Selective Flotation of Barite and Associated Minerals: A Comparative Study

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Abstract

In the present socio-economical difficult context and with the oil prices fall, Algeria aims to develop its economy. For this purpose, it has to research, work and valorize not only its hydrocarbons resources, but also mineral ones, among which barite and fluorite, two industrial minerals of great importance.

Because Algeria is a producer of gas and oil and a member of the OPEC, it needs important quantities of barite. This mineral plays a leading role in the oil industry, where it's a major ingredient of the drilling muds. As for fluorite, it is essentially used as flux in metallurgy, especially as the country has a huge iron deposit in Gara Djebilet, with a potential of 2,5 billions tons, that will support the steel platform of Algeria. Particularly interesting areas with reserves of almost 300 000 tonnes of fluorite have been highlighted in the Hoggar in Sahara.

In order to answer the requirements of the mentioned uses, barite and fluorite ores have to undergo an appropriate processing. The method here applied is flotation, during which different reagents, both anionic and cationic, have been tested in order to choose those who give the best results.

The aim of our study is, in a first step, a systematic flotation behaviour of barite and associated minerals, during which various collectors, combined with modifiers have been tested. Then, an artificial mixtures flotation was carried out and all the optimal conditions of flotation were applied to barite and fluorite-barite ores.

Definitive choice of optimal flotation requirements focused on Petronate L (1000 g/t ; pH 6.5) for barite flotation and on Flotbel R171A (100 g/t ; pH 9) for fluorite, combined with potassium dichromate as depressing agent for quartz and barite.

The final flotation treatment has led to the obtention of a barite concentrate with a 93,4% $BaSO_4$ grade and a fluorite concentrate with 93,6% CaF_2,both answering the users'requirements.

Keywords: flotation, barite, fluorite, calcite, quartz, collector, pH

Introduction

In the present socio-economical difficult context and with the oil prices fall, Algeria aims of developing its economy. So, it's imperative for the country to research, work and valorize its hydrocarbons resources, and mineral ones, among which barite and fluorite, two industrial minerals of first importance.

The former plays a prominent part in the oil industry, where it's used as a weighting agent in the drilling muds. Barite is also appreciated by the nuclear industry, as a constituent of heavy concretes and by the paint industry.

The latter is always principally used as flux in metallurgy and tends to make the chemical industry's largest market ; it's a raw material of hydrofluoric acid and fluorine, which are the key products of a new growing industry, that of fluorine chemistry.

To meet these different uses, barite and fluorite ores must undergo appropriate treatment. The process here applied in this study is flotation, without which the mining industry would not be what it is today. This concentration process allowed the exploitation of low-grade ores and complex ores (191).

The present work is a systematic experimental study of the flotation of the main minerals that may be associated with barite. The nature and the consumption of the collector, the influence of activators and depressors and the pH of the aqueous phase were the parameters studied.

The conclusions which were drawn in this preliminary work have been verified on artificial mixtures of minerals and ores.

Systematic behaviour study in flotation of barite and fluorite

The experimental part of this work concerns a systematic study of the flotation of pure minerals of barite and associated minerals which has been attempted. The flotations have been carried out with chosen various reagents, using different consumptions and in different pH conditions.

1. Samples brief description

Barite used for our tests is a gravity concentrate. Fluorite is light green in color and comes in pieces 2 to 3 cm; those contaminated by cop-

Tab. 1. Chosen reagents for the barite, fluorite, calcite and quartz flotation

Tab. 1. Wybrane odczynniki dla flotacji barytu, fluorytu, kalcytu i kwarcu

Reagents	Composition
Collectors	
Potassium Oleate	Oleic acid ($C_{17}H_{33}COOH$) salt
Aeropromoter 825	Mixture of sodium sulfonate, fuel oil and water, MW = ± 350
S 7723	Sulfonate
Sinclair S 40	Sodium sulfonate, MW = 461
Petronate L	Petroleum sulfonate, MW = 415-430
Sulfosuccinate 2875	$ROOC-CH_2-CH.COO^-M^+$ $SO_3^-M^+$ (on CH)
Sulfopon T35	Sodium Alkylsulfate
Sodium dodecylsulfate	$C_{12}H_{25}\ SO_4Na$
Flotbel R 159 A1	Sodium sulfate ester type
Flotbel R 171 A	Sodium salt o%f a phosphate ester
Armac 18	C18 primary amine acetate with formula : $R-NH_3^+\ CH_3COO^-$
Armacflote MFA 18	Cationic collector
Modulating agents	
Barium chloride	$BaCl_2$
Citric acid	$C_6H_8O_7$
Potassium dichromate	$K_2Cr_2O_7$
Sodium silicate	Na_2SiO_3
Aluminium chloride	$AlCl_3.6H_2O$
Quebracho	Tanins group compound

