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Prospects for Complex Use of Phosphate Ores Mineral Resources

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Abstract: The phosphate ores with siliceous and carbonated gangue are characterized by an unstable chemical composition and a high content of insoluble deposits. The aim of this study elaboration the working out of a separation technological diagram that would allow obtaining conditioned products from rough phosphate ore. The process used is flotation. The principal minerals which are included in the mineralogical composition are the phosphate, the dolomite, the calcite as well as the quartz and are used in the chemical industry for obtaining finished products.

Key words: Adsorption, fatty acids, amines, flotation, phosphate rock

INTRODUCTION

The development of the diagram of separation by flotation is carried out on the basis of the study of pure minerals flotability under various environment conditions in aqueous phase and with different concentrations of surfactants. This diagram relies also on the study of the adsorption of these surfactants on the minerals surface using FTIR spectroscopy, visible UV spectrophotometry and other physicochemical methods for the evaluation of the activity of mineral surfaces in flotation.

MATERIALS AND METHODS

The surfactants and minerals used: The surfactants used are the fatty acids fractions C_{10}-C_{18} synthesized from the paraffin oil by catalytic oxidation with the potassium permanganate during 24 h. The fatty acids are used in emulsion form. The cationic surfactant amines bases contain 50% of dodecylamine, 19% tetradecylamine, 14% hexadecylamine and some other fractions in small proportions.

The minerals used are the concentrated phosphate, the calcite, the dolomite, and the quartz; these minerals are selected by hand and finely crushed with less 160 μm and more 1μm.

Tests of flotation: Flotation is carried out on laboratory machine equipped with interchangeable plexiglas cells of volumes 100 and 300 mL. The 100 mL cell is used for the flotation of pure minerals whose test specimen is 2 g. The 300 mL cell is used for the flotation of the rough ore and the test sample is of 25 g.

Spectroscopic methods: The FTIR spectroscopy methods are used for the characterization of minerals and surfactants (collector) used, and also for the qualitative study of the adsorption forms of the latter on surfaces of studied minerals. The quantitative determination of adsorption is performed by visible UV spectrophotometry (The Ftir a Jasco 460 Plus spectrometer and Unisys spectrophotometer). Quantitative determination of the adsorption of the fatty acids on minerals surfaces in realized by the chloroform extraction of the blue complex, then by the measurement of the concentration on spectrophotometer (Rodier, 1996). The quantitative determination of the amines adsorption is based on the method of Silverstein (1963) or by using methyl orange. We obtain a yellow complex of amines which is extracted by chloroform and the concentration will be determined by spectrophotometer. The glassware used for the amines have to be in polyethylene. The study of adsorption is carried out by contact of the sample finely crushed with the surfactant used under the beforehand worked-out conditions of flotation while performing the study of the mono-mineral fractions flotation.

Evaluation of the activity of mineral surfaces in flotation: The activity of minerals surfaces in flotation, according to their solubilities and of the ionic composition of water, is

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evaluated by the study of the electric characteristic of these surfaces by the method based on the elect osmosis. This method is based on the velocity measurement of transfer of the liquid under the effect of the potential differences applied.

RESULTS AND DISCUSSION

Characterization of minerals and surfactant used: The infra-red concentrated phosphate spectrum (Fig. 1) has bands in the interval 1100 -950 cm^{-1}, characterizing the deformed oscillations P-O of bonds $PO4^{3-}$; bands of average intensity in the interval 1440-1420 cm^{-1} proving the existence of magnesium compounds $MgCO_3$, Mg $(OH)_2$. $3H_2O$; bands of low intensity in the interval 858-793 cm^{-1} and 644 cm^{-1} characterizing 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 unimportant intensity characterizing the oscillations P-O of $PO4^{3-}$bonds.

The carbonates are characterized by a large absorption band in infrareds in the interval 1400-1560 cm^{-1}. In the interval 670-730 cm^{-1}, rhomboedric and hexagonal carbonates give intensive narrow absorption bands which correspond to 713 cm^{-1} band in the Fig. 2a and 3a spectrum (Plousnina, 1975).

The dolomite spectrum (Fig. 3) presents peaks in the interval 1500-700 cm^{-1} characterizing the carbonates, a large peak at 1400 cm^{-1} for hexagonal and rhomboedric carbonates and two narrow peaks at 880 and 728 cm^{-1} (Zinouk, 1983).

The infrared pure quartz spectrum (Fig. 4) is characterized by an intensive large band between 1250 and 800 cm^{-1} and two narrow peaks with 880 and 728 cm^{-1} characterizing the asymmetrical oscillations O-Si-O (Plousnina, 1975).

