

# EFFICIENCY OF BARITE FLOTATION REAGENTS A COMPARATIVE STUDY

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## **Abstract**

Besides oil and gas, Algeria has important mineral resources which are a determining factor for the economic development of the country. Among these latter, barite is, for its specific properties, needed in big quantities in the oil industry as the major ingredient of drilling muds. Barite is also used as mineral filler, in barium chemistry (special glasses) and in the civil engineering and public works (heavy concretes). In order to answer the requirements of this use, barite ores have to be treated and the method here applied is flotation. Without this technique, there would be no mining industry as it is known today.

The present work concerns a long series of tests which allowed to specify the efficiency of various collectors (anionic and cationic) and modifiers (barium chloride, citric acid, potassium dichromate,...) during barite flotation. Besides the nature and consumption of the reagents, the influence of pH was also studied. After a comparative study of the various reagents used, the selected anionic collectors giving very good results were the sodium dodecylsulfate, petroleum sulfonate and sodium alkylsulfate Sulfopon T35. As for the cationic collector, Armac 18, a primary amine acetate, does not float barite and could be used in reverse flotation.

The conclusions which were drawn in this work have been then verified on artificial binary and tertiary mixtures of pure minerals and on a barite ore. The best performance was reached with the use of Petronate L (1000 g/t ; pH 6.5) for barite flotation, leading to the obtention of a barite concentrate with a 95.1% BaSO<sub>4</sub> grade answering the oil industry requirements.

**Keywords :** *flotation, barite, gangue minerals, collector, modifier, pH.*

## **I.Introduction**

Algeria is a producer of oil and gas and member of OPEC. Except these two energy sources, it has important mineral resources which are a determining factor for the economic development of the country. Among these latter, barite is, for its specific properties (high specific gravity = 4.5, high chemical stability, whiteness and low abrasiveness), needed in big quantities in the oil industry as the major ingredient of drilling muds. Barite is also used as mineral filler (paper, paint, plastics, etc.), in barium chemistry (special glasses) and in civil engineering and public works (heavy concretes).

In order to answer the requirements of these uses, barite ores have to be treated and the method here applied is flotation. Without the development of this technique, there would be no mining industry as it is known today. This shows the importance of this concentration process that allowed the exploitation of low grade ores and complex ores [13].

The present work concerns a long series of tests which allowed to specify the efficiency of various collectors (anionic and cationic) and modifiers (activating agents and depressants) during barite flotation. Besides the nature and consumption of the reagents, the influence of pH has been also studied. The conclusions which were drawn in this work have been then verified on artificial binary and tertiary mixtures of pure minerals in view of barite separation from both gangue minerals. The study finally ends by the application of the optimal flotation conditions to a barite ore, giving a concentrate answering the oil industry specifications.

## II. Efficiency study of flotation reagents

The flotation of barite was the subject of numerous studies of fundamental and applied type. The general conclusion to be drawn from them is that barite enrichment by flotation presents no great difficulties provided that the ore processed is not complex (barite-fluorite for example) or does not require forced grinding or low BaSO<sub>4</sub> content and with carbonate gangue.

Among the used or proposed collectors for the barite flotation, have to be mentioned carboxylates and especially oleic acid and its alkali salts, sodium cetyl sulfate, and some sulfonates of sulfonated lauryl alcohol. One could also consider the possibility of using cationic collectors (in the absence of a siliceous gangue) [2].

### II.1 Materials and Methods

#### *Materials*

As mentioned in a previous work [10], the materials used were a gravity concentrate of barite, a calcite sample, virtually free of impurities and a very pure quartz (99.9%). Except the latter mineral, all the other have been, after fragmentation, sieved and only the particle size range from 0.074 to 0.2 mm was used for flotation tests.

