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Synergism of octane phenol polyoxyethylene-10 and oleic acid in apatite flotation

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Abstract: The addition of octane phenol polyoxyethylene-10 (OP-10) to oleic acid via a reagent-combination technology was carried out and it was shown that OP-10 exhibited synergistic effects in the flotation performance of oleic acid. Single-mineral flotation tests, zeta-potential measurements, total-organic-carbon determination, and scale-up of continuous tests using raw ore were also carried out. Single-mineral flotation tests showed that OP-10 exhibited virtually no collecting performance for apatite, but it improved the flotation performance of oleic acid following its addition to oleic acid in small amounts at low temperature. Zeta-potential measurements and total-organic-carbon determination results indicated that the addition of 2.5% OP-10 to oleic acid increased the absolute value of the apatite surface potential and improved adsorption of oleic acid on the apatite surface at low temperature. A scale-up of the continuous test showed that application of OP-10 with industrial fatty acids led to good synergistic effects and contributed to effective separation of phosphate ore.

Keywords: *octane phenol polyoxyethylene-10, synergistic effect, flotation, apatite*

Introduction

Most global (> 60%) marketable phosphate is produced by flotation (USGS, 2007), and selection of an appropriate flotation reagent is critical for effective phosphate flotation. Depending on their purpose, reagents can be categorized as collectors, frothers and regulators, with collectors receiving the most attention (Moudgil and Gupta, 1989; Riggs, 1989; Abouzeid, 2008; Luo et al., 2014). Industrial phosphate-flotation collectors belong mainly to the fatty acid category, such as oleic acid, oxidized paraffin soap and tar soap (Houot, 1982; Prasad, 1992; Sisa and Chanderb, 2003; Guimarãesa et al., 2005). However, these collectors exhibit a poor solubility and dispersion in low-temperature flotation pulp, which results in a poor selectivity, a low flotation efficiency and the consumption of large quantities of reagent.

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To address such issues, a number of studies have focused on development of a novel reagent for phosphate beneficiation. For example, the novel chelating collector YH-2, which was developed by Ge at al. (2012), exhibited good selectivity and collection performance. Use of this reagent in the closed-circuit Dayukou phosphate test at ambient temperature as opposed to alternative direct reverse-flotation processes at high temperature, yielded an acceptable phosphate concentrate through single direct flotation (Ge at al., 2012). In terms of anionic collectors, Miller (2001) added polyethylene oxide (molecular weight 1000–8000) to an anionic collector to float the Florida phosphate ore. It was demonstrated that for a comparable phosphate recovery, the collector amount could be reduced significantly (~50% reduction) in the presence of polyethylene oxide (~10% of the collector weight) (Miller, 2001). It was also reported the use of an alcoholic solution of an alkyl hydroxamic acid collector for phosphate flotation (Miller, 2002). Huang et al. (2010) compounded a novel combined flotation collector by inducing elementary reactions of industrial rapeseed oil through saponification, acidolysis, chlorination and esterification. They also applied the collector in flotation of a medium–low grade phosphate, and demonstrated that this collector exhibited the improved water solubility and flotation performance compared with traditional fatty-acid collectors for phosphate flotation at ambient temperature (Huang et al., 2010).

Although the above reagents exhibit a good flotation performance for specific phosphates, their application in industrial production has been limited, because of their complex synthesis, high production costs and poor resistance to low temperature (Sisa and Chanderb, 2003; Abouzeid, 2008; Ge at al., 2012). In this paper we report application of a reagent combination technology, where octane phenol polyoxyethylene-10 (OP-10) is introduced into oleic acid to solve issues such as a poor tolerance and poor flotation effects at low temperatures. Because of its relatively low cost, the use of OP-10 can assist in the control of production costs. We also examine the mechanism of the synergistic effects of OP-10 on oleic acid through single-mineral flotation tests, zeta-potential analyses and total-organic-carbon (TOC) determination. The collector EM-C2 (compounded with 2.5% OP-10) was applied in scale-up flotation tests.

Experimental

Minerals and reagents

Apatite samples used in the single-mineral tests were provided by the Qingping Phosphate Company (Sichuan, China). The phosphorus-bearing mineral in the ore was fluorine-carbonate apatite. For single-mineral flotation and analytical tests, the raw ore was sorted manually, ground using a ceramic ball and screened to give a particle size from −0.10 to 0.037 mm. The apatite P_2O_5 grade was 40.69% from chemical composition analysis. An XRD analysis confirmed that the purity of the apatite sample was > 95% (Fig. 1), which met the test requirements.

