Flotation of pyrochlore from low grade carbonatite gravity tailings with benzohydroxamic acid

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ABSTRACT

The beneficiation of a low grade niobium tailings by flotation using benzohydroxamic acid (BHA) as a collector and sodium hexametaphosphate (SHMP) as a modifying agent has been studied. A concentrate containing approximately 3% Nb_2O_5 (with an upgrade ratio of 12) was obtained with nearly 80% Nb recovery in 6.5% of the mass after only one rougher flotation stage. After four rougher stages, a final concentrate containing 1.54% Nb_2O_5 with 93% Nb recovery in ~15% of the mass was obtained. A Box–Behnken experimental design was employed to analyze the effects of collector dose and dispersant dose and pulp temperature and to model the concentrate grade and niobium recovery during rougher–scavenger flotation. The results indicate that temperature has no significant effect on recovery at the 95% or 90% confidence level. Statistical insignificance of the temperature effect has been attributed to the collector mechanism, which essentially does not require BHA species beyond a maximum monolayer capacity that is potentially achievable within the solubility limit at room temperature. SHMP plays an important role in the selective recovery of pyrochlore. Its dispersing function is distinguished from its depressing function in the rougher stages through a positive interaction term together with BHA in both the recovery model and the grade model. The main negative effect of SHMP on niobium recovery emerges in the scavenger stages as a result of depressing action (e.g., targeting primarily the middlings). The effect of reagent dose and temperature on the grade and recovery are presented using 3D graphs from statistical models developed. Negative quadratic terms of the statistical models are discussed in reference to possible overdosing of SHMP on the middlings (involving pyrochlore and gangue) as well as a postulated change of orientation mode of BHA, also due to its overdosing.

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1. Introduction

Presently, nearly 99% of global ferroniobium production come from two countries; Brazil accounting for about 90% of global production and Canada with nearly 9% of the total production (US Geological Survey, 2013). While current production rates are sufficient to meet global demand well into the future, a niobium supply risk exists due to the geographic concentration of ferroniobium production (British Geological Survey, 2012). There are a number of known niobium resources around the world which could potentially diversify global production. However, many of these deposits are highly refractory and therefore uneconomical to exploit using currently employed methods of mineral processing (Bulatovic, 2010; de Oliveira Cordeiro et al., 2011).

Pyrochlore, $(Na,Ca)_2Nb_2O_6(OH,F)$, is the main economic niobium bearing mineral which has been mined and processed since 1953 in Söve, Norway (Ferguson, 1971). Typically, pyrochlore bearing ores are upgraded by flotation with cationic amine collectors in acidic pulp conditions. In some cases, in order to achieve and maintain a stable pulp pH, carbonate minerals must first be removed through a reverse gangue flotation step. Furthermore, amine collectors are sensitive to the presence of slimes, and it is common practice to reject the −15 μm size fraction prior to flotation. Consequently, the beneficiation circuit for the processing of niobium ores is often complicated with numerous unit operations which when compounded, result in significant niobium losses.

One method of recovering niobium from extremely fine grained material (i.e., <20 μm) is through flotation using chelating reagents such as hydroxamic acids. Alkyl hydroxamic acids have been tested

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as collectors for pyrochlore in real ore samples beginning in the 1960s in the USSR (Gorlovskii et al., 1966). They have been known to perform well in difficult flotation environments, which consist of extremely fine particles (typically below 10 μm) imposing serious slime problems. An example of such a successful application in commercial practice is purification of kaolin clay. Yoon et al. (1992) concluded that hydroxamate collectors are tolerant to high density slurries in conditioning and flotation as well as relatively insensitive to the dispersant type. Recently, using octyl hydroxamate, Ni et al. (2012) demonstrated that a rougher concentrate with an upgrade ratio of 2 could be obtained from Niobec ore, which recovered over 95% of niobium in 47% of the mass. Other hydroxamic acids, such as benzohydroxamic acid (BHA), have been shown as potentially selective collectors for pyrochlore over certain associated gangue minerals (mainly silicates) at the single-mineral micro-flotation level (Espinosa-Gomez et al., 1987). However, the effectiveness of this type of collector was not demonstrated on real niobium ore samples featured by multiple mineralogical components. Such ores usually demonstrate different behavior due to complex mineralogy affecting interactions among physical and chemical variables in flotation, which largely determine the grade and recovery performances. Statistical methods are well-suited to study relative significance and interactions of parameters in various process systems in an efficient and economic manner (Box et al., 2005).

