UTILISATION OF HYDROXAMATES IN MINERALS FROTH FLOTATION

S. M. ASSIS, L. C. M. MONTENEGRO and A. E. C. PERES

Dept. of Mining Engineering UFMG, Rua Espirito Santo, 35/702
30160-030 Belo Horizonte, MG, Brazil

ABSTRACT

Following a critical review of the utilisation of chelating reagents (hydroxamates) in minerals flotation, results of a series of experiments performed in the presence of an experimental commercial hydroxamate as collector, at bench scale with two different ores and in a microflotation cell with several combinations of minerals (most of them "sparingly soluble minerals") are presented. The conclusion is that the selectivity of minerals flotation with hydroxamates depends on a balance between the solubility of the mineral and the stability of the complex formed with the cation of the lattice. A favourable condition for the selective utilisation of hydroxamates as collectors is visualised if the mineral to be floated is the most soluble in the system and the chelate formed between the cation in the lattice and hydroxamate is the most stable.

INTRODUCTION

This introduction consists of a critical review of hydroxamates utilisation in minerals flotation. Following the presentation, discussion and conclusions of the experimental results, the findings of the present investigation are compared with the literature as "final considerations".

Chelating agents are commonly employed in analytical separations due to their specificity towards metals complexation. These compounds have been exhaustively tested as collectors, aimed at improving selectivity in comparison with conventional reagents. The hypothesis under investigation is a possible correlation between specific action with respect to cations in the minerals lattice and the stability constant $-K-$ of the corresponding metal complex.

Examples of successful bench scale separations employing chelating agents as collectors are reported in the literature [1], [2], [3], [4], [5]. Bogdanov *et al.* [6] and Gorlovkii *et al.* [7] describe industrial applications involving, respectively, the flotation of "wolframite–cassiterite–pyroclorite" and "rare-earth ores".

Theoretically, in analytical separation absolute specificity does not exist: most chelating agents complex almost all metals. The stability constants of these complexes differ from one metal to the other. Practically, these differences in K cause significant selectivity, which is affected by the factors that also have influence on the stability constant.

The utilisation of the complex formation stability constant as a criterion for a selection of chelating agents as flotation collectors requires caution. The reagent may present different behaviours in solution and at the mineral/solution interface. Some possible distinctions are mentioned in the literature:

i. in minerals, each cation is surrounded by several anions and only a share of its coordination sphere contributes to the formation of a surface compound; therefore, the first layer of the surface compound is different from the same species formed by a reaction in the bulk [9];

ii. in the case of the formation of surface chelates, account must be taken of the effect of donor atoms from the mineral lattice and not only the effect of the donor atoms from the ligand [8];

iii. steric effects play a significant role in surface reactions [9]; surface chelation is possible when the lattice atom has the correct orbitals oriented such that minimum steric hindrance exists between ligand molecules during bond formation on the surface;

iv. the mineral surface topography is an important factor in deciding the number of bonding orbitals available for the ligand molecule [9].

Some authors believe that the ability of a ligand to complex a surface cation also depends on the mineral lattice. The complex formation is rendered more difficult as a consequence of a more stable binding of the cation to the lattice, in other words a shorter length binding.

Results of several investigations dealing with the utilisation of chelating agents in adsorption and microflotation studies with pure minerals [1–6], [10–12] indicate a correlation between the stability constants of the complexes formed with the lattice cations, adsorption densities and microflotation recoveries. It is a consensus from these papers that "... the larger the difference between the stability constants of the complexes formed with the surface cations, the larger the difference in adsorption densities and flotation selectivity...". Flotation practice shows a different picture. In most cases, selectivity is achieved only through the action of depressants, despite indicated otherwise by adsorption density results.

Considering that hydroxamates complex almost all metals (with different stability constants), the authors believe that adsorption kinetics is a better selectivity indicator than adsorption density. It is important to identify the factors affecting the adsorption kinetics of hydroxamates on minerals.

The affinity between the lattice cation and the ligand, expressed by the stability constant, enhances the adsorption density and, certainly favours the adsorption kinetics, but this is not the only intervening factor and, maybe, not even the most important; in many instances the correlation between flotation selectivity and differences in stability constants is poor.

There are indications [10], [12] that the kinetics of hydroxamate adsorption are extremely slow and are related to the mineral solubility; the less soluble minerals exhibit slower kinetics. In the case of less soluble minerals, such as hematite, an increase in the conditioning time without collector improves the flotation recovery; for more soluble minerals, e.g., calcite, the opposite may happen [13].

