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The Effect of Different Auxiliary Collector in Flotation of Phosphate Ore

Melina Seyed Momen[1], Makan Etefagh[1], Amir Hassanjani-roshan[1] and Hassan Koohestani[2]

[1] Arvan Pod Company, Bahabad, Yazd Province, Iran
[2] Faculty of Materials and Metallurgical Engineering, Semnan University, Semnan, Iran

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ABSTRACT

Flotation is the main technique for extraction of elements from ores with suitable grades. Apatite with the formula of P_2O_5 can be extracted by flotation method. Fatty acids are the traditional collectors for apatite flotation but they have a poor selectivity against phosphate minerals. So, auxiliary reagents are needed. In this work, we formulated two collector packages with the same fatty acids and Nonylphenol ethoxylated (NPE) as anionic and nonionic surfactants but different in auxiliary reagents, and made a comparison between them in apatite flotation. Auxiliary reagents are polyethylene oxide (PEO) and paraffin. The results indicated that selectivity due to utilize PEO is better but for recovery, using paraffin is suitable.

Keywords: phosphate ore; Polyethylene oxide; paraffin; auxiliary reagents; fatty acids

INTRODUCTION

Phosphate is a main mineral source which is not replaceable or recyclable particularly in agriculture [1]. Apatite is a kind of group of phosphate-bearing mineral which has hexagonal crystal system and it is also the dominant source of phosphorous fertilizers [2]. Apatite has a general chemical formula $Ca_5(PO_4)_3(OH, F, Cl)$ which is called hydroxyapatite, fluorapatite and chlorapatite [3].

Phosphate rock minerals can be used for producing other industrial products such as animal feed supplements, anti-corrosion agents, pharmaceuticals and etc [4]. The Unites States and Morocco are the first and third largest producers and exporters of phosphate rock in the world, respectively. According to importance of phosphate in fertilizer industry, content of phosphate should have specified properties. For example the content of P_2O_5 must be larger than 30%. The ratio of CaO/P_2O_5 and MgO content should be less than 1.6 and 1% respectively [5].

Froth flotation has been used as a main method for purifying minerals from ore in recent years [6]. It is based on separating valuable particles from unwanted particles. All events are done in a pulp media containing ore and chemical reagents are used for this aim. Valuable particles are floatable because of hydrophobicity. Hence, they attached to air bubbles and carried up to the pulp surface by three

*Corresponding author: h.koohestani@semnan.ac.ir

phase foam which is called froth [7]. It can be noted that utilizing of phosphate resources is increasing. So, froth flotation is needed for processing of phosphate minerals [8, 9]. Fatty acids and their salts like oleic acid as anionic surfactants are used as traditional collectors for apatite flotation due to their low cost and collecting ability. Fatty acid can interact with Ca^{2+} ion on apatite surface with carboxylate group and will precipitated Ca^{2+} dicarboxylate, in the case of oleic acid calcium di-oleate, on apatite surface which is a primary mechanism for adsorption of fatty acids [10, 11]. The interaction strength between fatty acid and Ca^{2+} ion on the apatite surface results in an unsatisfactory separation of the two minerals at the industrial level. Fatty acid collectors are sensitive to slimes, pulp temperature and dissolved ions [10].

As mentioned earlier, some unwanted minerals (gunges) are existed in pulp during flotation. For example, for apatite flotation, hematite as Fe_2O_3 is one of the most important gunge minerals in phosphate ore. In this case utilizing some reagents which are called depressants will be needed. Sodium silicate, corn starch and guar gum are the famous depressants for iron minerals [12, 13]. In addition, fatty acids have poor selectivity against phosphate minerals. Therefore, auxiliary reagents such as oxime and phosphonate surfactants can be used for better performance of fatty acids in apatite flotation [14]. Generally, surfactant can have a number of synergistic advantages over the use of a single surfactant type. Addition of nonionic surfactant is found to improve the process of flotation by interacting with fatty acids. The depression of iron minerals in high-iron phosphate ores is usually achieved using starch as a modifier [5]. Polyethylene oxide (PEO) is nonionic polymer that improved phosphate recovery flotation during of using fatty acid collector. PEO can increase flotation recovery of coarse phosphate particles and reduce fatty acid/fuel oil consumption [15]. Paraffin has been used to stabilize the froth, as well as the results and the amount of weight concentrate indicated success [16].

Several factors can influence the floatability of apatite, such as its composition, particle size, the reagents used in the flotation process and the gangue minerals. In this work, we used mixture of fatty acids as main collector with paraffin and polyethylene oxide as auxiliary reagents and also Nonylphenol ethoxylated as nonionic surfactant for apatite flotation using apatite ore form Yazd province. Our aim is to compare the auxiliary reagents in final concentrate of P_2O_5.

EXPERIMENTAL

Materials

Apatite feed which is used in this study was taken from Yazd province in Iran. Chemical analysis of feed is shown in Table 1, that contains about 5.6% P_2O_5 and 43.2% Fe_2O_3. NaOH, Na_2CO_3 as pH modifiers were purchased from Neutron Chemistry Co. (Iran). Industrial grade sodium silicate (Na_2SiO_3) was used for Fe_2O_3 depressant. Fatty acids mainly oleic acid as collector of P_2O_5 and Paraffin, Polyethylene oxide (PEO) and Nonylphenol Ethoxylate (NPE) as the auxiliary reagents were used in the industrial grade.

