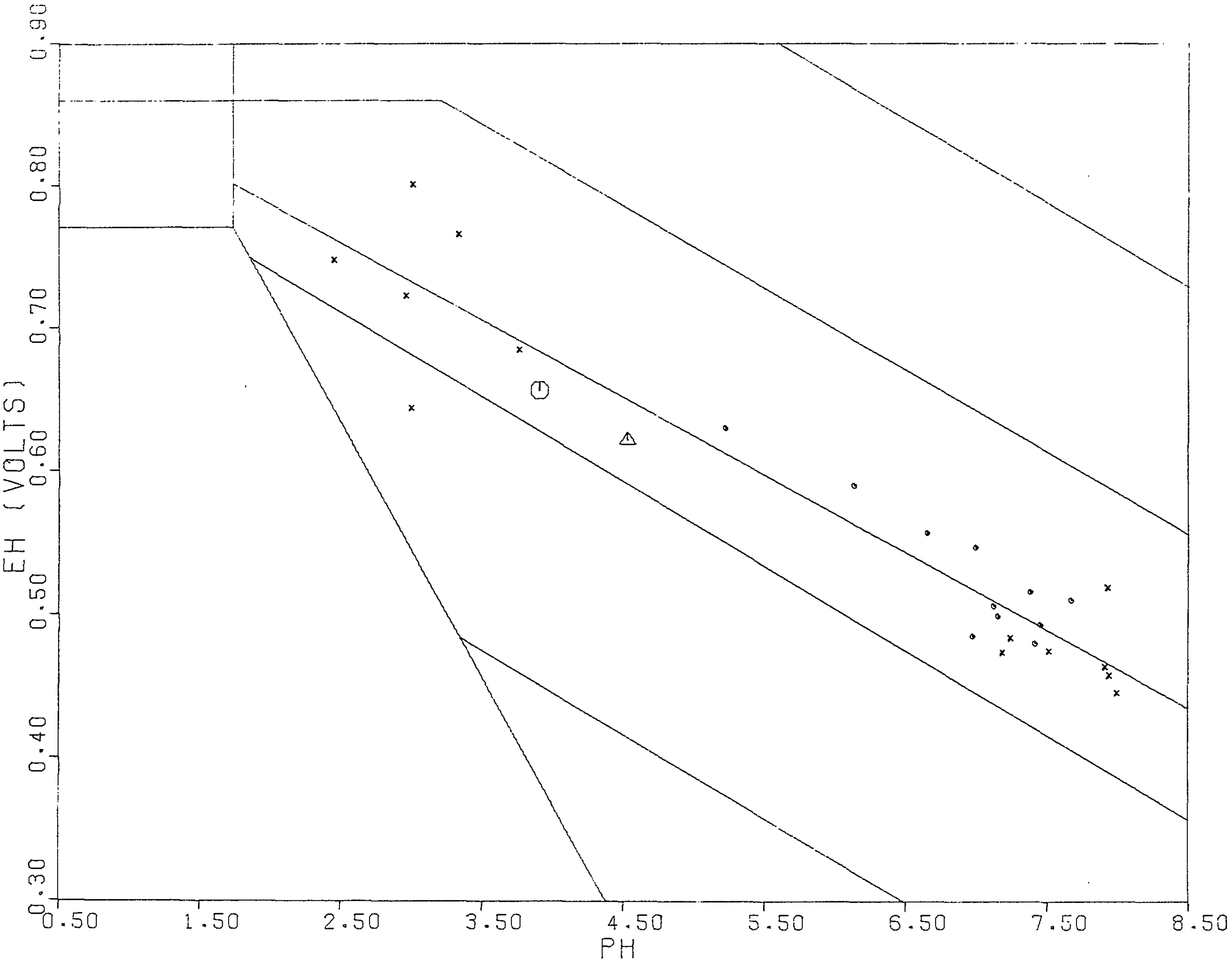
