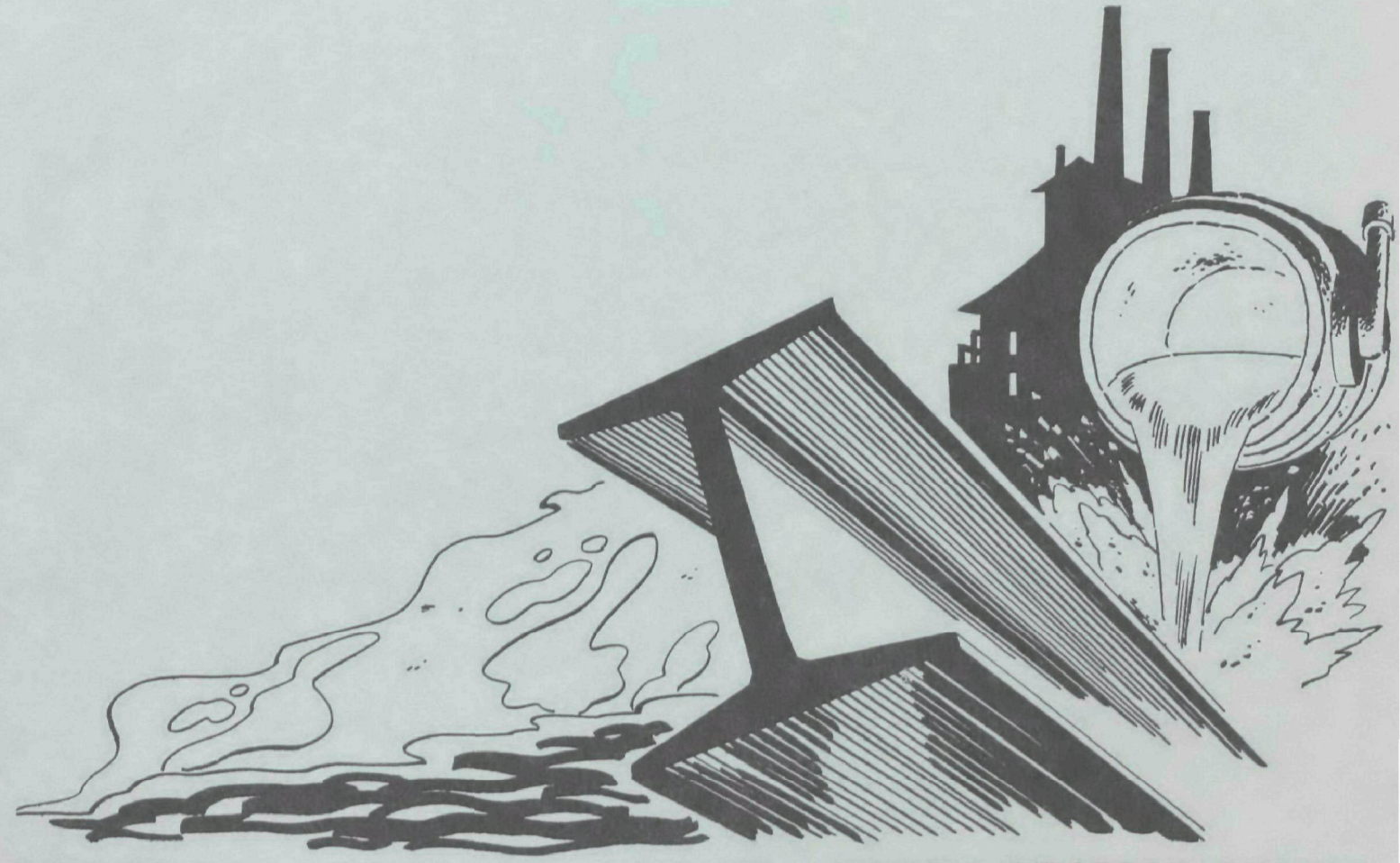
WATER POLLUTION CONTROL RESEARCH SERIES • 12010 DIM 08/70

Pyrite Depression by Reduction of Solution Oxidation Potential



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PYRITE DEPRESSION BY REDUCTION

OF

SOLUTION OXIDATION POTENTIAL

by

Department of Mineral Engineering

University of Utah

Salt Lake City, Utah 84112

for

ENVIRONMENTAL PROTECTION AGENCY
WATER QUALITY OFFICE

Grant Number 12010 DIM

December, 1970

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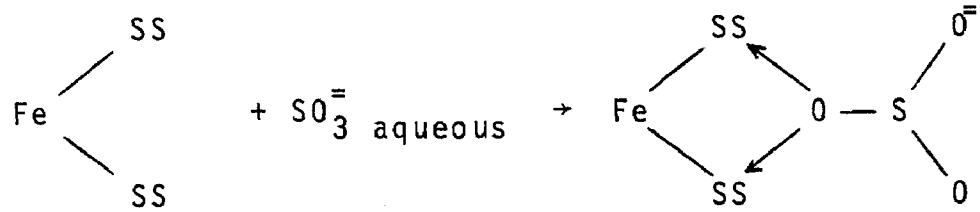
ABSTRACT

A study of pyrite depression by reducing agents with potassium ethylxanthate as collector indicates that pyrite may be depressed effectively in the flotation of both lead and copper sulfide ores without the use of poisonous cyanide salts. More specifically, the use of sodium sulfite as the depressant may result in metallurgical, economical, environmental and safety advantages over the poison, cyanide. For example, in the case of the copper ore, the best results with cyanide as the depressant were a rougher concentrate recovery of 90.2% and a grade of 4.3% Cu. However, when sulfite was used as the depressant for the same recovery a grade of 7.3% Cu was obtained.

Experimental results support the theory that dixanthogen is the collector species responsible for pyrite flotation. The study shows that pyrite depression is possible by maintaining a reduced solution oxidation potential thus preventing dixanthogen formation. Depression was effected with the following reducing agents and in all cases the results were similar; sulfite, sulfide, thiosulfate, hypophosphite and oxalate. The proposed mechanism of depression involves the adsorption of the reductant on surface active sites, thus preventing the adsorption and dissociation of molecular oxygen to nascent oxygen. In the case of sulfite the adsorption reaction is shown below:



Pyrite Surface Pyrite Surface

This report was submitted in fulfillment of Grant Number 12010 DIM between the Environmental Protection Agency (EPA) and the Grantee.

Key Words:

flotation

pyrite

depression

reducing agents

cyanide

sulfite

ethyl xanthate

oxidation potential

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CONCLUSIONS AND RECOMMENDATIONS

As was anticipated from the fact that dixanthogen is the collector species responsible for pyrite flotation, all reducing agents studied had the ability to depress pyrite when ethylxanthate was used as collector. Sulfite, a good reducing agent, appears to function exceptionally well as a pyrite depressant. Sulfite can be used as effectively as cyanide in galena-pyrite and chalcopyrite-pyrite ores with ethyl xanthate as the collector. In fact, sulfite exhibits no depressant effect on chalcopyrite, whereas excessive cyanide can completely depress chalcopyrite. In the case of the chalcopyrite-pyrite ore, a significant improvement in concentrate grade was obtained when sulfite rather than cyanide was used as the depressant. Equivalent metallurgical results were obtained with either sulfite or cyanide as depressants in the galena-pyrite ore.

Sulfite was shown to be potential determining for pyrite, which supports the mechanism proposed for pyrite depression by reducing agents. The solution potential reducing agents adsorb at the pyrite surface, preventing the adsorption and dissociation of molecular oxygen to nascent oxygen and in this manner, prevent oxidation of xanthate to dixanthogen and subsequent flotation. Meaningful oxidation potentials could not be obtained with a platinum electrode when oxyanion reductants were used to effect pyrite depression. However, the platinum electrode can be used as a monitor when sulfide

ion is used as the depressant.

Laboratory study has shown that poisonous cyanide salts need not be used, both from metallurgical and economical criteria, for the depression of pyrite in sulfide flotation systems. This is a most important conclusion in view of the recent interest of government and society on water pollution and safety. Consequently, it is recommended that this study be broadened in order to demonstrate that similar results can be obtained on an industrial scale. For such a study to be feasible an united effort and complete cooperation between the University, EPA , and industry is required.

INTRODUCTION

One of the principle means of processing the Nation's raw materials involves the technique of froth flotation. Froth flotation is the process whereby surfactants (termed collectors) are adsorbed on selected minerals in a particulate suspension. This renders the selected minerals hydrophobic and on passing air through the suspension, the hydrophobic particles concentrate in a froth column thus effecting their separation from the worthless gangue particles. Almost all sulfide ores are processed by the froth flotation technique, and in so doing the rejection or depression of pyrite, a common sulfide mineral, to the worthless gangue or tailing product is frequently required to make an effective separation. Industrially this is most readily accomplished with xanthate as collector for the valuable sulfides such as chalcopyrite and galena, and poisonous cyanide salts as a pyrite depressant, i.e., the cyanide salts prevent adsorption of the collector on the pyrite surface and subsequent flotation.

Dixanthogen, an oxidation product of xanthate, is the species responsible for pyrite flotation[1]. In most sulfide flotation systems pyrite depression is desired, therefore, it should be possible to use various chemicals to reduce the oxidation potential of the solution and depress pyrite by preventing the formation of the collector, dixanthogen. On this basis, the purpose of our research was to establish

that pyrite could be effectively depressed with non-toxic reducing agents which do not have the adverse ecological and emotional problems associated with the poisonous cyanide salts.

The first industrial technique of flotation[2,3] was to collect mineral particles in an oily layer which could then be separated from the gangue and water. The oil flotation procedure has been replaced by a method known as froth flotation, where bubbles carrying mineral particles rise to the surface and are removed in the froth, leaving the gangue behind.

The observation that different collectors changed flotation results and the patenting of xanthate, dithiocarbonate, in 1925 increased the use of flotation as a separation technique in mineral processing operations. Attention was then centered on means of floating one sulfide mineral away from others. This was accomplished by using various chemical reagents as depressants and activators. The depressants allowed one or more minerals to float while suppressing others with the gangue, while the activators caused otherwise unfloatable minerals to become floatable.

The first depressants were alkalis and cyanide compounds which were followed by many organic and inorganic compounds. The depressant effect of alkalis was investigated by Wark and Cox[5], and the depressant effect of cyanide has been the topic of many investigations[5-9].

Gaudin[10] has shown that many anions act as depressants for sulfide minerals, but little information on mechanisms was given. The mechanisms for depression of sulfide minerals have remained obscure, because the mechanisms for flotation have been obscure. This is evidenced by the number of theories proposed to explain the flotation mechanisms[11-14] Gaudin[11] proposed that the adsorption of xanthate on sulfide minerals was the result of an ion exchange mechanism. Wark[12] proposed that xanthates adsorb on a sulfide mineral by exchanging with hydroxyl and sulfur ions on the surface. Mellgren[15] presented evidence which supports a theory of insoluble salt formation between the collector and the mineral as a mechanism for flotation. Another mechanism, given by Cook and Nixon[14], is the chemical adsorption of a neutral molecule on the surface.

The mechanism for xanthate flotation of pyrite has been considered extensively[1,16-20]. Recently, Fuerstenau[1] showed that the oxidation product, dixanthogen, is the species responsible for pyrite flotation when xanthate is used as the collector. Majima and Takeda[18] verified the existence of dixanthogen on pyrite with infrared spectroscopy. Most probably dixanthogen is formed by adsorbed nascent oxygen oxidation of xanthate.

Since the pyrite flotation mechanism has been well established, it should be possible to analyze the depression of pyrite. The cyanide depression mechanism of pyrite has

been determined[6]. However, the mechanism of pyrite depression with other depressants, especially reducing agents, has not been analyzed in light of the recent theory advanced for pyrite flotation. Because of the environmental and safety problems presented by cyanide depression, research was initiated to determine the flotation response of pyrite in the presence of non-toxic reducing agents.

EXPERIMENTAL TECHNIQUES

The investigation included the four following techniques: flotation experiments with singular minerals, zeta potential experiments, oxidation potential measurements, and froth flotation experiments with ore samples.

Reagents

The reagents as discussed here, will apply to all of the experiments in this investigation.

Commercial potassium ethylxanthate (KEX) was purified by dissolving the xanthate in a minimum amount of acetone and recrystallizing the xanthate by the addition of cold petroleum ether[20]. After recrystallization the material was filtered, washed with petroleum ether, and dried. This purification method gives a purity of better than 99 percent. The purified xanthate was stored in an airtight container in a refrigerator until used.

Deionized, distilled water was used in all experiments except for the froth flotation experiments on ore samples, where tap water was used.

Pure pyrite mineral specimens and the galena-pyrite ore were obtained from Park City, Utah. Pure galena was obtained from Minerals Unlimited. The chalcopyrite-pyrite ore was typical of the southwestern copper porphory ores.

All of the chemicals used in this investigation were of reagent grade quality or better.

Flotation Experiments with Singular Minerals

A modified Hallimond tube flotation cell[21] was used to determine the effect of certain reducing agents on the flotation response of pyrite and galena with potassium ethylxanthate as the collector. The apparatus, described in Figure 1, consisted of a fritted-glass bottom tube through which air was controlled by a manometer, constant head reservoir, and a gas measuring burette. A magnetic stirrer with a teflon-coated stirring bar was used to maintain constant agitation.

The following procedure was used for both pyrite and galena mineral samples:

1. The mineral was dry-ground with a porcelain mortar and pestle, then sized with Tyler standard sieves within 24 hours prior to the flotation test.

2. A sized 1.0 gram sample was used as the flotation sample.

3. The flotation sample was deslimed 5 times with deionized water prior to each test.

4. Deionized water, xanthate, and reducing agent were mixed to yield the desired concentration of 130 milliliters total volume.

