

## THE USE OF SODIUM SULPHITE TO IMPROVE THE FLOTATION SELECTIVITY BETWEEN CHALCOPYRITE AND GALENA IN A COMPLEX SULPHIDE ORE

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### ABSTRACT

*The processing of complex sulphide ores by the sequential method of flotation requires maximal selectivity. In particular, the entrainment of galena into the chalcopyrite concentrate obtained with a dialkylthionocarbamate-type collector must be minimized. Use of sodium sulphite, in association with alkaline-earth or metal hydroxides released by the ore, helps to reduce the entrainment of lead into the copper ore.*

*We have observed these phenomena with pure minerals and then with a natural ore. Observations of the electrokinetic potential and surface adsorption phenomena of galena suggest a mode of action of  $Ca^{2+}$  and  $Ba^{2+}$  ions or metal hydroxides. The species formed by barium on galena were detected by diffuse reflectance infrared interferometry.*

### Keywords

Sodium sulphite; flotation; selectivity; galena; chalcopyrite

### INTRODUCTION

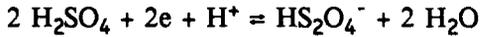
In the flotation of copper minerals from a complex sulphide ore, the choice of method may be sequential, almost invariably in the order copper, then lead, and finally zinc. Bulatovic and Wyslouzil [1] reviewed the reagents and operating conditions used in sequential flotation. Studies undertaken on a ore containing 3% Cu, 3.5% Pb, 12.6% Zn and 18% Fe, and whose mineralogy consisted of chalcopyrite, galena, sphalerite and pyrite associated with silicates (quartz, chlorite, micas), dolomite and traces of gypsum, found that the liberation size was 50  $\mu\text{m}$ , making the sequential method possible.

The reagents that gave good copper selectivity in the laboratory tests were N-ethyl O-isopropyl thionocarbamate (Dow Z-200 or Hoechst 1923-1) as the collector, associated with sodium sulphite as a depressor of galena, sphalerite and pyrite.

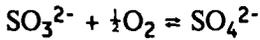
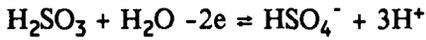
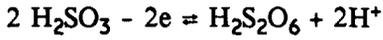
Little has been published on the collecting action of Z-200 on galena. Similarly, the depression of galena by sulphite when thionocarbamate-type collectors are used has not been described. Therefore we studied the mechanism of action of sulphite to avoid detrimental entrainment of galena into the chalcopyrite concentrate.

### PROPERTIES OF SODIUM SULPHIDE

Sodium sulphide ( $\text{Na}_2\text{SO}_3$ ) is a highly water-soluble crystalline white solid with sulphur in oxidation state IV. This compound has both oxidizing and reducing properties [2].

**Oxidizing Properties.**

$\text{H}_2\text{S}_2\text{O}_4$  = dithionous acid

**Reducing Properties**

The latter reaction takes place especially in solution on contact with oxygen dissolved in water. Thus assays of sulphite solutions are often distorted by alteration of the solutions.

Figure 1 reports assays of sulphite solutions at various times. A quarter of the initial concentration has disappeared by the end of 2 hours in the flask. At basic pH, the species  $\text{SO}_3^{2-}$  predominates over  $\text{HSO}_3^-$  and  $\text{H}_2\text{SO}_3$  ( $K_{a1} = 10^{-1.8}$ ,  $K_{a2} = 10^{-7.15}$ ).

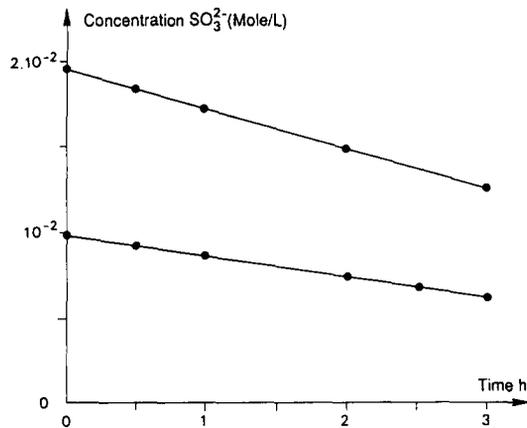


Fig.1 Sodium sulphite degradation as a function of time.

The sulphite ion reacts with a great many metal cations to form metal sulphites that are relatively insoluble in water but are soluble in acid media [2-6].

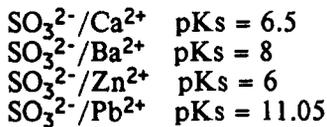
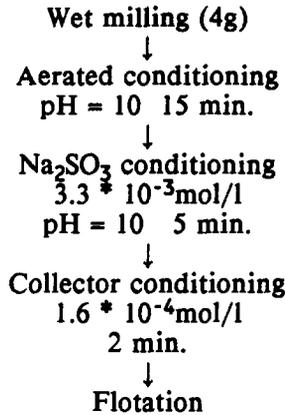


Figure 2 shows the stability of species involving  $\text{Ca}^{2+}$  and  $\text{SO}_3^{2-}$ , as a function of pH and  $\text{pSO}_3^{2-}$ .

