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REMOVAL OF DISSOLVED CONTAMINANTS FROM MINE DRAINAGE

By

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Project 14010 FKX

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ABSTRACT

Eleven mill tailing samples from locations throughout the Rocky Mountain region were tested for their effectiveness in removal of dissolved contaminants from mine drainage. With the exception of the sample of the Blaine Mill tailing, the average capacity of the tailings tested was 9.8 mg of iron per gram of tailing with a range of capacities from 6 mg/g to 15 mg/g. In batch tests the Blaine mill tailing exhibited a capacity in excess of 100 mg of iron per gram of tailing.

From these studies it was concluded that for all tailing samples, with the exception of the Blaine tailing, removal was accomplished mainly due to hydrolytic adsorption of metal ions with a small contribution due to the inherent basicity of the tailing. In the case of the Blaine tailing, removal occurred via reaction with calcareous components of the sample.

Continuous column, or stationary bed tests, in the laboratory and in the field were not nearly as effective. During the field test no aluminum was removed from the mine drainage and only 14 percent of the iron and copper were removed. During the test the pH rose from 2.85 to 3.5.

It appears that for effective removal a stirred tank reactor will be required. If the results obtained in the batch test can be duplicated in the field, it is estimated that from 4.5 to 45.0 tons of tailing per day, depending on the capacity, would be required to remove iron from a mine drainage similar to the Gennesse. For a tailing similar to the Blaine tailing, approximately 200 lb of iron could be removed per ton of tailing.

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Key words; mine drainage, mill tailing, adsorption, precipitation, Rocky Mountain Region.

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CONCLUSIONS AND RECOMMENDATIONS

Research has shown that the eleven mill tailing samples from the Intermountain Region have the ability to remove dissolved contaminants from mine drainage. The effectiveness of the mill tailing in removing contaminants depends on its mineralogical composition, size distribution and surface area. Engineering considerations include rate of removal and, naturally, reactor design. The most probable reactions which lead to the removal of contaminants are:

1) Adsorption of metallic cations on siliceous minerals,
2) Precipitation of metal hydroxides due to the natural basicity of the tailing,
3) Precipitation of metal hydroxides due to the reaction with calcareous components of the tailing.

With the exception of the Blaine Mill tailing, the average capacity for iron removal was found to be 9.8 mg per gram of tailing, with a range of capacities from 6 mg/g to 15 mg/g. Considering the adsorption of iron on siliceous minerals, the maximum capacity which could be achieved would be 7.3 mg/g. Also, the inherent basicity of the tailing samples due to addition of CaO in the milling procedure could account for a capacity of 2 mg/g. Thus, when both of these mechanisms are operative the total capacity could be on the order of 9.3 mg/g. which is nearly the same as the observed average capacity (9.8 mg/g). However, in the case of the Blaine tailing, a capacity in excess of 100 mg/g was obtained, accompanied by precipitation of ferric hydroxide. Since the Blaine mill tailing contained calcareous material, it is believed that the reaction responsible for iron removal was predominantly the precipitation of ferric hydroxide due to reaction with calcareous components of the tailing.

Ferrous iron could not be removed by the mill tailing samples. Therefore, in order to achieve the iron removal, it was necessary to oxidize ferrous to ferric, which was readily accomplished by the use of manganese dioxide. The removal of copper and zinc can be effected by the mill tailing samples, with capacities comparable to that for iron.

Results from continuous tests in the labroatory and in the field were not encouraging. During the field test, which involved the Blaine Mill tailing and the Gennesse mine drainage, plugging of the reactor due to the precipitation of iron salts was encountered. In the field test 14% of iron and copper were removed, but no aluminum could be removed.

On the basis of batch tests it is recommended that future continuous tests in the laboratory and in the field use a stirred tank reactor. If the capacities achieved in the batch tests could be realized in the field, from 4.5 to 45 tons of mill tailing per day, depending on the tailing sample, would be required to remove iron from a mine drainage similar to that of the Gennesse. When one considers that a small mill might handle 1000 tons per day and a large mill, 50,000 tons per day, the amount of tailing involved in treating mine drainage is rather small.

Also, in line with the recommendation by Wayman(8), diversion of mine drainage to abandoned tailing ponds is worthy of careful consideration.

INTRODUCTION

Pollution of our Nation's streams and rivers is a definite problem that has become an eyesore in recent years. One of the many sources of water pollution is mine drainage. In the eastern states, mine drainage pollution is due to the acid produced as a result of oxidation of pyrite (FeS_2), which occurs in coal seams. This has been recognized for some time, but no concrete solution has been found to solve the problem effectively, although the problem has been investigated extensively (1,2,3,4,5,6). In the western states, especially in the intermountain region, control of the mine drainage is more complex, due both to the chemistry of the system and to the large hydrostatic pressures developed as a result of the severe changes in elevation. The mine drainage occurs as a result of oxidation and subsequent leaching of many base metal sulfide minerals, such as galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). Consequently, western mine drainage contains relatively high amounts of sulfuric acid and metal ions. A typical analysis of mine drainage from one mine in the San Juan Mountains of Colorado is given in Table I. It can be seen from the table that the major constituents of the drainage are iron (Fe), aluminum (Al), zinc (Zn), copper (Cu), and sulfate ions. Also note that the drainage is quite acidic.

TABLE I

Analysis of Mine Drainage from San Juan Mountains, Colorado

	Concentration, mg per liter									
pH	As	Cd	Cu	Fe	Pb	Mn	Ni	Al	Zn	Sulfate
2.6	0.9	0.9	17.5	637	0.9	9.0	0.5	238	22.8	3310

Generally, mine drainage originates in an abandoned mine, from which the run-off joins, and pollutes, mountain streams. The observation is that from the point at which the mine drainage enters the stream, to a point further down the stream, no aquatic life exists. The non-existence of aquatic life is a result of the high acidity of mine drainage and the metal ion constituents. It is necessary to remove the metal ions in mine drainage and also to decrease its acidity before it joins a stream and thus preserve the stream's integrity.

A number of techniques are available for removal of metal ions and at the same time reduce the acidity of the drainage. The simplest one, is of course, precipitation of metal hydroxides by a limestone neutralization technique (3,4,5). Such a procedure involves a precipitation step, followed by a liquid-solid separation. The latter step presents a problem, since metal hydroxides generally form gelatinous precipitates, making the liquid-solid separation difficult.

Another scheme for removal of metal ions from mine drainage, takes advantage of the fact that the metal ions can be adsorbed on solid substrates. Evidence for this phenomenon and the critical conditions for its occurrence are well established for many oxides and silicate minerals (7). Such being the case, it is possible to use solid material of fine enough size (large surface area), to remove the metal ion contaminants from the mine drainage. If the selected substrate were to be discarded once loaded, an inexpensive material must be used. In this regard, mill tailings which frequently consist of oxides and silicate minerals, present an attractive solid material in that they are both inexpensive and of a relatively fine size. In this regard, Wayman (8) has proposed that mine drainage be diverted into nearby tailing ponds.

Based on the premise that mill tailings can be used for effective removal of metal ions by adsorption, a research program was devised to characterize the mill tailings from eleven different locations with respect to their adsorption capacities for various metal ions at different temperatures and different pH values. Such a characterization in the laboratory, thus, would determine the optimum conditions for adsorption, and the scheme could be tested in an actual system utilizing a particular mine drainage. Data from such work would show the feasibility of utilizing mill tailings to prevent pollution of streams by mine drainage. It was to this end that the following research program was conducted.

EXPERIMENTAL TECHNIQUES

The investigation included four distinct experimental areas: 1) determination of size analysis, mineralogical analysis, and surface area of the eleven mill tailings; 2) characterization of each mill tailing, by batch tests, with respect to its capacity; 3) continuous test in the laboratory to determine capacity; and 4) field testing with a particular mill tailing and mine drainage.

All the chemicals used in the batch and continuous laboratory tests were reagent grade. Distilled water was used in all cases to prepare the desired solutions. Mill tailings from the following locations were used:

	Mill Tailing	Location
1.	Arthur-Magna Mill, Kennecott Copper Corp. (KCC)	Salt Lake City, Utah
2.	Idarado Mining Company	Red Mountain Creek San Juan Mountains, Colo.
3.	Camp Bird Mill	Ouray, Colo.
4.	Standard Metal	Silverton, Colo.
5.	Highland Mary Mill, Dixilyn Corporation	Cunningham Creek East of Silverton, Colo.
6.	Idarado Mining Co.	Ironton, Colo.
7.	Idarado Mining Co.	Telluride, Colo.
8.	Blaine Mill, Argentine Mining Co.	Rico, Colo.
9.	Climax Molybdenum Corp.	Climax, Colo.
10.	Twin Buttes Mill, Anaconda Co.	Twin Buttes, Ariz.
11.	Bunker Hill Co.	Kellog, Idaho

Size Analysis, Mineralogical Analysis, and Surface Area Measurements:

Each of the eleven mill tailings were screened to obtain the size distribution of the sample. The sieving was accomplished on a standard set of sieves and a Ro-tap.

Mineralogical analyses were determined by an x-ray diffraction technique. Diffraction patterns for each tailing were made with a Norelco Diffractometer, CuK_α radiation.

The surface area determination was accomplished using nitrogen as the adsorbing gas and data analyzed using the B.E.T. method. The reproducibility of the data was checked and the technique was found to be quite accurate, ± 1 percent.

Batch Tests for Capacity Characterization:

The mill tailing samples were contacted with a solution of known amount of metal ion and pH for different lengths of time. The experiment was carried out in a beaker which was held in a constant temperature bath. The arrangement is shown in Figure 1. Effective mixing of the mill tailing with the solution was obtained by an overhead stirrer.

The following procedure was used in all experiments:

1. A solution of the desired concentration of metal sulfate was prepared in a 250 ml beaker and the pH adjusted to yield a final volume of 100 ml.

2. The beaker was placed in a constant temperature bath at the desired temperature. All tests were at 25°C unless otherwise noted.

3. A measured amount, 5 g., of mill tailing was introduced and agitation started.

4. After the desired contact time, the pulp was filtered, and the filtrate collected.

5. The filtrate was analyzed for the residual metal ion concentration on an Atomic Absorption Spectrophotometer.

Continuous Laboratory Experiments:

Using the Blaine Mill tailing material, which had the greatest capacity, a continuous laboratory experiment was conducted. A measured amount of mill tailing, 100 g., was placed in a glass column and a metal sulfate solution containing 1 gpl iron (III) at pH 1.8, was pumped through the column for a predetermined length of time. Samples of the solution were taken at fixed intervals of time, and analyzed for the metal ion concentration on the Atomic Absorption Spectrophotometer. The experimental arrangement is shown in Figure 2.

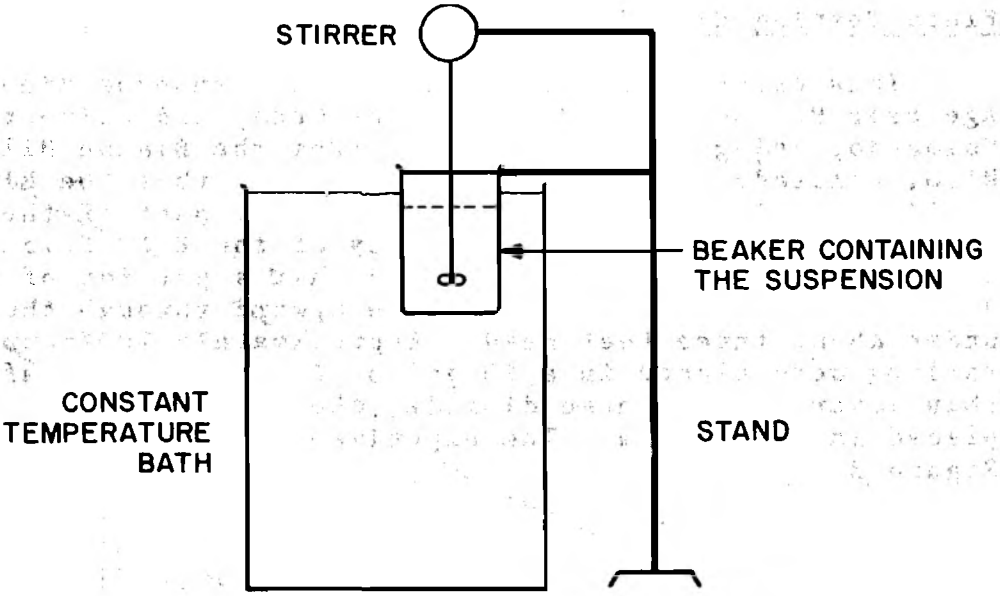


Figure 1 Schematic diagram of batch testing apparatus

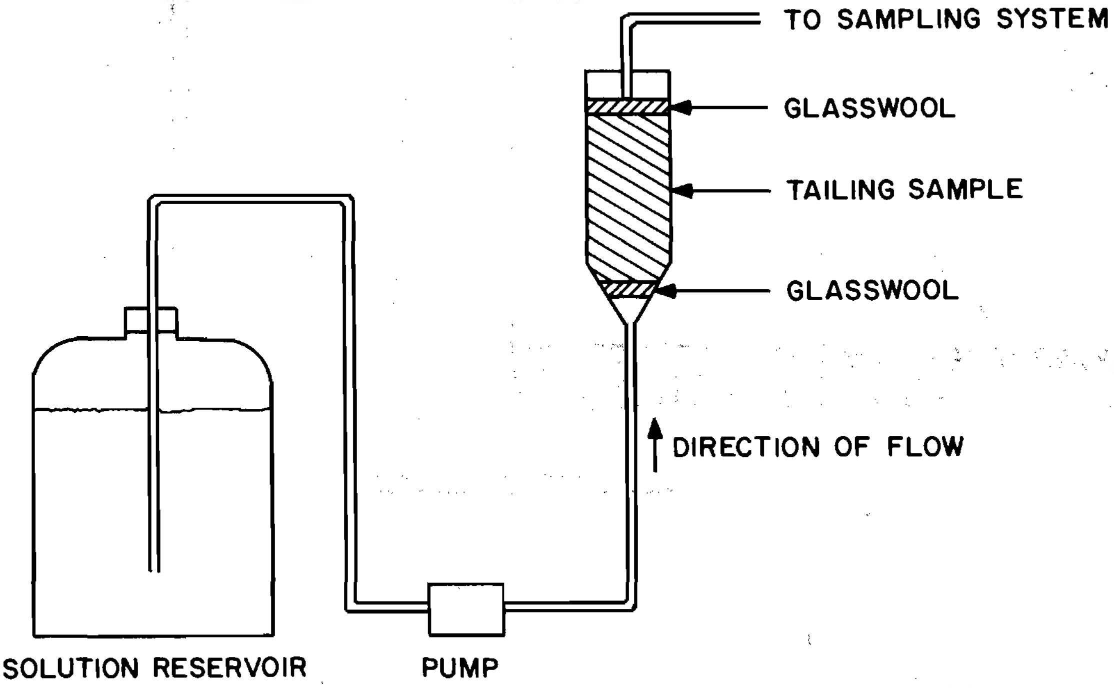
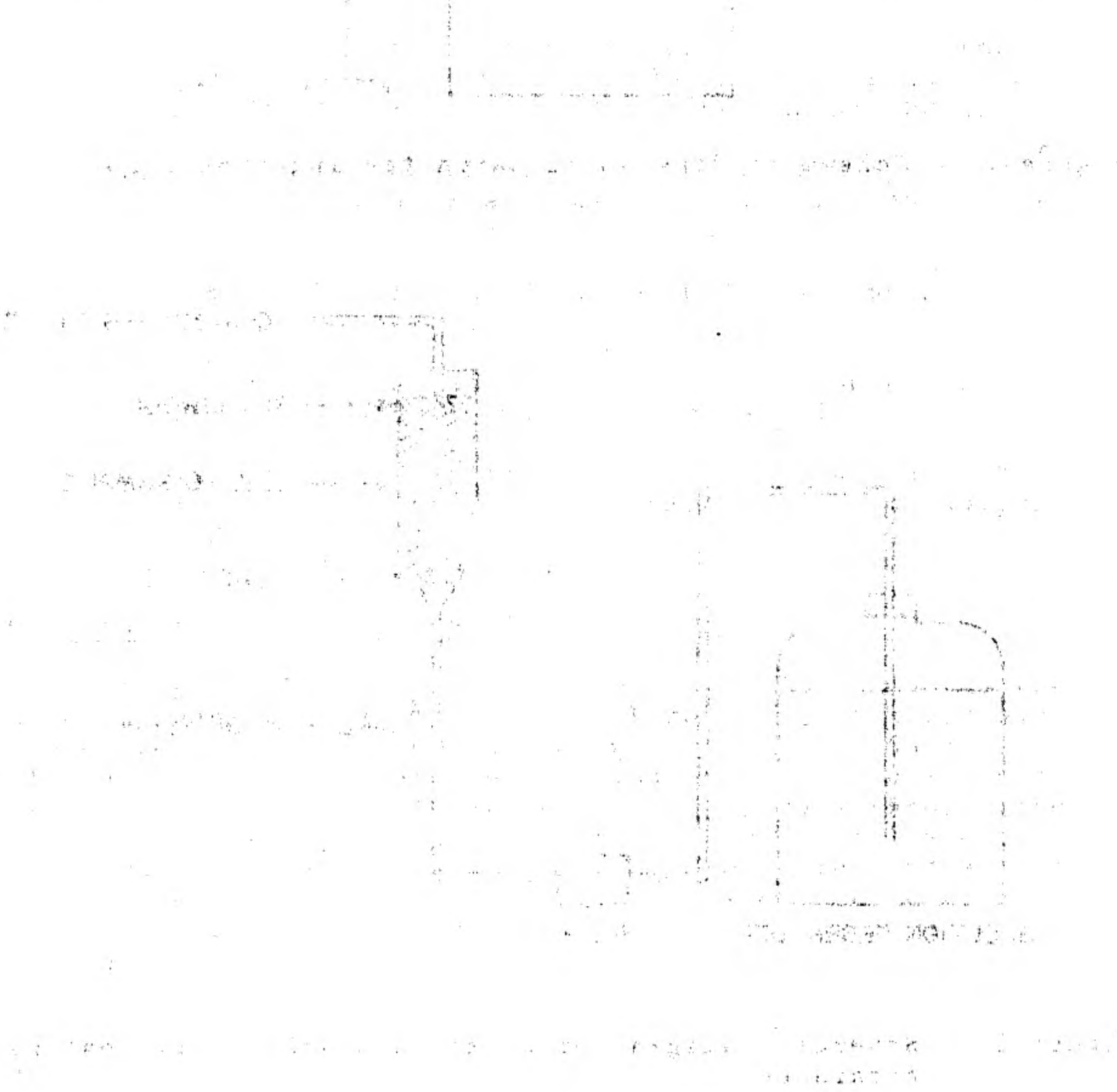


Figure 2 Schematic diagram of continuous laboratory testing apparatus

Field Testing Experiment:

This experiment was set up at the Gennesse Mine drainage near Red Mountain Pass between Ouray and Silverton, Colorado, using the mill tailing from the Blaine Mill at Rico, Colorado. It is important to note that the Blaine tailing sample used in the field was not part of the first sample which was obtained courtesy of the EPA office in Denver. The test was arranged so that a portion of the drainage was allowed to percolate upward through the tailing under about three feet head. Approximately 200 pounds of tailing were placed in a 20 gallon galvanized can after a thin layer of manganese dioxide, about 5 pounds, had been placed in the bottom. The experimental set-up is shown in Figure 3.