5. The desired solution pH was obtained with either KOH or HCl.

6. The deslimed mineral was added to the solution.

7. The pulp was conditioned for 3 minutes.

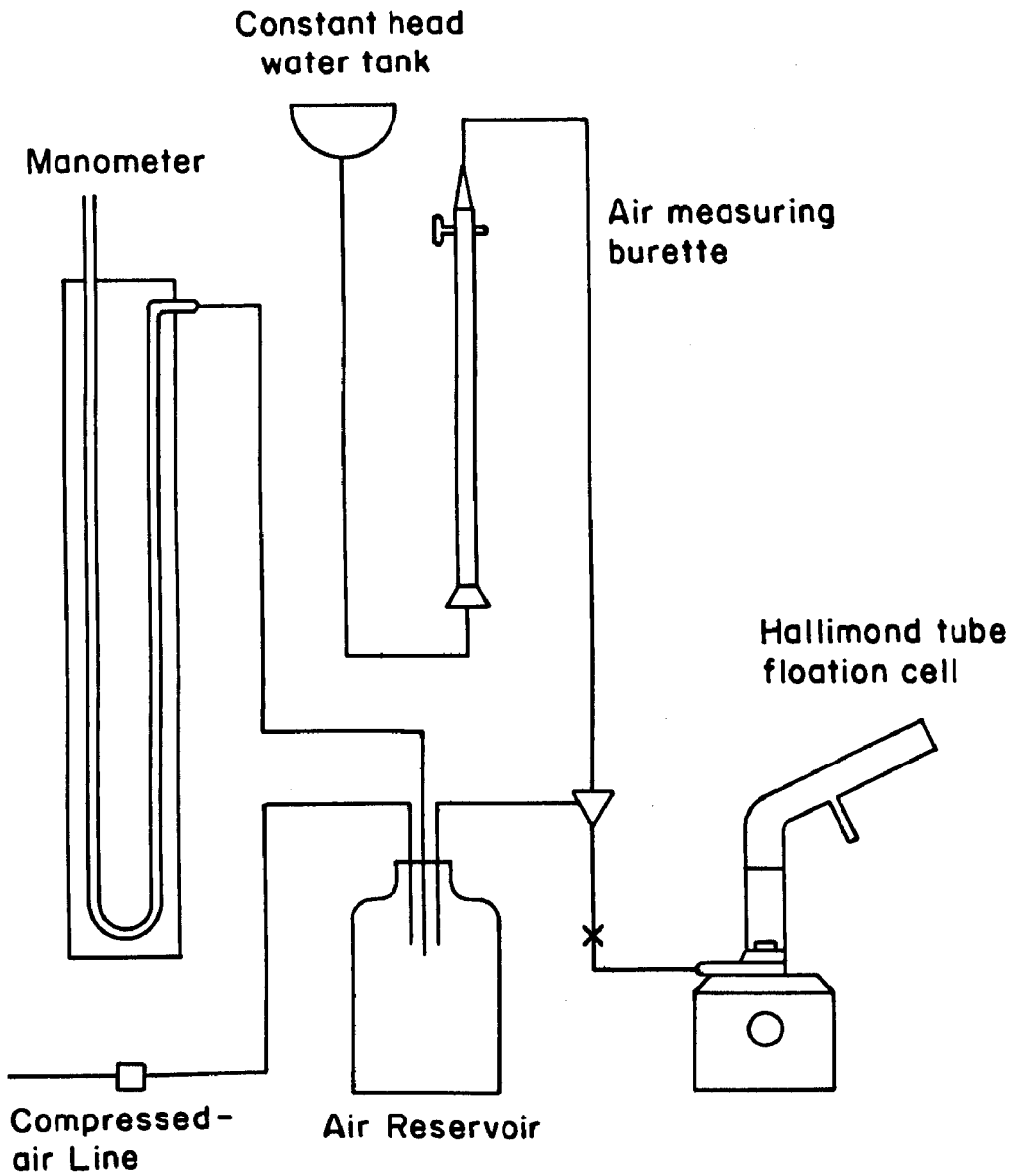


Figure 1. Schematic diagram of flotation apparatus.

8. The pH of the pulp was measured and recorded after conditioning.

9. The pulp was transferred to the Hallimond tube flotation cell and floated for 2 minutes at constant agitation and at 70 milliliters per minute air flow rate.

10. The pH was measured after flotation to determine if a significant change occurred.

11. The concentrate and tailing products were dried, weighed and the percent recovery calculated.

Zeta Potential Experiments

The zeta potential of pyrite was determined at various concentrations of sodium sulfite and at various pH values. The pH at which the zeta potential of the pyrite surface reached zero was determined graphically, and this pH is called the zero-point-of-charge (ZPC).

The equipment consisted of a Zeta Meter to determine the zeta potential at the pyrite surface and a Beckman Zeromatic II pH meter to measure pH. A magnetic stirrer with a teflon-coated magnetic stirring bar was used to maintain agitation during conditioning.

The following procedure was used to obtain the desired sample conditions for the zeta potential determinations.

1. The pyrite was dry-ground with a porcelain mortar and pestle, then screened through a 200 mesh Tyler sieve.

2. The minus 200 mesh pyrite was weighed out into 50 milligram samples.

3. Deionized water and sodium sulfite were added to a 150 milliliter beaker to give a total volume of 100 milliliters and the desired concentration of sodium sulfite.

4. The 50 milligram pyrite sample was added to the water and sodium sulfite solution.

5. The pH of the sample was adjusted with either HCl or KOH.

6. The sample was conditioned for 3 minutes to approximate the flotation conditions of the pyrite.

7. The pH of the sample was measured and recorded.

8. The resulting suspension was decanted into a plexiglass electrophoretic cell, electrodes inserted, and placed under the microscope.

9. A potential was applied across the electrodes.

10. The average time for a particle to move horizontally between two lines of the grid was recorded. This time was translated into zeta potential from standard charts. The measured zeta potentials were plotted against pH, and a ZPC was determined from the resulting curve.

Oxidation Potential Measurements

The apparatus used in these measurements consisted of a Beckman Zeromatic II pH meter, a calomel reference electrode, a platinum electrode, a glass electrode, magnetic stirrer with teflon-coated magnetic stirring bar, and a 250 milliliter beaker.

The following procedure was used in preparing the samples

and making measurements.

1. The pyrite was dry-ground with a porcelain mortar and pestle, then sized with Tyler sieves.

2. A 1.0 gram sample, 100 X 200 mesh, was used as in flotation experiments.

3. Deionized water, xanthate, and reducing agent were mixed to yield the desired concentrations of 130 milliliters total volume.

4. The pH was adjusted with either KOH or HCl.

5. The deslimed pyrite was added to the above solution.

6. The pulp was conditioned for 3 minutes.

7. The pH was measured and recorded.

8. The solution oxidation potential was measured and recorded.

9. The Eh was calculated from the cell potential, $E_h = E_{cell} + E_{ref}$.

Froth Flotation Experiments with Ore Samples

Experimental equipment consisted of an ore crusher, a rod mill, a Wemco froth flotation cell, a Beckman Zeromatic II pH meter, and a Mettler top load electronic balance.

The following procedure was used on both the galena and the chalcopyrite ores.

1. Approximately 100 lbs of ore was crushed, then coned and quartered, and split with a riffle until approximately 500 gram samples resulted.

3. 500 grams of a sample was weighed out on the top

loading balance and placed in the rod mill with 333 milliliters of tap water.

3. The ore was ground at 60 percent solids in the rod mill for 3 minutes and the resulting pulp was transferred to the flotation cell with 1667 milliliters of tap water.

4. Varying amounts of sodium sulfite or sodium cyanide and 0.05 pounds per ton KEX were added to the cell.

5. The pH was adjusted and the pulp was conditioned at 20 percent solids for 5 minutes.

6. 3 drops of Aerofroth 65 were added, the air was turned on, and the sample was floated for 8 minutes.

7. The concentrate and tailing products were dried, weighed, and analyzed to test the effectiveness of the depressant.

EXPERIMENTAL RESULTS

The flotation response of pyrite and galena in a Hallimond cell with KEX as the collector and various reducing agents as depressants was investigated. Zeta potential and solution oxidation potential measurements were made on these systems. Flotation tests with lead and copper ore samples were made to compare the effectiveness of sodium cyanide and sodium sulfite as depressants for pyrite. The experimental data from these tests are presented in this section.

Flotation Experiments with Singular Minerals

Various reducing agents at different concentration levels were tested to determine their ability to depress pyrite and to establish the mechanism for depression with KEX as the flotation collector.

The flotation response of pyrite with KEX in the presence of various additions of sodium sulfite is shown in Figure 2. When no sodium sulfite is present, complete depression is effected above pH 10: whereas, with increasing sulfite additions the pH for depression is lowered to what appears to be a minimum of pH 5 for additions of 10^{-3} M and greater.

The flotation response of pyrite with KEX in the presence and absence of zinc sulfite is shown in Figure 3. When zinc sulfite is present, complete depression is effected above pH 5.

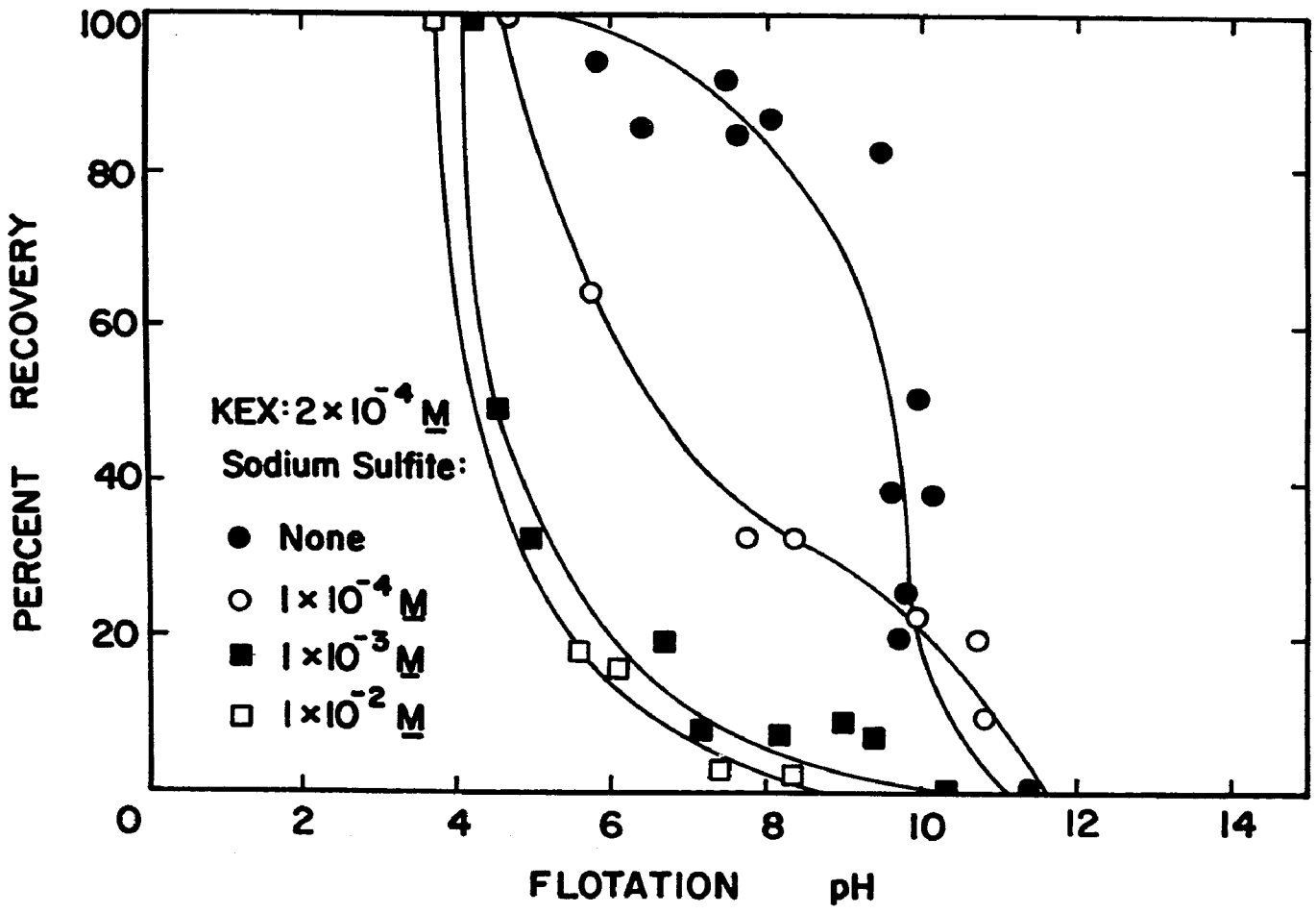


Figure 2. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2 x 10^{-4} M KEX and at four levels of addition of sodium sulfite.

