

# The interactive effects of the sulphite ion, pH, and dissolved oxygen on the flotation of chalcopyrite and galena from Black Mountain ore

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## SYNOPSIS

These effects were investigated in batch flotation studies, and by the measurement of rest and pulp potentials. At low additions of sulphurous acid as the pH regulator, flotation rate increased with increasing concentrations of dissolved oxygen. The recovery of chalcopyrite dropped significantly below a pH value of about 6,5 at 25 p.p.m. of dissolved oxygen, and below a pH value of about 6 at a dissolved-oxygen concentration of 8,2 p.p.m.

The rest and pulp potentials measured indicated that dixanthogen is the dominant species formed on chalcopyrite surfaces during flotation with sodium ethyl xanthate. The results suggested that the same species might have formed on galena surfaces in the pulp after the ore had been milled in a ceramic mill under nitrogen. Increased additions of sulphurous, sulphuric, and hydrochloric acids increased the rest potentials, while the addition of sodium sulphite decreased these potentials.

## SAMEVATTING

Hierdie effekte is ondersoek in lotflottasietoetse en deur rus- en pulppotensiaalmetings.

Met klein byvoegings van swaweligsuur as pH-reëlaar, het die flottasiereaksietyempo versnel met toenemende opgelostesuurstof-konsentrasies. Die herwinning van chalkopiriet het aanmerklik afgeneem by 'n pH-waarde laer as ongeveer 6,5 en 'n opgelostesuurstof-vlak van 25,0 d.p.m., en by 'n pH-waarde laer as 6,0 en 'n opgelostesuurstof-vlak van 8,2 d.p.m.

Die gemete rus- en pulppotensiale toon dat dixantogeen die belangrikste spesie is wat op chalkopirietoppervlakke gevorm word tydens flottasie met natriumetiexantaat. Die resultate dui daarop dat dieselfde spesie moontlik ook op loodglansoppervlakke in die pulp kon gevorm het nadat die erts in 'n keramiekmeul onder stikstof gemaal is. Groter byvoegings van swaweligsuur, swawelsuur en soutsuur het die ruspotensiale verhoog, terwyl die byvoeging van natriumsulfiet hierdie potensiale verlaag het.

## Introduction

Although the flotation of sulphide has been practised for many years, the interaction between the flotation variables remains largely unclear. Many investigators have undertaken basic work on pure minerals, and to a much lesser extent on ores, in order to gain an understanding of the various mechanisms involved in the flotation of lead, zinc, and copper sulphides. Of special interest are investigations into the depressing influence of the sulphite ion in the flotation of galena<sup>1</sup>, and the influence of the concentration of dissolved oxygen and the redox potential on the differential flotation of chalcopyrite and galena from Black Mountain ore<sup>2</sup>. Pulp potentials and the subsequent flotation of galena were studied by investigators<sup>3</sup> who correlated these results at Mount Isa, in Australia. Information on the reactions occurring at the surface of various sulphide minerals in xanthate solutions was obtained by the measurement of rest potentials<sup>4</sup>, and the same technique was used to show that isopropyl ethylthionocarbamate (Z-200) reacts with chalcopyrite but not with galena, although the mechanism remains unclear<sup>5</sup>.

In the flotation concentrator at Black Mountain, chalcopyrite, galena, and sphalerite are floated sequentially.

Both Z-200 and sodium ethyl xanthate are used as collectors in the copper-flotation circuit. Sulphurous acid is employed as a combined pH regulator and source of sulphite ions for the selective depression of galena. An increase in the pH of the flotation feed due to the back-filling of excavated mining areas posed metallurgical difficulties in flotation, since the copper rougher float is extremely sensitive to the rate and amount of sulphurous acid added<sup>2,6</sup>.

The purpose of the study described here was twofold: (1) to investigate the effect of the sulphite ion on the floatability of chalcopyrite and galena at different concentrations of dissolved oxygen, and (2) to provide a better understanding of the way and extent to which the different variables influence one another under regulated conditions.

## Experimental

Batch flotation tests were carried out in a 3-litre Wemco flotation cell with induced aeration, the impeller speed being kept constant at 900 r/min. Black Mountain ore, containing about 0,35 per cent copper, 6,5 per cent lead, and 2,2 per cent zinc, was used in all the experiments.

Before being floated, the ore was ground to 65 per cent smaller than 200 mesh (75  $\mu\text{m}$ ) under an atmosphere of nitrogen in a ceramic mill. The mill load was as follows: 1000 g of ore, ceramic balls, and 500 ml of deoxygenated tap water. After being milled, the ore was transferred to a

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flotation cell, deoxygenated tap water being added to bring the pulp density to 33 per cent solids.

So that the concentration of the dissolved oxygen in the pulp could be controlled during flotation, the entire flotation cell was placed inside an airtight container. The operator handled the concentrates and took the measurements using rubber gloves fitted to the Perspex frontispiece of the container.

Partial flushing of the container with oxygen allowed the desired oxygen level in the flotation atmosphere to be maintained. The concentration of dissolved oxygen in the pulp was measured with a Schott CG 867 dissolved-oxygen electrode, which was standardized in a saturated sodium sulphite solution. The pulp in the cell (with no chemicals added) was aerated inside the closed container until the oxygen concentration in the pulp was in equilibrium with the environment in the airtight container. An aeration period of about 5 minutes was required.

Aeration was then stopped, and the pulp was conditioned for 3 minutes with a pH regulator, sodium sulphite or sodium sulphate. Subsequently, the pulp was conditioned with a collector for another minute, which was followed by the addition of a frother and conditioning of the pulp for a further minute. The flotation reagents used in this study are summarized in Table I. After the total conditioning time of 5 minutes, the level of dissolved oxygen in the pulp was reduced by about 3 p.p.m. for the maximum addition of sodium sulphite. The previous equilibrium level of dissolved oxygen was reinstated by intermittent aeration of the pulp for about 1 minute. The flow of air was adjusted to prevent a froth overflow. The concentration of dissolved oxygen was monitored continuously.

After conditioning and pre-aeration to the desired level of dissolved oxygen, the pulp pH was measured with a Beckman  $\Phi 70$  pH meter. The ore was then floated for 3 minutes. Samples of the concentrate were collected at intervals of 1 minute by manual scraping. The pH value of the pulp was measured immediately after flotation, and it was found that it did not vary by more than 0,2 in extreme cases (i.e. at pH 5,3). The concentration of dissolved oxygen was monitored and stayed constant throughout the batch flotation test.

The possible effect of the sulphite ion at decreasing pH and also at constant pH was studied by increasing additions of sulphurous acid and sodium sulphite respectively. The corresponding effect of the sulphate ion was studied by

additions of sulphuric acid and sodium sulphate. Variation in mineral floatabilities with pH was investigated by the use of hydrochloric acid as a pH regulator.

Sulphurous acid was obtained from Black Mountain as a 1 per cent  $H_2SO_3$  solution. All the other acids and modulators were chemically pure.

Measurements of rest potential and pulp potential were taken at different pH values. These potentials were measured by the use of mineral electrodes (chalcopyrite from Prieska and galena from Tsumeb) and of platinum respectively. In all cases a saturated calomel electrode (SCE) was used as reference. In the preparation of the chalcopyrite and galena electrodes, a piece of mineral was sealed in the end of a glass tube, and contact was established through a layer of mercury above the mineral.