**CONDITIONS OF DEPRESSION OF PbS BY  $\text{Na}_2\text{SO}_3$** **Role of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions: Study on pure galena**

For these tests, galena was ground to a  $d_{80}$  of  $50 \mu\text{m}$  in a stainless-steel mill and floated in a  $250 \text{ cm}^3$  pneumatic microcell. The initial concentration of collector was constant at  $1.6 \text{ mg/L}$  \*

$10^{-4}$  mol/l, which corresponds to a flotation yield of 90% (NaOH as pH regulator). The galena flotation scheme was as follows:



Regardless of the dose of sulphite, galena was almost insensitive to the amount of NaOH used to maintain the pH (Fig.3). With lime or barium hydroxide used as regulator, however, depression was seen in the presence of sulphite, more so with Ba(OH)<sub>2</sub>. Regardless of what pH regulator was used, adding sulphite to the galena pulp produced a rise in pH (by 0.4 to 0.5 pH unit).

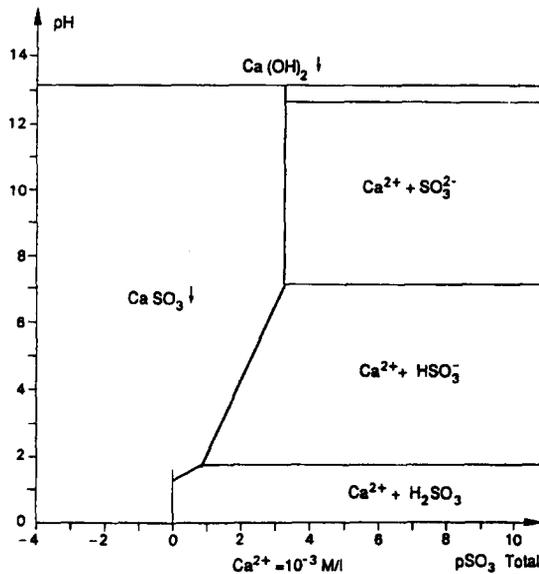


Fig.2 Calcium sulphite stability diagram.

At pH 10, calcium and barium occur as ions. In the absence of sulphite and with NaOH, when these ions were introduced as nitrates at various concentrations, flotation of galena was almost unchanged (Fig. 4). After conditioning with Ca<sup>2+</sup> or Ba<sup>2+</sup>, as nitrates, at doses above  $5 \cdot 10^{-4}$  mol/l, adding sulphite at  $3.3 \cdot 10^{-3}$  mol/l provoked depression of PbS. This proves that these ionic species participate in the depressive action of SO<sub>3</sub><sup>2-</sup>.

Besides this study, Duhamet [3] found that the concentrations of sulphite ( $3.3 \cdot 10^{-3}$  mol/l) and of collector ( $1.6 \cdot 10^{-4}$  mol/l) imply that the promoter is totally complexed by SO<sub>3</sub><sup>2-</sup>. Nevertheless, when Ca<sup>2+</sup> or Ba<sup>2+</sup> was absent, galena was collected; this complexation thus does not worsen the properties of collector.

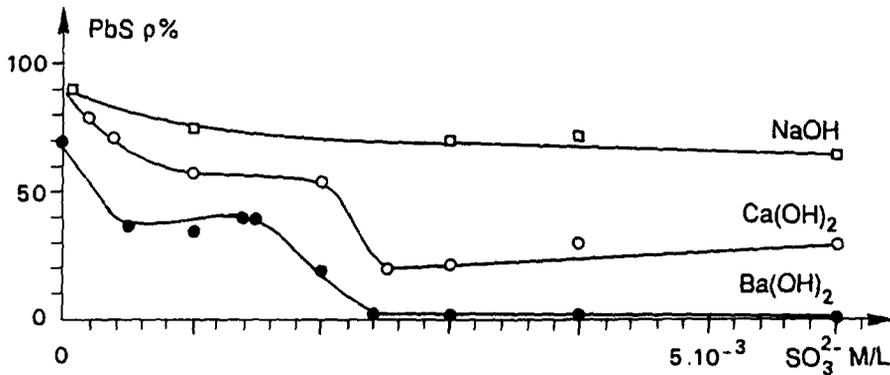


Fig.3  $\text{SO}_3^{2-}$  depressing effect on PbS.

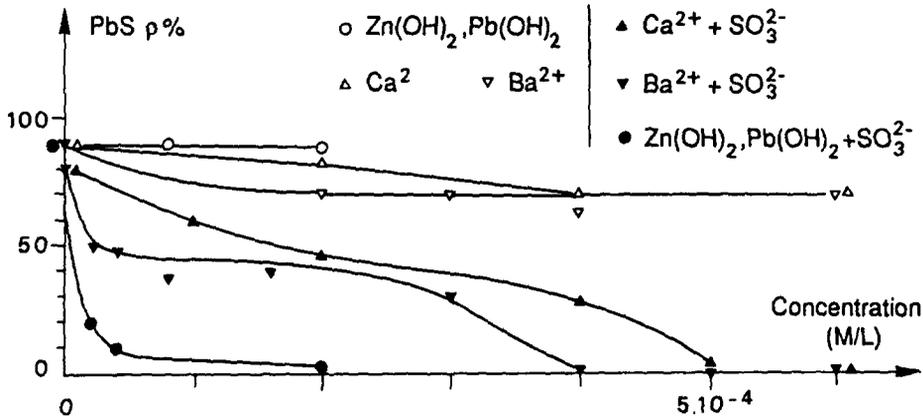


Fig.4 Ions and hydroxides action on galena flotation (with and without sodium sulphite).