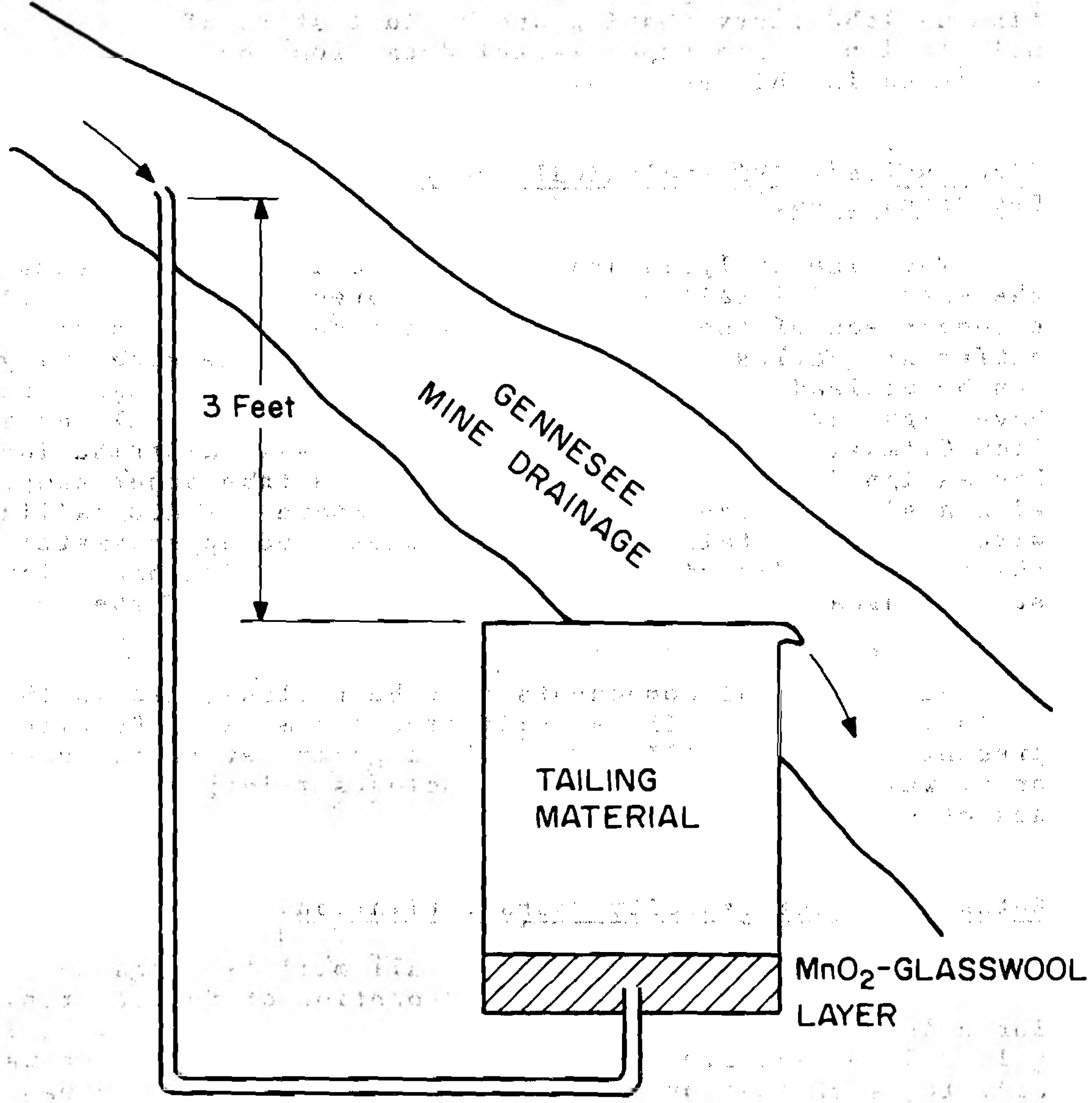


Figure 3 Schematic diagram of field testing apparatus

EXPERIMENTAL RESULTS

The size analysis, mineralogical analysis, and surface area measurements were made for each mill tailing. Batch tests to characterize each mill tailing with respect to their adsorption capacities were completed, followed by continuous laboratory testing and field testing of one particular mill tailing. The experimental data from these tests are presented in this section.

Size Analysis, Mineralogical Analysis, and Surface Area Determinations:

The size analysis and the surface area measurements of the eleven mill tailing samples are presented in Table II. A comparison of the size analyses and surface areas of different samples brings out the fact that the size analysis can be misleading and that some of the mill tailings tested have high internal porosity. For example, the mill tailing from Climax, which has one of the finer size distributions, has a significantly smaller surface area than other samples with a similar size distribution. Compare the KCC tailing with the Climax tailing. Both samples have approximately the same size distribution, but the KCC tailing has a larger surface area indicating the relative porosity of the two samples.

Mineralogical components have been classified in the following groups: silica, silicates and micas. Results are presented in Table III. The silica group refers to quartz only, while the silicate group includes feldspar, hornblende, and other silicates.

Batch Tests for Capacity Characterization:

The batch tests were done on all mill tailings to determine their capacities for adsorption of ferric iron. Three levels of ferric iron concentration were used: 0.1 gpl, 0.5 gpl and 1.0 gpl. The pH of the test solution was adjusted such that precipitation of ferric hydroxide was just prevented. The conditioning times for the test were 10 minutes, 30 minutes and 60 minutes. For the KCC tailing, the tests were done at two temperature levels, 10^{o}C and 25^{o}C.

1. KCC

Figures 4, 5, and 6 indicate that the adsorption reaction is not instantaneous but is rather slow. Consequently, long

Table II

Size Distributions and Surface Areas of the Mill Tailings

	Mill Tailing	Cumulative Percent Finer Than, mesh						Surface Area
		48	65	100	150	200	270	m^2/gm
1)	KCC	95.9	88.5	76.0	61.8	49.6	41.9	1.250
2)	Idarado (Red Mountain Creek)	93.3	70.6	46.5	26.8	13.6	7.9	1.502
3)	Camp Bird Mill	61.4	30.7	14.8	6.7	2.9	1.5	0.729
4)	Standard Metal	82.4	44.0	19.8	8.7	4.0	1.9	1.775
5)	Highland Mary	64.4	43.1	28.1	18.5	12.1	8.5	1.666
6)	Idarado (Ironton)	94.1	67.7	37.8	15.2	4.3	1.3	1.462
7)	Idarado (Telluride)	73.7	45.4	24.9	12.4	6.7	4.0	1.506
8)	Blaine Mill	91.4	77.1	48.4	41.7	28.3	18.9	1.257
9)	Climax	96.6	91.2	47.0	58.2	45.3	36.4	0.700
10)	Anaconda	94.5	89.4	78.3	61.8	49.7	43.1	1.000
11)	Bunker Hill	97.3	93.8	88.6	76.4	66.3	50.1	1.500

Table III

Mineralogical Classification of the Mill Tailings

Tailing	Silica	Silicates	Micas
KCC	X	X	X
Idarado (Red Mt. Creek)	X	X	X
Camp Bird Mill	X	X	
Standard Metal	X	X	
Highland Mary	X	X	X
Idarado (Ironton)	X	X	X
Idarado (Telluride)	X	X	
Blaine Mill	X	X	
Climax	X		X
Anaconda	X	X	
Bunker Hill	X	X	X

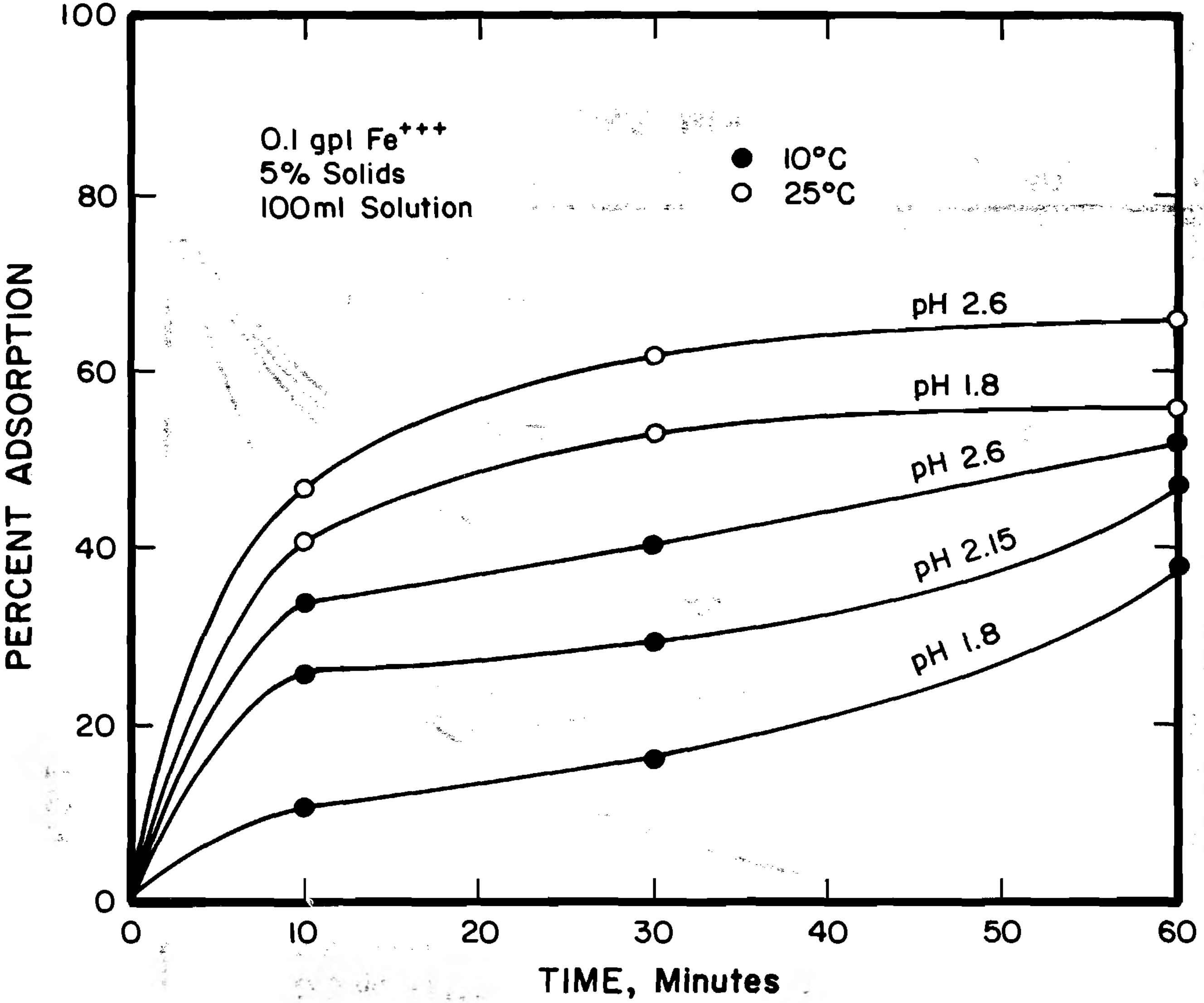


Figure 4 Adsorption of ferric iron, 0.1 gpl, on KCC tailing as a function of conditioning time

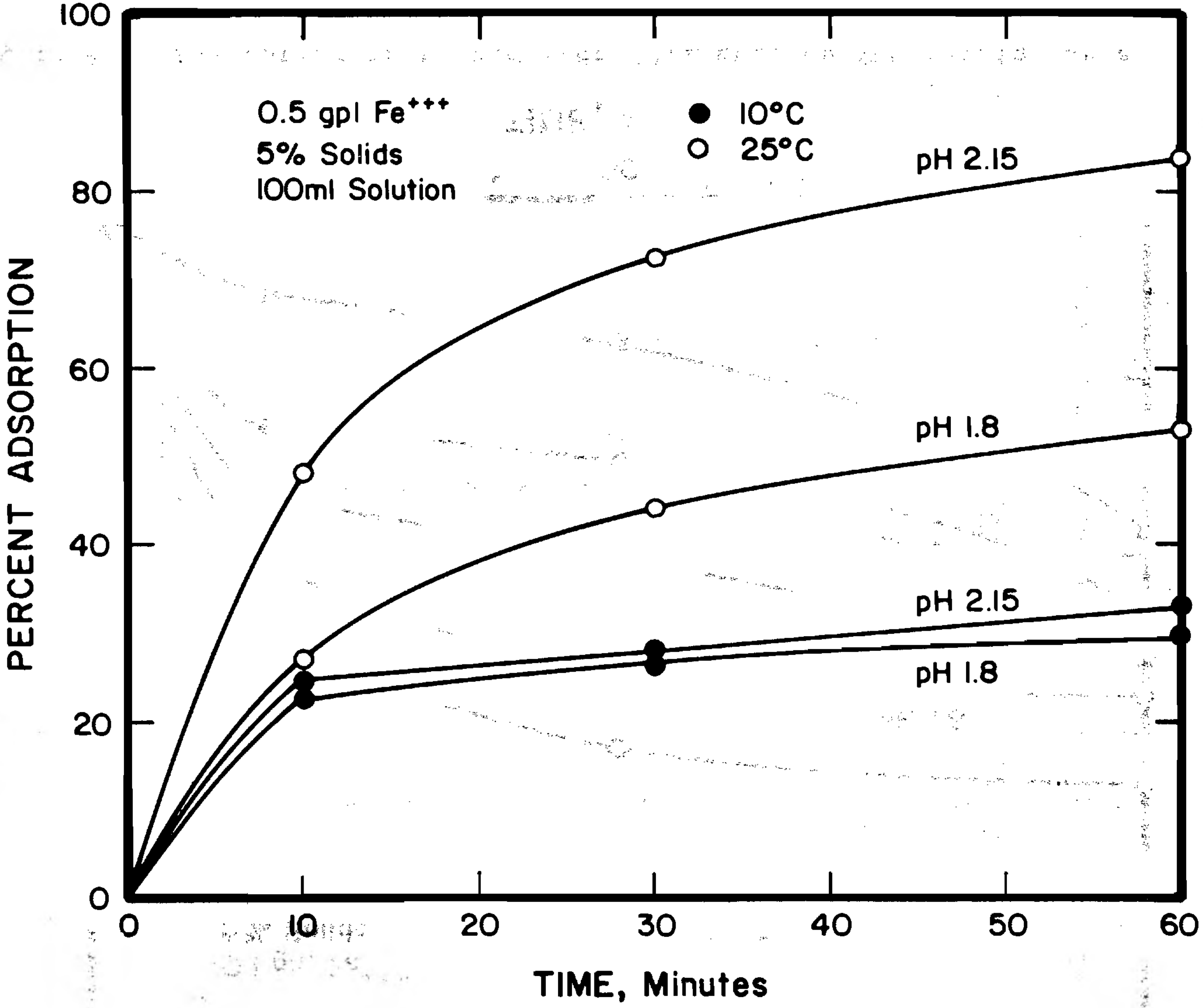


Figure 5 Adsorption of ferric iron, 0.5 gpl, on KCC tailing as a function of conditioning time.

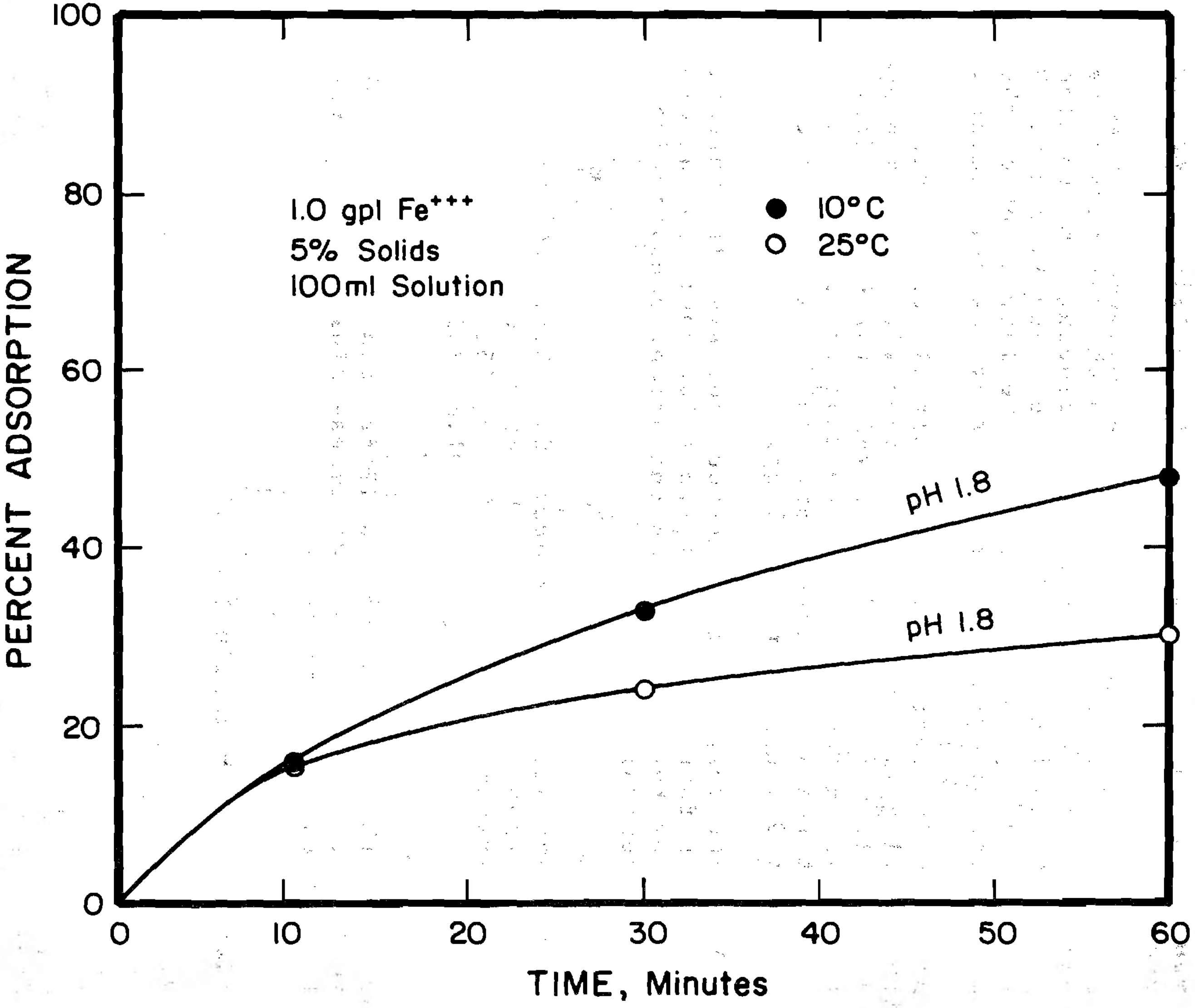


Figure 6 Adsorption of ferric iron, 1.0 gpl, on KCC tailing as a function of conditioning time

conditioning times have a tremendous effect on capacity. In all instances a higher initial pH results in an increased rate of adsorption. The limit placed on this parameter is that the pH for precipitation of ferric hydroxide or basic ferric sulfate is not exceeded. Note that at low ferric concentrations (0.1 and 0.5 gpl) adsorption increases with an increase in temperature, whereas at 1.0 gpl, the opposite effect is observed.

