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Technical Note

The flotation separation of scheelite from calcite using a quaternary ammonium salt as collector

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ABSTRACT

The flotability of scheelite and calcite was studied with Dioctyl dimethyl ammonium bromide (BDDA). The experiments were conducted on individual and mixed minerals as a function of pH with a micro-flotation cell. And oleic acid was tested for comparison. The flotation results revealed that the performance of BDDA is better than that of oleic acid and the best separation could be achieved with BDDA over the pH range 8–10. Through preliminary analysis, it is concluded that BDDA reacts with scheelite through electrostatic interaction.

1. Introduction

Scheelite, one of the most important tungsten-bearing minerals, is often associated with other salt-type minerals such as calcite, fluorite and apatite. Flotation techniques have been used to separate them. However, the flotation is difficult because of their similar surface properties and high surface reactivity with their conventional collectors such as fatty acid and alkyl sulphate (Houot, 1982; Mishra, 1982; Amakonah et al., 1985; Marinakis and Shergold, 1985a,b; Pugh et al., 1985; Shin and Choi, 1987). In practice, the general method to accomplish effective flotation is to add depressants in a large amount in association with fatty acids and to take some special treatments such as high-intensity agitating and heating (Hanna and Somasundaran, 1976). However, using large amounts of depressants may affect the following procedures or contaminate the environment. And the special treatments mentioned above are all high energy-consuming processes. Therefore, searching for collectors for effective flotation of scheelite at normal temperature is highly desirable.

Quaternary ammonium salts are extensively used as an efficient extraction reagent in tungsten hydrometallurgy for its high affinity to tungstate ions (Pzaitsev et al., 1992; Zhang and Zhang, 2003). Based on this, it is reasonable to imply that it would interact with scheelite but weakly with other associated salt-type minerals and thus exhibit high selectivity in the flotation of scheelite. In this study, the collecting properties of Dioctyl dimethyl ammonium bromide for scheelite and calcite were examined with flotation tests. The collector adsorption is confirmed by infrared spectroscopic characterization.

2. Materials and methods

2.1. Materials

Handpicked, high purity scheelite and calcite, taken from two Chinese mines, were ground in a porcelain mill. The ground samples were wet-sieved and the -74 μm-size fractions were collected and used in flotation tests. A portion of this size fraction particles were further ground in an agate mortar to obtain -5 μm particles for FTIR tests and zeta potentials measurements.

2.2. Reagents

Dioctyl dimethyl ammonium bromide (BDDA), as a collector, was provided by the Xirun Chemical Engineering and Technology Corporation of Shanghai. Oleic acid from Tianyu Oleo Chemical Corporation of Sichuan was tested for comparison. Analytical grade HCl and NaOH were used as pH modifiers. The distilled water was used in all the experiments unless otherwise stated.

2.3. Flotation tests

Flotation tests of individual minerals and artificially mixed minerals were both conducted. The mixture contains equal amounts of scheelite and calcite. All of the flotation tests were carried out in a micro-flotation cell. The mineral suspension was prepared by adding 2.0 g of -74 μm-size fraction minerals to 50 ml of solutions under agitation. The pH of the mineral suspension was first adjusted

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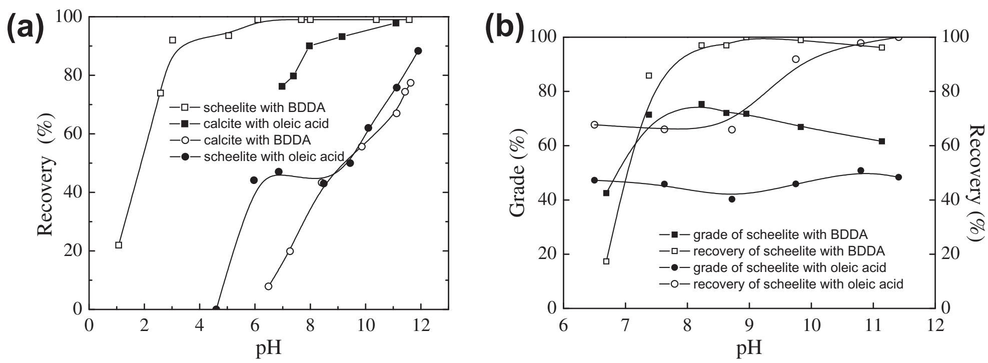

Fig. 1. Flotation results of individual minerals (a) and the mixed mineral (b) as a function of pH with BDDA and oleic acid as collector.

to a desired value by adding concentrated NaOH or HCl stock solutions. The prepared collector stock solution was added to a desired concentration while conditioning for 3 min. Flotation was allowed for a total of 4 min. The floated and unfloated particles were collected, filtered and dried in a well-ventilated oven at 120 °C for 2 h. The flotation recovery was calculated based on solid weight distributions between the two products. The grade of concentrates in the mixed-minerals flotation tests were expressed with the mass percents of scheelite.

3. Results and discussions

3.1. Flotation studies

Single-mineral flotation of calcite and scheelite was conducted as a function of pH using 0.2 mM BDDA and oleic acid as collector respectively. Fig. 1a shows that scheelite floated well with a recovery higher than 90% above pH 3 and almost 100% above pH 5. BDDA exhibits a strong collecting power for scheelite. In comparison, the recovery of calcite increases slowly over the pH range 6–12 and reaches 80% at pH 12. As calcite becomes soluble below pH 6, the acidic limit of the calcite pulp is pH 6. The single-mineral flotation results shown here suggest a preferential flotation separation of calcite from scheelite at a pulp pH between 7 and 9.

The flotation response of scheelite and calcite to oleic acid is almost contrary to the response of the two minerals to BDDA. Over the whole pH range tested, the recovery of calcite is above 80% and is higher than that of scheelite. Therefore, BDDA is superior to oleic acid in terms of selectivity for scheelite in single-mineral flotation tests.