#### Effect of $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ on the Ore

To confirm the role of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions in the depression of galena by  $\text{Na}_2\text{SO}_3$ , a series of flotations was performed on the ore. After milling in a ball mill to a  $d_{80}$  of  $50\mu\text{m}$ , the sequence of the standard test was as follows:

- 15 min. aerated conditioning with pH regulated at 10
- 5 min. conditioning with  $\text{Na}_2\text{SO}_3$  (4 kg/t)
- 2 min. conditioning with the collector (75 g/t)
- 5.5 min. flotation with 10 g/t of MIBC.

A test was carried out with NaOH, and several others with NaOH and various amounts of  $\text{Ca}(\text{NO}_3)_2$ . This showed that (Table 1) :

- 1) In spite of the absence of  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$ , little lead was entrained into the float product;
- 2) Adding  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  had only a limited and very localized effect on entrainment of galena over a range of concentrations from  $1.5 \cdot 10^{-4}$  to  $5 \cdot 10^{-4}$  mol/l.

**TABLE 1 Effect of Ca<sup>2+</sup> and Ba<sup>2+</sup> ions on the Cu-Pb-Zn content of chalcopyrite concentrate.**

EXPERIMENTAL	Content %			Recovery %		
	Cu	Pb	Zn	Cu	Pb	Zn
NaOH alone	18.1	3.71	9.15	91.95	18.44	10.95
Ca <sup>2+</sup> = 7.16 x 10 <sup>-5</sup> M/l	18.7	4.78	10.80	93.63	20.28	11.22
Ca <sup>2+</sup> = 1.43 x 10 <sup>-4</sup> M/l	21.2	4.31	8.66	92.95	18.02	8.75
Ca <sup>2+</sup> = 2.85 x 10 <sup>-4</sup> M/l	20.2	3.75	8.25	90.67	14.84	7.88
Ca <sup>2+</sup> = 5.70 x 10 <sup>-4</sup> M/l	21.2	3.69	8.42	93.30	16.55	8.53
Ca <sup>2+</sup> = 1.71 x 10 <sup>-3</sup> M/l	20.2	3.10	7.76	93.08	15.85	8.73
Ba <sup>2+</sup> = 7.16 x 10 <sup>-5</sup> M/l	19.1	4.68	9.56	93.27	18.16	9.42
Ba <sup>2+</sup> = 1.43 x 10 <sup>-4</sup> M/l	20.8	3.84	8.50	90.27	15.75	8.36
Ba <sup>2+</sup> = 2.85 x 10 <sup>-4</sup> M/l	20.2	3.75	8.25	90.67	14.84	7.88
Ba <sup>2+</sup> = 5.70 x 10 <sup>-4</sup> M/l	19.5	4.10	8.85	92.99	17.88	9.34
Ba <sup>2+</sup> = 1.71 x 10 <sup>-3</sup> M/l	18.9	4.19	8.88	92.83	18.17	9.00

An explanation for these results must be sought in the liberation of ions or of metal hydroxides by the ore itself. In particular, the hydroxides of lead and zinc must take the place of the action of calcium.

#### Influence of Pb(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> on Pure Galena

The involvement of these hydroxides was confirmed using pure minerals. The species Pb(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> were produced in the pulp by addition of nitrates of lead and of zinc. Preconditioning galena with these elements even at very low concentrations (5 \* 10<sup>-5</sup> mol/l) leads later to a total depression of galena with 3.3 \* 10<sup>-3</sup> mol/l of sulphite (Fig. 4).

#### Conclusion

The mechanism by which Na<sub>2</sub>SO<sub>3</sub> depresses galena can be studied only by considering soluble species and not precipitated hydroxides. For the latter, adsorptions cannot be determined. Studies with Ca<sup>2+</sup> and Ba<sup>2+</sup> will allow the construction of a model.

### MECHANISM OF DEPRESSION

#### Adsorption of Ca<sup>2+</sup> and Ba<sup>2+</sup> Ions

Ten grams of galena were conditioned in solutions of Ca<sup>2+</sup> and Ba<sup>2+</sup> (nitrates), and the residual ions were assayed, to show whether calcium and barium ions were adsorbed onto galena prior to any sulphite action. The barium assay revealed strong adsorption of ions onto PbS. Figure 5 shows the adsorption isotherms at pH 10, with and without aeration, and at pH 7. At pH 10, adsorption was greater with aeration than without it. Adsorption of Ba<sup>2+</sup> was weaker at pH 7. The assay of calcium solutions in the presence of galena revealed no ion adsorption.