At 0.5 gpl ferric iron and pH 2.15 the capacity increases from about 5 mg/g for 10 minutes conditioning time to almost 9 mg/g for 60 minutes conditioning time. See figure 5. Ultimately the capacity is determined by the initial pH of the system, and for all practical purposes by the temperature.

As shown in Figure 4, with an initial ferric iron concentration of 0.1 gpl, adsorption increases with conditioning time at both 10°C and 25°C. The results for 0.5 gpl ferric iron are shown in Figure 5. Notice that the decrease in adsorption at the lower temperature, 10°C, is even more pronounced at 0.5 gpl than at 0.1 gpl.

Adsorption response for ferrous iron was also investigated. It was found that the ferrous ion would not adsorb, at any level of ferrous iron concentration, conditioning time, or temperature tested:

Concentrations of ferrous: 0.1, 0.5, 1.0 gpl
Conditioning times: up to 60 minutes
Temperatures: 10, 25, and 45°C
pH: 1.8, 2.15, 2.6

It was found that the conversion of ferrous to ferric iron is almost instantaneous, when manganese dioxide (MnO_2) was used for the oxidation reaction.

2. Idarado (Red Mountain Creek)

Figures 7, 8, and 9 show the response of this mill tailing when exposed to ferric iron solutions. From Figure 4, it can be seen that the concentration of dissolved iron at the end of the conditioning time was less than the initial concentration. However, Figures 8 and 9 conclusively show that initial adsorption does take place, and then the iron concentration in the solution increases. A closer examination of the tailing material showed the presence of metallic iron to the extent of 0.10% by weight. Dissolution of the iron filings may account

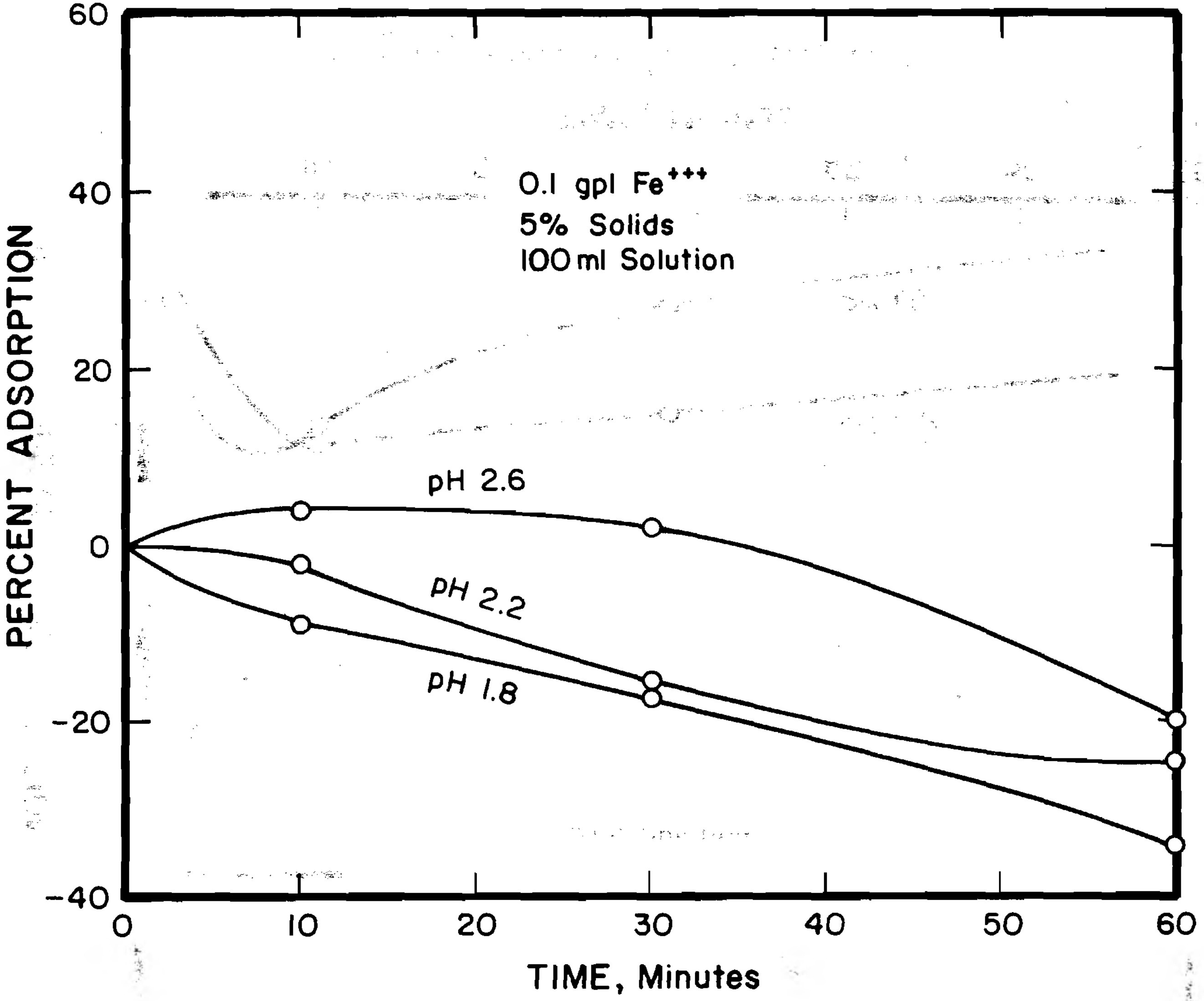


Figure 7 Adsorption of ferric iron, 0.1 gpl, on Idarado Red Mountain Creek tailing as a function of conditioning time

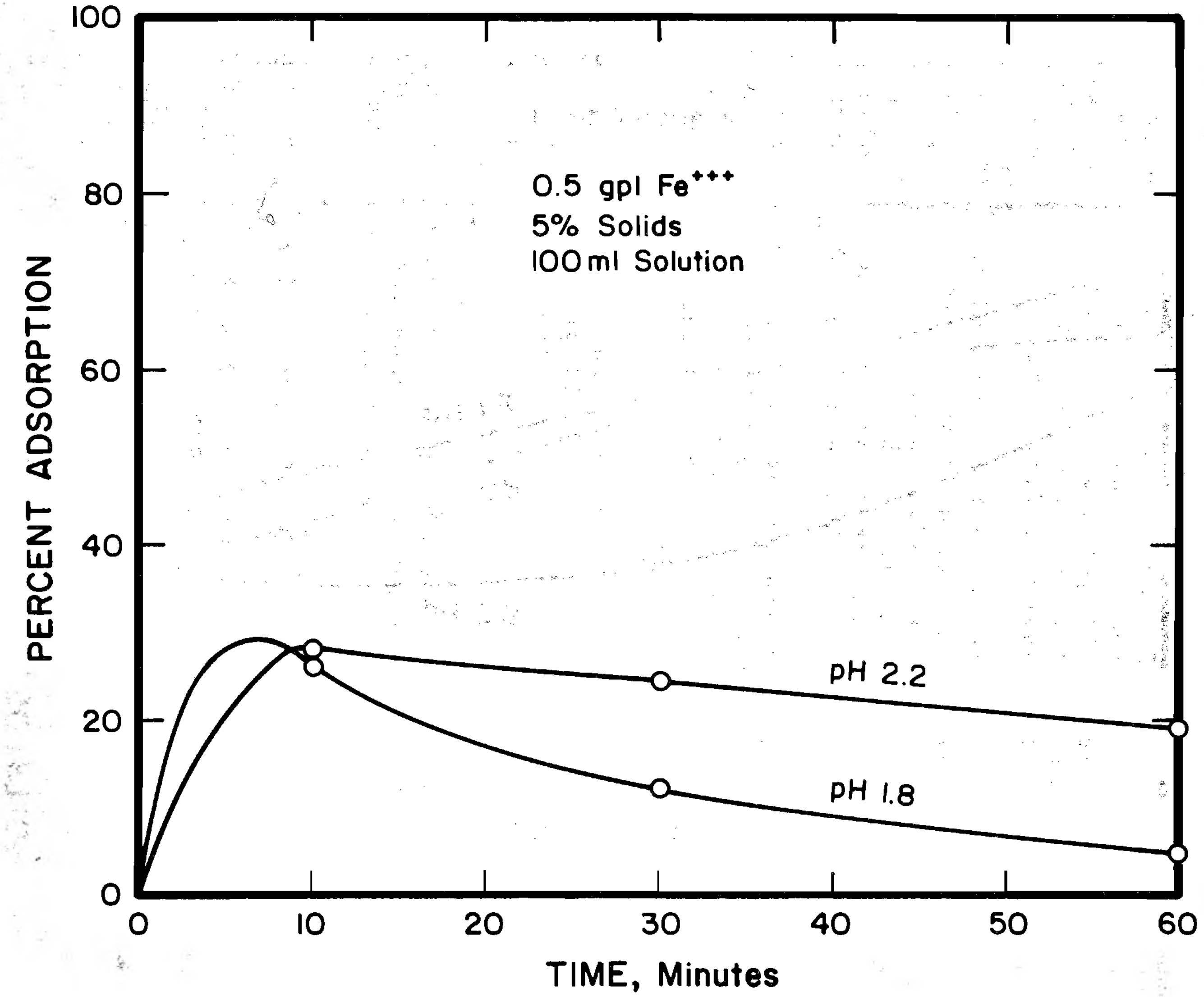


Figure 8 Adsorption of ferric iron, 1.0 gpl, on Idarado Red Mountain Creek tailing as a function of conditioning time

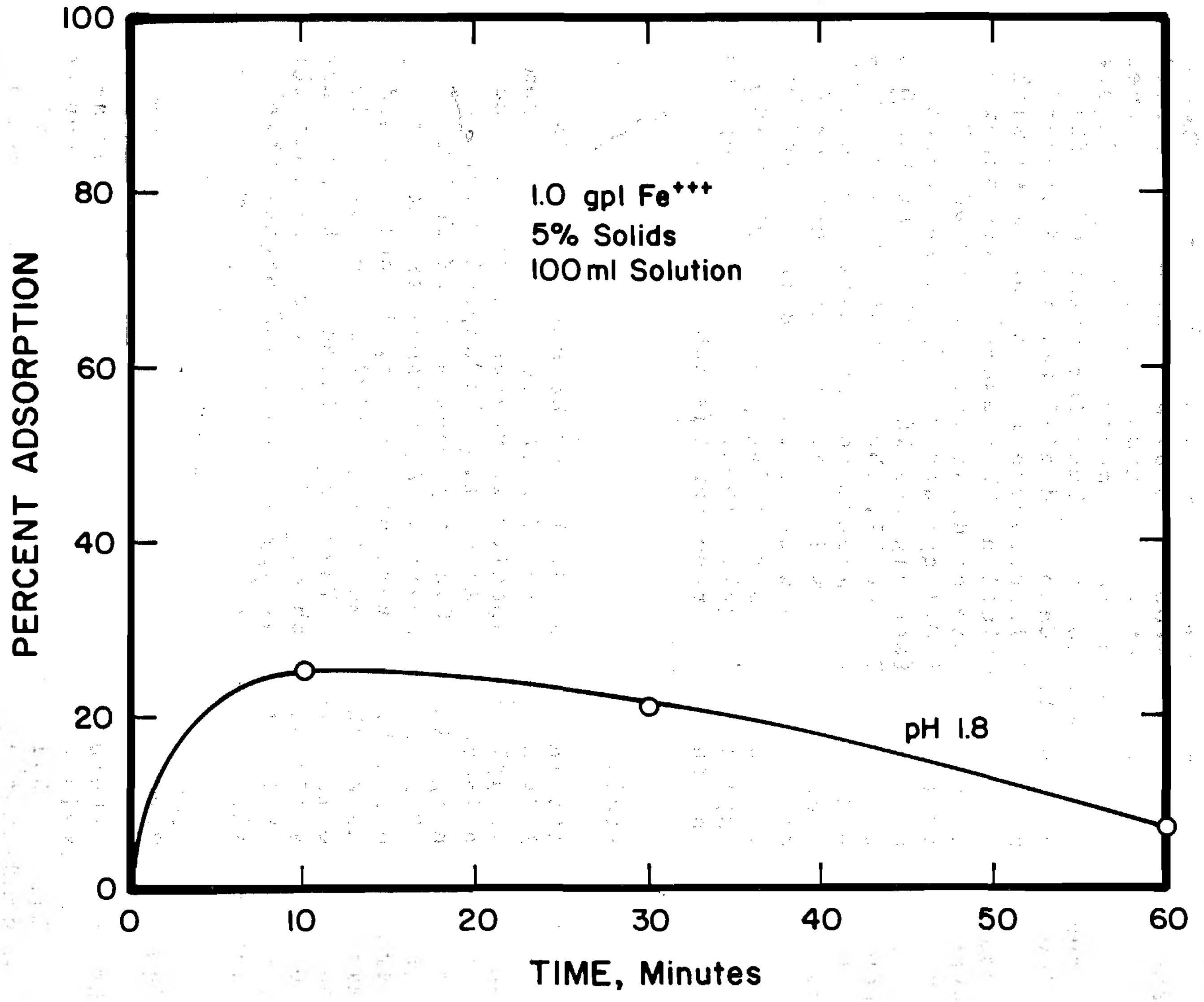


Figure 9 Adsorption of ferric iron, 1.0 gpl, on Idarado Red Mountain Creek tailing as a function of conditioning time

for the anomalous effect observed. Removal of iron filings by magnetic separation should lead to comparable adsorption capacities for ferric iron.

3. Camp Bird

Presence of metallic iron (0.1% by weight) was also noticed in this tailing. Consequently, the iron filings were removed by magnetic separation prior to the adsorption study. Figures 10, 11, and 12 show the adsorption behavior observed. The adsorption capacity of the Camp Bird mill tailing increased not only with an increased iron concentration, but also with an increase in pH of the solution. For example, the adsorption capacity for a 10 minute conditioning time at pH 2.2 and iron concentrations of 0.1 gpl and 0.5 gpl were respectively 1 mg/g and 4 mg/g (see Figures 10 and 11). At the 0.5 gpl concentration level, Figure 11, the adsorption capacities at pH 1.8 and pH 2.2 for a 30 minute conditioning time were 4.5 mg/g and 7.5 mg/g respectively. Also notice that the adsorption capacity increased with an increase in conditioning time from 10 to 60 minutes reaching 100% adsorption in the case of 0.1 gpl and 0.5 gpl. These capacities are approximately the same as those observed for the KCC tailings.

4. Standard Metal

From the data in Figure 13, it can be seen that this tailing material is suitable for ferric iron adsorption from solution. At 0.1 gpl the capacity increases as pH and conditioning time are increased. At pH 1.8 the capacity for 60 minute conditioning time is 0.8 mg/g, but at a pH of 2.6, the capacity is 2 mg/g or greater. At a concentration of ferric iron of 0.5 gpl, the maximum capacity is not reached in 60 minutes and at pH values of 1.8 and 2.2 the capacities were found to be 11.5 mg/g. These capacities are higher than those for KCC tailings, which may be due to the fact that the surface area of Silverton tailing is about 40% higher than that for KCC tailing.