The most probable currently accepted mechanisms of hydroxamates adsorption indicate that a certain solubility of the mineral is required for adsorption to occur. Hydrolysis of the lattice cation, hydroxy complex formation in solution followed by precipitation/adsorption at the interface take place first for the most soluble mineral. This mineral will be "ready" for hydroxamate adsorption faster than the less soluble ones.

MATERIALS AND METHODS

Two phosphate ores from Arafertil and Fosfertil were utilised in the bench scale flotation studies.

Arafertil ore

Mineralogical composition: apatite, barite, quartz, gorceixite, micas, magnetite, limonite/goethite, calcite and hematite.

Chemical composition: P_2O_5 9.0%; CaO 13.7%; Fe_2O_3 10.8%; MgO 10.1%; BaO 1.4%; SiO_2 26.8%; TiO_2 4.4%; Al_2O_3 3.3%.

Fosfertil ore

Mineralogical composition: apatite, magnetite, hematite, micas, anatase, diopside, calcite, quartz and hematite.

Chemical composition: P_2O_5 8.4%; TiO_2 1.5%; Fe 12.,7%

Both ores were ground to − 149 μm and deslimed at 10 μm.

Samples of the minerals calcite, fluorite, apatite, siderite and hematite employed in microflotation tests were at least 95% pure. Preparation consisted of grinding in an agate mortar and screening to a size range − 210 μm + 105 μm. Whenever necessary a Frantz Isodynamic Magnetic Separator was used for further purification of the samples. Mixtures 1:1 were prepared with individual minerals: calcite/apatite, hematite/apatite, calcite/fluorite, calcite/siderite, calcite/hematite and apatite/fluorite.

Aiming at clarifying some of the results with pure minerals, some microflotation tests were performed with the mixtures described as follows:

i.   90% apatite + 10% anatase, obtained directly from purification of the Fosfertil ore in the Frantz Isodynamic Separator;
ii.   30% malachite + 55% calcite + 8% hematite + impurities.

Analytical grade HCl and NaOH were used for pH control. An experimental commercial hydroxamate, Flotinor V3759, supplied by Hoechst, was utilised as collector.

Bench scale flotation tests were performed in a 500 ml cell. Operation conditions, unless otherwise specified, were: 1300 RPM, 60% solids during conditioning, 30% solids in flotation, pH = 8.5.

The procedure adopted was: slurry conditioning for 2 min; collector addition and conditioning for 2 min; slurry dilution to 30% solids; air introduction and flotation until froth exhaustion.

The sequence of steps in the microflotation tests was: introduction of 1 g of the mixture in the tube; collector solution addition at the concentration and pH set for the test; starting agitation (constant for all tests); conditioning for 2 min; air injection at a flowrate of 100 ml/s; flotation for 1.5 min.

RESULTS AND DISCUSSION

The reduction in the grade of impurities, such as iron and aluminum present in some phosphate ores represents a difficult task. Aiming at increasing P_2O_5 content and reducing iron grade in the concentrates, a hydroxamate was chosen as collector with the objective of pre-floating iron and titanium oxides, representing an attempt of reverse flotation. The choice of hydroxamate was based on considerations from the literature:

i.   possibility of improving selectivity with hydroxamic acids in comparison with fatty acids due to larger differences in stability constants for the complexes formed with hydroxamates;

ii.   preferential floatability of iron and titanium bearing minerals with respect to apatite, with hydroxamates. The low stability of the complex between hydroxamate and Ca^{2+} suggests poor floatability of apatite. Pradip and Fuerstenau [13] present the following stability constants (log Kt) for metal/hydroxamate complexes at 20°C: Ca^{2+} 2.4; Fe^{3+} 11.4; Fe^{2+} 4.8.