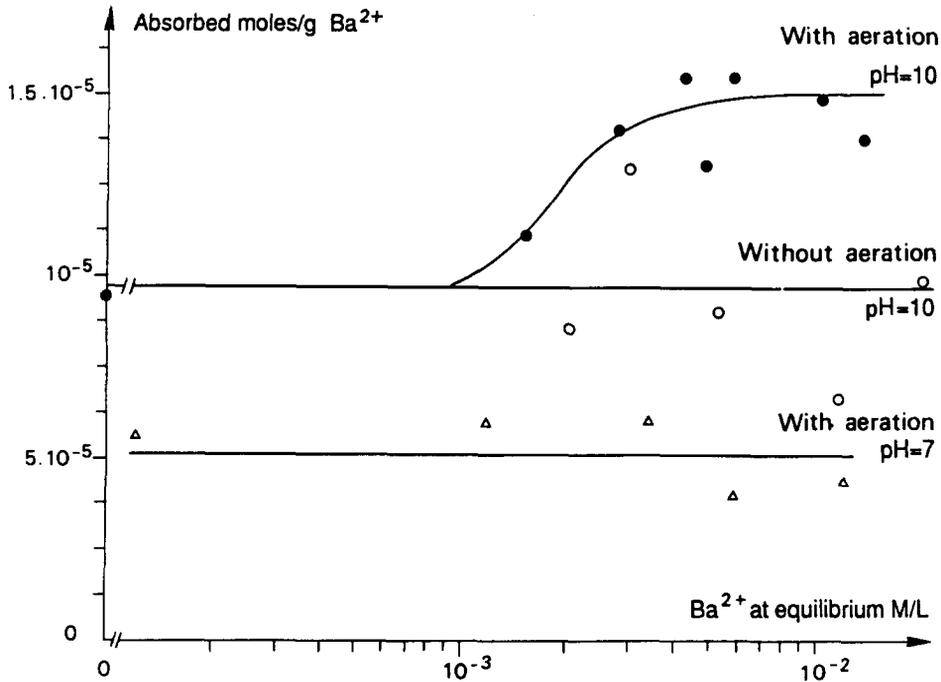


Fig.5  $Ba^{2+}$  adsorption isotherm on galena.

#### Measurement of Electrokinetic Potential

The zeta-potential was measured using a Laser Zee Meter Model 501 equipped with a video system [7].

#### Electrokinetic potential of pure galena as a function of pH

After milling at the natural pH (about 7) in a 18/8 stainless-steel rod mill (0.15m diameter \* 0.25m), followed by conditioning in distilled water for 12h, the surface of the galena was measured as a function of pH (see Fig.6, curve 3). This galena sample proved to have a positive surface charge, as after milling in an acidic medium, and in contradiction with other previously published data [5].

It can be seen that galena dry-milled (Fig.6, curve 5) and conditioned overnight in water has a negative surface charge and that the shape of the curve is very like that obtained with wet milling (Fig.6, curve 3): there is a shift of only about 20mV.

In order to find out whether the manner of milling was crucial, tests were carried out in the same conditions on some galena known to have a normal zeta-potential curve (see Fig.7) and used by Cases and Kongolo [5,7]. For this reference galena, it appeared that the electrokinetic-potential curve as a function of pH was positive if the measurements were not made until after 30 min. of conditioning in water (before adjustment of pH); after 12h, it became negative.

In Figure 6, our galena sample, with conditioning times of half an hour (curve 2) and 12 hours (curve 3) shows only a shift of the peak. Only milling at pH 12 (curve 4) succeeded in giving it a negative or zero charge.

This comparison with a reference galena eliminated any possibility of pollution due to the mill; this phenomenon of positive charge is linked with only one galena. Moreover, it is not very important, since measurements of electrokinetic-potential are useful more to detect relative variations than to determine absolute values.

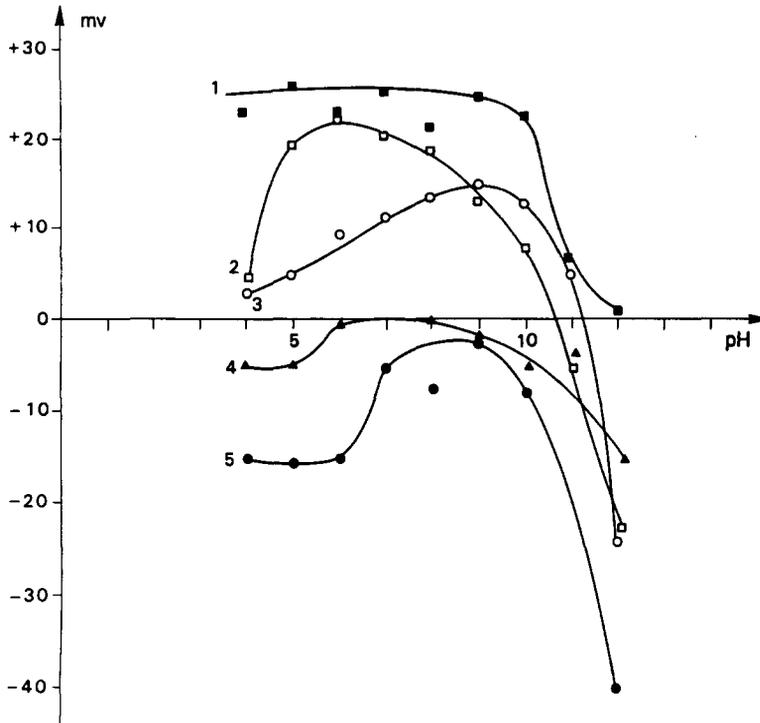


Fig.6 Galena Electrokinetic potential.