Before the measurements of rest potential were made, the surface of the electrode was cleaned thoroughly with a piece of waterpaper to ensure an uncontaminated surface. The rest and pulp potentials respectively were measured after the electrodes had been immersed for 10 minutes in a 25 mg/l sodium ethyl xanthate solution and in a pulp containing 33 per cent solids. The collector added to the pulp was a solution consisting of 20 mg of xanthate to 1 litre of water, which is equivalent to 40 mg of xanthate per kilogram of ore. Different amounts of sodium sulphite, sodium sulphate, sulphurous acid, sulphuric acid, and hydrochloric acid were added to the pulp and solutions. The rest and pulp potentials were converted to the standard hydrogen electrode (SHE) scale.

All the measurements of rest and pulp potentials were conducted in solutions or pulps in which the concentration of dissolved oxygen was kept constant at 8,2 p.p.m. Even with the most concentrated sodium sulphite solutions used (i.e. 300 mg/l) with no aeration to maintain a constant level of dissolved oxygen, the rest potentials were found to be only 6 mV lower than when the dissolved oxygen was kept constant at 8,2 p.p.m.

The concentrations of residual sodium ethyl xanthate after 10 minutes of pulp conditioning were used in the calculation of  $X_2/X^-$  reduction potentials at different pH values. At similar pH values, a slightly higher xanthate uptake was measured with hydrochloric acid than with sulphurous acid. In the calculation of the maximum  $X_2/X^-$  reduction potentials, the former was used as a pH regulator but the pulp conditions were identical to those used in the measurement of rest potentials. After a conditioning time

TABLE I  
REAGENTS USED IN BATCH FLOTATION TESTS

Reagents	Dosage
pH regulators: $H_2SO_3$	Varying
$H_2SO_4$	Varying
HCl	Varying
Modulators: $Na_2SO_3$	Varying
$Na_2SO_4$	Varying
Collectors: Sodium ethyl xanthate (NaEtX), Karbochem	20 g/t
Isopropyl ethyl thionocarbamate (Z-200), Dow	20 g/t
Frother: Tri-ethoxybutane (TEB) Senmin	0,1 ml/kg ore

TABLE II  
CALCULATED DIXANTHOGEN/XANTHATE REDUCTION POTENTIALS AT DIFFERENT pH VALUES IN PULP AFTER 10 MINUTES

Conditions:  
Concn of diss.  $O_2$  8,2 p.p.m.  
Temperature 25°C  
Initial NaEtX concn in solution 20 mg/l =  $1,39 \times 10^{-4}$  M

pH	Xanthate uptake, % of initial concn	Residual xanthate $M \times 10^5$	$E_{calc}$ mV
8,2	51,7	6,70	+187
7,0	64,7	4,90	+195
6,5	68,6	4,36	+198
5,5	74,2	3,58	+203
5,0	76,1	3,32	+205

of 10 minutes, a representative sample of pulp was taken and immediately vacuum filtered. The clear filtrate was titrated with a standard solution of potassium dichromate, and the amount of dissolved oxygen was determined. The concentration of dissolved oxygen was monitored and stayed constant throughout the flotation test. Sodium ethyl xanthate was implemented as a collector at a dosage of 20 g/t.

These diagrams show that the maximum copper grade, as well as the maximum copper recovery and copper-lead selectivity, occurs at a pH value of about 6,0. Whereas galena is steadily depressed by increasing amounts of sulphurous acid, the recovery and grade of chalcopyrite

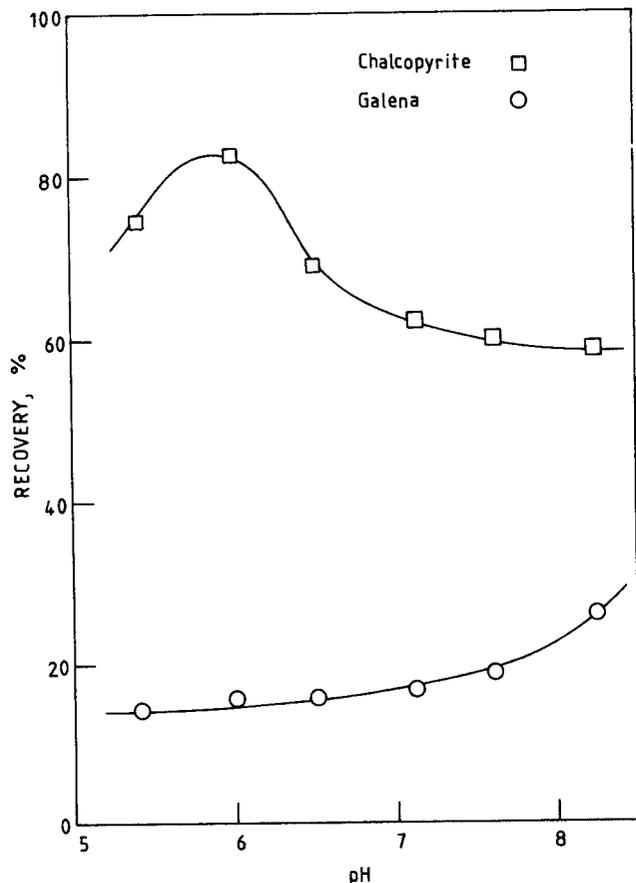
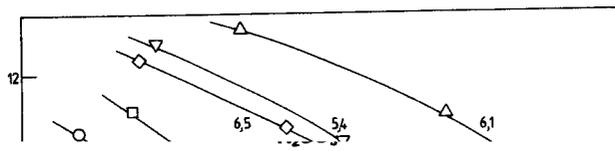


Fig. 1—Variation in the recovery of chalcopyrite and galena for ore milled in a steel mill. NaEtX addition: 20 g/t, pH regulator:  $H_2SO_3$



increase as the pH is decreased. Below pH 6, the decrease in both the grade and the recovery of chalcopyrite may be caused by the reaction of the collector with soluble salts, thereby reducing the effective concentration of collector in the pulp<sup>7</sup>.

A comparison of these results with the results obtained when the ore was milled under an atmosphere of nitrogen in a ceramic mill shows that milling in a steel mill followed by pre-aeration to a dissolved-oxygen concentration of 7,5 p.p.m. results in much higher copper grades.