Results of P_2O_5 and Fe_{total} grade and recovery as a function of pH obtained with Arafertil's ore are presented in Figure 1. An almost flat region of maximum recovery of both, P_2O_5 and Fe_{total} starts at pH = 8.5. The highest P_2O_5 grade in the concentrate (19.3%) was achieved at pH = 8.5. Above pH = 4.5, P_2O_5 recovery in the concentrate is always higher than Fe_{total} recovery and the difference increases towards the alkaline region.
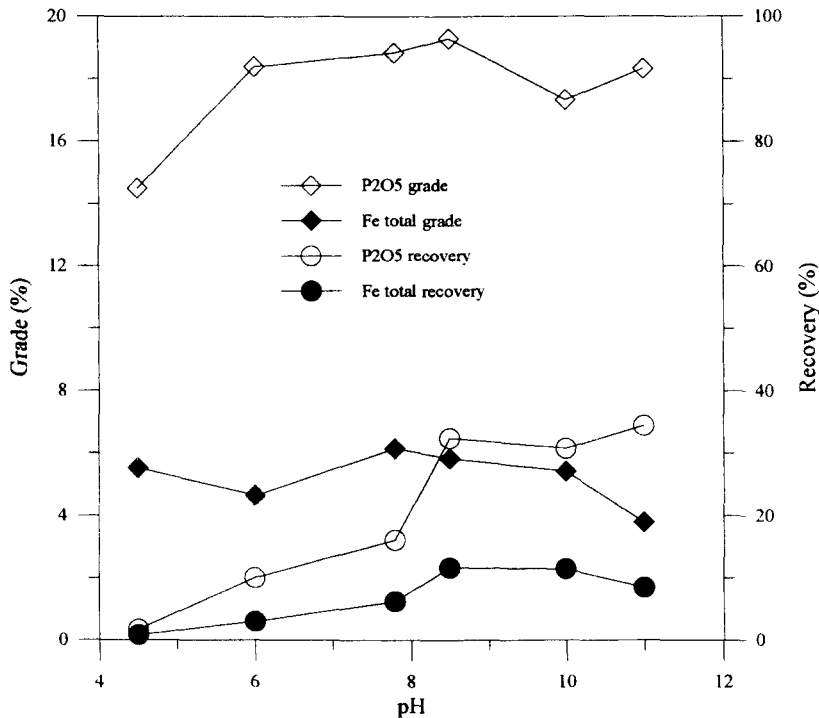

Fig.1 Effect of pH on bench scale flotation of Arafertil's ore.

For most mineral systems, flotation with hydroxamates shows a coincidence between the pH of best floatability and the pH of maximum concentration of the first hydroxy complex of a lattice cation available in solution. If dissolved iron is present as ferrous ion, $Fe(OH)^+$ may be responsible for the behaviour of the ore at pH = 8.5.

Under the hypothesis that the lattice cation controls the hydroxy complex formation and the stability of the complex hydroxamate/cation is an indication of floatability, hematite should float better than apatite, even taking into account that ferrous hydroxamate is less stable than the ferric species.

Results obtained with an ore from Fosfertil are illustrated in Figure 2. The highest P_2O_5 grade is reached at pH = 8.5. Except for the very acidic pH region, a much larger recovery is observed for P_2O_5 than for Fe_{total}. This behaviour is more noticeable in the pH range of predominance of the ferric hydroxy complex.