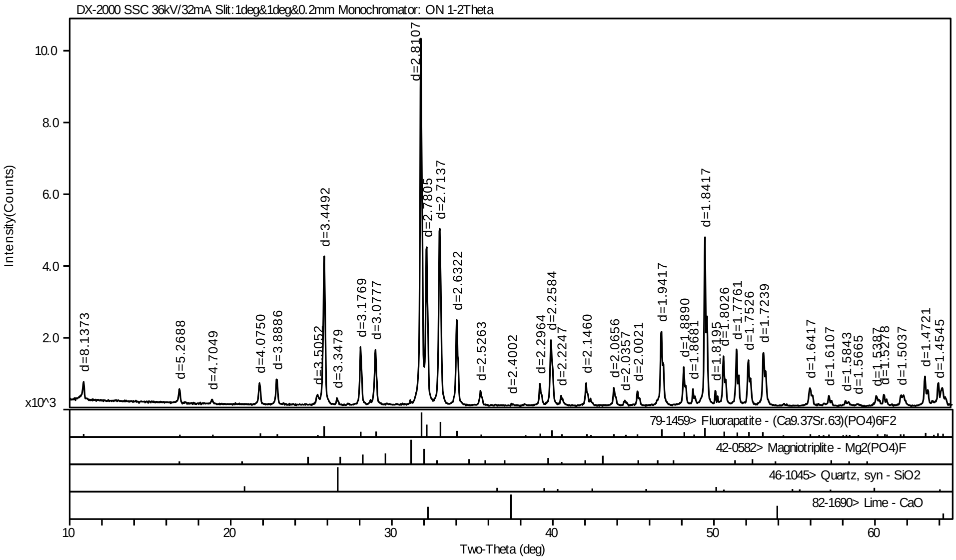

Fig. 1. XRD spectrum of apatite sample

The chemical composition of the ore sample is given in Table 1 and shows 22.50% P_2O_5, 16.25% SiO_2, and 3.32% MgO. The mineral composition of the ore is given in Table 2, as determined by the X-ray diffraction, infrared spectroscopy and mineral liberation analysis. Details of the various reagents used in the measurements and tests are given in Table 3.

Table 1. Chemical composition of raw ore

Compound	P_2O_5	MgO	SiO_2	Al_2O_3	Fe_2O_3	CaO	F^-
wt%	22.50	3.32	16.25	4.18	1.96	35.75	2.07
Compound	K_2O	Na_2O	REO	Loss-on-ignition		Insoluble in acid	
wt%	0.61	0.12	0.038	10.21		18.71	

Table 2. Mineral composition of raw ore

Mineral	Apatite	Svanbergite	Carbonate (e.g., dolomite)	Silicoide (e.g., quartz)	Others
wt %	55.05	4.98	17.99	18.16	3.82

Oleic acid was obtained by saponification of NaOH (i.e., HOL). Modified oleic acid I (or 2.5% OP-10) is the saponified oleic acid that is compounded with 2.5% OP-10. Modified oleic acid II (or 5.0% OP-10) is the saponified oleic acid that is compounded with 5.0% OP-10, and EM-C2 is the cotton oil fatty-acid soap that is compounded with 2.5% OP-10.

Table 3. Reagents used in measurements and tests

Reagent	Formula or abbreviation	Purity	Manufacturer
Hydrochloric acid	HCl	Analytical-reagent (AR) grade	Chengdu Kelong Chemical Reagent Factory, China
Sulfuric acid	H_2SO_4	AR grade	Chengdu Kelong Chemical Reagent Factory, China
Sodium hydroxide	NaOH	AR grade	Chengdu Kelong Chemical Reagent Factory, China
Sodium carbonate	Na_2CO_3	AR grade	Chengdu Kelong Chemical Reagent Factory, China
Oleic acid	$C_{17}H_{33}COOH$	AR grade	Chengdu Kelong Chemical Reagent Factory, China
Octane phenol polyoxyethylene-10	OP-10	AR grade	Chengdu Kelong Chemical Reagent Factory, China
Cotton oil fatty-acid soap		Industrial product	Sichuan Lutianhua Company Limited, China

Batch flotation tests

To obtain an appropriate ground sample, an XMB-70 rod mill was used to grind the ore sample, with a fixed spindle speed of 233 r/min, the addition of 250 g ore sample into the mill with 167 cm^3 water, and by grinding for 12 min (grinding fineness of 79% –0.074 mm, see Fig. 2). The grinding pulp was used as a flotation feed.

