



Two-stage reverse flotation process for removal of carbonates and silicates from phosphate ore using anionic and cationic collectors

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Abstract

Phosphate rock contains various gangue minerals including silicates and carbonates which need to be reduced in content in order to meet the requirements of the phosphate industry. Froth flotation has become an integral part of phosphate concentration process. In this study, double reverse flotation was applied to recover apatite from phosphate ore. H_3PO_4 and CaO were used as phosphate depressants, in acidic and alkaline conditions. Fatty acids and amines were added as carbonate and silicate collectors respectively. An experimental protocol devised to optimize the grade and recovery of phosphate using anionic–cationic method was found effective. Consequently, a required high quality of phosphate concentrate containing 30.1% P_2O_5 was obtained, with a recovery of 94%. X-ray diffraction and optical microscopy studies were performed to define the main minerals.

Keywords Phosphate ore · Characterization · Fatty acids · Amines · Flotation

Introduction

Phosphates are some of the most important minerals on Earth as they are the indispensable fertilizing raw material for agriculture and also the essential feedstock of chemical industries such as cleaning agents, dental creams, and flame retardants. A large proportion of the world's phosphate reserves are sedimentary deposits containing a considerable amount of carbonate minerals. Phosphate beneficiation from carbonate-rich sedimentary phosphate deposits is not effortless and requires further investigation (Al-Fariss et al. 1991). Phosphate ore processing techniques are dependent on the type of phosphate minerals and associated gangue. Froth flotation is a widely used physicochemical beneficiation technique in mineral processing industry for separating finely ground valuable minerals from a mixture of gangue minerals (Wills and Nappier-Munn 2006; Miller et al. 2002). The efficiency of a flotation circuit operation depends on several factors related to nature and structure of associated minerals together

with the type of instrumentation and operational variables which have been extensively investigated (Ralston and Dukhin 1999; Lima et al. 2009; Dos Santos et al. 2012; Feng and Aldrich 2004; Eigels 1967; Liu et al. 2011).

Phosphate ores are mainly accompanied with various associated gangue minerals like clays, silica, calcareous minerals (mainly calcite and dolomite), carbonaceous matter, and iron oxides. Various separation methods have been developed for phosphate ores; however, most of them have posed problems for upgrading the ores due to similarities in the apatite and associated gangue minerals in terms of physical properties (density, particle size, particle shape, etc.) and physico-chemical properties of carbonate and apatite minerals (Abouzeid et al. 2009; Bogdanov and Maximov 1990). Various beneficiation schemes have been established for improving phosphate grade including scrubbing/washing and size classification, gravity separation, magnetic separation, and flotation (Al-Fariss et al. 1991, 2013; Unkelbach and Wasmuth 1991; Abu-Eishah et al. 1991; Abdel-Khalek 2000; Deghani et al. 2012). In order to be considered successful; the beneficiation method must be able to increase P_2O_5 content above 30%. Applying a two-stage reverse flotation process for removal of carbonates and silicates from phosphate ore using anionic and cationic collectors, this work aims at illustrating the effect of collector's concentrations or dosage and pH on flotation performance of carbonates and quartz from phosphate ore.

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Materials and methods

Materials

Phosphate ore and pure minerals The samples were collected from Djebel Onk deposits in Algeria. The phosphate ore sample and pure minerals such apatite, dolomite, and quartz were ground below 0.16 mm for flotation studies. The phosphate analyzed 24.7% P₂O₅ with 9.4% insolubles.

Flotation reagents The flotation reagents used in the first stage are fatty acid fractions of C₁₀–C₁₈ synthesized from the paraffin oil by catalytic oxidation using potassium permanganate (Doudenkov and Choubov 1969). The composition of the used fatty acid, determined by gas chromatography, contains a significant percentage of carbon atoms in the molecule, from C₁₀ to C₁₇ equals 89.8% and the remaining C₇ to C₉; C₁₈ to C₂₀ equals 10.2%. The fatty acids were used in emulsion form, with phosphoric acid as depressant for phosphate and pH modifier.

The reagent scheme in the second stage flotation included an amine-based cationic collector containing 50% dodecylamine (C₁₂), 19% tetradecylamine (C₁₄), 14% hexadecylamine (C₁₆), and some other fractions in small proportions with CaO as pH modifier.

Methods

Flotation tests

Microflotation tests of pure minerals (2 g)—dolomite, quartz, and apatite—were conducted in a monobubble Hallimond tube. The Reynolds number of the bubble produced in monobubble Hallimond tube is more than 385 indicating a near turbulent flow in the layer of water behind the bubble and vertical velocity of the bubbles was found to be within 13.1 cm/s (Drzymala 1994).