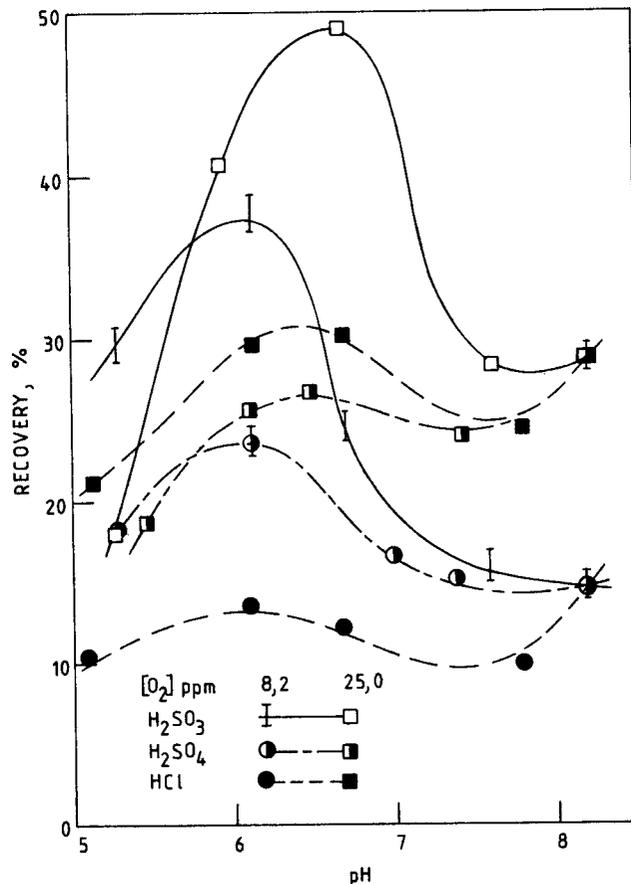


Fig. 3—Comparison of pH regulators in the recovery of chalcopyrite. NaEtX addition: 20 g/t. I and  $\Phi$  indicate the variation in recovery obtained from two independent experiments carried out under identical conditions

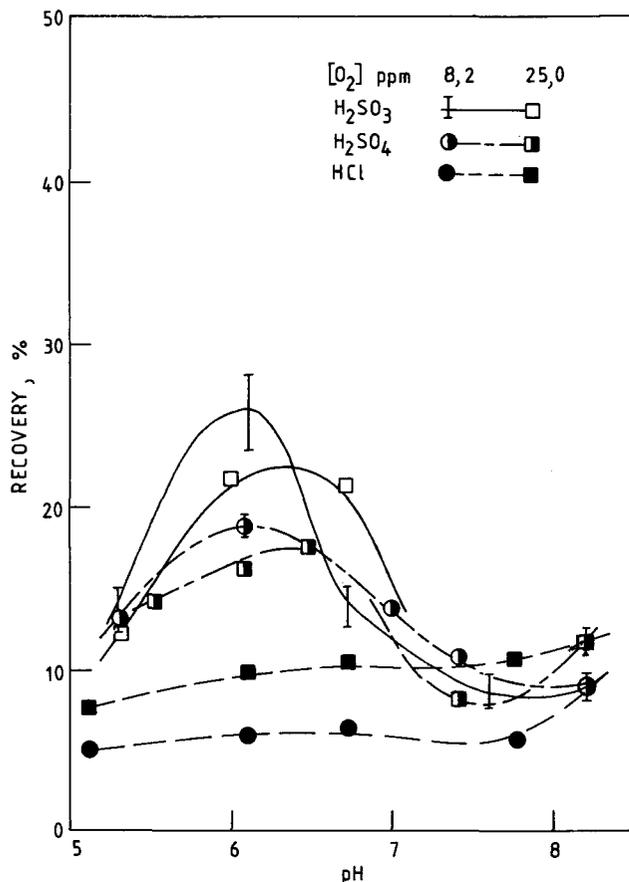


Fig. 4—Comparison of pH regulators in the recovery of galena. NaEtX addition: 20 g/t. I and  $\Phi$  indicate the variation in recovery obtained from two independent experiments carried out under identical conditions

#### Comparison of the pH Regulators Used

Figs. 3 and 4 illustrate the variation in the recoveries of chalcopyrite and galena when different pH regulators were used for a flotation time of 3 minutes. As indicated, the reproducibility of these results is satisfactory.

There was little variation in the recovery of both chalcopyrite and galena when hydrochloric acid was used as a pH regulator at a constant level of dissolved oxygen. The recovery of both minerals increased when the concentration of dissolved oxygen increased. Also, during the collectorless flotation of ore milled in a steel mill, it was observed that pre-aeration of the pulp before the addition of frother resulted in an increase in the recovery of chalcopyrite over that when there was no pre-aeration. Although it cannot be proved, a possible explanation for the increase in recovery of the minerals may be that increased adsorption of molecular oxygen promotes dehydration of the sulphide minerals, which renders them more hydrophobic.

Very low copper grades (about 0,5 per cent) were obtained when the ore was milled under an atmosphere of nitrogen in a ceramic mill and subsequently aerated before being floated. With increasing additions of sulphurous acid at a dissolved-oxygen concentration of 8,2 p.p.m., the recovery of water increased until a pH value of 6,1 was used, after which the recovery of water decreased slightly. Under these conditions, the froth poured over the lip of the

cell during the initial stages of flotation (the first 2 minutes). Initially, the froth was very loose and runny, but it changed later to a foamy, solid texture. Whereas the concentrates recovered after 1 minute were very dark-coloured, those during the later stages of flotation became greyish. The copper grade increased slightly with flotation time. Although an attempt was made to facilitate the drainage of gangue particles to the pulp by flotation at a froth height of 7 cm, the copper grade was still very low. In many instances, the copper content of the first concentrate was lower than the copper content of the ore (0,35 per cent), which gives an indication of the extent to which the gangue was entrained. After 3 minutes of flotation, the copper grade increased to only about 0,9 per cent.

These froth effects vanished when the ore was milled in an iron mill, and a good copper grade and recovery were obtained easily. No explanations for this difference can be proposed at this stage.

The possible effect of the sulphite ion on the flotation of chalcopyrite and galena at different pH values is illustrated by the recoveries obtained when sulphurous acid and hydrochloric acid were used as pH regulators respectively (Figs. 3 and 4). At both concentrations of dissolved oxygen, there is a marked increase in the recovery of chalcopyrite when sulphurous acid is used as a pH regulator instead of hydrochloric acid. At pH values below 7, the recovery of galena is also increased if sulphurous acid is used as a pH regulator instead of hydrochloric acid.

When sulphuric acid is used as a pH regulator instead of hydrochloric acid, the recovery of chalcopyrite is increased at a dissolved-oxygen concentration of 8,2 p.p.m. but decreased at a dissolved-oxygen concentration of 25 p.p.m. In the recovery curves for chalcopyrite in Fig. 3, with sulphuric acid as the pH regulator, the effect of dissolved oxygen diminishes as the pH is decreased. Fig. 4 shows that, at both levels of dissolved oxygen, sulphuric acid, in comparison with hydrochloric acid, increases the recoveries of galena at pH values below 7. For both chalcopyrite and galena at both levels of dissolved oxygen, sulphurous acid gives higher recoveries than either hydrochloric or sulphuric acid. No explanation can be given for these phenomena.

Fig. 3 shows that, at pH values higher than about 5,8, the recovery of chalcopyrite increases when the concentration of dissolved oxygen is increased, while the opposite situation occurs at pH values lower than about 5,8 when sulphurous acid is used as the pH regulator. At a dissolved-oxygen level of 8,2 p.p.m., the maximum recovery of chalcopyrite occurs at a pH of about 6,1, while this maximum occurs at a pH of about 6,8 when the level of dissolved oxygen is 25 p.p.m. The occurrence of a maximum chalcopyrite recovery can be explained by the possible cleaning effect of the sulphite ion to render the chalcopyrite more hydrophobic, which is opposed by the possible formation of surface oxidation products as the pH is decreased. The higher dissolved oxygen level (25 p.p.m. as compared with 8,2 p.p.m.) shifts the occurrence of a maximum chalcopyrite recovery to a higher pH value when sulphurous acid is used as the pH regulator.

