



# The effect of dissolution kinetics on flotation response of apatite with sodium oleate



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## ABSTRACT

Different flotation strategies are used to concentrate apatite from phosphate rock around the world. There is evidence that the flotation performance of apatite can be influenced by its dissolution kinetics. The objective of this study was to investigate the effect of dissolution kinetics parameters on the flotation response, with sodium oleate, of apatite samples from different origins and genesis. The samples were firstly purified and characterized by X-Ray Fluorescence (XRF) and the Rietveld method applied to X-Ray Diffraction data (RXD). Surface area, specific mass and porosity were also determined. Apatite dissolution experiments were carried out in an automated reactor. The apatite flotation responses were determined by means of microflotation experiments. Both types of tests were performed at pH 8 and 10. By means of exponential adjustment of the dissolution curves (accumulated amount of dissolved  $\text{Ca}^{2+}$  ions as a function of time) it was possible to calculate the maximum amount of dissolved  $\text{Ca}^{2+}$  ions ( $\text{Ca}^{2+}_{\text{MAX}}$ ) and the kinetic constant ( $k$ ). The initial dissolution rate ( $R_i$ ) was determined by linear adjustment of the first minutes of reaction. It was observed that the initial dissolution rate, as well as the floatability, is greater at pH 8 than at pH 10. In addition, by comparing apatites from different origins it was found that the floatability increases with  $R_i$  and  $\text{Ca}^{2+}_{\text{MAX}}$ . The results indicate that the flotation performance is improved by the increase in the amount of  $\text{Ca}^{2+}$  ions that are available to interact with oleate molecules. This result supports the relevance of the surface precipitation mechanism governing the adsorption of oleate on the apatite surface.

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**Table 1**  
Flotation strategies applied to concentrate apatite from phosphate rock from different regions (Horta, 2013).

Genesis	Origin	Flotation route	Collector	Modifiers	pH
Sedimentary	China	Reverse anionic	Fatty acid	H <sub>2</sub> SO <sub>4</sub> and H <sub>3</sub> PO <sub>4</sub>	<5
	Brazil <sup>(a)</sup> Mozambique and Brazil				
Igneous	South Africa	Direct anionic	Alkyl sarcosinate <sup>(b)</sup> Alkyl sulfosuccinamate <sup>(c)</sup>	Starch NaOH	>10.5
		Direct anionic	Fatty acid	Sodium silicate Gum arabic Nonylphenol	Natural (8–8.5)
Metamorphic	Brazil	Reverse anionic	Fatty acid <sup>(d)</sup>	H <sub>3</sub> PO <sub>4</sub>	Acidic medium
	India	Direct anionic	Alkyl sarcosinates	Starch	Basic medium

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## 1. Introduction

Phosphate rock is a primary, nonrenewable, source of phosphorous (P) for inorganic fertilizers. The total demand must be met through the mining, beneficiation and chemical processing of apatite. More than 60% of the phosphate in the world is concentrated by froth flotation (Abouzeid, 2008; Sis and Chander, 2003a). The marketable phosphate concentrate must display contents of P<sub>2</sub>O<sub>5</sub> ≤ 30%, CaO/P<sub>2</sub>O<sub>5</sub> < 1.6, MgO/P<sub>2</sub>O<sub>5</sub> < 0.022 and MgO < 1% (Abouzeid, 2008; Lawendy and McClellan, 1993; Sis and Chander, 2003a, 2003b).

Apatite is the phosphorus (P) bearing mineral of phosphate deposits with different genesis: igneous (as in the carbonatite-alkaline complexes of Russia, Uganda, Brazil and South Africa); sedimentary (marine fosforites as in the north of Africa and Florida) and phosphates of organic accumulation (like the deposits of guano in Peru and Chile). Deposits from different genesis are characterized by the presence of several types of apatite: fluorapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>) in igneous rock; hidroxiapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) from biogenic origin; cloroapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>) in igneous rock, rocks affected by metasomatism with chlorine (Cl) and in some sedimentary environments; and Carbonate-fluorapatite ((Ca,Na,Mg)<sub>10</sub>(PO<sub>4</sub>,CO<sub>3</sub>)<sub>6</sub>(F,OH)<sub>2</sub>) in sedimentary rock (Abouzeid et al., 1980; Toledo and Pereira, 2001).

Industrial practices and laboratory investigations have provided strong evidence that a flotation strategy, which is suitable to concentrate a specific phosphate ore, can completely fail to concentrate others. This fact is evidenced in Table 1, which shows that for some ores it is more worthwhile to accomplish direct flotation of apatite. Conversely, for other ores, it is more effective to conduct reverse flotation of carbonates (Abdel-Khalek, 2000; Assis et al., 1985; Leal Filho et al., 2010; Pugh and Stenius, 1985; Zheng et al., 2006).

