Fizykochemiczne Problemy Mineralurgii, 32 (1998), 243–253

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FLOTATION OF LOW GRADE SILICEOUS CALCAREOUS PHOSPHATE ORE

This investigation deals with the concentration of low grade siliceous-calcareous phosphate ore by flotation. The ore consists mainly of friable fragments, collophane, carbonate and hydroxyapatite associated with quartz, calcareous and clayey materials. An attempt of upgrading this phosphate ore, assaying 14.37% P_2O_5, 40.65% CaO, 8.85% MgO, 2.55% R_2O_3, 17.05% SiO_2 and 16.6% CO_2, by flotation was made using an adopted technique of bulk-roughing flotation. A new flotation machine, of 'mechanical type', with previously established optimum design parameters was successfully used. Optimization of the main concerning variables of the flotation process including chemical reagents, modifiers, depressant, collector, pulp density, air flowrate and time, was conducted. Concentration of the phosphate ore was successfully achieved by anionic flotation with fatty acid collector 3.5 kg/ton, 20% oleic acid in kerosene, and depression of siliceous-calcareous gangue with water glass 0.2 kg/ton at low pulp density (14% solids) and an air flow rate of 0.22 $m^3/min/m^2$. A rougher flotation concentrate of high recovery 88.8% and grade 29.12% P_2O_5 was obtained. Cleaning gave rise to phosphoconcentrate of very high grade 32.41% P_2O_5%, and recovery (overall recovery 68.78%), and very low silica content 1.91%, which seems to be a suitable marketable concentrate grade.

INTRODUCTION

Flotation is a process of concentrating finely divided mineral particles in water on the basis of variations of their ability to keep themselves on a phase interface and its usual method is the froth flotation. The flotation process has been investigated based on three groups of variables: the fixed properties of the ore mineral, the physical and chemical effects imposed on them to influence their floatability and the flotation machine characteristics, which realize their potential (Arbiter and Harris, 1962). The complexity of the problem due to the large number of variables and the inconclusive results led some investigators to study some of them separately (Dell, 1964). This work is devoted to the optimisation of chemical and operating variables of the flotation of a low grade siliceous-calcareous phosphate ore, using a specially designed flotation machine whose mechanical parameters are optimized (Salwa, 1984).

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Phosphate rock has many applications such as fertilizers and industrial phosphorus compounds. Phosphate rocks have one common property that belong to the apatitic minerals, which were formed under igneous, metamorphic and sedimentary environments. The phosphate composition is nearly similar to that of fluorapatite and carbonate fluorapatite (francolite) in igneous and sedimentary deposits, respectively (Mc.Clellan et al., 1969). Sedimentary phosphates show a wide diversity in the gangue minerals compositions, e.g. siliceous, carbonaceous and clayey phosphate ores. Recently, phosphate rocks have been classified according to quality and content of harmful ingredients into premium grade, non-premium grade and marginal phosphate. Because of the variable composition of the phosphate ores, a wide range of beneficiation methods are employed to upgrade the phosphate ores to marketable concentrates according to the ore characteristics and the end-use products. These upgrading procedures are usually crushing, grinding, screening, washing, classification, flotation, calcination, magnetic and electric separation and partial acidulation.

Flotation of phosphate minerals is becoming increasingly more important as more half of the world's marketable phosphate is produced by it. Sedimentary phosphate rocks may be consolidated rocks, cemented by silica, silicates, carbonates or Fe and Al oxides, or unconsolidated ores of various sizes and structures. In Central Florida phosphate plant, the coarse fraction is handled by skin flotation after conditioning with anionic collector, tall oil (1–2 kg/t) at 70% solids, pH ~9 and the finer one by froth flotation. The rougher concentrate is de-oiled and subjected to cationic froth flotation to float most of the remaining silica (Lawver et al., 1978). In Upper Pensula of Michigan phosphate, the process required fine grinding 45 μm and direct flotation of phosphate using fatty acid–fuel oil–petroleum sulphonate emulsion and produced a concentrate of 30% P_2O_5 and 72% recovery after 3 cleaning steps (Rule, 1979). Flotation of siliceous Indian phosphates without desliming was conducted using sodium silicate, $K_4Fe(CN)_6$, and fatty acid collectors at pH ~8.5 producing a concentrate of very high grade and recovery (Anon, 1976).