per sulfides were manually sorted and removed. Another batch contains green fluorite, calcite , quartz and sulfides.

Studied gangue minerals are calcite and quartz. The first is virtually free of impurities. As for the second, it is very pure (99,9% SiO_2). Except the latter mineral, all the others have been, after fragmentation, sieved and only the particle size range from 0.074 to 0.2 mm was used in our preliminary flotation tests.

2. Reagents'choice

Research in the field of industrial minerals flotation (barite and fluorite and associated quartz and calcite) allowed us to choose a priori both anionic and cationic reagents, which may float these minerals.

The chosen collectors are mentioned in the first part of the table 1, meanwhile the activators and depressors are in the second part.

3. The experiments

3.1. Operating mode

During the systematic behaviour study in flotation of barite and fluorite, we opted for the following procedure :

– All the flotations have been performed in batch mode in a Fagergreen cell of 500 ml capacity.

– The same experimental conditions, common to all tests, were the following:

• the solid content of the pulp was set at 20%;

• the water used was distilled water;

• pH was adjusted by addition of sulfuric acid or whitewash, followed by a 5 minutes conditioning;

• after adding a possible modulating agent, if any, the collector is allowed to act during 10 minutes;

• when necessary,oil pine is added as frother.

3.2. Results

3.2.1. Among all the tests realized – when the collector is the only reagent added – we selected those that gave the best results. They are essentially the sodium dodecylsulfate (cf. fig.1), Petronate L (fig. 2) and Sulfopon T 35 (fig. 3) for barite, with respective consumptions : 200, 1000 and 1000 g/t, particularly in the pH interval 6–9,5 (cf. fig. 5).

These results confirm the efficiency of the dodecylsulfate, already tested on Chaillac samples [6] and reported by Pryor [10], Hanna and Somasundaran [5], Eigeles [2], Gaudin [3], Klassen and Mokroussov [7].

Tab. 2. Artificial mixtures flotation optimal conditions of barite, fluorite, calcite and quartz

Tab. 2. Optymalne warunki flotacji dla mieszaniny barytu, fluorytu, kalcytu i kwarcu

Collector (g/t) ; pH	Depressing agent (g/t)	Float Balance		Sink Balance	
		T (%)	Rc (%)	T (%)	Rc (%)
$BaSO_4$ (0,074 – 0,1 mm) / SiO_2 (0,2 – 0,3 mm)					
Dodecylsulfate (200) ; 7	-	99,2	98,4	98,2	99,4
Petronate L (1000) ; 6,5	-	98,4	98,8	98,2	99,2
Dodecylsulfate (100) ; nat	Na Silicate (1000)	99,6	94,9	95,0	99,7
$BaSO_4$ (0,074 – 0,1 mm) / $CaCO_3$ (0,2 – 0,3 mm)					
Sulfopon T 35 (500) ; 6,5	-	98,2	98,4	98,2	99,2
$BaSO_4$ (0,074 – 0,1 mm) / CaF_2 (0,2 – 0,3 mm)					
Dodecylsulfate (100) ; 6	Citric acid (500)	98,1	93,0	93,3	98,4
CaF_2 (0,074 – 0,1 mm) / SiO_2 (0,2 – 0,3 mm)					
Flotbel R171A (100) ; 9	Citric acid (500)	99,3	96,6	96,9	99,4
Aero 825 (1000) ; nat	-	95,6	95,6	95,2	100,0
CaF_2 (0,2 – 0,3 mm) / $CaCO_3$ (0,074 – 0,1 mm)					
Armacflote MFA 18 (500) ; nat	-	95,9	92,7	92,4	96,5
CaF_2 (0,2 – 0,3 mm) / $BaSO_4$ (0,074 – 0,1 mm)					
Flotbel R171A (100) ; 9	Dichromate de K (500)	96,3	86,2	87,1	97,6
$BaSO_4$ (0,074 – 0,1 mm) / SiO_2 + $CaCO_3$ (0,2 – 0,3 mm)					
Dodecylsulfate (100) ; 6,5	-	96,4	93,8	95,6	99,0
$BaSO_4$ (0,074 – 0,1 mm) / CaF_2 (0,1 – 0,2 mm) / SiO_2 (0,2 – 0,3 mm)					
Dodecylsulfate (200) ; nat	Citric acid (500)	99,2	92,4	95,2	99,5

