Abstract. Reagentizing at elevated temperature, reported in the past as beneficial for the flotation of hematite using oleate, is studied here as a function of collector concentration, solution pH and ionic strength at various levels of conditioning temperature. The study revealed strong interactions between variables; particularly, the effect of conditioning temperature was found to strongly depend on the ionic strength of the solution. Thus, while an increase of conditioning temperature at lower ionic strengths or that of ionic strength at lower temperatures resulted in an increase of both flotation and grade, an increase of the former at higher ionic strength or that of the latter at higher temperatures caused a significant decrease in both responses. These observations have been explained in terms of the increased chemisorption of oleate at elevated temperatures and the temperature effect of ionic-strength on the salting out of the oleate from the bulk solution. The above effects which were first observed during Hallimond cell flotation tests were subsequently tested with Denver cell using low-grade iron ore. The results obtained using the two test procedures were in agreement with each other. The implications of these effects and interactions for process control of optimum flotation performance must be noted since variation in the levels of the above parameters are likely under plant conditions.

Use of temperature effects in mineral processing operations such as flotation and flocculation is to date limited to a very few cases. Elevated temperature is used during conditioning for the flotation of hematite and fluorite at a few plants. In addition, there have been a few laboratory studies reporting an improvement in flotation owing to an increase in reagentizing temperature. For example, Cook, et al., have shown that at pH 6 the increase in the operating temperature will increase the selectivity index of the flotation of hematite from quartz. There has not been, however, a detailed basic study of the effects of reagentizing temperature as a function of relevant operating variables such as pH, ionic strength, and collector concentration. These effects are technically important since their utilization can result in better mineral recovery and grade, particularly from finely dispersed ores. Furthermore, effect of seasonal variations in temperature can be better controlled if the interactions are understood. Toward this purpose, a detailed study of the effects of temperature and other relevant process variables in hematite flotation using oleate was made at the Henry Krumb School of Mines. In this paper, certain new effects and interactions observed for this flotation are described. It was found that all the stated variables have strong influence on the flotation recovery of hematite and that they exhibit complex interactions with each other.

Experimental

Materials

Minnesota massive red hematite purchased from Wards Natural Sciences Establishment crushed and sized to 100 x 150 mesh fraction was used for Hallimond tube studies and a sample of low-grade iron ore of -65 mesh size fraction from upper Michigan peninsula was used for the Denver cell studies. The Ward sample was of 94% purity with quartz as the major impurity. These impurities were very finely dispersed and were not liberated even after grinding to -325 mesh. The low-grade iron ore was of 40% Fe grade with mainly quartz and magnetite in the nonhematitic portion. This ore was used as received.

Oleic acid, purchased from Applied Sciences Laboratories, in 1 g sealed ampoules had a specification of 99% purity and was not further purified. It was refrigerated until use. A stock solution of 7.5 x 10^{-4} mole/L potassium oleate was prepared by dissolving appropriate amounts of oleic acid in deaerated water containing enough potassium hydroxide to yield a pH of 11.2 after saponification. The stock solution was refrigerated under a nitrogen atmosphere. Storage under nitrogen was found helpful to avoid irreproducibilities owing to any slow oxidation. It must be noted in this regard that technical grade oleic acid (88% pure) exhibited strong aging effects on flotation obtained even on refrigeration under a nitrogen atmosphere. Reagent grade oleic acid (99% pure) did not exhibit such effects under these conditions. Because of the above problems with technical grade oleic acid, all the other results given here were obtained using reagent grade sample.

Fisher certified grade potassium nitrate and potassium chloride were used to vary the solution ionic strength while same grade potassium hydroxide and nitric acid were used to obtain the desired solution pH. Ultrapure potassium chloride purchased from PCR, Inc., was used in selected tests in order to ascertain that the effects ob-
tained upon adding salt were due to an increase in ionic strength and not due to the heavy metals such as lead and/or polyvalent ions present in reagent grade chemicals. Total impurity level for all the polyvalent ions and heavy metal contaminants in the ultrapure KCl amounted to less than 120 ppb as against 12.5 ppm for the reagent grade KCl. Triple distilled water, distilled in a pyrex still and collected and stored in teflon bottles, was used for making all solutions.

Methods

Modified Hallimond cell and 250/300 g Denver cell were used for all flotation experiments. Two special features of the present Hallimond cell setup were automatic control of flotation time and stirring intensity and time. Hallimond test procedure consisted of desliming 0.8 g of the sample until free of visible fines and then transferring it to a cylinder to which the desired collector solution is added. It was then conditioned by placing it in a water/oil bath maintained at desired reagentizing temperature for 10 min, stirring for the next 10 min, and finally placing it in a 24°C bath for another 10 min. By examining the temperature profile for selected cases, it was confirmed that the selection of time interval was satisfactory. Also stirring speed was selected with care to avoid any contact of the mineral particles with bubbles. After conditioning, the pH of the pulp supernatant was measured and the pulp was transferred to the cell. Flotation was conducted for 10 sec at a nitrogen flowrate of 20 mL/min.