Beneficiation of low grade-calcareous phosphates has been a challenging job associated with considrable significance. Most of the elements of carbonaceous sedimentary phosphates react with collectors, particularly fatty acids and their salts, sometimes, at very definite pH ranges, the floatabilities are different, thus allowing selective flotation. International Minerals and Chemical Corporation has developed a process to beneficiate low grade sedimentary deposits, high in shale and carbonate, using anionic flotation followed by de-oiling and amine silica flotation (Lovell et al., 1976). Some investigators (Awasthi et al., 1977) studied direct flotation of phosphate with depression of carbonate gangue. Others studied reverse flotation of carbonaceous gangue with the depression of phosphates by phosphoric acid, fluosilicic acid (Rule et al., 1975) or by aluminium sulphate–tartarate complex (Smani et al., 1975). A well known industrial application of this flotation technology for sedimentary phosphates is that of Karatou (USSR). Carbonate flotation using C_{10}–C_{16} fatty acid collectors and phosphoric acid as a selective depressant for apatite at pH ~4.8–5 is employed, followed by direct flotation of phosphate from siliceous gangue minerals by tall oil, kerosine and water glass at pH ~8 (Ratobyliskaya, 1975)

EXPERIMENTAL PROCEDURE

Table 1. Operating conditions for the flotation of phosphate ore

Variables	Test No.									
	1	2	3	4	5	6	7	8	9	Optimum
Cell type	Fagergreen	→	→	→	new cell	→	Fagergreen	new cell	→	new cell
Conditioning										
Feed size, mm	–0.25 + 0.038	→	→	→	→	→	→	→	→	–0.25 + 0.038
Pulp density,%	50	→	→	→	→	→	→	→	→	50
Impeller speed r.p.m.	1500	→	→	→	→	→	→	→	→	1500
Time, min	7	6	6	7	9	9	8	10	9	9
Modifier, pH	n	n	c	9	→	→	→	→	→	9
Depressant,kg/t	0.4	0.4	0.4	0.4	c	0.22	→	→	→	0.22
Collector, kg/t	changed in steps 1.1 + 1.1			1.1	3.5	c	1.1 + 1.1	→	→	3.5
Collector /Kerosene, %	14	14	6	c	20	20	6	20	→	20
Frother, kg/t	–	–	–	–	0.25	→	–	0.25	→	0.25
Flotation										
Pulp density,%	10	10	10	10	14	→	10	14	c	14
Air flowrate l/min	nat.	nat.	nat.	nat.	1.62	→	nat.	1.62	→	1.62
Impeller speed, r.p.m.	1000	1000	1500	1500	1000	→	1500	1000	→	1500
Time, min	3	succ.	5.25	3	5	→	5.25	6.5	5	

* n – normal, ** c – changed.

The phosphate ore used in this investigation is from Gebel Hamadat, Kossier Area (bed C), Red Sea, Egypt. The phosphate deposits in this area occur in 3 layers (A, B, C), which vary in thickness and P_2O_5 content. The high quality ore is produced by selective mining, leaving the low grade ore, bed C, “Terso Banko” for its high content of siliceous and calcereous matters.The flotation tests were preferably conducted on this low grade phosphate ore to achieve more reasonable variations in the metallurgical performance due to variations in the levels of the optimisation parameters. Variable factors affecting the flotation process, liberation size, slimes, qualities and quantities of modifier, depressant, collector and frother as well as mode of addition, conditioning and flotation time, etc, were studied using a specially designed flotation machine. Optimum levels of these variable parameters established from this investigation were consequently used in the optimisation of the main design parameters of this flotation cell (Salwa, 1984).

RESULTS AND DISCUSSION

General characteristics of the phosphate ore sample

The phosphate ore sample consists mainly of collophane and bone fragments together with considerable amounts of calcareous minerals, detrital and silty quartz and some clay material. The phosphate grains vary from coarse to very fine and the phosphate fragments vary from friable to very hard, usually cemented with dolomite. The major constituents of the flotation concentrate are hydroxyapatite and francolite whereas those of the tailing are dolomite, and quartz (Salwa, 1984).