The results, obtained with Petronate L agree with Van Lierde's observations [12]. The best performance achieved with this collector is 99% at pH = 6.

Among the cationic reagents, it was noticed that Armac 18, with a consumption of 500 g/t, doesn't float barite and could therefore be used in reverse flotation, as also proposed by Ghiani (cited in [11], Carta and Massacci [4].

For the fluorite flotation, most collectors have given satisfactory results, summarized in figure 4. The maximum yields are averaging 95–96% for consumptions about 1000 g/t and in a pH range between 4 and 10,5. Among these reagents, it was opted for Sulfosuccinate 2875, Potassium oleate, Aeropromoter 825 and Armacflote MFA 18, as being the best ones.

3.2.2. When a modulating agent is added to a collector

Barite and fluorite being associated in the nature with gangue minerals such quartz and calcite, the use of collectors allowing selective flotation of useful minerals often requires the use of modifiers. It's in the context of such separations that we have systematically studied the action of various collectors mentioned above, in combination with depressing and activating various minerals considered, i.e. barium chloride, citric acid, potassium dichromate and sodium silicate, etc. (cf. table 2).

At the end of this systematic study of barite, fluorite, quartz and calcite flotation with various collectors, whose action was combined with mod-

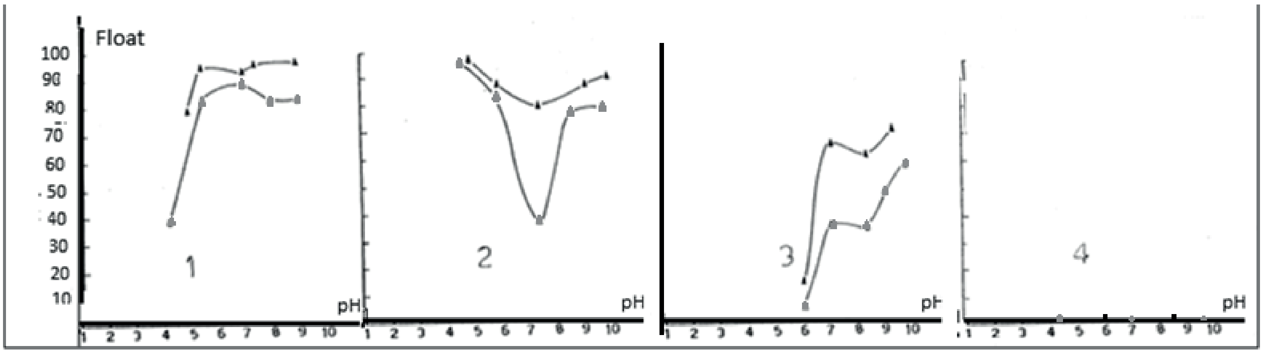

Fig. 1. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Na dodecylsulfate (▲200 g/t ; Δ 100 g/t) – Influence of pH

Rys. 1. Flotacja barytu (1), fluorytu (2), kalcytu (3) i kwarcu (4) za pomocą dodecylosiarczanu Na (▲200 g/t ; Δ 100 g/t) –wpływ pH