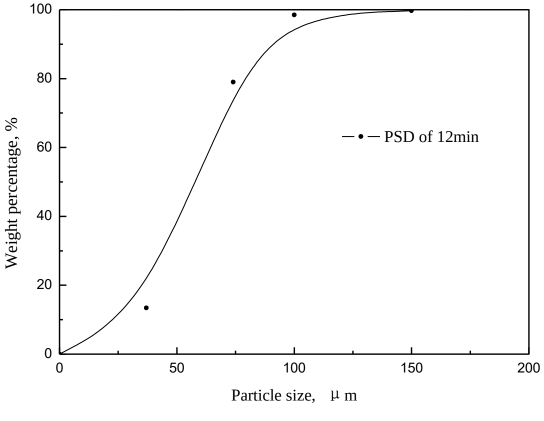

Fig. 2. Ground particle-size distribution

A 0.75 dm^3 XFD single-cell flotation device was used for batch flotation tests. The grinding pulp, and then Na_2CO_3, were added into the float cell and stirred for 2 min. Sodium silicate was added and the mixture was stirred for 2 min. A collector was added and the flotation pulp was stirred for the next 2 min. The vessel was filled with gas and the froth was baffled for 5 min to yield the desired froth and trough products. The flotation products were filtered, dried, weighed and sampled for chemical analysis.

Single-mineral test

A XFG II hanging-cell flotation machine was used for single-mineral flotation tests, with a spindle speed of 1992 rpm. For each test, an ore sample (5 g) was placed in the flotation cell and deionized water (50 cm^3) was added to the cell. After stirring for 1 min, the pH regulator was added, the mixture was stirred for 2 min, and the collector was added. After stirring for a further 2 min, the flotation pulp pH was measured and the froth products were collected for 5 min. After flotation, the baffled froth products (concentrate) were dried and weighed and the recovery was calculated.

Zeta-potential measurements

A Zetasizer Nano Zs90 (Malvern) was used to measure the zeta potential. Initially, single-mineral apatite was ground to < 37 μm. A sample of pure apatite (0.1 g) was added to deionized water (100 cm^3), OP-10 (40 mg/dm^3), oleic acid (40 mg/dm^3), or 2.5% OP-10 (40 mg/dm^3), and stirred for 10 min using a magnetic stirrer. The mixtures were left to stand for 10 min, and the supernatant liquid was transferred to the Zetasizer Nano Zs90 analyzer. The slurry temperature during the zeta-potential measurements was 10 °C. Measurements were carried out three times (the standard deviations of the zeta-potential measurements were 0–0.5 mV) and an average was taken.

TOC determination

A vario TOC cube (Elementar, Germany) was used to determine the sample TOC. Initially, the pure apatite mineral was ground to < 37 μm, and a sample of the powder (1 g) was added to the collector solution (100 cm^3) at pH 9.5 and 10 °C. The resulting mixture was stirred for 20 min, and a sample of the upper suspension (20 cm^3) was treated by centrifugation for 5 min. Thereafter, the supernatant was subjected to TOC determination. To determine the collector adsorbance on the mineral surface, TOC analysis was also carried out for the collector. The slurry temperature during TOC determination was 10 °C. TOC measurements were conducted three times for each sample (the standard deviations of the TOC determination were $0–0.5 \times 10^{-1}$ mg/g) and an average was taken.

Scale-up flotation test

A scale-up flotation test was carried out at the Emei Base of Institute of Multipurpose Utilization of Mineral Resources of the Chinese Academy of Geological Sciences, which has a handling capacity of ± 1.73 Mg/d. Direct-reverse flotation processes were applied. An EM-C2 collector (cotton oil fatty acid compounded with 2.5% OP-10) was used in the direct flotation and the collector for reverse flotation was EM-D10 (independently developed anionic collector for reverse flotation of phosphate). A flow chart of the test process is shown in Fig. 3.

