Investigation of surface properties of gangue minerals in platinum bearing ores

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The large proportion of gangue minerals present in platinum bearing ores in South Africa provides challenges to the flotation and down stream processes. In order to take effective measures to reduce their recovery in flotation an understanding of the mechanisms and factors influencing their behaviour is needed. Typical gangue minerals are pyroxene, feldspar, quartz, chromite and talc. Of these, talc is a naturally hydrophobic mineral and although it is present in relatively small quantities, it has a disproportionate effect as it has a strong froth stabilizing effect, increasing the recovery of other gangue minerals by entrainment. Talc recovery is effectively reduced with the addition of polymeric depressants. Although the other gangue minerals are assumed to be hydrophilic and their recovery by entrainment is expected to follow the water recovery, there is some evidence that they may be activated by the typical reagent suites used. Reagents such as copper sulphate, added as an activator, and collectors are used to selectively induce hydrophobicity on the sulphides. It has been shown that some of these gangue minerals can be activated. This research work investigates whether inadvertent copper activation is mineral specific and evaluates the mechanisms and factors affecting the reversal of activation with the addition of the depressants using electrokinetic measurements, adsorption and microflotation tests.

Results are presented that show that the selected minerals do respond differently and that the reversal of activation is dependent on mineral type, depressant type, dosage and ionic strength of the electrolyte.

Introduction

The recovery of platinum group minerals (PGM) and associated sulphides by froth flotation from the Bushveld Igneous Complex is complicated by the presence of naturally floatable gangue minerals such as talc. Although talc is present in small quantities it has a disproportionate effect by enhancing froth stability and increasing the entrainment of other gangue minerals. However, there is an indication that some of the other gangue minerals, which are normally considered to be hydrophilic, such as chromite and pyroxene, report to the concentrate as floatable particles. In practice, polysaccharide depressants, such as carboxymethyl cellulose (CMC) and modified guar gums, are used to reduce the floatability of naturally floatable gangue and it is important to examine whether the use of these depressants can also prevent the flotation of gangue minerals that have been copper-activated and rendered hydrophobic by the addition of collector.

Much work has been done on the activation of sulphide minerals by metal ions (Acar and Somasundaran, 1992; Finkelstein and Alison, 1997; Laskowski, Liu and Zhan, 1997) and the mechanism of activation has been well established particularly in the acid pH range. The activation of sulphide minerals in alkaline solutions (typically found in South African flotation plants) is slightly more complex but has also been well described (Malysiak, 2002). Less work has been done on the activation of oxide and silicate minerals. Fuerstenau in 1975 showed that oxide minerals could be activated with metal ions such as copper and lead and subsequently floated with a collector. Nagaraj (1995)

also showed that pyroxene could be activated with Cu(II) and addition of a collector led to the formation of a Cu(I)-collector at the surface of the mineral. Wesseldijk (1999) more recently found chromite could be copper activated and readily floated with xanthate in a microcell at pH 9. In addition, Malysiak and Shackelton (2003) showed that both pyroxene/pentlandite and feldspar/pentlandite systems could be copper activated. TOF-SIMS analysis showing much greater activation of the pentlandite but still some activation and reaction with the collector for the silicate mineral. Mailula (2004) studied the effect of presence and concentration of calcium ions on the activation by copper ions of pyroxene and feldspar. He also carried out some microflotation studies on the activation with copper ions and subsequent flotation behaviour, in the presence of xanthate, of the two minerals. He found strong floatability of the activated minerals but found that the addition of a depressant such as guar or CMC could cause some reduction in their floatability. Both Malysiak and Shackelton (2003) and Mailula (2004) included in their studies the effect of the presence of calcium on the copper activation. There appeared to be a competitive adsorption in that calcium reduced the effect of the activation.

This study examines the copper activation of a range of minerals, namely pyroxene, feldspar, chromite and talc as well as the classical oxide quartz, using zeta potential measurements and then compares their floatability after activation and collector adsorption in the presence of a modified guar and a CMC depressant. Although quartz is not a major gangue component in PGM ores it was selected

since it is a strongly negatively-charged mineral in the alkaline range and therefore likely to respond to copper activation. Steenberg and Harris (1984) found that polymers such as guar and CMC did not appear to adsorb to a significant level on quartz.