#### *Methods*

In order to study the efficiency of the various collectors and modifiers during the barite flotation, it is necessary to specify that all the flotation experiments have been performed in batch mode in a Fagergreen cell (capacity of 500 ml), in the same following conditions :

- use of distilled water ;
- solid content of the pulp = 20% ;
- pH adjusted by H<sub>2</sub>SO<sub>4</sub> or whitewash, followed by a 5 mn conditioning ;
- after an optional addition of a modulating agent, the collector is allowed to act during 10 mn ;
- addition of oil pine as frother, when necessary.

### II.2 Results and discussion

#### II.2.1 The anionic reagents

Research conducted in the area of flotation of non-metallic minerals, especially barite (and associated calcite and quartz), allowed us to choose a priori anionic as well as cationic reagents, that may float these minerals. The tests were realized with the following collectors and gave the results mentioned hereafter :

\***Sulfopon T35** is a sodium alkylsulfate, product of tallow fatty alcohol sulfonation. It consists of a white paste, poorly soluble in water. According to the literature [3], increasing the temperature would favorably influence the collector efficiency. Also note that the collector is self foaming.

Barite flotation with Sulfopon, realized with 1000 g/t of collector, extends to a wide pH range (4.3 – 10.2) with average recoveries of 94%. The best results are reached at natural pH (6-6.3).

The flotation yield of calcite is much lower ; indeed, between pH 7 and 8.7, flotation of carbonate gives a recovery of about 50% for a collector consumption of 1000 g/t. At pH 500 g/t, flotation rate decreases with pH up to 6.2, value  $\hat{Z}$ at which performance is canceled and below which it cannot go down because of the mineral dissolution. Quartz hardly floats with Sulfopon in a wide pH range (between 4.2 and 10).

\***Sodium dodecylsulfate (SDS)** is an anionic surfactant known as lauryl (C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na) which is considered as "type-collector" in non metallic minerals flotation. It consists of a white paste, easily

soluble in water. Taking into account the low consumptions used (100 and 200 g/t), it's the collector which has given the best results in barite flotation. Indeed, from figure 1, it follows that sodium dodecylsulfate is particularly efficient for the flotation of barite at pH higher than 6 (consumption : 200 g/t).

SDS acts also as calcite collector. It can be noticed that performance increases with pH, from natural pH (7.2). In acid medium (pH = 6.2), flotation is almost zero, always for the same consumption of 100 g/t. In the pH zone (between 4 and 9.5), SDS didn't float quartz ; this is valid, in general, for all the anionic collectors.

**\*Sulfonate Sinclair S-40** : it is a sodium sulfonate of molecular weight 461, mahogany colour, water emulsifiable. Its composition is following : sulfonate : 41.5% ; Na carboxylate : 0.95% ; salt : 1.08% ; water : 4.37% ; petroleum : 52.1% [7].

Barite flotation tests carried out in the pH range comprised between 3 and 10 have given a maximum flotation rate at natural pH (6.2), with a consumption of 500 g/t. This recovery decreases up to 33% and up to 62%, respectively at pH 3 and pH 10, which gives a bell-shape curve. Increasing of the collector consumption to 1000 g/t didn't led to a significant performance improvement (augmentation < 5%). The figures 500 g/t and pH 6.2 will be therefore retained for which the best results were obtained.

For the calcite flotation with a consumption of 1000 g/t and at pH 8 to 10, recovery was 96% on average. With 500 g/t, recovery of this carbonate is poor, while it's about 12% at acid pH (6.2).

**\*Petronate L** is a petroleum alkylsulfonate containing 62% of sulfonates of molecular weight from 415 to 430. Like all the sulfonates, Petronate L is completely miscible in oil and can be water-dispersible (preferably hot water). It is particularly useful as emulsifier and wetting agent for various solvent systems [14].

To assess the interest of this collector, barite and calcite have been floated under the same conditions as those used during testing with Sinclair S-40. From figure 2, it can be observed that Petronate L floats barite with significantly better recoveries (100% at pH 6).