Table 1. Chemical composition of apatite ore

Component	F_2O_3	CaO	P_2O_5	MgO	Al_2O_3	SiO_2	L.O.I
wt%	43.2	12.7	5.6	4.05	3.3	22.2	8.5

Flotation Process

Flotation tests were carried out in a Denver laboratory machine with 1200 rpm (Figure 1). 700 g of apatite feed was put into flotation cell with 20% solid in pulp. Direct flotation process for beneficiation of apatite ore in this project has 5 steps (3 roughers and 2 cleaners). Figure 2 is a flowchart of flotation process in this research. At first, sodium silicate with 600 gr/t) dosage as a depressant was added. In each step of process, NaOH and Na_2CO_3 were used to adjuste the pH of pulp to 10. Then, the collector was added in 3 rougher stages with 250, 150 and 100 gr/t dosages, respectively. In this study, two collector packages (similar to Table 2) with the same concentration were used for comparison.

Fig. 1. Images of laboratory flotation machine.

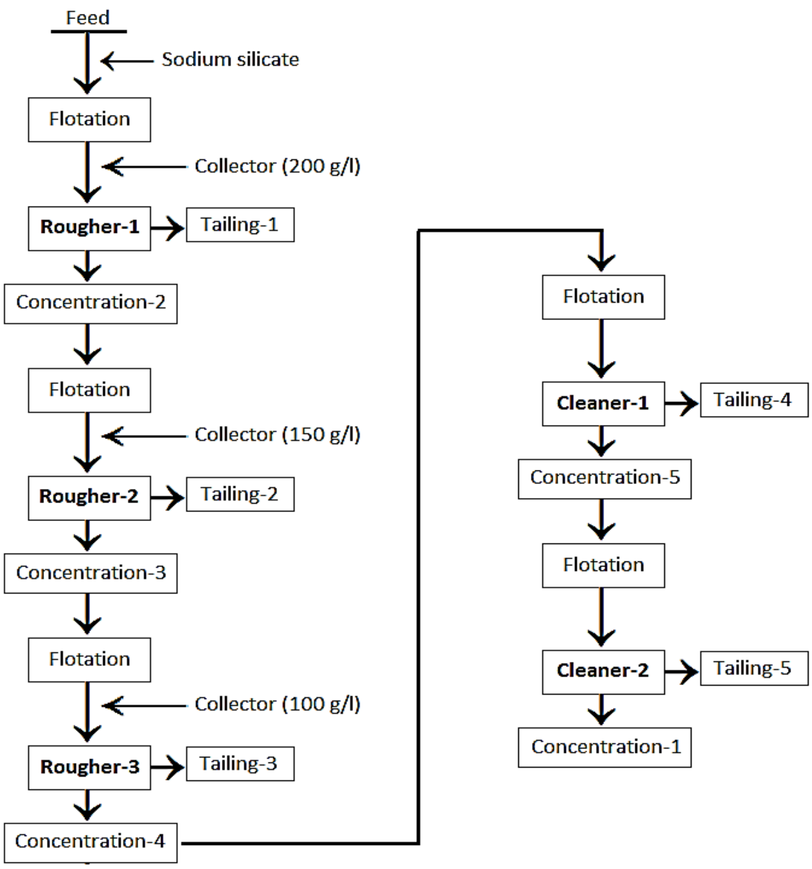

Fig. 2. Flowchart of flotation process in this research.

Table 2. Components of two collector packages

Package	Collector	Auxiliary reagents	
Sample 1	Fatty acids	NPE	PEO
Sample 2	Fatty acids	NPE	Paraffin

Each stage of rougher takes 5 min including 2 min for conditioning time and 3 min for froth collecting time. The total concentrates of previous stages were used in two cleaner steps. In cleaner stages we didn't add collector, but adding modifiers for increasing pH to 10, and 2 min for conditioning time and 3 min for collecting froth were necessary. Final concentrate-5 was dried in oven at 100^{o} C. The flotation recovery was calculated by the following formula [3]:

$$\% \text{ Recovery} = \frac{\text{C.c}}{\text{F.f}} \times 100 \qquad (1)$$

Which C and c represent the concentrate weight the concentrate grade, respectively. F and f show the feed weight and feed grade, respectively. Finally, the Concentrate-5 was investigated for element contain.

Characterization

Amounts of P_2O_5 and Fe_2O_3 in feed were determined by X-ray fluorescence (XRF) spectroscopy (Philips X-Unique-II, Germany). The grade of P_2O_5 in concentrates was analyzed by UV-Visible spectroscopy (Perkin Elmer-Lambda 850, USA). Grades of P_2O_5 in feed and concentrates were analyzed by UV spectroscopy in λ_{max} = 420 nm.