Flotation experiments for phosphate ore (300 g) were conducted in a flotation cell of 1-L capacity at the impeller rate of 1200 rpm. The rate of removal particles with bubbles in flotation cell is given by Ralston and Laskowski (1992), Pyke et al. (2003). However, the effect of bubble size attachment, attachment efficiency, and velocity given by Reay and Ratcliff (1973), Kouachi et al. (2010) has shown that the bubble velocity equal 18 cm/s.

Spectroscopic methods

FTIR spectroscopy was used for the characterization of studied phosphate ore. The FTIR spectra were measured by Jasco 460 Plus spectrometer (Tokyo, Japan) with resolution 2 cm⁻¹.

c-X-ray diffraction and optical microscopy

Identification of the minerals in the raw phosphate ore was performed using XRD Bruker diffractometer (AXS-8D) operating at 45 kV and 40 mA with CuK α radiation (1,5406 Å) and also a microscope equipped with a trinocular head, infinitely corrected lenses with transmitted and reflected light, and a 360° rotating polarizer.

Results and discussion

Characterization of phosphate ore

Mineralogical analyses

The X-ray diffraction pattern of the phosphate ore sample presented in Fig. 1 shows a significant difference between phases. The main mineralogical phases identified are apatites. On the basis of International Centre for Diffraction Data (ICDD)

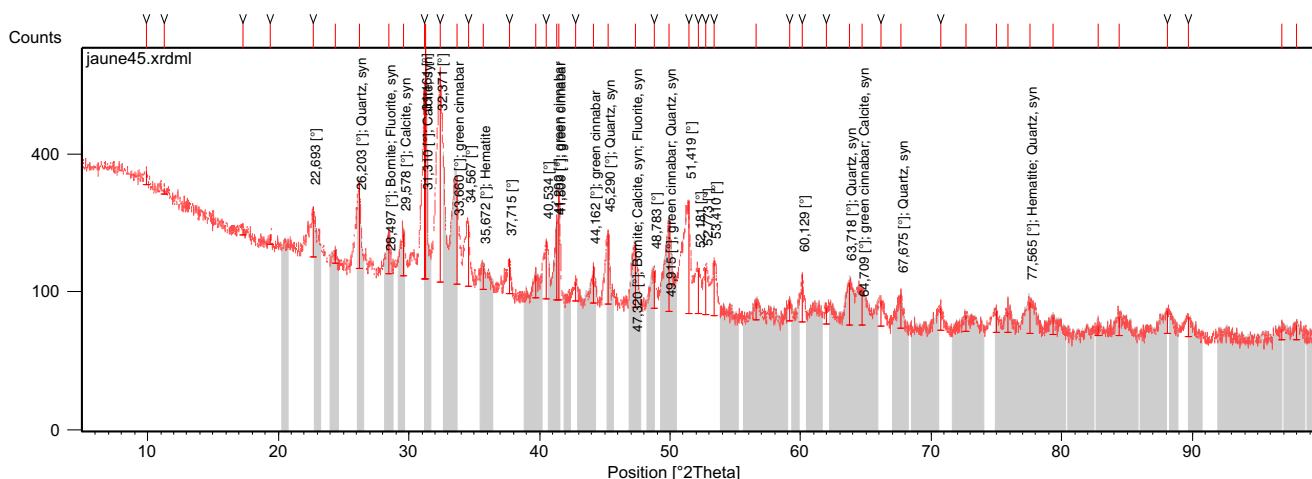


Fig. 1 XRD diagram of phosphate ore 1–47 μm size

Table 1 Candidates patterns of phosphate ore phase 1–45 μm

No.	Compound name	Chemical formula	Reference code	Score	Scale factor
01	Quartz	SiO ₂	27-1402	27	0.143
02	Calcite	CaCO ₃	05-0586	11	0.105
03	Hematite	Fe ₂ O ₃	33-0664	19	0.192
04	Green cinnabar	Cr ₂ O ₃	38-1479	15	0.228
05	Bornite	Cu ₅ FeS ₄	73-1667	11	0.104

Table 2 Measured values and pattern values of chlorapatite in phosphate ore phase 1–45 μm

Compound name	Chemical formula	Position [°2Theta]		d-Spacing [Å]		ICCD Reference
		Measured	Reference	Measured	Reference	
Chlorapatite–calcium chloride phosphate	Ca ₅ (PO ₄) ₃ Cl	31.31–100%	31.353–100%	2.854	2.853	24-0214
		32.371–86%	32.26–55%	2.765	2.770	