5. Highland Mary

The data gathered for different ferric iron concentrations and pH levels at varying conditioning time is presented in Figure 14. At 0.1 gpl, maximum capacity is reached only with long conditioning time and is 2 mg/g at pH 2.6. But as the concentration of ferric iron is increased, the capacities increase. At 0.5 gpl, a maximum capacity of 5 mg/g seems to

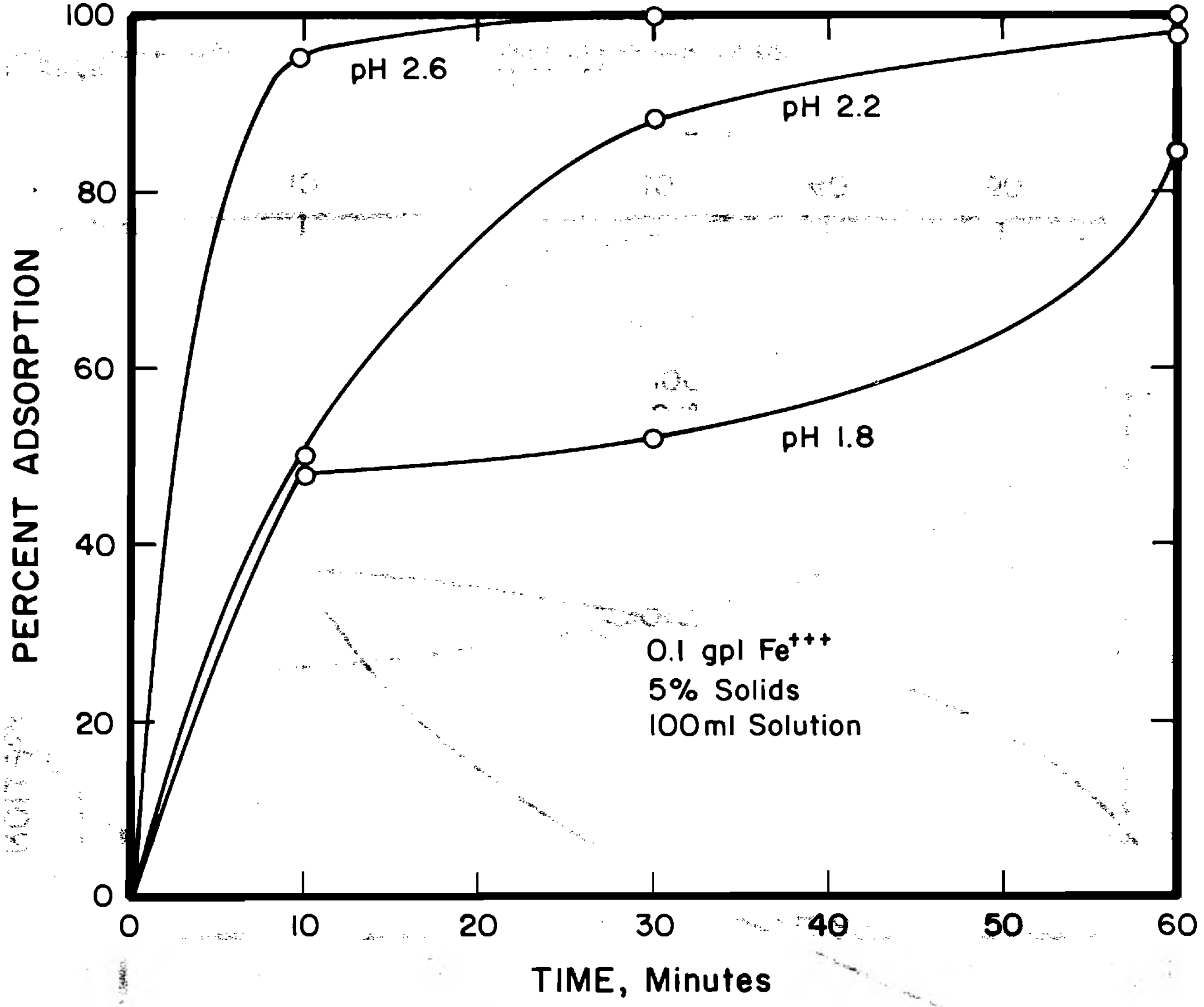


Figure 10 Adsorption of ferric iron, 0.1 gpl, on Camp Bird tailing as a function of conditioning time

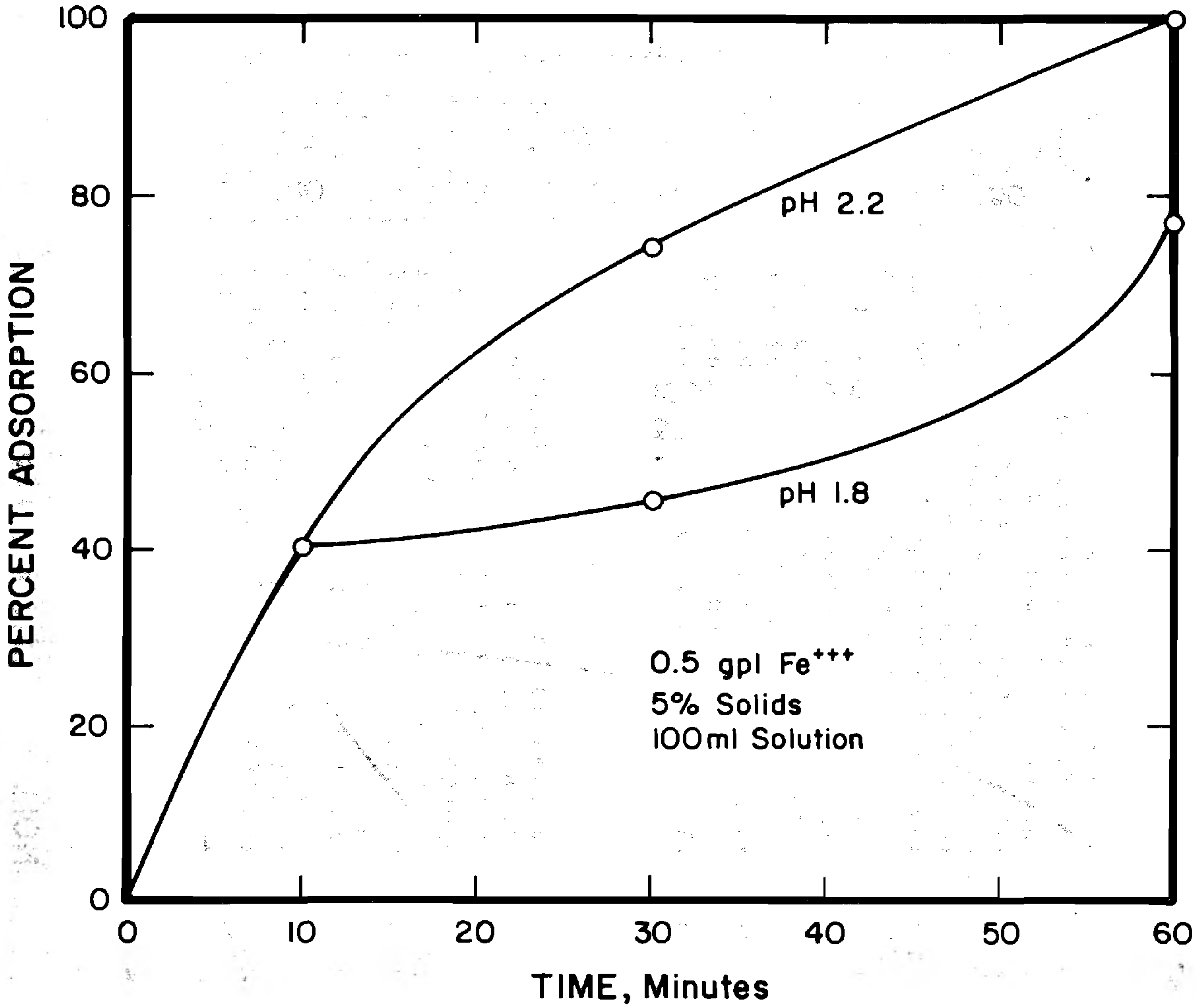


Figure 11 Adsorption of ferric iron, 0.5 gpl, on Camp Bird tailing as a function of conditioning time

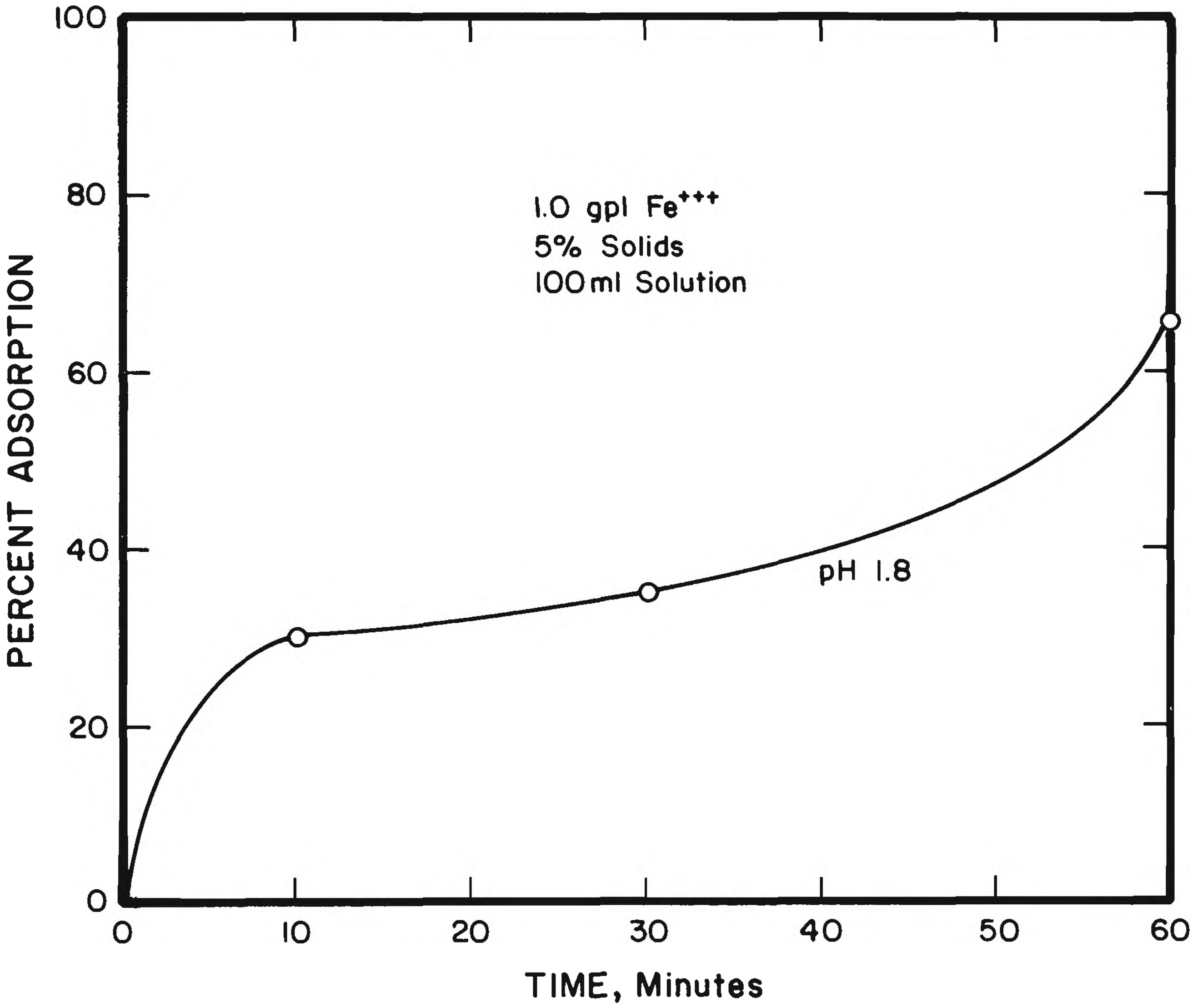


Figure 12 Adsorption of ferric iron on Standard Metal tailing as a function of conditioning time

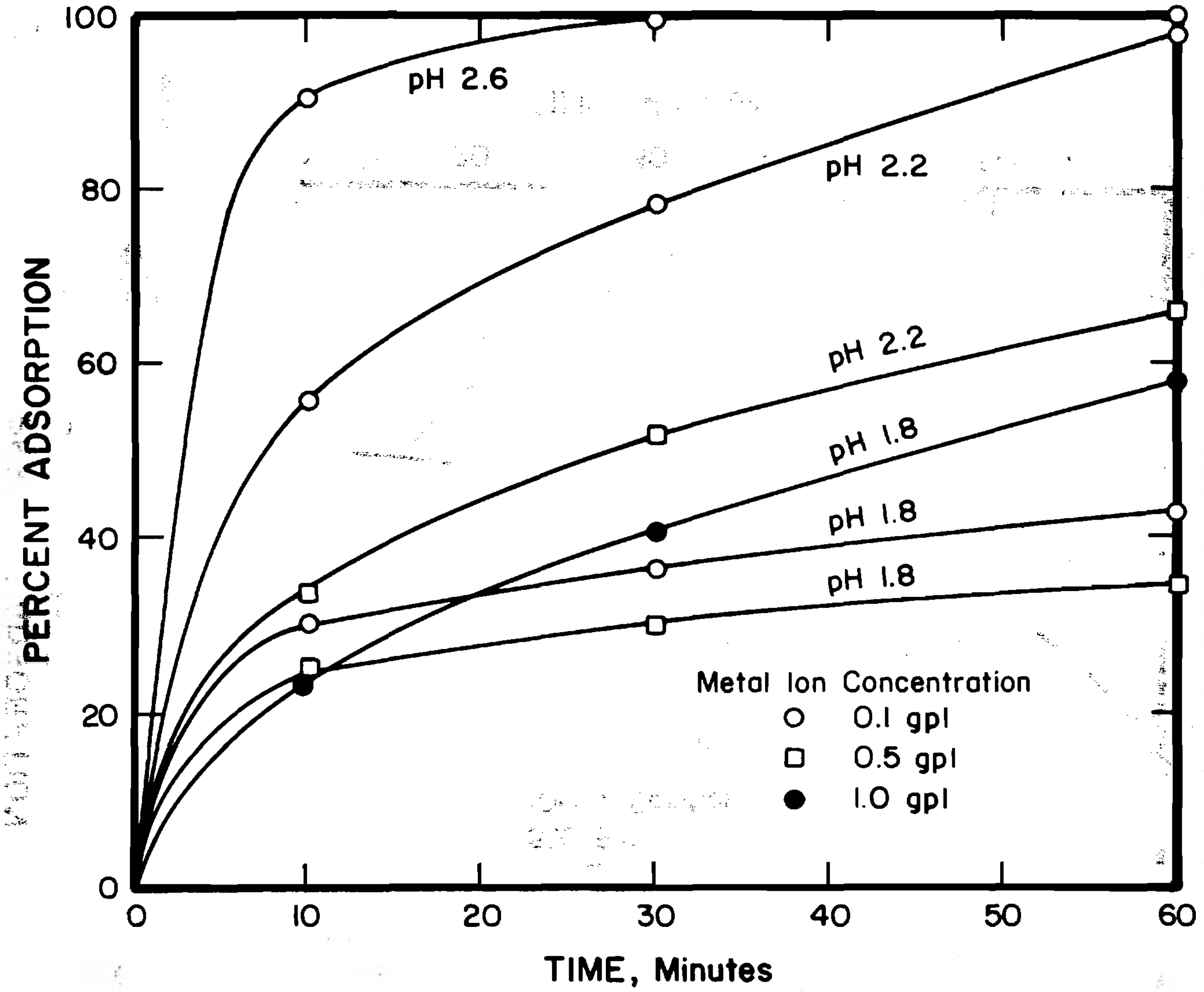


Figure 13 Adsorption of ferric iron on Standard Metal tailing as a function of conditioning time

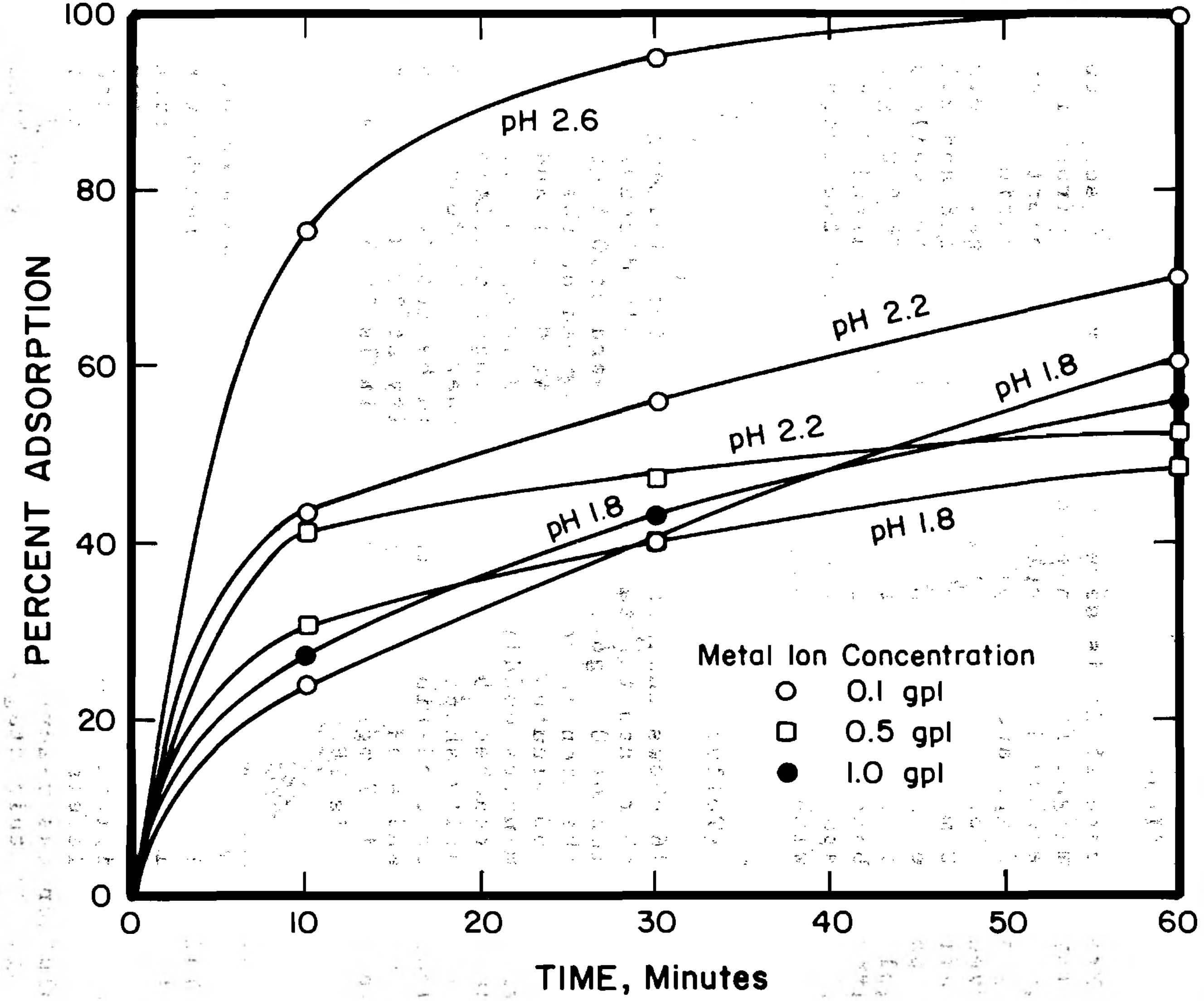


Figure 14 Adsorption of ferric iron on Highland Mary Mill tailing as a function of conditioning time

be reached in 60 minutes and the dependence of capacity on pH of solution is not very noticeable. At 1.0 gpl, the maximum capacity after 60 minutes of conditioning is 11.0 mg/g, while at 10 minutes conditioning time the capacity was only 5 mg/g. Thus, the capacity of the Highland Mary Mill tailing is comparable to the Standard Metal tailing, which has a similar surface area.

