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Flotation study of fine grained carbonaceous sedimentary apatite ore – Challenges in process mineralogy and impact of hydrodynamics

Duong Huu Hoang[a,b,c,*], Nathalie Kupka[a], Urs Alexander Peuker[c], Martin Rudolph[a]

[a] Department of Processing, Helmholtz-Institute Freiberg for Resource Technology, Helmholtz-Zentrum Dresden-Rossendorf, Chemnitzer Straße 40, Freiberg, Germany
[b] Department of Mineral Processing, Faculty of Mining, Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem, Hanoi, Viet Nam
[c] Institute of Mechanical Process Engineering and Mineral Processing, TU Bergakademie Freiberg, Agricolastraße 1, Freiberg, Germany

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ABSTRACT

The flotation beneficiation of apatite for phosphate production is challenging for finely disseminated sedimentary ores rich in carbonates. Similarities in surface properties of the semi-soluble salt-type carbonate and phosphate calcium minerals combined with fine intergrowth are the main reasons for poor grade and low recoveries. Imperfect depression of the calcium/magnesium carbonate minerals, e.g. calcite and dolomite, will lead to weak hydrophobic surface properties and thus true flotation of this gangue. Furthermore, fine particles, even though sufficiently liberated, strongly affect the bubble-particle collection due to negative rheological effects within the pulp leading to a drop in flotation kinetics of the fine valuables and an increase in entrainment of fine gangue particles.

This study presents the results and discussions based on automated mineralogy (conducted with a Mineral Liberation Analyzer – MLA) of size-by-size-by-liberation analyses for various mineral groups. In addition, results on different turbulent hydrodynamic parameters are presented based on various tests in a lab cell.

1. Introduction

Phosphate rock is the primary source of phosphorus, e.g. the production of phosphoric acid used in agricultural fertilizers, pharmaceuticals, cosmetics and the chemical industry in general. The world's demand for fertilizers is expected to continuously increase due to the population growth. The demand for phosphate fertilizers (P_2O_5) is forecasted to grow annually by 2.2% from 2015 to 2020 (FAO, 2017).

Sedimentary phosphate ores make up approximately 80% of the world's total phosphate rock production (Zapata and Roy, 2004; Oelkers and Valsami-Jones, 2008). Typical gangue minerals associated with these include carbonates (dolomite, calcite and ankerite), clays and silica. The beneficiation process becomes increasingly difficult in the presence of significant amounts of carbonate minerals finely intergrown with the phosphate minerals. Many separation methods have been investigated, but there is still no widely accepted economically efficient methods for separating carbonates from phosphates (Komar Kawatra and Carlson, 2014).

1.1. Challenges in selectivity of phosphates against carbonates

Froth flotation is considered as the most effective process for the beneficiation of the sedimentary phosphate ore, with more than 60% of the marketable phosphate in the world being processed by flotation (Abouzeid, 2008). For carbonaceous sedimentary phosphate ores, flotation is facing various challenges due to mineralogical surface property similarities between carbonate and phosphate minerals. The carbonaceous sedimentary phosphate ores contain similar constituent minerals such as calcium/magnesium carbonates and calcium phosphate, which exhibit similar surface properties. All minerals, apatite ($Ca_{10}(PO_4)_6F_2$), dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) belong to the group of semi-soluble salt-type minerals with similar cations (Ca^{2+}) (Komar Kawatra and Carlson, 2014).

Apatite, dolomite and calcite minerals are sparingly soluble and will release their lattice constituents into the solution. Sedimentary carbonaceous ores contain a significant amount of $(CO_3)^{-2}$ and F^- substituted for $(PO_4)^{-3}$, along with the cationic substitutions of Mg^{2+} for Ca^{2+} (Komar Kawatra and Carlson, 2014; Baudet and Save, 1999; McClellan and Van Kauwenbergh, 1991). These dissolved ions and their species can also interact with various minerals changing their surface

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[*] Corresponding author at: Department of Processing, Helmholtz-Institute Freiberg for Resource Technology, Helmholtz-Zentrum Dresden-Rossendorf, Chemnitzer Straße 40, Freiberg, Germany.

E-mail address: d.hoang@hzdr.de (D.H. Hoang).

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properties which interfere with the added reagents. Such interferences are the main reason for poor reagent adsorption selectivity (Somasundaran and Wang, 2006). Solution thermodynamics of systems containing various suspended semi-soluble salt-type minerals and flotation reagents are rather complex. In addition to the dissolution of minerals and adsorption of dissolved mineral and reagent species at the interface, interactions between these species in the bulk can lead to complicated phenomena such as surface and bulk precipitation as well as re-dissolution of adsorbed species (Somasundaran and Wang, 2006). Due to a surface reaction, the lattice is disrupted and a new phase is formed, so that surface precipitation may occur in the interfacial region (Fuerstenau and Deason, 1991).

Dissolved mineral species and similarly charged collector species compete for adsorption sites which can result in depression of the minerals. The reagents interact with the exposed surface of phosphates and also interact with carbonate minerals which have weak hydrophobic surface properties, leading to true flotation of this gangue.

1.2. Challenges of fine particle flotation – impact of turbulent hydrodynamics

There are a number of additional properties of sedimentary phosphate ores that are unfavorable to flotation, including:

- *High slimes production*: Because of the soft nature of sedimentary phosphate ore, specifically the softer dolomite-rich pebbles, large amounts of slimes are produced during the comminution and the conditioning stage. This can significantly increase reagent consumption while reducing the selectivity of the flotation process (Wiegel, 1999).