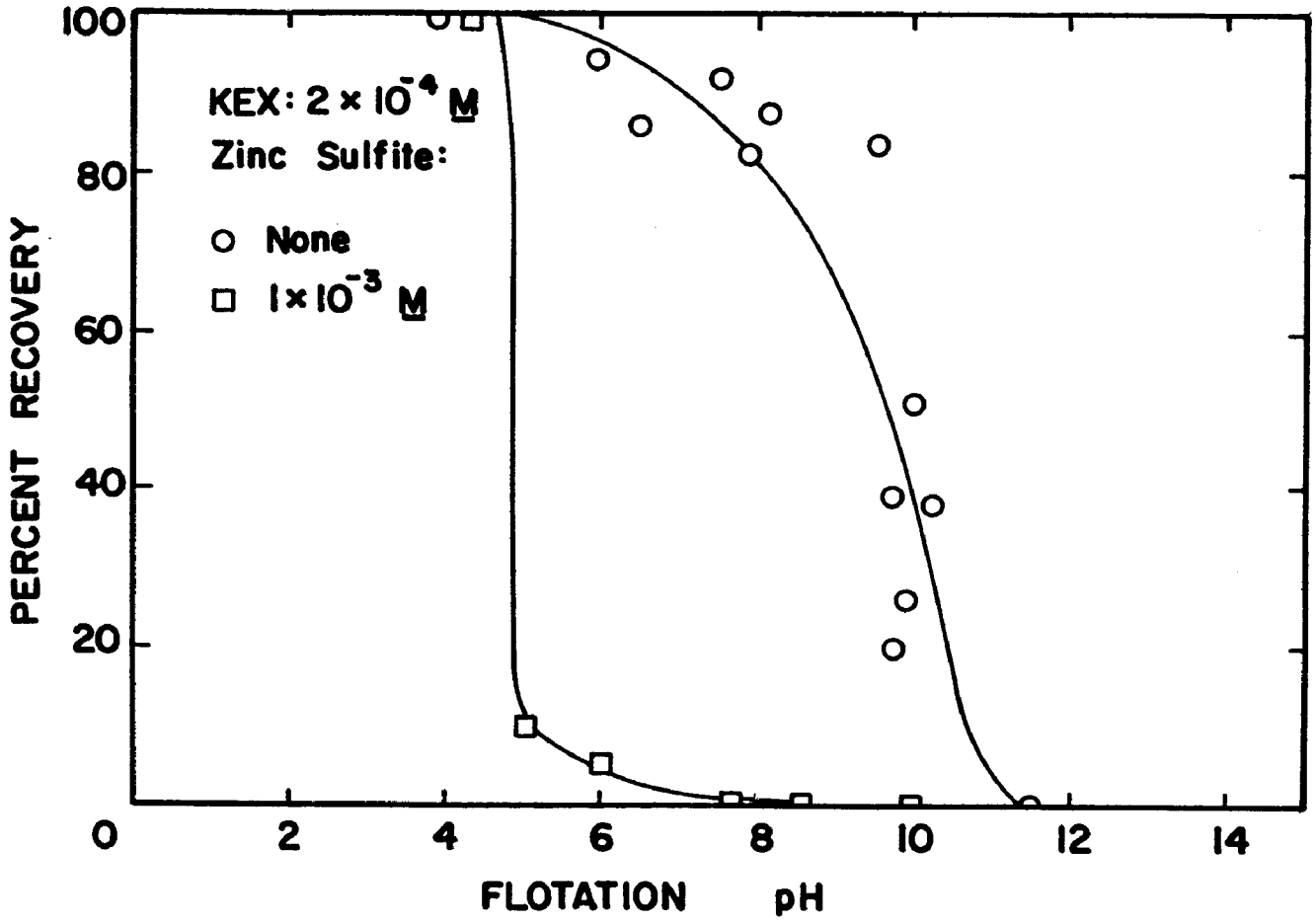


Figure 3. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2 x 10^{-4} M KEX in the presence and absence of zinc sulfite.

The flotation response of pyrite with KEX in the presence of various additions of sodium sulfide is shown in Figure 4. Addition of 10^{-3} M sodium sulfide is required to depress pyrite, while additions of 10^{-5} M sodium sulfide have no effect on the flotation response.

The flotation response of pyrite with KEX in the presence and absence of sodium thiosulfate is shown in Figure 5. Sodium thiosulfate acts as a depressant at pH 7 and above, but shows little effect below pH 7.

The flotation response of pyrite with KEX in the presence and absence of sodium hypophosphite is shown in Figure 6. Sodium hypophosphite is a pyrite depressant above pH 6, but shows little effect on pyrite below pH 6.

The flotation response of pyrite with KEX in the presence of various additions of sodium oxalate is shown in Figure 7. Sodium oxalate is not as effective as the other reducing agents in pyrite depression. Depression occurs only above pH 8.

Figures 2 thorugh 7 show that sulfite is one of the most effective depressants tested. These figures aloo show that the best pyrite depression occurs in basic media and that below pH 4.5, no depression is observed with any depressant.

Figure 8 indicates that the effectiveness of sodium sulfite is long-lasting, in that pyrite is depressed as well, or even better, after a ten minute conditioning time

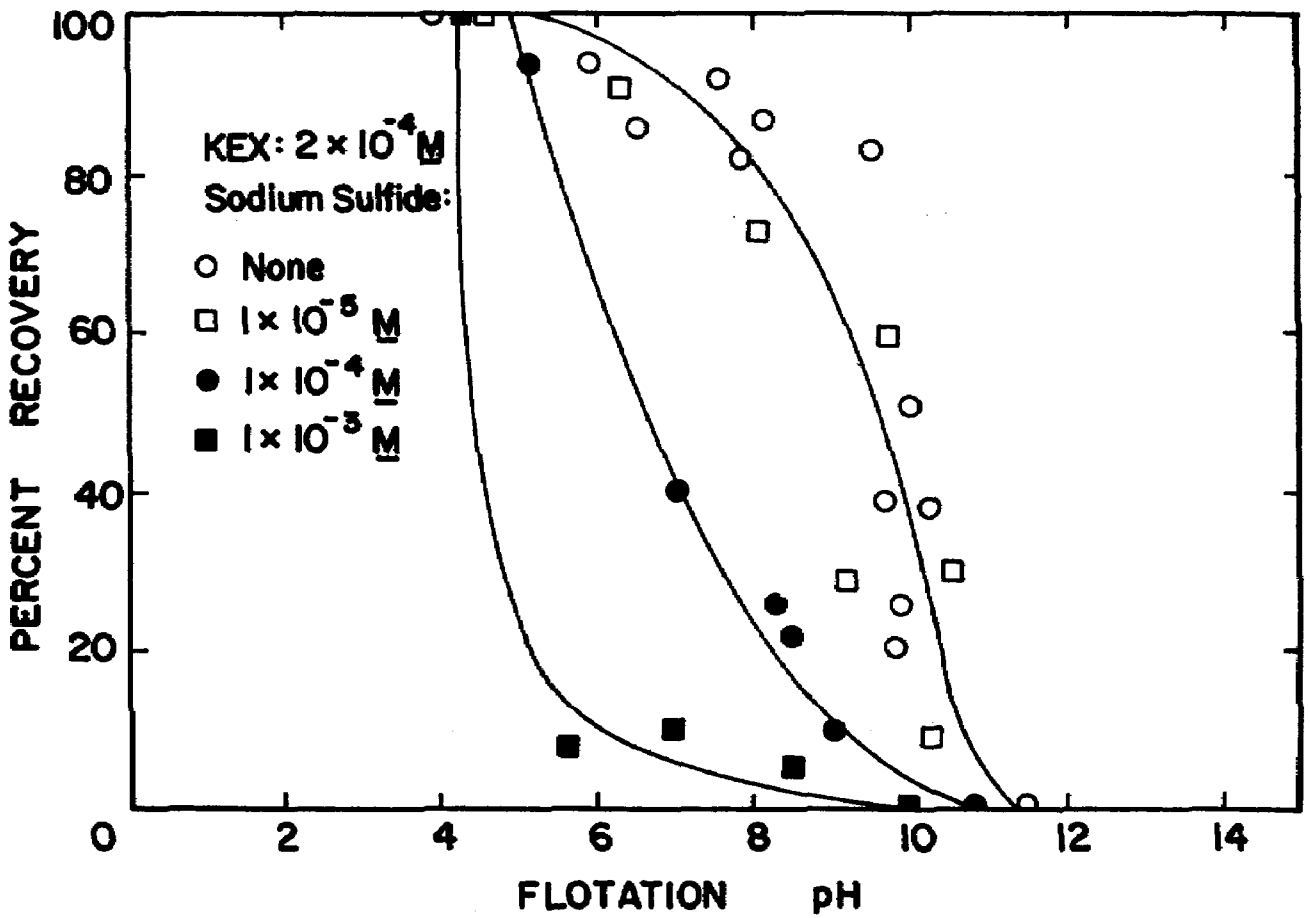


Figure 4. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2 x 10^{-4} M KEX, and at four levels of addition of sodium sulfide.

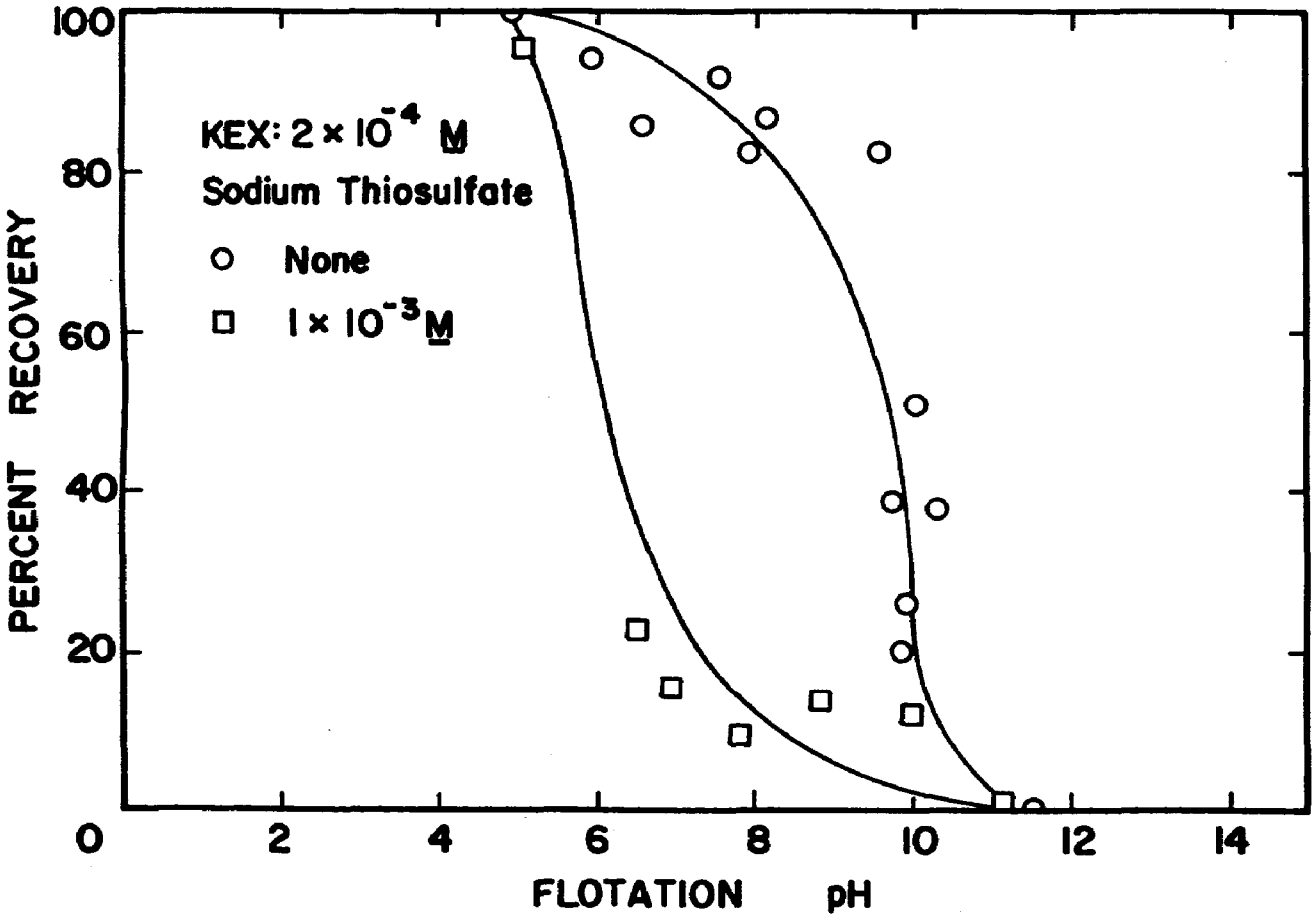


Figure 5. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2 x 10^{-4} M KEX in the presence and absence of sodium thiosulfate.

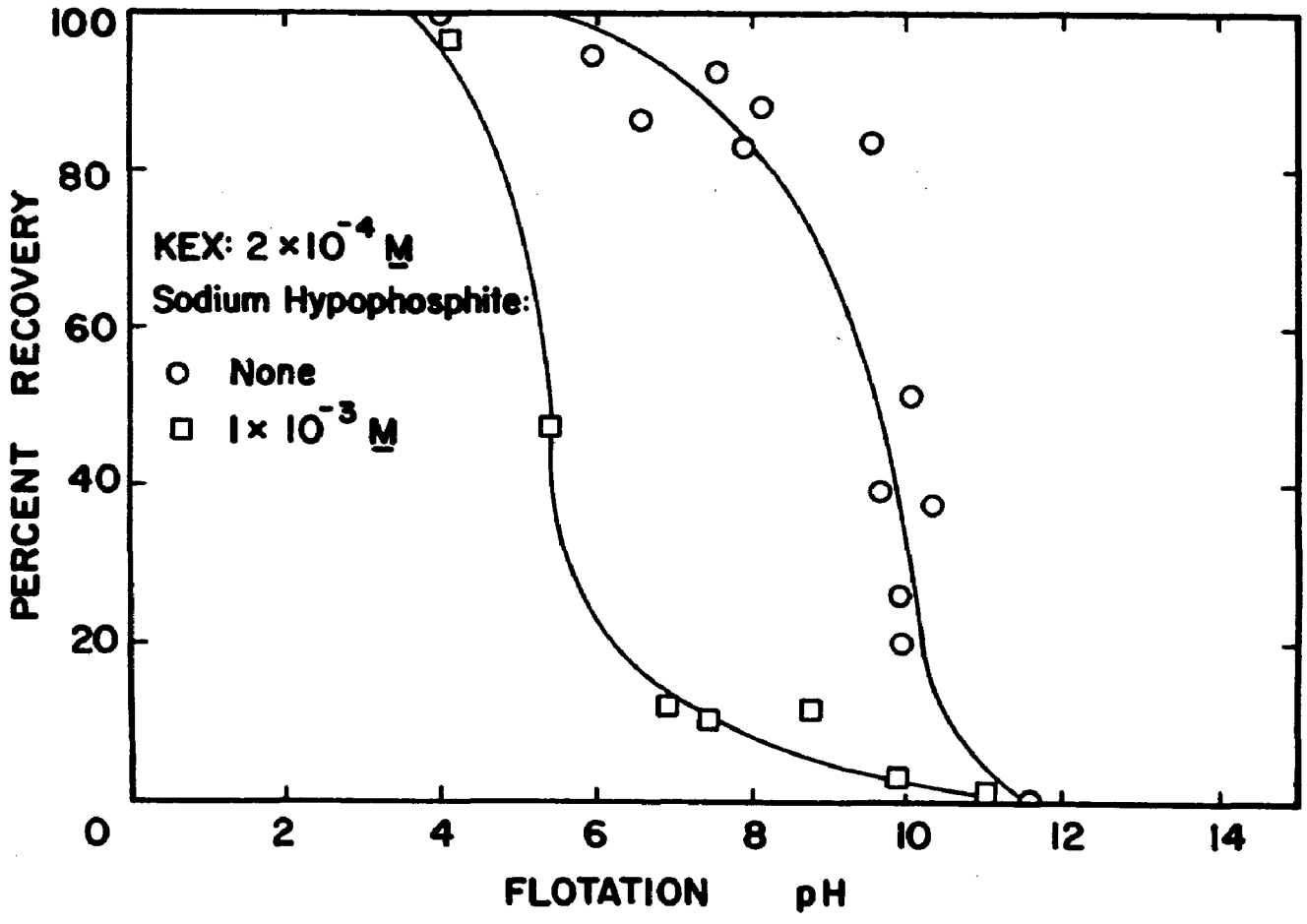


Figure 6. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2×10^{-4} M KEX in the presence and absence of sodium hypophosphite.