(Hounslow and Chao 1970; Brophy and Nash 1968; Hendricks et al. 1932) and using the X’Pert HighScore software, we were

able to identify the mineralogical composition of the raw phosphate ore. All the indications shown in the X-ray diagrams con-

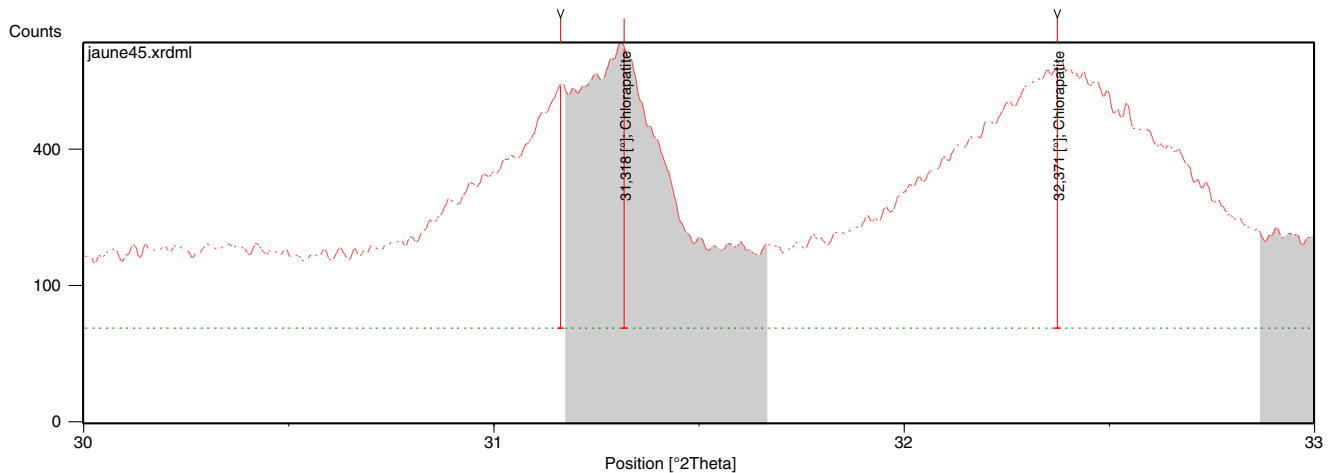


Fig. 2 XRD diagram of phosphate ore phase 1–45 μm shows chlorapatite

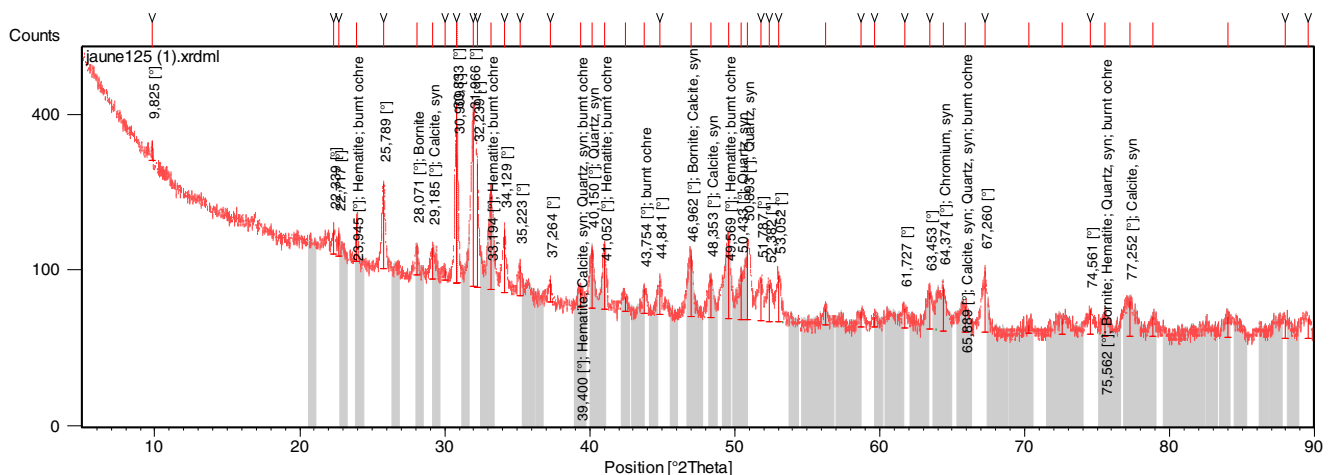


Fig. 3 XRD diagram of phosphate ore 45–125-μm size

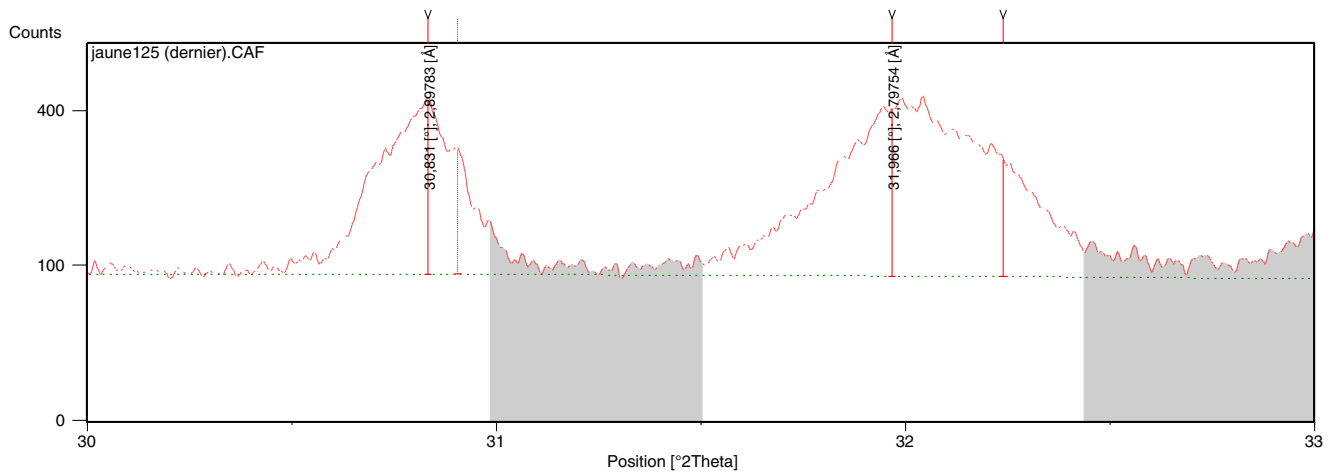


Fig. 4 XRD diagram of phosphate ore phase 45–125 shows dolomite and fluorapatite

Table 3 Candidates reference patterns of phosphate ore 45 to 125 μm

No.	Compound name	Chemical formula	Reference code	Score	Scale factor
01	Bornite	Cu ₅ FeS ₄	73-1667	20	0.183