Figures 3 and 4 show the effect of collector concentration on P_2O_5 and Fe_{total} grade and recovery of these ores from Arafertil and Fosfertil, respectively. In all cases P_2O_5 grades and recoveries surpass those for Fe_{total}.
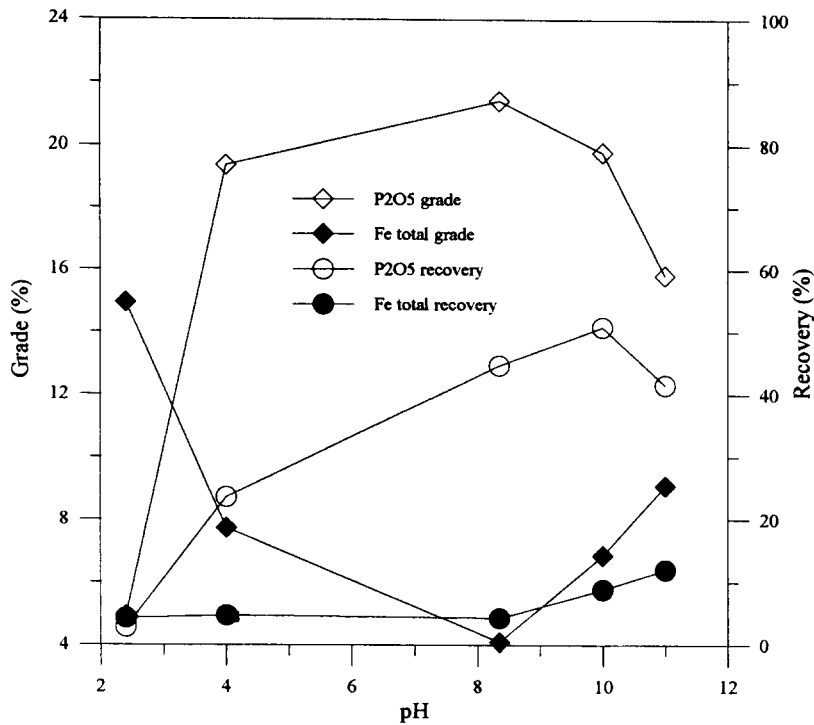
Fig.2 Effect of pH on bench scale flotation of Fosfertil's ore.
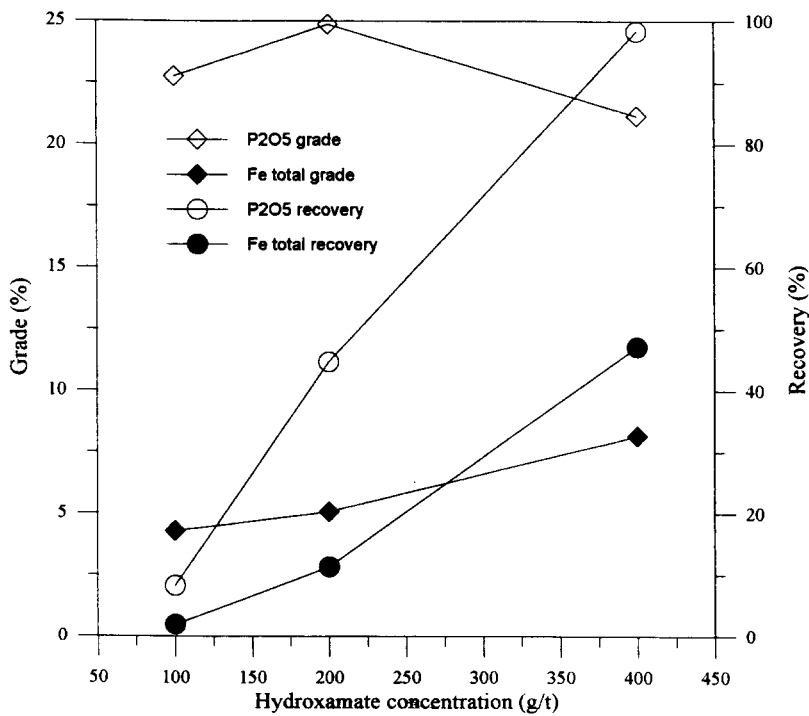

Fig.3 Effect of collector concentration on bench scale flotation of Arafertil's ore

Tests employing different conditioning times, before and after collector addition, collector addition after slurry dilution to 30% and flotation of coarse and fine particles separately did not change the trend of apatite floating better than hematite with hydroxamates.

The bench scale tests also indicated a preferential flotation of apatite with respect to anatase and very poor flotation of micas.
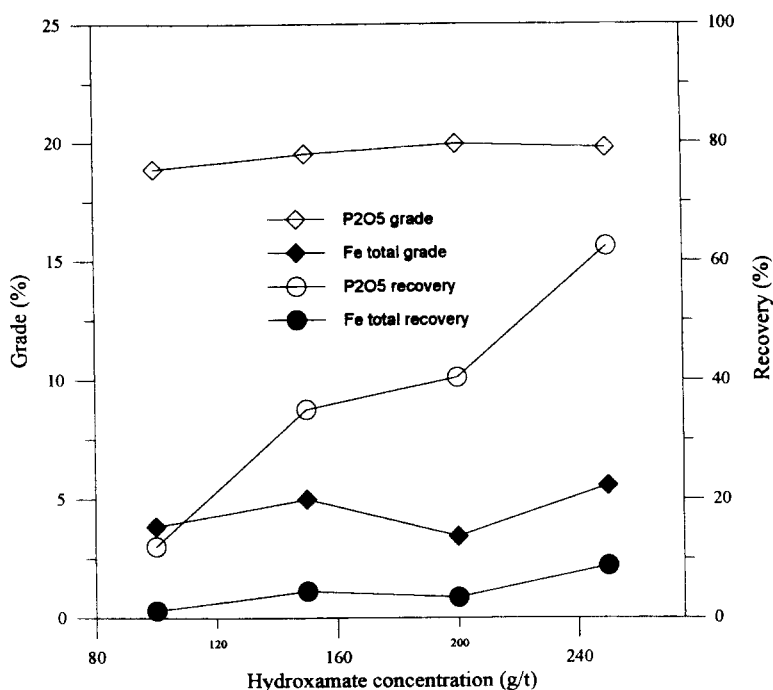
Fig.4 Effect of collector concentration on bench scale flotation of Fosfertil's ore.