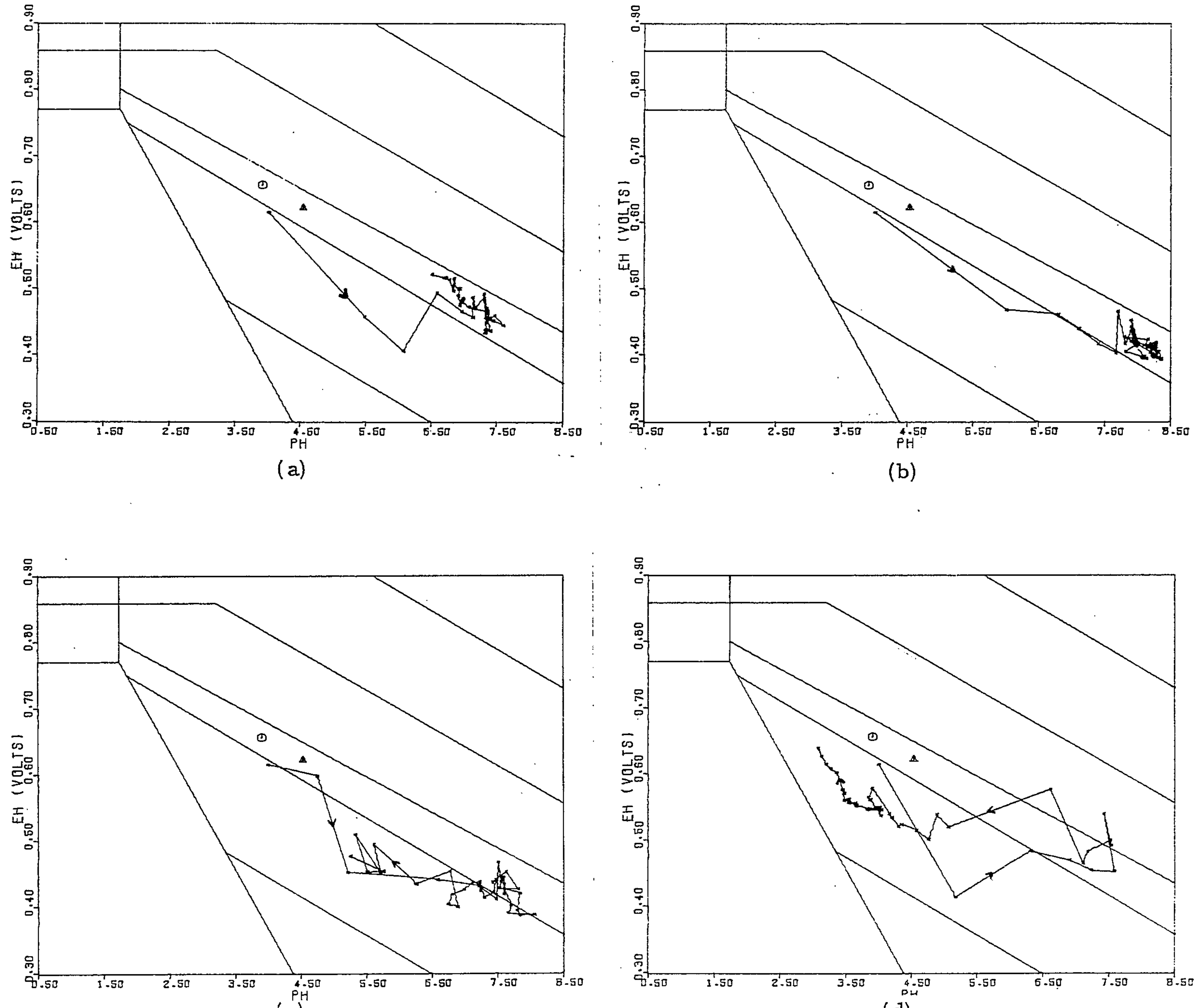