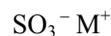
As for calcite, it floats with 250 g/t at pH 6, reaching a yield of almost 40%, a figure that rises with the reagent consumption, from 1000 g/t, to a maximum value of 97-98% in the pH range 6 - 9.7 .

**\*Aeropromoter 825** : a mixture of sodium sulfonate, fuel oil and water, mahogany brown, made by the US company Cyanamid. Its molecular weight is low (about 350). It is present in viscous form which heating increases the fluidity [4]. It can be dispersed in hot water.

As the sulfonates above mentioned, the Aeropromoter 825 floats barite effectively at a rate of 500 g/t. The recovery is 75%, at pH 6. In order to improve this latter, barite has been floated with 1000, then 2000 g/t. The best result was obtained at natural pH (yield of 95%). At acidic pH, the efficiency of this collector is showing a considerable fall.

Calcite floats to almost 100 % for a reagent consumption of 1000 g/t and this in the same basic range as barite. As for quartz, it doesn't practically float in the pH range 3-9.

**\*Sulfosuccinate 2875** : it's a reagent which formula is :  $\text{ROOC} - \text{CH}_2 - \text{CH}.\text{COO}^- \text{M}^+$  [174]



It is used as wetting agent, auxiliary collector and fatty acid emulsifier for a variety of flotation processes. The flotation tests of the considered minerals, carried out at different values, cover the area from 3 to 10.5 . The flotation barite performance remains constant for consumptions higher than 500 g/t and reaches 100% for 1000 g/t. For a lower consumption (250 g/t), it passes through a maximum between pH 6 and 9.

For calcite, the consumption of 1000 g/t is sufficient to achieve an average yield of 94% in the alkaline range (pH 7 to 9).

At acidic and neutral pH, sulfosuccinate action on the flotation of quartz is zero. This mineral abruptly and totally floats from pH 8.

### II.2.2 The cationic reagents

Among the amines, Armac 18, Armacflote MFA 18 and amine triisooctyl have been used.

\***Armac 18** is a primary amine acetate formula  $R-NH_3^+ CH_3COO^-$  where R is an alkyl radical containing 18 carbon atoms or 16-18 carbon atoms saturated chains by hydrogenation ; the  $R_{18}$  amine itself is insoluble in water.

The pH range for which a maximum flotation is observed with Armac 18 is indicated in the table 1 below :

**Table 1.** Flotation with Armac 18

pH range	Mineral	Reagent consumption, g/t	Yield, %
7.0 – 9.5	Barite	2000	Between 92 and 98 %
7.0 – 10.5	Calcite	1000	
6.0 – 8.5	Quartz	500 (250)	

\***Armacflote MFA 18** : with a consumption of 500 g/t, it floats barite at pH 4.5-9.5 with a poor yield of 5-8%. When flotation tests of gangue minerals (calcite and quartz) are conducted at 500 g/t, a very low recovery of calcite (5-15%) is noticed between pH 6 and pH 9.8 . As for quartz, it floats to 98 % at pH 6. This yield decreases slightly with increasing pH up to 10. For a consumption of 250 g/t, quartz remains at the bottom of the flotation cell and only 4% float at pH 4 (Figure 3).

At the end of the barite flotation experiments that were realized with different anionic and cationic reagents, a comparative study has allowed to test the efficiency of these latter. So, were selected those that gave the best results : **Sodium dodecylsulfate, Petronate L and alkylsulfate Sulfofon T35**, with respective consumptions 200, 1000 and 1000 g/t, particularly in the pH range between 6 and 9.5 . It must be added that the best yield (99%) was reached with sodium dodecylsulfate at pH 6.

Among the cationic reagents, it has been noticed that **Armac 18**, with 500 g/t, does not float barite and could therefore be used in reverse flotation, as it was proposed by italian authors [5],[16].

### II.2.3 Efficiency study of the modifiers

Barite is often associated in nature with gangue minerals such as calcite, quartz, etc. The use of collectors allowing the selective flotation of the useful mineral often requires the use of modifiers such as barium chloride, citric acid, sodium silicate, potassium dichromate, quebracho, etc. [15].