The following results refer to microflotation experiments.

A sample composed of 90% apatite and 10% anatase was floated at different levels of pH and collector concentration. Apatite floated better than anatase in all cases, despite the fact that the titanium/hydroxamate complex is more stable than calcium hydroxamate.

Supposing that hydroxamate adsorption mechanisms involve surface reaction, or even adsorption with surface reaction (hypothesis supported by mechanistic studies and other evidences) [13], the mineral solubility must play a prominent role in hydroxamate adsorption. The cation should detach from the mineral lattice, otherwise hydroxamate adsorption is unlikely.

The authors believe that the affinity between hydroxamate and the lattice cation plays a role but the overall interaction will depend, among other factors, on a balance between affinity (stability constant K) and mineral solubility.

Microflotation tests with binary mixtures of minerals were planned aimed at checking the effects of minerals of different solubilities and lattice cations. The goal of this stage was to find a profile of minerals amenable to separation with the collector under investigation.

Despite the dependence of the minerals' dissolution kinetics on factors such as particle morphology, lattice impurities, etc., the parameter chosen for discussion was the solubility product PK_{SO}: calcite = 8.35; siderite = 10.40; fluorite = 10.30; apatite = 119.10.

Results of microflotation with binary mixtures of sparingly soluble minerals are shown in Figures 5, 6 and 7.

Figures 5 and 6 deal with mixtures of minerals bearing the same cation (Ca^{2+}). Both, calcite and fluorite, float better than apatite, the least soluble mineral among the three.

Selectivities similar to those illustrated in Figures 5 and 6 are not expected at bench scale. Microflotation experiments are fast. Flotation starts 2 min after the water/mineral contact. This short contact time will render only the surface of the more soluble mineral "ready" for collector adsorption. In bench scale tests

the contact between the minerals and water is longer. All the minerals will, then, be ready for collector adsorption, impairing the selectivity.
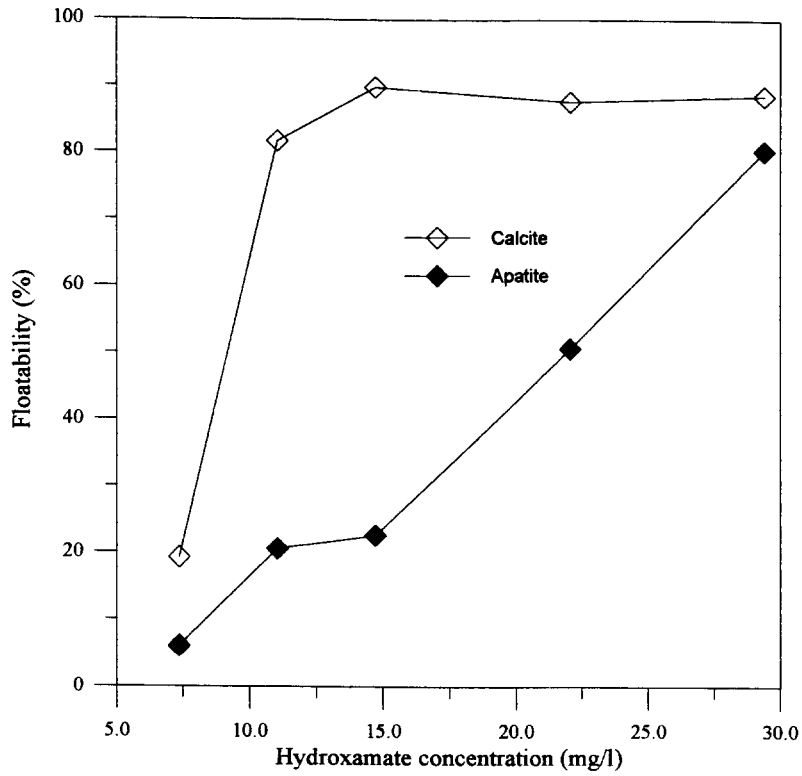