- *Porous nature of sedimentary phosphates*: Sedimentary phosphate particles are typically made up of very small mineral grains, which results in micron-sized pores. These “micropores” can significantly increase total surface area of the particles and increase reagent consumption (Save, 1999; Baudet and Save, 1999).

- *Very fine liberation size*: Phosphate particles can contain fine (micron to submicron-sized) dolomite inclusions. Grinding to such a size as to liberate the fine dolomite inclusions would significantly reduce selectivity of flotation processes (Save, 1999; Baudet and Save, 1999; Moudgil and Ince, 1991) and is therefore not done.

In addition, fine particles, even though sufficiently liberated, strongly affect the bubble-particle collection due to negative rheological effects within the pulp leading to a drop in flotation kinetics of the fine valuables (affecting the recovery) and an increase in entrainment of fine gangue particles (affecting the grade). The main reason for poor recovery is the low frequency of collision between particles and bubbles Z_{PB} (Leistner, 2016; Leistner et al., 2017; Trahar and Warren, 1976; Trahar, 1981). Fine particles with low mass rather follow fluid streamlines around air bubbles than collide with them. Hence, the efficiency of collision E_c is set in relation to the ratio of particle size and bubble size (Leistner et al., 2017; Trahar and Warren, 1976; Dai et al., 2000; Luttrell and Yoon, 1992; Yoon et al., 2016; Do, 2010; Sherrell, 2004).

$$E_c = \tanh^2\left[\sqrt{\frac{3}{2}\cdot\left(1+\frac{3/16\cdot Re}{1+0.249\cdot Re^{0.56}}\right)}\left(\frac{d_p}{d_b}\right)\right] \tag{1}$$

where Re is the Reynolds number, and d_p and d_b are the diameter of particle and bubble, respectively.

The collision probability is governed by the physics of the process (or hydrodynamics), while attachment probability and stability of attachment include a surface chemical component (particle hydrophobicity) (Wills and Finch, 2016). Therefore, turbulent hydrodynamics in a flotation cell play a very important role, especially for fine particle flotation.

In this study, automated mineralogy by MLA is applied on size-by-size-by-liberation classes to obtain a better understanding of the effect of size, liberation and various mineral groups on the flotation performance. Furthermore, the effects of different turbulent hydrodynamic parameters are being investigated in order to determine the role of turbulence in fine particle flotation.

2. Materials and methods

2.1. Ore

The apatite samples for this study were provided by the Vietnam Apatite Limited Company. Detailed information of the sample preparation procedures can be found in the study by Leißner et al. (2016a, 2016b). The apatite samples were used for flotation tests after 8 min of grinding (particle size distribution parameters $D_{10,3} = 5.3\ \mu m$, $D_{50,3} = 27.9\ \mu m$, and $D_{90,3} = 67.1\ \mu m$). All the samples (four size fractions of feed, tailings and four subconcentrates) were sent for chemical assaying by ICP-OES and Mineral Liberation Analysis (MLA).

2.2. Reagents

Sodium hydroxide (NaOH) with analytical grade ≥99% was supplied by Carl Roth GmbH & Co. KG, Germany and used to gelatinize corn starch.

Sodium carbonate (Na_2CO_3) with analytical grade of 99.9% was supplied from VWR Company, Belgium. It is applied as a pH modifier to achieve alkaline environment. A 2% solution was prepared for application.

Sodium silicate (Na_2SiO_3) with analytical grade of 99% was supplied by Zschimmer & Schwarz GmbH & Co. KG, Germany. It is used not only to depress the silicates and carbonates gangue but also as a dispersant of fine particle flotation.

Corn starch ($(C_6H_{10}O_5)_n$) was supplied by Carl Roth GmbH & Co. KG, Germany. It is gelatinized with NaOH at a 4:1 ratio Starch:NaOH. This modified corn starch was used as a carbonate mineral depressant.

Methyl isobutyl carbinol (MIBC) was used as a frother, provided by Sigma-Aldrich, Germany.

The different types of collectors used in the direct flotation of apatite are long chain fatty acids or fatty acid derivatives and their salts, i.e. hydroxamate, phosphoric esters, sodium oleate, etc., The collector in use is Berol 2015, a formulation of an amphoteric collector and a nonionic secondary collector. It is special product supplied by AkzoNobel Surface Chemistry, Sweden. Berol 2015 is intended to be used as a collector for the flotation of oxide and salt type minerals such as apatite, scheelite and fluorspar.

2.3. Froth flotation procedure

The batch flotation tests are performed using an MVTAT flotation cell built at the Technische Universität Bergakademie Freiberg. In order to minimize the impact of froth recovery, the flotation test was developed by using shallow froth levels and frequent froth removal (Dobby and Savassi, 2005). Fig. 1 provides an overview of the flotation process and reagent regimes.

Four sub-concentrates were taken, C1 (0 – 0.75 min), C2 (0.75 – 1.5 min), C3 (1.5 – 3 min), C4 (3 – 6 min). After completion of the flotation tests, the concentrate and the tailings products were filtered, dried, weighed and analyzed.

The flotation tests were conducted in five replicates, in order to be left with sufficient sample mass of the different streams for characterizing the sample.

2.4. Chemical assay – ICP-OES

The feed, flotation products and tailings and all the size-by-size subsamples after sieving were taken as representative samples for chemical assays using ICP-OES at the Technische Universität Bergakademie Freiberg. The sample was digested in 8 ml of acid composed of