Given the large number of combinations related to the flotation tests conducted in the presence of collectors used alone, different modifiers will be combined only with the collectors that gave the best results, i.e. Sulfofon T35, sodium dodecylsulfate and Petronate L.

The main conclusion of this study is that the distinction between an activating and a depressing agent is not as clear as one might think. A reagent may act as activating agent of a mineral with a given collector and as depressant with another ; furthermore, it can activate the flotation of a mineral in a pH range and, with the same collector, depress this mineral in another pH area.

\***Barium chloride** : is an inorganic compound with the formula  $BaCl_2$ . It's a white chlorine and barium salt, soluble in water. Like other barium salts, it is relatively toxic.

Combined with :

-Sulfofon T35, BaCl<sub>2</sub> depresses barite, mainly at natural pH while it has no effect on gangue minerals, but with a low depression of calcite at basic pH in presence of 500 g/t of Sulfofon. With a double amount of the same collector, barium chloride activates calcite.

-Sodium dodecylsulfate (100 g/t), BaCl<sub>2</sub> (500 g/t) gives a maximum flotation yield (85%) for barite in basic area (pH 9.5). Note that if the amount of barium chloride is increased while maintaining the same collector consumption, a depressing effect on barite is obtained, on the other hand. For gangue minerals, it is noticed that calcite is activated and quartz doesn't react at all and that, for the same combination of reagents.

-Petronate L : the action of BaCl<sub>2</sub>, when combined with this petroleum sulfonate at 1000 g/t and pH 6, is only interesting for barite which it activates ; indeed, adding BaCl<sub>2</sub> improves the recovery from 35 to 60% and even 70% (at pH 10.2). In these conditions, quartz doesn't float while calcite floats to 93% (Figure 4).

-Among the cationic collectors, it is Armac 18 (or primary amine acetate) that has been added in the cell after BaCl<sub>2</sub>. Barite which floats at 1000 g/t of Armac 18 with a maximum yield of 80% at pH 7, is activated by BaCl<sub>2</sub> and reaches a maximum recovery of 85% at pH 7.5 . This upper limit decreases progressively as the pH increases. For calcite, floated at 500 g/t of collector in the basic range, it's depressed by BaCl<sub>2</sub> allowing only a recovery of 20% at pH 9.5 ; this one becomes zero at pH 6. It is known that quartz floats with amines.

\***Citric acid** is an organic acid of formula C<sub>6</sub> H<sub>8</sub> O<sub>7</sub>. Will be considered the same collectors used in combination with BaCl<sub>2</sub> . Note that in all tests, citric acid was added at 500 g/t.

-Sulfofon T35 : as previously mentioned (§ II.1), Sulfofon T35 exerts a good action as collector on the grains of pure barite and mainly at natural pH, where recovery reaches 94% when collector consumption is 500 g/t. As soon as it is added the same amount of citric acid, the mineral is completely depressed over the studied entire pH range. In the same conditions, it appears unnecessary to add the depressant in flotation of calcite and quartz with Sulfofon as both gangue minerals float, the first quite little and the second, not at all.

-In the presence of sodium dodecylsulfate (100 g/t), citric acid is an activating agent of barite at acidic pH and depresses this one beyond pH 6 and pH 8.8 (Figure 5). Calcite, which floats with dodecylsulfate from natural pH, undergoes the depressing action of citric acid. Quartz does not react at all in the presence of citric acid. From pH 8, quartz is depressed when Petronate L is used as collector and combined with citric acid. As for calcite, it is activated by citric acid in the presence of Petronate L (especially at pH 6 where recovery reaches 96%).

-It was also tried to estimate the action of citric acid on the considered minerals in presence of cationic collectors. As mentioned before, Armac 18 alone floats the three minerals. Adding citric acid depresses them. This depression is important especially at pH 9.5 for barite (for a consumption of acid of 2000 g/t). Note that when the collector consumption is multiplied by 4 :

- calcite is totally depressed between pH 7 and 10.5 ;
- quartz undergoes the depression effect in the pH range 6-9.