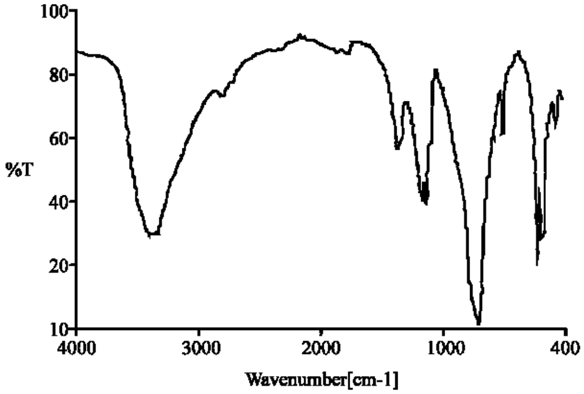

Fig. 1: Infrared phosphate spectrum

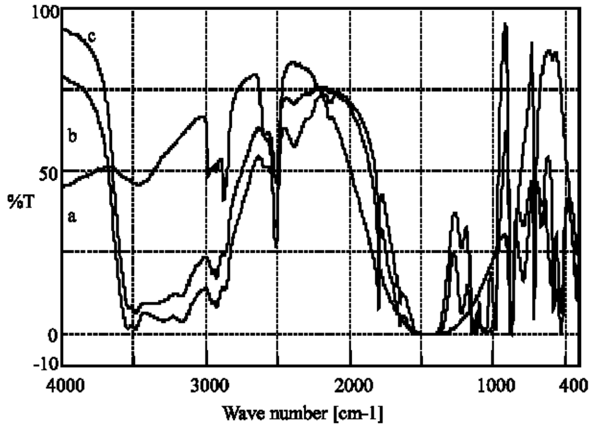

Fig. 2: Infrared spectrum of pure calcite (a), calcite treated by the fatty acids (b), calcite treated by the fatty acids with washings (c)

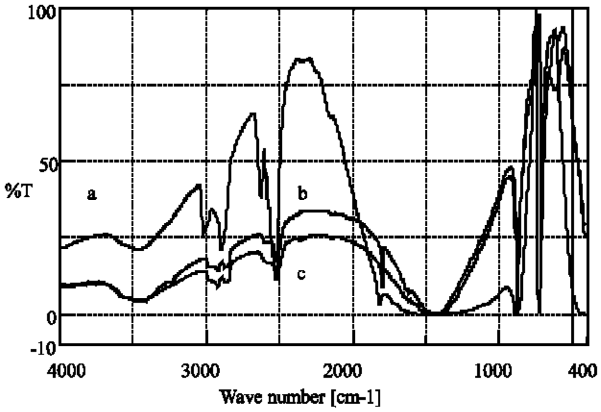

Fig. 3: Infrared spectrum of pure dolomite (a), dolomite treated by the fatty acids (b), dolomite treated by the fatty acids with washings (c)