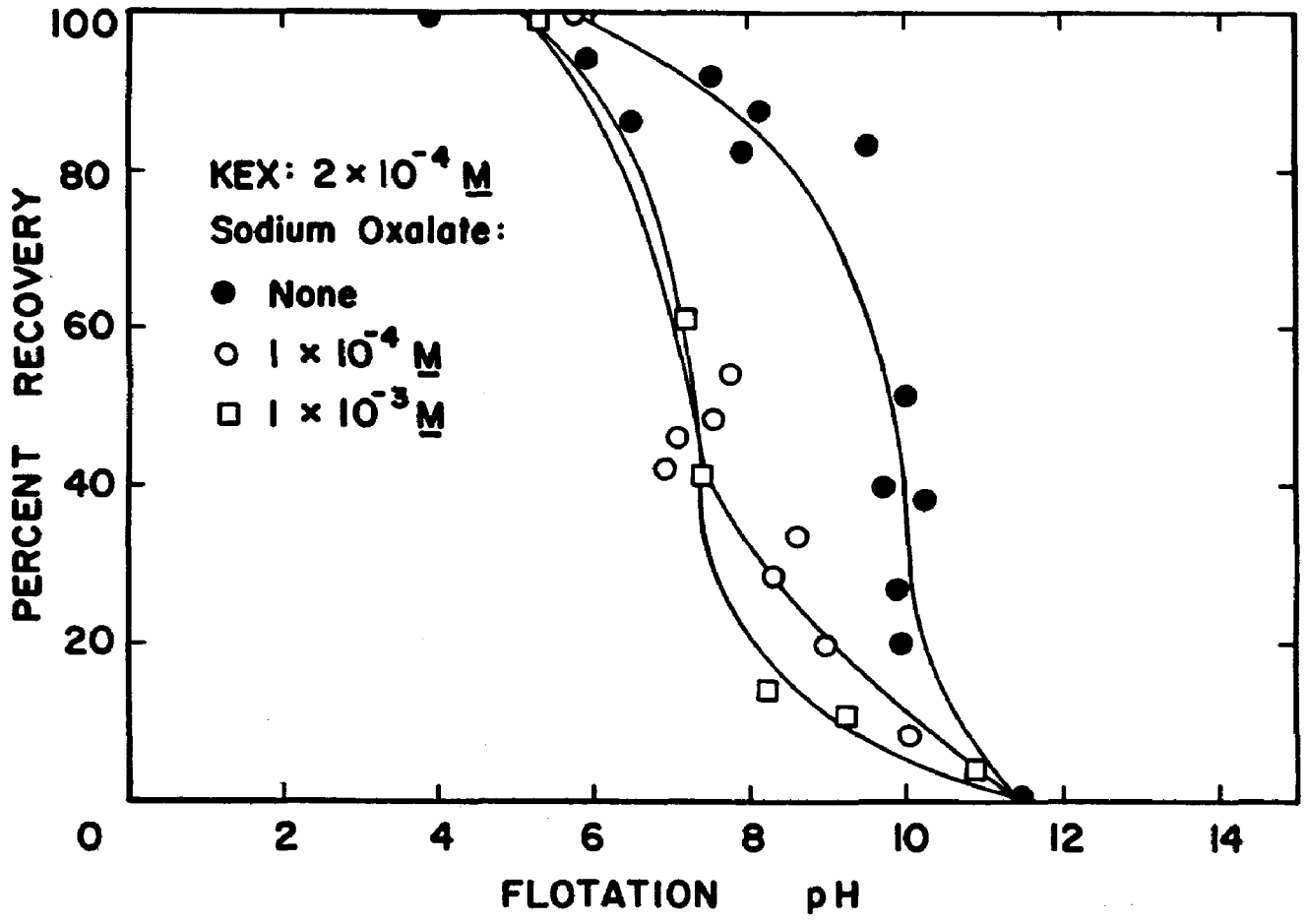


Figure 7. Flotation recovery of pyrite, 100 x 200 mesh as a function of pH with 2 x 10^{-4} M KEX and at three levels of addition of sodium oxalate.

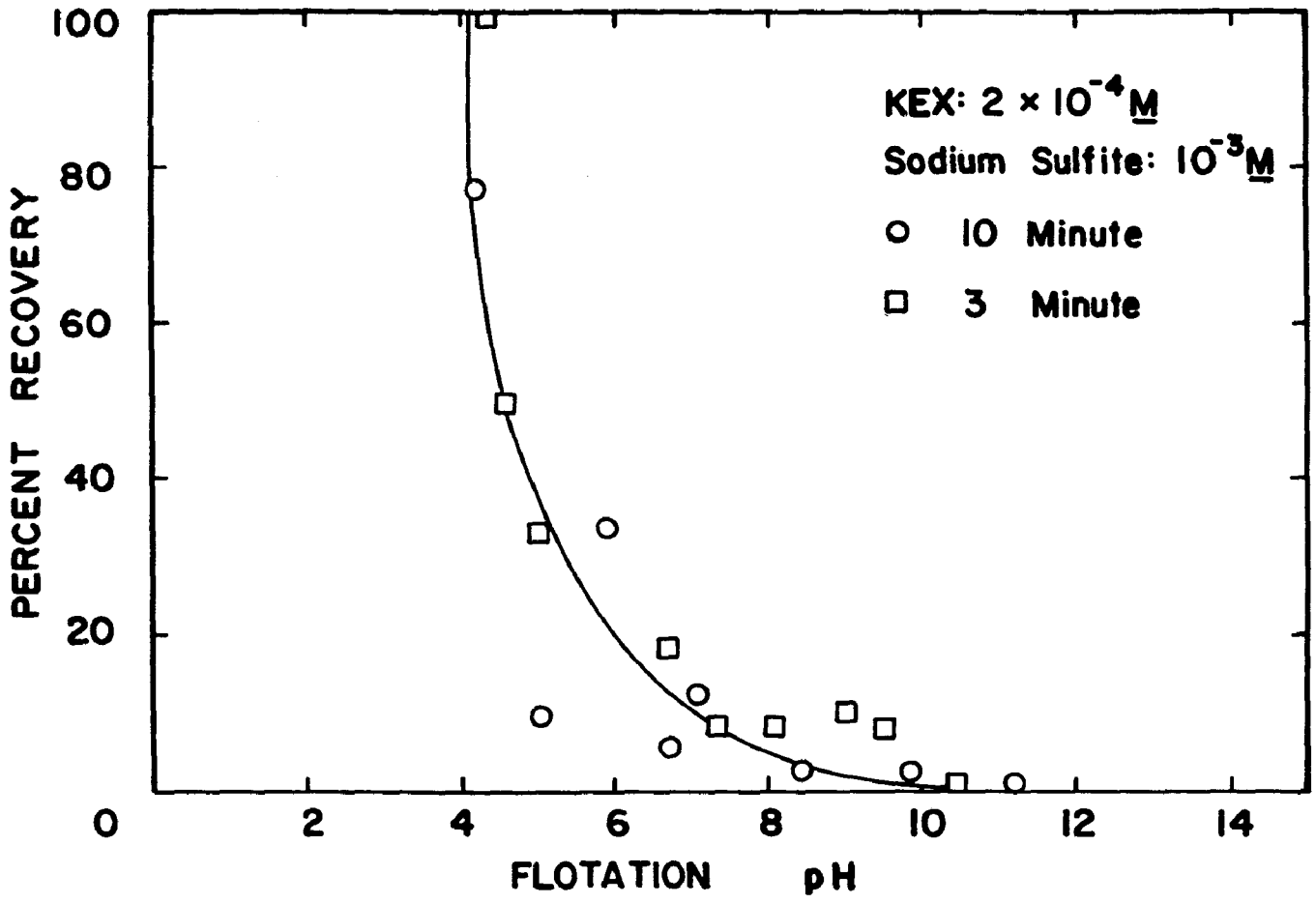


Figure 8. Flotation recovery of pyrite, 100 x 200 mesh, as a function of pH with 2×10^{-4} M KEX and 1×10^{-3} M sodium sulfite for two different conditioning times.

as it was after a three minute conditioning time.

As can be seen in Figure 9, pyrite flotation response does not change considerably from a KEX concentration of 2xx 10^{-4} mole per liter to a KEX concentration of 5 x 10^{-5} mole per liter. This determination was made because the ore samples were floated at a KEX level of about 5 x 10^{-5} mole per liter.

Figures 10 and 11 illustrate that the size of the pyrite particles are relatively unimportant in the sodium sulfite depression system.

Oxyanion reductants do not affect the flotation response of galena, as Figure 12 illustrates. The galena floats as well in the presence of the reductants as in their absence.

Zeta Potential Experiments

The zeta potential of pyrite in the absence of sulfite and at two levels of sulfite addition was determined as a function of pH. See Figure 13. It appears that the sulfite anion has a special affinity for the pyrite surface, in that the ZPC is pH 7 with no sulfite addition, pH 6 with 10^{-4} M sulfite, and pH 5 with 10^{-3} M sulfite.

Oxidation Potential Measurements

Solution oxidation potential measurements of each pyrite flotation system were attempted; however, in oxyanion reductant systems, it was not possible to obtain meaningful measurements. No variation in the platinum-calomel cell potential could be detected, even though the concentration

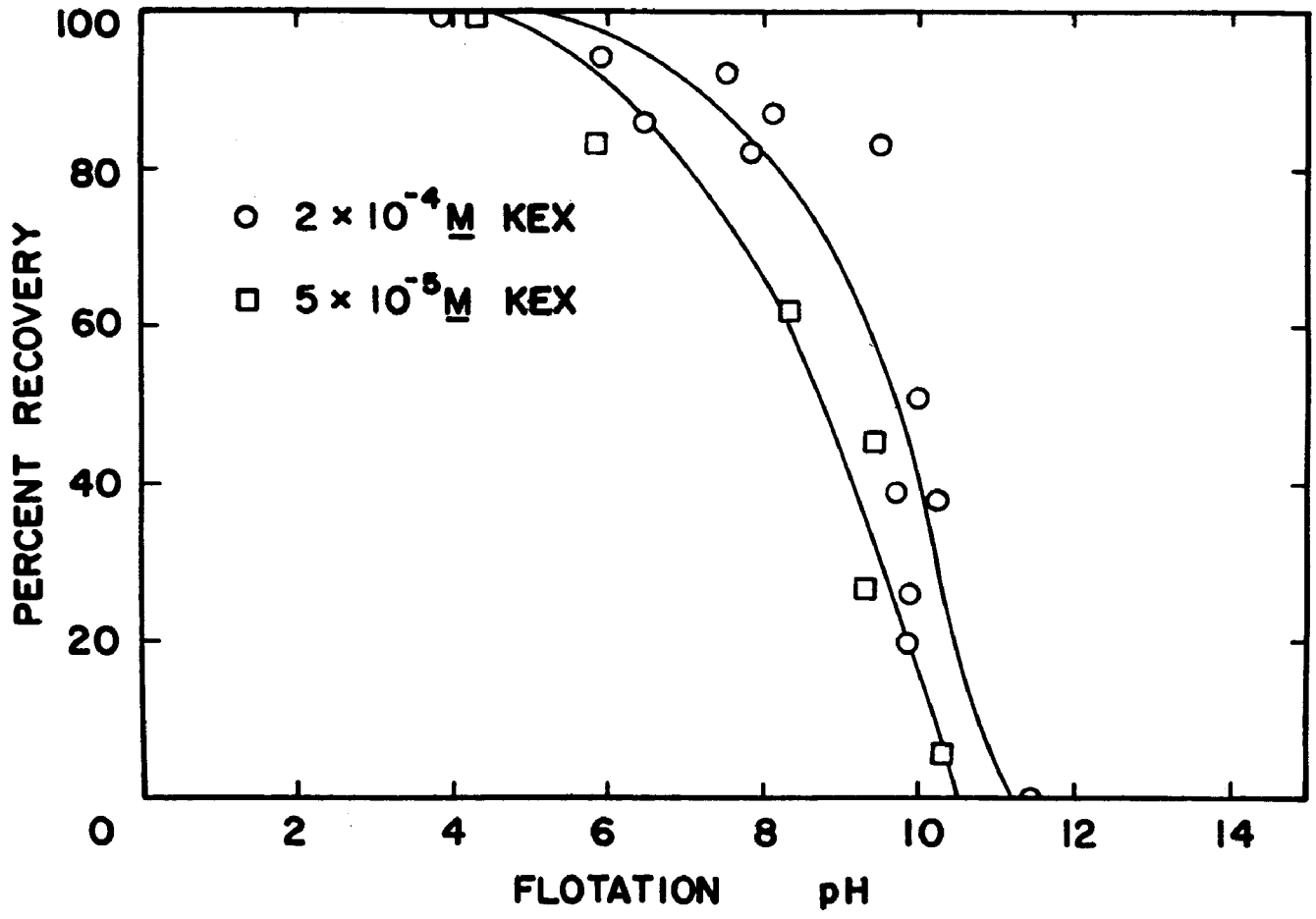


Figure 9. Flotation recovery of pyrite, 100 x 200 mesh as a function of pH at two levels of addition of KEX.