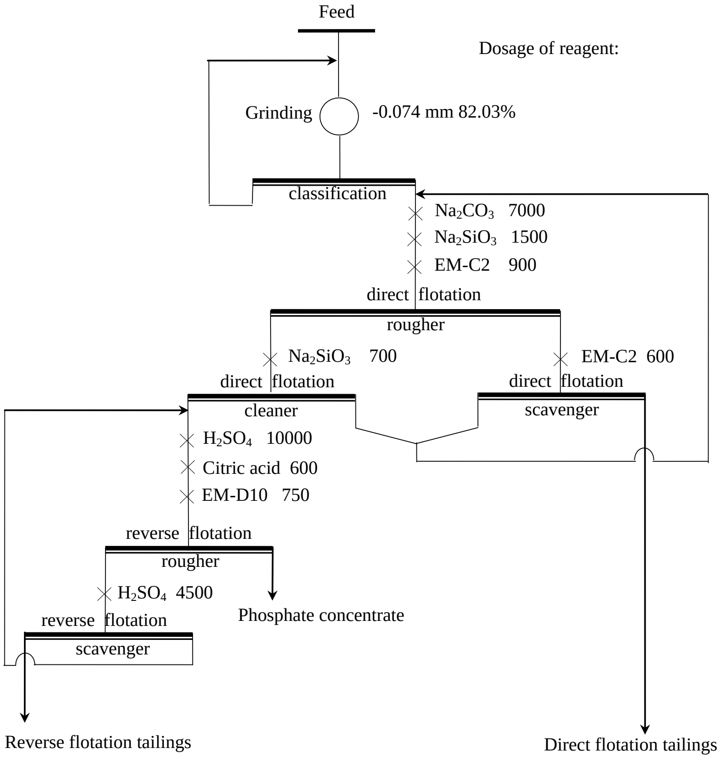

Fig. 3. Flow chart of scale-up flotation test

Results and discussion

Batch flotation test

The following test conditions were used in the batch flotation test and the results are outlined in Table 4 (sodium carbonate dosage = 5 kg/Mg, where kg/Mg refers to the reagent dose per Mg of phosphate rock, water glass dosage = 2 kg/Mg, collector dosage = 1.0 kg/Mg, test temperature = 15 °C).

Table 4. Comparison of direct flotation results using two different collectors

Collector	Product	Production (%)	P_2O_5 grade (%)	P_2O_5 recovery (%)
HOL	Concentrate	75.71	24.35	82.03
	Tailings	24.29	16.63	17.97
	Raw ore	100.00	22.48	100.00
2.5% OP-10	Concentrate	82.12	24.85	90.69
	Tailings	17.88	11.71	9.31
	Raw ore	100.00	22.50	100.00

As demonstrated in these tests, at a low temperature (i.e., 15 °C), the combination of OP-10 with oleic acid can improve the flotation performance of the reagent significantly. Compared with HOL, the 2.5% OP-10 collector yielded increase in phosphate concentrate production (6.41%) and recovery (8.66%), and reduction in the P_2O_5 grade of the tailings from 16.63 to 11.71%. Thus, OP-10 addition showed synergistic effects in the flotation performance of oleic acid.

Single-mineral tests

pH test

The flotation pulp pH is an important factor in determining the flotation separation effect (Hernainz et al., 2004; Sophia et al., 2015). The flotation pulp pH was tested at ambient temperature (20 °C) with an oleic acid collector dosage of 80 mg/dm^3 (Fig. 4).

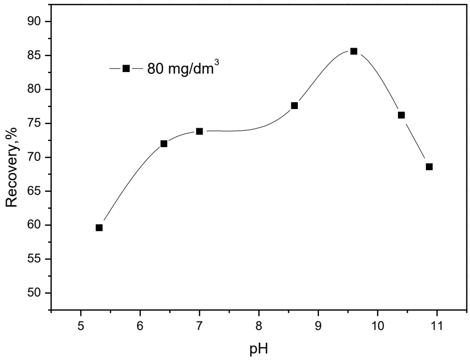

Fig. 4. Effect of pH on apatite recovery using sodium oleate as collector

As shown in Fig. 4, with an increase in pH of the flotation pulp from 5.31 to 9.60, the apatite recovery increased gradually from 59.6 to 85.6%. After NaOH addition to increase the pH to 10.87, the recovery dropped rapidly to 68.6%. In weak alkaline solutions, ions and ion–molecule complexes of oleic acids existed in the collector solutions. These species can adsorb at the apatite surface, which improved the hydrophobicity of the apatite significantly. However, at a pH above 9.6, the oleic-acid dimers became major species in which two oleic-acids ions were arranged in reverse. Therefore, when an oleic-acid dimer adsorbed on the apatite surface, the head group of one molecule in the dimer must face the solution, which resulted in a decrease in apatite flotation recovery (Lu et al., 1998; Nunes et al., 2011; Cao et al., 2015). This confirms that the optimal pH of the flotation pulp of the oleic-acid system is ~9.60. This result is consistent with those of previous studies (Lu et al., 1998; Nunes et al., 2011; Cao et al., 2015).

Flotation tests with four reagents at different temperatures

To study the flotation performance of oleic acid, modified oleic acid I, modified oleic acid II, and pure OP-10, dosage tests were carried out at 10, 20, and 35 °C, and the results are shown in Figs. 5–7.