-The tests with Armacflote MFA 18 have been limited to the consumption of 1000 g/t of the collector which, when combined with citric acid (500 g/t), allowed the obtention, at pH 9.5, of a rate barite flotation of 62%, hence the role of activating agent played here by citric acid. This role is also found with calcite which yield is much more important (95% at pH 9.5). Quartz finally undergoes depression at pH 6.

\***Potassium dichromate** is a common inorganic chemical agent (formula  $K_2Cr_2O_7$ ) with a very bright, red-orange color. This mineral salt, indicated in the literature as a depressant of barite, was found effectively as such in certain limits of pH during the flotation tests carried out with all the collectors used in our study, except Petronate L. When combined with this latter, the dichromate has an inverse effect on barite flotation, and slightly activates it especially at pH 6-8.

Note that the dichromate was used everywhere at 500 g/t.

-Sulfofon T35 : according to the figure 6, it is noticed that the dichromate activates calcite at pH 8 when collector is Sulfofon T35 and that it depresses it at the same pH when dodecylsulfate is used. The quartz flotation is not at all influenced par the addition of dichromate.

\***Sodium silicate** is an inorganic salt, odorless and very soluble in water. There are two definable silicates : metasilicate ( $Na_2SiO_3$ ) and disilicate ( $Na_2O.2SiO_2$ ) [12]. It is the influence of the former on the action of the various collectors that has been investigated.

Added at 1000 g/t in all flotations, the metasilicate generally depressed barite, when used in presence of all the studied anionic reagents, with the exception of sulfonates Petronate L and Aero 825 with which it activates the heavy mineral. However, it is noticed that  $Na_2SiO_3$  still depresses barite at pH 8.5 . Calcite is also depressed, especially at pH 9.5, in presence of the same two collectors ; on the other hand, it is activated by sodium silicate when this one is combined with the already mentioned sulfonates. It appears that sodium silicate addition has no influence on quartz flotation with used carboxylate, alkylsulfate and sulfonate, except for the former in presence of which quartz is depressed from pH 9.

\***Quebracho** is an important compound of the tannins (complex mixtures of polyphénols), produced from a plant grown in Mexico. It has been recognized by many researchers ([1], [6], [8], [11]) as depressant of calcite. Indeed, this action has been confirmed during the tests realized with potassium oleate, dodecylsulfate and petroleum sulfonate Petronate L.

Combined with all these collectors at 500 g/t, quebracho totally depresses calcite at basic (pH>7). With 100 g of dodecylsulfate per ton, calcite is depressed by quebracho over the entire pH range (6-10).

### III. Artificial mixtures flotation

To verify studied reagents' efficiency for the separation of barite from the gangue minerals, artificial binary and ternary mixtures of these minerals were realized. Their particle size was comprised between 0,3 mm (48 mesh) and 0,074 mm (200 mesh) (the most 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.1 .

#### Barite (0.074-0.1 mm) / Quartz (0.2-0.3 mm) mixture

Although barite-quartz differential flotation has become an almost routine operation in industrial practice, the tests performed in this study seem to open new paths. Indeed, the best results were obtained in the following conditions, as mentioned in tables 2 and 3 :

-dodecylsulfate (200 g/t) allowed barite float at pH 7, thus obtaining a 99.2%  $BaSO_4$  concentrate with a 98.4% recovery and a tailing grading 98.2%  $SiO_2$  with a recovery of 99.4% .

- Petronate L (1000 g/t) and at pH 6.5, gave a barite concentrate at 98.4%  $BaSO_4$  (recovery 98.8%) and a tailing with same  $SiO_2$  content and recovery than before.