02	Hematite	Fe ₂ O ₃	24-0072	16	0.157
03	Calcite	CaCO ₃	35-0816	32	0.121
04	Chromium	Cr	06-0694	18	0.093
05	Quartz	SiO ₂	46-1045	03	1.538

Table 4 Measured values and pattern values of dolomite and fluorapatite in phosphate ore phase 45 to 125 μm

Compound name	Chemical formula	Position [°2Theta]		d-spacing [Å]		ICCD Reference
		Measured	Reference	Measured	Reference	
Dolomite–calcium magnesium iron carbonate	Ca(Mg,Fe)(CO ₃) ₂	30.831	30.84	2.897	2.899 Å	34-0517
Fluorapatite–calcium fluoride phosphate	Ca ₅ (PO ₄) ₃ F	31.966–100%	31.936–100%	2.797 2.774	2.796 2.772	15-0876
		32.239–59%	32.26–55%	2.696	2.702	
		33.196–44%	33.127–60%			

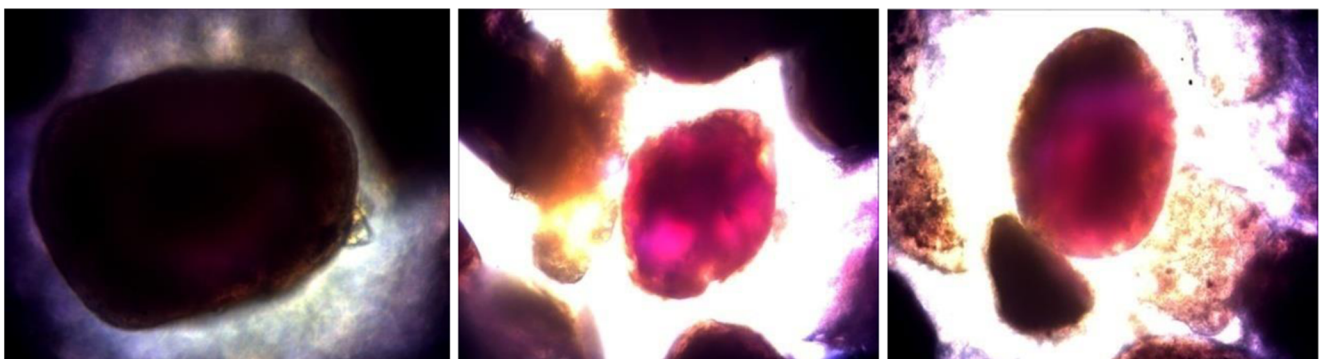


Fig. 5 Microphotography of a dark red spherical hematite mineral in the studied phosphate ore (× 400)