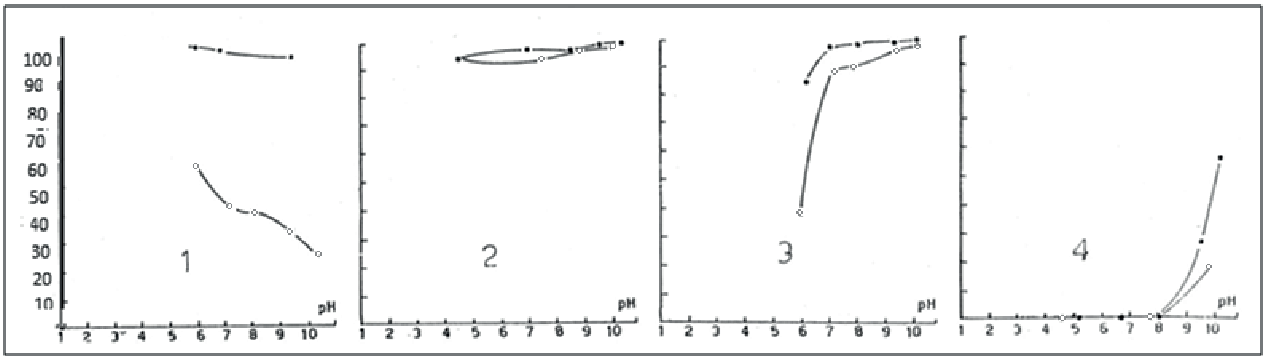

Fig. 2. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Petronate L (● 1000 g/t;○ 500 g/t) – Influence of pH

Rys. 2. Flotacja barytu (1), fluoryt (2), kalcyt (3), kwarc (4) odczynnik Petronate L (● 1000 g/t;○ 500 g/t) – wpływ pH

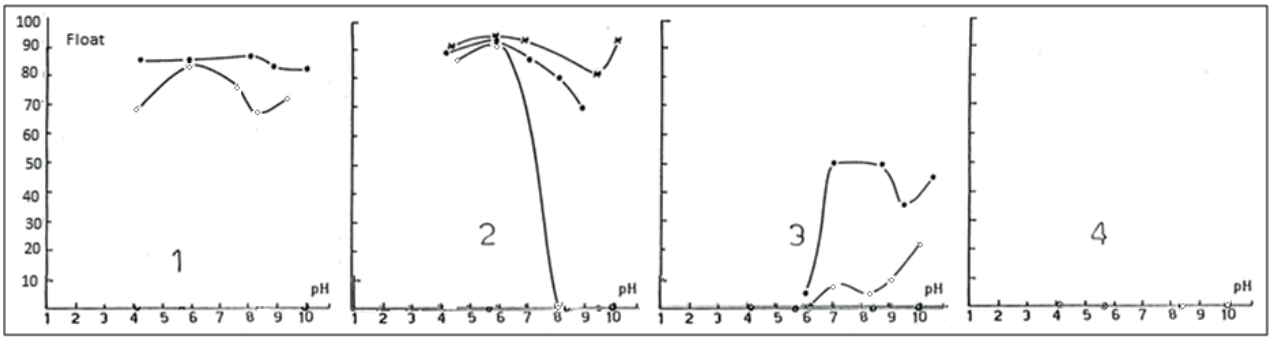

Fig. 3. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Sulfopon T35 (* 2000 g/t ● 1000 g/t ;○ 500 g/t) – Influence of pH

Rys. 3. Flotacja barytu (1), fluoryt (2), kalcyt (3), kwarc (4) z odczynnikiem Sulfopon T35 (* 2000 g/t ● 1000 g/t ;○ 500 g/t) – wpływ pH

ifiers, it appears the interest of these latter. Indeed, those should allow the separation of valuable minerals from the gangue and the valuable minerals between themselves.

On the basis of the results of this previous work, were identified the most favorable conditions it would be useful to study for the separation of mixtures, which is the subject of the next section.

