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New collectors for sphalerite flotation

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Abstract

A series of *N*-arylhydroxamic acids (31) were synthesized and tested as collectors to float sphalerite from a Canadian copper–zinc ore. The compounds were classified into four types namely, *N*-aryl-*C*-alkyl, *N*-aryl-*C*-aryl, *N*-aryl-*C*-aralkyl, and dihydroxamic acids based on the type of substitution. Dihydroxamic acids were found to be poor mineral collectors while the efficiency of sphalerite flotation increased in the order *N*-aryl-*C*-aryl < *N*-aryl-*C*-alkyl < *N*-aryl-*C*-aralkyl. Sphalerite was floated without activation by copper sulfate, and the best sphalerite recovery of about 80% (grade 32%) was achieved with *N*-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA) 67 g/t collector dosage. However, pyrite also floated along with sphalerite and this appeared as a major disadvantage to be addressed.

Keywords: flotation; sphalerite; arylhydroxamic acid

1. Introduction

Xanthate reagent scheme for the flotation of base metal sulfide ores is widely accepted and extensively used by operating mills all over the world. Activation of zinc minerals, especially sphalerite, by copper sulfate in xanthate-based flotation is a well known phenomenon (Finkelstein, 1997, 1999), and the amount of copper sulfate needed varies based on the zinc content of the ore. Some mills have to use as high as 1 to 1.2 kg of copper sulfate per tonne of the ore. Thus an operating mill that processes about 20,000 tonnes of ore per day dumps nearly 20 tonnes of copper sulfate per day, which imparts toxicity to the effluents. Also, copper sulfate being a very corrosive chemical reduces the equipment life. Thus, mills processing zinc ores not only have to spend lot of money on copper sulfate, which is the most expensive auxiliary chemical in the flotation circuit, but also end up producing toxic wastes.

Let us consider the Canadian scenario in the production or processing of zinc minerals. Canada produces about 70,000 tonnes of zinc concentrate per month (http://mmsd1.mms.nrcan.gc.ca/mmsd/data/04MTLY09.XLS) and the zinc content varies from 4% to about 25%. If one considers an average ore concentration of about 10–15% zinc minerals, the total amount of zinc ore to be handled would be about 700,000 to 1,000,000 tonnes per month. Calculation based on an approximate consumption of 1 kg of copper sulfate per tonne of ore to activate zinc shows that the Canadian mineral industry on an average

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consumes about 700 to 1000 tonnes of copper sulfate per month. Thus the money spent on copper sulfate (@ $ 2.80/kg) is around 2–2.8 million dollars per month. A collector that could float zinc minerals without activation by copper sulfate will result in significant saving because of the elimination of copper sulfate from the circuit. In addition to this direct benefit, the indirect benefits include (1) extended equipment life, and (2) less toxic industrial effluent that can meet the environmental compliance more easily.

The authors synthesized and tested a few cupferron-derivatives (Natarajan, 1995) to float zinc minerals without activation by copper sulfate and found (Natarajan et al., 1997) *p*-nonlycupferron was able to float 95% zinc without adding copper sulfate. They also reported (Nirdosh and Natarajan, 2002) that flotation of sphalerite from a copper-rougher tails obtained from a Canadian mill occurred without activation with copper sulfate, and this finding was verified by a Canadian industry (Fortin et al., 1999). High cost of manufacture of the cupferron derivatives, the flotation of pyrite with sphalerite and cupferron derivatives (*N*-nitroso compounds) being suspect carcinogens, were the negative aspects due to which further work on this class of collectors was not pursued.

Hydroxamic acids have structural similarity to cupferron and belong to the O–O type chelating collectors and had been used as analytical reagents (Lutwick and Ryan, 1954; Shendrikar, 1969). Pradip and Fuerstenau (1983, 1985, 1989, 1991), and Fuerstenau and Pradip (1984) tested alkylhydroxamates as collectors for oxidized copper minerals and rare earth minerals. Yoon et al. (1992) reported the use of hydroxamates for an entirely different purpose namely, in the beneficiation of kaolin clay. Recently Sreenivas and Padmanabhan (2002) tested alkylhydroxamates for the flotation of cassiterite. Owing to the vast scope for structural modifications, Natarajan and Nirdosh (2001) preferred *N*-arylhydroxamic acids to alkylhydroxamates, and synthesized and tested seventeen *N*-arylhydroxamic acids as mineral collectors for the flotation of a copper–zinc ore. They also attempted (Natarajan and Nirdosh, 2003) Quantitative Structure–Activity Relationship (QSAR) modeling of the results and showed that the flotation results were amenable to the structure–activity (flotation) modeling. The prime objective of the current study was to float zinc mineral without adding copper sulfate. Results of laboratory flotation tests on a copper–zinc ore from Canada using thirty one *N*-arylhydroxamic acids is reported in the paper. Except *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA) that is commercially available, all the other hydroxamic acids reported in the paper were synthesized and characterized.

2. Materials and methods

2.1. Synthesis

N-arylhydroxamic acids were synthesized following the procedure reported by Priyadarshini and Tandon (1967) and Natarajan and Nirdosh (2001). The two-step synthesis scheme and the structures of the *N*-arylhydroxamic acids used in the current study are given in Table 1 along with their abbreviated names. Six of the compounds reported in an earlier study by the authors (Natarajan and Nirdosh, 2001) were used in the current study also, and they are included in Table 1. All synthesized *N*-arylhydroxamic acids were colorless crystalline solids and were crystallized either from benzene–hexane mixture or from aqueous alcohol. The solids had a very long shelf-life and did not decompose on storing. All synthesized compounds were characterized by elemental analysis and spectroscopic methods.

2.2. Flotation tests

Flotation tests were done on a Canadian ore that contained about 2–3% copper, 7–8% zinc and about 15–20% iron. Chalcopyrite, sphalerite and pyrite were the main sulfidic mineral constituents of the ore.

2.2.1. Procedure for flotation tests

350 g of the ore was ground in a polyurethane-lined rod mill with stainless steel grinding medium for 8 min at 67% solids so that 50% the ore passed through 150 μm mesh. Mild steel grinding mill was not used to prevent addition of extraneous iron in the system for fear of masking the results with the newly synthesized collectors. Methyl isobutyl carbinol (0.1% aqueous solution) was used as the frother, and lime water and sulfuric acid solution (1 M) were used for pH adjustments. Water at pH 9.0 (the pulp pH during flotation) was used occasionally to wash the sides of the flotation tank while pulling the froth, to compensate for the loss of water and maintain the pulp level. The complete procedure for flotation tests is outlined in the form of a scheme in Fig. 1. The flotation samples (floats and tails) were acid digested using HNO_3–HF mixture in Teflon crucibles and analyzed for copper, zinc and iron by inductively coupled argon plasma atomic emission spectrometer (ICAP).

3. Results and discussion

Head assays based on the mineral distribution in the floats and tails of all the experiments matched very closely to the ore assay. This supported the data reliability and