

T 994

AN INVESTIGATION OF THE FLOTATION OF CHROMITE

by

L. Raul Reyes A.

ProQuest Number: 10795615

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10795615

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 – 1346

A thesis respectfully submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

Signed:



L. Raul Reyes A.

Approved:



M. C. Fuerstenau,  
Thesis Advisor

Golden, Colorado

Date: February 14<sup>th</sup>, 1964



A. W. Schlechten, Head  
Department of  
Metallurgical Engineering

## ABSTRACT

Micro-flotation studies with chromite were undertaken to determine first the response of chromite to flotation with high-molecular-weight sulfonate as collector and secondly the mechanism of collection involved.

The experimental results indicate that flotation can occur by two different mechanisms, dependent on the pH of the system and on the absence or presence of added metal ions. Below pH 10 and in the absence of added metal ions, flotation appears to result from the formation of aluminum, chromium, and iron sulfonates at the surface of the chromite. Above pH 10 and in the presence of metal ions capable of hydrolyzing to their first hydroxide complex, flotation results from the formation of a metal-hydroxy-sulfonate which apparently hydrogen bonds to an oxygen of the surface.

## CONTENTS

	Page
ABSTRACT. . . . .	iii
LIST OF ILLUSTRATIONS . . . . .	v
ACKNOWLEDGMENTS . . . . .	vi
INTRODUCTION. . . . .	1
EXPERIMENTAL MATERIALS AND PROCEDURE. . . . .	2
Chromite . . . . .	2
Water. . . . .	3
Reagents . . . . .	3
Micro-Flotation Apparatus. . . . .	3
Experimental Procedure . . . . .	6
EXPERIMENTAL RESULTS. . . . .	7
DISCUSSION OF RESULTS . . . . .	18
SUMMARY AND CONCLUSIONS . . . . .	28
BIBLIOGRAPHY. . . . .	31

## LIST OF ILLUSTRATIONS

Figure	Page
1. Photograph of the micro-flotation cell. . . .	4
2. Photograph of the experimental apparatus. . .	5
3. Curve relating recovery vs sulfonate concentration . . . . .	8
4. Curve relating recovery vs pH at constant sulfonate. . . . .	10
5. Curve relating recovery vs calcium concen- tration at constant pH and constant sulfonate concentration . . . . .	11
6. Curve relating recovery vs magnesium concentration at constant pH and constant sulfonate concentration . . . . .	12
7. Curve comparing flotation response when no metal ion is added and also when calcium is added. . . . .	15
8. Curve relating recovery vs sulfonate concen- tration in presence of various magnesium concentrations. . . . .	17

## ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor M. C. Fuerstenau for guidance and constructive criticisms which made the completion of this investigation possible. The author is also indebted to Professor H. Frost, Jr. for the interest shown in this research program and helpful encouragement given.

The author also wishes to acknowledge the financial support provided by Universidad Industrial de Santander and Icetex, which supported his study at the Colorado School of Mines.

Lastly the author wishes to thank Mr. A. L. Pierce for the chemical analyses of the mineral samples.

## INTRODUCTION

The flotation of oxide minerals of chromium, copper, iron, lead, and zinc has, in general, been problematic. This can probably be attributed to a number of factors, notably a lack of understanding of the basic mechanism of collection involved, the role that metal ion hydrolysis assumes in such systems<sup>(8)</sup>, the non-selectivity associated with fatty acid flotation, and in some cases, the high surface area of the mineral.

Previous investigations of chromite flotation have generally involved the use of fatty acids, amines, alkyl sulfates, soaps, and various additives<sup>(1,3,4,6,11,16,19)</sup>. In particular Weinig suggested the use of caustic, kerosene, and an  $\text{NH}_4$  soap of tall oil or other fatty acid with previous conditioning with  $\text{Na}_2\text{SiF}_6$ ,  $\text{NaF}$ ,  $\text{NaHF}_2$  or  $\text{HF}$ <sup>(21)</sup>. Flotation with a soap and sodium metaphosphate as a modifier was reported by MacDonald in 1937<sup>(15)</sup>. Erlenmeyer reported the use of 8-hydroxyquinoline as collector on oxide compounds in the presence of metal salts<sup>(5)</sup>.



## EXPERIMENTAL MATERIALS AND PROCEDURE

Chromite

The chromite used in the experimental investigation came from the Transvaal region of South Africa. A chemical analysis of the mineral appears in Table 1.

Table 1. -- Chemical Analysis of the Chromite used in the Experimental work

FeO	21.10 percent
Cr <sub>2</sub> O <sub>3</sub>	43.15
Al <sub>2</sub> O <sub>3</sub>	14.00
MgO	11.18
SiO <sub>2</sub>	5.72
MnO	3.00
CaO	Tr.

As listed, this chromite contained 21.10 percent FeO and 43.15 percent Cr<sub>2</sub>O<sub>3</sub> as opposed to the theoretical 32 percent FeO and 68 percent Cr<sub>2</sub>O<sub>3</sub>. A chromite containing the theoretical amounts of iron and chromium oxides is difficult

to find in nature because of the frequent replacement of iron by magnesium and chromium by aluminum and ferric iron<sup>(4)</sup>.

An x-ray powder pattern showed that the mineral was magnesio-chromite or chrome-spinel.

### Water

Conductivity water was used in all of the experimental work. This water was made by passing distilled water through an ion exchange resin (anion and cation).

### Reagents

With the exception of the sulfonate, all of the chemicals were reagent grade quality.

A sodium alkyl aryl sulfonate, chosen as collector, had the following physical properties<sup>(18)</sup>:

Physical form	Solid finely ground
Sulfonate content (% weight)	95 to 97
Molecular weight	450 to 470
Number of carbon atoms in hydrocarbon chain	25 to 30
Melting point (Deg. F)	250 to 260

### Micro-Flotation Apparatus

A small glass micro-flotation cell was used in the investigation; see figure 1. This cell, constructed from a 150-cc Buchner funnel (fritted glass filter) has two principal advantages: (1) system contamination can be kept to a

minimum since no metallic components are involved, and (2) small charges (2 g in this case) of pure mineral may be used.

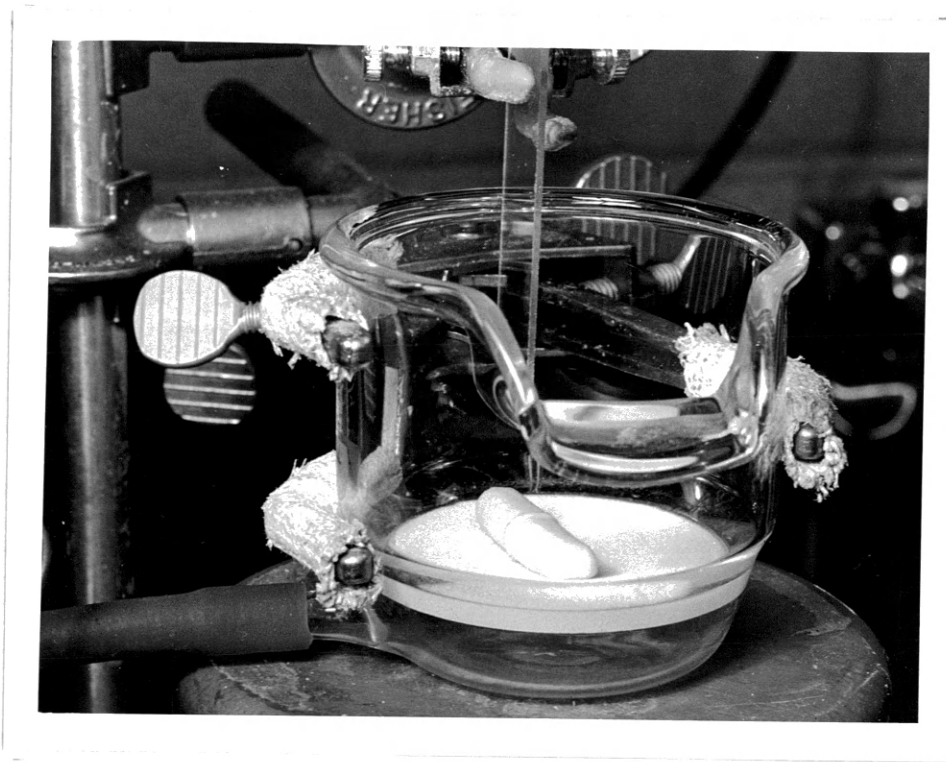


Figure 1 - Micro-flotation cell

A photograph of the complete experimental apparatus is shown in figure 2. The magnetic stirrer used for system agitation can be noted directly under the flotation cell (see figure 1) as can the constant head tank in the upper portion of the photograph (see figure 2).