As the surface properties of salt-type minerals are affected greatly by each other in solution, flotation tests of mixed minerals were carried out to further investigate the performance of BDDA. Because of the existence of calcite, the pulp pH ranges from 6 to 12. As shown in Fig. 1b, the recovery of scheelite exhibits a similar trend to the case of individual-mineral flotation and reaches greater than 90% above pH 8. It indicates that BDDA has strong collecting power for scheelite even when calcite coexists. Furthermore, the selectivity of BDDA for scheelite was also good in this case. The grade of scheelite reaches 80% at pH 8 and above pH 8 it reduces slightly as the collectivity of BDDA for calcite is increased. According to the results, effective separation of scheelite from calcite occurs over the pH range from 7 to 9 which is consistent with the conclusions of single-mineral flotation tests.

When oleic acid was used as collector, the recovery of scheelite is lower than that when BDDA was used although the recovery was improved compared to that in individual-mineral flotation. And the grade of concentrates does not change much from the one of the feed, which is 50%. It indicates that oleic acid cannot effectively separate scheelite from calcite when these two minerals coexist. This is consistent with the fact that some depressants are required when oleic acid is used as collector in the flotation practice of scheelite.

BDDA demonstrates both higher collectivity and selectivity for scheelite than oleic acid does in both individual mineral and mixed-minerals flotation. Therefore, BDDA is more effective in the flotation of scheelite than oleic acid.

3.2. Adsorption mechanism analysis

In respect of the electronic structure of nitrogen and the spatial structure of BDDA, its mechanism of adsorbing chemically on the scheelite through the nitrogen atom could be excluded. Specifically, on the one hand, the surface atoms of scheelite are inaccessible for the nitrogen atom because of the steric effects of its four alkane substituents. On the other hand, the ionic form of nitrogen of BDDA has no lone electron pair to form covalent bonds with metallic atoms.

Therefore, BDDA is most likely to physically adsorb on scheelite through electrostatic reaction. And similar mechanisms involved quaternary ammonium salts were proposed by some other researchers (Xia et al., 2009; Wang and Ren, 2005). Our previous work revealed that scheelite exhibits an iep of pH 2 and is negatively charged in the wide range of pH, while the iep of calcite is pH 11 (Xu and Hu, 2003). And the maximum zeta potential differential between scheelite and calcite was observed over the pH range from 8 to 10 which corresponds well with the maximum separation of scheelite from calcite over the same pH range as shown in Fig. 1.

4. Conclusion

BDDA exhibits selective collection for scheelite when calcite coexists, allowing preferential flotation separation by control of pulp pH. The individual and mixed mineral flotation tests indicate that the maximum separation of scheelite from calcite occurs over the pH range from 8 to 10. Through analyzing the structure of BDDA and the zeta potentials of scheelite and calcite, it is concluded that electrostatic interaction is the major mechanism of BDDA adsorbing on the scheelite.

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References

Amakonah, J.O., Somasundaran, P., Anathapadmanabhan, K.P., 1985. Effect of dissolved mineral species on the dissolution precipitation characteristics of calcite and apatite. Colloids Surf. 15, 295–307.

Hanna, H.S., Somasundaran, P., 1976. Flotation of salt-type minerals. In: Fuerstenau, M.C. (Ed.), Flotation, A.M. Gaudin Memorial Volume, vol. 1. AIME, New York, pp. 197–272.
Houot, R., 1982. Beneficiation of phosphatic ores through flotation: review of industrial applications and potential development. Int. J. Miner. Process. 9, 353–384.
Marinakis, K.I., Shergold, H.L., 1985a. Influence of sodium silicate addition on the adsorption of oleic acid by fluorite, calcite and barite. Int. J. Miner. Process. 14, 177–193.
Marinakis, K.I., Shergold, H.L., 1985b. The mechanism of fatty acid adsorption in the presence of fluorite, calcite and barite. Int. J. Miner. Process. 14, 161–176.
Mishra, S.K., 1982. Electrokinetic properties and flotation behavior of apatite and calcite in the presence of sodium oleate and sodium metasilicate. Int. J. Miner. Process. 9, 59–73.
Pugh, R., Stenius, P., et al., 1985. Solution chemistry studies and flotation behavior of apatite, calcite and fluorite minerals with sodium oleate collector. Int. J. Miner. Process. 15, 193–218.
Pzaitsev, V., Ivanov, I.M., Kalesh, N.K., et al., 1992. Scientific foundations of a new extraction technology for the processing of tungsten containing solutions[C]. In: Proceedings of the Second International Conference on Hydrometallurgy (ICHM). International Academic Publishers, Changsha, pp. 768–772.
Shin, B.S., Choi, K.S., 1987. Adsorption of sodium metasilicate on calcium minerals. Miner. Metall. Process. 2, 226.
Wang, Y.H., Ren, J.W., 2005. The flotation of quartz from iron minerals with a combined quaternary ammonium salt. Int. J. Miner. Process. 77, 116–122.
Xia, L.Y., Zhong, H., Liu, G.Y., Huang, Z.Q., Chang, Q.W., Li, X.G., 2009. Comparative studies on flotation of illite, pyrophyllite and kaolinite with Gemini and conventional cationic surfactants. Trans. Nonferr. Metal Soc. China 19, 446–453.
Xu, Z.H., Hu, Y.H., 2003. Interaction of amphoteric amino phosphoric acids with calcium-containing minerals and selective flotation. Int. J. Miner. Process. 72, 87–94.
Zhang, G.Q., Zhang, Q.X., 2003. A new clean production technology for tungsten hydrometallurgy. Chin. J. Rare Metals 23, 254–257.