Curve	Mill	Milling	Conditioning	pH
1	iron	wet	2h	nat.
2	stainless	wet	0.5h	nat.
3	stainless	wet	12h	nat.
4	stainless	wet	12h	12
5	agate	dry	12h	nat.

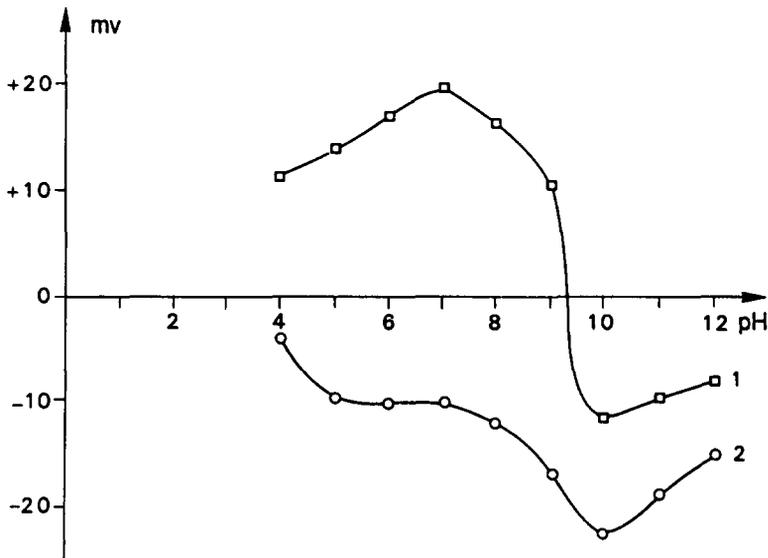


Fig.7 Reference galena electrokinetic potential.

Curve 1 : after 30 min. conditioning.

Curve 2 : after 12 h. conditioning.

### Measurement of electrokinetic potential in the presence of $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ ions

Electrokinetic potential measurements (see Fig.8) made on galena conditioned with several concentrations of these ions showed the following:

- With  $\text{Ba}^{2+}$ , the electrokinetic potential rose sharply with ion concentration, then stabilized at a plateau. The plateau given by assay (adsorption isotherm) does not coincide with that measured from the surface potential.
- With  $\text{Ca}^{2+}$ , the potential rose, but much less.

Thus, for  $\text{Ba}^{2+}$ , the adsorption was characteristic both as regards chemical assay (adsorption) and electrokinetic potential. For  $\text{Ca}^{2+}$ , only the zeta potential showed that some calcium was bound to the galena.

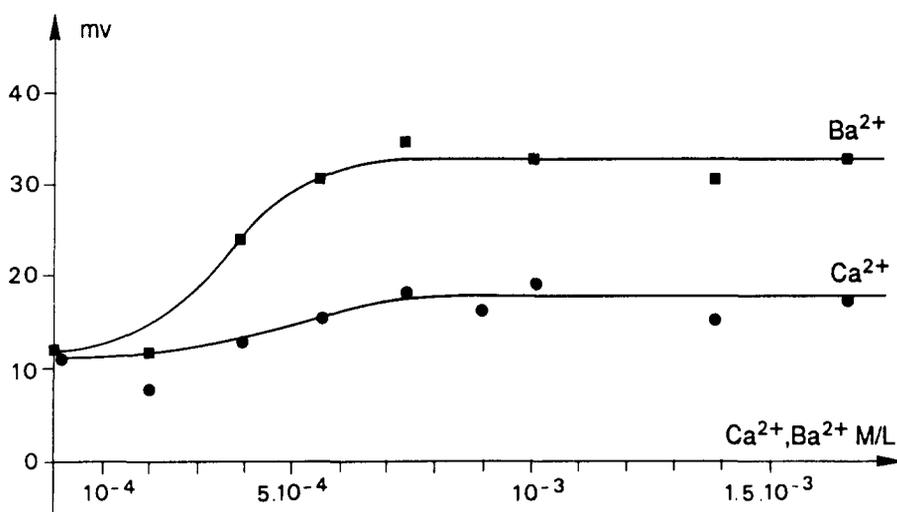


Fig.8 Galena zeta-potential as a function of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  addition.

### Effect of sulphite, measurement of electrokinetic potential

It is difficult to characterize the reaction of sulphite with galena by assaying residual sulphite, because sulphite is oxidized in the presence of  $\text{O}_2$  dissolved in water.