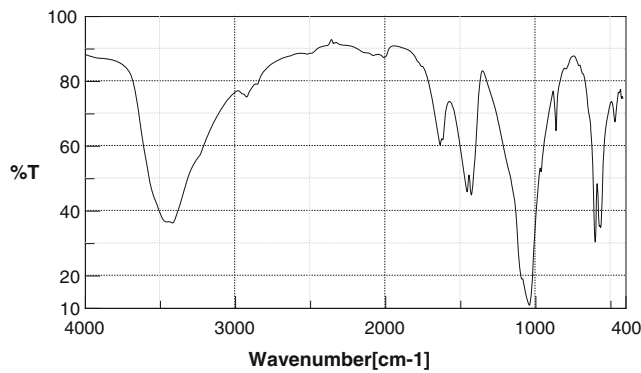


Fig. 6 Infrared spectrum of studied phosphate ore

cern two phases of the phosphate ore, the 45–125 μm phase and the 1–45 μm phase; – 20-μm size was removed.

Phase 1—45 μm The studied phase on minus 45 μm showed the existence of several phases containing calcite, quartz, hematite, green cinnabar, fluorite, bornite, and calcium chloride phosphate (Tables 1 and 2 and Figs. 1 and 2).

Phase 45–125 μm On the other hand, the 45–125-μm size range contained calcium fluoride phosphate (Howie and Broadhurst 1958); dolomite was proportionally found more prevalent than other secondary minerals than that shown on Figs. 3 and 4 and Tables 3 and 4.

Optical microscopy

The identification of the major contained minerals in the phosphate ore has been done with the use of an optical microscope. We focused on the phosphate ore particles of different sizes (45–180 μm). Some inclusions of magnetic dark red spherical minerals in Fig. 5 indicate the presence of hematite mineral.

Infrared spectroscopy characterization of phosphate ore

The infra-red phosphate spectrum (Fig. 6) shows bands in the interval of 1100–950 cm⁻¹, characterizing the deformed oscillations of P–O of bonds PO₄³⁻; bands of

Table 5 Chemical composition of the phosphate ore studied

Feed size, mm	Content, %				
	P ₂ O ₅	CO ₂	CaO	MgO	SiO ₂
– 0.160 + 0.125	29.8	6.50	50.66	0.89	2.36
– 0.125 + 0.100	28.8	7.70	48.96	1.25	3.46
– 0.100 + 0.080	25.4	11.50	43.18	3.30	6.81
– 0.080 + 0.040	23.8	12.60	40.46	4.11	7.03
< 0.040 mm	22.4	13.90	38.08	4.88	7.12

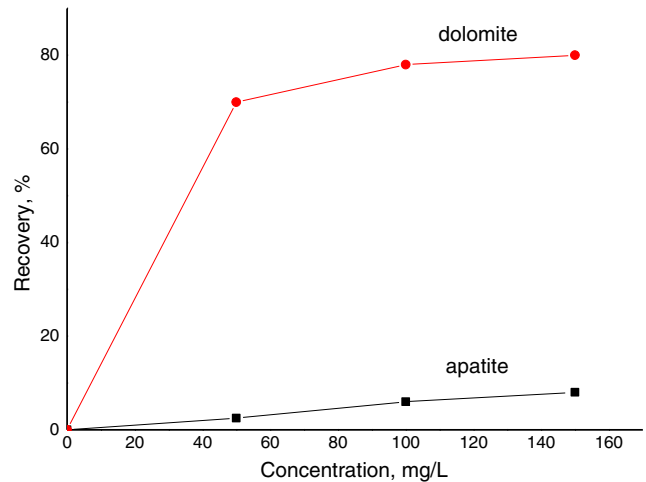


Fig. 7 Effect of fatty acid concentration on recovery of dolomite and apatite at pH 4.8–5.2 in the presence of H₃PO₄

average intensity in the interval 1440–1420 cm⁻¹ confirm the existence of magnesium compounds; bands of low intensity in the interval of 858–793 cm⁻¹ and 644 cm⁻¹ characterize the deformed oscillations of groups OH of the hydrogen bond; and doublets of average intensity in the interval 600–568 cm⁻¹ and the bands between 465 and 420 cm⁻¹ of relatively insignificant intensity characterize the oscillations P–O of PO₄³⁻ bonds.