The flotation performance of the four reagents was affected by the flotation pulp temperature and reagent dosage. A higher pulp temperature gave a higher apatite recovery because the increase in temperature can accelerate the thermal motion of molecules, which benefitted reagent dispersion and dissolution and improved the chance and speed of reagent adsorption on the mineral surface. The collecting performance of flotation reagents can be enhanced (O'Connor and Mills, 1990; Luo, 1998; Wei, 2009). OP-10 demonstrated a poor collecting performance to apatite.

Figure 5 shows that oleic acid, modified oleic acid I and modified oleic acid II exhibited a good collecting performance at 35 °C. With an increase in oleic-acid dosage from 5 to 20 mg/dm^3, the apatite recovery increased from 8.0 to 79.6%. However, at a high oleic-acid dosage of 60 mg/dm^3, the apatite recovery increased only slightly to 82.6%. The flotation performance curves of modified oleic acid I and modified oleic acid II were comparable with that of oleic acid, although apatite recoveries were 5–10% higher than when oleic acid alone was used. This result suggested that OP-10 exhibited synergistic effects on oleic acid with heating (i.e., at 35 °C), although these effects were not very apparent.

Figure 6 shows that the collecting performance of oleic acid, modified oleic acid I, and modified oleic acid II at 20°C was poorer than at 35 °C. At 20 °C, the apatite recovery was 78.4% with an oleic-acid dosage of 40 mg/dm^3, which is 1.2% lower than the recovery at 35 °C in the presence of 20 mg/dm^3 oleic acid. However, with the addition of synergist OP-10, the apatite recovery increased by > 10% at low dosages (0–20 mg/dm^3), which demonstrated the synergistic effects of OP-10 on oleic acid at 20 °C.

Figure 7 shows that OP-10 exhibited the synergistic effect on oleic acid for apatite flotation at 10 °C from 0–60 mg/dm^3. The apatite recovery was only 61.6% in the presence of 40 mg/dm^3 oleic acid, and increased to 82.6% in the presence of 40 mg/dm^3 modified oleic acid I. To obtain a comparable apatite recovery in the presence of oleic acid, the dosage must be increased to 60 mg/dm^3, which gave an overall increase of 50%. These results confirm the synergistic effects of OP-10 on oleic acid for apatite flotation at low temperatures (i.e., 10 °C) and low dosages (i.e., 0–40 mg/dm^3).

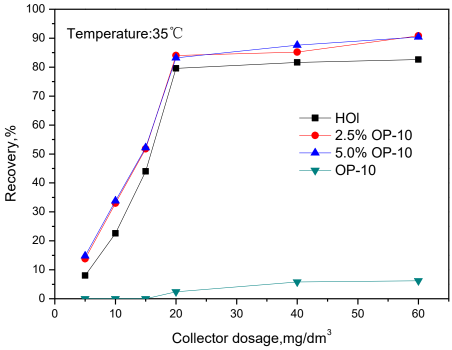

Fig. 5. Effect of collector dosage on apatite recovery at 35 °C

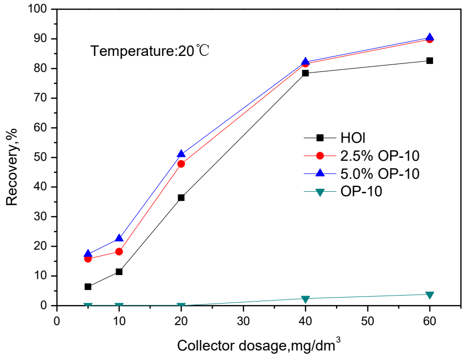

Fig. 6. Effect of collector dosage on apatite recovery at 20 °C

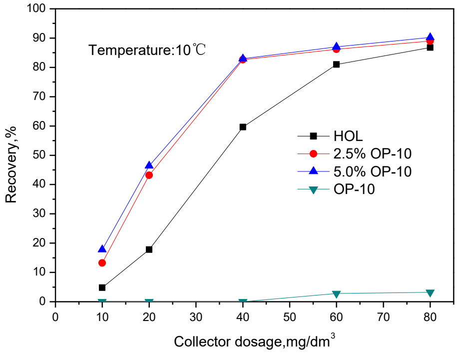

Fig. 7. Effect of collector dosage on apatite recovery at 10 °C

Zeta-potential measurements

Because the surface potential of a mineral is often studied in mineral-flotation studies (Pugh and Stenius, 1985; Pavez et al., 1996; Prakash et al., 1999; Keith, 2016), we investigated the relationship between the zeta potential of the apatite surface and the pH of four solutions (i.e., deionized water, 40 mg/dm^3 OP-10, 40 mg/dm^3 HOL, and 40 mg/dm^3 2.5% OP-10) (Fig. 8). The slurry temperature during the zeta-potential measurements was 10 °C.