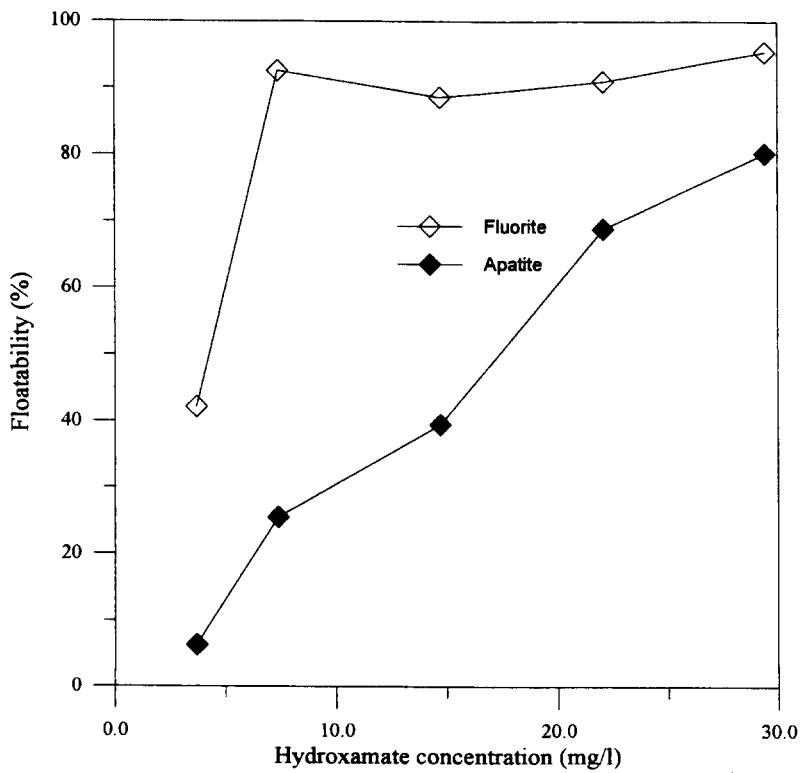Fig.5 Microflotation of calcite/apatite mixtures.

Fig.6 Microflotation of fluorite/apatite mixtures.

The floatability of minerals in the mixture calcite/siderite is shown in Figure 7. Calcite floats better than siderite, despite the fact that the hydroxamate complexes of iron are more stable than those of calcium. The more soluble mineral floated better.
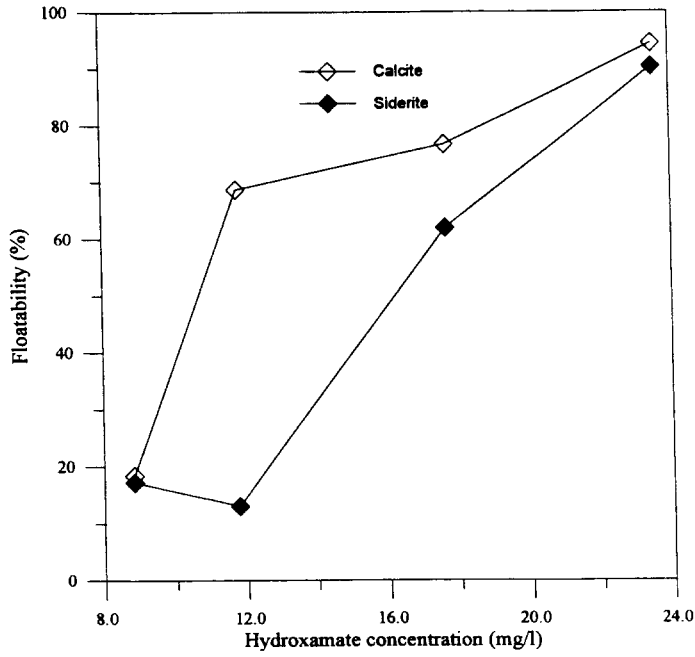

Fig.7   Microflotation of calcite/siderite mixtures.