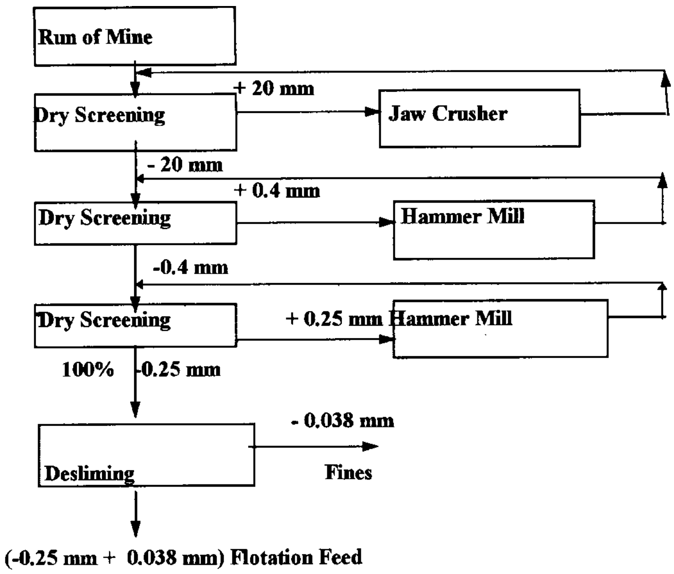

Fig. 1. Flowsheet for preparation of the flotation feed

Preparation of the flotation feed (–0.25 + 0.035 mm) was conducted by crushing, grinding and screening of the phosphate ore in closed-circuit to avoid overgrinding, followed by desliming according to the flowsheet (Fig.1). Complete chemical analysis of the phosphate ore sample, as well as the screen and chemical analysis of the flotation feed are given in Table 2, which shows that the ore is relatively of low phosphorus, and high siliceous and calcareous matters. Moreover, the MgO content is considerably high and most of it is found in the ore as carbonate.

Table 2. Chemical analysis of the phosphate ore and the flotation feed (–0.25 +0.038 mm)

Component	Wt. %	P_2O_5 %	Insol. %	CaO %	MgO %	CO_2 %	Fe_2O_3 %
Phosphate ore –0.25 mm	(	14.37	17.05	40.65	8.85	16.60	2.00
(0.25 + 0.149 mm	20.73	16.51	19.26	33.98	2.25	16.56	1.70
(0.149 + 0.074 mm	15.81	15.47	16.10	29.97	6.15	18.85	1.77
(0.074 + 0.038 mm	43.29	13.06	18.20	34.59	8.19	22.26	1.57
(0.038 mm	20.17	10.09	26.77	29.06	8.27	19.04	2.78
Total	100	13.56	19.82	32.62	6.65	19.97	1.87
Flotation Feed	79.83	14.44	18.06	33.52	6.24	20.10	1.64

Operating conditions of the flotation tests

An adopted technique of bulk-roughing flotation in one step was usually conducted in preference to the various stages of flotation for reasonable assessment in flotation performance due to variations in the levels of its parameters. The experimental conditions of the operating variables of the flotation tests are given in Table 1, which indicates for each test, the levels of the variables studied, those which were kept constant and the optimum level found.

Preliminary flotation tests (Test 1)

Table 3. Results of preliminary flotation tests

Collector kg/ton	Product	Wt. %	P_2O_5 %	Recovery %	Insol. %
	C	49.51	18.32	77.43	7.52
0.49	T	50.49	5.24	22.57	29.16
	Total	100.00	11.72	100.00	18.45
	C	72.91	16.61	92.28	8.43
4.98	T	27.09	3.74	7.72	46.64
	Total	100.00	13.12	100.00	18.78
Cumulative	Step-wise addition of collector				
1.00	C1	13.56	13.26	13.53	12.46
1.74	C2	26.2	15.51	30.57	10.27
3.24	C3	49.17	18.66	69.07	8.16
4.73	C4	62.87	18.54	87.71	8.49
6.23	C5	69.79	17.95	94.29	9.16
	T	30.21	2.51	5.71	44.80

	Total	100.00	13.25	100.00	19.93

Preliminary flotation tests were conducted in batches of 500 g each, using the Fagergreen cell and the results indicate the floatability of phosphate ore (Table 3).