6. Idarado (Ironton)

From Figure 15 it is seen that the maximum adsorption capacity, 2 mg/gm, for a concentration of ferric iron of 0.1 gpl is reached in 60 minutes. At higher concentrations, namely at 0.5 gpl and 1.0 gpl, the maximum capacities observed are lower than for the previous tailings. At 0.5 gpl, after 60 minutes of conditioning, at pH's 1.8 and 2.2, the capacities are 4 mg/g and 5 mg/g respectively, while at 1.0 gpl ferric iron concentration the capacity is 9.0 mg/g. Compared to both the Standard Metal and the Highland Mary Mill, this capacity is lower. Also notice that the increase in capacity with conditioning time is slower.

7. Idarado (Telluride)

Figure 16 shows that the capacity of this tailing is considerably higher than the tailings previously discussed. At a concentration of 0.1 gpl, at all pH's and at 0.5 gpl and pH 2.2, all the iron in solution is adsorbed on the tailing in less than 60 minutes. The capacity at 0.5 gpl and pH of 2.2 with 60 minutes conditioning time is 10 mg/g. At 1.0 gpl the capacity reaches 15 mg/g and with longer conditioning time the capacity should increase further. The dependence of capacity on conditioning time should be noted. For example, for 1.0 gpl and a pH of 1.8 the capacity at 10 minutes conditioning time is 7 mg/g, at 30 minutes it is 10.5 mg/g and at 60 minutes it is 15 mg/g.

8. Blaine Mill

This tailing has an exceptional ability to remove ferric iron from solution. The removal is a result of two simultaneous processes: (1) adsorption of ferric iron on the surface and (2) precipitation of ferric hydroxide. It was noticed that at all levels of ferric iron concentration, all the iron in solution was removed within the first ten minutes of conditioning. At this stage, further tests were done with higher concentrations of ferric iron, up to 50 gpl. (It should be

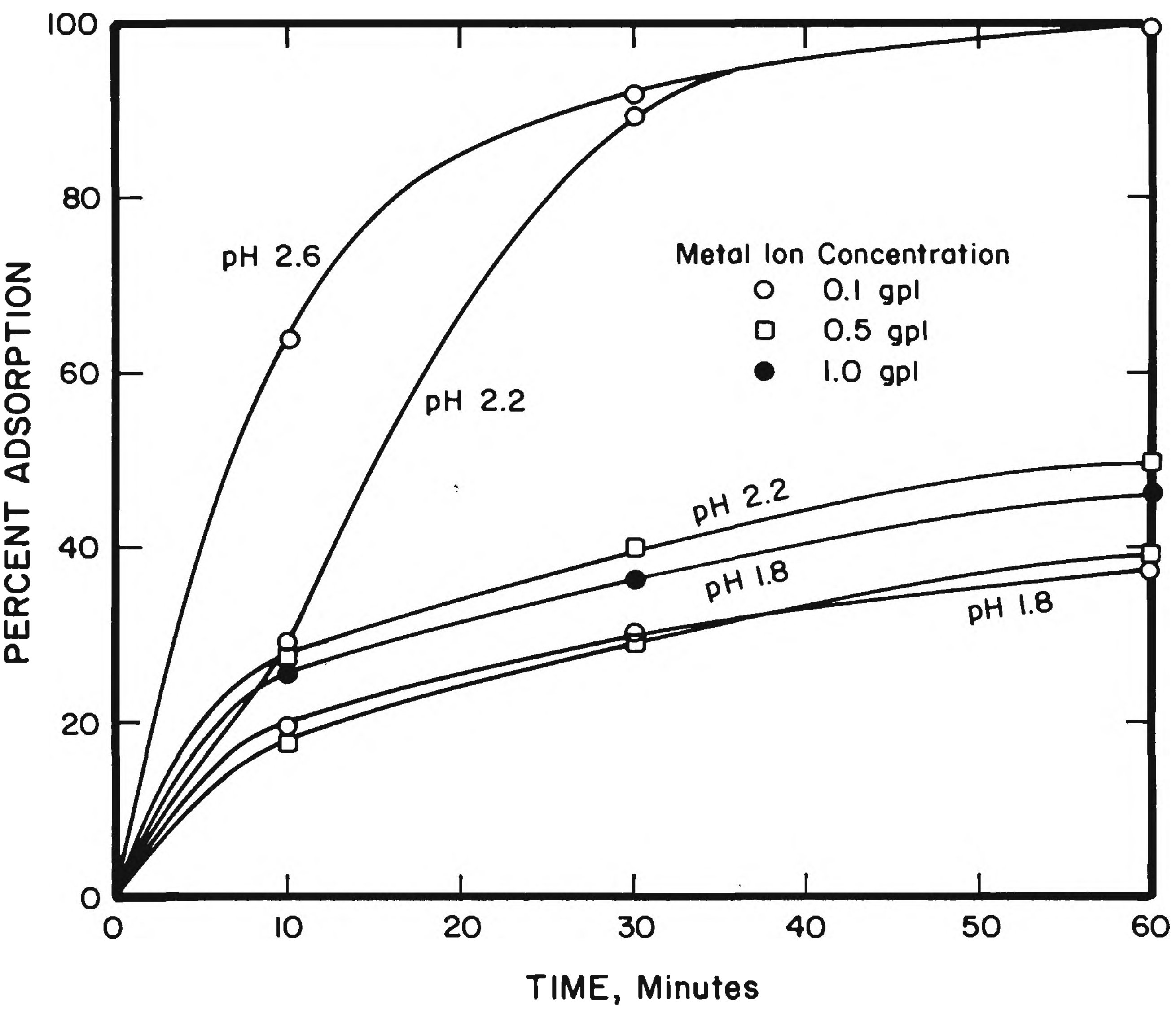


Figure 15 Adsorption of ferric iron on Idarado Ironton tailing as a function of conditioning time

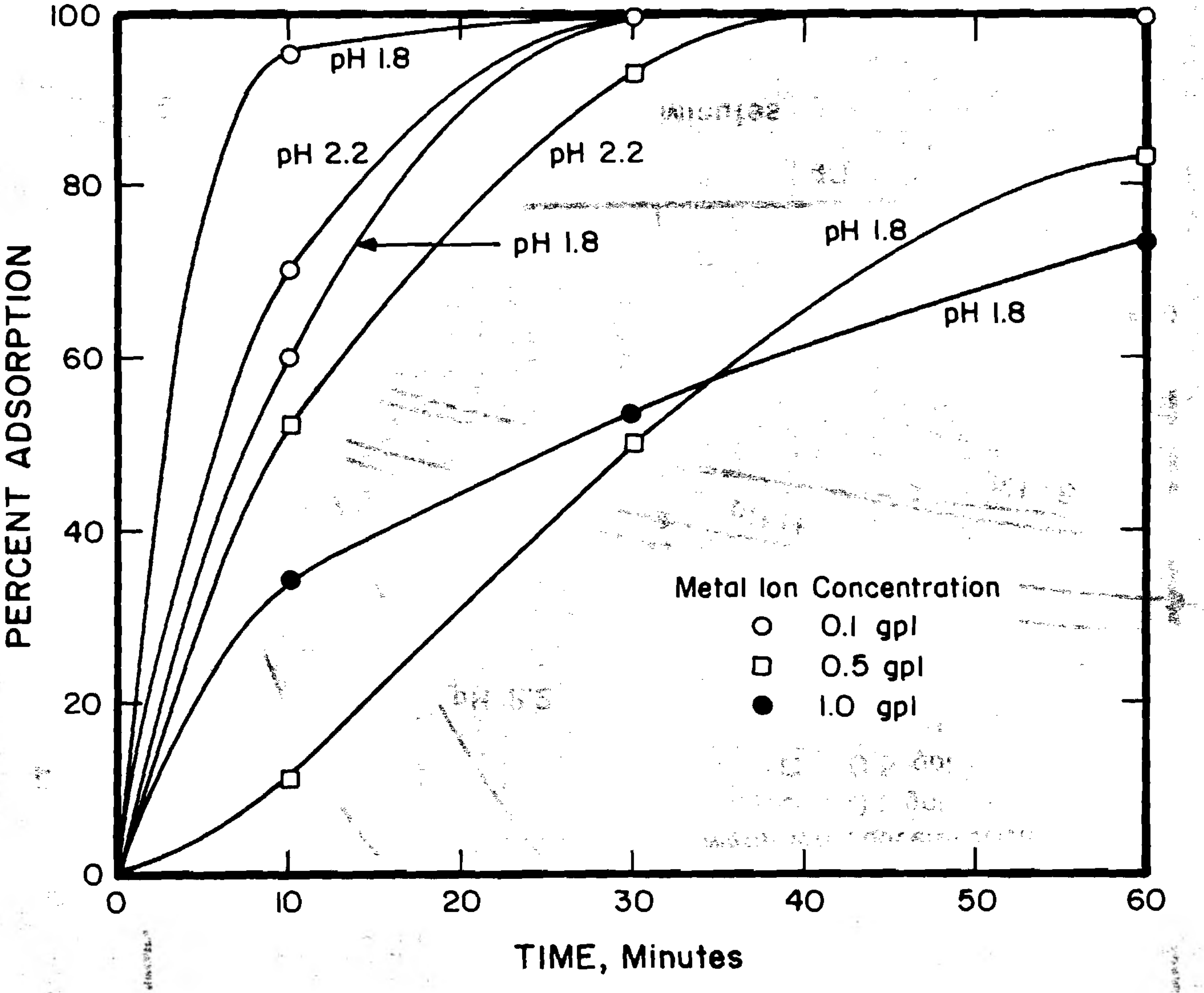


Figure 16 Adsorption of ferric iron on Idarado Telluride tailing as a function of conditioning time

be noted that the pH of the solution was decreased to obtain such concentrations of ferric iron.) Even at such high levels no iron was left in the solution at the end of a 10 minute conditioning time. No difficulty in making solid-liquid separation was encountered due to the fact that the tailing probably acted as a nucleation site for precipitation and prevented the formation of a gelatinous precipitate. The Blaine Mill tailing is capable of removing in excess of 100 mg of ferric iron per gram of tailing.

9. Climax

The data in Figure 17 shows that ferric iron adsorption capacities of this tailing are small compared to the other tailings. Even with longer conditioning time the capacity achieved at 0.1 gpl and pH 2.6 is 1.2 mg/g. At a ferric iron concentration of 0.5 gpl and pH of 2.2 the capacity after 60 minutes conditioning is 4.0 mg/g. While at 1.0 gpl, the capacity is only 7.6 mg/g. Thus, the capacity of this tailing is quite small compared to the other tailings tested. Also the rate of adsorption is relatively slow.

10. Anaconda

Figure 18 shows the character of ferric iron adsorption. It is noticed that more than 70% of the adsorption capacity is reached within the first ten minutes, at all concentration levels. The maximum adsorption capacity of 9.0 mg/g is reached in 60 minutes at a concentration of 0.5 gpl (pH 2.2) and 1.0 gpl (pH 1.8). The adsorption characteristics are very similar to the KCC tailing material.

11. Bunker Hill

It can be seen in Figure 19 that the adsorption capacity of this tailing is considerable at high concentration of ferric iron in solution. At 1 gpl, the capacity is 14 mg/g after 60 minutes of conditioning, but at 0.5 gpl (pH 1.8) the capacity is only 4.1 mg/g. At 0.1 gpl (pH 1.8) it is only 1.8 mg/g. Thus, the capacity is very much dependent not only on the pH of the solution, but also on the concentration of ferric iron in solution.

Table IV gives a summary of the ferric iron adsorption experiments. With the exception of the Blaine tailing and Idarado's Red Mountain, the maximum capacity ranges from 6.0 mg/g to 15.0 mg/g, with an average of 9.8 mg/g.

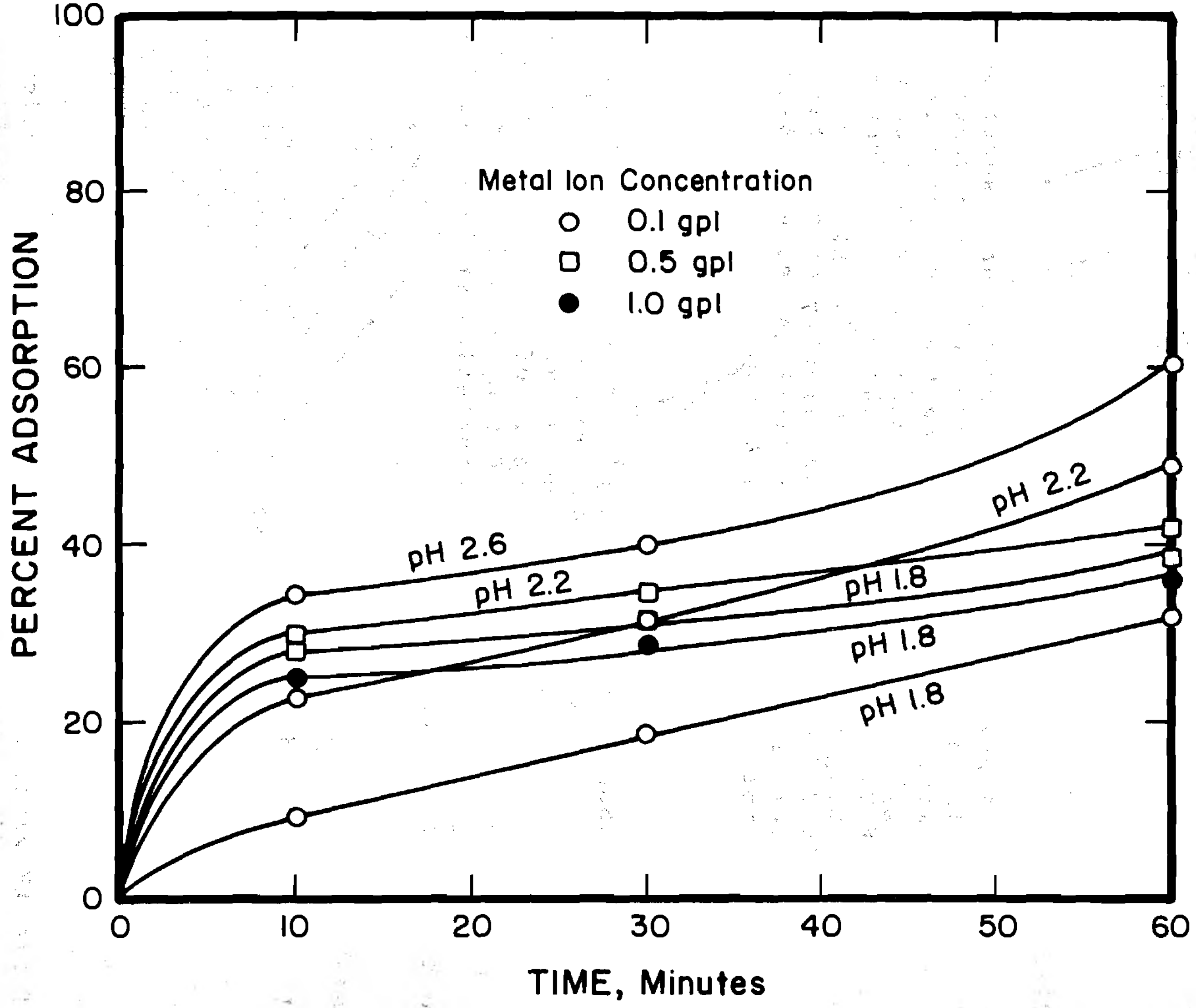


Figure 17 Adsorption of ferric iron on Climax tailing as a function of conditioning time

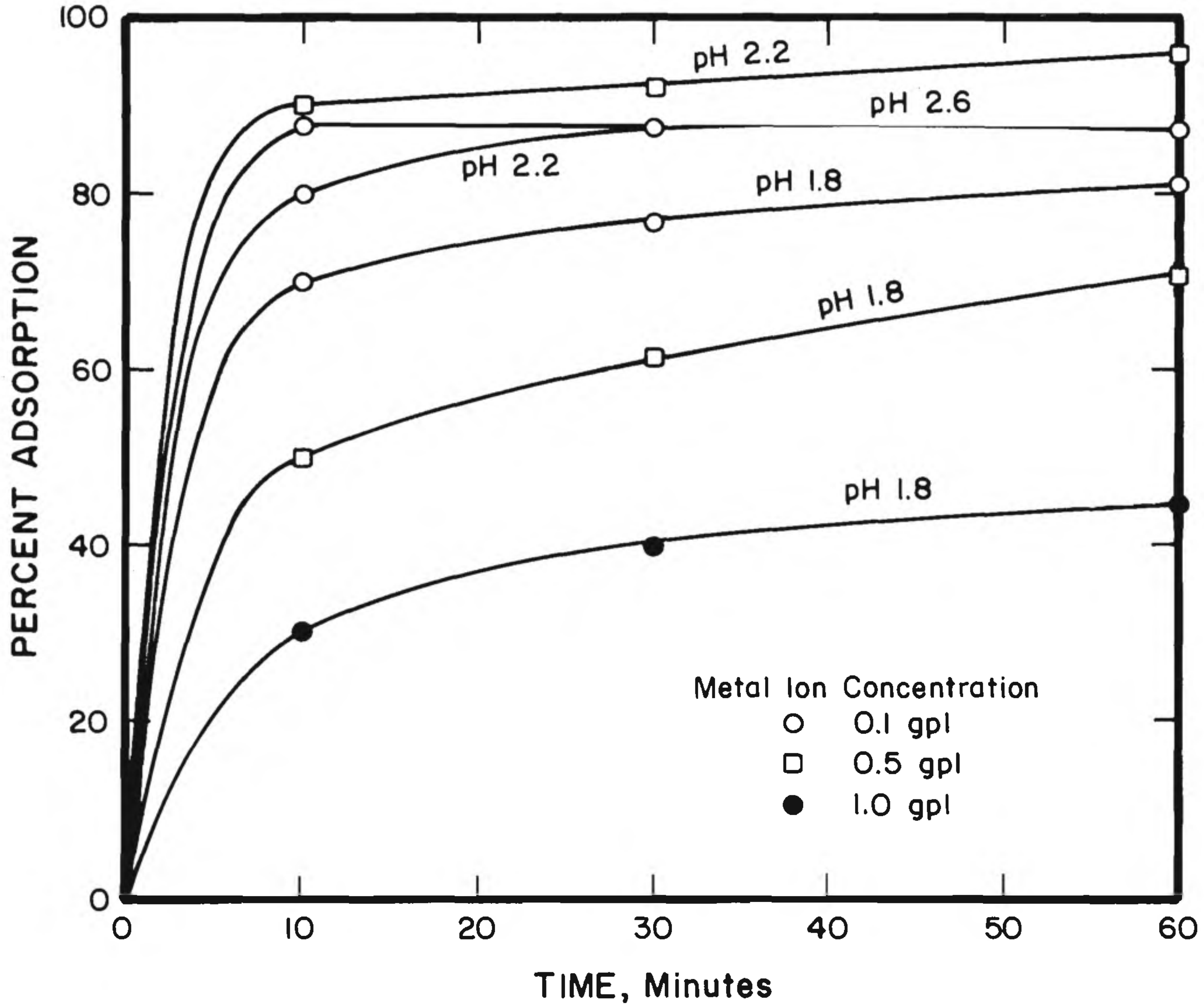


Figure 18 Adsorption of ferric iron on Anaconda tailing as a function of conditioning time