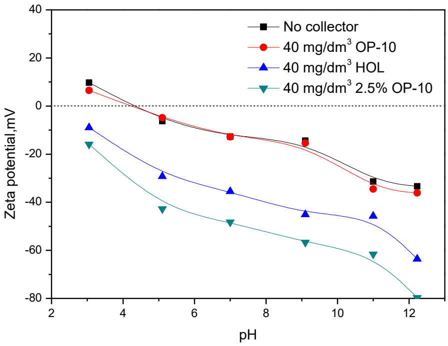

Fig. 8. Effect of pH on zeta potential of apatite

Figure 8 shows that, in deionized water alone (black plot), the apatite surface potential decreased with the pH increase in the solution. Under acidic conditions (pH < 4.3, i.e., with relatively high hydrogen-ion dosages in solution) the apatite surface potential was positive, and hydrogen ions absorbed at the phosphate radical position on the apatite surface to counteract the negative charges. Therefore, positively charged calcium atoms and residual hydrogen ions on the surface resulted in the development of a positive surface potential. Under neutral and alkaline conditions, the hydroxide ions in solution reacted with calcium atoms on the apatite surface to counteract the positive charges. In this case, the negatively charged phosphate ions and redundant hydroxide ions rendered the mineral surface negatively charged. These results indicated that the point-of-zero-charge potential of the apatite was close to pH 4.3, which was consistent with previous studies (Hu and Xu, 2003; Cao et al., 2015).

As reported by Rogan (1994) and Pavez et al. (1996), reagent adsorption on a mineral surface can be divided into two classes, namely physical and chemical absorption. After OP-10 addition, the apatite surface potential remained constant, which indicated that OP-10 did not exhibit chemical absorption on the apatite surface. OP-10 is a polar molecule and the zeta potential of a mineral changes if electrostatic adsorption occurs on the mineral surface. It appears that OP-10 did not exhibit electrostatic adsorption on the apatite surface. In contrast, with either oleic acid or modified oleic acid I addition, the zeta potential decreased, which indicated that oleic acid absorbed on the apatite surface. According to a study on the oleic-acid adsorption mechanism, during apatite flotation in the presence of oleic acid, oxygen atoms of the carboxyl functionality on the reagent formed an ionic bond with a calcium atom of the mineral surface to generate a compound that was similar to calcium carboxylate (Lu et al., 1998). Because a number of positive charges on the mineral surface were counteracted following formation of an ionic bond, the reagent was unable to interact with the phosphate radical of the mineral surface to influence the negative potential. This resulted in the zeta potential of the apatite mineral surface becoming more negative.

As shown in Fig. 8, at an oleic-acid dosage of 40 mg/dm^3 and a 9.6 of pH, the apatite surface potential was −44.5 mV. However, in the presence of modified oleic acid I, the potential decreased to −56.8 mV. This indicates that the combination of a small quantity of synergist OP-10 in oleic acid improved the oleic acid adsorption on the apatite surface significantly and increased the absolute value of the apatite surface potential.

TOC determination

The TOC contents were determined in 1 mg/dm^3 HOL and 1 mg/dm^3 2.5% OP-10 at a range of collector dosage up to 60 mg/dm^3, which gave a 50% increase. At pH 9.6 before and after apatite absorption (Fig. 9), the slurry temperature during TOC determination was 10 °C. Because of the positive correlation between the organic carbon and collector dosage, the content of collector adsorbed on the apatite surface can be calculated, which allows for a subsequent calculation of the ratio of collector absorbed on the apatite surface in 2.5% OP-10 to that absorbed in pure oleic acid, as outlined in Table 5.

As shown in Fig. 9, the collector adsorption on the apatite surface increased with an increase in reagent dosage. In 10 mg/dm^3 oleic acid, the collector adsorption on the apatite surface was 0.24×10^{-1} mg/g, whereas in 10 mg/dm^3 2.5% OP-10, the adsorbance increased to 0.77×10^{-1} mg/g. With an increase in oleic-acid dosage to 40 mg/dm^3, the adsorbance was 11.87×10^{-1} mg/g, whereas in 40 mg/dm^3 2.5% OP-10, this value increased to 15.59×10^{-1} mg/g. With a further increase in the collector dosage, the 2.5% OP-10/HOL ratio became relatively constant despite the increase in adsorbance. This is likely because of the formation of micelles or micelle double layers of ions on the mineral surface after saturation of the initial mineral surface with oleic acid (Wei, 2009).