Artificial mixtures flotation

1. Operating mode

To verify studied reagents' efficiency for the separation of valuable minerals from those of the gangue and the valuable minerals between themselves, we made artificial binary and ternary mixtures of these minerals. Their particle size was different according to the constituent, but always comprised between 0,3 mm (48 mesh) and 0,074 mm (200 mesh) (the most

Tab. 3. Barite ore cell flotation results

Tab. 3. Wyniki flotacji rudy barytu

Product	Weight Yield (%)	$BaSO_4$ Balance		SiO_2 Balance		Remainder Balance	
		Content (%)	Rec (%)	Content (%)	Rec (%)	Content (%)	Rec (%)
R O U G H I N G							
F1	77.8	95.1	89.4	01.0	14.1	03.9	25.9
C1	22.2	39.7	10.6	21.3	85.9	39.0	74.1
Feed	100.0	82.8	100.0	5.5	100.0	11.7	100.0
S C A V E N G I N G							
F2	28.0	97.7	68.9	00.2	00.3	02.1	01.5
C2	72.0	17.1	31.1	29.5	99.7	53.4	98.5
	100.0	39.7	100.0	21.3	100.0	39.0	100.0
G L O B A L B A L A N C E							
F1	77.8	**95.1**	**89.4**	01.0	14.1	03.9	25.9
F2	06.2	97.7	07.3	00.2	00.2	02.1	01.1
C1	16.0	17.1	03.3	29.5	85.7	53.4	73.0
Feed	100.0	82.8	100.0	05.5	100.0	11.7	100.0

fragile minerals being the finest). The proportions of the constituents in the binary and ternary mixtures were systematically 50:50 and 40:30:30. The procedure adopted is that described in section II.3.1 .

The test conditions achieved for each collector, either alone or in combination with an activator (or depressing agent) were selected from the results acquired during the flotation contents being estimated by sieving.

2. The tests and conclusions

We took in table 2 overall optimum flotation conditions of the artificial mixtures concerning the four studied minerals and the corresponding results.

We find that without depressing agent, Na-dodecylsulfate, Petronate L and Sulfopon T 35 are the reagents that helped to separate barite from the two gangue minerals. It is the same about Aeropromoter 825 for fluorite.

When the mixture consists only of fluorite and calcite, it is the cationic collector Armacflote MFA18, which allows the most selective flotation of the valuable mineral.

When quartz and barite are present simultaneously with fluorite, they are depressed by citric acid and potassium dichromate, respectively. Therefore, for the application to ores, our final choice of optimal flotation requirements focused on Petronate L (1000 g/t) used at pH 6,5 for the flotation of barite, the Flotbel R171A (100 g/t, pH 9) for the flotation of fluorite and potassium dichromate (500 g/t) as a depressing agent of barite.

Application to ores

The final optimal conditions we have chosen will focus on a barite ore and a barite-fluorite ore. In this section, are summarized the experimental conditions in cell flotation and the obtained results.

1. The samples

1.1. The barite ore

The ore sample that was used in our tests is almost entirely movable and has a particle size ranging from a fine dust to blocks of about 10 cm. It essentially contains barite (82,8% $BaSO_4$) and quartz (5,5% SiO_2), the remainder being various impurities (clay, iron hydroxides,…). Barite is released at a size greater than 0,4 mm (35 mesh) while quartz is released under 0,3 mm (48 mesh). It is under this last dimension that our samples were ground.

1.2. The fluorite-barite ore

The used sample of the fluorite-barite ore contains essentially fluorite (50,2%), barite (17,6%) and quartz (14,7%) and various other gangue minerals. Barite and fluorite are released at, at least, 82,5% in the fraction 0,1–0,2 mm (65–150 mesh) and the gangue is released at 82% in the same fraction.

2. Experimental conditions in cell flotation and results

2.1. Barite ore

For the cell flotation of the barite ore, two steps (roughing and scavenging) have been nec-

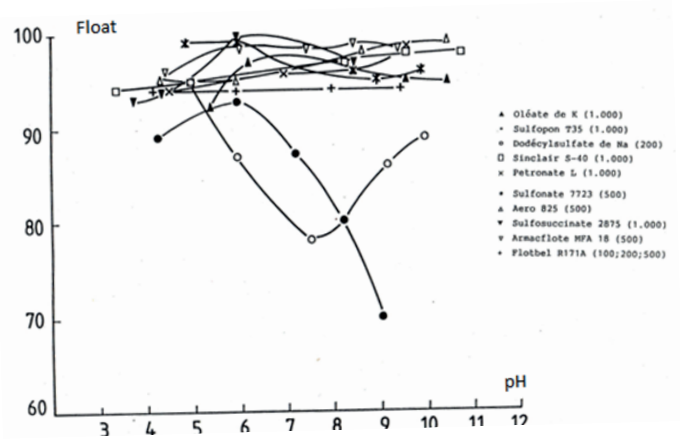

Fig. 4. Flotation of fluorite in presence of various collectors – Influence of pH (the number between parenthesis indicate the consumption in g/t)