Figure 14. Eh-pH values of water samples collected from or near tailings ponds of mining operations in N. E. Ontario and N. W. Quebec.

x Waters definitely connected with mining operations (tailings ponds).
o Waters possibly connected with mining operations.



(a)

(b)

(c)

(d)

Figure 15. Eh-pH values of water samples from runs in which the tailings were increasingly diluted with sand.

a Run No. 3, 100 g tailings.

b Run No. 6, 100 g tailings + 100 g sand.

c Run No. 10, 100 g tailings + 350 g sand.

d Run No. 9, 10 g tailings + 450 g sand.

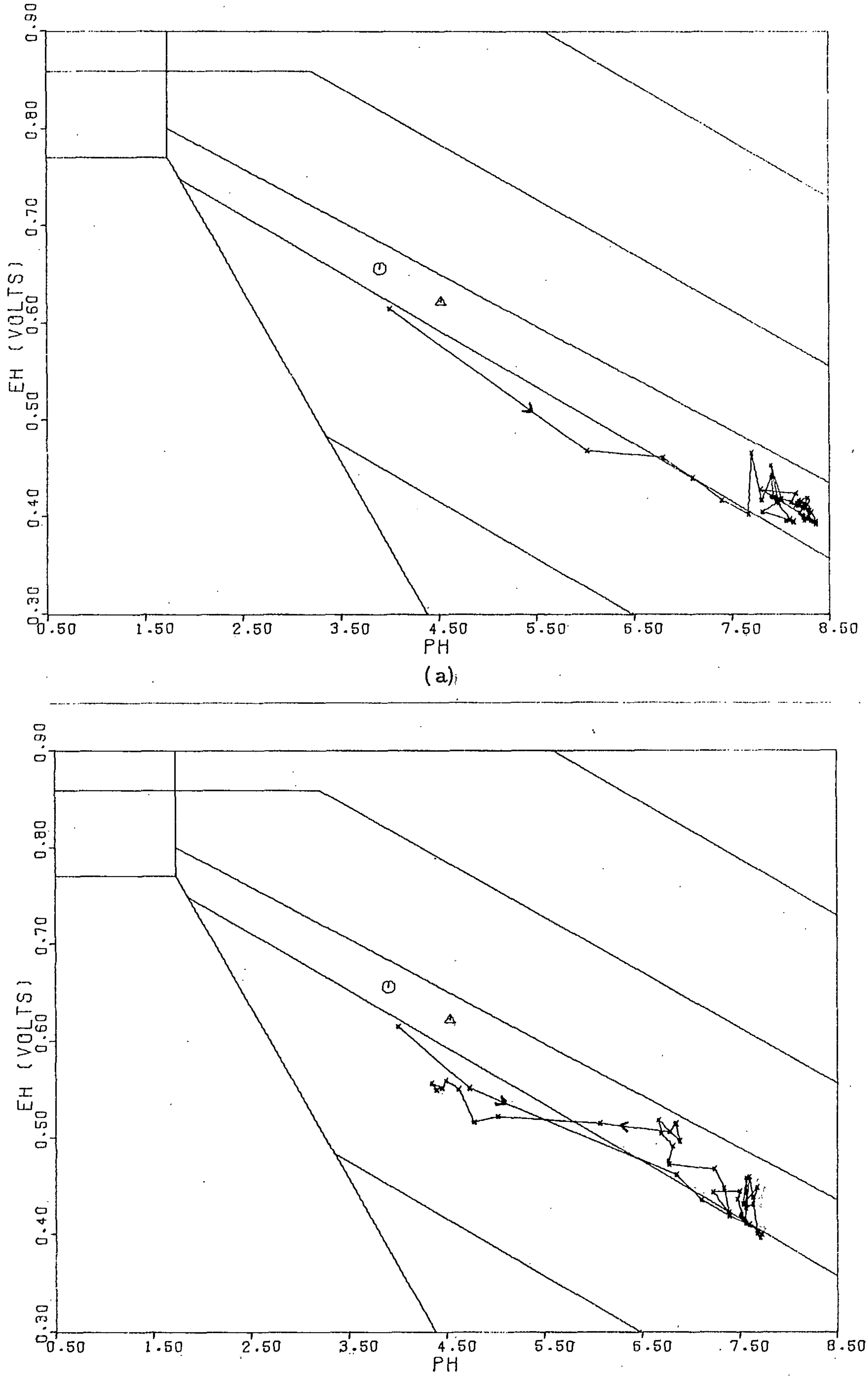
The measured values have been connected to indicate the variation in time as shown by the arrows. Both water samples No. 3 and No. 6 appear to move along the direction of Sato's upper limit (line 5, Figure 13) to reach an equilibrium near neutrality. A similar trend is shown by the values of water sample No. 10. However, during the latter part of the run, the values moved in the direction of the intersection of lines 2 and 4, which trend was shown to a greater extent by sample No. 9. During the latter part of the run, the Eh-pH values of sample No. 9 even followed a line parallel to line 2, which showed the principal reaction concerned to be the oxidation of ferrous ions.

A movement of the Eh-pH values parallel to Sato's line probably indicates a variation in the ferrous/ferric ratio which increases towards line 2. A movement of the Eh-pH values parallel to line 2 may indicate a variation in the oxygen partial pressure or an oxidation of ferrous ions and a simultaneous precipitation of ferric hydroxide. However, the more ferrous ions that are involved in the equilibrium, the more the system is complicated by the dissociation of sulphides and by the participation of sulphur compounds in the reactions. The position of the stability field of ferric hydroxide will be shown later in this report.

The temporary conclusion, however, is that the greater the exposed surface area of the grains in the tailings is, the more the oxidation from ferrous to ferric ions may be involved in the weathering process.