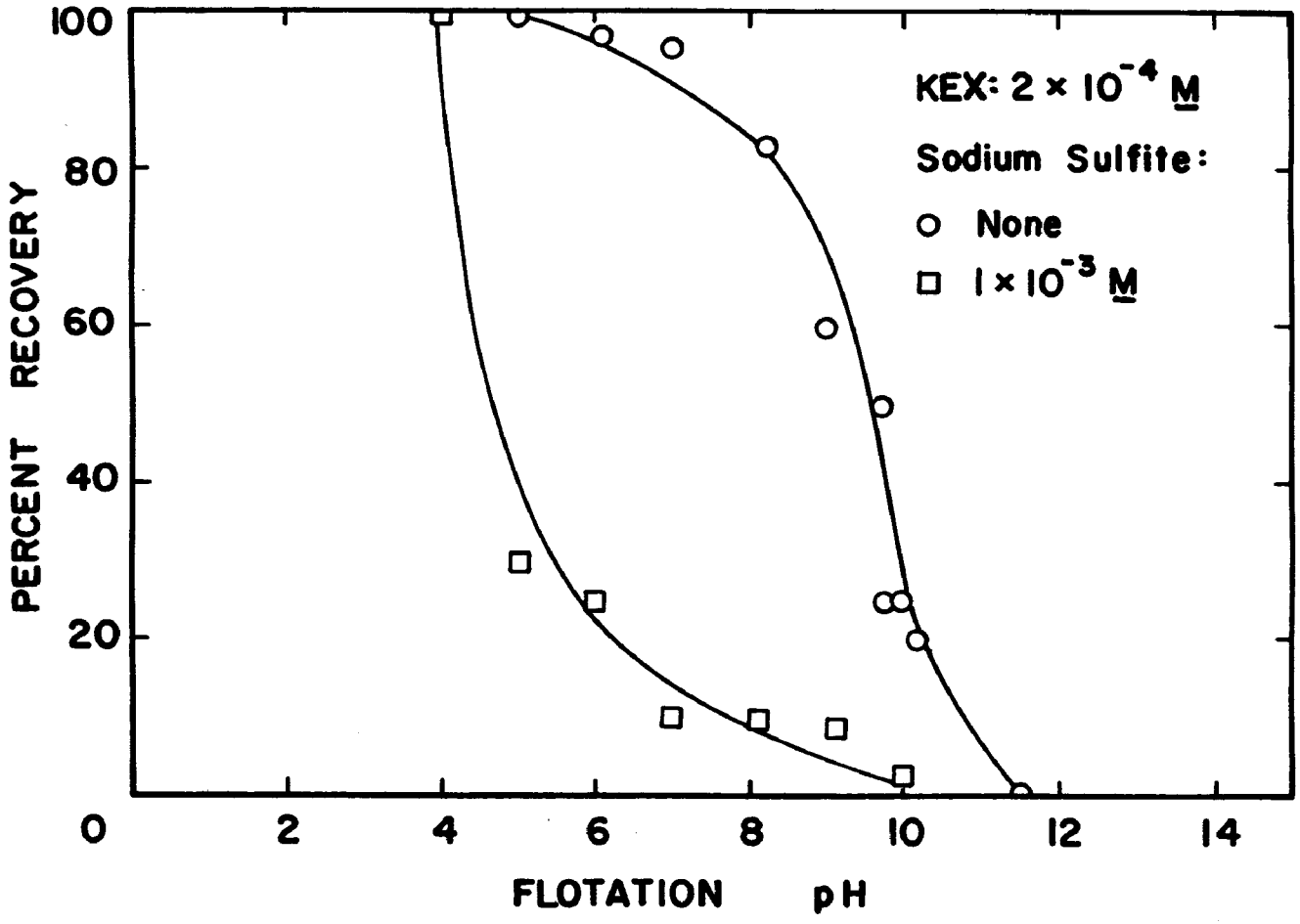


Figure 10. Flotation recovery of pyrite, 65 x 100 mesh, as a function of pH with 2×10^{-4} M KEX in the presence and absence of sodium sulfite.

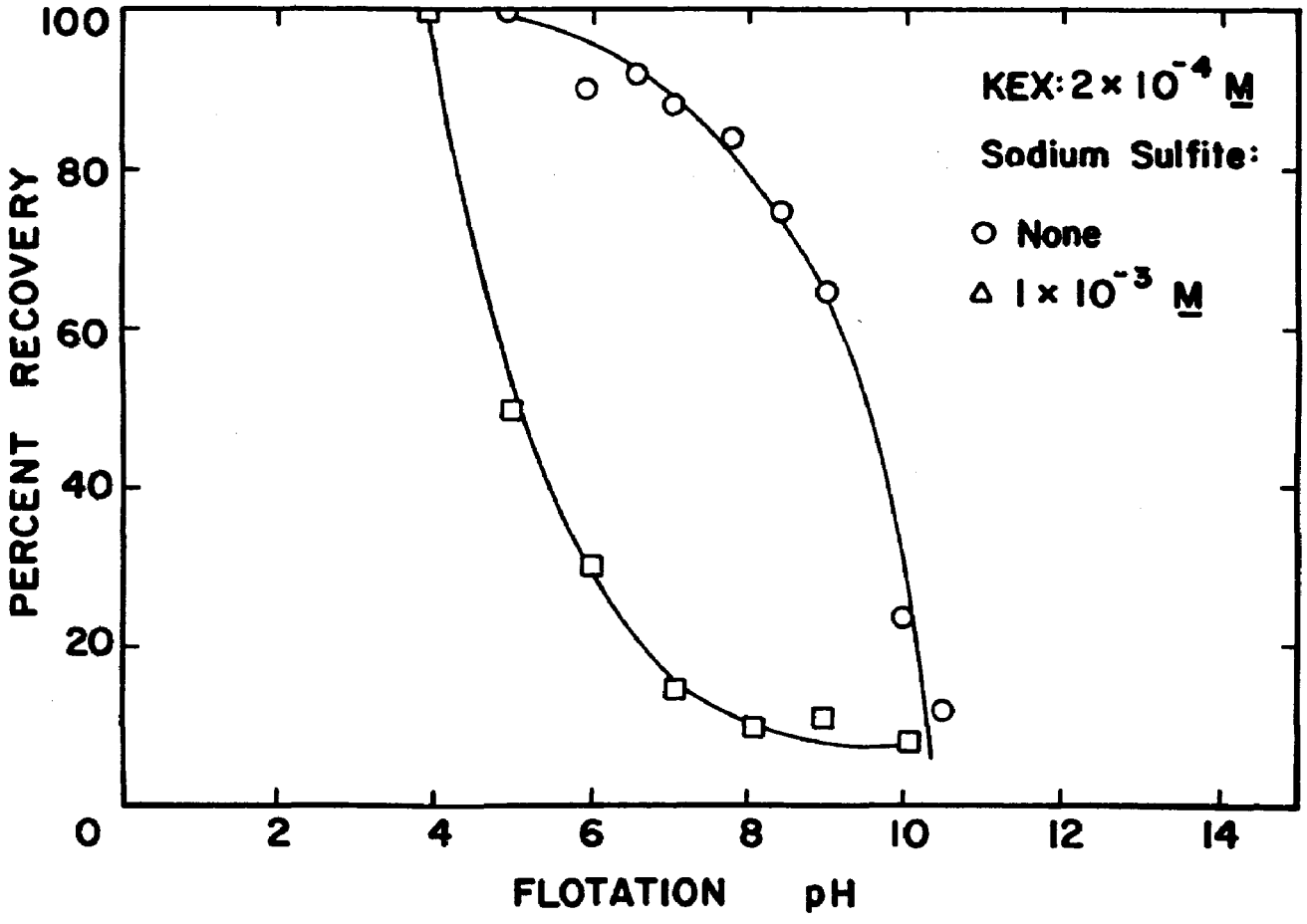


Figure 11. Flotation recovery of pyrite, minus 200 mesh, as a function of pH with 2 x 10^{-4} M KEX in the presence and absence of sodium sulfite.

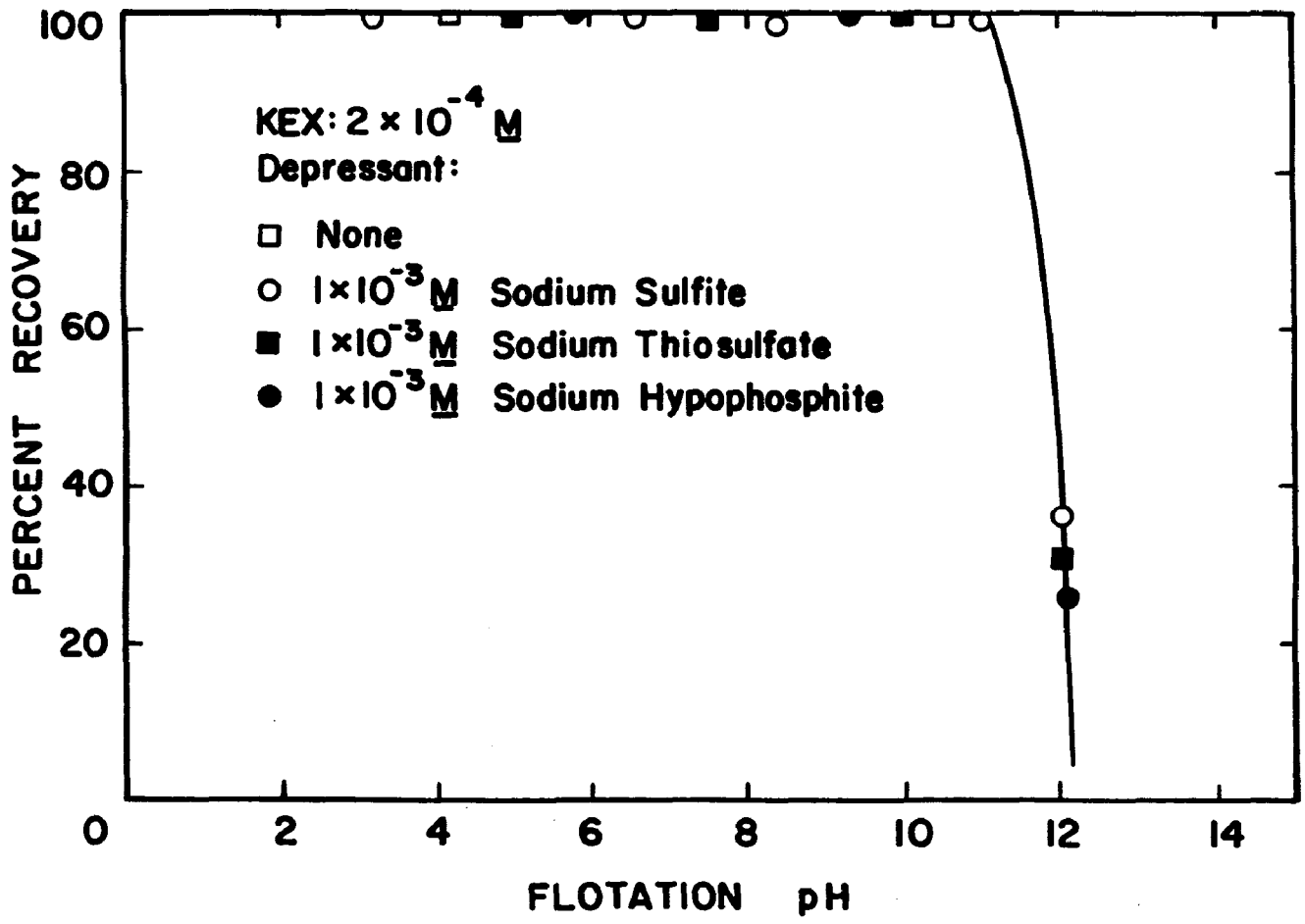


Figure 12. Flotation recovery of galena, 100 x 200 mesh, as a function of pH with 10^{-3} M additions of several reducing agents and 2 x 10^{-4} KEX.