Fig. 4 shows that, with sulphurous acid, a maximum recovery of galena occurs at a slightly higher pH at a dissolved-oxygen concentration of 25 p.p.m. than at 8,2 p.p.m. For pH values higher than about 6,4, an increase in the level of dissolved oxygen increases the recovery of galena, while the opposite happens at pH values lower than about 6,4. An increase in the level of dissolved oxygen decreases the maximum recovery of galena, as opposed to the effect of oxygen on the recovery of chalcopyrite. Optimum copper-lead selectivity can be attained from flotation at a dissolved-oxygen level of 25 p.p.m. in the pH range between about 5,8 and 6,4. It is expected that a higher level of dissolved oxygen will slightly increase this optimum pH value.

Flotation studies with isopropyl ethylthionocarbamate (Dow Z-200) have indicated that this collector can be combined effectively with xanthate in the separation of chalcopyrite and galena. Essentially the same recovery-pH trends were observed with Z-200 as with sodium ethyl xanthate, but the selectivity is better with the former at higher concentrations of dissolved oxygen (Figs. 5 and 6). As with xanthate, maximum recoveries of both chalcopyrite and galena were observed at higher pH values when the level of dissolved oxygen was 25 p.p.m. instead of 8,2 p.p.m. Bench-scale flotation tests in the flotation concentrator at Black Mountain indicated that a combined collector concentration of about 20 g/t (xanthate 7 g/t and Z-200 13 g/t) not only yields a higher copper recovery than when only xanthate is used, but the copper-lead selectivity is also greatly improved.

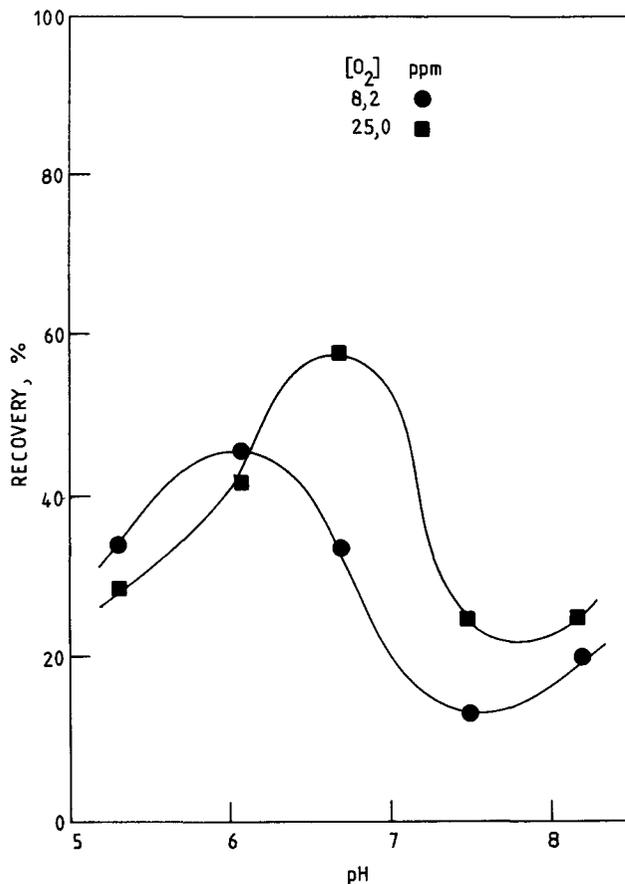


Fig. 5—Recovery of chalcopyrite, with Dow Z-200 (20 g/t) and H<sub>2</sub>SO<sub>3</sub> as pH regulator

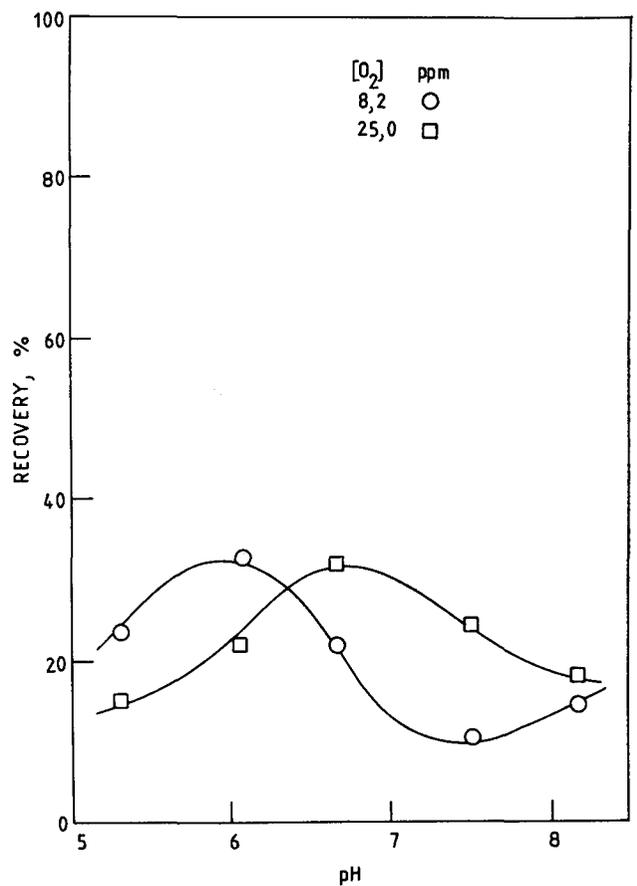


Fig. 6—Recovery of galena, with Dow Z-200 (20 g/t) and H<sub>2</sub>SO<sub>3</sub> as pH regulator

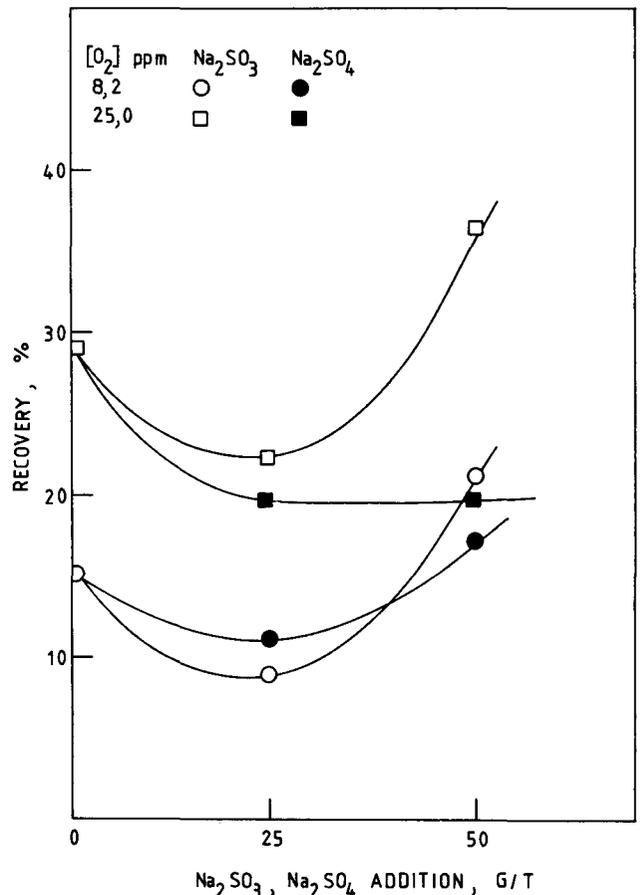


Fig. 7—Influence of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> on recovery of chalcopyrite. NaEtX addition: 20 g/t, pH: 8,2