These results were consistent with those of the low-temperature single-mineral flotation test, because, at low temperatures and low dosages, OP-10 promoted the hydrolysis and dispersion of oleic-acid ions to increase its adsorption on the apatite surface. However, with an increase in oleic-acid dosage, excess oleic-acid ions in solution saturate the mineral surface. With OP-10 addition, as opposed to promoting oleic-acid absorption on the mineral surface and the subsequent formation of additional adsorption structures, it reduced the recovery of apatite. Therefore, at low temperatures and low dosages, OP-10 addition improved the oleic-acid adsorption on the mineral surface, and exhibited a synergistic effect on the flotation performance of oleic acid.

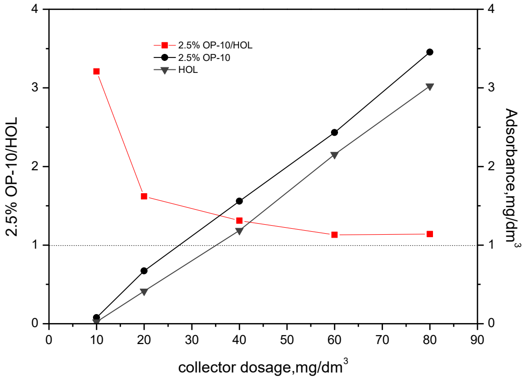

Fig. 9. Relationship between collector adsorbance on apatite surface and collector dosage

Table 5. Collector adsorbance on apatite surface

Collector dosage (mg/dm^3)	Collector adsorption on apatite surface ($\times 10^{-1}$ mg/g)		2.5% OP-10/HOL ratio
	HOL	2.5% OP-10	
10	0.24	0.77	3.21
20	4.14	6.71	1.62
40	11.87	15.59	1.31
60	21.53	24.31	1.13
80	30.25	34.54	1.14

Scale-up flotation test

Scale-up flotation tests were carried out after laboratory and closed-circuit flotation tests. All experiments were carried out at ambient temperature (20–22°C), with the results as outlined in Table 6.

Table 6. Results of scale-up flotation tests

Product	Production rate (%)	P_2O_5 grade (%)			P_2O_5 recovery (%)		
		P_2O_5	MgO	SiO_2	P_2O_5	MgO	SiO_2
Phosphate concentrate	63.70	30.47	0.67	12.70	86.22	13.25	49.91
Tailings of direct flotation	12.48	8.56	1.12	46.15	4.74	4.33	35.53
Tailings of reverse flotation	23.82	8.54	11.14	9.91	9.04	82.41	14.56
Total tailings	36.30	8.55	7.70	22.37	13.78	86.75	50.09
Raw ore	100.00	22.51	3.22	16.21	100.00	100.00	100.00

The results in Table 6 show that collophanite (P_2O_5 grade of 22.51%, MgO grade of 3.22%, and SiO_2 grade of 16.21%) ground to a –0.074 mm particle size (82.03%) with the direct flotation collector EM-C2 and the reverse flotation collector EM-D10 gave an acceptable phosphate concentrate (63.70% production rate), with a P_2O_5 grade of 30.47%, a P_2O_5 recovery of 86.22%, and the MgO content of only 0.67%. This indicates that OP-10 also exhibited good synergistic effects when combined with industrial fatty acids.

Conclusions

A combination of small quantities of synergist OP-10 (2.5%) in oleic acid improved the apatite flotation recovery substantially and increased the absolute value of the apatite surface potential. At low temperature (10 °C) and low dosage, OP-10 improved adsorption of oleic acid on the apatite surface and exhibited synergistic effects on the flotation performance of oleic acid. Results of the scale-up flotation test confirmed that OP-10 exhibited good synergistic effects following its application to industrial fatty acids, and should have good market application prospects.

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References

ABOUZEID, A.Z.M., 2008, *Physical and thermal treatment of phosphate ores – an overview*, Int. J. Miner. Process. 85(4), 59-84.

CAO, Q.B., CHENG, J.H., WEN, S.M., LI, C.X., BAI, S.J., 2015, *A mixed collector system for phosphate flotation*, Miner. Eng. 78, 114-121.