Effect of step-wise addition of collector (Test 2)

Comparing results of step-wise addition of the collector with those of one step-addition (Table 3), it will be seen that the latter case is preferable since it allows more chance for conditioning and dispersing the total amount of collector at high pulp density.

Effect of varying the hydrogen ion concentration, pH (Test 3)

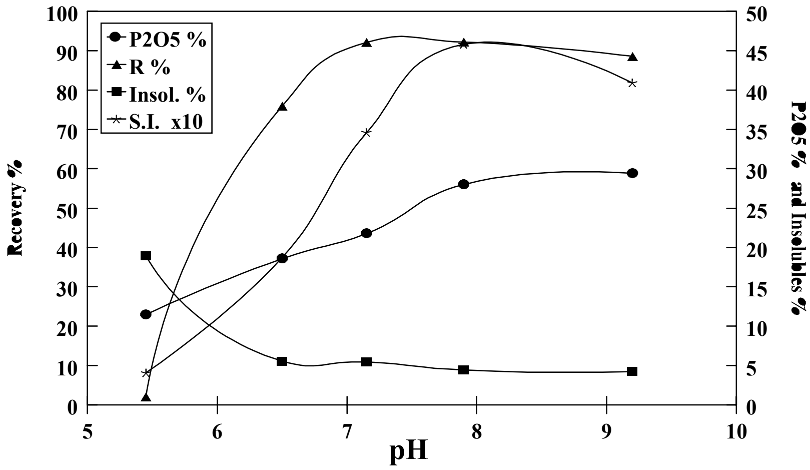

Fig. 2. Effect of varying pH on concentrate

The effect of varying the hydrogen ion concentration in the anionic flotation of the phosphate ore was investigated by conditioning the pulp at 50% solids with different additions of HCl or NaOH before the addition of depressant and collector and the flotation results are given in Fig. 2. It will be seen that both the grade and the recovery of the concentrate increase largely on increasing the pH up to about 7, above which the grade increases and the recovery remains substantially constant. The improvement in both recovery and grade seems to be due to favourable ionization or dissociation of the oleic acid collector, resulting in increasing the amount of collected phosphate particles and improvement in the selectivity in the alkaline side. Consequently, the flotation of this phosphate ore is successful in alkaline pulp at pH ~8–9 (1.25 kg NaOH/ton) giving a concentrate of high grade (28 to 30% P_2O_5) and recovery 90 to 89%. Most investigators found that optimum results were obtained when the anionic flotation process of phosphate was carried out in alkaline pulp, at pH from ~9 to 9.5

(Lovell et al., 1976) and pHfrom ~9 to 11 (Smani et al., 1975). Small differences in the optimum pH value may be due to differences in the types of collectors and ores.

Effect of kerosine as a dispersing agent for the collector (Test 4)

The flotation results in which the volume per cent of oleic acid in kerosine was varied, are shown in Table 4. The concentrate of high grade and recovery was achieved when 20% oleic acid to kerosine was added. The advantage of kerosine as a hydrocarbon extender and dispersing agent breaks oleic acid into minute droplets which favour more coating of the phosphate particles containing more fracture, which agrees with the previous work (Orphy et al., 1968).