One of the only methods available to characterize the reaction  $\text{PbS} - \text{SO}_3^{2-}$  in-situ is to measure the electrokinetic potential. In Figure 9, curve 1, it can be seen that sulphite gives galena a negative charge. Its effect on galena preconditioned with  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  is reflected in a rise of the zeta curves towards less negative potentials.

In the presence of calcium, curve 5 falls exactly on the preceding curve 4, a curve obtained at the  $\text{Ca}^{2+}$  concentration where the plateau of calcium adsorption on galena appears (Fig.8). This indicates that calcium saturating the surface of galena reacts with  $\text{SO}_3^{2-}$  and that the excess ions in solution do not provoke any additional precipitation, particularly of calcium sulphite, on this mineral.

With barium (Fig.10), at the lower concentrations of  $\text{Ba}^{2+}$  ions (up to  $3.85 \times 10^{-4}$  mol/l), the curves all lie in the same region. The rise in potential towards less negativity appears only afterwards. In addition, the zeta potential does not stabilize with increasing doses of  $\text{Ba}^{2+}$ , as the surface of the galena is not saturated. The threshold at  $3 \times 10^{-3}$  mol/l given by chemical analysis is not reached.

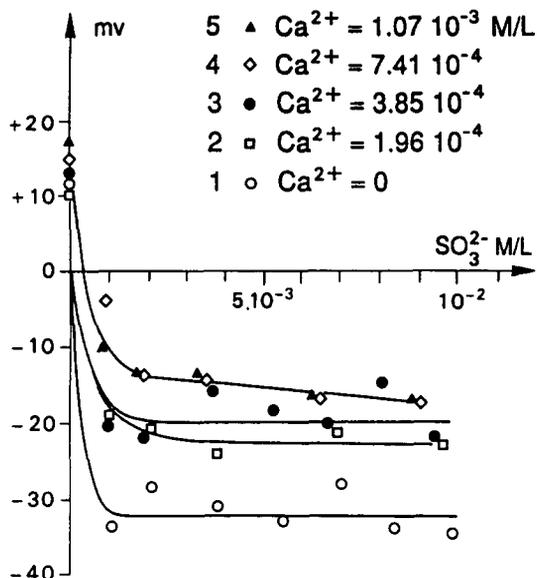


Fig.9 Galena zeta-potential (after  $\text{Ca}^{2+}$  conditioning) as a function of sodium sulphite concentration (pH = 10).

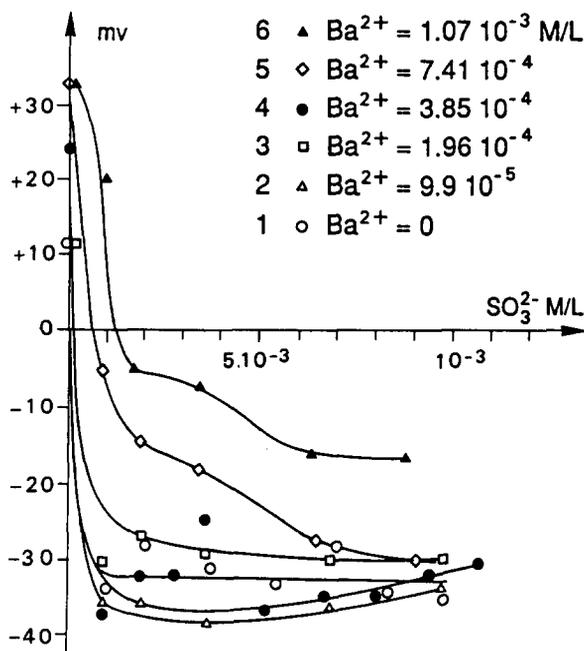


Fig.10 Galena zeta-potential (after  $\text{Ba}^{2+}$  conditioning) as a function of sodium sulphite concentration (pH = 10).

#### CHARACTERIZATION OF THE SPECIES FORMED BY DIFFUSE REFLECTANCE INFRARED INTERFEROMETRY

The Fourier transform infrared (F.T.I.R.) spectra were recorded using a Bruker IFS 88 spectrometer equipped with a globar source, Ge/KBr beam splitter and a broad banded mercury-cadmium-telluride liquid-nitrogen-cooled detector (range  $5000\text{--}600\text{cm}^{-1}$ ). The

diffuse reflectance unit was obtained from Harrick Scientific Corporation [7]. The intensity unit was defined by  $\log(R_0/R)$  where  $R_0$  and  $R$  are the reflectivities of pure finely powered KBr and the sample, respectively.

Figure 11 represents three surface states of galena. Curve 1 is for raw galena wet-milled in a stainless-steel mill. Curve 2 is for the same galena conditioned with lime for 15 min. with aeration at pH 10 : the peak at  $1400\text{cm}^{-1}$  is for lead carbonate, which always appears when galena is conditioned in neutral or basic media [4]. Curve 3 results from the preceding steps followed by 5 min. of conditioning with  $3.3 \cdot 10^{-3}$  mol/l of  $\text{Na}_2\text{SO}_3$ . In the latter case, far from showing up new peaks, for example of  $\text{CaSO}_3$  (Fig.12), the sulphite largely cleans the mineral surfaces.