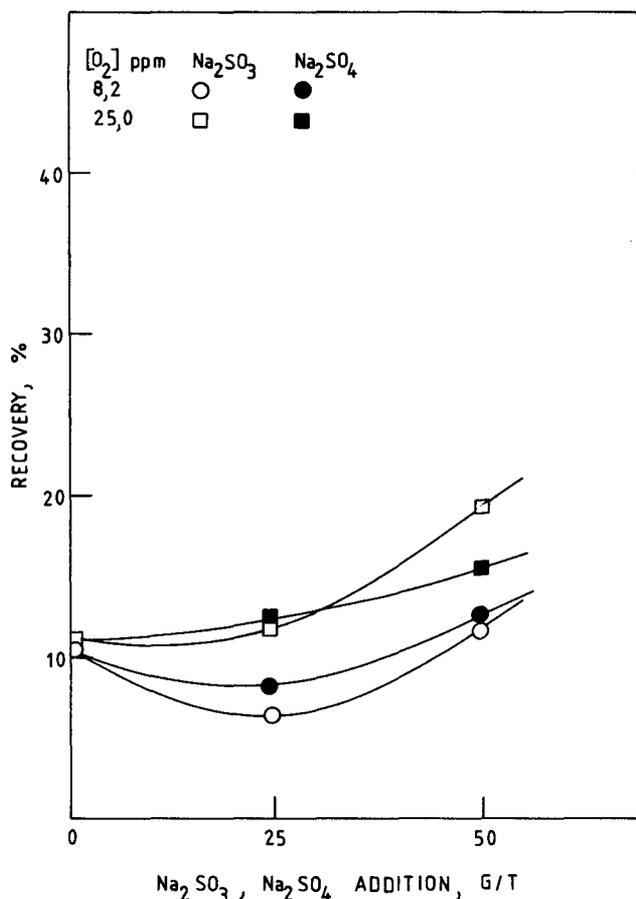


Fig. 8—Influence of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> on the recovery of galena. NaEtX addition: 20 g/t, pH: 8,2

#### The Effect of Sulphite and Sulphate at Constant pH

Batch flotation with sodium sulphite and sodium sulphate was conducted at a constant pH of 8,2 so that the isolated effects of the sulphite and sulphate anions respectively could be investigated on the recovery of chalcopyrite and galena (Figs. 7 and 8).

At increasing sodium sulphite additions of up to 25 g/t, the recovery of chalcopyrite decreased, while galena was slightly depressed at low concentrations of dissolved oxygen. At higher sodium sulphite concentrations, however, the recovery of both minerals increased, together with a significant increase in the recovery of water. This complements the flotation results obtained with sulphurous acid as the pH regulator. These results show that increased additions of sulphite ion increase entrainment in the froth, although the effect on chalcopyrite is more pronounced than that on galena.

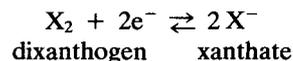
Increasing additions of sodium sulphate up to 25 g/t reduced the recovery of chalcopyrite, but higher additions increased its recovery only at lower levels of dissolved oxygen. The same effect was observed when sulphuric acid was used as the pH regulator. This may indicate that most of the variations in recovery obtained with sulphuric acid can be attributed to the effect of the sulphate ion, which does not influence the recovery of galena significantly.

Figs. 7 and 8 show that higher concentrations of dissolved oxygen promote copper-galena selectivity.

#### Measurement of Rest Potentials

The rest potentials of chalcopyrite and galena were studied in an effort to elucidate the reactions occurring on the respective mineral surfaces during flotation. Measurements of rest potentials in a  $1,92 \times 10^{-4}$  M sodium ethyl xanthate solution, as well as in an aerated pulp (with an initial xanthate concentration of  $1,39 \times 10^{-4}$  M), are presented in Figs. 9 to 12. Oxidation of the collector to its dimer occurs only on those minerals that display a rest potential above the corresponding reversible potential for dimer formation<sup>4,8</sup>. Metal-collector compounds are formed instead for those sulphides that give a rest potential below this value.

The reduction potentials for the dixanthogen/xanthate couple



under the above-mentioned conditions were calculated according to the Nernst equation:

$$E_{\text{X}_2/\text{X}^-} = E^\circ + 0,0128 \ln (a_{\text{X}^-})^{-2}$$

at a temperature of 25°C. The standard potential<sup>4</sup>  $E^\circ$  of -0,06 V was assumed to stay constant over the pH range studied. The *minimum* reduction potential for the conditions in the  $1,92 \times 10^{-4}$  M NaEtX solution was calculated as +156 mV, indicated by dotted lines in Figs. 9 to 12. In other words, if allowance is made for a possible decrease in the concentration of the collector, the X<sub>2</sub>/X<sup>-</sup> reduction potential would increase.

Likewise, if allowance is made for the decrease in the concentration of xanthate in the pulp due to possible adsorption or reaction with the other species present, the dixanthogen/xanthate reduction potential increases. The *maximum* reduction potential at each pH value was calculated by use of the concentrations of residual xanthate in the pulp after 10 minutes and the Nernst equation. These potentials are presented in Table II as a function of pH and percentage of initial xanthate taken up. The initial concentration of xanthate was 40 mg per kilogram of ore, or  $1,39 \times 10^{-4}$  M in the solution in the pulp. These potentials are indicated as broken lines in Figs. 9 to 12.

Figs. 9 and 10 show that the rest potentials of chalcopyrite and galena in the aerated pulp after 10 minutes are higher than the maximum X<sub>2</sub>/X<sup>-</sup> reduction potentials at all pH values. This indicates that dixanthogen is probably formed on both minerals in the pulp. It is possible, however, that rest potentials may differ depending on the origin of the mineral<sup>4</sup>. For this reason, although measurements of rest potentials may yield valuable information regarding the processes possible on the mineral surface, no absolute conclusions can be drawn from these data.

Measurements of rest potentials obtained in the  $1,92 \times 10^{-4}$  sodium ethyl xanthate solution suggest that dixanthogen is probably the dominant surface species formed on chalcopyrite surfaces at pH values less than 7,0. However, lead xanthate is probably formed on galena because the rest potentials are lower than the calculated minimum reduction potential.

The formation of dixanthogen on chalcopyrite surfaces is in agreement with observations made by Allison *et al.*<sup>4</sup>

Richardson and Maust<sup>9</sup> have discussed contrasting results published on the formation of galena surface species. For example, Allison *et al.*<sup>4</sup> found that lead xanthate,  $PbX_2$ , was the major product formed when galena was treated with xanthate solutions under conditions corresponding to an essentially unlimited oxygen supply. This is in agreement with the results shown in Fig. 10 for pure solutions with pH values higher than about 4. The results of Allison *et al.*<sup>4</sup> are in contrast to the results of Fig. 10 for an aerated pulp, but those investigators did not determine rest potentials in pulps, but merely in pure solutions.

Figs. 9 and 10 reveal a linear relationship between rest potential and pH for chalcopyrite in pulps and xanthate solutions, and for galena in the pulp when hydrochloric acid is used as pH regulator. This supports an electrochemical oxidation of xanthate and the formation of dixanthogen on chalcopyrite in pulps and solutions at pH values below 7, as well as on galena in pulps. No such linear relationship between rest potential and pH exists for galena in solution, which may support the formation of lead xanthate under these conditions.