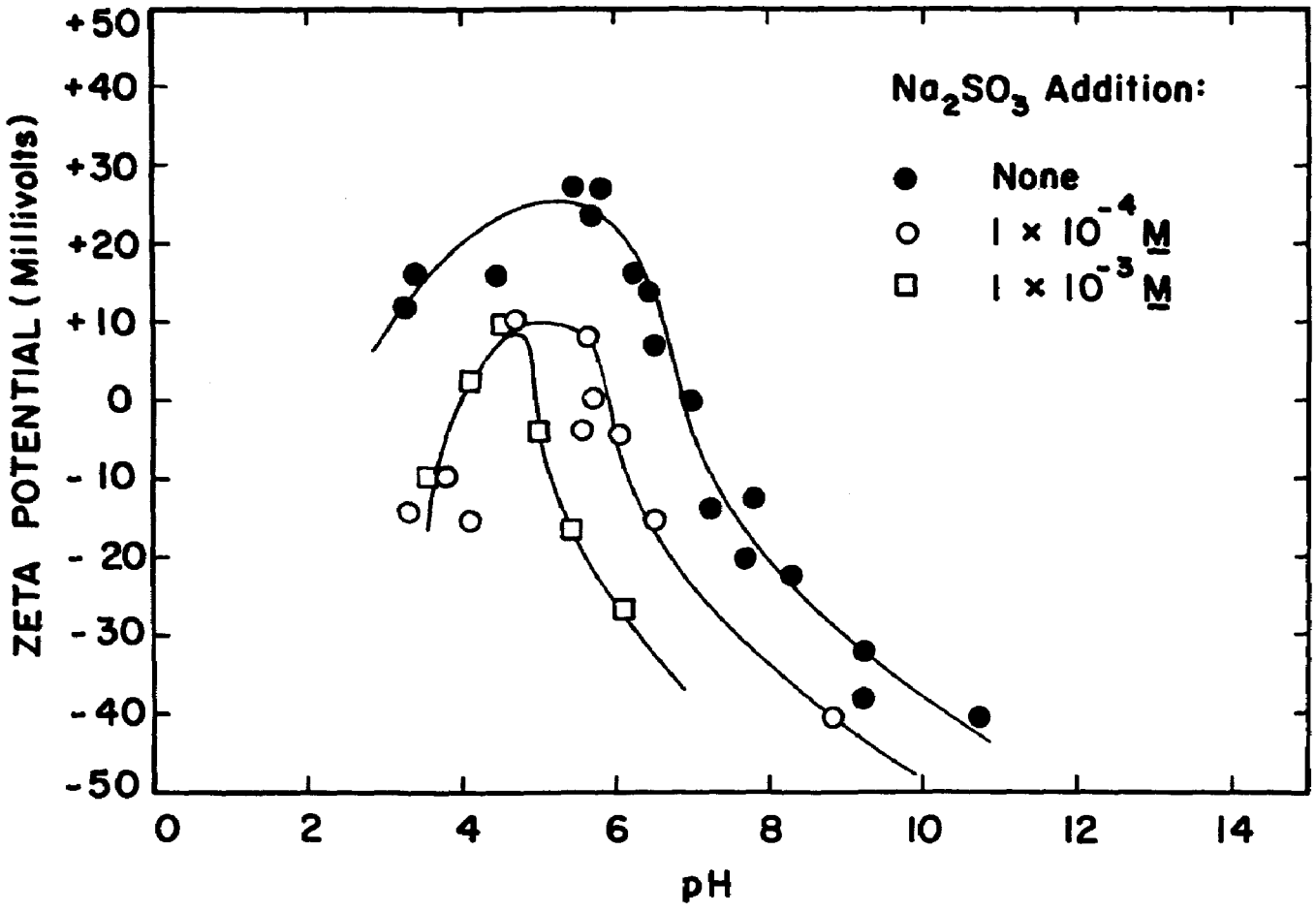


Figure 13. Zeta potential of pyrite as a function of pH in the absence and presence of various additions of sodium sulfite.

of reductant was changed by several orders of magnitude. Meaningful solution oxidation potential readings were obtained in the sodium sulfide system, as illustrated in Figure 14. The potential readings in this figure have been converted to Eh (hydrogen electrode reference), and are plotted against pH. The dotted line drawn through the data represents the 50 percent recovery isotherm, as determined from flotation experiments. Above the dotted line, good flotation response is obtained and below the dotted line, poor flotation response is obtained.

Froth Flotation Experiments with Ore Samples

Tables I and II show the flotation results of the chalcopyrite-pyrite ore when sodium cyanide and sodium sulfite, respectively, were the depressants. By comparing these two tables the relative effectiveness of each depressant can be determined. The columns labeled Fe Units and Cu Units, are weights of the respective elements based on a total weight of 100 grams. The distribution percentages of Fe and Cu show that sodium sulfite is just as effective as sodium cyanide for depressing pyrite in a chalcopyrite ore. Graphical representation in Figures 15 and 16 show that Fe percent recovery falls off with increasing depressant addition in both cyanide and sulfite systems. This means that both sodium cyanide and sodium sulfite can effectively depress pyrite.

Comparison of the Cu percent recovery of both curves,

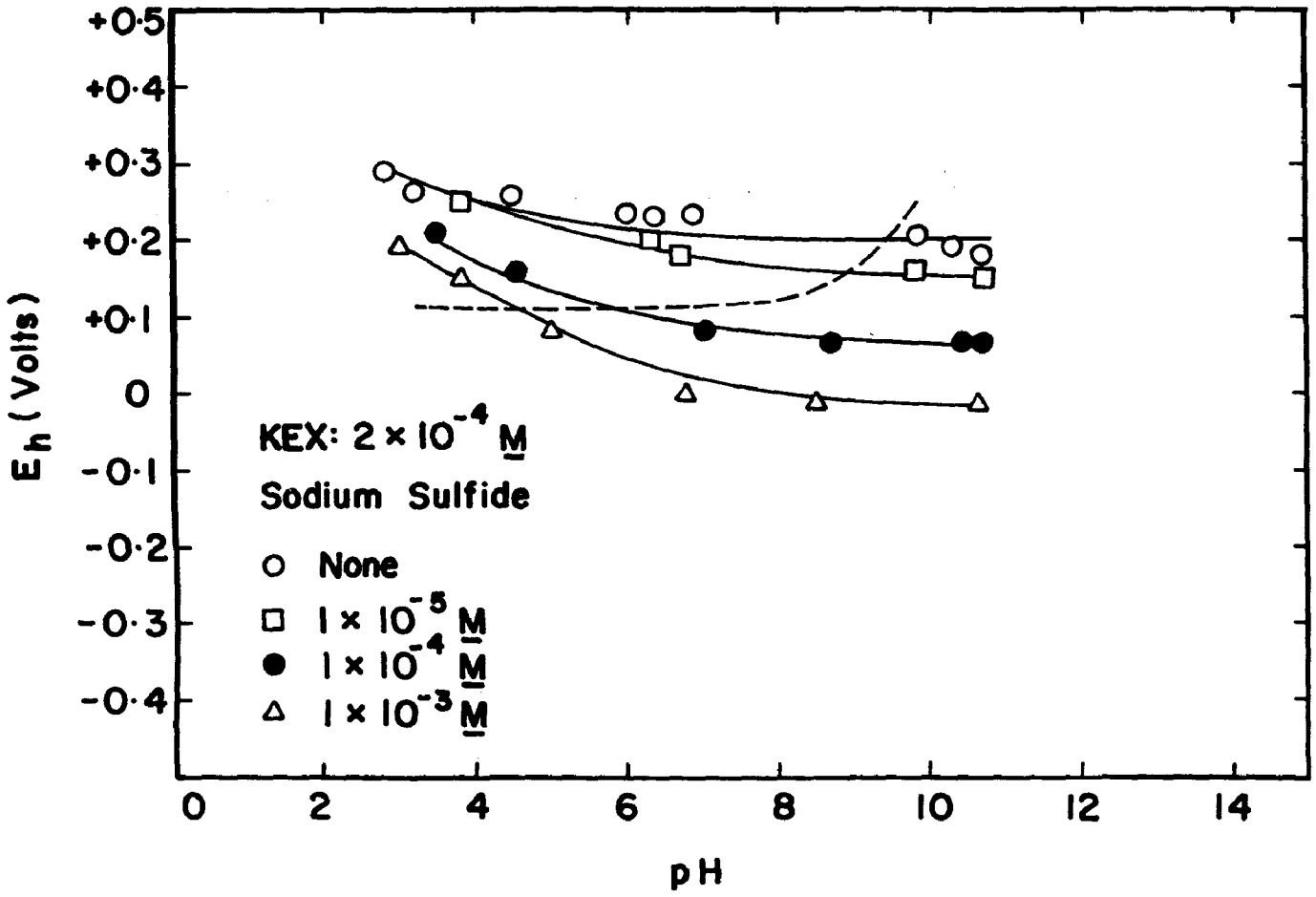


Figure 14. Solution oxidation potential as a function of pH, pyrite (100 x 200 mesh), 2 x 10^{-4} M KEX, and various levels of addition of sodium sulfide (European Convention).

TABLE I

Experimental Flotation Results Obtained With Chalcopyrite-Pyrite Ore With 2.0 lb per ton CaO and Various Amounts of NaCN Depressant

pH	Depressant Amount	Product	Product Wt, grams	Wt,%	Fe,%	Cu,%	Fe Units	Cu Units	Fe Distribution,%	Cu Distribution,%
		Concentrate	82	16.6	20.4	4.30	3.39	0.710	60.9	90.5
		Tail	412	83.4	2.6	0.09	2.17	0.075	39.1	9.5
8.5	None	Total		100.0			5.56	0.785	100.0	100.0
		Concentrate	72	14.5	15.7	4.30	2.26	0.620	47.8	90.2
	0.05 lb	Tail	425	85.5	2.9	0.08	2.46	0.067	52.2	9.8
8.65	per ton	Total		100.0			4.72	0.687	100.0	100.0
		Concentrate	60	12.0	16.6	4.60	2.00	0.560	26.1	84.2
	0.10 lb	Tail	443	88.0	6.4	0.12	5.67	0.106	73.9	15.8
8.65	per ton	Total		100.0			7.67	0.666	100.0	100.0
		Concentrate	40	8.5	9.3	2.30	0.74	0.180	15.6	31.0
	0.50 lb	Tail	434	91.5	4.6	0.67	4.00	0.580	84.4	69.0
8.80	per ton	Total		100.0			4.74	0.760	100.0	100.0

TABLE II

Experimental Flotation Results Obtained With Chalcopyrite-Pyrite Ore Using Various Amounts of Sodium Sulfite Depressant at pH 8

Depressant Amount	Product	Product Wt, grams	Wt,%	Fe,%	Cu,%	Fe Units	Cu Units	Fe Distribution,%	Cu Distribution,%
	Concentrate	53	10.7	26.8	5.90	2.84	0.620	58.3	90.2
	Tail	443	89.3	2.3	0.08	2.04	0.070	41.7	9.8
None	Total		100.0			4.88	0.690	100.0	100.0
	Concentrate	55	11.0	24.4	5.80	2.68	0.640	56.8	90.2
0.25 lb	Tail	443	89.30	2.3	0.08	2.04	0.070	43.2	9.8
per ton	Total		100.0			4.72	0.710	100.0	100.0
	Concentrate	44	8.9	28.0	7.30	2.46	0.640	26.0	89.9
0.50 lb	Tail	453	91.1	7.7	0.08	7.00	0.072	74.0	10.1
per ton	Total		100.0			9.46	0.712	100.0	100.0
	Concentrate	43	8.7	23.8	6.20	2.04	0.536	31.6	82.0
0.75 lb	Tail	453	91.3	4.9	0.13	4.44	0.118	68.4	18.0
per ton	Total		100.0			6.48	0.654	100.0	100.0
	Concentrate	39	7.8	28.0	7.70	2.18	0.600	14.1	86.0
1.00 lb	Tail	461	92.2	14.5	0.10	13.34	0.092	85.9	13.4
per ton	Total		100.0			15.52	0.692	100.0	100.0

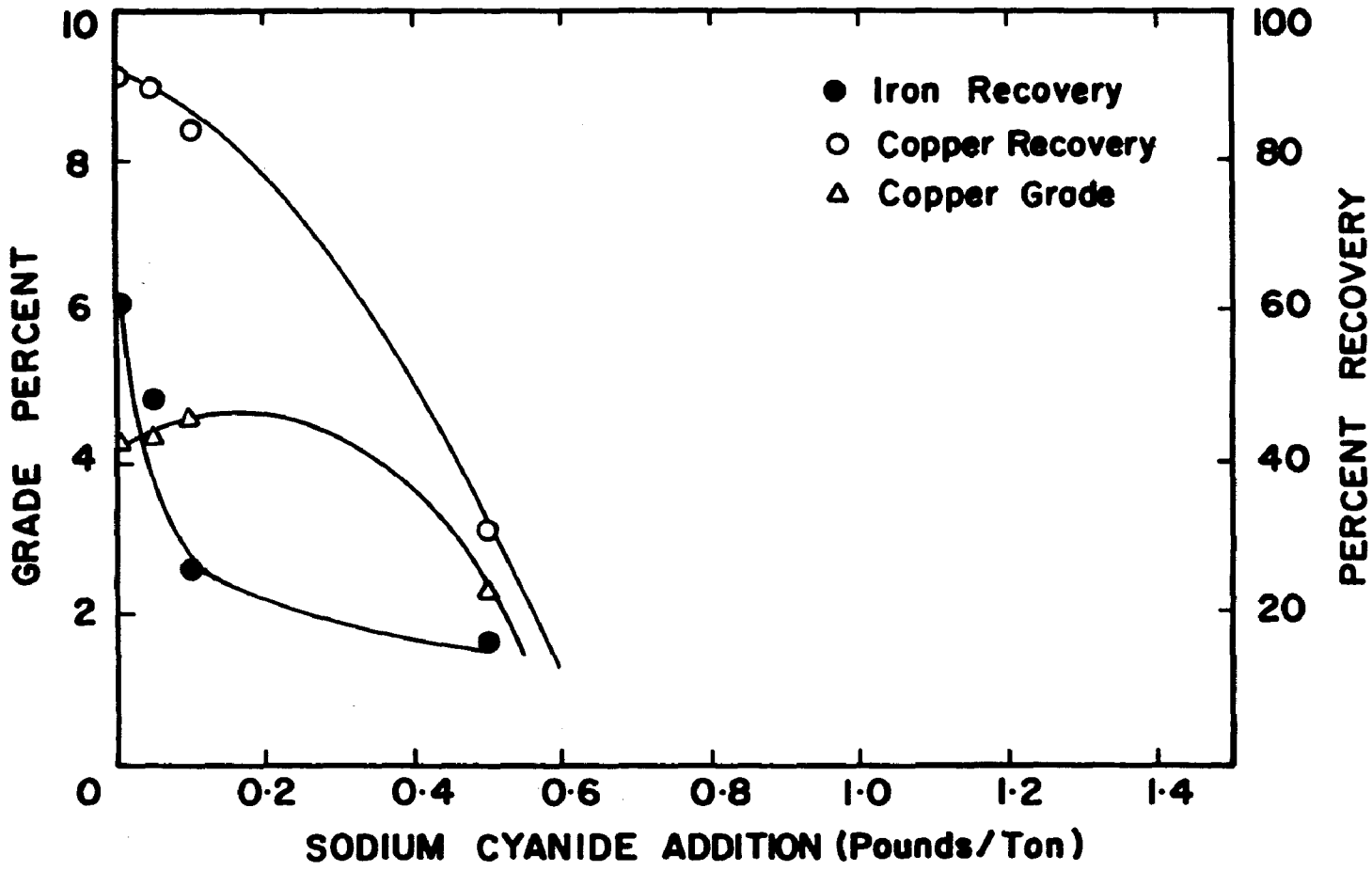


Figure 15. Percent recovery and grade percent of chalcopyrite-pyrite ore with KEX as a function of sodium cyanide addition.