Chemical analyses

The chemical analysis of the studied phosphate ore is presented in Table 5.

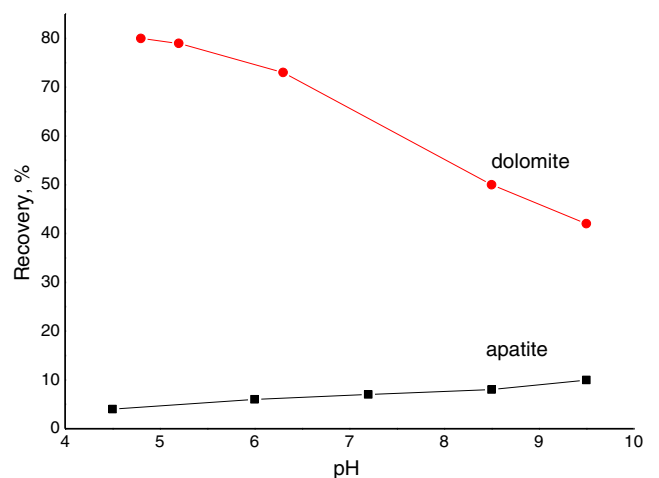


Fig. 8 Effect of pH on recovery of dolomite and apatite using H₃PO₄ and CaO at concentration of fatty acids 150 mg L⁻¹

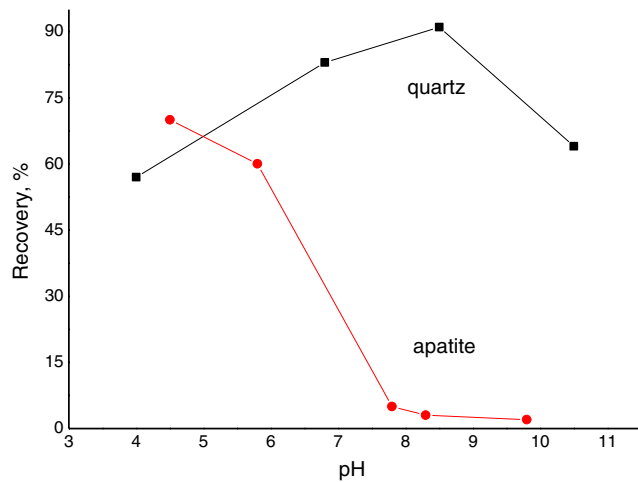


Fig. 9 Effect of pH on recovery of quartz and apatite using H_3PO_4 , CaO at mixed amine concentration of 30 mg.L^{-1}

Micro-flotation of pure minerals with fatty acids and amines

Flotation of dolomite and apatite using fatty acids

In the system $CaO-P_2O_5-H_2O$ system, the passage from the basic and neutral medium to the acid medium of less than 6, the solubility of the phosphate increases from 0.003 to 0.15 g/L (Shuvalova and Ratobilskaia 1984). In this case, there is a transfer of Ca^{2+} cations to the liquid phase, which reduces the number of active sites causing a significant decrease in the adsorption of anionic collectors. On the other hand, the dissolution of the carbonates in the acid medium increases the number of active sites, which increases the adsorption of anionic collectors.

The solution chemistry of fatty acids is an important factor in anionic flotation where Ca^{2+} is present in the solution. The depression of phosphate is possibly due to formation of aqueous $CaHPO_4$. The selective flotation of carbonates from phosphate in

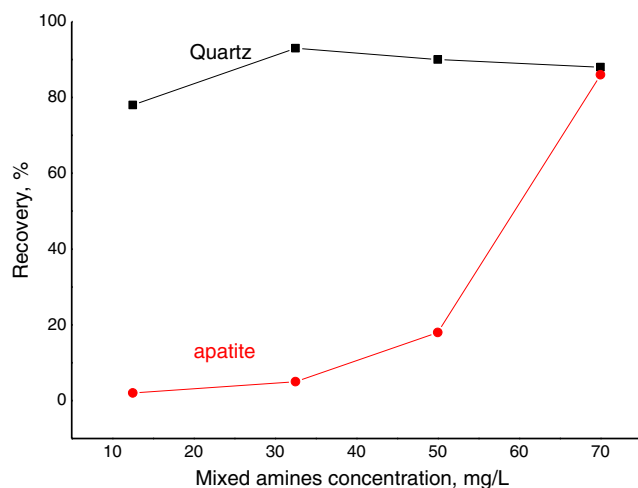


Fig. 10 Effect of mixed amines concentration on recovery of quartz and apatite at pH = 7.8–8.5 using CaO as regulator