When sulphurous or sulphuric acid is used instead of hydrochloric acid, the reduced rest potentials observed are probably due to an interaction between the sulphite or sulphate ions in solution and the electrode surface.

The increase in the rest potentials of both chalcopyrite and galena at pH values less than 3 in the solutions concerned is presumably caused by hydrolysis of the sulphite and sulphate ions respectively. This may be the reason for the uncontrolled activation of galena at low pH values observed in the flotation circuit at Black Mountain<sup>7</sup>.

Studies of contact angles have shown<sup>8</sup> that, when dixanthogen is the dominant species formed on a mineral surface, a strongly hydrophobic surface results. Although electrochemical measurements have indicated that the initial chemisorbed xanthate layer on galena is hydrophobic and that flotation commences at potentials where this species is formed with only small amounts of dixanthogen present, this does not exclude the possibility that dixanthogen also plays an important supporting role<sup>8</sup>. The formation of dixanthogen on galena surfaces in copper-lead separation would be seriously detrimental to the depression of galena because of the irreversibility of the xanthate adsorption reaction when the dimer is formed<sup>10</sup>.

Figs. 11 and 12 show that, in solutions and pulps at a pH of 8.2, increasing additions of sodium sulphite result in a decrease in the rest potentials of both chalcopyrite and galena. The results indicate that dixanthogen is possibly formed on galena in the pulp at concentrations of up to 50 g of sodium sulphite per ton of ore, which was the concentration range used in the experiments illustrated in Fig. 8. Lead xanthate may be formed on galena surfaces in the solution. Fig. 11 shows that dixanthogen is probably formed on chalcopyrite surfaces in the pulp at sodium sulphite additions of up to about 138 g/t, which was higher than the concentrations used for the results shown in Fig. 7. Dixanthogen is probably not formed on chalcopyrite in the xanthate solution at a pH value of 9.6, as indicated in Fig. 11. Increasing additions of sodium sulphate have

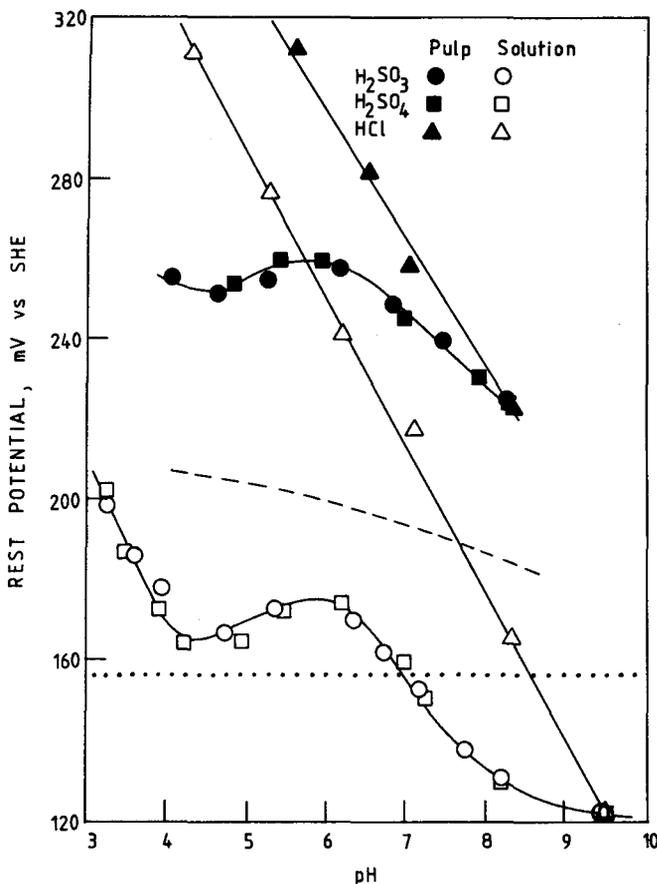


Fig. 9—Effect of pH regulators on the rest potential of chalcopyrite.  $X_2/X^-$  reduction potentials: solution ····, pulp ———

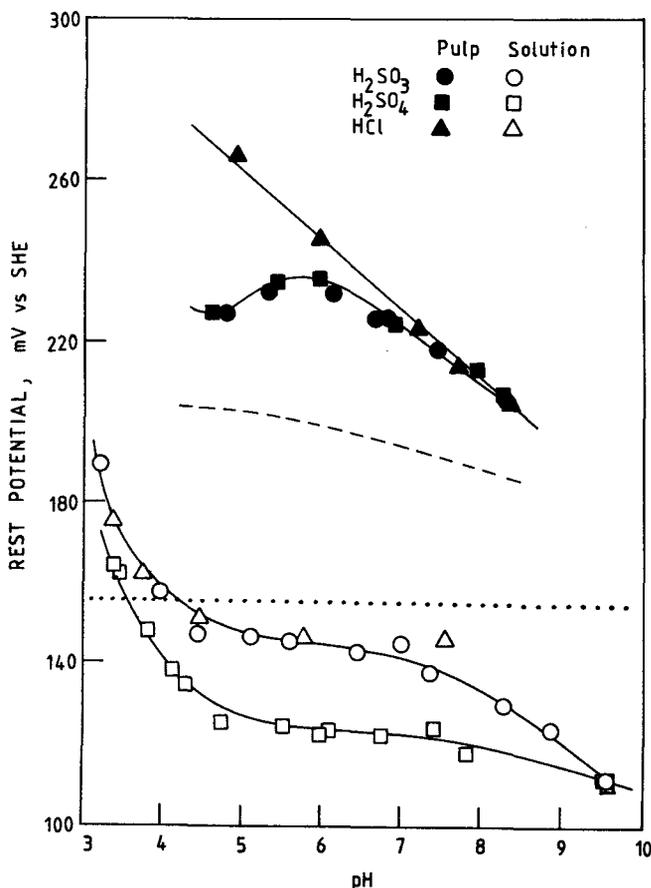


Fig. 10—Effect of pH regulators on the rest potential of galena.  $X_2/X^-$  reduction potentials: solution ····, pulp ———

virtually no effect on the rest potentials of either chalcopyrite or galena in both the pulp and the solutions.

The milling environment and the concentration of dissolved oxygen greatly affect the rest potentials of both chalcopyrite and galena in the pulp. Milling under a reducing atmosphere (dissolved-oxygen concentration 0,1 p.p.m.) results in low rest potentials for both minerals, as shown in Table III. Although no dixanthogen is formed on chalcopyrite under these circumstances, the dominant species formed on galena surfaces is probably chemisorbed xanthate. Subsequent aeration of the pulp (dissolved-oxygen concentration 8,2 p.p.m.) greatly increases the rest potentials of both chalcopyrite and galena. While dixanthogen is probably formed on chalcopyrite, imposing hydrophobicity on that mineral, the possible formation of multilayers of lead xanthate on galena would render the mineral hydrophilic and less floatable. These results are in accordance with the flotation results presented in Fig. 1.