GE, Y.Y., ZHANG, M., ZHANG, Y.L., LI, H.Q., JIANG, Z.S., 2012, *Study on flotation of low-grade collophanite with a new chelating collector YH-2*, Mining and Metallurgical Engineering 32(1), 25-28.

GUIMARAESA, R.C., ARAUJOB, A.C., PERESC, A.E.C., 2005, *Reagents in igneous phosphate ores flotation*, Miner. Eng. 18(2), 199-204.

HERNAINZ, F., CALERO, M., BLAZQUEZ, G., 2004, *Flotation of low-grade phosphate ore*, Adv. Powder Technol. 15 (4), 421-433.

HOUOT, R., 1982, *Beneficiation of phosphatic ores through flotation: Review of industrial applications and potential developments*, Int. J. Miner. Process. 9(4), 353-384.

HU, Y., XU, Z., 2003, *Interactions of amphoteric amino phosphoric acids with calcium-containing minerals and selective flotation*, Int. J. Miner. Process. 72(1-4), 87-94.

HUANG, Q.M., DENG, C.B., XIANG, P., PAN, Z.Q., LUO, H.H., 2010, *Synthesis and application of α-chloro fatty acid monoester of citric acid as a phosphate ore collector*, Mining and Metallurgical Engineering 30(2), 31-34.

KEITH, Q., 2016, *Literature review on the interaction of oleate with non-sulphide minerals using zeta potential*, Miner. Eng. 94, 10-20.

LU, Y., DRELICH, J., MILLER, J.D., 1998, *Oleate adsorption at an apatite surface studied by ex-situ FTIR internal reflection spectroscopy*, J. Colloid Interface Sci. 202 (2), 462-476.

LUO, H.H., RAO, H.H., YANG, J.L., LI, C.X., 2014, *Alkalescent mixed-regulators in collophanite beneficiation*, J. Wuhan Inst. Tech. 36(5), 20-23.

LUO, L.M., 1988, *Emulsification and flotation temperature*, Ind. Miner. Process. 17(3), 20-22.

MILLER, J.D., 2001, *Improved Phosphate Flotation with Nonionic Polymers*, Publication No. 02-113-150, FIPR.

MILLER, J.D., 2002, *A Selective Collector for Phosphate Flotation*, Publication No. 02-142-187, FIPR.

MOUDGIL, B., GUPTA, D., 1989, *Advances in Coal and Mineral Processing Using Flotation*, Engineering Foundation Conference, Palm Coast, Fl., USA, 164-168.

NUNES, A.P.L., PERES, A.E.C., DE ARAUJO, A.C., VALADAO, G.E.S., 2011, *Electrokinetic properties of wavellite and its floatability with cationic and anionic collectors*, J. Colloid Interface Sci. 361 (2), 632-638.

O'CONNOR, C.T., MILLS, P.J.T., 1990, *The effect of temperature on the pulp and froth phases in the flotation of pyrite*, Miner. Eng. 3(6), 615-624.

PAVEZ, O., BRANDAO, P.R.G., PERES, A.E.C., 1996, *Adsorption of oleate and octyl-hydroxamate on to rare-earths minerals*, Miner. Eng. 9(3), 357-366.

PRAKASH, S., DAS, B., MOHANTY, J.K., VENUGOPAL, R., 1999, *The recovery of fine iron minerals from quartz and corundum mixtures using selective magnetic coating*, Int. J. Miner. Process. 57, 87-103.

PRASAD, M.S., 1992, *Reagents in the mineral industry — recent trends and applications*, Miner. Eng. 5, 279-294.

PUGH, R., STENIUS, P., 1985, *Solution chemistry studies and flotation behaviour of apatite, calcite and fluorite minerals with sodium oleate solutions*, Int. J. Miner. Process. 15, 193-218.

RIGGS, W.F., 1989, *Frothers — an operators guide. In: Malhotra, Riggs (Eds.), Chemical Reagents in Mineral Processing Industry*, SME, 113-116.

ROGAN, K.R., 1994, *Adsorption of oleic acid and triolein onto various minerals and surface treated minerals*, Colloid Polym. Sci. 272, 82-98.

SISA, H., CHANDERB, S., 2003, *Reagents used in the flotation of phosphate ores: a critical review*, Miner. Eng. 16(7), 577-585.

SOPHIA, J.S., KEITH, Q., JASON, N.C., 2015, *Effects of Eh and pH on the oleate flotation of iron oxides*, Miner. Eng. 83, 97-104.

USGS: Electronic Communication with USGS Staff, 2007.

WEI, D.Z., *Solid material separation research*, Metallurgical Industry Press, 292-294, 2009 [in Chinese].