Rys. 4. Flotacja barytu z różnymi odczynnikami – wpływ pH (liczby w nawiasach oznaczaja zużycie w g/t)

Tab. 4. Fluorite-Barite ore cell flotation results

Tab. 4. Wyniki flotacji fluorytu-baryt

Product	Weight Yield (%)	CaF_2 Balance		$BaSO_4$ Balance	
		Content (%)	Rec (%)	Content (%)	Rec (%)
R O U G H I N G					
F1	53.9	89.7	96.3	05.6	17.2
C1	46.1	04.0	03.7	31.6	82.8
Feed	100.0	50.2	100.0	17.6	100.0
C L E A N I N G					
F1	87.3	93.6	91.1	05.63	87.8
C1	12.7	62.8	08.9	05.4	12.2
Feed	100.0	89.7	100.0	O5.6	100.0
B A R I T E F L O T A T I O N					
F1	28.1	06.2	43.6	93.4	83.1
C1	71.9	03.1	56.4	07.4	16.9
Feed		04.0	100.0	31.6	100.0
G L O B A L B A L A N C E					
Con A CaF_2	47.1	**93.6**	**87.8**	05.7	15.2
Con B CaF_2	06.8	62.8	08.5	05.4	02.1
Con $BaSO_4$	13.0	06.2	01.6	93.4	69.0
Sink	33.1	03.1	02.1	07.4	13.7
Feed	100.0	50.2	100.0	17.6	100.0

essary. Given the constitution of the ore (cf. table 2), roughing was done in presence of Petronate L (1000 g/t) at pH 6. The sinking product of this operation had a content of 39,7% $BaSO_4$; so we found it useful to enrich it in a scavenging step, carried out under the same conditions as those used for roughing, but with reduced collector consumption by half.

The results for barite ore cell flotation are summarized in table 3.

It should also be noted that the $BaSO_4$ and SiO_2 contents in run-of-mine and flotation products were obtained by titration of Ba and Si , the first by gravimetric method and the second by plasma emission spectrometry.

2.2. Fluorite-barite ore

The table 2 from which have been chosen the final optimum flotation conditions suggests the use of Flotbel R171A for the flotation of fluorite,

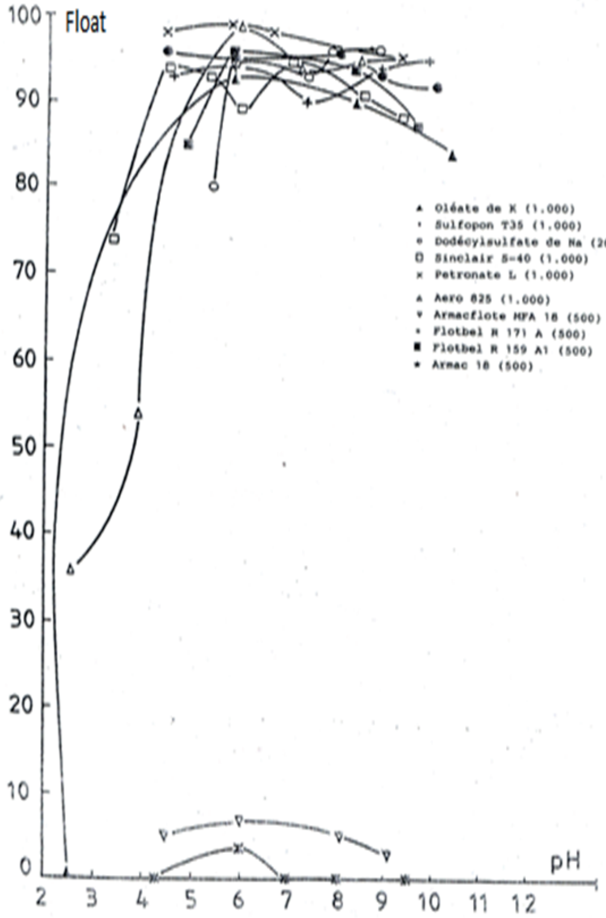

Fig. 5. Flotation of barite in presence of various collectors – Influence of pH (the number between parenthesis indicate the consumption in g/t)

