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Reactive oily bubble technology for flotation of apatite, dolomite and quartz

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ABSTRACT

Reactive oily bubble technology was applied to selectively floating apatite from dolomite and quartz. Kerosene containing 100 ppm fatty acid was chosen to generate reactive oily bubbles. Zeta potential and contact angle were measured to investigate the surface properties of reactive oily bubbles and single minerals. The induction time was determined to evaluate the effect of different bubbles on bubble–mineral attachment. This novel technology was compared with conventional air bubble flotation in which collectors were added in the pulp. A shorter induction time and hence a stronger collecting power of the reactive oily bubbles attaching to the unconditioned minerals than the air bubbles attaching to the collector-conditioned minerals were observed.

With the addition of sodium silicate as depressant at pH 9, the induction time of reactive oily bubble attaching to dolomite becomes much longer than that attaching to apatite as a result of smaller contact angle of dolomite than apatite, which is opposite to the case of conventional air bubble flotation with collectors added in the pulp. Therefore, a novel phosphate flotation technology is proposed and tested. In this novel technology, apatite is separated from dolomite and quartz using reactive oily bubble with sodium silicate as depressant, followed by separation of dolomite from quartz with conventional air bubble flotation. The results of micro-flotation tests demonstrated a better flotation separation using the proposed novel technology.

1. Introduction

Phosphate rock, a main raw material of phosphatic fertilizer and phosphorus chemical industry, is one of the most important non-renewable mineral resources. The only way to provide phosphate is through the mining and beneficiation of natural resources. Most of the world's phosphate reserves are in the sedimentary and igneous deposits, which contain a considerable amount of gangue minerals. The treatment of phosphate ores is therefore needed to reduce these indigenous gangue minerals to meet the requirement of the phosphate industry (Sis and Chander, 2003a). The separation of apatite [$Ca_5(PO_4)_3(F,Cl,OH)$], a valuable mineral of phosphate ores, from the gangue minerals such as dolomite [$(Ca,Mg)(CO_3)_2$] and quartz [SiO_2] is the most critical step in the phosphate processing.

Many beneficiation methods such as heavy media separation, roasting, calcinations, leaching and flotation are applied to phosphate rock processing. When silica is the main gangue mineral, conventional flotation is the most widely used mineral processing technology. For the Jordanian phosphate ore, for example, collectors are added in the pulp, and air bubbles or oil droplets are used as carrier to separate the phosphate minerals from gangue with sodium silicate [Na_2SiO_3] as the depressant of silica (Salah et al., 2011). When carbonate is the main gangue mineral, the presence of carbonates in the phosphate rock requires the addition of sulphuric acid during the production of phosphoric acid and results in a low quality product of phosphoric acid. It is difficult to separate the carbonate gangue minerals efficiently from such phosphate ores by conventional flotation technology (Gharabaghi et al., 2010). Due to the similarity of the physical–chemical properties of the carbonate gangue minerals and phosphate valuable minerals (apatite [$Ca_5(PO_4)_3(F,Cl,OH)$]) and complex solution chemistry from the dissolution of salt minerals, the processing of such phosphate ores has always been a big challenge (Abouzeid et al., 2009).

Many researchers have devoted their efforts to developing a suitable and economic approach to improve the phosphate recovery from low grade and high dolomite content phosphate ores. The methods include the use of novel flotation systems, development of new flotation equipment, and use of high temperature to improve the solubility of collector or alternative flotation reagents. Calcination and selective leaching with organic acids are also used to upgrade the phosphate ores which are difficult to be treated (Abouzeid, 2008; Gharabaghi et al., 2010). However, all these methods either increase the energy consumption or have limited operability. None of these methods have been proven economically competitive to the conventional flotation and sufficiently efficient to

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upgrade poor grade ores. Thus, further improvement of the current technology or a novel method is required.

In past few years, addition of oil in flotation as flotation carrier has been proven to be a great success to some extents. Ralston et al. (1984) used polymer-stabilized oil droplets to efficiently separate fine calcite particles from fine quartz gangue. Another technique of using aerosol (air or nitrogen bubbles coated with silicone oil) to enhance de-inking efficiency was demonstrated, where oil-coated bubbles act as carrier. It is believed that using oily bubble instead of pure air bubble facilitates the liquid film drainage between air bubble and mineral surfaces, thus increasing the flotation rate (Gomez et al., 2001; Maiolo and Pelton, 1998). A novel concept of reactive oily bubbles (i.e., bubbles covered by a thin layer of oil containing oil-soluble collectors) was proposed and successfully used to float sulfide minerals (Liu et al., 2002). The results showed a great improvement in flotation efficiency by the reactive oily bubbles. Compared with air bubble, oil droplet and oily bubble used in conventional flotation, the advantages of using reactive oily bubbles include: fine-tuning surface properties of reactive oily bubbles; less consumption of collectors and oil; larger buoyancy force than flotation using simple oil droplets; and increased hydrophobicity of solid surfaces. More importantly due to the addition of oil-soluble collectors in the oil phase the reactive oily bubble technology can avoid unnecessary synergistic interactions and undesired activation of gangue particles by other inherent chemical species present in the pulp and the collectors added in the aqueous phase (Liu et al., 2002). Considering these distinct features, reactive oily bubble technology is believed to be a good alternative to process phosphate ores, especially the high dolomite content phosphate ores.

