Minerals Engineering 123 (2018) 85–94

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

New reagent formulations for selective flotation of scheelite from a skarn ore with complex calcium minerals gangue

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ARTICLE INFO

Keywords:
Scheelite
Fluorite
Flotation
Collectors blend
Adsorption
DFT modeling

ABSTRACT

The approach using synergistic effects of the blend of carboxylic collectors was applied to process the Tabuaco tungsten skarn ores (Portugal) by flotation. However, a very complex mineral composition with high amounts of the fluorite (> 10%) and apatite (3–5%), as well as the presence of more than 40% of vesuvianite, a silicate of calcium, implied that such separation is highly challenging. In this work, the influence of sodium silicate and sodium carbonate on the selective flotation of scheelite has been investigated. A study of depressants dosage allowed to reach a selective flotation of scheelite from calcium minerals at 1125 g/t, except from fluorite. The use of sodium carbonate with sodium silicate showed synergistic effects, increasing the WO_3 grade from 6.6% to 11.2% without impacting the recovery. Collector formulations were created in the laboratory by mixing the commercial fatty acids, in which oleic and linoleic acid predominated, in various proportions with rosin acids while the ratio between oleic and linoleic acids was kept constant. The tungsten recovery increased significantly, up to 98%, with the amount of rosin acids in the mixture while the concentrate grade decreased from 16% WO_3 grade to 10.5% WO_3 grade impacting the selective flotation of scheelite from an ore with 0.9% WO_3 grade. The optimal ratio of fatty and rosin acids was then experimentally set to 5/1-6/1. An unprecedented increase of the flotation selectivity between scheelite and fluorite was obtained when the saturated acids were introduced in the formulation. The concentrate grade reached 27% WO_3 grade for the same ratio between anionic reagents. Thus, the new reagent formulation allowed to obtain a tungsten concentrate after only one cleaner stage without additional use of thermal treatment or activating heavy metals salts or specific depressants.

1. Introduction

Tungsten has been classified as a critical metal by the European Union in 2011, for its economic importance and its high supply risk (European Commission, 2010). Wolframite and scheelite are main source minerals for tungsten extraction. In scheelite ores, especially in skarns, fluorite, apatite and calcite constitute common gangue minerals. Nowadays, the main route for scheelite beneficiation is the flotation (Atademir et al., 1981; Deng et al., 2016; Liu et al., 2016). Cationic collectors such as amines showed good efficiency in scheelite flotation, though they are not recommended when silicates are the main gangue minerals (Hiçyìlmaz et al., 1993; Gao et al., 2015b; Yang et al., 2015). In such cases, a large range of anionic collectors can be used with very good results, including fatty acids, sulfonates, sulphates, sulphosuccinamate, hydroxamic acids and sarcosinate (Atademir et al., 1981; Ozcan et al., 1994; Zhao et al., 2013). However, fatty acids and particularly sodium oleate are the main collectors for the flotation of calcium-bearing minerals, due to their low cost and their high efficiency (Agar, 1982; Yongxin and Changgen, 1983; Miller and Misra, 1984; Rao and Forssberg, 1991; Pugh and Stenius, 1985; Filippova et al., 2014; Bo et al., 2015).

Separation of calcium-bearing minerals from themselves is very difficult because of their same surface properties (Pugh and Stenius, 1985; Marinakis and Shergold, 1985a). This is due to the presence of the same cation, Ca^{2+}, at the surface and very similar anions, WO_4^{2-}, CO_3^{2-} and PO_4^{3-} (Marinakis and Shergold, 1985b; Filippova et al., 2014). The low selectivity of fatty acids, inducing a global flotation of the calcium minerals, is linked to the chemisorption of sodium oleate onto Ca^{2+} of the surface (Atademir et al., 1981; Marinakis and Shergold, 1985a; Marinakis and Kelsall, 1987; Rao and Forssberg, 1991). Nevertheless, an efficient flotation of scheelite from other calcium-bearing mineral has been reached using specific depressants

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https://doi.org/10.1016/j.mineng.2018.05.001
Received 4 January 2018; Received in revised form 26 April 2018; Accepted 1 May 2018

(Yongxin and Changgen, 1983; Ozcan and Bulutcu, 1993; Liu et al., 2014; Bo et al., 2015; Gao et al., 2016; Liu et al., 2016). The main depressant used in the selective separation of scheelite from gangue minerals is sodium silicate (Qi et al., 1993; Marinakis and Shergold, 1985b; Marinakis and Kelsall, 1987; Liu et al., 2016), with a better efficiency when it is used with sodium carbonate (Agar, 1982; Lu et al., 2014; Liu et al., 2014). Besides, researchers have shown that selectivity between Ca-bearing minerals and mineral recovery can be enhanced by using combinations of fatty acids with different molecular structures or combinations of anionic and non-ionic reagents (Somasundaran et al., 1991; Filippov et al., 1993; Filippov and Houot, 1997; Filippov and Filippova, 2006; Filippov et al., 2012; Filippova et al., 2014).