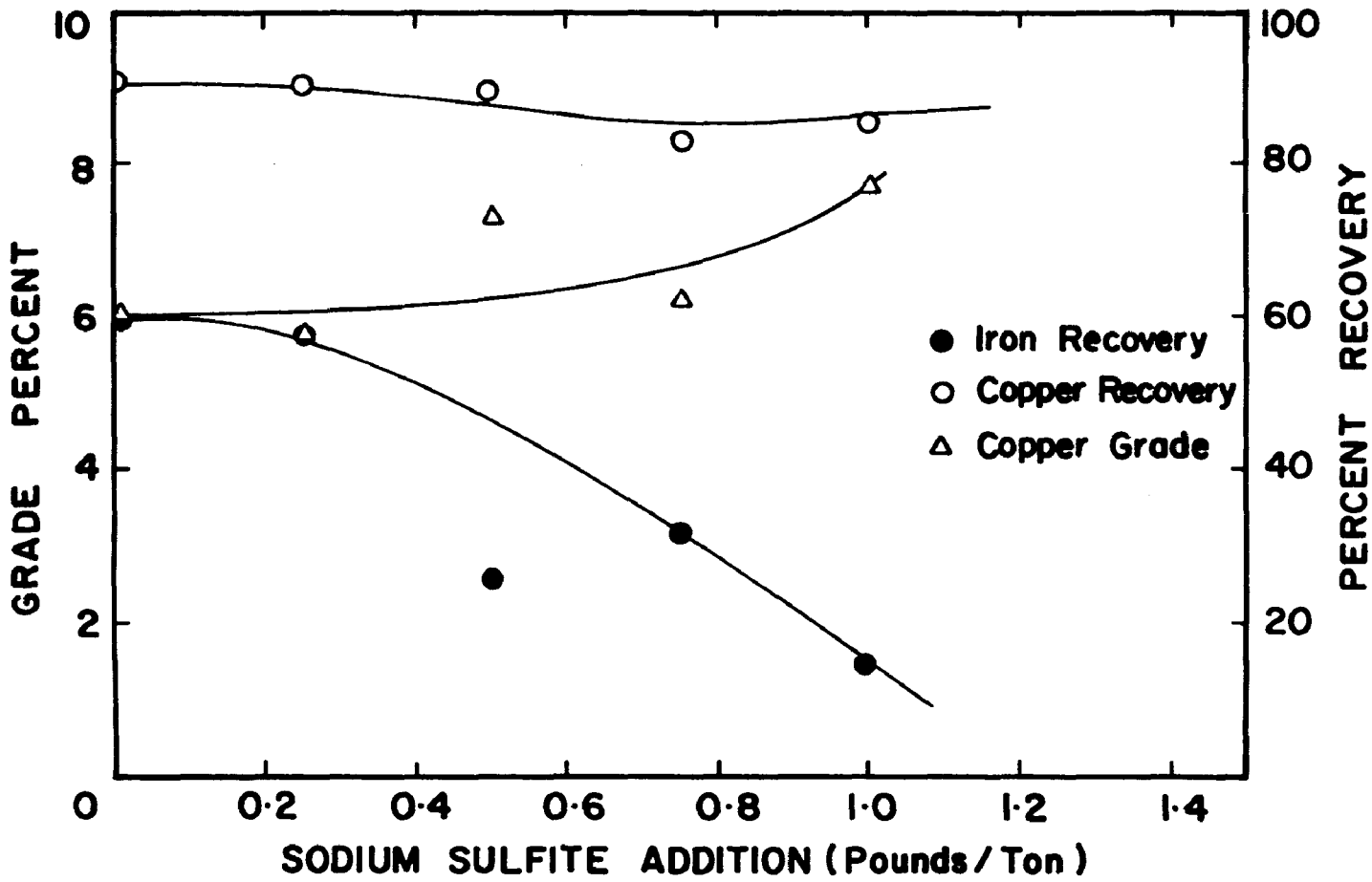


Figure 16. Percent recovery and grade percent of chalcopyrite-pyrite ore with KEX as a function of sodium sulfite solution.

reveals that sodium cyanide not only depressed pyrite but also depressed the chalcopyrite. Recovery dropped from about 90 percent at .05 lb per ton to 30 percent at 0.5 lb per ton. Sodium sulfite had little effect on the flotation recovery of chalcopyrite. Recovery decreased from 90 percent at 0.25 lb per ton to 86 percent at 1.0 lb per ton. Comparison of concentrate grade, percent Cu, of the cyanide and sulfite systems indicates the same results, sulfite is a depressant for pyrite but not for chalcopyrite whereas, cyanide can be depressant for both pyrite and chalcopyrite. For example, with sodium sulfite the percent copper in the concentrate increases from about 6 percent at 0.25 lb per ton to almost 8 percent at 1.0 lb per ton. This is to be compared with results in the cyanide system in which the percent copper in the concentrate drops from about 4.5 percent at low levels of cyanide to about 2.5 percent at 0.5 lb per ton.

Table III and IV show the flotation results of the galena-pyrite ore when sodium cyanide and sodium sulfite were the depressants. Again, the columns labeled Fe Units and Pb Units refer to the weight of the respective elements based on a total weight of 100 grams. Comparison of these tables gives the relative effectiveness of each depressant. Both depressants are effective for pyrite depression.

Figures 17 and 18 graphically demonstrate that both cyanide and sulfite depress pyrite in a galena-pyrite ore.

TABLE III

Experimental Flotation Results Obtained With Galena-Pyrite Ore Using Various Amounts of Sodium Cyanide Depressant at pH 8.0

Depressant Amount	Product	Product Wt,grams	Wt,%	Fe,%	Pb,%	Fe Units	Pb Units	Fe Distribution,%	Pb Distribution,%
	Concentrate	251	50.7	20.9	30.5	10.6	15.50	62.7	94.0
	Tail	244	49.3	12.8	2.0	6.3	0.99	37.3	6.0
None	Total		100.0			16.9	16.49	100.0	100.0
	Concentrate	102	21.6	5.8	46.0	1.19	9.48	4.4	66.4
0.10 Lb	Tail	393	79.4	32.6	6.0	25.85	4.76	95.6	33.6
Per Ton	Total		100.0			27.04	14.24	100.0	100.0
	Concentrate	106	21.4	4.7	54.6	1.00	11.70	5.4	70.6
0.25 Lb	Tail	389	78.6	22.7	6.2	17.85	4.88	94.6	29.4
Per Ton	Total		100.0			18.85	16.58	100.0	100.0
	Concentrate	99	19.8	11.6	49.0	2.30	9.71	11.5	60.4
0.50 Lb	Tail	400	80.2	22.1	8.0	17.70	6.42	88.5	39.6
Per Ton	Total		100.0			20.00	16.13	100.0	100.0
	Concentrate	112	22.5	5.8	43.3	1.30	9.75	8.4	64.2
0.75 Lb	Tail	387	77.5	18.3	7.0	14.20	5.42	91.6	35.8
Per Ton	Total		100.0			15.17	15.17	100.00	100.0
	Concentrate	117	23.6	8.1	43.3	1.91	10.20	9.7	63.0
1.00 Lb	Tail	380	76.4	23.3	7.8	17.80	5.95	90.3	37.0
Per Ton	Total		100.0			19.71	16.15	100.0	100.0

TABLE IV

Experimental Flotation Results Obtained With Galena-Pyrite Ore Using Various Amounts of Sodium Sulfite Depressant at pH 8.0

Depressant Amount	Product	Product Wt,grams	Wt,%	Fe,%	Pb,%	Fe Units	Pb Units	Fe Distribution,%	Pb Distribution,%
	Concentrate	251	50.7	20.9	30.5	10.6	15.50	62.7	94.0
	Tail	244	49.3	12.8	2.0	6.3	0.99	37.3	6.0
None	Total		100.0			16.9	16.49	100.0	100.0
	Concentrate	148	29.8	11.6	43.3	3.5	12.90	19.1	79.5
0.25 Lb	Tail	349	70.2	20.9	4.7	14.6	3.30	80.9	20.5
Per Ton	Total		100.0			18.1	16.20	100.0	100.0
	Concentrate	111	22.5	16.3	46.6	3.4	10.50	17.0	76.0
0.50 Lb	Tail	383	77.5	23.0	4.3	17.8	3.33	83.0	24.0
Per Ton	Total		100.0			21.5	11.58	100.0	100.0
	Concentrate	87	17.5	9.9	44.0	1.7	7.70	7.8	66.7
0.75 Lb	Tail	410	82.5	25.0	4.7	20.6	3.88	92.2	33.3
Per Ton	Total		100.0			22.3	11.58	100.0	100.0
	Concentrate	91	18.2	7.6	56.6	1.4	10.30	11.8	68.0
1.00 Lb	Tail	407	81.8	12.5	6.0	10.2	4.90	88.2	32.0
Per Ton	Total		100.0			11.6	15.20	100.0	100.0

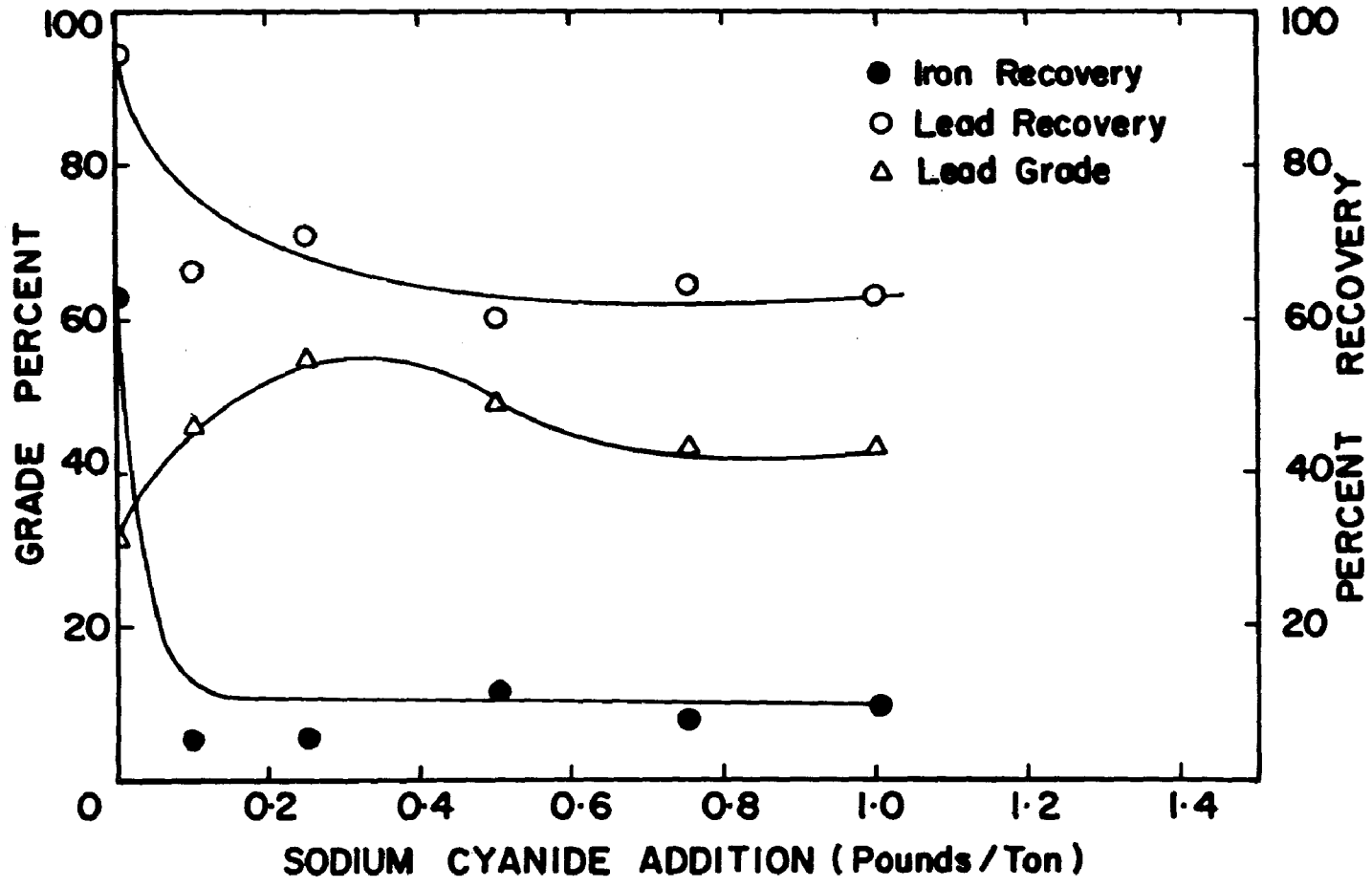


Figure 17. Percent recovery and grade percent of galena-pyrite ore with KEX as a function of sodium cyanide addition.