Table 4. Effect of kerosene as a dispersing agent for the oleic acid

Oleic acid %	Product	Wt. %	P_2O_5 %	Recovery %	Insol. %
10	C	22.59	24.53	45.01	4.36
	T	77.41	8.75	54.99	24.22
	Total	100.00	12.31	100.00	19.73
15	C	25.60	26.75	49.21	5.88
	T	74.40	9.50	50.79	25.20
	Total	100.00	13.92	100.00	20.25
20	C	42.41	24.49	75.34	4.94
	T	57.59	5.90	24.66	32.12
	Total	100.00	13.78	100.00	20.62

Effect of varying the quantity of depressant (Test 5)

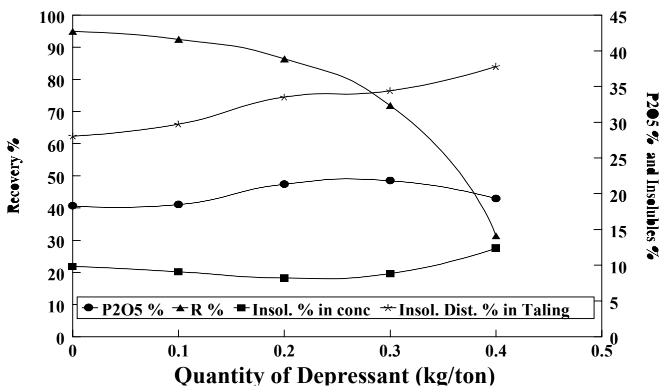

Fig. 3. Effect of varying the quantity of depressant on concentrate

The results of the flotation tests for the gangue minerals in which the quantity of depressing agent (sodium silicate) was varied, are given in Fig. 3. On increasing the quantity of the depressant, the concentrate grade (P_2O_5 %) increases and its recovery decreases slightly up to a value of 0.2 kg/ton, above which the grade remains nearly constant and the recovery decreases largely. The improvement in the flotation selectivity is due to the depression of the floated gangue minerals with sodium silicate as shown by the increase in the distribution percent of the insolubles in the tailing. Some investigators (Rambabu et al., 1976) found that attrition-scrubbing with sodium silicate is essential for affecting proper conditioning of phosphate particles and to depress quartz and shales.

Effect of varying the quantity of collector (Test 6)

The results of the flotation tests of varying the quantity of the collector (20% oleic acid in kerosine) are illustrated in Fig. 4. Increasing the collector dosage increases largely the recovery and slightly the grade percents and decreases the insolubles percent in the concentrate up to a value of about 3.5 kg/t, above which the recovery becomes substantially constant, while the grade decreases slightly. The increase in both grade and recovery of the concentrate and the decrease in its insoluble content on increasing collector dosage up to 3.5 kg/t could be attributed to the increase in the amount of coated phosphate particles i.e. more selectivity. While, the decrease in the concentrate grade beyond this optimum dosage may be due to crowding of more coated particles resulting in less selectivity. Some investigators (Güven, 1973) found that the highest recovery was obtained at the dosage of 4 kg/t of sodium oleate and others (Narayanna, 1946) found that the consumption of oleic acid for flotation was 3.5 kg/t, which seems to be in agreement with this work.

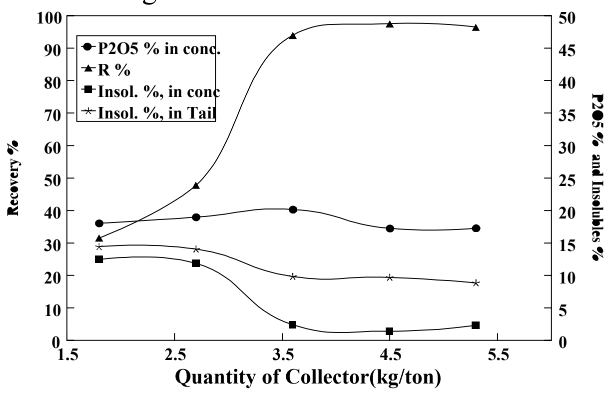

Fig. 4. Effect of varying quantity of collector on concentrate

Effect of cleaning (Test 7)

In the cleaning tests, the pulp was conditioned with two successive additions of collector followed by removing two successive froth products and tailing was remained in the cell. The two roughing products were refloated without any collector addition giving clean froth concentrate and the middling remained in the cell. The results of the cleaning process (Table 5) show that a clean phosphoconcentrate of very high grade 31 to 32% P_2O_5, and recovery 80 to 85% was obtained. The flotation process of two successive roughing steps followed by one cleaning step is similar to the Release Analysis Flotation Method (Dell, 1961). Lamont et al. (1971) found that multiple-cleaning of the rougher phosphate concentrate was required to produce high grade concentrate.