A constant 30 cc of purified nitrogen was passed through the cell at a flow of about 120 cc per min. against a constant

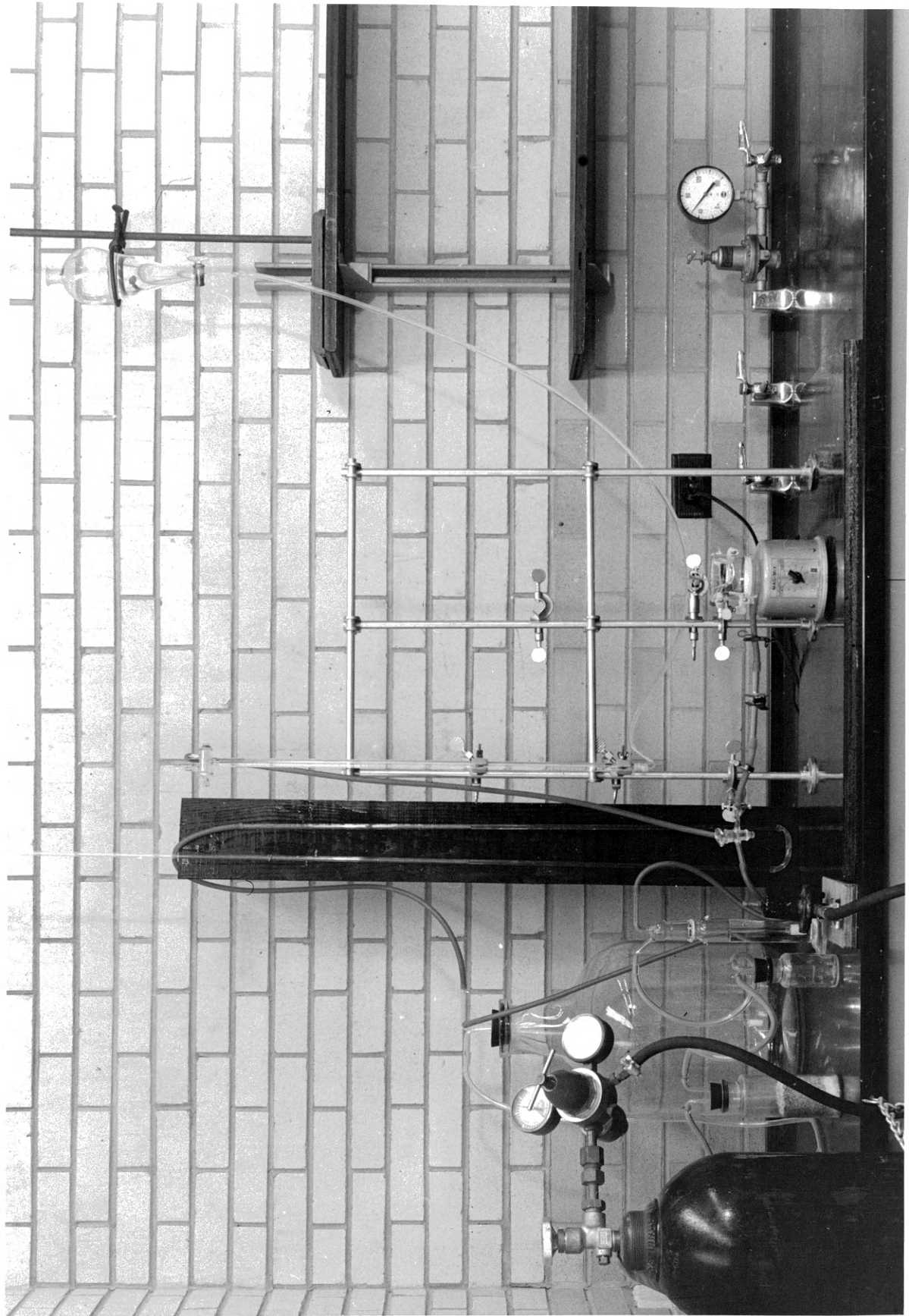


Figure 2 - Micro-flotation apparatus.

pressure head of water (35 inches).

#### Experimental Procedure

The chromite was ground with mortar and pestle to avoid contamination and dry-screened to -65 +100 mesh. The residual material finer than this size was removed by slurring the sized chromite in conductivity water and decanting.

Two grams of mineral was added dry to a constant volume of 140 cc of solution (water, sulfonate and salt solutions). In more detail, the experimental flotation procedure involved the following:

- 1) Predetermined amounts of water and salt solution were combined and the pH adjusted to a given value.
- 2) A given amount of sulfonate was added so that the final solution volume was 140 cc.
- 3) One drop of n-amyl alcohol was added as frother.
- 4) Two grams of chromite were added and the system was conditioned for  $2\frac{1}{2}$  minutes.
- 5) The pH of the system was measured (termed flotation pH).
- 6) Thirty cc of purified nitrogen were passed through the cell at an average flow of 120 cc per min.
- 7) The pH of the system was measured (termed final pH).

## EXPERIMENTAL RESULTS

The first parameter investigated was the effect of sulfonate concentration on flotation response at constant pH, in this case neutral pH. As shown in figure 3, recovery increased with increasing collector concentration until a recovery of about 75 percent was achieved at  $10^{-4}$  mole per liter sulfonate. Increasing the sulfonate concentration above this level resulted in a decrease in recovery, that is a recovery of about 25 percent was obtained at  $10^{-3}$  mole per liter.

Excluding choice of collector, one of the most important parameters in any flotation system is hydrogen ion concentration. The effect of hydrogen ion concentration was examined in a series of experiments in which the sulfonate concentration was maintained constant at  $7.15 \times 10^{-5}$  mole per liter, while the pH was varied. See figure 4. This figure reveals an optimum value of pH for optimum flotation response; that is, a recovery of 90 percent was obtained at

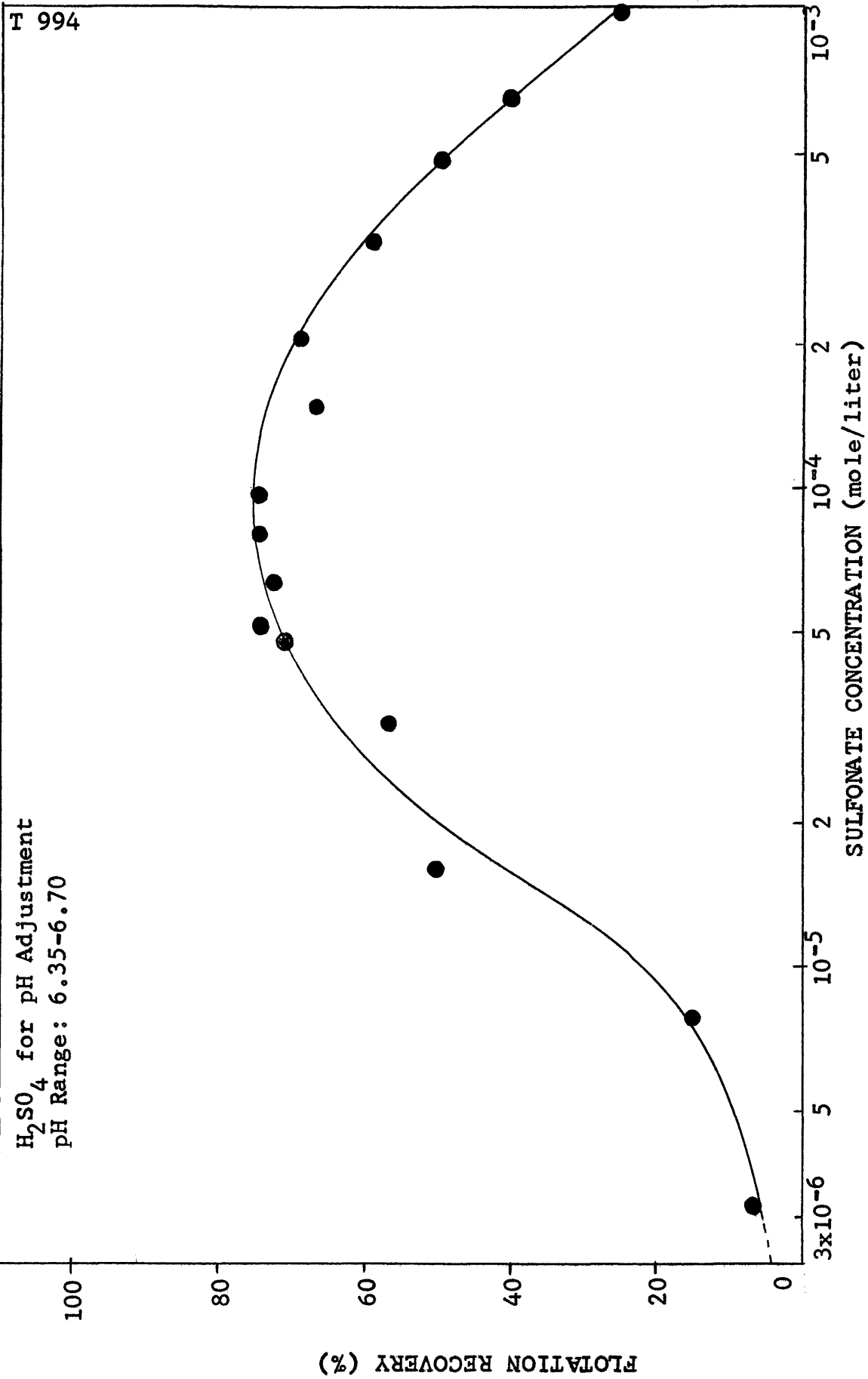


Figure 3 - Curve relating recovery and sulfonate concentration at constant pH.

pH 4. Above and below pH 4, recovery was noted to decrease. Finally, at pH 11, the system was essentially depressed. Even large additions of sulfonate at pH 11 did not result in improved flotation response. That is, about 10 percent recovery was obtained with  $3 \times 10^{-4}$  mole per liter sulfonate.