Experimental methods

Minerals

Talc from Scotia Mine, chromite from the Ntuane Chrome Mine in the Bushveld Complex, feldspar and orthopyroxene from Merensky Reef and quartz from Delmas mine were used. The ore samples were dry milled in a laboratory rod mill, dry screened and the $+75\mu m$ to $-106\mu m$ size fraction selected. XRD measurements revealed that all selected minerals were free of major impurities and were more than 95 per cent pure.

Reagents

Copper sulphate, potassium nitrate and calcium nitrate were used to introduce the desired concentration of copper, potassium and calcium. A stock solution of acid (10^{-2}M HNO_3) and base (10^{-2}M KOH) were used for pH adjustment as required. These reagents were all analytical grade and solutions were prepared in deionized water. For microflotation sodium isobutyl xanthate (SIBX) obtained from SENMIN was used as the collector. The carboxymethyl cellulose (FF30) from Noviant and modified guar gum (APX4M) from Agricultural Product Exchange were used as depressants. FF30 has a purity of 98 per cent and degree of substitution (DS) of 0.76 and APX4M a purity of 89 per cent.

Zeta potential determinations

Zeta potential determinations were carried out on dilute dispersions of the individual minerals using a Malvern Zetasizer 4. Potassium nitrate at 10^{-3} M (equivalent to an ionic strength (IS) of 10^{-3}) was used as an indifferent electrolyte for all zeta potential determinations. All the minerals were ground with a ceramic pestle and mortar to obtain sub $15\mu m$ particles. During the experiments the

effect of potassium (10^{-2} IS), calcium (10^{-3} and 10^{-2} IS) and copper ions (1 x 10^{-4}M) on the zeta potential of the minerals was investigated. The instrument gives the electrophoretic mobility from which the zeta potential was calculated using the Smoluchowski equation, since k_a<< 1, k_a is the ratio of particle radius to double layer thickness (Hunter, 1993). The mineral zeta potential measurements were started at pH 10 down to pH 3 to prevent leaching out of ions present in the selected mineral at acidic pH values which could influence the results. In the presence of copper sulphate, measurements had to be started at low pH, since the precipitation of $Cu(OH)_2$ at alkaline pH values was expected to influence the measurements.

Microflotation tests

A microflotation cell (volume 250 cm³) was used to determine the flotation response and the floatability of pure minerals. The cell consists of a conical tapered cylindrical tube with air-introduced through a needle at the base of the cell (Bradshaw and O'Connor, 1996).

Microflotation was conducted in calcium nitrate solution at an IS of 10^{-2} (3.33 x 10^{-3} M calcium nitrate) and the pH was adjusted to pH 9. These values were chosen to simulate conditions of water on a typical platinum concentrator in a plant. Reagents conditioning was done in a 100 ml beaker with electrolyte solution and the pH adjusted before transferring the pulp into the microfloat cell The reagents were conditioned for the following times and order:

- 5 minutes for $CuSO_4$
- 2 minutes for SIBX
- 2 minutes for depressant.

An air flowrate of 10 cm³/min was used and the peristaltic pump set at 100 rpm.

Concentrates were collected at time intervals of 1.5, 5 and 10 minutes.

Results and discussion

Zeta potential determinations

The zeta potentials for all 5 minerals over the pH range of 3 to 10 are shown in Figures 1 and 2.
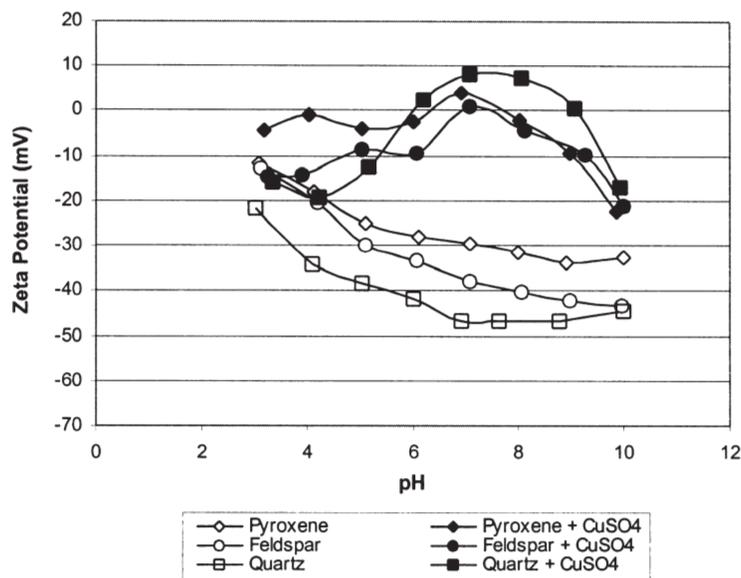