**Table 2.**  $BaSO_4/SiO_2$  separation using sodium dodecylsulfate (200 g/t) at pH 7

Product	Weight Yield,%	$BaSO_4$ balance		$SiO_2$ balance	
		Content,%	Rec., %	Content,%	Rec.,%
Concentrate	49	99.2	98.4	0.6	0.6
Tailing	51	1.6	1.6	98.2	99.4
Restored feed	100	49.4	100.0	50.4	100.0
Feed		50		50	

**Table 3.** BaSO<sub>4</sub>/SiO<sub>2</sub> separation using Petronate L (1000 g/t) at pH 6.5

Product	Weight Yield,%	BaSO <sub>4</sub> balance		SiO <sub>2</sub> balance	
		Content,%	Rec., %	Content,%	Rec.,%
Concentrate	49	98.4	98.8	0.8	0.8
Tailing	51	1.2	1.2	98.2	99.2
Restored feed	100	49.8	100.0	50.5	100.0
Feed		50		50	

**Barite (0.2-0.3 mm / Calcite (0.074-0.1 mm) mixture**

Recall that in order to not dissolve calcite, precaution was taken to not drop below acid pH 6-6.5 .

It is at pH close to this area that the two minerals could be separated. Table 4 gives the best result obtained with Sulfofon T35 (500 g/t) ; this allowed to reach content and recovery higher than 98%, both in concentrate and in tailing ( table 4). This separation is the best, especially as the collector is used alone and without addition of frother, hence the economic benefit.

**Table 4.** BaSO<sub>4</sub>/SiO<sub>2</sub> separation using Sulfofon T35 (500 g/t) at pH 6.5

Product	Weight Yield,%	BaSO <sub>4</sub> balance		CaCO <sub>3</sub> balance	
		Content,%	Rec., %	Content,%	Rec.,%
Concentrate	49.3	98.2	98.4	0.8	0.8
Tailing	50.7	1.6	1.6	98.2	99.2
Restored feed	100	49.2	100.0	50.5	100.0
Feed		50		50	

**Barite (0.074-0.1 mm / "Quartz +Calcite" (0.2-0.3 mm) mixture**

Barite was effectively separated from the two other minerals thanks to sodium dodecylsulfate (100 g/t), sulfonate S-40 (500 g/t) and sulfosuccinate 2875 (500 g/t) at pH 6.5. The comparison of the flotation parameters (content and recovery), allows to affirm that the results obtained using the sodium dodecylsulfate are excellent, as it is shown on Table 5.

**Table 5.** BaSO<sub>4</sub>/SiO<sub>2</sub> + CaCO<sub>3</sub> separation using sodium dodecylsulfate (100 g/t) at pH 6.5

Product	Weight Yield,%	BaSO <sub>4</sub> balance		SiO <sub>2</sub> + CaCO <sub>3</sub> balance	
		Content,%	Rec., %	Content,%	Rec.,%
Concentrate	37.3	96.4	93.8	1.6	1.0
Tailing	62.7	3.8	6.2	95.6	99.0
Restored feed	100	38.3	100.0	60.5	100.0
Feed		40		60	