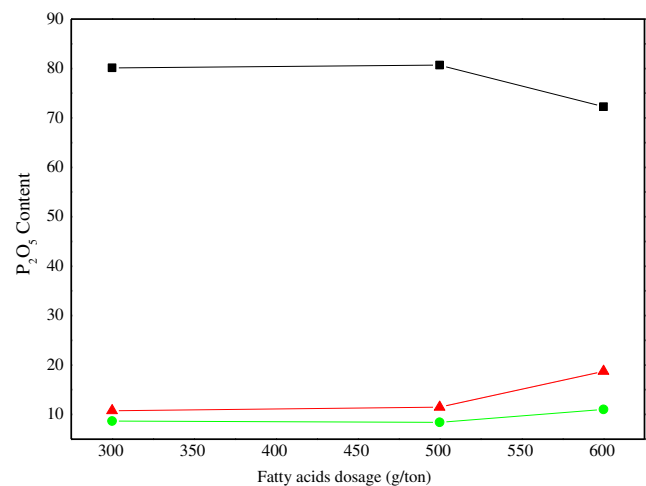


Fig. 11 Effect of fatty acids dosage on P_2O_5 content in closed circuit flotation of phosphate ore using $H_3PO_4 = 5 \text{ kg/ton}$ at pH = 4.8–5.2 ■ phosphate concentrate, (▲) carbonate product, (●) quartz product

acidic media can be enhanced by minimizing free Ca^{2+} in solution (Mohammadkhani et al. 2011; Snow and Zhang 2002).

Flotation of dolomite and apatite under various conditions of pH and different concentrations of fatty acid emulsions is illustrated in Figs. 7 and 8. The flotation tests of these minerals was carried out at 50, 100, 150 mg/L concentrations of fatty acids and constant pH of 4.8–5.2 adjusted by phosphoric acid. As seen in Fig. 7, while apatite floated at negligible amounts, dolomite floated well with increasing the concentration of fatty acid. The concentration of 150 mg/L was selected as an optimum collector concentration and the effect of pH was further investigated at this particular fatty acid concentration.

The flotation of dolomite and apatite minerals against the pH range of pH 4.8–9.5 is presented in Fig. 8 at 150 mg/L of collector concentration in the presence of H_3PO_4 and CaO to both adjust the pH and depress apatite. Evidently, there is a considerable difference between the floatability of the two

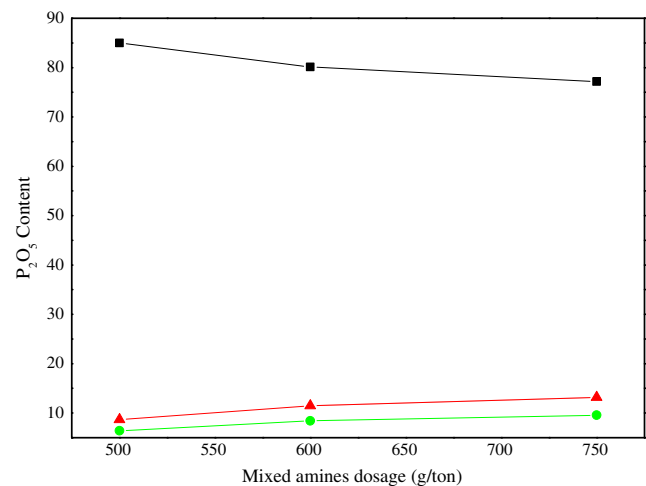


Fig. 12 Effect of amines dosage on P_2O_5 content in closed circuit flotation of phosphate ore using CaO at pH = 7.8–8.5 ■ phosphate concentrate, (▲) carbonate product, (●) quartz product

Table 6 Results of phosphate ore flotation in closed circuit

Product	Weight (%)	Content in %			Recovery %		
		P ₂ O ₅	MgO	Insoluble deposits	P ₂ O ₅	MgO	Insoluble deposits
Phosphate concentrate	77.1	30.1	1.05	11.7	94.00	28.90	60.1
Float product—carbonate	11.7	4.0	15.8	3.7	1.90	66.10	2.90
Float product—quartz	11.2	9.0	1.25	49.6	4.1	5.00	37.00
Feed	100	24.70	2.80	15.0	100	100	100

minerals at acidic and neutral pH but decreased at alkaline pH. Accordingly the acid medium of pH 4.8–5.2 was selected to achieve apatite–dolomite separation using fatty acids (Fig. 8).