For Denver cell tests, 300-g sample of the ore was deslimed twice with 1800 mL of distilled water and then reagentized at 60% solid content at desired temperature for 10 min. Pulp was then transferred into the Denver cell and floated for 30 sec at 20% solid content.

Results and Discussions

Results obtained during the exploratory part of this study showed the ionic strength (as adjusted by the added potassium nitrate) of the pulp to have an interesting influence on the flotation of hematite using oleate as collector. The effect of the ionic strength on the flotation of hematite at pH 8.0 is shown in Fig. 1. The activating effect of the increase in the ionic strength on the flotation response is to be noted. This effect of the ionic strength was in contrast with the previously reported depressive effect on the oxides flotation of addition of inorganic salts that do not activate by specific adsorption or chemical adsorption. For oxide flotation systems in which electrostatic interactions between the mineral surface and the collector ions are predominant, the commonly encountered depressing effect of inorganic salts is attributed to the competition that is offered to the collector species for adsorption. Evidently such effects dependent upon competitive interactions do not play a governing role for the hematite-oleate system. This observation is consistent with the results given in Fig. 2 in that the maximum flotation of hematite is obtained under pH conditions where both hematite and oleate exhibit relatively low charge characteristics. Maximum floatability obtained in the 7 to 7.5 pH range is in agreement with the data in literature. It can be seen from an examination of the results given in Fig. 2 that the nature of the effect of the ionic strength on flotation is pH dependent. The activating effect of the inorganic salt was found to be significant only above pH 6.0. The effect of the ionic strength increase could be attributed to its salting-out effects on the solubility of oleate and thereby on its adsorption at the hematite/solution as well as solution/air interfaces. Alternatively, it could be due to the reduction in the coulombic repulsive forces between the negatively charged hematite surface and similarly charged oleate ions in the basic pH range.

On the basis of the above results the variables selected for the present study were ionic strength, collector concentration, and pH in addition to the conditioning temperature that was a variable of major interest here. It can be seen from the results given in Fig. 2 that it is necessary to keep a close control of solution pH. However, due to the strong buffering tendency of the hematite
Fig. 3—Effect of conditioning temperature on the hematite flotation.

sample, it was difficult to achieve a predetermined pH value. The pH of the solution drifted during conditioning toward 7 to 8, the final value being found to depend on the conditioning temperature and ionic strength. It is the final value obtained after conditioning that is reported here. Maximum pH drift, which occurred during the first 3 min of conditioning, was about 1 unit. Owing to the above drifting pH characteristics, present tests were done as a function of pH at selected levels of the other three variables.

The effect of conditioning temperature on flotation under low ionic strength conditions as a function of pH is given in Fig. 3. It can be clearly seen that an increase in temperature is beneficial under these conditions, particularly in the acid pH range. The effect of temperature on flotation is thus different from that obtained for the ionic strength, which affected the flotation response in the basic pH range only. The beneficial effect of temperature is proposed to be due to the enhanced dispersion of the collector as well as enhanced chemisorption of the collector species at the mineral surface. The mechanisms have been studied in detail with the help of adsorption and solubility, and surface tension experiments. It might be noted that the pH of maximum flotation does shift to lower values with increasing conditioning temperature. Most importantly, however, this beneficial effect of an increase in temperature is found to be limited to low ionic strength conditions. Simultaneous variation in conditioning temperature and ionic strength on the basis of a statistical design showed the effects of these variables to be complex. A summary of the results obtained is given in Fig. 4 where the flotation recovery at selected pH values (interpolated when necessary) is plotted as a function of reagentizing temperature at low and high ionic strength conditions. The detailed results are given in reference 20. It can be seen from this figure that an increase in conditioning temperature at low ionic strength does cause a decrease in the beneficial effects of hot reagentizing. In fact, an increase of ionic strength to levels of $10^{-2}$ M is found to totally reverse the temperature effect. It can be similarly seen that while an increase in ionic strength was beneficial for flotation under ambient temperature conditions, it was detrimental at elevated temperatures.

The above interaction between variables observed for Hallimond cell flotation of hematite mineral was checked for the flotation of the low-grade iron ore sample in the Denver cell. The results obtained given in Figs. 5 to 7 show the interaction to be present also for the Denver cell flotation of iron ore. It is to be noted from this correlation that Hallimond cell tests, normally used only for studying flotation chemistry aspects, did give general agreement with the Denver cell tests for the case discussed here. It can be seen from Fig. 7 that both the recovery and the grade are improved upon increasing the conditioning temperature under low ionic strength conditions, whereas they are decreased upon increasing the ionic strength under high temperature conditions. Thus both recovery and grade undergo similar change upon altering the levels of the above variables. This observation is in contrast with the normal inverse dependence between flotation recovery and grade but are consistent with those observed by Cooke, et al. It might, however, be noted that while maximum recovery was obtained at 25°C and $2 \times 10^{-1}$ M ionic strength, best grades were obtained at high levels of the conditioning temperature and low levels of the ionic strength. Furthermore, while the flotation recoveries were sensitive to pH in the range of 6.5 to 8.5, the grade of the floated product was found to remain practically constant.