Figures 8, 9 and 10 show microflotation results of an oxide (hematite) mixed with sparingly soluble minerals (calcite, siderite and apatite, respectively). The stable complex was formed with the hematite lattice and the other mineral was more soluble than hematite. Hematite floated better than the sparingly soluble mineral in all cases. It was verified that the higher the solubility of the sparingly soluble mineral, the less sharp was the separation.
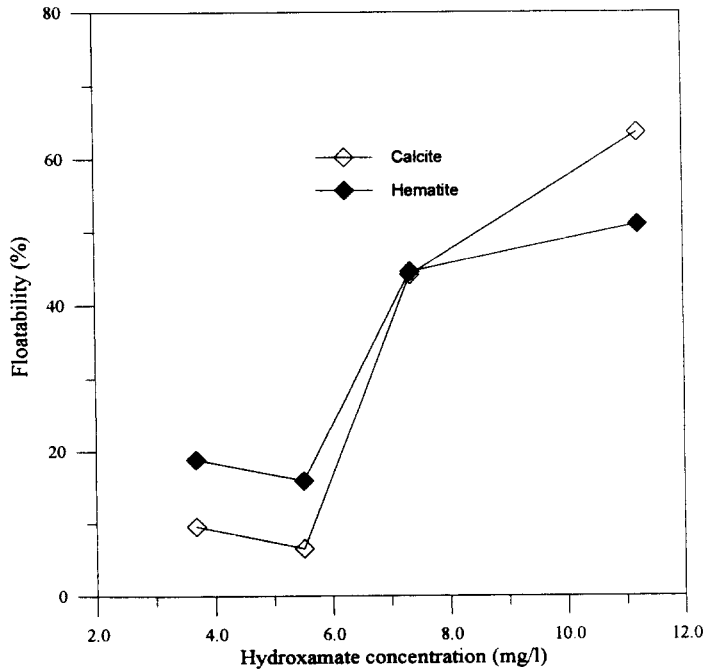

Fig.8   Microflotation of calcite/hematite mixtures.
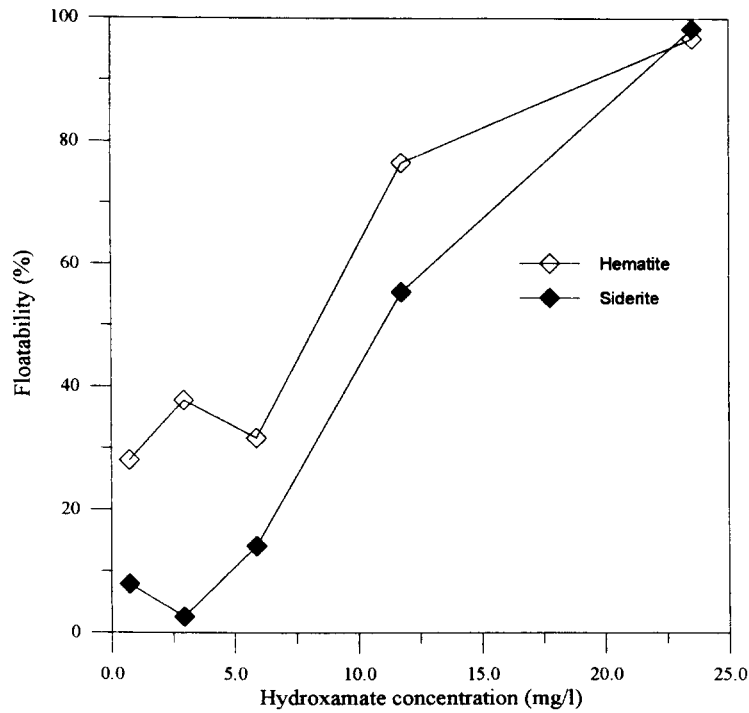
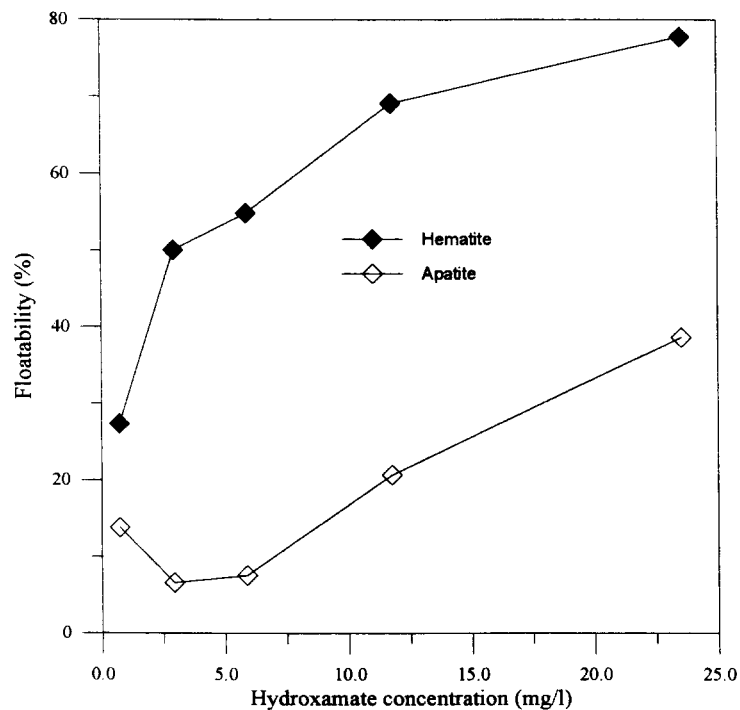Fig.9 Microflotation of hematite/siderite mixtures.