Rys. 5. Flotacja barytu z różnymi odczynnikami – wpływ pH (liczby w nawiasach oznaczaja zużycie w g/t)

combined with potassium dichromate which plays the of depressing barite and quartz. The flotation tests have been then carried out, with these reagents,on the ore in question. In a first step (roughing), the consumptions of collector and depressing agent are, respectively, 100 g/t and 500 g/t, with a pH = 9 (using whitewash); according to the table 2, it is possible to first float barite (sodium dodecylsulfate as collector, 200 g/t and citric acid to depress fluorite and quartz, 500 g/t), then fluorite with Aeropromoter 825 (1000 g/t). Given the low CaF_2 content of the float, it was necessary to carry outa cleaning, in order to get a marketable product. This goal has been achieved by using 50 additional grams of collector and 500 g of potassium dichromate per ton, but at natural pH this time.

The sinking product of fluorite roughing operation contained 31,6% of $BaSO_4$ and in the second step, we attempted to separate barite, previously depressed, from the gangue. Among the optimum flotation conditions capable of leading to interesting results and shown in table 2, it is the combination Na-dodecylsulfate/Na-silicate we opted for. The table 4 summarizes the results of the cell flotation of fluorite – barite ore.

3. Results – Conclusions

Samples of the two minerals were ground under 0.3 mm (48 mesh) and under 0.2 mm, respectively. Then, the selected optimum conditions were adopted during the flotation of these two ores. Tables 3 and 4 show the good results obtained regarding the $BaSO_4$ content of the roughing concentrate, which is 95,1% for the barite ore and the CaF_2 content (93,6%) obtained during fluorite concentrate cleaning (for the fluorite-barite ore).

These products answer the users' requirements.

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Flotacja barytu i minerałów towarzyszących: analiza porównawcza

W obecnej trudnej sytuacji socjoekonomicznej, w połączeniu ze spadkiem ceny ropy, Algieria jest nastawiona na rozwój ekonomiczny. W tym celu należy przeprowadzić badania, prace i waloryzację zasobów nie tylko surowców węglowodorowych , lecz również mineralnych, do których można zaliczyć baryt i fluoryt – dwa istotne minerały przemysłowe.
Z racji tego, że Algieria prowadzi wydobycie gazu i ropy oraz jest członkiem OPEC, ma wysokie zapotrzebowanie na baryt. Minerał ten ma kluczowe znaczenie w przemyśle naftowym jako główny składnik iłowych płuczek wiertniczych. Fluoryt jest używany jako substancja zmiękczająca w metalurgii. Jest to istotne z powodu dużego złoża znajdującego się w tym kraju w GaraDjebilet, której zasoby sięgają 2,5 miliardy ton. Szczególnie interesujące tereny z zasobami fluorytu dochodzącymi do 300 000 ton mieszczą się w Hoggar na Saharze.
W odpowiedzi na zapotrzebowanie przemysłu rudy barytu i fluorytu muszą być poddawane wzbogacaniu. Zastosowano flotację, podczas której badano odczynniki, zarówno anionowe jak i kationowe.
Celem badań, w pierwszym etapie, było określenie wyników (efektów) flotacji barytu i minerałów towarzyszących , podczas której testowano różne kolektory wraz z ich modyfikatorami.
Następnie przeprowadzono flotację sztucznych mieszanek oraz określono optymalne warunki flotacji rud barytu i fluorytu.
Ostateczny wybór najlepszych parametrów technologicznych flotacji, został oparty na odczynniku zbierającym Petronate L (1000 g/t; pH=6,5) dla flotacji barytu oraz na Flotbel R171A (100 g/t; pH=9) dla fluorytu, w połączeniu z dichromianem potasu, jako czynnika depresyjnego dla kwarcu i barytu. Optymalny proces flotacji doprowadził do otrzymania koncentratu barytu z BaS04 na poziomie 93,4% i koncentratu fluorytu zawierającego 93,6% CaF2. Oba spełniają wymogi użytkowników.

Keywords: barite, fluorite, flotation, flotation reagents, pH