A comparison between the Eh-pH values of water samples Nos. 6, 8,and 7 again indicated that the process moves along line 5 to reach the basic part of the system.

Because the Eh-pH values of the water samples Nos. 6 and 8 had the same trend, only those of sample No. 6 are shown in Figure 16, where they are compared with the Eh-pH values of water sample No. 7. In the latter, the trend of returning in the direction of the ferrous ion field is indicated. Although sample No. 8 contained less kaolin than sample No. 7, it is quite possible that the effective surface area of the kaolin in sample No. 8 was larger than that in sample No. 7. In sample No. 7,the packing may have been



igure 16. Eh-pH values of water samples from runs in which kaolin was increasingly substituted for quartz. (a) Run No. 6, 100 g tailings + 100 g sand.
(b) Run No. 7, 75 g tailings + 75 g kaolin.

fairly dense as the grain sizes of both the tailings and of the kaolin were very small. Hence, the effective surface area of the kaolin in its mixture with sand in sample No. 8 may have been greater than the effective surface area in sample No. 7. Consequently, the ion-exchange capacity in sample No. 7 might have reached its limit sooner than in sample No. 8. However, in view of the continuity of the conductivity curves (Figure 6), this assumption is very tentative.

The difference in reaction between the tailings and FeS is shown in Figure 17, where the Eh-pH values of water samples Nos. 9 and 11 are compared. The values of water sample No. 11 (FeS), remain concentrated below the line 6 and move gradually towards the ferrous ion field. The Eh-pH values of water sample No. 9 (the tailings), move initially to the basic area above line No. 6 and, then, below line No. 6 towards the ferrous-ion field, so that only the initial trend is possibly different due to the presence of gangue minerals in the tailings.

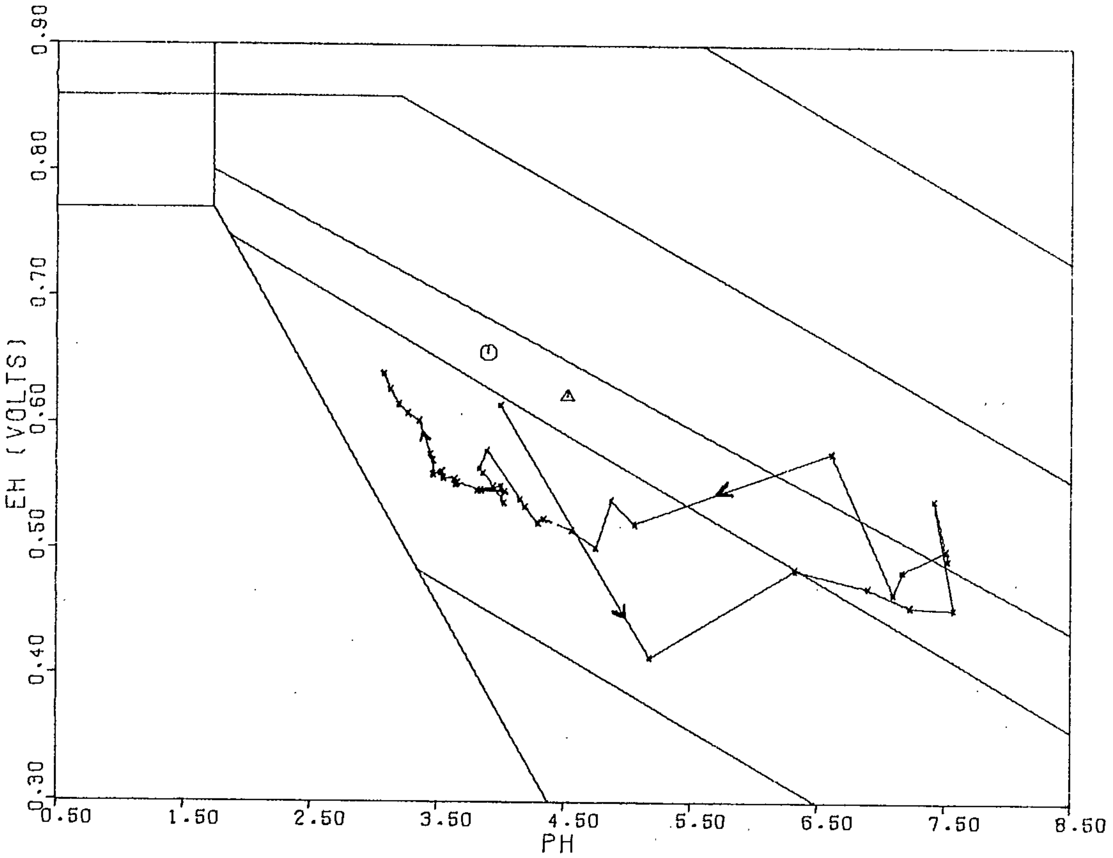
The differences between the Eh-pH values of both pairs of water samples No. 3 and No. 4, as well as No. 11 and No. 12, of which one of each pair was inoculated with bacteria, were not very marked. Hence, the comparison of the Eh-pH values of these water samples is not shown.