Fig.10 Microflotation of hematite/apatite mixtures.

It may be seen from Figure 10 that in a microflotation experiment hematite floats much better than apatite, in contrast to results from bench scale.

Figure 11 shows the floatabilities of calcite, hematite and malachite, components of a mixture consisting of 55% calcite, 30% malachite and 8% hematite. The observed floatability sequence is: calcite > malachite > hematite. The floatability of calcite is larger than that of hematite (probably due to the small proportion of hematite in the mixture), a result different from that obtained for a 1:1 mixture (Figure 8). An

explanation for this behaviour may be the lower probability of a hydroxamate species finding Fe (hematite) than Ca (calcite) when the proportion of the former mineral in the mixture is small. This may have enhanced apatite flotation with respect to hematite at bench scale.
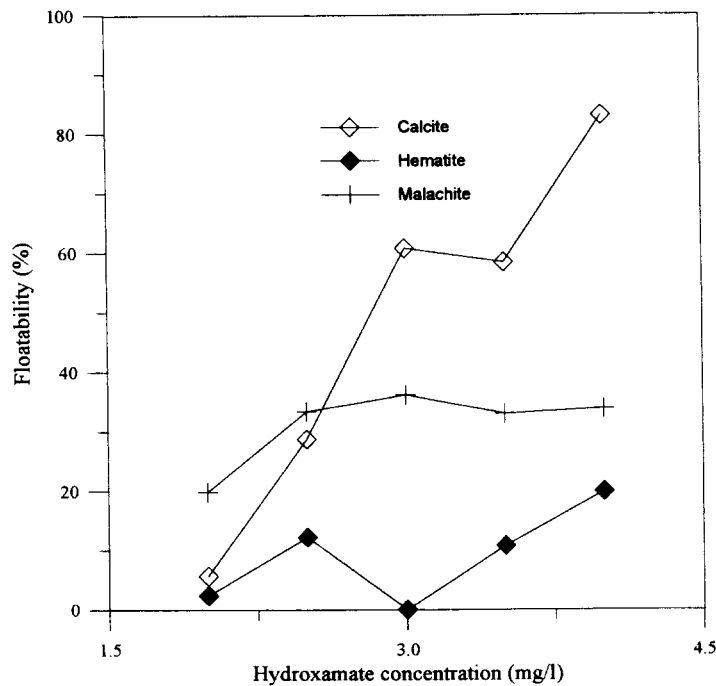

Fig.11 Microflotation of calcite/hematite/malachite mixtures.

CONCLUSIONS

In bench scale tests apatite always floated better than iron and titanium bearing minerals.

Microflotation experiments with mixtures of sparingly soluble minerals with the same lattice cation showed better floatability of the more soluble mineral, with reasonable selectivity. In the case of different lattice cations, the more soluble being those of smaller stability constant, the more soluble mineral floated better, with a less sharp selectivity.

In microflotation experiments with 1:1 mixtures of an oxide (hematite) and a sparingly soluble mineral (calcite, siderite or apatite) hematite always floated better and a higher mineral solubility hindered selectivity.

In microflotation tests of a mixture containing 55% calcite, 30% malachite and 8% hematite, the sparingly soluble minerals floated better than hematite. Hematite floatability depends, probably, on its proportion in the mixture.

FINAL CONSIDERATIONS

The selectivity of minerals flotation with hydroxamates depends on a balance between at least two characteristics: mineral solubility and the stability constant of the complex hydroxamate/lattice cation.

A higher adsorption density is expected for minerals bearing strongly complexing cations; nevertheless, if the mineral solubility is small the kinetics of hydroxamate adsorption will be very slow. The selectivity between this mineral, and another having higher solubility and a weaker complexing ability, will be poor.

A favourable prediction for the use of hydroxamates contemplates the flotation of the most soluble mineral containing a lattice cation that forms the most stable chelate with the collector.

These conclusions are supported by the following data from the literature:

i. hydroxamates adsorption kinetics are very slow and depend on the mineral solubility;

ii. evidence suggests a most probable mechanism for hydroxamates adsorption: cations from the mineral surface hydrolyse in solution forming hydroxy complexes that chemisorb at the interface, providing conditions for collector adsorption.

ACKNOWLEDGEMENTS

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