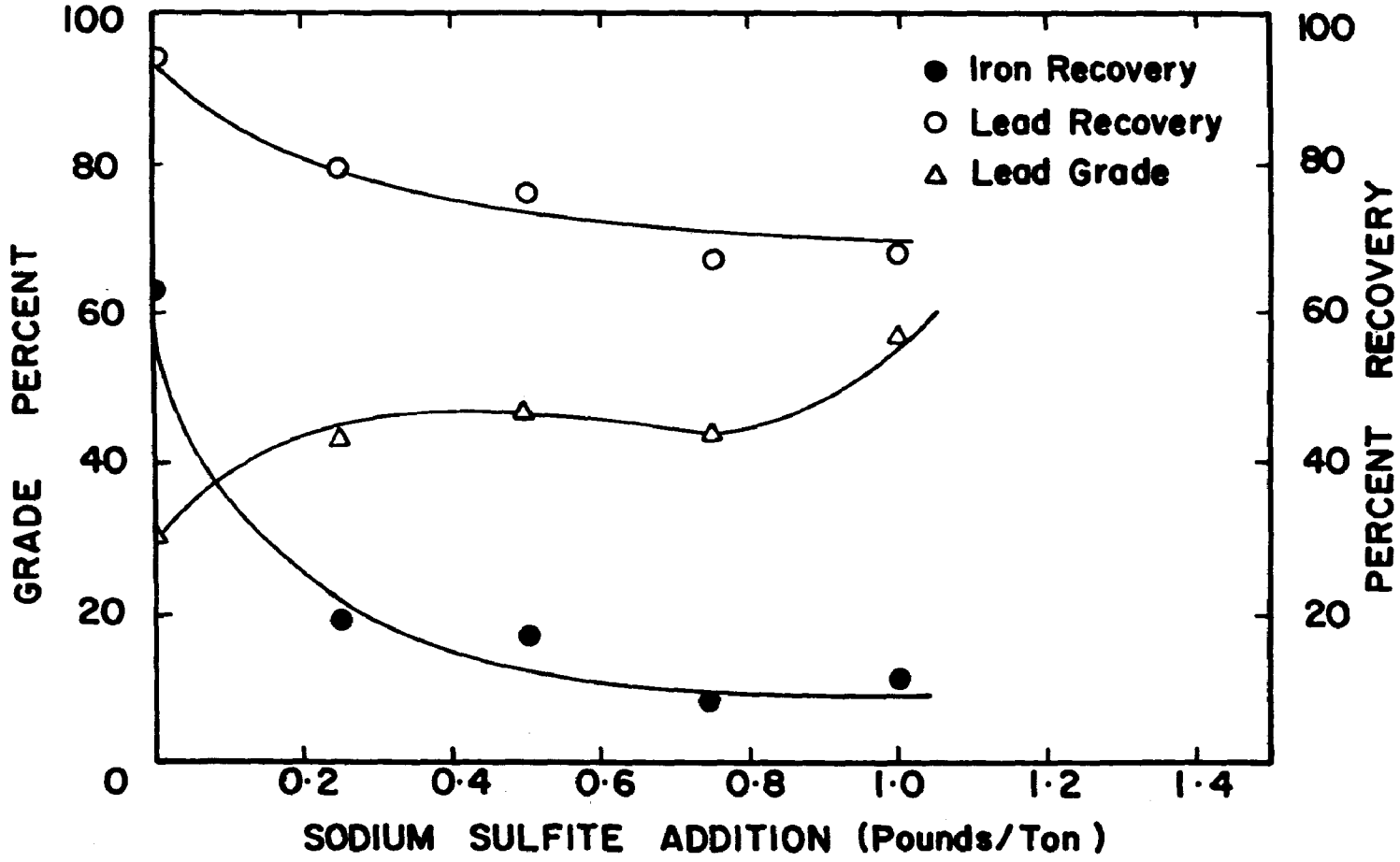


Figure 18. Percent recovery and grade percent of galena-pyrite ore with KEX as a function of sodium sulfite addition.

The lead recovery drops slightly in both the cyanide and sulfite systems, which is an indication that both cyanide and sulfite may have a small depressing effect on galena. Lead recovery in the cyanide system drops quickly from about 95 percent to about 65 percent with small additions of the depressant. On the other hand, lead recovery in the sulfite system is not affected to the same extent. In this case, the lead recovery decreases slowly and only at large additions of sodium sulfite (1.0 lb per ton) is the recovery less than 70 percent. In both systems iron recovery is reduced to 10 percent at moderate additions of depressant.

DISCUSSION OF RESULTS

The common technique of cyanide depression of pyrite in flotation milling of a complex sulfide ore has been thoroughly investigated[5-8]. The mechanism responsible for depression is the formation of a ferrocyanide complex on the pyrite surface[5]. The industrial use of cyanide is undesirable, however, both from the standpoint of the potential pollution problem and safety hazard it presents.

The depression of pyrite with reducing agents has not been investigated as extensively as has cyanide. However, reducing agents have been observed to depress pyrite[22]. Sulfite, which is a good reducing agent, has been observed to depress pyrite[22-25]. In addition, ferrous ion, which is also a good reducing agent, has been observed to depress pyrite[1].

Since dixanthogen is the species responsible for pyrite flotation, any chemical which is more reducing than the xanthate-dixanthogen couple should be capable of depressing pyrite. The average value of the standard half cell potential (E°), according to the European sign convention, for the xanthate-dixanthogen system was found to be minus 0.044 volt by Huiatt[20] and minus 0.049 volt by Majima[17]. The half cell reactions and their corresponding potentials for the reducing agents considered in this study are presented in the following equations, written according to the European sign convention[26]:

$$SO_3^{--} + 2OH^- = SO_4^{--} + H_2O + 2e^- \qquad E° = -0.93$$

$$H_2PO_2^- + 3OH^- = HPO_3^{--} + 2H_2O + 2e^- \qquad E° = -1.57$$

$$S^{--} = S + 2e^- \qquad E° = -0.48$$

$$H_2C_2O_{4(aq)} = 2CO_2(g) + 2H^+ + 2e^- \qquad E° = -0.49$$

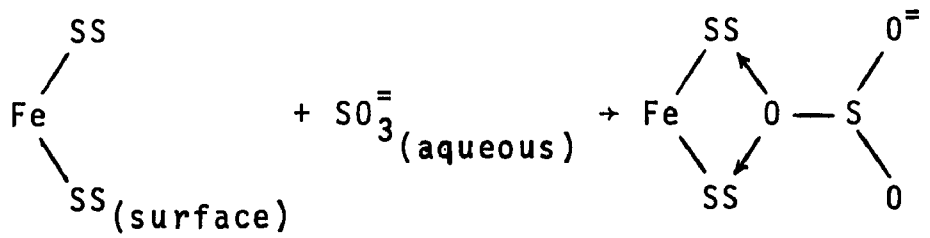
$$S_2O_3^{--} + 6OH^- = 2SO_3^{--} + 3H_2O + 4e^- \qquad E° = -0.58$$

The flotation results of pyrite using the reducing agents, which are represented in the preceding half cell reactions, are shown in Figures 2 through 7. The figures indicate that all these reducing agents act as depressants for pyrite. These results present more evidence that dixanthogen is the species responsible for pyrite flotation, since in these systems the dixanthogen molecule would be thermodynamically unstable. Other indirect evidence for dixanthogen as the collector species for pyrite arises because: ferric xanthate is an unstable compound, decomposing into ferrous ion and dixanthogen;[16] ferrous xanthate is too soluble to form at the concentration used, and while electrostatic adsorption is possible in acid solutions it should not be possible in basic solutions where both the pyrite surface and xanthate ion are negatively charged.

Comparison of Figures 2 through 7, indicate that sulfite is one of the better depressants for pyrite. This can be accounted for, since sulfite is such a strong

reducing agent ($E° = -0.93$) and since sulfite is potential determining for pyrite, as shown in Figure 13.

Because sulfite is potential determining for pyrite, the depressant effect should arise both from its reducing interactions in solution and its adsorption on the pyrite surface. The latter effect is probably more important, because recent work indicates that the oxidation of xanthate to dixanthogen is accomplished catalytically by nascent oxygen on the pyrite surface[18,20]. The sulfite would then prevent the adsorption of molecular oxygen and formation of active nascent oxygen sites as indicated by the following reaction:



Such a mechanism accounts for depression by occupying the sites for the effective oxidant and is substantiated by zeta potential measurements. The results illustrated in Figure 13 show that the zeta potential becomes more negative as sulfite is added. This is in accord with the proposed mechanism. Other reducing agents, which also act as depressants, probably function in a similar manner.

Figure 12, shows that reducing agents are not depressants for galena and that it should be possible to separate galena

from pyrite in an ore containing both minerals. This may be somewhat surprising because galena as well as all other sulfides adsorb oxygen at their surface readily. Consequently, one might expect depression as in the case of pyrite. Such is not the case, because unlike ferrous ethyl xanthate, lead ethyl xanthate is a very stable compound and has been observed by infrared techniques on the galena surface[27]. As a result, galena is not depressed by reducing agents.

To depress pyrite from galena and other sulfides, it would be desirable to be able to monitor the solution oxidation potential and determine whether enough reducing agent is in solution to prevent dixanthogen formation. Meaningful measurements of solution oxidation potentials were not possible with oxyanion reductants because these reductants are not reversible to the platinum electrode, probably due to the fact that there is an oxygen transfer involved in the oxidation-reduction couple, in addition to the simple electron transfer. However, meaningful measurements were made using sulfide ion for the depressant, as shown in Figure 14. Comparison of Figure 14 with Figure 4 indicates that for a pH less than 8, pyrite depression occurs at Eh values less than 0.1 volt; and that good flotation occurs at Eh values greater than 0.1 volt. Above pH 8, it is believed that pyrite depression occurs for an entirely different reason. It is well known that pyrite is

depressed in a basic media of pH 11 and above. This phenomenon is attributed to the formation of ferric hydroxide, on which dixanthogen cannot adsorb. This reasoning is supported by the fact that flotation cannot be effected at high pH even when a moderate oxidizing agent is added to the system to form dixanthogen. If measurements of oxyanion solution potentials were possible, it is expected that an Eh response similar to the sulfide system would exist.

Sodium sulfite has relatively long-lasting effectiveness, since it depresses pyrite well, even after a ten minute conditioning time. This is demonstrated in Figure 8 and indicates that the oxidation kinetics of sulfite in the pyrite system is slow and therefore not a hindering factor in depression.

The flotation results shown in Figures 2, 10 and 11 indicate that depression of pyrite is not a function of particle size, since almost identical flotation curves were obtained for three different mesh sizes.

An evaluation of the theory proposed was made by testing both a lead and copper ore. The results of tests on the copper ore are shown in Table I and II. These results show that both sodium cyanide and sodium sulfite are depressants for pyrite, since in both cases the weight percent of concentrate, the percent of iron in the concentrate and the iron distribution in the concentrate decrease as the level of depressant addition increases. The copper

distribution in the concentrate drops from 84 percent with 0.10 lb per ton sodium cyanide to 31 percent with an addition of 0.5 lb per ton. This response is not observed when sodium sulfite is used as the depressant, since recovery is still 86 percent even at an addition of 1.0 lb per ton. These results indicate that cyanide will depress both chalcopyrite and pyrite with additions of more than 0.10 lb per ton, but that sulfite is a depressant for pyrite only and will not influence chalcopyrite flotation at any level. Figures 15 and 16 illustrate these results graphically. Approximately five times more sulfite than cyanide is required for adequate depression of pyrite; however, the rougher concentrate grade is significantly greater with sulfite, 7 percent Cu, than with cyanide, 4.3 percent Cu, at the same recovery. The minimum price of alkaline sulfites is 4 cents a pound, while the price of sodium cyanide is about 20 cents a pound[28]. At these prices the cost of using sulfite is the same as the cost for using cyanide. Because the economics are the same and because sulfite is more efficient metallurgically, it appears that sulfite would be a better depressant for pyrite in copper porphory ores. In addition, pollution danger is reduced and monitoring costs for the poisonous cyanide are eliminated.

It has been reported that sulfite is an effective depressant for galena[23] and that galena is not influenced by cyanide[29]. However, the results of this investigation

tabulated in Tables III and IV and illustrated in Figures 17 and 18, do not support prior findings. Galena floats as well with sulfite additions as with cyanide additions. Both cyanide and sulfite appear to depress galena to a slight extent in ore flotation but the effect seems greater with cyanide than with sulfite. Pyrite is effectively depressed with both cyanide and sulfite, but more sulfite is required than cyanide to accomplish the same results. Other than the level of reagent addition, there seems to be little difference in metallurgical results of sulfite and cyanide in the case of the lead ore. To depress pyrite more sulfite than cyanide is required; however, this is offset by the fact that cyanide is five times more expensive than sulfite. Therefore, on the basis of both metallurgy and economics, sulfite and cyanide are equivalent as pyrite depressants for lead ore.

ACKNOWLEDGMENTS

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PYRITE DEPRESSION BY REDUCTION OF SOLUTION OXIDATION POTENTIAL

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27 Abstract

A study of pyrite depression by reducing agents with potassium ethylaxanthate as collector indicates that pyrite may be depressed effectively in the flotation of both lead and copper sulfide ores without the use of poisonous cyanide salts. More specifically, the use of sodium sulfite as the depressant may result in metallurgical, economical, environmental and safety advantages over the poison, cyanide as the depressant were a rougher concentrate recovery of 90.2% and a grade of 4.3% Cu. However, when sulfite was used as the depressant for the same recovery a grade of 7.3% Cu was obtained.

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