The extraordinary effects that metal ions display in flotation systems, when they are added in a pH region in which they are hydrolyzing, have already been reported<sup>(8)</sup>. Various metal ions were added to this system both in the region where they were hydrolyzing and also where they were simply hydrated cations, to extend the understanding of the mechanism of collection involved.

To start with,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were added in the pH regions where they start to hydrolyze which is also where the chromite is naturally depressed. See figures 5 and 6. Figure 5 shows flotation recovery as a function of  $\text{Ca}^{++}$  concentration at constant sulfonate concentration ( $1 \times 10^{-4}$  mole per liter) and constant pH. As shown, recovery increases with increasing  $\text{Ca}^{++}$  concentration until a recovery of about 80 percent is achieved at  $10^{-4}$  mole per liter  $\text{Ca}^{++}$ , and about 90 percent at  $10^{-3}$  mole per liter.

Figure 6 reveals two phenomena that are dependent on the amount of sulfonate added. When  $1 \times 10^{-5}$  mole per liter sulfonate was present, no flotation could be effected, even



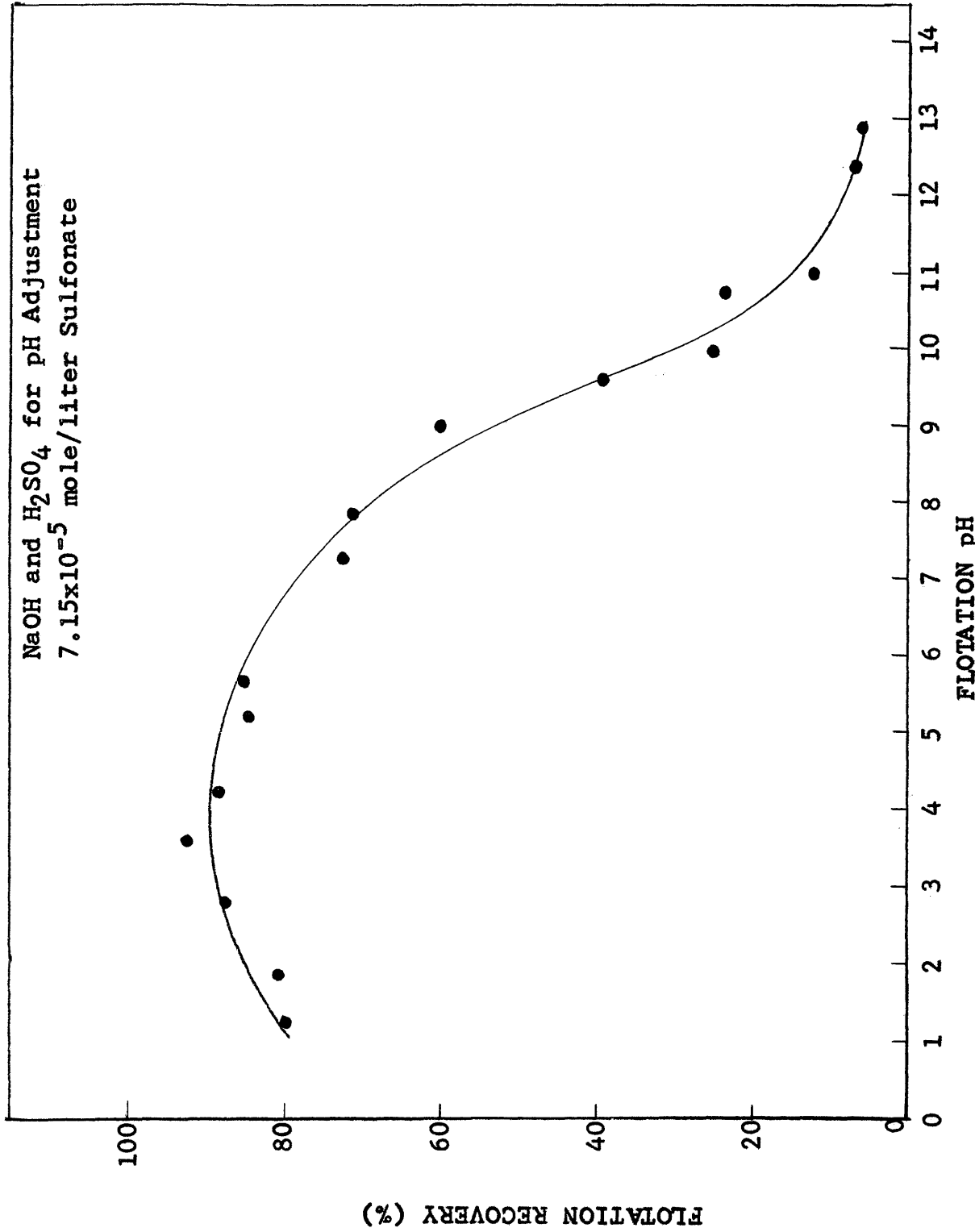


Figure 4 - Curve relating recovery and pH at constant sulfonate concentration.

NaOH for pH Adjustment  
pH Range: 11.82-12.10  
1x10<sup>-4</sup> mole/liter Sulfonate

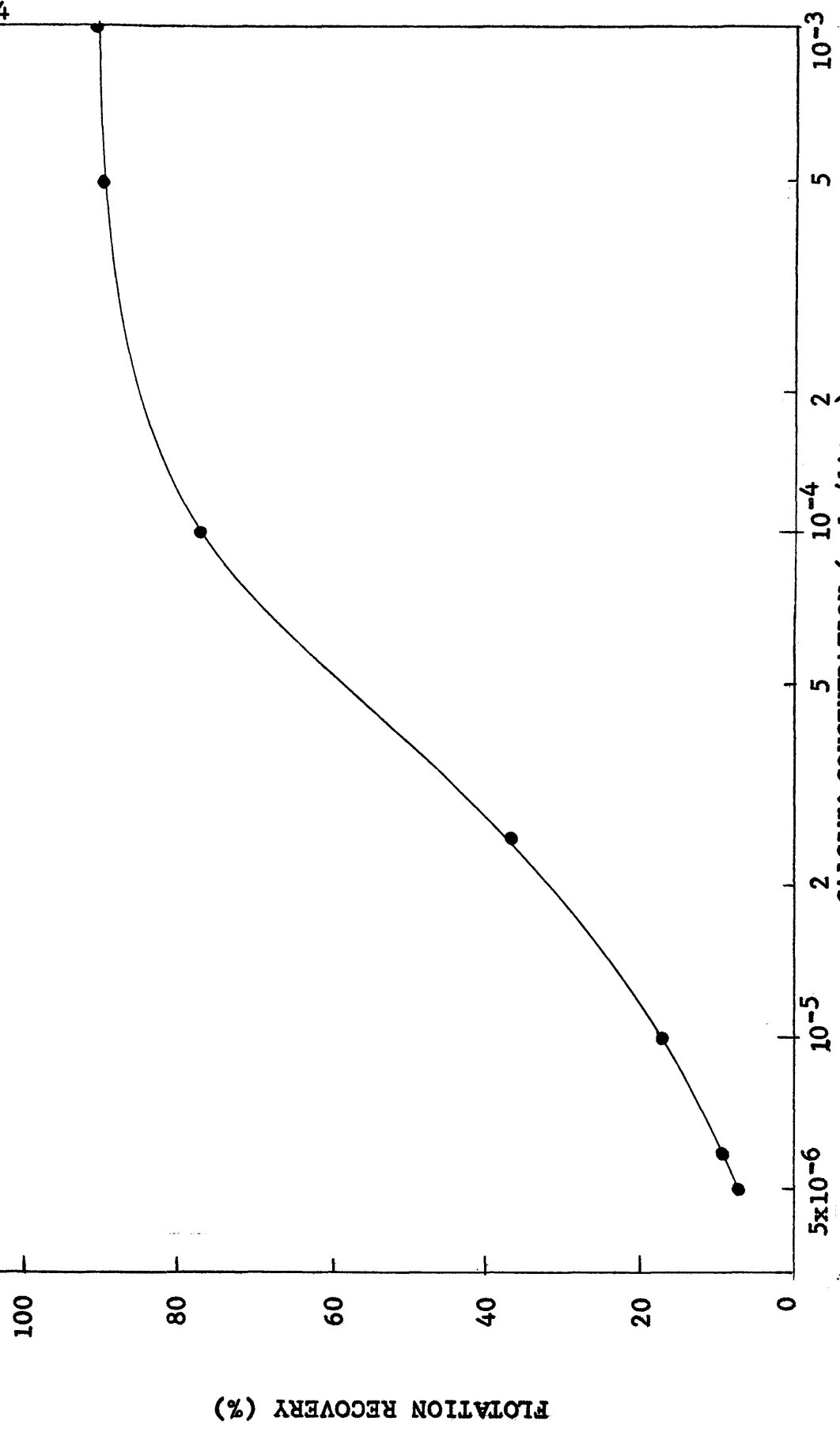


Figure 5 - Curve relating recovery and calcium concentration at constant pH and constant sulfonate concentration.

with the addition of  $1 \times 10^{-4}$  mole per liter  $Mg^{++}$ . When  $1 \times 10^{-4}$  mole per liter sulfonate was added, however, a recovery of 70 percent was obtained with  $1 \times 10^{-4}$  mole per liter  $Mg^{++}$  present and 90 percent with  $5 \times 10^{-4}$  mole per liter  $Mg^{++}$ .