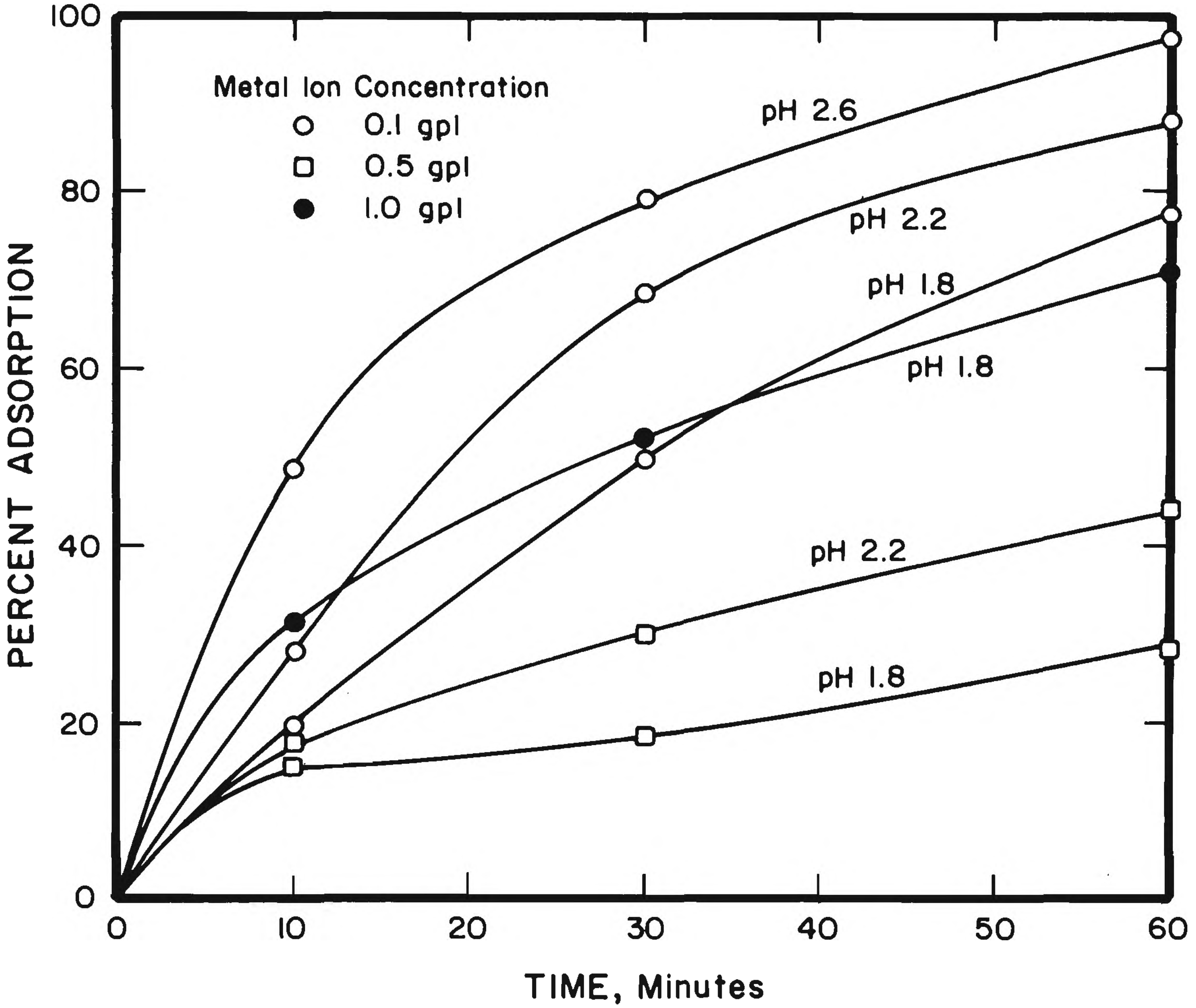


Figure 19 Adsorption of ferric iron on Bunker Hill tailing as a function of conditioning time

Table IV

Summary of Ferric Iron Adsorption Study on Mill Tailings

Tailings	Surface Area m^2/g	Capacity* mg/g
KCC	1.25	6.0
Idarado (Red Mountain Creek)	1.50	2.0
Camp Bird Mill	0.73	13.0
Standard Metal	1.78	11.5
Highland Mary	1.67	11.0
Idarado (Ironton)	1.40	9.0
Idarado (Telluride)	1.51	15.0
Blaine Mill	1.20	100.0**
Climax	0.70	7.6
Anaconda	1.00	9.0
Bunker Hill	1.50	14.0
Average	1.29	9.8

*60 minute conditioning time at 1.0 gpl Fe^{+++}, pH 1.8, and 25°C.

**It is important to note that a capacity in excess of 100 mg/gm can be obtained with the Blaine Tailing at higher Fe^{+++} additions.

Copper adsorption behavior was studied with two mill tailings, the exceptional Blaine Mill tailing and the Camp Bird tailing, typical of all the other tailings. Figure 20, shows the response obtained with the Blaine Mill tailing, at pH 2.0. It is noted that at the lower concentration level of 0.1 gpl all the copper was removed by the tailing within 30 minutes. However, at higher concentrations, maximum capacities were approached with 60 minutes conditioning time. The initial rate of adsorption was slow. At 0.5 gpl the capacity was 9.6 mg/g, while at 1.0 gpl the capacity was found to be 12.6 mg/g. No precipitate was observed as in the case of the ferric iron adsorption study. The adsorption curves in Figure 21 show that the adsorption capacity of the Camp Bird tailing for copper at pH 2 is poor. At 0.1 gpl the capacity is 0.3 mg/g, at 0.5 gpl the capacity is 7.5 mg/g, and at 1.0 gpl the capacity is 8.2 mg/g. Thus, the capacity for adsorption is proportional to the concentration of copper ions in solution, and is very sensitive to the concentration in the lower concentration range.

Similarly, zinc adsorption was studied with the same tailings, the Blaine and the Camp Bird. The adsorption response of the Blaine tailing at various concentrations of zinc and pH 2.0 is presented in Figure 22 as a function of conditioning time. The adsorption capacities for zinc are dependent on concentration. The capacities after 60 minutes conditioning time are: at 0.1 gpl, 1 mg/g; at 0.5 gpl, 5.3 mg/g; and at 1.0 gpl, 14 mg/g.

The data in Figure 23 shows surprisingly that for high zinc ion concentrations, the adsorption capacity of the Camp Bird tailing at pH 2 is greater than that of the Blaine tailing. At 0.1 gpl, the capacity is 17.0 mg/g, after 60 minutes of conditioning time.

Notice that the Blaine tailing is not nearly as effective for zinc as it was for iron III and copper. On the other hand, the Camp Bird tailing adsorbed zinc significantly better than iron III and copper.

Continuous Laboratory Experiment:

The continuous laboratory test was conducted with a 100g. sample of the Blaine Mill tailing which exhibited the greatest capacity of all tailings tested. A 1.0 gpl solution of iron (III) as ferric sulfate at pH 1.8, was pumped through the sample at a rate of 30 ml per min, which gave an effective retention time of the solution in the column of 1.29 minutes. The effluent solution was analyzed for iron at regular time

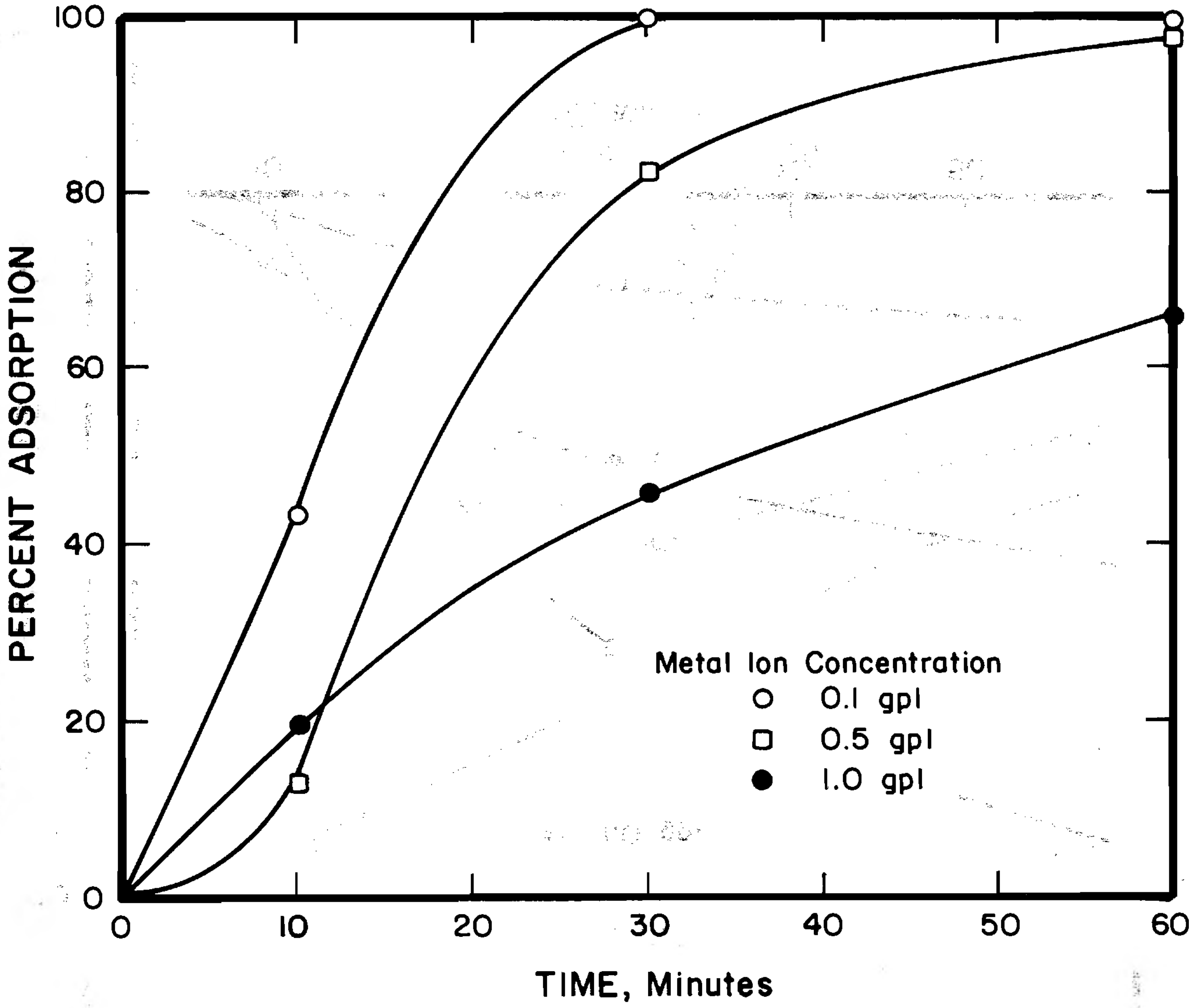


Figure 20 Adsorption of copper at pH = 2.0, on Blaine tailing as a function of conditioning time

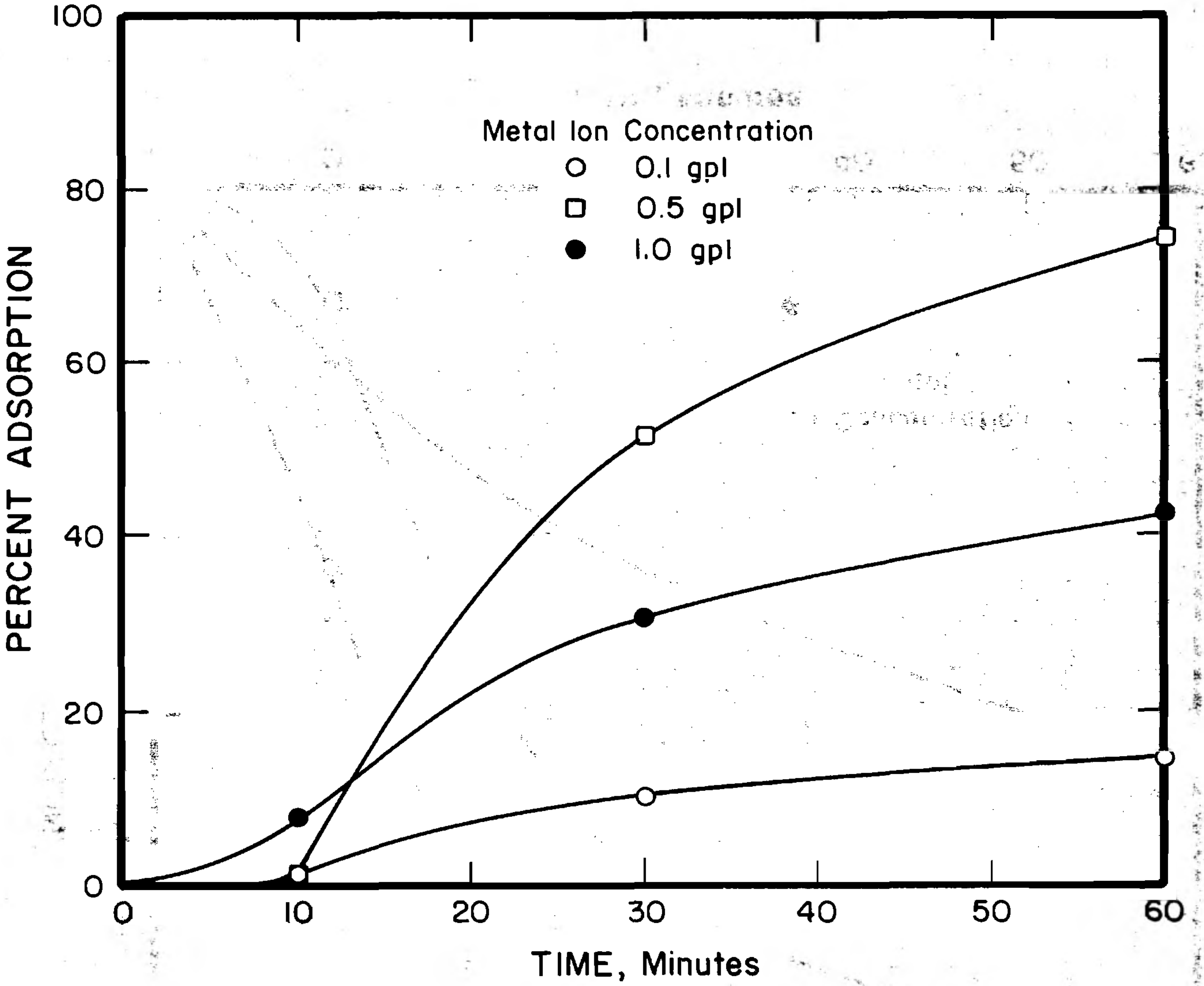


Figure 21 Adsorption of copper at pH = 2.0, on Camp Bird tailing as a function of conditioning time