The main objective of this study is to improve the separation contrast between calcium minerals. A combination of depressants and new collector formulations was used to reach this aim. First, depressants were studied and optimized until they show their limitation in terms of selectivity. The impact of the quantity of sodium silicate on the flotation selectivity was investigated. Then, with a set sodium silicate concentration, sodium carbonate was introduced in the flotation process to quantify its influence. Under optimal depressants conditions, collectors was studied, to highlight their real effect on the flotation selectivity. All the flotation tests were carried out with Tall Oil Fatty Acids, a by-product of the Kraft process in paper industry commonly used in the flotation (Sis and Chander, 2003; Pearse, 2005; Kou et al., 2010). These collectors contain fatty acids but also rosin acids, big-sized hydrophobic terpene-derived components among them abietic, pimaric and palustric acids are dominant (Logan, 1979). The rosin acids content in these commercial collectors can change significantly, depending on the geographic origin and on the species of the pines used to produce them (Logan, 1979). Even if some authors proposed that rosin acids do not adsorb onto mineral surfaces (Pearse, 2005), their impact on the scheelite flotation has not been studied. Furthermore, other fatty acids were studied and formulations containing saturated fatty acids were tested. Differences in terms of flotation selectivity and flotation efficiency are discussed in this paper, on the basis of an extended experimental work supported by molecular modeling.

2. Material and methods

A. Characterisation of the ore

The ore used in this work was sampled at Tabuaço deposit (Northern Portugal). It is a tungsten-bearing skarn, mainly composed by silicates (85%), among which most of them are calcium-bearing silicates (vesuvianite, zoisite, grossular). The other silicates are feldspars and quartz. The remaining fraction (15%) is constituted by fluorite (11%), apatite (3%) and scheelite (1%). The liberation mesh of the scheelite is estimated between 150 and 200 μm using optical microscopy.

B. Comminution for flotation tests

Blocs of the ore were crushed in 3 successive jaw crushers and a gyratory crusher to obtain −4 mm size fraction. To reach the liberation mesh, this product was wet sieved at 150 μm and the non-passing fraction was ground in a laboratory ball mill, during 6 min. For each stage, 1 kg of +150 μm size fraction was used with 10 kg of steel balls, at 66% of solid in the pulp. The ground ore was wet sieved at 150 μm. The passing fractions were all mixed and deslimed at 10 μm using a 2-inches hydrocyclone. The underflow (−150 +10 μm) constituted the flotation feed.

C. Pure minerals

Pure minerals were used in micro-flotation. The pure minerals sources were as follows: calcite from France, apatite from Madagascar, fluorite from France and scheelite from China. To determine impurities in minerals samples, chemical analyses were performed (Filippova et al., 2014). Scheelite was analysed through inductively coupled plasma mass spectrometer (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). It contains 63.71% W, 19.82% CaO with very low contents in impurities.

Table 1
Composition of commercial and created collector formulations, with different content in rosin acids.

Collector composition	BD2	2/3 BD2 + 1/3 BD30	BD15	1/2 BD2 + 1/2 BD30	1/3 BD2 + 2/3 BD30	BD30
Oleic acid (%)	47	39	36	36	32	25
Linoleic acid (%)	34	28	25	26	23	18
Palmitic acid (%)	2	1.3	–	1	0.7	–
Linolenic acid (%)	–	0.7	2	1	1.3	2
Rosin acids (%)	2	11.3	15	16	20.7	30
Oleic acid/Linoleic acid	1.38	1.38	1.44	1.39	1.39	1.39
Oleic acid + Linoleic acid (%)	81	68	61	62	55	43

D. Flotation

1. Reagents

For all the flotation tests, three different commercial mixtures of tall oil fatty acids, BD2, BD15 and BD30, were used as collectors. They are supplied by MWV, which also gave the compositions in terms of different molecules. The main fatty acids of these collectors are oleic acid and linoleic acid, with small amounts of palmitic acid and linolenic acid (Table 1). The 2, 15 and 30 are the weight percentage of rosin acids contained in the mixture. As mentioned previously, rosin acids are mostly abietic acid, pimaric acid and palustric acid. Collector formulations were created in the laboratory by mixing the commercial fatty acids, in which oleic and linoleic acid predominated, in various proportions with rosin acids. The ratio between oleic and linoleic acids was kept constant at 1.3–1.4, and the percentage of rosin acids within the mixture was experimented at 2–30% range (Table 1). All the formulations and the commercial mixtures were prepared as an aqueous solution at alkaline pH, obtained with the addition of sodium hydroxide. All the other fatty acids were 100% pure, supplied by Sigma Aldrich. As well, sodium silicate and sodium carbonate were supplied by Sigma Aldrich, in technical quality. In micro-flotation tests, sodium abietate is used to model all the rosin acids, as they have very similar structures.

2. Tests

Batch flotation tests were performed in an AGITAIR LA-500 rotor–stator apparatus with a 1.5 L cell by using 500 g of −150 +10 μm size fraction samples for each test. The rotational speed in the cell during conditioning and flotation was 900 rpm. The solid-liquid ratio was 33%. The samples were conditioned in the cell with water at pH 9 for 1 min, with depressant for 2–5 min and with 200 g/t of collector for 3 min. The pH was adjusted to 9 with addition of NaOH. The tests were conducted at room temperature, around 20 °C. The pulp was aerated with an airflow set at 0.27 m^3/h and the froth was collected manually every two seconds for a total time of 3 min.

Micro-flotation tests were conducted in a Hallimond tube with 200 mL volume, using 0.5 g of 40–100 μm size fraction of pure mineral for each test. The samples were conditioned in 100 mL of deionized water with collector, during 5 min. The pH was adjusted to 9–9.5 with addition of NaOH during the conditioning and before the flotation. Flotation tests were performed with N_2, at 20 °C, during 5 min. After the