The effects of  $Al^{+++}$ ,  $Cr^{+++}$ ,  $Fe^{+++}$ , and  $Pb^{++}$  on flotation response at pH 10.5 are listed in table 2. Constant sulfonate and metal ion concentrations of  $1 \times 10^{-4}$  mole per liter were used.

Table 2 Flotation Recoveries in the Presence and Absence of Various Metal Ions		
Metal Ion	Flotation Recovery (%)	Flotation pH
No added salt*	20.0	10.50
$Al^{+++}$	6.6	10.53
$Cr^{+++}$	9.1	10.51
$Fe^{+++}$	3.5	10.69
$Pb^{++}$	62.8	10.53

\*Determined with  $7.15 \times 10^{-5}$  mole per liter sulfonate.

As can be noted, the only ion of the four that exhibited a major effect on flotation response was  $Pb^{++}$ .

The effect of  $Ca^{++}$  on flotation response was examined further in a series of experiments in which a constant

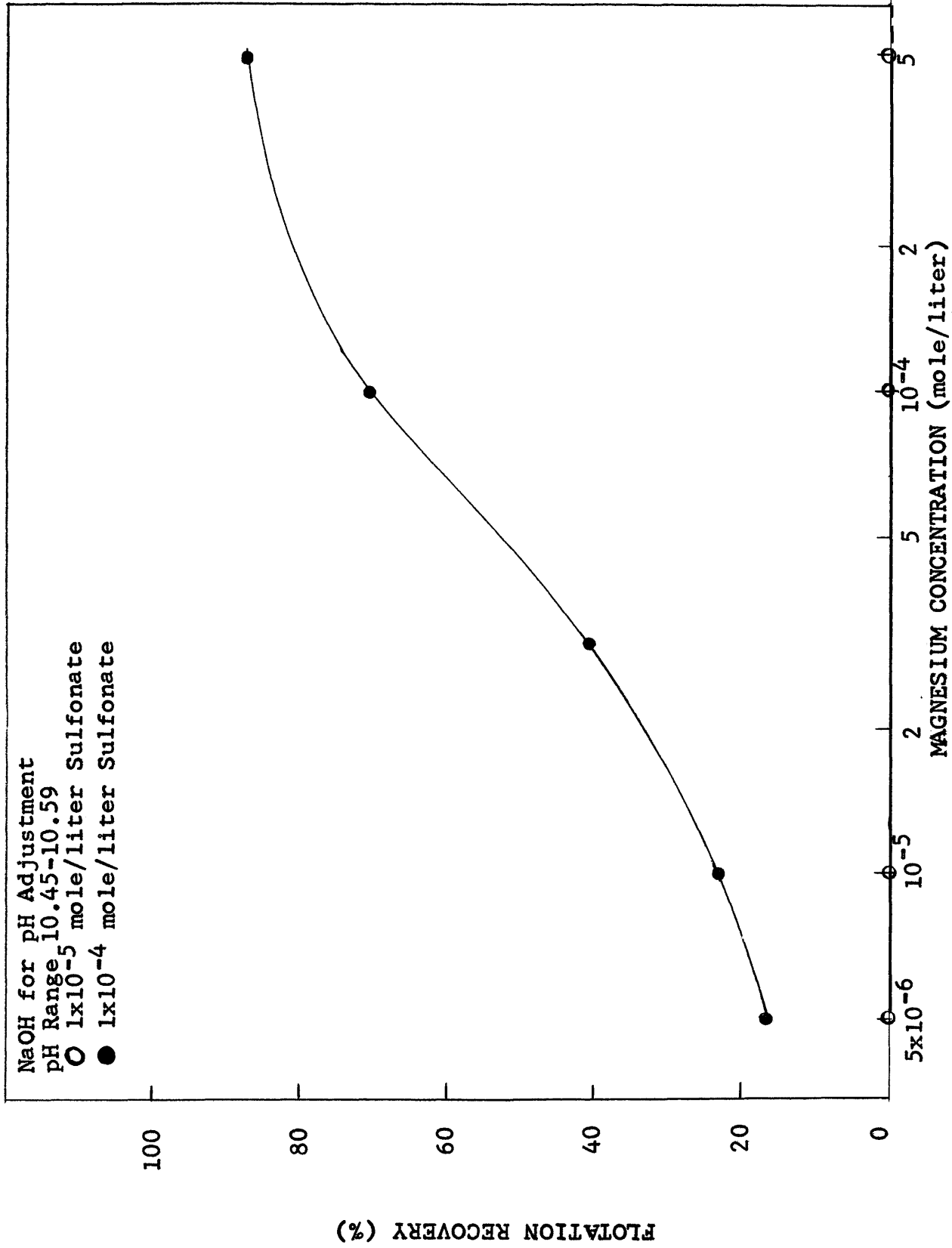


Figure 6 - Curve relating recovery and magnesium concentration at constant pH and constant sulfonate concentration.

sulfonate concentration ( $7.15 \times 10^{-5}$  mole per liter) and constant  $\text{Ca}^{++}$  ( $1 \times 10^{-3}$  mole per liter) were maintained, while pH was varied over the complete range (1.58 to 13.4). Figure 7 shows a comparison between data determined in the presence and absence of added  $\text{Ca}^{++}$ . Two phenomena are seen to result when  $1 \times 10^{-3}$  mole per liter  $\text{Ca}^{++}$  was added; that is, below pH 9 flotation recovery is actually decreased by about 15 percent from that obtained in the absence of added  $\text{Ca}^{++}$ . Above pH 9, and especially at pH 11 and 12, flotation recovery is increased markedly in the presence of  $1 \times 10^{-3}$  mole per liter  $\text{Ca}^{++}$ . Above pH 13, however, recovery is again noted to decrease.

Finally, previous work with quartz revealed that flotation response depended on the ratio of sulfonate to metal ion; in fact, it was shown that this ratio determined whether any flotation was possible at the pH involved. Accordingly, experiments were conducted with variable  $\text{Mg}^{++}$  and sulfonate concentrations at constant pH to determine whether this same phenomenon occurs in this system.

Figure 8 shows flotation recovery charted as a function of sulfonate concentration for three different concentrations of  $\text{Mg}^{++}$  at constant pH. As illustrated, an optimum recovery was obtained at  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and  $5 \times 10^{-4}$  mole per liter sulfonate with the addition of  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and

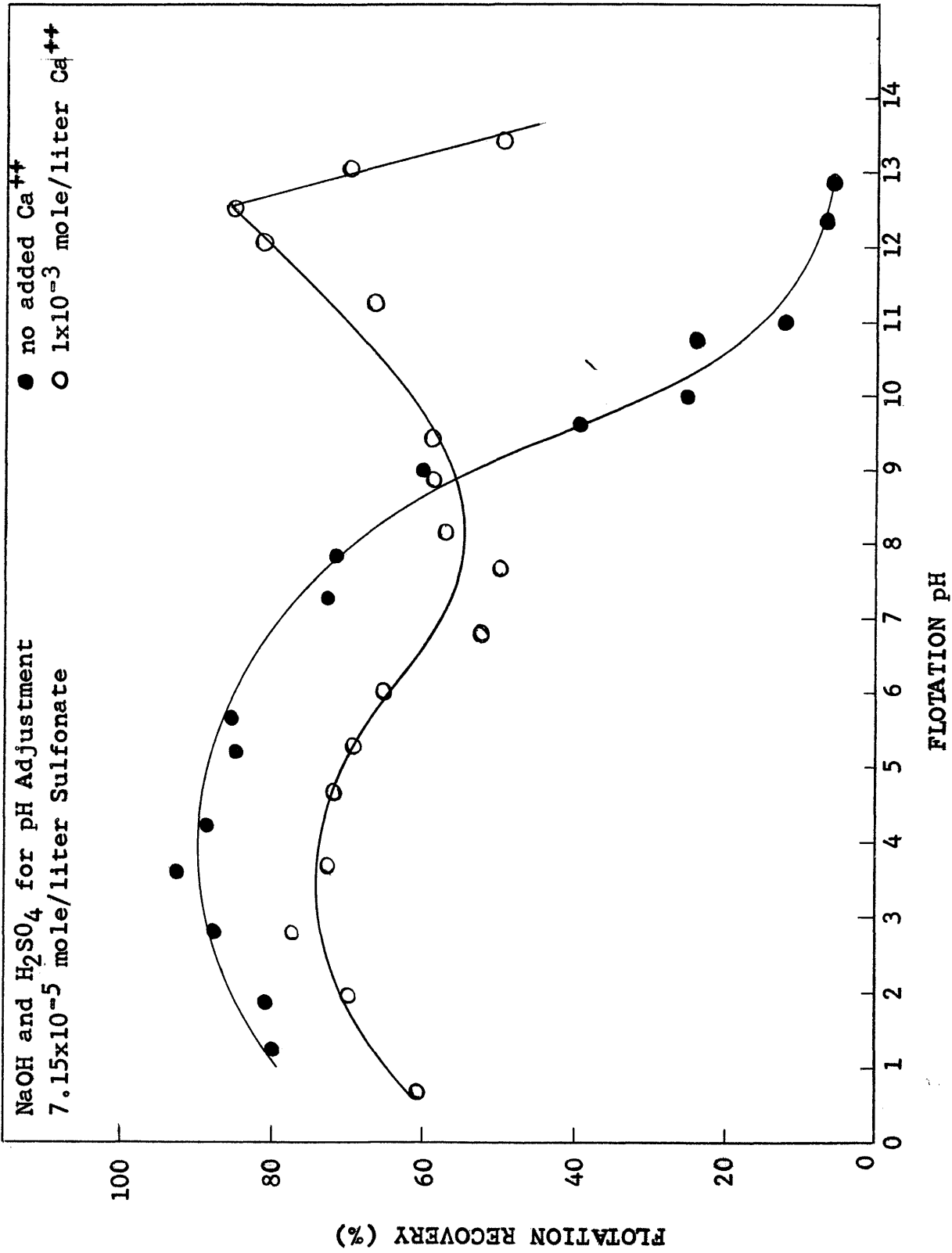


Figure 7 - Relation between flotation recovery and pH in presence of Ca<sup>++</sup> and when no metal ion is added.