This paper investigates the upgrade potential of a niobium tailing by rougher–scavenger flotation with benzohydroxamic acid and sodium hexametaphosphate as input factors. In addition, the effect of pulp temperature as an input factor on concentrate grade, recovery and mass pull as response factors has been examined using a Box–Behnken methodology of experimental design.

2. Materials and methods

A series of bench scale flotation tests were carried out on a fine-grained, pyrochlore-containing, carbonatite ore, which was the tailings product from a gravity separation circuit. The assay of the flotation feed material can be found in Table 1. Preliminary analysis using a Malvern Metasizer revealed that the feed material was 80% passing 53.9 μm. QEMSCAN analysis identified that the sample contained primarily dolomite (∼85%), apatite (∼6%), and calcite (∼3.6%), as well as minor quantities (<1%) of Fe-oxides, pyrite, silicates, pyrochlore, columbite, and monazite.

A Box–Behnken experimental design was employed to examine the main and interaction effects of benzohydroxamic acid (BHA) dosage, pulp temperature, and sodium hexametaphosphate (SHMP) dosage. BHA was used to assess its function as a pyrochlore collector. As a variable, temperature was selected to enhance the collector action of BHA due to expected increase in its solubility. SHMP was selected as a modifier as it has been reported to improve selectivity in flotation of niobium minerals by acting as a dispersant as well as carbonate gangue mineral depressant (Bulatovic, 2010; Ni and Liu, 2013). The Box–Behnken design is a class of three-level incomplete factorial experimental design with fewer points than central composite designs (Box and Behnken, 1960). The design also avoids axial points, which is beneficial if certain operating conditions may be disadvantageous or impractical. For example, particularly high flotation pulp temperatures may be undesirable from an operability and economic standpoint. Thus,

one can stay away from their inclusion in experimental design space of the Box–Behnken method so that the design points selected are limited to a more relevant operating window. A schematic of the Box–Behnken design space is presented in Fig. 1.

Experimental run order as well as coded and actual variable levels (uncoded) for this particular experimental design can be found in Table 2.

BHA (99% pure) was purchased from Alfa Aesar and dissolved in water at 60 °C. SHMP was purchased in the form of Calgon (i.e., the brand name for sodium hexametaphosphate available in Canada and the United States). Oreprep®549 frother from Cytec was added at a rate of 2.5 g/t in each rougher stage. Pulp temperature was adjusted with a 750 Watt silica cased immersion heater. Pulp temperature was maintained within ±2 °C of the set point temperature using a Digi-Sense® temperature controller.

The flotation tests were carried out in Denver flotation cell on 2 kg charges of ore at a natural pH of around 8. No desliming was performed prior to flotation. For each test, four rougher flotation stages were performed, each four minutes in length. Reagent addition at each stage was made in equal dosage levels based on feed tonnage at equal time intervals according to Box–Behnken design so that statistical analysis could be carried out stage-wise to consider cumulative effects (Nanthakumar and Kelebek, 2007). In all tests, Calgon was added to the pulp prior to BHA. Note that the reagent dosages listed in Table 2 are for each individual rougher stage. During scoping testwork, it was observed that froth was stable and consistent through all rougher stages with minimal frother addition. Thus, frother was not considered as an input factor for this study and its addition rate was held constant for all experimental runs.

3. Results and discussion

3.1. Metallurgical performance and implication of model terms

Grade–recovery curves, as well as mass–pull recovery curves for all fifteen runs can be found in Figs. 2 and 3, respectively. The
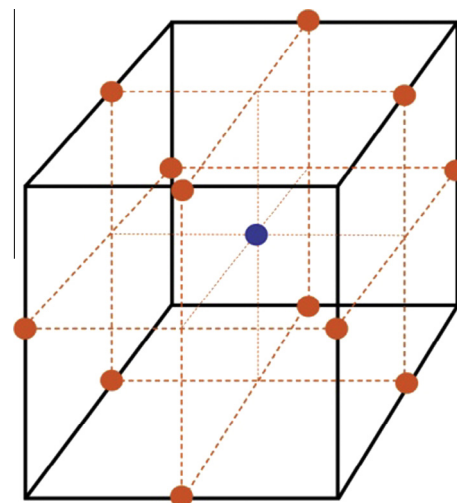

Fig. 1. The Box–Behnken design space.

Table 1
Head assay of flotation feed for Box–Behnken bench scale flotation experiments.

Assay (%)												
Sample	Nb_2O_5	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	SUM
Flotation feed	0.25	1.77	0.33	5.04	15.7	31.4	0.07	0.07	0.1	4.05	0.56	38.8	98.14