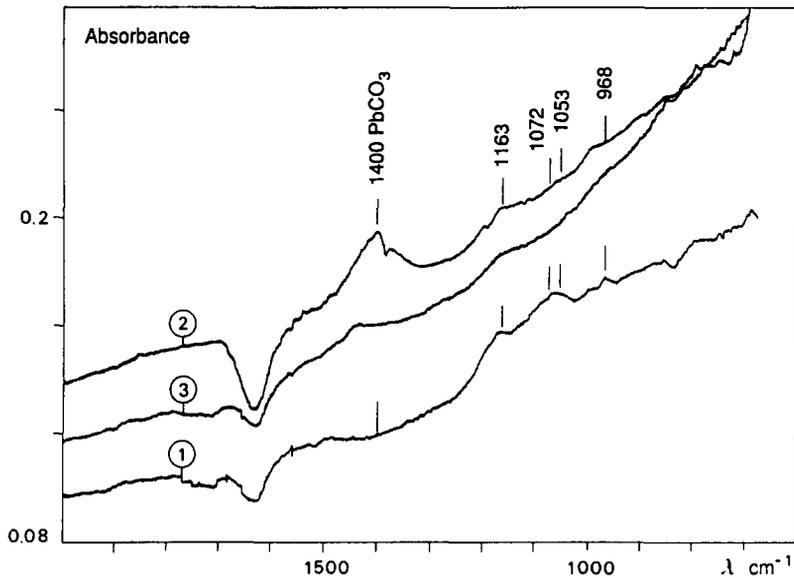


Fig.11 Diffuse reflectance Fourier transform infrared spectrum (F.T.I.R.) of galena

Curve 1 : Ground at natural pH.

Curve 2 : 15 min. CaO conditioning and aeration.

Curve 3 : 5 min.  $3.3 \cdot 10^{-3}$  M/l  $\text{Na}_2\text{O}_3$  conditioning.

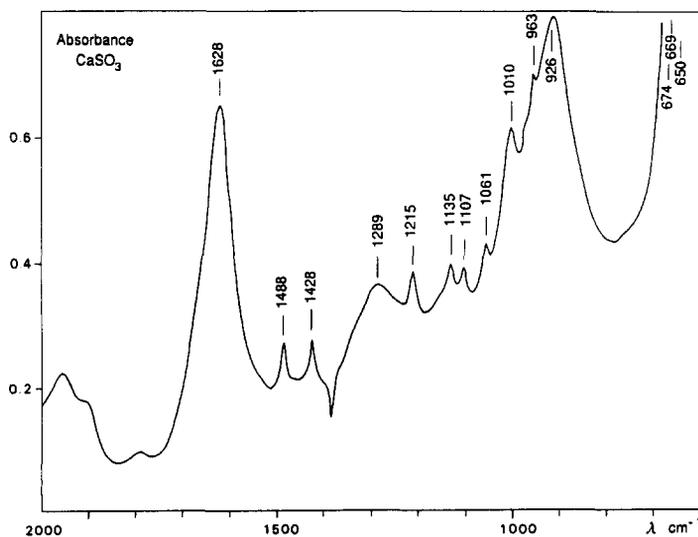


Fig.12 Diffuse reflectance F.T.I.R. spectrum of calcium sulphite.

Additional experiments were carried out using calcium and barium nitrates. Figure 13 shows the surface state of galena conditioned at pH 10 (with NaOH) for 45 min. with an ion concentration of  $8 \cdot 10^{-4}$  mol/l. In both cases, conditioning at basic pH developed lead carbonate (peak at  $1400 \text{ cm}^{-1}$ ). In addition, galena conditioned with barium produced three peaks ( $1210$ ,  $1100$  and  $1080 \text{ cm}^{-1}$ ) which are for barium sulphate. In the presence of sulphite (after 3h of conditioning) two other peaks emerge, at around  $1000$  and  $940 \text{ cm}^{-1}$  (Fig.14), which can be attributed to barium sulphite (Fig.15). As regards calcium, no new peak was detected, after the addition of either calcium nitrate or sodium sulphite (see Figs.13 and 14).

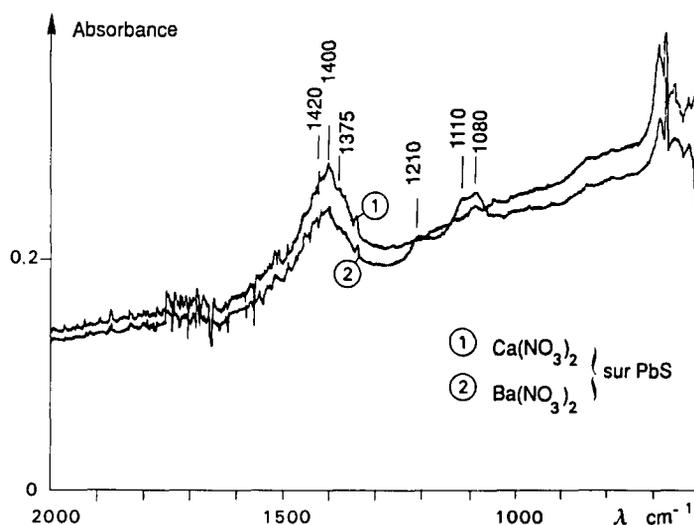


Fig.13 Diffuse reflectance F.T.I.R. spectrum of with  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , 45 min. conditioning galena (pH =10).