Variances in mineralogical composition and P<sub>2</sub>O<sub>5</sub> content are not sufficient to explain the dissimilar flotation response of phosphate ores from different origins (Table 1). Several works from 1985 to 1990 alerted to the influence of the intrinsic characteristics of minerals that compose the ore on the interaction between minerals and flotation reagents. Chemical heterogeneity, surface texture, crystallinity and dissolution degree are examples of intrinsic characteristics (Assis et al., 1987; Horta, 2013; Leal Filho, 1991; Silva et al., 1985).

In addition, the flotation success depends on the range of chemical reagents added to the system in order to control the surface characteristics of the minerals, determining the selectivity degree. Different types of reagents are used in the flotation of phosphate ores, such as collectors, depressants, and auxiliary reagents. Long chain anionic collectors such as fatty acids and alkyl sarcosinates, sulfosuccinates and sulfosuccinamates have been used for Ca-bearing minerals as observed in Table 1 (Hanna and Somasundaran, 1976; Leal Filho et al., 2010; Snow and Zhang, 2006; Yehia et al., 1993).

Sodium oleate (fatty acid) is the collector used in most of the works in the literature (Amankonah et al., 1985; Finkelstein, 1989; Hanna and Somasundaran, 1976; Lu et al., 1998; Marinakis and Shergold, 1985;

Young and Miller, 2000). Three oleate adsorption mechanisms at the surface of salt-type minerals are proposed in the literature: (1) chemisorption that results from the direct interaction between oleate molecules and the Ca<sup>2+</sup> ions exposed at the mineral surface; (2) surface precipitation whereby Ca<sup>2+</sup> ions interact with the oleate molecules immediately after leaving the mineral lattice. The formed calcium oleate then precipitates at the mineral surface; and (3) bulk precipitation that assumes that interaction between Ca<sup>2+</sup> ions and collector takes place in the solution bulk. The formed calcium oleate colloids can cover the mineral particles (heterocoagulation) depending on conditions that are governed by the DLVO theory (Finkelstein, 1989; Hanna and Somasundaran, 1976).

Lu et al. (1998) analyzed adsorption isotherms of oleate onto an apatite surface and compared their results with literature information about the adsorption of oleate on fluorite and calcite at pH 9.5. The authors observed that for oleate concentrations between  $2 \times 10^{-6}$  and  $2 \times 10^{-5}$  mol dm<sup>-3</sup> the preferential adsorption order is: fluorite (surface calcium density =  $11.1\text{--}12.9 \mu\text{mol m}^{-2}$ ) > calcite ( $8.2 \mu\text{mol m}^{-2}$ ) > apatite ( $5.1\text{--}6.6 \mu\text{mol m}^{-2}$ ). This adsorption order is proportional to the calcium density at the mineral surface. On the other hand, for an oleate concentration greater than  $2 \times 10^{-5}$  mol dm<sup>-3</sup>, the adsorption order changes to: calcite (solubility product (K<sub>ps</sub>) =  $4.6 \times 10^{-9}$ ) > fluorite ( $5.0 \times 10^{-11}$ ) > apatite ( $6.3 \times 10^{-126}$ ). This adsorption sequence is relative to the solubility product of minerals. These results indicate that surface precipitation takes place preferentially on the more soluble minerals (Lu et al., 1998). Nevertheless, the K<sub>ps</sub> parameter is relative to an equilibrium condition, which probably does not take place during the flotation process. Therefore, it is necessary to study the dissolution kinetics of salt-type minerals in order to predict the behavior of these minerals in real systems.

Very few studies in the scope of mineral processing have been dedicated to investigate the influence of solubility/dissolution on flotation response of sparingly soluble minerals (Amankonah et al., 1985; Lu et al., 1998; Marinakis and Shergold, 1985). Marinakis and Shergold (1985) studied the effect of the presence of sodium oleate in the solubility of different salt-type minerals. It was observed that the dissolution of apatite, fluorite and calcite is inhibited by the oleate addition, probably due to the covering of the mineral surface by calcium oleate.

If different sparingly soluble minerals are present in solution, the dissolution of one phase can affect the dissolution of the others. According to Amankonah et al. (1985), although the apatite solubility is different from the calcite solubility in pure water, an intermediated value is reached as the reaction takes place in the supernatant of the other mineral. The found behavior was explained as a consequence of the formation of a third phase with characteristics of both calcite and apatite, and called "capatite" by the authors. Finkelstein (1989), however, suggested the formation of monetite (calcium hydrogenophosphate, CaHPO<sub>4</sub>), whose solubility is less than that of calcite and greater than that of apatite.

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