$1 \times 10^{-3}$  mole per liter  $Mg^{++}$ , respectively. However, when the sulfonate concentration was increased, the curve of recovery vs sulfonate concentration dropped rather markedly when  $5 \times 10^{-5}$  mole per liter was present and less so when  $1 \times 10^{-4}$  mole per liter  $Mg^{++}$  was present. A reduction in recovery when  $1 \times 10^{-3}$  mole per liter  $Mg^{++}$  was present occurred only when a sulfonate concentration in excess of  $1 \times 10^{-3}$  mole per liter was involved.

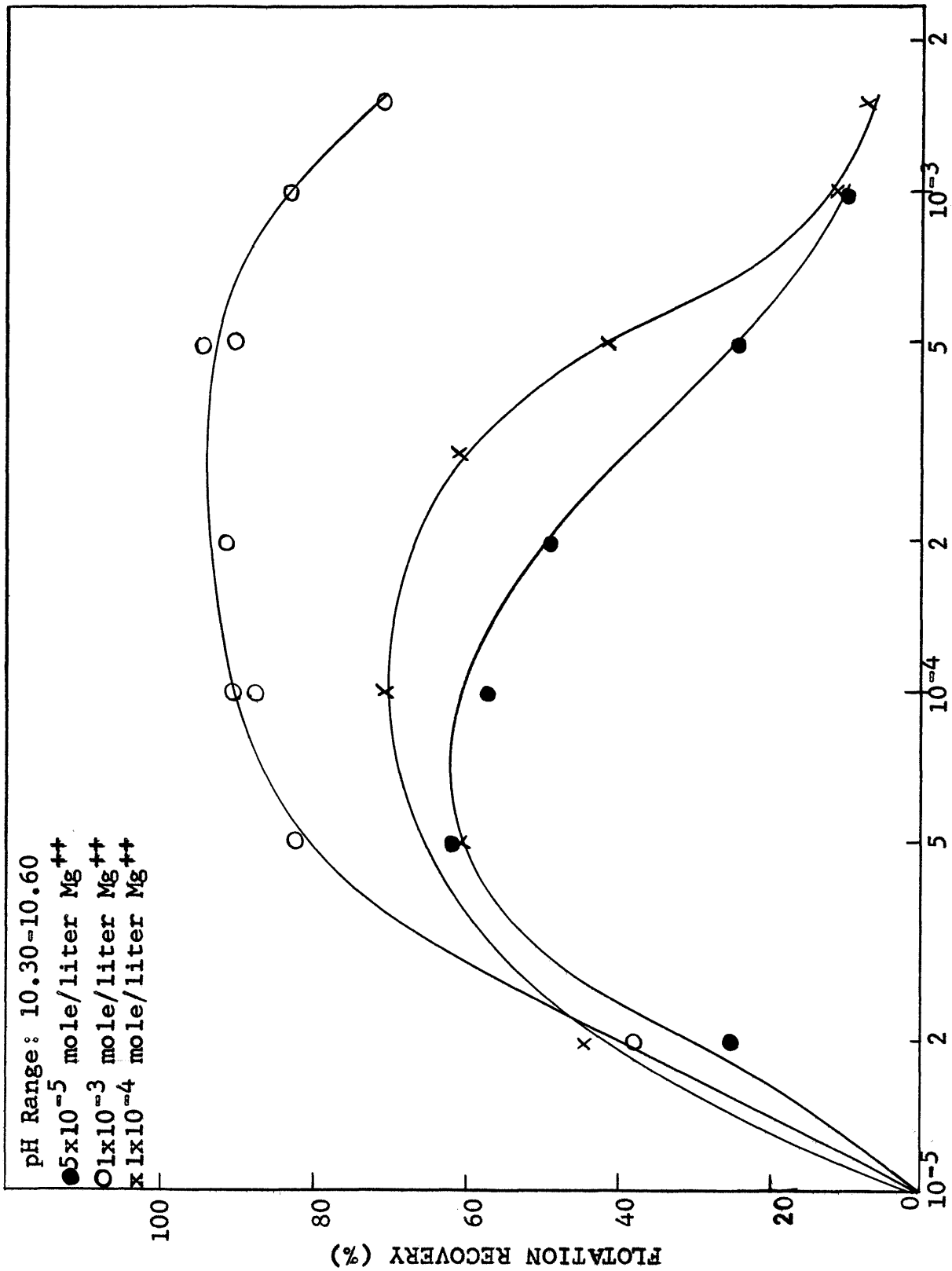


Figure 8 - Curve relating recovery and sulfonate concentration in presence of various magnesium concentrations.



## DISCUSSION OF RESULTS

The experimental results revealed a number of interesting and important phenomena; that is, chromite was found to respond well to sulfonate flotation in the absence of added metal ions. Also, when chromite is naturally depressed by  $\text{OH}^-$  at higher values of pH, the addition of metal ions, that will hydrolyze in that pH region, results in essentially complete flotation.

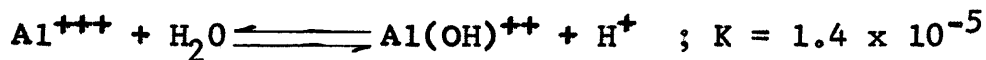
These data suggest that two mechanisms are responsible for flotation in this system and related systems. Both mechanisms apparently involve metal ion hydrolysis, one completely and the other in part; this will be seen from the data listed in tables 3 and 4 (2,10,12,13,14,17).

Table 3. First Stage of Hydrolysis of Various Metal Ions

$\text{Al}^{+++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})^{++} + \text{H}^+$	;	$K = 1.40 \times 10^{-5}$	Ref. 12
$\text{Pb}^{++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})^+ + \text{H}^+$	;	$K = 6.67 \times 10^{-7}$	Ref. 13
$\text{Zn}^{++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{OH})^+ + \text{H}^+$	;	$K = 2.45 \times 10^{-10}$	Ref. 14
$\text{Mn}^{++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Mn}(\text{OH})^+ + \text{H}^+$	;	$K = 2.38 \times 10^{-11}$	Ref. 10
$\text{Mg}^{++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})^+ + \text{H}^+$	;	$K = 3.40 \times 10^{-12}$	Ref. 2
$\text{Ca}^{++}$	+	$\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})^+ + \text{H}^+$	;	$K = 2.96 \times 10^{-13}$	Ref. 2

Table 4. Solubility Products of Various Metal Hydroxides	
Hydroxide	$K_{sp}^{(14)}$
Fe(OH) <sub>3</sub>	$1 \times 10^{-38}$
Al(OH) <sub>3</sub>	$1 \times 10^{-33}$
Pb(OH) <sub>2</sub>	$1 \times 10^{-16}$
Mn(OH) <sub>2</sub>	$1 \times 10^{-14}$
Mg(OH) <sub>2</sub>	$6 \times 10^{-12}$
Ca(OH) <sub>2</sub>	$8 \times 10^{-6}$

For example, in the hydrolysis of aluminum ion to the first hydroxide complex:

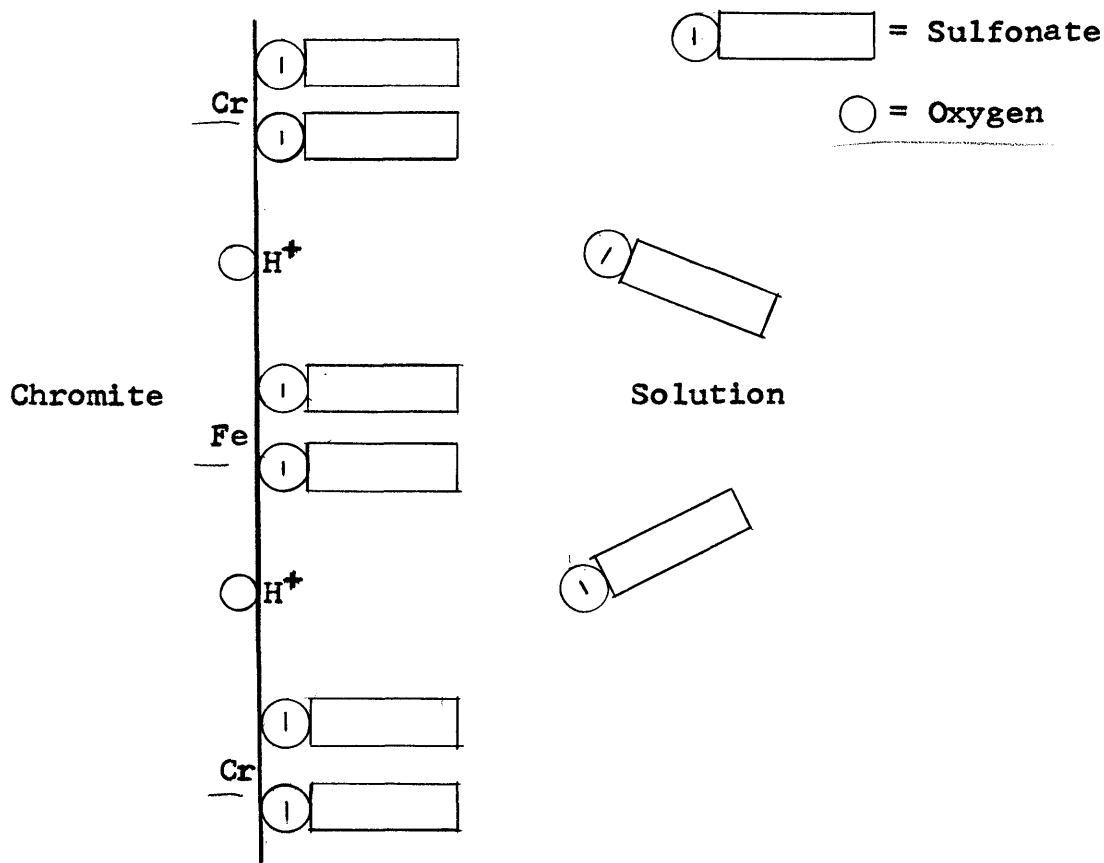


at pH 4, about 12 percent of the total aluminum added will be in the form of  $\text{Al(OH)}^{++}$ , while 88 percent will be hydrated  $\text{Al}^{+++}$  ion.

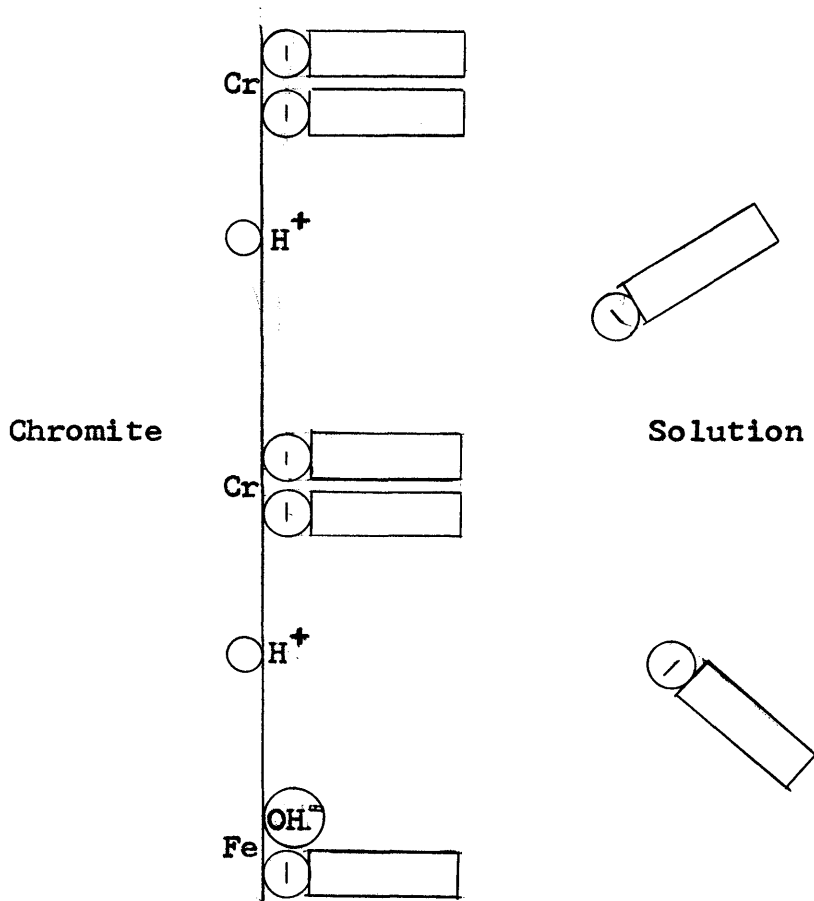
Further, the addition of small amounts of any metal ion (on the order of 1 ppm) to a dilute solution of this sulfonate (also on the order of 1 ppm) results in the precipitation of metal sulfonate<sup>(8)</sup>. It should be mentioned that the solubility products of the various metal sulfonates and metal-hydroxy-sulfonates were not measured in this work; this determination requires special equipment that was not avail-

able. In the case of the metal ion addition, however, the various metal sulfonate precipitates could be readily seen by eye.

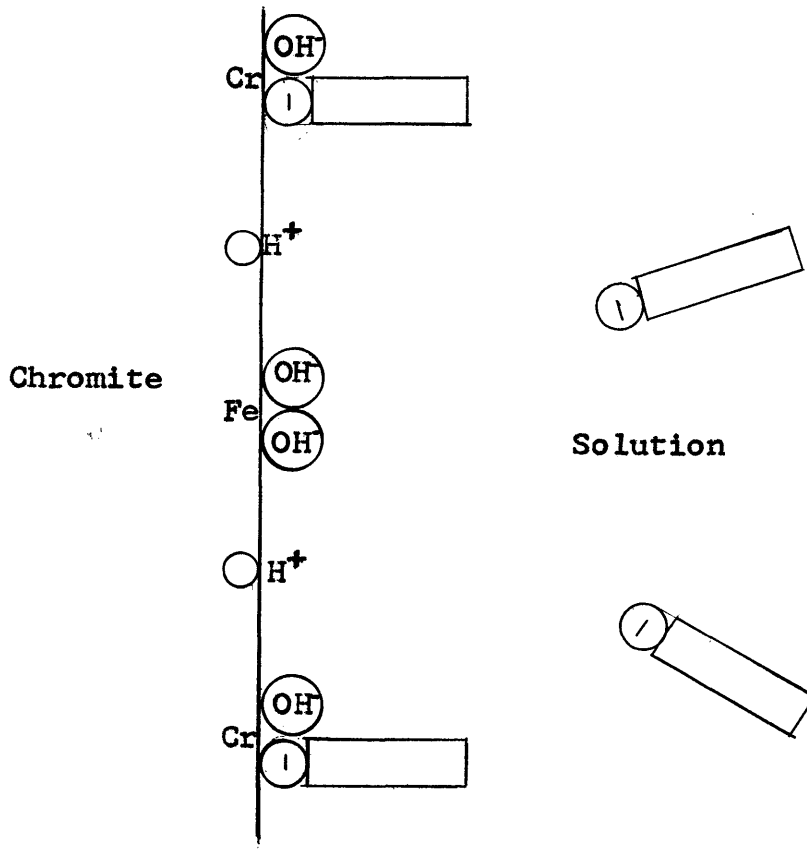
The data shown in figure 4 revealed that chromite responded well to flotation from pH 1 to 7. With reference to tables 3 and 4, it can be seen that none of the metal ions present in chromite will start to hydrolyze at pH 1. In view of this, it would appear that simple iron, and chromium sulfonates are forming at the surface. This is represented pictorially below:



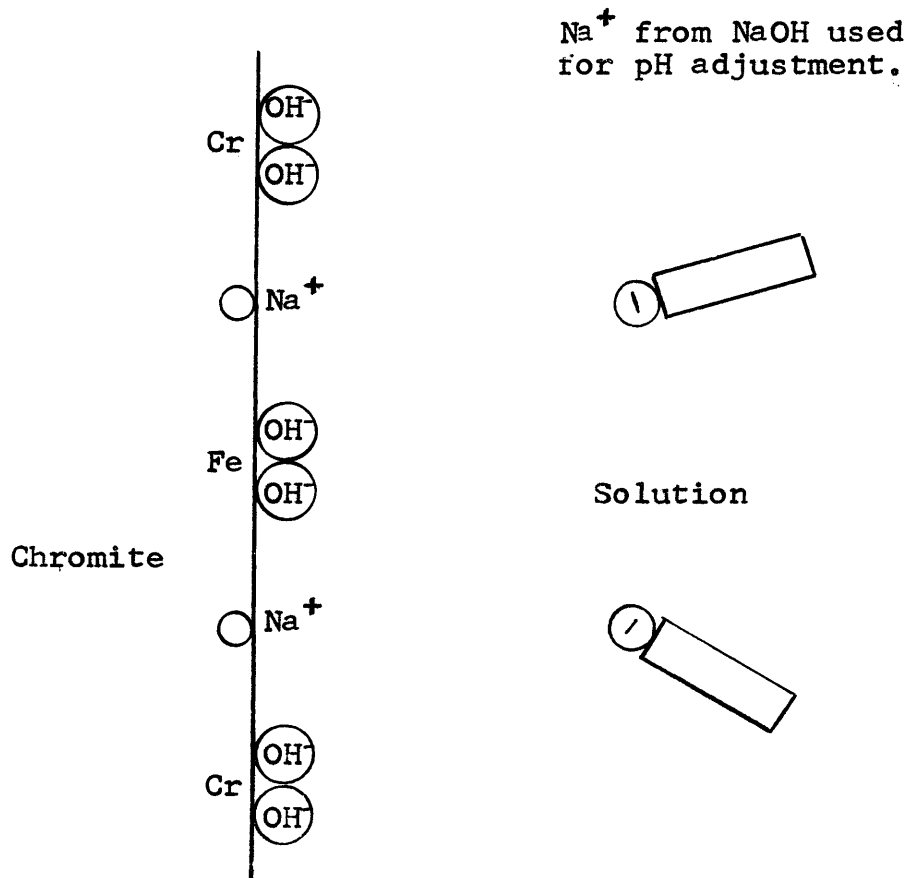
At slightly higher pH, e.g. 2.5,  $\text{Fe}^{+++}$  will start to hydrolyze to the hydroxide complex, and the following model may be represented:



Since ferrous iron is known to oxidize readily to ferric iron, it seems reasonable to predict hydrolysis of the surface iron at pH 2.5. At pH 5,  $\text{Cr}^{+++}$  will start to hydrolyze to the  $\text{Cr}(\text{OH})^{++}$  but  $\text{Fe}^{+++}$  will have hydrolyzed to ferric hydroxide. As such, the following model can be presented:



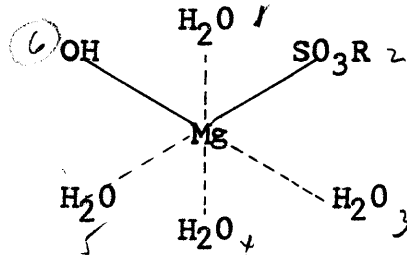
At higher values of pH, e.g. 11, both iron and chromium will have hydrolyzed to their insoluble hydroxides. When this happens, complete depression should occur. The surface might then look as follows:



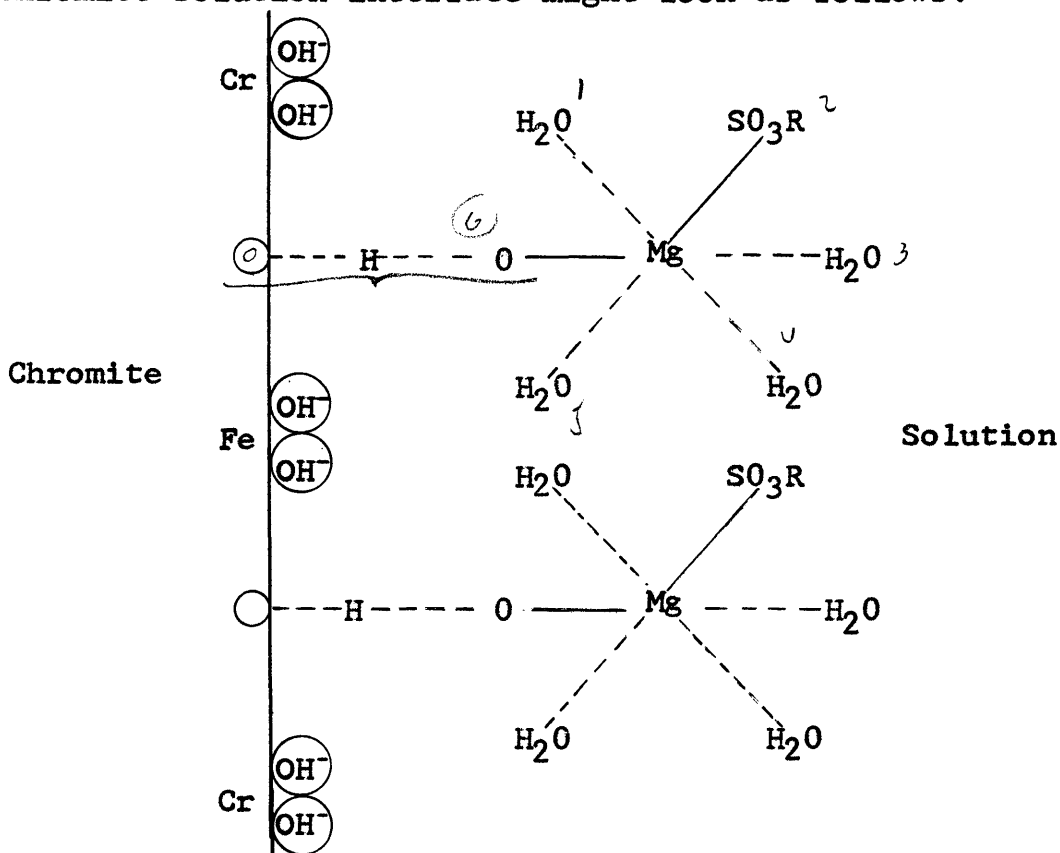
The model has been developed with only iron and chromium at the surface. Chemical analysis showed that aluminum was present in substantial quantity (about 15 percent). Tables 3 and 4 show that  $\text{Al}^{+++}$  starts to hydrolyze at pH 4 and is surely involved in the mechanism. For simplicity's sake, it was omitted in the previous discussion, since it will function similarly to  $\text{Fe}^{+++}$  and  $\text{Cr}^{+++}$ .

Figures 5 and 6 showed that when  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$  were added at pH 10.5 and 11.9, respectively, essentially complete flotation was again affected. This is especially interesting and important, since quartz was found to respond similarly by

others<sup>(8)</sup>. As suggested by Fuerstenau, Martin, and Bhappu, precipitated metal-hydroxy-sulfonates apparently function as collectors. They have represented the basic unit of magnesium-hydroxy-sulfonate as follows:



Bonding to the surface occurs apparently as a hydrogen bond between the oxygen of the compound and an oxygen of the surface. With  $Mg^{++}$  and sulfonate present at pH 10.5, the chromite solution interface might look as follows:



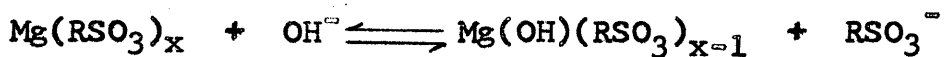
It will be apparent then that the metal ions of the surface are involved in the flotation process below about pH 10. Above this pH, they will have hydrolyzed to their insoluble hydroxides. At this point, though, if a metal ion is added to the system that is capable of hydrolyzing to its first hydroxide complex, for example,  $\text{Pb}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ , the collector, lead-hydroxy-sulfonate, will form in solution and bond through the hydrogen of the hydroxyl to an oxygen of the surface. The data contained in table 2 showed that  $\text{Pb}^{++}$  improved flotation recovery markedly, whereas the addition of  $\text{Cr}^{+++}$ ,  $\text{Al}^{+++}$ , and  $\text{Fe}^{+++}$  actually decreased flotation response. At this pH,  $\text{Cr}^{+++}$ ,  $\text{Al}^{+++}$ , and  $\text{Fe}^{+++}$  have hydrolyzed to their insoluble hydroxides, whereas some  $\text{Pb}^{++}$  was still  $\text{Pb}(\text{OH})^+$ .

The competition of  $\text{Ca}^{++}$  in solution and iron and chromium at the surface for the sulfonate is illustrated in figure 7. Below about pH 11,  $\text{Ca}^{++}$  will be present predominantly as hydrated calcium ion. Since the solubility product of calcium sulfonate has been exceeded under these conditions, some sulfonate will be consumed in precipitating calcium sulfonate. The data show the relative solubilities of chromium, iron, and calcium sulfonates in that the relatively large addition of  $\text{Ca}^{++}(10^{-3}\text{M})$  resulted in a decrease in recovery of only about 15 percent from that obtained in the absence of added  $\text{Ca}^{++}$ . Above pH 11,  $\text{Ca}^{++}$  is hydrolyzing to  $\text{Ca}(\text{OH})^+$  and calcium



hydroxy-sulfonate is functioning as the collector.