Table 5. Effect of cleaning the phosphate concentrate

<table>
<tr><td>pH</td><td colspan="2">Product</td><td>Wt.%</td><td>$P_2O_{5\%}$</td><td>Recovery%</td><td>Insol.%</td><td>Insol. Dist.%</td></tr>
<tr><td rowspan="5">7.9</td><td colspan="2">Rougher conc.</td><td>48.90</td><td>28.02</td><td>92.19</td><td>4.43</td><td>12.03</td></tr>
<tr><td colspan="2">Clean conc.</td><td>40.97</td><td>31.19</td><td>85.97</td><td>2.58</td><td>5.87</td></tr>
<tr><td colspan="2">Middling</td><td>7.93</td><td>11.66</td><td>6.22</td><td>3.98</td><td>6.16</td></tr>
<tr><td colspan="2">Tailing</td><td>51.10</td><td>2.27</td><td>7.81</td><td>30.99</td><td>87.97</td></tr>
<tr><td colspan="2">Total</td><td>100</td><td>14.86</td><td>100</td><td>18.01</td><td>100</td></tr>
<tr><td rowspan="5">9.2</td><td colspan="2">Rougher conc.</td><td>45.17</td><td>29.43</td><td>88.54</td><td>4.24</td><td>10.31</td></tr>
<tr><td colspan="2">Clean conc.</td><td>38.22</td><td>31.51</td><td>80.22</td><td>2.88</td><td>5.92</td></tr>
<tr><td colspan="2">Middling</td><td>6.95</td><td>17.99</td><td>8.32</td><td>11.75</td><td>4.39</td></tr>
<tr><td colspan="2">Tailing</td><td>54.83</td><td>3.15</td><td>11.46</td><td>30.40</td><td>89.69</td></tr>
<tr><td colspan="2">Total</td><td>100</td><td>15.02</td><td>100</td><td>18.59</td><td>100</td></tr>
<tr><td>Product</td><td>P_2O_5%</td><td>SiO_2%</td><td>Fe_2O_3%</td><td>Al_2O_3%</td><td>I.L.%</td><td>CaO%</td><td>MgO%</td></tr>
<tr><td>Clean conc.</td><td>31.51</td><td>1.91</td><td>1.24</td><td>0.16</td><td>3.40</td><td>59.72 (24.13)</td><td>2.05 (1.46)</td></tr>
<tr><td>Tailing</td><td>3.15</td><td>29.08</td><td>2.43</td><td>0.83</td><td>5.70</td><td>37.07 (22.78)</td><td>11.73 (7.79)</td></tr>
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() – leached.

Effect of addition of starch (Test 8)

Table 6. Effect of addition of starch

Starch, kgl/t	Product	Wt. %	P_2O_5 %	Recovery %	Insol. %	Insol.dist. %	CO_2 %
0.2	C	36.12	23.35	59.29	9.69	19.31	
Roughing	M	16.63	15.78	18.45	9.28	8.51	
	T	47.25	6.70	22.26	27.69	72.18	
	Total	100.00	14.22	100.00	18.13	100.00	
0.2	C	56.29	22.75	93.02	5.72	16.80	18.51

Cleaning	M	11.54	3.27	2.35	13.17	7.93	35.39
	T	32.17	2.31	4.63	44.86	75.27	18.44
	Total	100.00	13.77	100.00	19.17	100.00	20.44

The effect of starch in the anionic flotation of phosphate by oleic acid and depressing the calcarceous-silicous gangue by water glass was investigated by changing its mode of addition and the results are given in Table 6. It appears that the addition of starch in the cleaning step is more preferable than its addition in roughing as it results in a clean concentrate of high recovery (93.02%) and grade (22.75% P_2O_5) and rejection of most of the carbonate in the middling.