Figure 1. The effect of 10^{-4} M copper sulphate addition on the zeta potential values of pyroxene, feldspar and quartz with 10^{-3} M of potassium nitrate as indifferent electrolyte at pH of 3 to 10
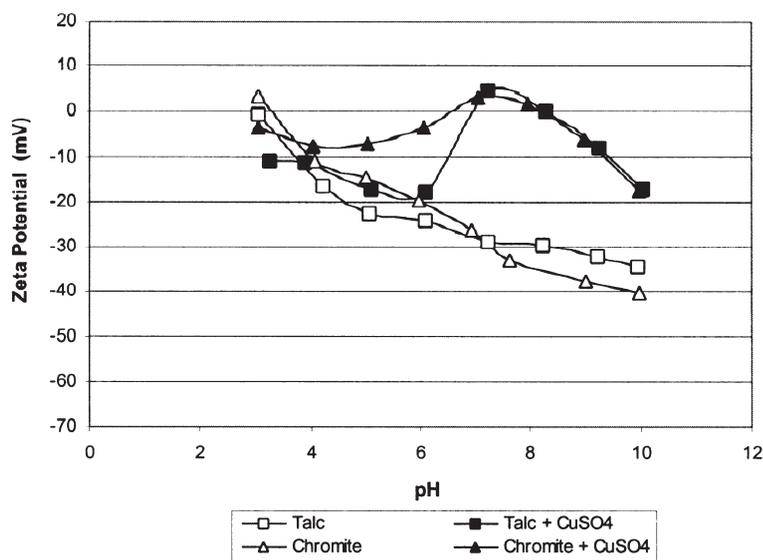
Figure 2. The effect of 10^{-4} M copper sulphate addition on the zeta potential values of talc and chromite with 10^{-3} M of potassium nitrate as indifferent electrolyte at pH of 3 to 10
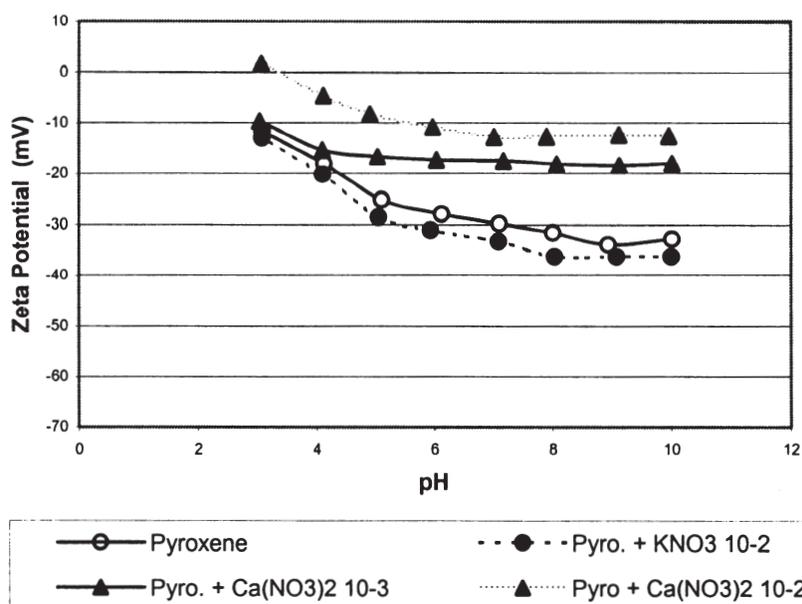

Figure 3. The effect of calcium ions and different ionic strength (10^{-3}; 10^{-2}) on the zeta potential values of pyroxene