RESULTS AND DISCUSSION

As mentioned in previous sections, we have comprised two collector samples to evaluate the effect of surfactants (auxiliary reagents) in final concentrates. Each sample has mixture of fatty acids and NPE but they are different in other auxiliary reagents. Grades of P_2O_5 in concentrates and recovery are collected in Table 3.

Nonylphenol ethoxylate (NPE) with chemical structure in Figure 3, is a nonionic surfactant with hydrophobicity conferred by the branched alkyl group and hydrophilicity by their polar polyethoxy moiety. NPE has been the dominating auxiliary reagent used as a co-collector in selective flotation of apatite from phosphate ores [17, 18]. The measurement of the contact angle of sodium oleate on the apatite surface in the absence and presence of the NPE showed that the beneficial effect of the nonionic surfactant was achieved at low oleate concentrations (0.1-5 mg/L). It was further confirmed that the activity of ionic surfactants is enhanced with the addition of nonionic surfactant due to the synergistic effect in the formation of mixed micelles and the reduction of surface tension [19, 20]. Somasundaran and Maltesh (1997) used an ethoxylated sulfonate and ethoxylated nonylphenol phosphate for flotation of phosphate minerals [24]. They found the presence of secondary (auxiliary) reagent very beneficial in the experiments. The most important reason proposed for the improved flotation was the protection of anionic collector from the harmful effect of the slimes and dis-solved ions (e.g., Ca^{2+} and Mg^{2+}) which react with collector ions to form an insoluble salts that, in turn, precipitate on the minerals nonselectively.

Table 3. UV-Vis analysis of final concentrates

Collectors	Grade (% P)	% phosphate Recovery
Sample 1	% 15	% 32
Sample 2	% 12	% 51

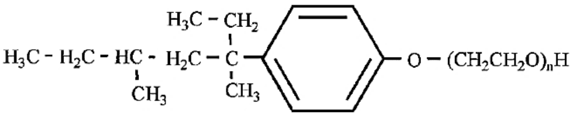

Fig. 3. Chemical structure of nonylphenol ethoxylate [17].

On the basis of Table 3, using PEO can improve the grade of P_2O_5 whereas, paraffin enhances the recovery. Fatty acids, including oleic acid, show poor performance at lower temperatures, which can be a problem for plants in winter or in cold regions [21]. Reagents are added to perform specific roles to manipulate the pulp chemistry and enhance the differences in mineral surface hydrophobicity to facilitate the separation. In the other words, PEO can improve selectivity of the collector but paraffin can increase the collecting ability. PEO ($C_{2n}H_{4n+2}O_{n+1}$) with chemical structure depicted in Figure 4, could flocculate hydrophobic particles (e.g. talc, graphite and chalcopyrite) better than hydrophilic ones (e.g. rutile, quartz, copper, and silica). It was observed during flotation experiments that there was a more stable froth developed when PEO was used. Moreover, when the hydrophilic minerals were treated to be more hydrophobic, the flocculation caused by the PEO could also be promoted [22]. Miller had shown that the addition of PEO nonionic polymers can both reduce fatty acid consumption and increase the flotation recovery of coarse phosphate particles [15].

In principle, all PEO investigated in this study would form mixed micelles with the fatty acid collector. Hence preventing the transformation of most of the collector into all ineffective insoluble precipitate found in solution. This however, is not that is needed to ensure a successful apatite flotation recovery [23]. PEO, particularly with longer oxyethylene chains, are not capable of bringing about a successful apatite recovery, in spite of 'protecting' the collector from Ca^{2+} in the mixed micelle. Other factors, i.e. the adsorption of PEO, which is controlled by the mixed micelle, also play a role, and this affects the hydrophobicity of the minerals [23]. PEO in the phosphate rougher flotation system may influence both the hydrophobicity of the particle and frothing behavior, which is good for improving the recovery of coarse phosphate particles [15].

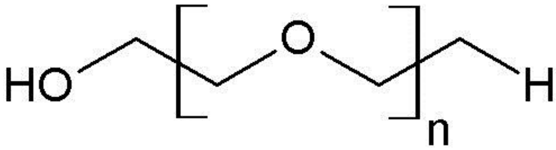

Fig. 4. Chemical structure of polyethylene oxide.

A reasonable pH for the application of the fatty acid collector was determined to be at pH of 10 by the experiments and these auxiliary reagents have a proper functional in pH= 10 according to the literatures [16]. The pH controls the dissociation of fatty acid, the distribution of acid/soap species in solution, and the interfacial properties of the flotation system. Flotation recovery with coarse feed drops dramatically when the conditioning pH is decreased. Under low pH, few bubbles were generated during flotation and the froth was very weak.

CONCLUSION

In this work, we made a comparison between two collector packages in direct flotation of apatite ore from Yazd province in laboratory scale. In these packages, mixture of fatty acids mainly oleic acid and NPE but different in auxiliary reagents were used. Flotation feed includes about 5.6% P_2O_5. This grade was enhanced of 32% and 51% in final concentrates by samples 1 and 2, respectively. It can be concluded that using PEO can enhance the grade of P_2O_5 more effectively than paraffin but the recovery is reverse.

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