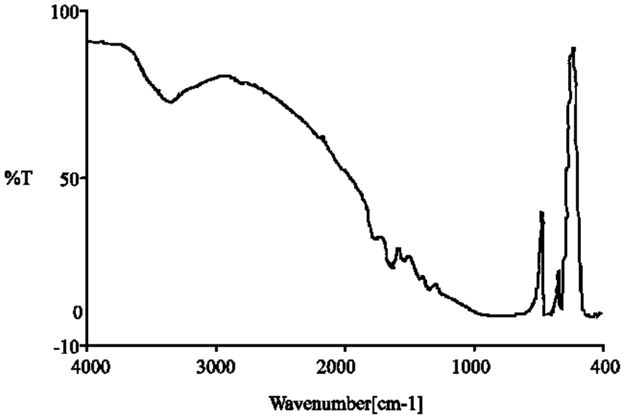

Fig.4 : Infrarouge pure quartz spectrum

Adsorption of the fatty acids: The study of the adsorption of the fatty acids is conducted out in the case of pure minerals flotability. The adsorption of the fatty acids on calcite, dolomite, phosphate and quartz in slightly acid environment pH = 4,8-5,2 created by the phosphoric acid is given with a concentration of these acids equal to 300 mg l^{-1}. The qualitative study of the adsorption of the latter on surfaces of these minerals needed the preparation of a standard solution with a concentration of mg l^{-1}. The analysis of FTIR spectra of calcite (Fig. 3) treated by the fatty acids fractions C_{10}-C_{18} showed absorption bands of group C = O to 1700 cm^{-1} characterizing the molecular form, and a 1650 cm^{-1} band corresponding to the asymmetrical deformation of the carboxylate group proving the existence of the ionic shape of these acids, and that is confirmed by the analysis of spectra FTIR of calcite treated without washing and treated calcite followed by two distilled hot water washings. On the spectrum of the calcite treated and followed by two washings, the 1700 cm^{-1} band disappears gradually, which suggets that the adsorption of the fatty acids fractions C_{10}-C_{18} is favored by the combined action of the two forms of adsorption (Vijaya, 2002). The analysis of FTIR spectra of dolomite treated by the fatty acids fractions C_{10}-C_{18} depicted the existence of a 1660 cm^{-1} absorption band characterizing group C = O of the molecular shape of fatty acids RCOOH (Bogdanov and Maximov, 1990). The examination of the spectrum of the dolomite treated under the same conditions followed by two washings with distilled hot water distilled raised disappearance of the 1660 cm^{-1} absorption band (Fig. 4), which imply that the adsorption of the fatty acids fractions C_{10}-C_{16} on the dolomite surface is furthered by the action of the molecular form (Ratobylskaya and Boyka, 1977; Moudjil, 1992; Snow and Zhang, 2001). The molecular form only, does not allow a total flotation of dolomite Which must be reached instantaneously in a very short time. For calcite, flotation can be total by the combined action of the two forms of adsorption; ionic and molecular. The quantitative study of the adsorption of the fatty acids on calcite and dolomite under the same conditions confirms the results of the qualitative analysis, where one notes a definitely higher adsorption on calcite than on dolomite. On the other hand the adsorption of these acids on quartz and phosphate is practically unimportant (Fig. 5).

The adsorption of the fatty acids on calcite and phosphate is in favour of the flotation of carbonated minerals and that is confirmed by the study of the flotability of pure minerals dolomite and phosphate (Fig. 6). The dolomite flotability of calcite and dolomite is definitely higher than that of phosphate in slightly acid environment created by the phosphoric acid. Thus when pH≤ 6, there is a dissolution of phosphate with transfer of the cations Ca^{2+} in the liquid phase, which accelerate the hydration of the phosphate surface and decreases the adsorption of the collector at the time of the dissolution of dolomite. Then a transfer of CO_3^{2-} occurs in the liquid phase which contributes to the appearance of new active centres of adsorption, and increases adsorption.

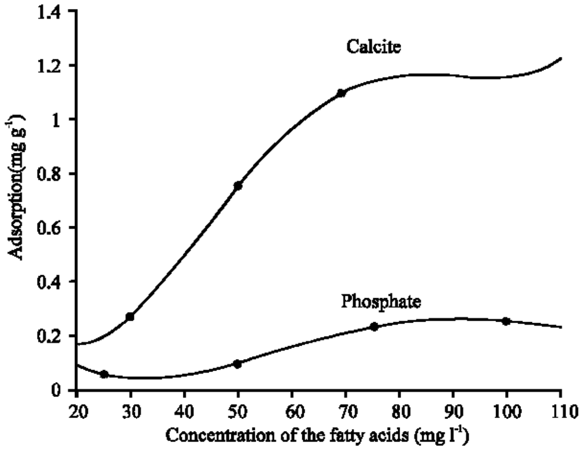

Fig. 5: Variation of the adsorption of the fatty acids according to the concentration

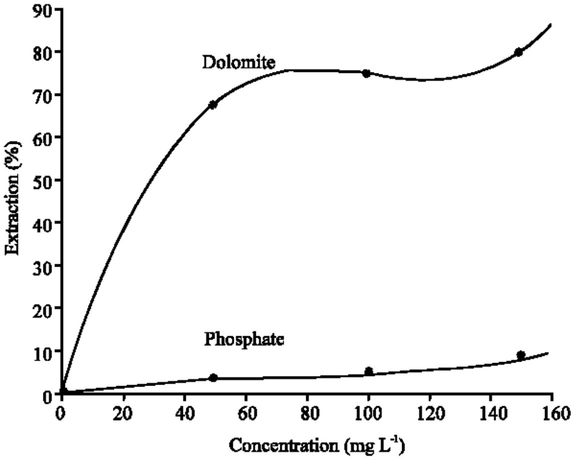

Fig. 6: Flotability of pure minerals according to the concentration of fatty acids at pH 4,8-5,2

Adsorption of the amines: The adsorption of the amines is carried out under the conditions of flotability of quartz and phosphate in slightly basic environment pH = 7, 8-8, 5 created by CaO. The adsorption of the amines on quartz is purely physical: It is due to bonds detected on the infrared spectra. There is a doublet of low intensity in the interval 2350-2332 cm^{-1} characterizing the valent oscillations valences group NH+ and two peaks of low intensity at 3477 and 3392 cm^{-1} characterizing the NH groups oscillations and the intermolecular hydrogen bonds of OH and NH^+ groups, which proves the fixation of the amines on the quartz surface. Practically, the quartz spectrum treated by the amines followed by two distilled hot water washings is identical to the pure quartz spectrum which confirms the low solidity of fixation. Quartz in neutral and slightly basic environments has a negative charge, but with the increase in acidity, the Zeta-potential of quartz decreases up to the point of null charge to pH 4 and zeta-potential becomes positive. Quartz zeta-potential reaches a maximum-18 mv with pH 7, 8-8, 5, an environment favourable to the interaction of the amines with quartz (Bouhenguel, 1991). Measurements of zeta-potential showed that the increase in the concentration of the amines causes a reduction in the negative potential of mineral surfaces of quartz and phosphate, but the variation is apparent from 10 to 30 mg L^{-1} concentration favourable to a maximum degree of flotability of quartz (Fig. 7 and 8). For higher concentrations, there is a reduction in the flotability of phosphate that can be attributed to the appearance of a micelles deposit (Kunio and Minoru, 1997) on the quartz surface.