Over this range, all minerals, with the exception of chromite at pH 3, displayed a negative zeta potential with the zeta potential increasing negatively as the pH is raised. The point of zero charge (PZC) of chromite was found to be close to pH 3.6, which is similar to that obtained by Wesseldijk (1999) for chromite from the same source. As expected, the quartz sample displayed the highest negative zeta potential. The addition of copper sulphate (10^{-4} M) caused a significant change in the zeta potential of all minerals in the alkaline range, indicating a strong interaction of the copper with all minerals. In all cases at around pH 7 the zeta potential becomes positive. This charge reversal is indicative of a specific adsorption occurring at the surface and corresponds to the pH at which the maximum concentration in solution of the hydrated copper species CuOH+ occurs (Wesseldijk, 1999). The fact that all minerals behave the same shows that the copper activation (or 'inadvertent' activation) is not specific for

any of the minerals examined. It is of interest to note that the largest charge reversal occurred with the mineral quartz where the zeta potential stayed positive from pH 6 to pH 9 showing strong adsorption on a mineral, which possessed the most negative natural zeta potential.

At acid pH values (pH 4) the copper is present in the form of free Cu^{2+} ions. At pH 7 the amount of CuOH+ present becomes significant, while at pH 9 the majority of the copper is present as $Cu(OH)_2$ with a small quantity of CuOH+ based on the following equilibria (Figure 5, Wesseldijk, 1999):

$Cu^{2+} + OH^- \Leftrightarrow CuOH^+$

and

$CuOH^+ + OH^- \Leftrightarrow Cu(OH)_{2(s)}$
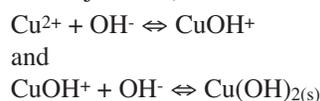
Consequently, it would also be expected that a significant quantity of $Cu(OH)_2$ is likely to be co-adsorbed on the surface of the mineral via hydrogen bonding to the

specifically adsorbed CuOH⁺. The presence of the neutral $Cu(OH)_2$ species would not be observed by zeta potential measurements.

Malysiak and Shackelton (2003) found that calcium competed with the copper ions in adsorption on pyroxene and feldspar, and Mailula (2004) found that the presence of calcium reduced the floatability of the activated silicate mineral. This is only likely if the calcium ion shows a strong interaction with the mineral surface. Zeta potential measurements were carried out on all minerals in the presence of calcium ions at 10^{-3} IS and 10^{-2} IS. The zeta potential of the minerals was also examined under a higher background electrolyte (10^{-2} M K⁺, 10^{-2} IS) to eliminate the possibility that changes in zeta potential were simply due to a contraction of the double layer at the higher ionic strength. Again the response for all minerals was the same and therefore only the behaviour of pyroxene in the presence of calcium is shown in Figure 3.

A change in the IS of the indifferent electrolyte resulted in a very little change in zeta potential over the whole pH range. The presence of even a low concentration (10^{-3} IS) of calcium causes a significant move in the zeta potential in the positive direction, particularly at alkaline pH values. At the higher concentration (10^{-2} IS) the curve is shifted positively over the whole pH range, implying a strong interaction of calcium ions with the mineral surface. The increase in the PZC also indicates a specific adsorption.

Zeta potential measurements were not done in the presence of both copper and calcium ions since they are both positively charged ions and therefore the adsorption of one cannot be distinguished from the other.

The zeta potentials of all the minerals were measured in the presence of the two depressants evaluated during this study to establish whether adsorption was occurring. The CMC, FF30, has a high DS and thus a high negative charge, whereas the guar, APX4M, has a very low charge. Both these polymers have relatively high molecular masses and would therefore be expected to cause a change in the zeta potential if adsorption is occurring. The change in the zeta potential would not give an indication of the extent of adsorption but simply that some adsorption has taken place. The depressants were added at a concentration of 10 ppm.

All minerals reacted in the same way and the typical behaviour is shown in Figure 4 for feldspar.

A significant increase in the negative zeta potential on the addition of FF30 showed that adsorption of the CMC was occurring under these conditions and the high negative charge on the polymer was overcoming any reduction in zeta potential that would be expected by the expansion of the double layer to accommodate the large molecules. On the other hand, the decrease in the negative zeta potential in the presence of guar again indicates adsorption but, since this polymer has almost no charge, the expansion of the double layer and inclusion of counter ions in the double layer leads to lower zeta potential values. This behaviour was also observed for quartz and strongly negative zeta potentials in the region of –70 mV were observed in the presence of FF30. Steenberg and Harris (1984) found similar types of polymers adsorbed on talc and some sulphide and oxide minerals. However, contrary to this work, they were not able to measure adsorption on quartz.