Therefore, it is established that the selectivity of separation by flotation of dolomite from apatite is induced with the use of phosphoric acid and fatty acids as collector in acidic medium created part of the depressing action of apatite.

Flotation of quartz and apatite using amines

Flotation of quartz and apatite was carried out with the use of amine collector. The amines were used with the addition of phosphoric acid and CaO to make acidic basic medium, respectively. The flotation results presented in Fig. 9 show that quartz in acidic medium is relatively less floatable and reaches its peak value at pH 8.5 and then decrease upon increasing pH to 10.5. Interestingly, the pH range of 7.8–8.5 appears to be the best for flotation of quartz and beyond pH 9 the hydrolysis of amine resulted in the depression of quartz. On the other hand, the floatability of apatite in Fig. 9 steadily decreased with increasing pH from 4.5 up to 7.8 and then remained almost constant all the way in alkaline medium. The concentration of the mixture of amines at 30 mg/L represents an optimum to reach a window of selectivity between quartz and apatite at pH 7.8–8.5. Further experiments shown in Fig. 10 as a function of amine concentration reveal that indeed the selected concentration of 30 mg/L provides indeed the best selectivity between quartz and apatite minerals.

Closed circuit of phosphate ore flotation

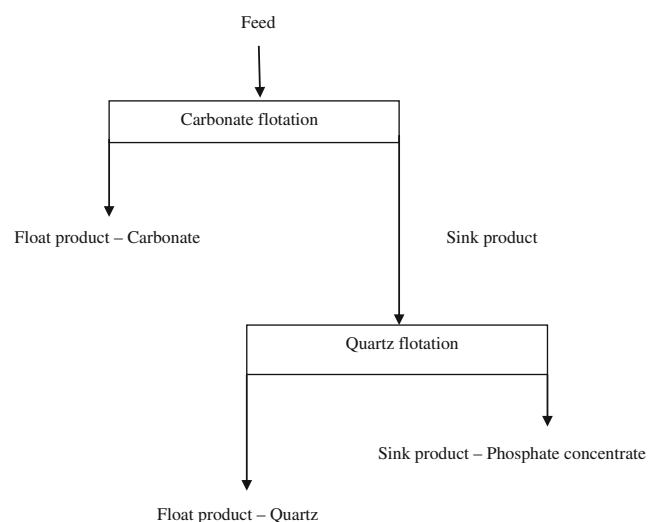
The difficulty of enriching carbonated phosphate ores, having a complex mineralogical composition, lies in the high dispersion of apatite; the existence of calcium and magnesium carbonates with similar floatability to that of apatite with a difficulty of separation of dolomite. The studied phosphate ore contains some oxides that not only decrease the difference in floatability of minerals but are found in the phosphate concentrate and reduce its quality. They also contain clay impurities

which give rise to a large quantity of slimes having a great influence on the flotation process.

Figure 11 shows the results obtained in presence of 5 kg/ton H₃PO₄ at pH 4.8–5.2 at first flotation stage using fatty acids 300, 400, 500 g/ton. Best results were obtained when 5 kg/ton of H₃PO₄, 500 g/ton fatty acids were used with feed size fraction—160 + 20 μm.

Figure 12 shows the results obtained using amines at 500, 600, and 750 g/ton in the presence of CaO as regulator at pH 7.8–8.5 at second flotation stage. The increase in the consumption of amines causes a decrease in recovery of P₂O₅ in phosphate concentrate and an increase in float products of quartz and carbonate. The cationic stage (flotation of silicate minerals—quartz) using amine collector was then carried out and final phosphate concentrate obtained.

The results in closed flotation circuit are displayed in the Table 6 and Fig. 13 shows that one can obtain a phosphate concentrate with a high content of P₂O₅ up to 30% with a relatively low MgO content of about 0.8–1.05% and insoluble residue of 11.7%.

**Fig. 13** Closed circuit flotation for the removal carbonates and silicates from phosphate ore

Conclusion

The flotation method proposed give satisfactory experimental results for the flotation of a carbonate and silicates rich phosphate ore. Flotation in this case is carried in two stage operation. Anionic–cationic double reverse flotation was found to be an appropriate method to upgrade grade phosphate rocks. The two steps process is to float the carbonates at pH = 4.8–5.2; the second stage includes flotation of the quartz at pH = 7.8–8.5. Using fatty acids (0.5 kg/ton) in the first flotation stage and mixed amines (0.5 kg/ton) in the flotation second stage gave good results, concentrate assayed 30.1 P₂O₅% at a recovery of 94%.

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