It is well established that the wetting properties of mineral surface control the selective flotation. The most basic measure of wettability for a particular liquid/mineral combination is the contact angle (David and Neumann, 2014). The induction time has been proven to be a critical parameter to evaluate the efficiency of particle–bubble attachment and hence flotation as it incorporates the dynamic nature of bubble–particle interactions. Under a given hydrodynamic condition, the shorter the induction time, the higher the flotation recovery (Yoon and Yordan, 1991; Gu et al., 2003). In this study, contact angle of the mineral solid and the induction time of reactive oily bubbles attaching to mineral particles were measured to investigate the feasibility of applying reactive oily bubble technology to the separation of phosphate ores by flotation. Zeta potential of the mineral particles and oil droplet were measured to investigate the properties of the interested interfaces. The micro-flotation test was conducted to demonstrate the use of reactive oily bubble in the processing of phosphate ores.

2. Materials and methods

2.1. Materials

Kerosene (Fisher Scientific) was used as the model oil. Fatty acids and sodium silicate (Fisher Scientific) were used as collectors and depressant, respectively. Reagent grade HCl and NaOH (Fisher Scientific) were used as pH modifiers, while ultra-high purity KCl (>99.999%) also from Fisher Scientific was used as the supporting electrolytes to prepare 1 mM KCl solutions. The single minerals of apatite, dolomite, and quartz were purchased from Ward's Natural Science Establishment (Canada). The single mineral chunks were hand-crushed by a hammer, ground and sieved to obtain particles in different size fractions suitable for various measurements. The composition of the single minerals was analyzed by the X-Ray Fluorescence micro-probe (EDAX ORBIS XRF) and the results are shown in Table 1.

Table 1
Composition of single minerals used in this study (wt %).

Components	Apatite	Dolomite	Quartz
Na_2O	2.19	–	–
MgO	–	36.06	1.30
Al_2O_3	0.21	0.77	1.00
SiO_2	1.36	1.25	96.02
P_2O_5	46.06	–	1.18
SO_3	1.11	0.68	0.27
CaO	48.18	60.27	0.23
CeO_2	0.77	0.07	–
Fe_2O_3	0.12	0.91	–

2.2. Zeta potential measurement

The zeta potential distribution of the oil droplets and mineral particles was measured using a Zetaphoremeter III (SEPHY/CAD). To prepare an oil-in-water emulsion for zeta potential distribution measurement, 5 droplets of kerosene with and without fatty acid were placed in 100 mL 1 mM KCl solutions. The mixture was then placed under a 550 sonic dismemberator (Fisher) for 15 min to make micron size oil droplets. The obtained emulsion was then creamed for 30 min to stabilize the oil droplets. The oil droplets remained in the emulsions had an average diameter of 504.2 ± 73.7 nm, suitable for zeta potential distribution measurement using the Zetaphoremeter. Before zeta potential distribution measurement, the oil emulsion was diluted with 1 mM KCl solutions to an oil droplet concentration that was suitable for the test. The mineral particles with diameter smaller than 20 μm were mixed with the test solution to prepare a 0.01–0.1 wt.% suspension and used for zeta potential distribution measurement. Once prepared, the suspension was left for 10 min for the mineral particles to reach equilibrium. The upper layer of the suspension was then used for zeta potential distribution experiment.

The Zetaphoremeter III (SEPHY/CAD) consists of a rectangular electrophoresis cell containing a pair of hydrogenated palladium electrodes at both ends, a laser-illumination and a digital-video-viewing system. The details on the experimental procedures can be found elsewhere (Liu et al., 2002). About 30 mL of the prepared suspension or emulsion samples at a given pH was used for zeta potential distribution measurement. The zeta potential distributions obtained were used to calculate the average zeta potential values for each measurement. The measurements were repeated for three times for the same suspension/emulsion and three sets of suspensions/emulsions were used for a given experimental condition. The average values as well as the standard deviations of nine measured average zeta potential values of a given sample were reported. The measurement was conducted at ambient temperature of 22 ± 0.5 °C.

2.3. Contact angle measurement

The contact angle of reactive oily bubble on the mineral surfaces was measured in testing solutions using the technique described by Liu et al. (2002). In this method a block of mineral was firstly ground and then polished to create a smooth surface. After polishing, the surface was rinsed with ethanol followed by de-ionized water and dried under an ultra-pure nitrogen stream to remove all possible contaminations on the surface. The cleaned mineral surface was placed in a 2 cm × 2 cm square-shape glass cell filled with the testing solutions. A reactive oily bubble, i.e., air bubble covered by a thin layer of kerosene with desired concentration of fatty acid was generated and placed on the mineral surface. After 1 min of contact with the mineral surface, the bubble was retracted back slowly, while the images of bubble in contact with mineral surface were recorded by a CCD camera. An image analysis software was then used to analyze the video images, and the frame right before the three phase contact (TPC) moves was analyzed to obtain the advancing contact angle. As illustrated in Fig. 1, the oil/aqueous solution interface was advancing on a mineral surface, a tangent line was drawn on the oil/aqueous solution interface at the TPC point. The angle between the tangent line and the mineral/water interface was measured and considered as advancing contact angle (θ_a). The contact angle on