Microflotation tests

Microflotation tests were also performed at pH 9 in the presence of calcium at a concentration of 10^{-2} IS to compare to conditions found in practice and allow the extrapolation of the zeta potential behaviour.

The activator copper sulphate was added at a concentration of 10^{-4} M and the collector (SIBX) at a similar concentration of 10^{-4} M. As discussed previously, the copper at this pH value would be present as CuOH⁺ and $Cu(OH)_2$. Both copper species should then be available for reaction with the xanthate collector through the following mechanisms (Fornasiero and Raston, 1992):

$$Cu(OH)_2 + 2X^- \Leftrightarrow CuX_2 + 2OH^-$$
$$CuOH^+ + 2X^- \Rightarrow CuX_2 + OH^-$$
$$CuX_2 \Rightarrow CuX + \tfrac{1}{2}X_2$$
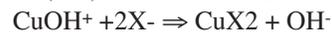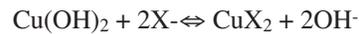
The stoichiometry of these reactions imply that one molecule of copper reacts with two molecules of xanthate to form a Cu(II) xanthate, which decomposes rapidly to form Cu(I) xanthate and dixanthogen. Consequently, since the copper sulphate and xanthate are added in equimolar concentrations, only 50 per cent of the copper would be present as Cu(I) xanthate and 50 per cent remain in the
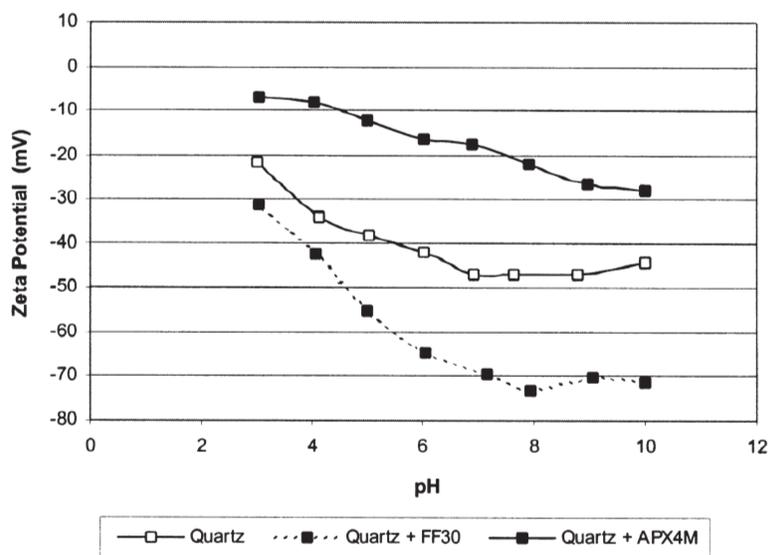

Figure 4. The effect of polymeric depressants on the zeta potential values for quartz with 10^{-3} M of potassium nitrate as an indifferent electrolyte

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form of $Cu(OH)_2$. However, this assumes that the presence of species such as $Cu(OH)X$ at the surface is very small. The dosages of depressant of 50 and 100 ppm were selected as being similar to those typically found in practice.

Figure 5 shows the typical flotation behaviour of the minerals in the microflotation cell without activation or collector addition, i.e. the natural floatability of the minerals. As expected, only talc showed natural floatability. The remaining minerals had very low recoveries. The slight natural floatability of the chromite was unexpected but it was insufficient to interfere with the copper activation studies.

Figures 6 and 7 show the effect of copper activation and collector addition on the floatability of the five minerals and also show the effect of depressant addition on this 'inadvertent' floatability.

The actual recovery values obtained after 10 minutes flotation are shown in Table I for all the minerals and conditions tested. The decrease in floatability in the presence of a polymer does not imply that the hydrophobic copper xanthate has actually been removed from the surface (i.e. deactivation). The polymer may simply be co-adsorbing at the surface and, because of the large size of the polymer, simply prevent particle-bubble attachment. However, the adsorption of the polymer may, in fact, lead to deactivation but confirmation of this is beyond the scope of the present project. The important finding is that copper activated minerals can be depressed in the presence of a polymer.