Finally, the positions of the aqueous ferrous- and ferric-ion field boundaries, in relation to the metastable ferric hydroxides, are shown in Figure 18 and they are compared with the position of the ferric oxide boundary used in the foregoing figures.

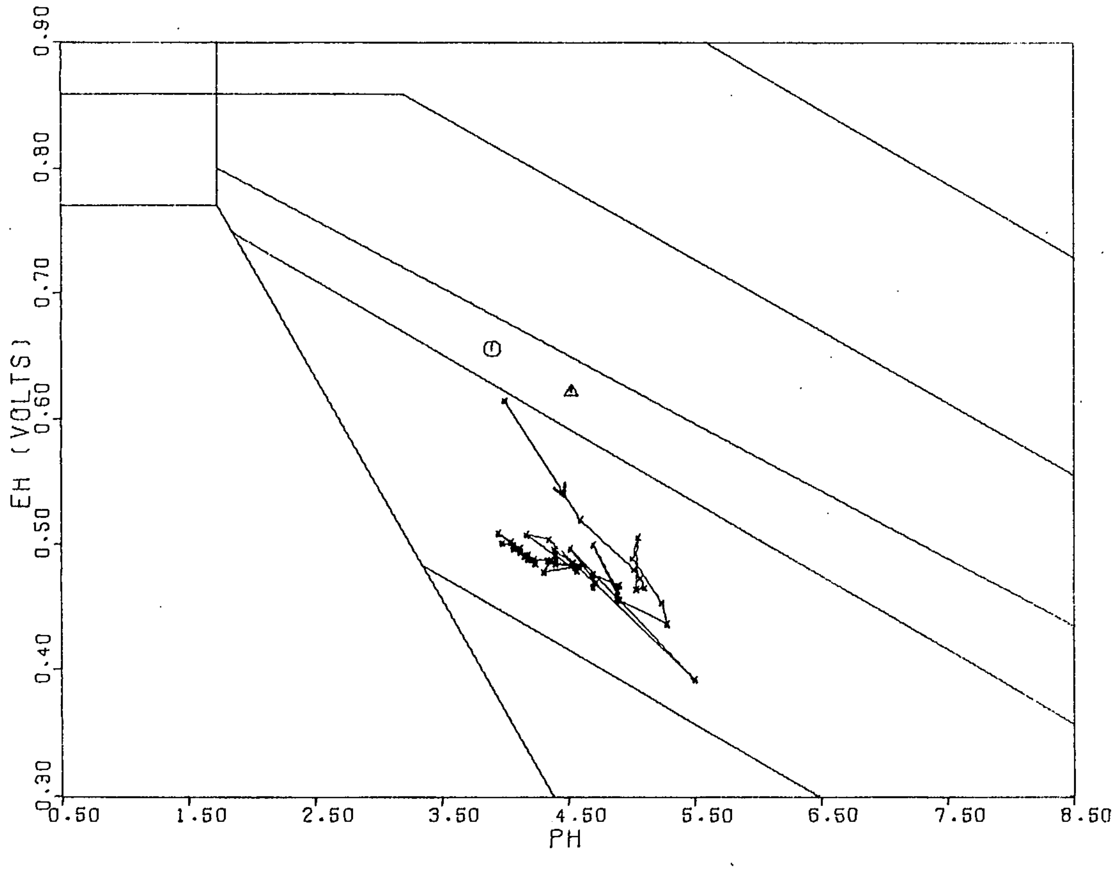
The Eh-pH values of water samples Nos. 7, 10, 9, and 11 that contain iron, as is described in the next section, are compared with each other in Figure 18.

The iron contents of the water samples appear to be related to the extent with which the lines have moved in the aqueous ferrous-ion field at the end of the experiment.