Effect of varying the pulp density (Test 9)

The results of the flotation tests when varying the pulp density (Fig. 5), show that on increasing the pulp density, the grade of the concentrate decreases and the recovery increases slightly initially, then remains substantially constant, which is due to the increase in the weight percent of the floated material. This seems to be due to increasing the levitating effect and reaction rates which were enhanced by increasing the reagent concentration in the solution i.e. more crowding in the pulp. Consequently, better selectivity is achieved in less thicker pulp (about 14% solids) which is recommended for one roughing flotation step in preference to higher pulp density.

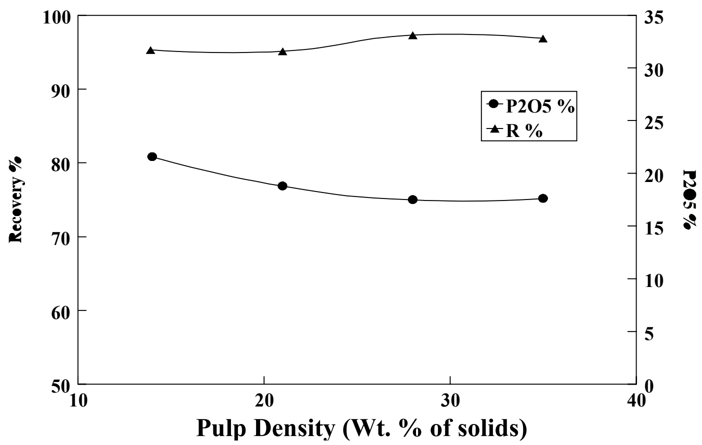

Fig. 5. Effect of varying pulp density on concentration

CONCLUSIONS

This low grade siliceous calcaerous phosphate ore under investigation consists of collophane, bone fragments, hydro-oxyapatite, quartz, calcareous and clayey materials. Preparation of the flotation feed in closed circuit is advantageous to minimize slimes and fine gangue minerals. Concentration of this phosphate ore by flotation was successfully achieved at optimum levels of the main variables: pH 8–9, 1.25 kg/t Na OH, depressant sodium silicate 0.2 kg/t, collector oleic acid in kerosine (20%) 3.5 kg /t, pulp density 14% solids, air flow rate 0.22 $m^3/min/m^2$. Rougher phosphoconcentrate of 29.12% P_2O_5 and 88.9% recovery as well as clean phosphoconcentrate of 32.41% P_2O_5, and 68.78% overall recovery were obtained.

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Mostafa S.I., Sadda M.Y., Boulis S.N., Hawash S.I. Flotacja ubogich krzemianowo-węglanowych rud fosforytowych. *Fizykochemiczne Problemy Mineralurgii*, 32, 243–253 (w jęz. angielskim)

Badana ruda zawierała kolofan, węglany i hydroksyapatyt związane z kwarcem, węglanami i materiałem gliniastym. Flotacji poddano rudę zawierającą 14.37% P_2O_5, 40.65% CaO, 8.85% MgO, 2.55% R_2O_3, 17.05% SiO_2 i 16.6% CO_2. Flotację przeprowadzono w nowego typu maszynie flotacyjnej stosując wcześniej określone optymalne parametry jej pracy. Przeprowadzono optymalizację głównych zmiennych procesu flotacji tj. stężenia kolektora, depresora, modyfikatorów, gęstości pulpy, przepływ powietrza i czas flotacji. Osiągnięto zadawalające wzbogacenie rudy fosforytowej stosując flotację anionowymi kwasami tłuszczowymi przy stężeniu 3.5 kg/Mg rudy i depresję krzemianowo-węglanowego składnika płonnego za pomocą szkła wodnego w ilości 0.2 kg/Mg przy niskiej zawartości ciał stałych (14%) w pulpie oraz przy przepływie powietrza wynoszącym 0.22$m^3/min/m^2$. Uzyskany we flotacji

głównej koncentrat zawierał 29.2% P_2O_5 przy uzysku 88.8% tego składnika. Czyszczenie tego koncentratu pozwoliło uzyskać bogaty końcowy koncentrat fosforytowy zawierający 32.4% P_2O_5 przy 68.78% całkowitym uzysku i przy niskiej zawartości krzemionki wynoszącej 1.91%. Wydaje się więc, że uzyskano koncentrat spełniający wymagania koncentratów handlowych.