Results for talc indicated that, after adding copper sulphate and collector, the floatability was actually reduced from 61 to 42 per cent. Although activation must have occurred (see zeta potential data) the reaction with collector most probably led to the formation of a copper xanthate complex away from the talc surface, implying that the hydrophobic xanthate complex was not stably adsorbed. This phenomenon appears to be specific for talc with its naturally hydrophobic planes. The excess $Cu(OH)_2$ would still remain adsorbed at the surface, leading to a lower floatability.

For all the other minerals, the floatability after copper activation and collector addition was significantly enhanced, indicating the formation of a reasonably stable hydrophobic copper xanthate attached to the surface. The

addition of the modified guar gum, APX4M, (Figure 6) resulted in a significant decrease in the floatability of the copper-activated mineral. The floatability of talc in particular was significantly reduced to between 10 and 15 per cent. For all the other minerals, the floatability caused by the activation could be significantly reduced but could not be completely removed in the presence of APX4M. Increasing the concentration from 50 to 100 ppm did not, apart from pyroxene, increase the degree of depression. The effect of the CMC, FF30, on the copper activated floatability was much less than that found for the guar (Figure 7). In fact, in two cases, talc and quartz, the floatability increased on the addition of 50 ppm FF30. Increasing the concentration of the CMC to 100 ppm always led to an increase in the extent of the depression. However, recoveries of more than 30 per cent of all the minerals could still be obtained.

These results imply that the depressant did not lead to a deactivation of the mineral but rather a co-adsorption of the depressant on the mineral. However, this conclusion is speculative, as the experimental technique does not measure the amount of copper at the surface. It would be expected that the presence of a copper xanthate at the surface would create a more negative surface due to its hydrophobic nature and the adsorption of the strongly negatively charged CMC would therefore be more difficult due to the charge repulsion. This repulsion would not affect the low-charged guar to the same extent. The increase in the floatability of talc and quartz in the presence of 50 ppm CMC suggests that $Cu(OH)_2$ was present on the mineral surfaces since CMC forms a strong complex with copper. The precipitation of CMC by copper ions is used as a quantitative method for the determination of its degree of substitution. The enhanced floatability of talc and quartz can be attributed to the complexation and dispersion of the $Cu(OH)_2$ leaving only the stable copper xanthate at the surface. The high floatabilty of quartz would be expected since the zeta potential data indicated that the adsorption of the copper was greater on quartz than on the other minerals.

Conclusions

The zeta potential determinations indicate the activation by copper ions at alkaline pH values is not specific to the
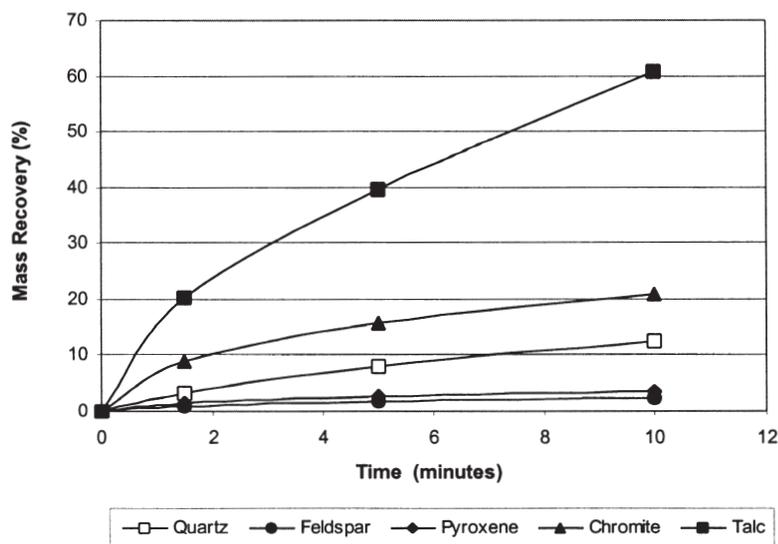