TABLE III  
INFLUENCE OF DISSOLVED OXYGEN ON REST POTENTIALS

Dissolved O <sub>2</sub> p.p.m.	Rest potentials, mV vs SHE	
	Chalcopyrite	Galena
0,1	78	65
8,2	198	146

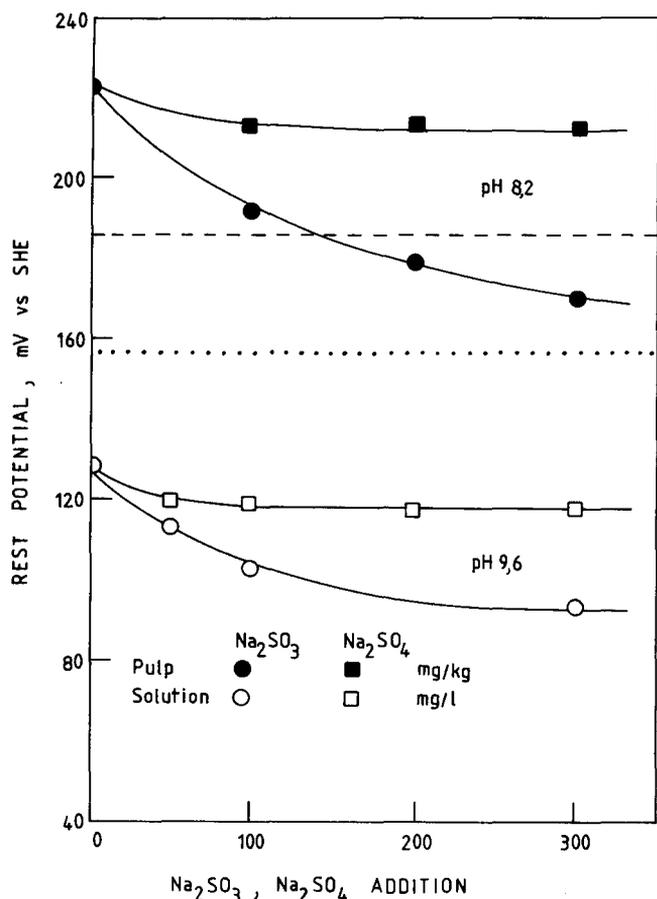


Fig. 11—Influence of sulphite and sulphate concentrations on the rest potential of chalcopyrite. X<sub>2</sub>/X<sup>-</sup> reduction potentials: solution ···, pulp ---

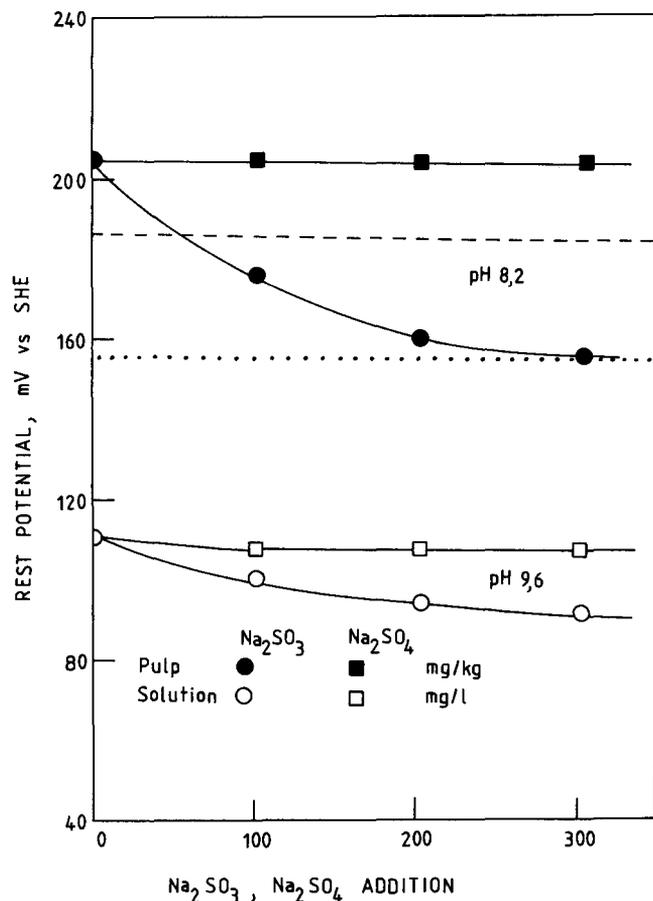


Fig. 12—Influence of sulphite and sulphate concentrations on the rest potential of galena. X<sub>2</sub>/X<sup>-</sup> reduction potentials: solution ···, pulp ---

#### Pulp Potential

The pulp potential (Eh) is an important electrochemical parameter that has been correlated with flotation results<sup>2,3</sup>. It is measured as the potential of a platinum wire relative to a saturated calomel electrode (SCE), both of which are inserted into a stirred pulp. The potential is then converted to the standard hydrogen electrode (SHE) scale. Information regarding these potentials can be very useful in the prediction of regions of optimal flotation<sup>3</sup>, although the 'meaning' of the pulp potential in a complex pulp remains obscure. The Eh monitors the relevant electrochemical parameter that may determine the condition of the sulphide surface.

Eh measurements are presented in Figs. 13 and 14. Notable is the increased Eh when the addition of sulphurous acid is increased (as was observed with rest potentials). Increased additions of sodium sulphite result in a decrease in pulp potential, as indicated in Fig. 14. At no stage, however, was a potential in the region of +150mV approached, which was observed to cause the effective depression of galena at Mount Isa in Australia<sup>3</sup>.

Laboratory batch flotation tests have shown that the initial Eh has a major influence on the flotation of chalcopyrite<sup>2</sup>, as well as of galena<sup>3</sup>. With the sulphite, the addition of the galena was suppressed for only a small decrease in Eh. This depression was due to the sulphite ion<sup>3</sup> and not because of the slight variation in Eh. The results obtained

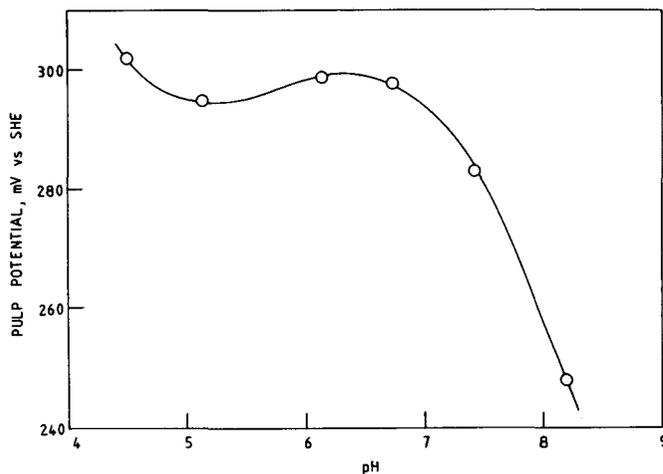


Fig. 13—The effect of  $H_2SO_4$  as pH regulator on the pulp potential, Eh. NaEtX addition: 20 g/t

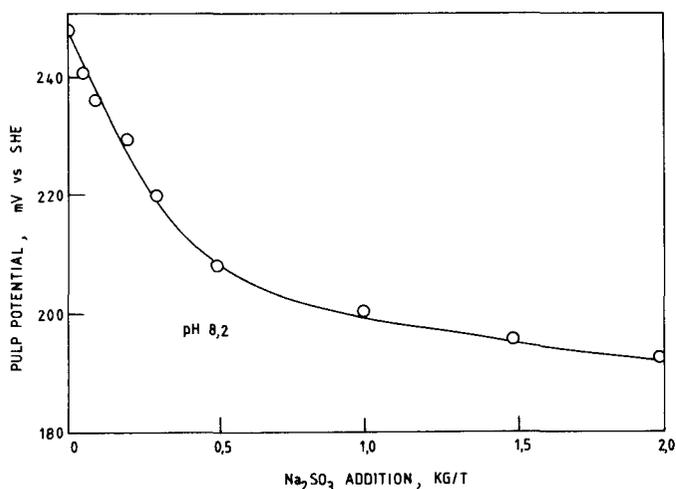


Fig. 14—Variation of pulp potential (Eh) with  $Na_2SO_3$  addition. NaEtX addition: 20 g/t, pH: 8,2

in the present study agree with these findings.