The complexity of the problem, however, is indicated by the facts that, in run No. 10, far more iron was dissolved and precipitated than in runs Nos. 9 and 11, and that, in run No. 7, no precipitate could be observed.

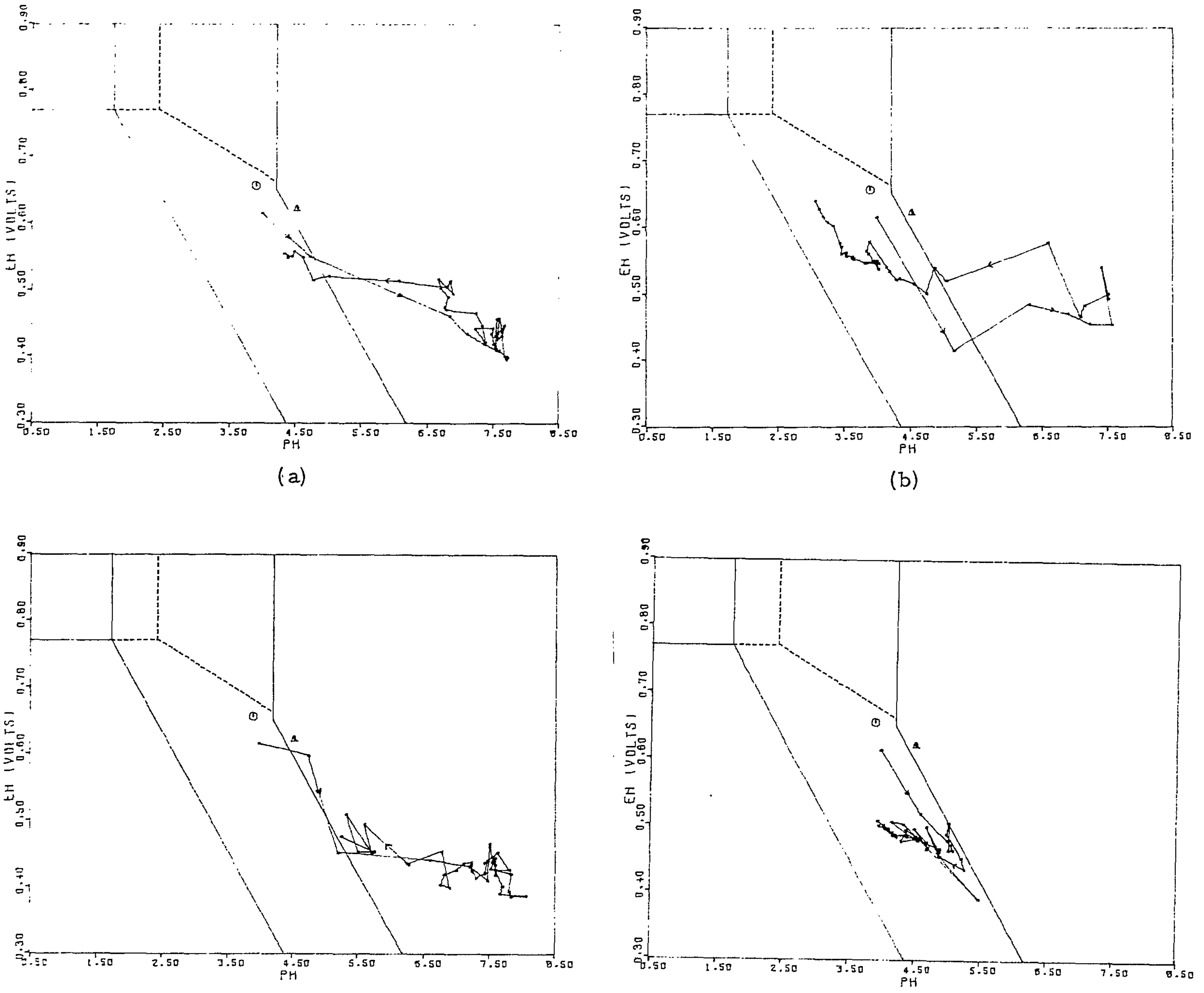


(a)



(b)

Figure 17. Eh-pH values of water samples from runs that compared the dissolution of iron sulphide with that of the tailings. (a) Run No. 9, 10 g tailings + 450 g sand. (b) Run No. 11, 10 g FeS + 450 g sand.



(a) (b) (c) (d)

Figure 18: Eh-pH values of water samples containing various quantities of iron at the end of the experiment.
(a) Run No. 7, 75 g tailings + 75 g kaolin. (b) Run No. 9, 10 g tailings + 450 g sand.
(c) Run No. 10, 100 g tailings + 350 g sand. (d) Run No. 11, 10 g FeS + 450g sand.