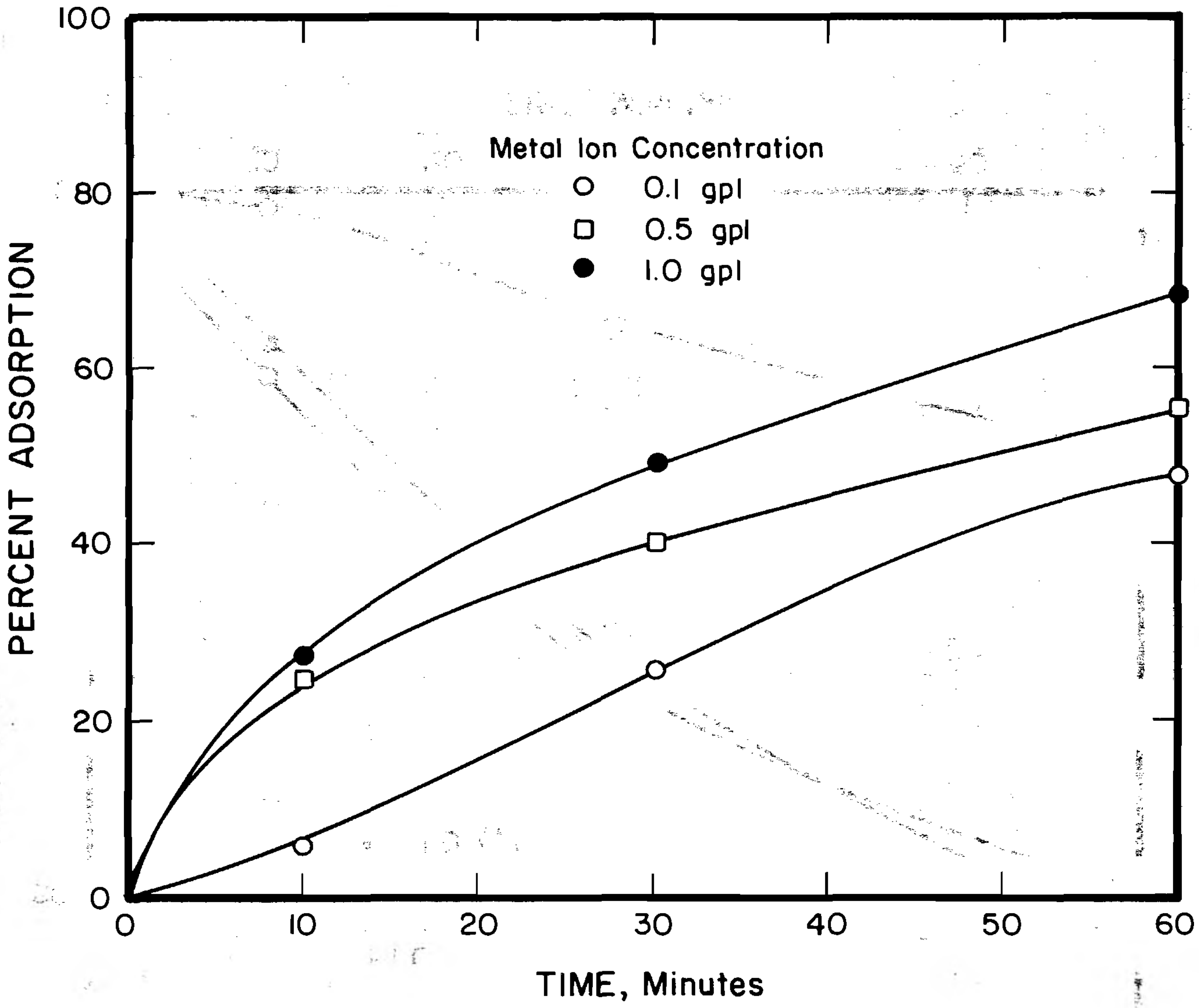


Figure 22 Adsorption of zinc at pH = 2.0, on Blaine Mill tailing as a function of conditioning time

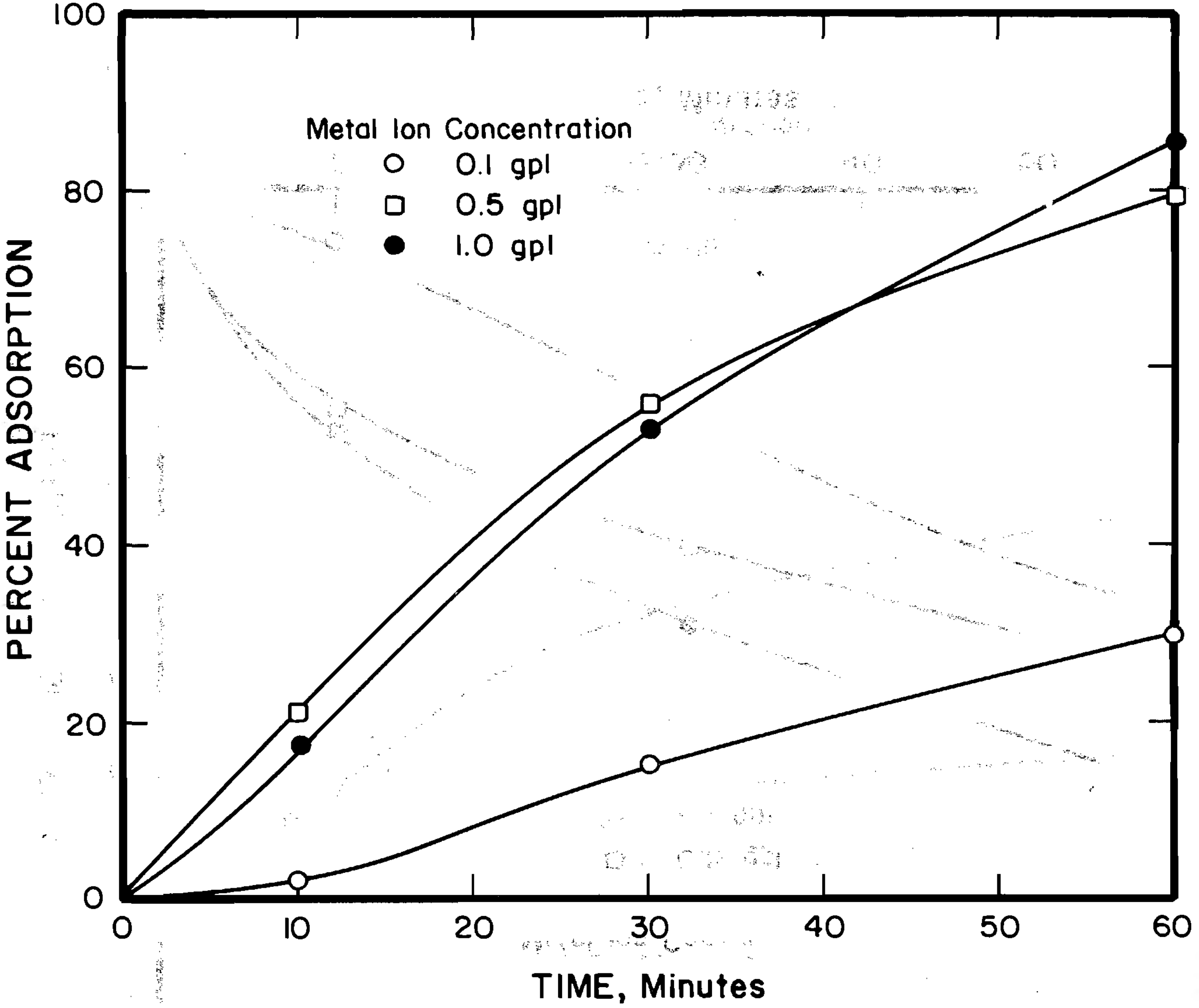


Figure 23 Adsorption of zinc at pH = 2.0, on Blaine Mill tailing as a function of conditioning time

intervals. The data is shown in Figure 24. After the initial adsorption reaction had occurred, the concentration of the effluent solution reached a steady value of 600 mg/liter, indicating that the iron was being removed at a rate of about 12 mg/min in the small sample of mill tailing. The flow rate was increased further to 60 ml/min and a similar rate was approached.

Field Testing Experiment:

A field experiment was conducted in the San Juan Mts., using the Gennesse Mine drainage on the 23rd and 24th of August, 1971. The average analysis of the drainage is shown in Table V. These results can be compared with, and are very similar to, other measurements which had been made and are recorded in Table VI (9).

TABLE V

Average Analysis of Gennesse Mine Drainage

pH = 2.85
Iron = 720 ppm
Copper = 14.6 ppm
Aluminum = 245 ppm

TABLE VI

Previous Chemical Analyses of Gennesse Mine Drainage(9)

Date	pH	Flow gpm	Concentration, ppm iron	copper	aluminum
August 5, 1968		120	660	18	254
August 14, 1968		120	658	18	261
August 28, 1968		107.5	661	18.4	255
September 12, 1968	3.4	103	649	18.4	252
October 1, 1968	2.6	90	637	17.5	238
October 24, 1968	3.3	72	636	16.8	249
November 8, 1968		60			

Figure 25 shows the flow rate of the mine drainage through the reactor containing a 200 pound sample of the Blaine Mill tailing as a function of time. The decrease in flow rate from 5 liters per minute to 1 liter per minute is due to the clogging

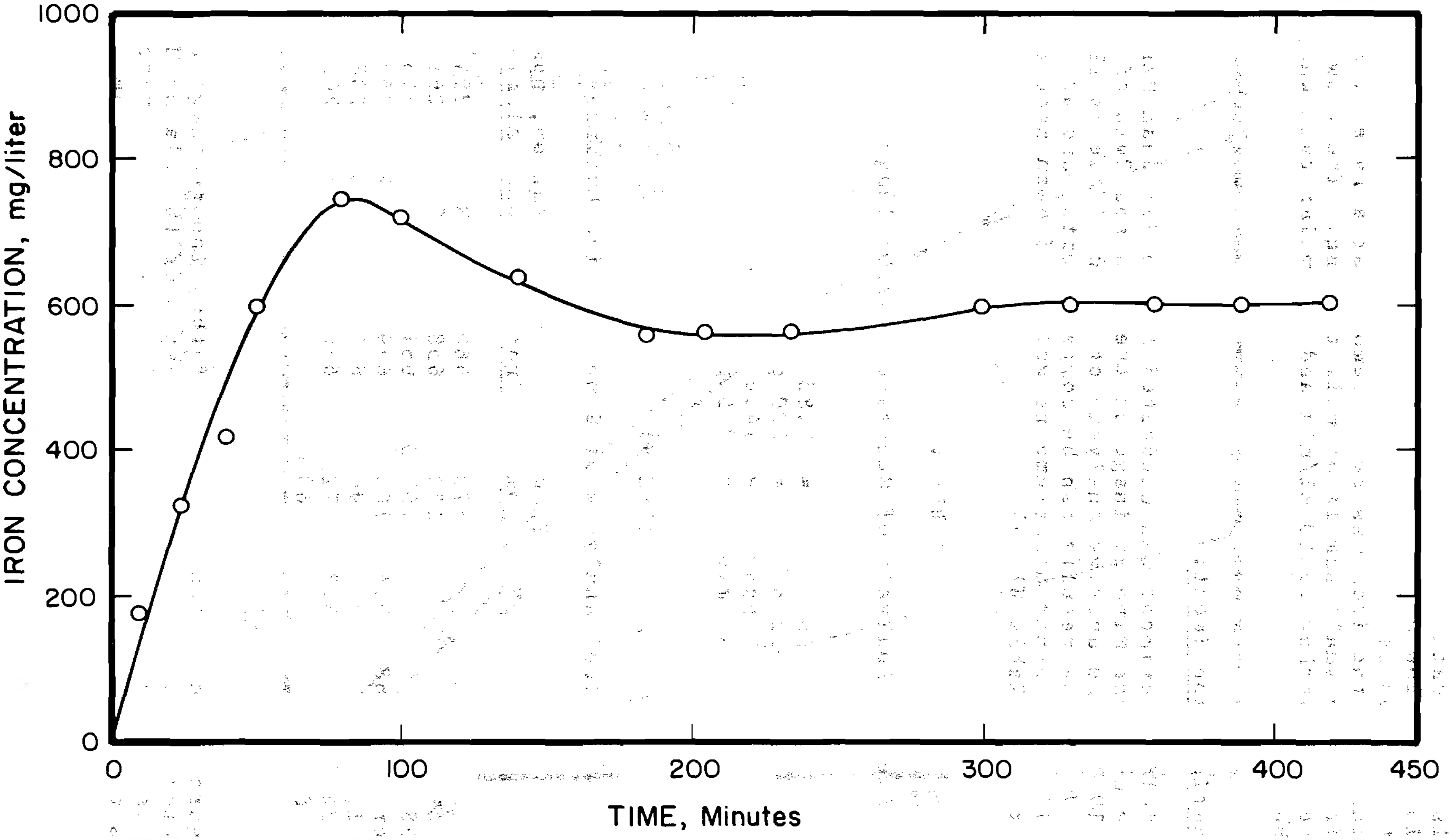


Figure 24 Adsorption of ferric iron, 1.0 gpl, on Blaine Mill tailing on a continuous laboratory test

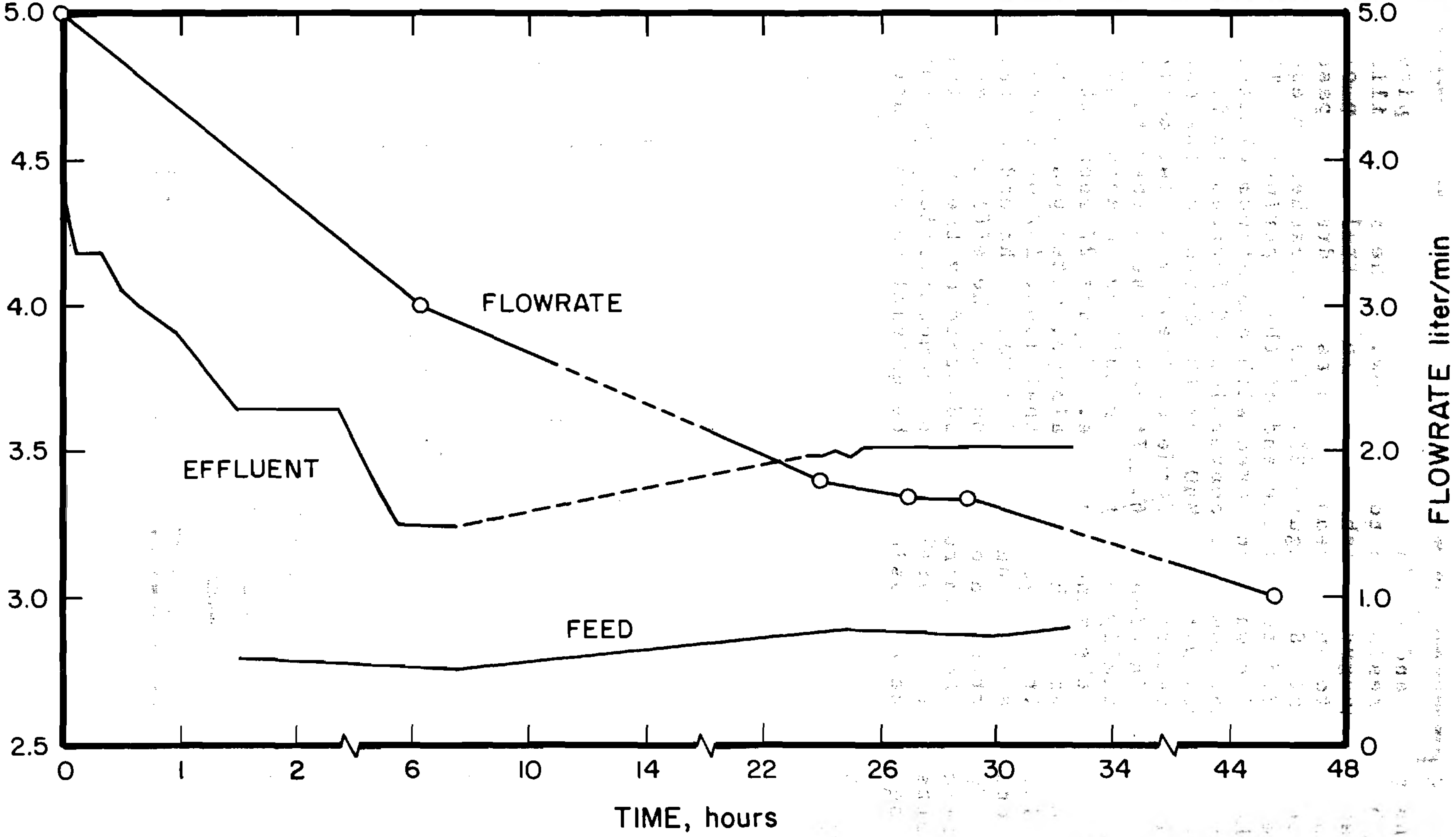


Figure 25 Variation in pH and flow rate during the field testing experiment

of the pores and voids between particles by precipitate, leading to a higher resistance to the flow. The mill tailing contains calcareous gangue, which results in neutralization of the acid, giving rise to an increase in pH as the drainage passes through the container. See Figure 25. The pH reached an equilibrium value of pH 3.5 toward the end of the experiment. The potential of the solution was monitored with a platinum electrode and indicated that complete conversion of ferrous to ferric was being achieved with the MnO_2 at the bottom of the container. The iron concentration of the effluent was also monitored, and is shown in Figure 26. It can be seen that the removal of iron was partially effective, resulting in about 14% removal of iron from the mine drainage. Figure 27 shows the concentration of copper in the mine drainage, after passing through the container. It is again seen that about 14% of copper from mine drainage is being removed towards the end of the experiment. Concentration of aluminum in the effluent was also determined. No aluminum was adsorbed by the mill tailings. The attempt to measure the zinc concentration was futile, because of the corrosion of the galvanized container.