A comparison of the rest potentials of chalcopyrite and galena after 10 minutes (Figs. 9 and 10) with the Eh measurements given in Fig. 13 under the same conditions indicates that Eh may prove a useful control parameter to ensure the formation of dixanthogen in the flotation of chalcopyrite (Table IV). The relationship between the rest potentials of chalcopyrite in the pulp and the Eh when sulphurous acid is used as the pH regulator is given by

$$E_{cha} = Eh - 45 \text{ (mV)}.$$

For galena, the relationship is given by

$$E_{gal} = Eh - 67 \text{ (mV)}.$$

TABLE IV  
RELATIONSHIP BETWEEN REST POTENTIAL AND PULP POTENTIAL (mV vs SHE)

pH	Rest potentials, E		Eh	Eh-E	
	Chalcopyrite	Galena		Chalcopyrite	Galena
7,4	239	218	283	44	65
6,7	249	225	298	49	73
6,1	257	232	299	42	67
5,1	250	232	295	45	63
Average				45	67
Standard deviation				2,94	4,32

## Conclusions

The recoveries of chalcopyrite and galena are sensitive to the amount of sulphurous acid or sodium sulphite added. When either sodium ethyl xanthate or isopropyl ethylthionocarbamate is used as the collector, both minerals reveal a pH value at which maximum recovery is obtained when sulphurous acid is added as the pH regulator. This pH value increases slightly as the level of dissolved oxygen is increased.

Sulphite additions of more than 25 g/t result in an increased recovery of both chalcopyrite and galena, which is accompanied by a higher recovery of water.

Under the aeration conditions studied, poor copper grades are obtained when the ore is milled in a ceramic mill. Milling in a steel mill, followed by pre-aeration, greatly improves the copper grades and copper-lead selectivity when sulphurous acid is used as the pH regulator. In this case, an optimum pH also exists at which the recovery of chalcopyrite is at a maximum.

Although it cannot be proved, the sulphite ion appears to have a cleaning effect on chalcopyrite to increase recovery of the mineral.

The measurements of rest and pulp potentials showed that, at pH values of less than 8, increased additions of sulphurous acid increased these potentials. Dixanthogen was formed on chalcopyrite surfaces in the pulp and in the xanthate solution at pH values lower than about 7 when sulphurous acid was used as the pH regulator. Dixanthogen appeared to be formed on galena surfaces in the pulp, but lead xanthate was presumably formed on galena in solutions at pH values higher than about 4.

The effect of an increased concentration of dissolved oxygen on the recovery of chalcopyrite may suggest that, in practice, longer pre-aeration periods will slightly increase the pH values at which maximum copper recoveries will be obtained.

## Acknowledgements

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## Shock-wave and high-strain-rate phenomena

EXPLOMET '85, an International Conference on Metallurgical Applications of Shock Wave and High-strain-rate Phenomena, is to be held in Portland, Oregon, from 28th July to 1st August, 1985.

EXPLOMET '85 will provide a forum for the exchange of information on the metallurgical and other materials effects and applications of shock wave and high-strain-rate phenomena. The excellent response obtained from survey cards sent with the initial announcement indicates that the conference will be as successful as the original EXPLOMET '80 held in Albuquerque, New Mexico. EXPLOMET '85 will consist of invited/plenary talks addressing broader areas and summarizing aspects of generic areas, and contributed talks reporting research efforts. The following keynote talks are currently confirmed:

- T.Z. BLAZYNSKI (The University of Leeds): Explosive Compaction of Polymeric and Ceramic Powdered Materials.
- A.A. DERIBAS (Novosibirsk, U.S.S.R.): Shock Wave Applications in the U.S.S.R.
- G.E. DUVALL (Shock Dynamics Laboratory, WSU): Shock Dynamics Overview — Linking Shock Physics and Shock Dynamics Applications.
- H. KUNZE (Fraunhofer-Institut für angewandte Materialforschung): Materials for Extreme Dynamic Loads.
- V.D. LINSE (Battelle — Columbus): The Particulate Nature of Dynamic Compaction.
- M.A. MEYERS, K.P. STAUDHAMMER, and L.E. MURR (U.S.A.): A Review of Some Contemporary Metallurgical Applications of Shock and High-Strain-Rate Phenomena.
- R. PRÜMMER (Fraunhofer-Institut für Werkstoffmechanik): New Trends in Explosive Powder Metallurgy.
- A. SAWAOKA (Tokyo Institute of Technology): New Aspects of Materials Synthesis by Quenching from a Highly Dense Plasma-like State.
- M. STELLY, and R. DORMEVAL (C.E.A., France): Adiabatic Shearing.
- V.M. TITOV (Novosibirsk, U.S.S.R.): Modification of Materials and Properties by Shock Waves.

Contributed papers describing the results of research and/or developments and applications, especially novel applications of shock wave and high-strain-rate technologies in any of the following areas are solicited:

- High-strain-rate Deformation and Forming
- Explosive Metal Working
- Dynamic Fracture (Including Spallation)
- Hypervelocity Impact
- Adiabatic Shearing and Shear-band Phenomena
- Dynamic Consolidation (Metals/Ceramics/Composites)
- Novel Applications of Explosive and High-strain-rate Technologies
- Modification of Materials and Properties by Shock Waves
- Laser Shock Effects in Materials
- Applications in the Megabar Regime

There will be no concurrent or parallel sessions, and each session will be structured to allow for considerable discussion and exchange of ideas; special workshop sessions will be developed. The papers presented will be edited and published in a book by a major international publishing house similar to those of EXPLOMET '80, which was published as 'Shock Waves and High-strain-rate Phenomena in Metals: Concepts and Applications' (edited by M.A. Meyers and L.E. Murr) by Plenum Publishing Corp. in 1981.

EXPLOMET '85 will have as one of its objectives the acceleration of progress in the field of high-strain-rate deformation and fabrications. It will emphasize applications of shock physics and other fundamental high-strain-rate phenomena. It is intended to provide a forum for the exchange of state-of-the-art information on the metallurgical effects of high-strain-rate deformation and fabrication, and other shock-wave and explosive-technology applications in the materials sciences and engineering.

An abstract of 250 words or less detailing the work to be presented for consideration by the Conference organizers should be sent to the address below. The deadline for abstracts will be 1st March, 1985. Manuscripts of acceptable papers to be presented will be required for the Conference proceedings in a format to be sent with the notice of acceptance. Deadline for the (camera-ready) paper submission will be 15th June, 1985. Invited papers will be allowed 30 text pages while contributed papers will be allowed 15 pages.

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