In order to elucidate the mechanism of the above effects, the adsorption at solid/liquid and liquid/gas interfaces of the hematite/oleate solution/gas system was studied. Correlation obtained between solid/liquid and liquid/gas interfacial
properties and flotation has been examined elsewhere.\textsuperscript{18,19,21} The results suggested that consideration of the properties of all the interfaces to be important for an understanding of the flotation behavior of minerals. For example, surface tension studies\textsuperscript{19} of olate solutions as a function of temperature and ionic strength yielded data which clearly suggested the salting-out of olate upon the addition of the potassium nitrate to be significant for the present system at room temperature. Magnitude of this effect was found to decrease at elevated temperatures, possibly due to the fact that the increased thermal agitation will reduce the salting-out. Also, the increase in ionic strength should enhance adsorption on hematite above the point of zero charge of it by reducing electrostatic repulsion. This effect of salt addition can also be expected to be of a lower magnitude at elevated temperatures because the electrostatic repulsion itself will then be lower. The olate adsorption on hematite occurs due to physical and/or chemical forces depending on the solution conditions. While under lower pH and/or higher ionic strength conditions physical adsorption will be favored, elevated temperature conditions will promote chemical adsorption and decrease physisorption. The observed flotation interactions can be explained on the basis of the above effects. Elevation of temperature under ordinary conditions increases the chemisorption of olate on hematite and thereby flotation. Elevation of ionic strength at room temperature on the other hand causes salting-out of olate and thereby its adsorption on both hematite and the air bubble. Increase in ionic strength under elevated temperature conditions does not produce such effects, however, since salting-out under such thermal conditions can be expected to be minimal.

These temperature-ionic strength effects on olate adsorption are described in detail elsewhere.\textsuperscript{18-21}

A question of practical interest was that whether the observed effect was indeed due to an increase in ionic strength or due to the heavy metals present in most reagent grade chemicals. At ionic strength values as high as $2 \times 10^{-1} N$ that was used here, the concentration of heavy metals such as lead does reach a significant value of about 45 ppb that cannot be ignored when reagent
grade salts are used. It was therefore considered necessary to ascertain whether the observed ionic strength effect was due to heavy metal activation of hematite or of unliberated quartz. Towards this purpose, several flotation tests were conducted with "ultrapure" potassium chloride and the results were compared with those obtained using "reagent" grade potassium chloride. In addition, effect of impurities present in reagent grade chemicals was examined by adding known amounts of such impurities to "ultrapure" potassium chloride. The results given in Fig. 8 show that the ionic strength effects do exist, possibly even to a larger extent, when the "ultrapure" chemical is used.

The implications of the ionic strength-temperature interactions to actual hematite ore beneficiation must be noted. The results have clearly demonstrated the reasentinning is to be effective for the present case only below about 1 x 10^{-2}N. This ionic strength is, interestingly, close to the average value of ionic strengths of twenty different lake and river waters in the U.S. In fact, measurement of ionic strength of a pulp supernatant from an operating iron ore beneficiation plant gave us a value of 3 x 10^{-3}N. The present results therefore suggest the measurement and control of ionic strength to be important for optimum flotation operation.

Summary

1) In addition to the usually studied variables such as collector concentration and pH, both the conditioning temperature and ionic strength were found to markedly affect the flotation recovery and grade of hematite using oleate.

2) The ionic strength and conditioning temperature were also found to interact strongly with each other. An increase in conditioning temperature is beneficial for increasing both the recovery and the grade but only under low ionic strength conditions. In fact, at higher ionic strengths (>10^{-2}N) hot conditioning was found to be detrimental. Temperature also interacted with the effect of ionic strength on flotation in a similar manner.

3) The possibility of the observed effects due to the presence of heavy metals present in reagent grade chemicals was eliminated on the basis of results obtained with "ultrapure" chemicals.

4) Good agreement was obtained between the effects and interactions observed during the Hallimond cell tests and those observed during the laboratory Denver cell tests. This correlation, hitherto unconfirmed, shows the potential of such micro flotation tests not to be limited to the study of flotation chemistry alone.

5) The ionic strength-temperature effects and interactions result from the enhancing effect of temperature on the chemisorption of oleate on hematite and that of the ionic strength on the salting-out of oleate from the bulk aqueous solution. At elevated temperatures salting-out effects should be minimal.

Acknowledgments

The authors acknowledge the American Iron and Steel Institute (23-274) and the National Science Foundation (EMC-71-02405A01) for support of this research.

References