3.2.3.4. Chemical Analyses

Chemical analyses for a number of elements were planned to be done every day or on alternate days. The requirements for the chemical analytical methods include not only the determination of low metal contents, but also that these determinations be done on 1 to 2-ml samples, in view of the limited capacity of the percolating water and the duration of the runs. These requirements might only be met by the application of specialized instrumentation that is not yet available.

However, in order to obtain some information on the chemical composition and, possibly, on the trends in the changes of the chemical composition of the waters, 50-ml samples were taken after 36 and after 55 days. The results of the chemical analyses of the first batch of samples and of the samples taken at the end of the run (75 days) are listed in Table 4. The second batch of samples, taken after 55 days, was unfortunately never analysed. Although attempts were also made to determine the Al content of the waters, the analytical chemical method has not been developed sufficiently to produce results.

Although most elements appeared to have increased during the run, the Zn content in a few samples had apparently decreased. Because the results of the chemical analyses were not available shortly after the samples were taken, it remains uncertain how meaningful the analyses are. Did some elements precipitate during the run or upon standing? The conditions in the water change during standing in a way similar to natural waters becoming stagnant.

Precipitation of iron hydroxides had already taken place during the run in some of the percolators and it is not known whether the reported Fe contents refer to some precipitate that was sampled along with the water or to iron in solution. The precipitation of iron compounds unfortunately coincided with the difference in the experimental arrangement. In the percolators No. 3 to No. 8 in which Soxhlet extractor thimbles were used, no precipitate could be observed but, in the percolators No. 9 to No. 12 in

TABLE 4

Chemical Analysis of Waters in the Percolators

Element	Composition in ppm											
	Percolator Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Na	0.76	0.09	3.38	3.38	0.80	1.38	1.77	1.64	1.17	1.13	1.83	2.25
	0.76	-	3.41	3.69	1.72	2.35	1.86	2.04	1.33	1.27	1.75	2.21
K	0.32	0.06	3.58	3.40	0.36	0.28	0.80	0.50	0.90	0.67	0.54	1.91
	0.04	-	3.83	3.59	0.70	0.61	0.92	0.65	0.87	1.25	0.57	2.05
Ca	1.15	-	358	348	332	334	288	353	50	339	2.15	6.59
	1.15	-	390	378	503	361	342	428	44	405	2.33	3.28
Mg	0.09	0.01	48	44	39	42	40	45	10.5	63	0.37	1.45
	0.10	-	61	58	58	58	57	68	13.0	92	0.37	1.28
Si	0.51	0.97	0.85	0.78	1.47	1.33	1.91	2.45	6.45	0.78	0.70	3.14
	0.56	1.1	1.1	0.94	1.7	1.4	2.90	2.60	9.30	1.90	0.85	3.10
Fe	-	-	-	-	-	-	-	0.28	25	1.40	99	226
	-	-	-	-	-	-	3.55	-	33	6.42	212	343
Cu	-	-	-	-	-	-	-	-	0.66	-	-	-
	-	-	-	-	-	-	0.30	-	1.04	-	-	-
Zn	0.02	0.01	4.14	0.87	2.30	0.24	9.10	6.40	8.20	2.60	0.02	0.06
	0.02	-	8.26	0.23	1.31	0.19	20.1	9.92	9.76	17.9	0.02	0.03

NOTES: - = nil

The figures listed in the upper row for each element represent the composition after 36 days, and those in the lower row, that at the end of the run.

which glass wool was used to retain the samples, various amounts of precipitate could be observed. The first precipitate started to develop in percolator No. 10 after only a few days, then in No. 9 after 26 days, in No. 12 after 29 days and, finally, in No. 11 after 37 days. It is possible that iron hydroxides precipitated in percolators No. 3 to No. 8 immediately after solution and remained in the thimble while the glass wool did not retain these precipitates. It is also possible that the large amount of sand in percolators No. 9 to No. 12 and the subsequent acidity of the water is connected with the foregoing and that the filter arrangement is coincidental.

The results of the chemical analyses, however, indicated that the quantity of lime dissolved out of the tailings represents almost all that is present in the tailings. The form in which calcium is held in solution is obviously unknown. The analysis of the waters was not extended to include sulphate or carbonate and, even if these ions were determined, the complexity of the multi-component system would not have been reduced.