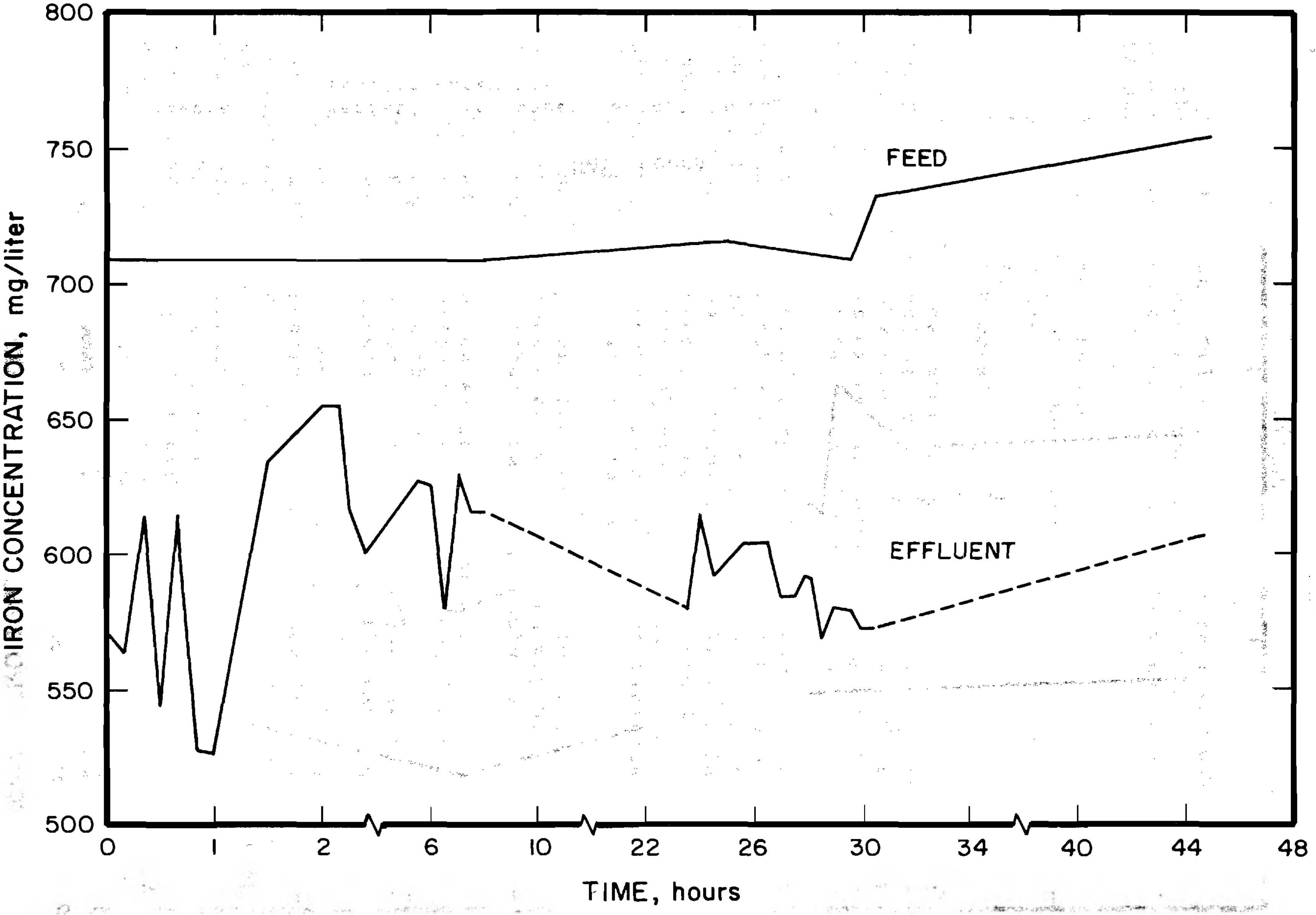


Figure 26 Variation in iron content during the field testing experiment

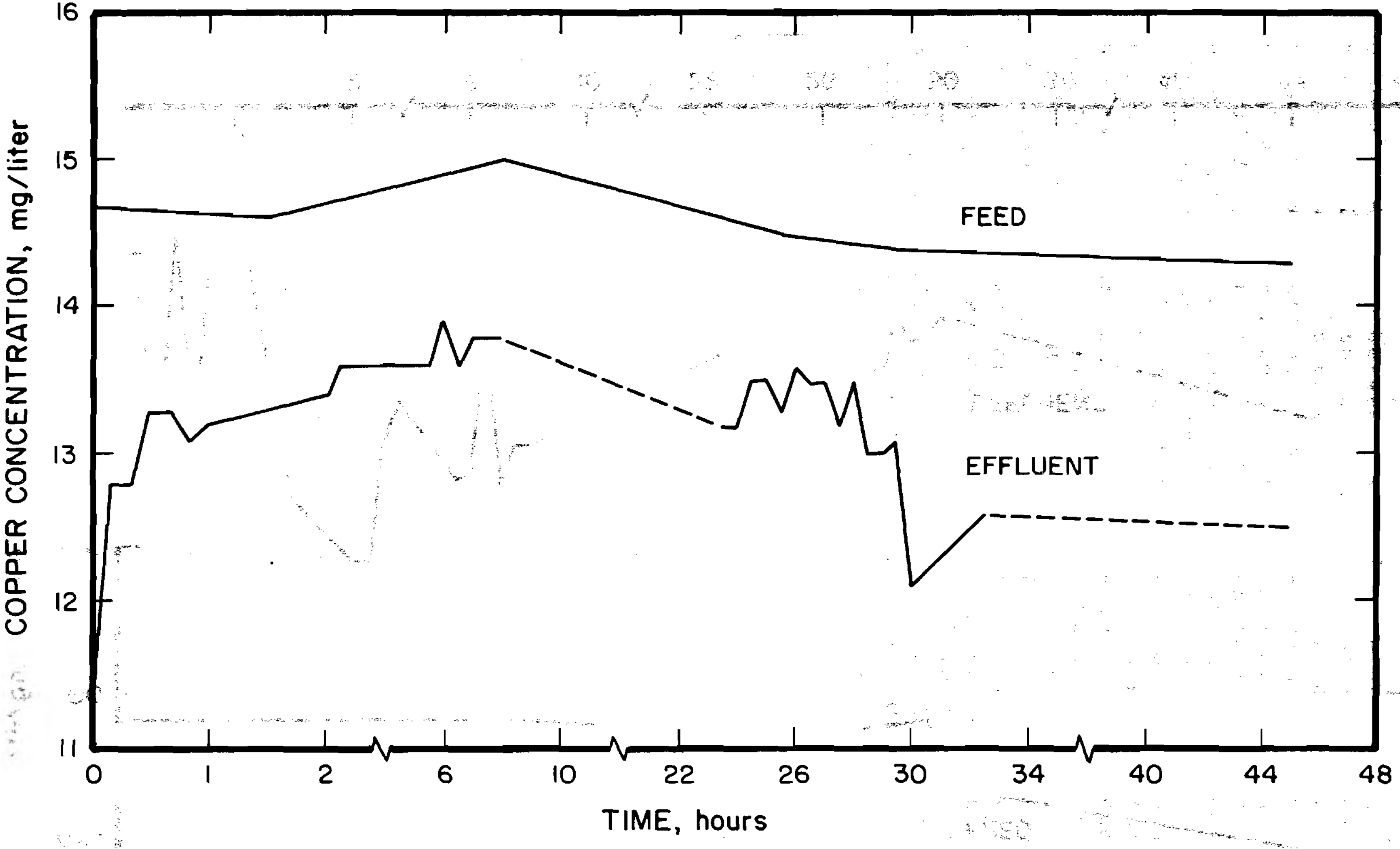


Figure 27 Variation in copper content during the field testing experiment

DISCUSSION

Mill tailing samples can be characterized, with regard to their effectiveness in the removal of metal ions from mine drainage, on the basis of the following interrelated properties:

1. Size Distribution
2. Mineralogical Composition
3. Surface Area
4. Capacity
5. Rate of Removal

The first three parameters, intrinsic properties of the tailing, may be indicative of the mill tailings effectiveness, but ultimately some direct measure is required. Consequently, the most direct and most meaningful of these parameters are the last two; capacity and rate.

For the purpose of comparison, the capacity of the mill tailing samples is taken under conditions where maximum loading is observed, i.e. 1.0 gpl, (in the case of iron) pH 1.8, and 60 minutes conditioning time. In most instances this condition represents a reasonable measure of the extent to which the mill tailing can remove metal ion contaminants. Also, the rate of removal is an important parameter, whose definition is not quite as arbitarary.

In complex systems such as those encountered in this study, many different types of reactions may be occurring. Three of the most probable reactions would be:

1. Adsorption on siliceous minerals
2. Precipitation of metal hydroxides due to the basicity of the tailing
3. Precipitation of metal hydroxides due to reaction with calcareous components of the tailing

Research has shown that adsorption of multivalent cations on oxide substrates occurs at specified values of pH depending on the cation involved (7). The mechanism appears to be controlled by the extent of hydrolysis of the cation, with the formation of hydroxy complexes being mandatory. The effect is illustrated in Figure 28 for the lead-alumina and iron-alumina systems. A similar effect for the adsorption of iron (III) was observed in these studies. At higher pH values, adsorption was faster and more complete.

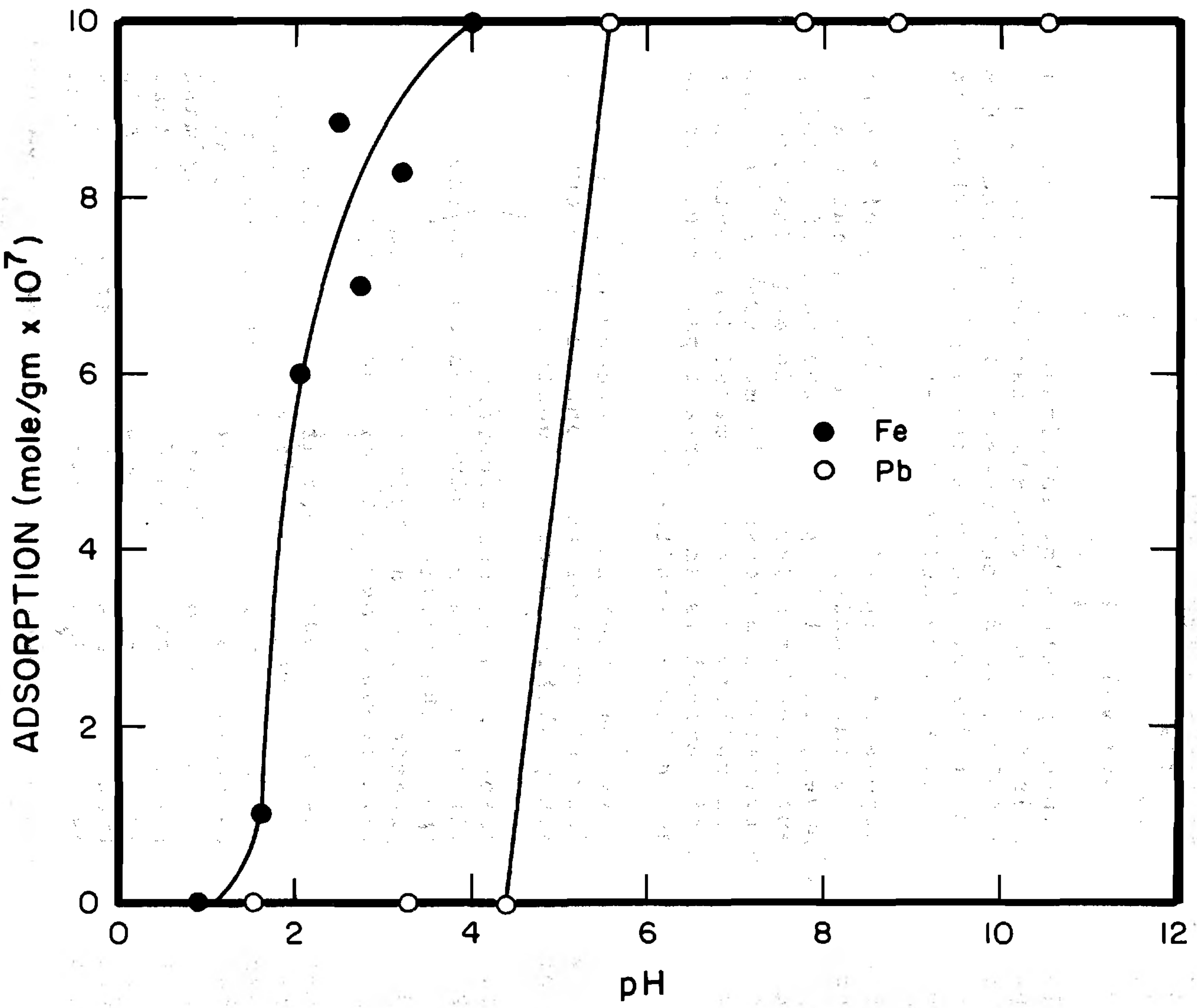


Figure 28 Adsorption of ferric iron and lead species on sapphire as a function of pH

In an adsorption process, the capacity of the substrate is limited by the surface area of the substrate in the absence of any multilayer adsorption or chemical reaction, which would be the case in these systems involving charged ions rather than neutral molecules. Consequently, the maximum capacity which could be achieved by an adsorption process is limited by surface area considerations. The average surface area of the mill tailing samples is 1.29 m2/g. Assuming close packing of dehydrated iron atoms on the surface, each with an effective parking area of 1.64 $\overset{o}{A}2$, the maximum adsorption which could be obtained would be 7.3 mg/g. For a partially hydrated ferricion the effective parking area would be approximately 4$\overset{o}{A}2$, which would correspond to a capacity of 3 mg/g. Most tailing samples exhibit a capacity of this order (average capacity = 9.8 mg/g) and with the exception of the Blaine tailing, the adsorption process could account for a good portion of the capacity observed in these systems.

The rate studies can be analysed in terms of the first mechanism. Taylor (10) referred to adsorption processes such as this as "activated: adsorption, represented by the following reaction;

$$S + A \underset{k_b}{\overset{k_f}{\rightleftarrows}} \; || \; S \cdot A$$

where

S is a surface reaction site
A is the adsorbate
S·A is the adsorbate on the surface

If θ represents the fraction of available surface covered, the rate of change of θ can be written:

$$\frac{d\theta}{dt} = (1 - \theta)A \cdot k_f - \theta k_b$$

where

k_f - specific rate constant for forward reaction
k_b - specific rate constant for backward reaction

The rate expression can also be written in terms of the equilibrium constant, K, for the adsorption reaction:

$$\frac{d\theta}{dt} = \frac{k_f}{K} \{K(A) - [K(A) + 1]\theta\}$$

As this equation indicates, the rate of adsorption would continually decrease with decreasing concentration of A and increasing θ. Most of the tailing samples responded in this fashion.

The second mechanism suggested, i.e. precipitation of metal hydroxide due to the inherent basicity, appears to be of rather minor importance. Most of the tailing samples are strictly siliceous and their acquired basicity comes from prior treatment in the mill. The tailing samples come from a variety of mills; complex lead - zinc, copper porphyry, and molybdenum, all of which make a flotation separation in alkaline solution. The alkalinity is generally controlled with either soda ash or lime, and in any event the reagent consumption rarely exceeds 4 lbs per ton. If these reagents were retained by the tailing, and used to remove metal ions by precipitation, the maximum capacity that could be achieved if this mechanism alone were operative would be 2 mg/g. Notice that the sum of the capacities predicted by adsorption, 7.3 mg/g, and by precipitation, 2 mg/g, is very close to the average capacity for all systems, 9.8 mg/g.

The final mechanism suggested is that observed in the case of the Blaine tailing sample which had definite quantities of calcareous minerals evidenced by the evolution of CO_2 in acid media. This mechanism is essentially the well-known limestone neutralization process. The capacity is strictly dependent on the carbonate content of the ore. Extremely high capacities can be obtained when this mechanism is operative, for it is a chemical reaction of major significance rather than a surface adsorption process. The high capacities observed suggest that this is the predominate mechanism for removal of contaminates by the Blaine Mill tailing.

For copper and zinc, capacities similar to that for iron were obtained with the exception of the Blaine tailing. The Blaine tailing did not exhibit the large capacity, which it had for iron.

Results from the continuous test in the laboratory, with the Blaine tailing were not as encouraging as the batch testing. The rather high effluent concentration of 600 mg/liter may be due to the short retention time of 1.29 minutes in the column.

The field test was not particularly encourageing. Some iron removal, 14%, and copper removal, 14%, was attained, but no aluminum could be removed. The field test was complicated further by the fact that a new sample of Blaine tailing had to be acquired. It appeared that this sample, unlike the one obtained previously via EPA in Denver, contained appreciable amounts of pyrite. Of course, a high pyrite content is detrimental to the object of the exercise in that pyrite will oxidize and generate more iron.

Another detrimental effect which was realized during the field test was the plugging of the reactor due to the precipitation of iron salts. From the results of this cursory field test, it appears that a stirred tank reactor would be much more effective than a packed column.

On the basis of the batch tests, in order to remove the iron from the Gennesse drainage (.720 gpl iron and 100 gallons per minute effluent) with Blaine tailing (100 mg/g capacity), 4.5 tons of tailing per day would be required. With a less effective tailing (10 mg/g capacity) in which removal is solely an adsorption process, 45 tons per day would be required. The above estimates are for properly designed reactors in which the batch test data can be duplicated.

ACKNOWLEDGMENTS

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REFERENCES

1. Anonymous, Coal Mine Drainage Research, Coal Mine Drainage Symposium III, Coal Industry Advisory Committee, Cincinnati, Ohio, 413 pages, (1970).

2. Anonymous, "Inert Gas Neutralizes Coal Mine Acid," New Scientist, London, 47 (709), 81, (1970).

3. Browning, J. E., "Freshening of Acid Mine Waters," Chemical Engineering, 77 (1), 40-42, (1970).

4. Deul M., Mihok, E. A., "Mine Water Research: Neutralization," U. S. B. M. Report of Investigation No. 6987, (1967).

5. Mihok, E. A., Deul M., Chamberlain, C. E., and Selnecai J. G., "Mine Water Research: The Limestone Neutralization Process," U. S. B. M. Report of Investigation No. 7191, (1970).

6. Sterner, J. J., and Conahon, H. A., "Ion Exchange Treatment of Acid Mine Drainage," Proceedings of Industrial Waste Conference, Part I, 101-108, (1968).

7. Fuerstenau, M. C., Elgillani D. A., and Miller, J. D., "Absorption Mechanism in Non-metallic Activation Systems," Trans. A. I. M. E., 247, p. 11, (1970).

8. Wayman, C. H., "Abatement Procedures Related to Acid Mine Drainage," Proceedings of Industrial Process Design for Water Pollution Control, Volume II, A.I.Ch.E., Water Committee 102, (1970).

9. Rouse, J., Private Communication, August 1969.

10. Taylor, H. S., J. American Chemical Society, 53, 578, 1931; Chem. Rev., 9, 1, (1931).

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Adsorption, Mill tailings, San Juan Mts. Colorado, Metal ions

27 *Abstract*

Eleven mill tailing samples from locations throughout the Rocky Mountain region were tested for their effectiveness in removal of dissolved contaminants from mine drainage. With the exception of the sample of the Blaine Mill tailing, the average capacity of the tailings tested was 9.8 mg of iron per gram of tailing with a range of capacities from 6 mg/g to 15 mg/g. In batch tests the Blaine mill tailing exhibited a capacity in excess of 100 mg of iron per gram of tailing.

From these studies it was concluded that for all tailing samples, with the exception of the Blaine tailing, removal was accomplished mainly due to hydrolytic adsorption of metal ions with a small contribution due to the inherent basicity of the tailing. In the case of the Blaine tailing, removal occurred via reaction with calcareous components of the sample.

Continuous column, or stationary bed tests, in the laboratory and in the field were not nearly as effective. During the field test no aluminum was removed from the mine drainage and only 14 percent of the iron and copper were removed. During the test the pH rose from 2.85 to 3.5.

It appears that for effective removal a stirred tank reactor will be required. If the results obtained in the batch test can be duplicated in the field, it is estimated that from 4.5 to 45.0 tons of tailing per day, depending on the capacity, would be required to remove iron from a mine drainage similar to the Gennesse. For a tailing similar to the Blaine tailing, approximately 200 lbs. of iron could be removed per ton of tailing.

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