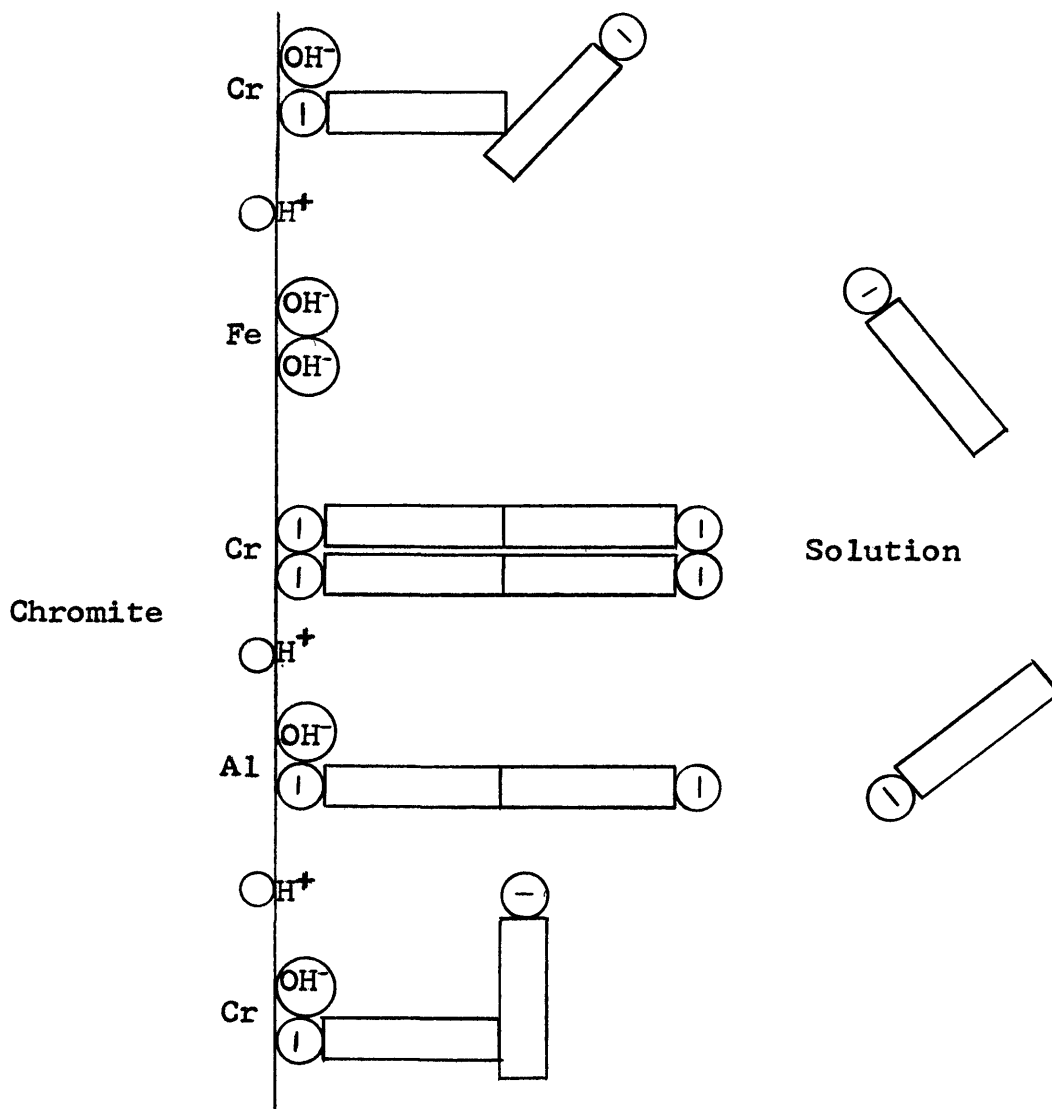
Previous work with quartz<sup>(8)</sup> has shown that flotation response is dependent on the relative concentration of sulfonate and metal ion. Experiments, similar to those conducted with quartz, were conducted to determine whether this same phenomenon occurs with chromite. As shown in figure 8, when  $5 \times 10^{-4}$  mole per liter sulfonate was added at pH 10.4 to systems containing  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and  $1 \times 10^{-3}$  mole per liter  $Mg^{++}$ , flotation recoveries of about 25, 40, and 95 percent, respectively, were obtained. These data can probably be explained with the following equilibria:



where x is a real number, as yet not determined for  $Mg^{++}$ .

Finally, the effect of sulfonate concentration in the absence of added metal ions has been illustrated. Figure 3 showed that when  $1 \times 10^{-5}$  mole per liter sulfonate was added, there was insufficient absorption to render the chromite particles hydrophobic. The optimum sulfonate concentration was found to be about  $1 \times 10^{-4}$  mole per liter; a sulfonate concentration of  $1 \times 10^{-3}$  mole per liter was found to decrease flotation recovery drastically.

At this later condition, the chromite-solution interface probably looks like the following:



Micelles have formed at the surface in which the polar part of sulfonate is projecting into the solution phase. Under these conditions, the chromite surface will be hydrophylic and nonfloatable.

## SUMMARY AND CONCLUSIONS

A micro-flotation technique was used to determine the mechanisms involved in sulfonate flotation of chromite. The results of this investigation lead to the following conclusions:

1. Chromite responds well to flotation with a high molecular weight sulfonate as collector. This observation is most important practically, as chromite has been difficult to concentrate with other flotation techniques.
2. An optimum sulfonate concentration of about  $1 \times 10^{-4}$  mole per liter was determined at neutral pH for this system. A sulfonate concentration of  $1 \times 10^{-3}$  mole per liter results in micelle formation at the chromite-solution interface, with subsequent reduction in recovery.
3. Chromite responds well to sulfonate flotation from pH 1 to pH 7 with  $7.15 \times 10^{-5}$  mole per liter sul-

fonate present. Above pH 7, recovery is decreased and is essentially zero at pH 11 due to  $\text{Cr}^{+++}$ ,  $\text{Fe}^{+++}$ , and  $\text{Al}^{+++}$  hydroxide formation at the surface. The optimum pH appears to be between pH 4 and 5.

4. The addition of a relatively large quantity of  $\text{Ca}^{++}$  to the system below pH 10 resulted in a slight (15 percent) reduction in flotation recovery.
5. The addition of the same amount of  $\text{Ca}^{++}$  above pH 10 resulted in a significant increase in recovery.
6. Two mechanisms of collection are possible, dependent on the pH and the absence or presence of metal ions. In the absence of added metal ions and below pH 10, collection is apparently due to the formation of aluminum, chromium, and iron sulfonates at the surface. Above pH 10, in the presence of an added metal ion capable of hydrolyzing to its first hydroxide complex, the mechanism of collection involves the formation of a metal-hydroxy-sulfonate which bonds to a surface oxygen through the hydrogen of the hydroxyl contained in the metal-hydroxy-sulfonate.
7.  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{+++}$ , do not function as "activators" above pH 10 because they will have hydrolyzed to

their insoluble hydroxides at this pH.

8. The ratio of sulfonate to added metal ion is critical. For example, when the ratio was 2:1, 1:1, and 0.1:1 sulfonate to  $Mg^{++}$  at pH 10.5, recoveries of 58, 72, and 90 percent were obtained. However, when the ratios were 20:1, 10:1, and 1:1 at the same pH, flotation recoveries were 10, 12, and 83 percent, respectively.



## BIBLIOGRAPHY

1. Borjes, Trojano Roberto, 1943, Treatment of the chromite of Santo Antonio, State of Baia: Ministerio Agr., Dept. Nacl. produçao Mineral Lab. Produçao Mineral (Brazil). Tests on treatment of ore, bol. 7, p. 9-26.
2. Butler, J. N., 1964, Ionic equilibrium, a mathematical approach: Reading, Mass., 1st ed., Addison-Wesley Pub. Co., Inc.
3. Davis, C. W., and others, 1938, Establishment of ore testing procedures: U. S. Bur. Mines Rept. Inv. 3370, p. 75-161.
4. de Wet, J. F. (South African Council Sci. Ind. Research), 1953, Classification of chromites in the Transvaal: Jour. Chem. and Mining Soc. S. Africa, v. 53, p. 1-10.
5. Erlenmeyer, H., Hazium Kam, and Theilheimer, W., 1943, Flotation experiments with 8-hydroxyquinoline as collector. v. Flotation experiments on oxide compounds in the presence of metal salts: Helv. Chem. Acta 26, p. 1129-31.
6. Falconer, S. A., and Crawford, B. D., 1944, Froth flotation of some nonsulfide minerals of strategic importance: AIME tech. Pub. 1754, 16 p.
7. Fuerstenau, M. C., and Bhappu, R. B., 1963, Sulfonate flotation of beryl: AIME Trans. v. 226, p. 174-184 (June).
8. Fuerstenau, M. C., Martin, C. C., and Bhappu, R. B., 1963, The role of hydrolysis in sulfonate flotation of quartz: AIME Trans. v. 226, p. 449-454 (Dec.).

9. Gaudin, A. M., 1957, Flotation: New York, 2nd ed., McGraw Hill Co.
10. Hem, Hohn D., 1963, Chemical equilibria and rates of manganese oxidation: Wates-Supply Paper 1667-A, p. A-8.
11. Hovens, Richard, 1946, Froth flotation of chromite with fluorides: U. S. Pat. No. 2,412,217, Dec. 10.
12. Latimer, W. M., 1953, Oxidation potentials: Englewood Cliffs, N. J., 2nd ed., Prentice Hall, Inc., p. 281.
13. Ibid. p. 151
14. Ibid. p. 170
15. MacDonald, Wm. T., 1937, A useful new selectivity modifier in nonsulfide flotation: Mining Met. v. 18, p. 285-6.
16. Morawietz, Hans J., 1959, Chromite flotation: Z. Ergbergbau U. Metallhüttenw v. 12, p. 309-321, 388-393.
17. Pauling, Linus, 1956, General Chemistry: San Francisco, W. H. Freeman and Co., pp. 446-464.
18. Shell Chemical Co., 1961, Industrial Chemical Div., Preliminary Data Sheet, July.
19. Shroder, A. A., 1936, Flotation of slimes from chromite concentration plants: Gorno-Obogatitel, No. 5, p. 35-40.
20. Sutherland, K. L., and Wark, I. W., 1955, Principles of flotation: Australasian Institute of Mining and Metallurgy.
21. Weinig, Arthur J., 1949, Selective flotation of chromite ores: U. S. Pat. No. 2,469,422, May.