Figure 5. Natural floatability of all selected gangue minerals under 10^{-2} calcium nitrate ionic strength
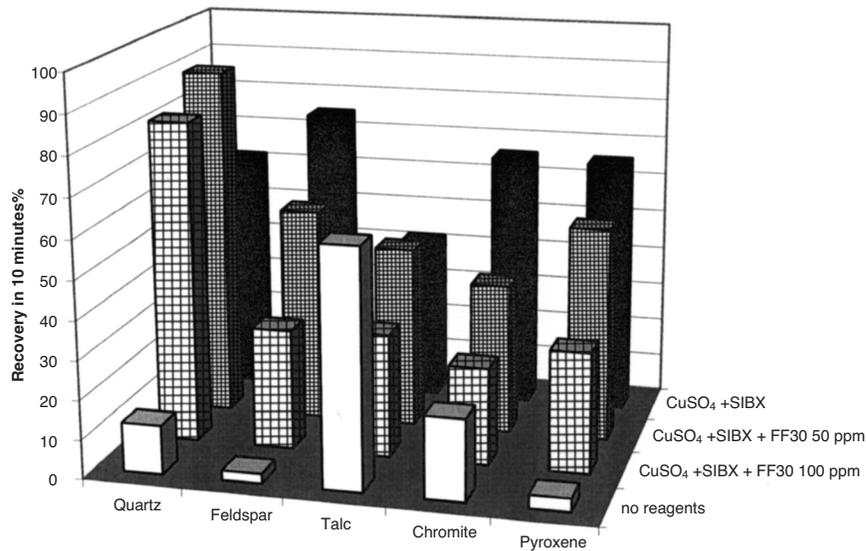
Figure 6. The effect of adding reagents with CMC (FF30) as a depressant on the floatability of quartz, feldspar, talc, chromite and pyroxene (as mass recovery percentage)
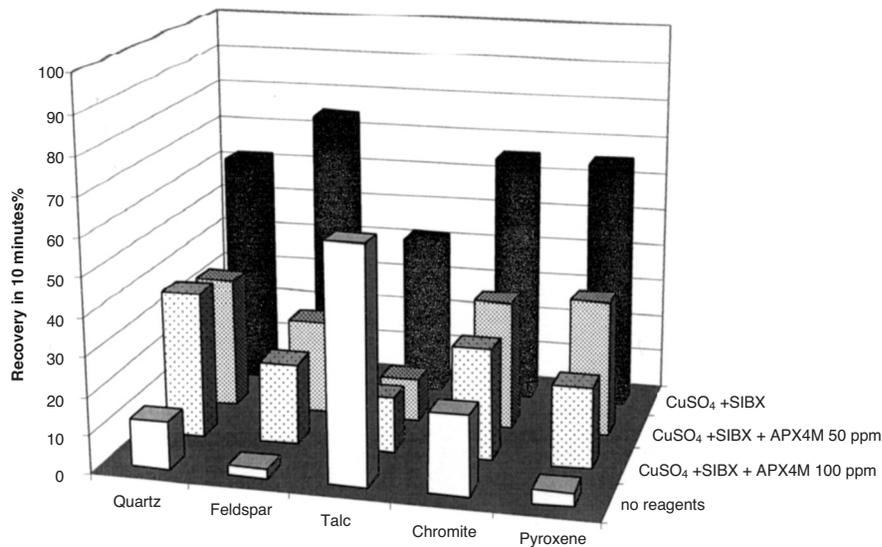

Figure 7. The effect of adding reagents with guar gum (APX4M) as a depressant on the floatability of quartz, feldspar, talc, chromite and pyroxene (as mass recovery percentage)

Table I
Percentage of recovery after 10 minutes for microflotation tests at various conditions

Minerals	No reagents	$CuSO_4$ + SIBX	$CuSO_4$ + SIBX + APX4M (50 ppm)	$CuSO_4$ + SIBX + APX4M (100 ppm)	$CuSO_4$ +SIBX + FF30 (50 ppm)	$CuSO_4$ + SIBX + FF30 (100 ppm)
Quartz	13	62	34	38	90	82
Feldspar	3	75	25	21	55	31
Talc	61	42	11	14	47	32
Chromite	21	66	33	29	39	25
Pyroxene	3	65	35	21	55	31

mineral type. Microflotation tests showed that copper activation and collector addition could lead to the formation of very floatable gangue minerals. The use of depressants can reduce this inadvertent floatability, guar gum being much stronger than CMC. However, the floatability could not be completely removed at the dosages used. The results suggest that, apart from talc, relatively stable copper xanthate complexes are formed on these gangue minerals.

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