The results of flotation of the mineral mono fractions allowed the development of a diagram of separation for a siliceous phosphate ore and carbonated gangue considering at first stage the separation of carbonates by addition of the fatty acid solutions in the emulsion forms in acid environment pH 4,8-5,2, and at the second stage the quartz separation by addition of solutions of amines in slightly basic environment pH7, 8-8, 5 (Bouhenguel *et al.*, 1991). At the bottom of the flotation cell, the phosphate deposits are recovered as concentrated phosphate. The results displayed in Table1 show that one can obtain a phosphate concentrate with a high content of P_2O_5 up to 32-33% and an unimportant content of MgO of about 0,3-1%. The carbonates and quartz can be used for obtaining finished products: Pure quartz having good optical properties and magnesia from carbonates.

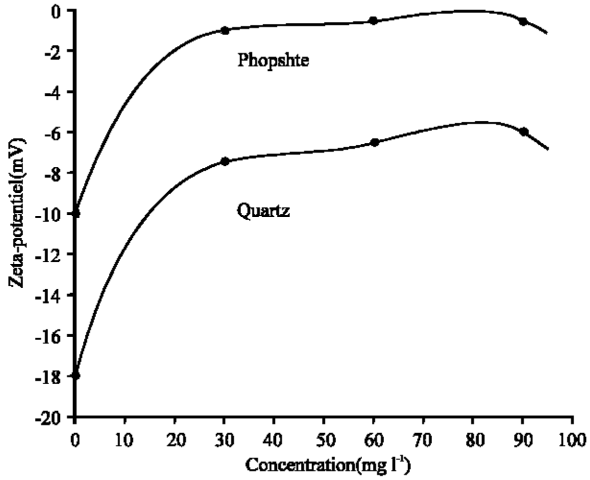

Fig. 7: Variation of Zeta-potential according to concentration of amines

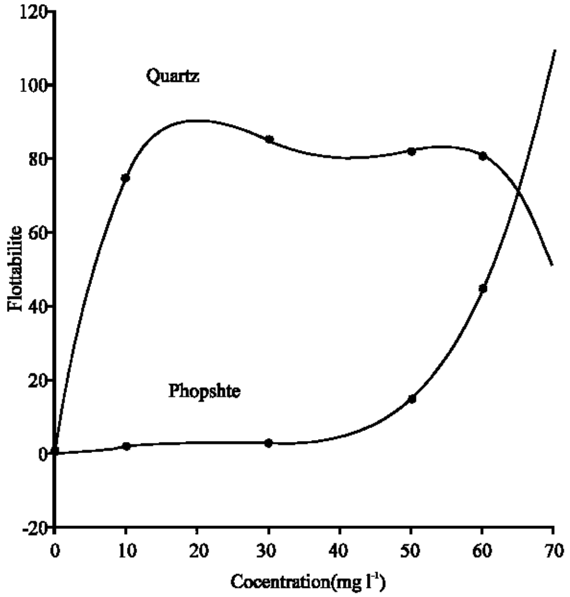

Fig. 8: Quartz and phosphate flotability according to concentration of amines at pH = 7.8-8.5 created by CaO

Table 1: Results of flotation of a phosphate ore with siliceous and carbonated

		Content (%)			Extraction degree (%)		
Products	Products in (%)	P_2O_5	MgO	Insoluble deposits	P_2O_5	MgO	Insoluble deposits
Phosphate	62.043	32.66	0.30	4.50	79.21	7.04	26.31
Carbonates	25.25	12.44	9.30	7.50	12.46	89.36	18.07
Quartz	12.32	16.23	0.80	49.50	7.63	3.6	55.62

CONCLUSION

The study of the flotation collectors adsorption of the collectors proposed under beforehand-established conditions allowed the development of a diagram of separation in closed loop and obtaining conditioned products of good quality. This diagram also allows the recycling and the saving reduction of solid wastes mass of the mineral industry of phosphates. The use of the two stages of successive flotation's by addition of anion collectors for the separation of carbonates and of cation collectors based on amines for the quartz separation, makes it possible to reach a content of P_2O_5 in the phosphate concentrates up to 32-33% and MgO of about 0,3-1 %.

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