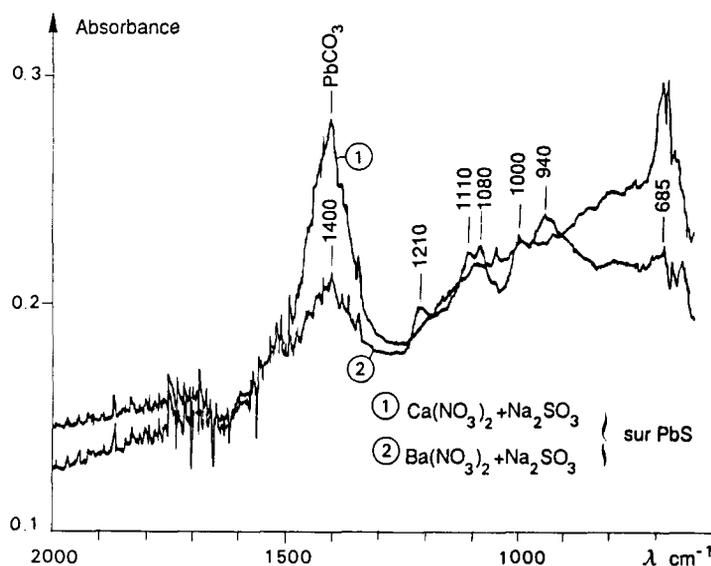


Fig.14 Diffuse reflectance F.T.I.R. spectrum of with firstly  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  and secondly with sodium sulphite conditioning galena.

In both cases ( $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ ), addition of  $\text{SO}_3^{2-}$  did not lessen the amount of lead carbonate. This was because of the long conditioning time of the sulphite with galena : lead carbonate was formed again.

Note : The species formed on PbS following the action of  $\text{SO}_3^{2-}$  could not be characterized by measurement of the electrokinetic potential since the sulphites of calcium and barium do not have any point of zero charge.

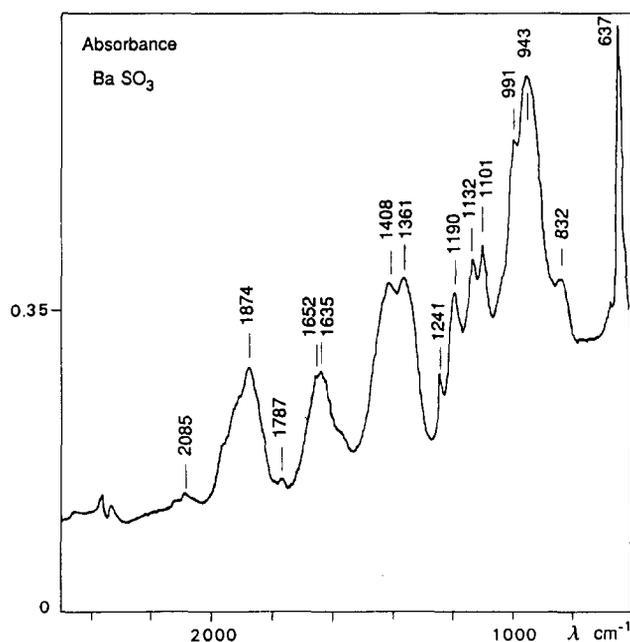


Fig.15 Diffuse reflectance F.T.I.R. spectrum of barium sulphite.

### CONCLUSIONS

On pure galena floated with a dialkyl-thionocarbamate-type collector, depression by sodium sulphite is not linked to complexation of the collector with  $\text{SO}_3^{2-}$ . This reaction does not deprive the promotor of its collector properties.

Depression of galena by  $\text{Na}_2\text{SO}_3$  is seen only if this compound has been previously conditioned with metal ions or hydroxides whose reactions in aqueous solution produce relatively insoluble sulphites. With  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , the mechanism of depression takes place in steps :

1. Adsorption of metal ions to the surface of the mineral.
2. Reaction of sodium sulphite with this ion, leading to the formation of a sulphite that prevents subsequent binding of the collector.

With  $\text{Ca}^{2+}$ , though diffuse reflectance interferometry did not identify calcium sulphite, it may still have been present in small quantities, since a depressive effect of the combination  $\text{Ca}^{2+}$ - $\text{SO}_3^{2-}$  was seen.

The adsorption of barium was detected by infrared interferometry : some sulphite with the remaining adsorbed  $\text{Ba}^{2+}$  ions leads to the formation of  $\text{BaSO}_3$ .

In the case of an ore,  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  ions participated very minimally in the effectiveness of  $\text{NaSO}_3$ . Metallic hydroxides released by the ore at more strongly, but the mechanism may well be similar.

### ACKNOWLEDGEMENTS

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