4. DISCUSSION

A few trends were indicated in Experiment No. 2 as follows.

a) The systems in which water percolates through tailings are not stable and certain transient conditions in the process are probably producing the undesirable acidity of the waters seeping from the Heath Steele tailings pond.

b) The attempt to get an impression about the best proportion of tailings sample in a mixture with sand in order to obtain the optimum exposed surface area, to avoid clogging, and to have reaction rates suitable for the experiments, indicated that reactions took place too rapidly when a 100-g tailings sample was diluted with 350 g sand.

   The sample containing 10 g tailings and sand indicated that the reaction moved too much towards the oxidation of ferrous ions to allow the alkaline reaction to take place sufficiently. Therefore, 50 g tailings might be a preferable quantity for the next experiment.

c) The addition of kaolin to the mixture initially had some effect, but it remains a question what the effects of kaolin are over a long period of time. It is very probable that the initial chemical effect is due to the saturation of the ion-exchange capacity. In the long run, the physical aspects due to grain size may have the largest effect on the composition of the water.

d) The most important phenomenon was the trend of the waters to become acid when the tailings samples were mixed with sand. A few of the variables involved in this phenomenon are (1), the reaction rate in the interaction between the individual mineral species with water, (2), the exposed surface area of the minerals due to their total quantity as well as to their grain-size distribution, (3), the initial pH of the water, (4), the treatment of the sample, e.g., sterilization, (5), possible differences between the apparatus, e.g., filtering action. Although it is clear that the exposed surface area of the iron sulphides due to the total quantity in the tailings (see Table 3) is greater than that of the gangue minerals (quartz not included), not much is known proportionally about the effect of the other variables. In the future study of the interaction between minerals, attempts will be made to obtain information on these problems by experimenting with mixtures and conditions in which the number of variables is reduced.

e) Initially there was some indication of increased rates of solution of iron sulphides due to bacterial activity. However, the observation that the microbial population decreased during the runs and the possibility that the composition of a microbial population from one specimen of tailings may not be as effective in another type of tailings, suggested the desirability of a study of the microbial ecology of several tailings ponds before confining the investigation of the microbial action to the effect of iron and sulphur bacteria.

f) The daily variations of the pH measurements in Experiment No. 2, being slightly greater than those in Experiment No. 1, may have been caused partly by the use of different pH meters. However, it is quite possible that the Heath Steele tailings, with their greater content of iron sulphides, are more sensitive to the dailing variations of uncontrollable parameters than are the Hudson Bay tailings.

Some of the uncontrollable parameters follow.

(a) Temperature. Because all the samples were run simultaneously and were subject to the same variations in room temperature, the temperature factor could be practically eliminated in the comparison of the preliminary experiments. A record of the room temperature over a certain period indicated a maximum variation between 14° and 26°C. Any instrumentation to maintain the temperature of the solutions slightly above the maximum room temperature is cumbersome, although it could possibly be installed. Air-conditioning may then be the preferable alternative.

(b) The oxygen partial-pressure. Variations due to changes in atmospheric pressure were the same for all percolators. However, differences in water-flow rates due to clogging and, consequently, in air-flow rates did occur. The possible variation due to the degree of air saturation of the water will be incorporated in future experiments. Although the action of the stopcocks was improved with the installation of metering valves for Experiment No. 3, clogging will remain a problem.

(c) The daily tapping of water samples is a factor in the daily fluctuations of the electrochemical properties, but it should not have an influence on the comparison among the results obtained in the different runs.

(d) The daily variations in Experiment No. 2 were also caused by small experiments concerning the effects of interrupting the water flow, temporarily saturating the samples with water, etc. These experiments were done to get an impression about the magnitude of variables not included in the experiments.

The effect of the bacterial action, as well as the physical effects due to the small grain-size of the tailings, seem to be subjects in which several variables can be distinguished; therefore, the plan of study is to do at least one more general series of runs on the Heath Steele tailings in order to get an impression about the effect of aeration, the effect of the incorporation of an ion-exchange resin, and the effect of lime in the water-flow circuit.

The physical aspects of the problem such as the effects of grain size, packing, layering, temporary drying, depth penetration, etc., for which different types of apparatus have been designed, are being investigated. After completion of the experiments using actual tailings samples, it is planned that experiments on mixtures of iron sulphides and sand should be started to investigate certain aspects of the chemical interaction of minerals with the solution. The effects of other gangue minerals will be included later.

A preliminary study on the specificity of the microbial population using available samples has also been started and these results will be integrated after sufficient progress has been made.

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