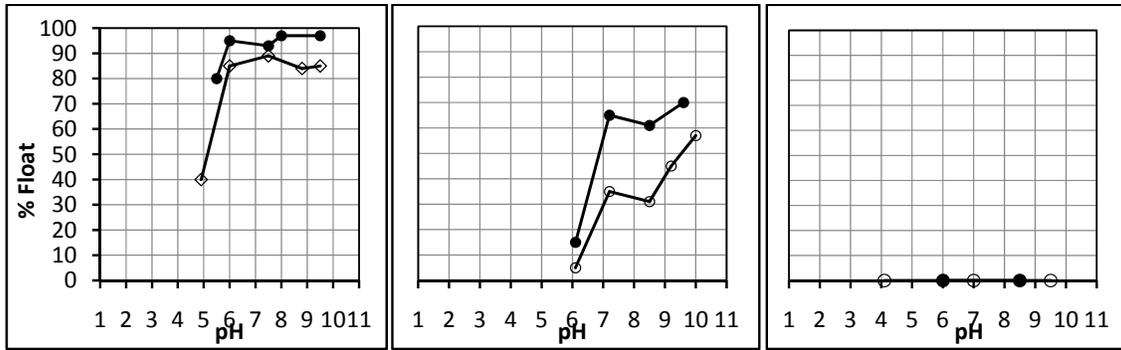
**IV. Conclusion**

After a theoretical research on flotation of barite, a systematic experimental study of the heavy mineral and associated gangue minerals (calcite and quartz) was carried out with various collectors and modifiers, at different consumptions and pH of the aqueous phase.

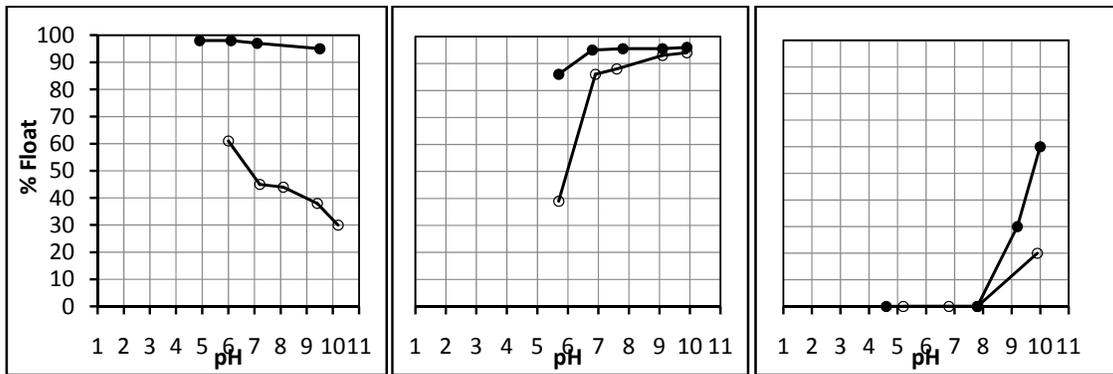
A comparative study allowed to test the efficiency of the reagents used and led to the selection of sodium dodecylsulfate, petroleum alkylsulfonate Petronate L and sodium alkylsulfate Sulfofon T35, among which the first has given the best results. These conclusions have been then verified on artificial binary and tertiary mixtures and on a barite ore, in view of separation of barite from gangue minerals. The application of the optimal flotation conditions resulted in obtaining a barite concentrate with a content higher than 95% BaSO<sub>4</sub>, a content which answers the oil industry users demand.

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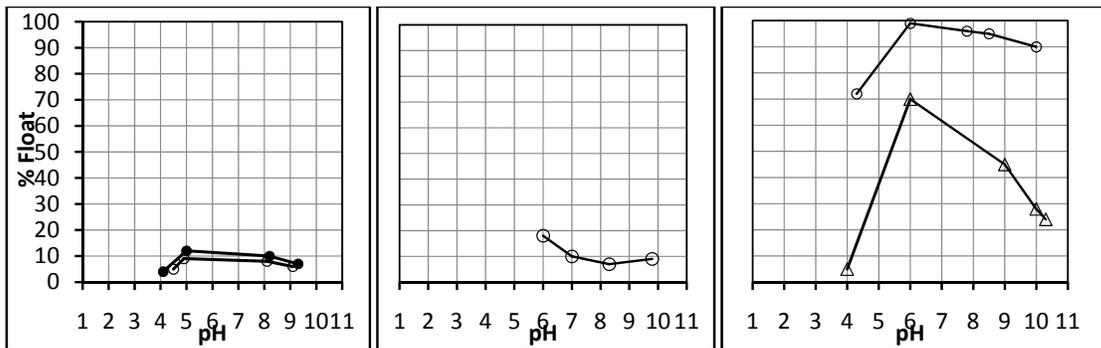
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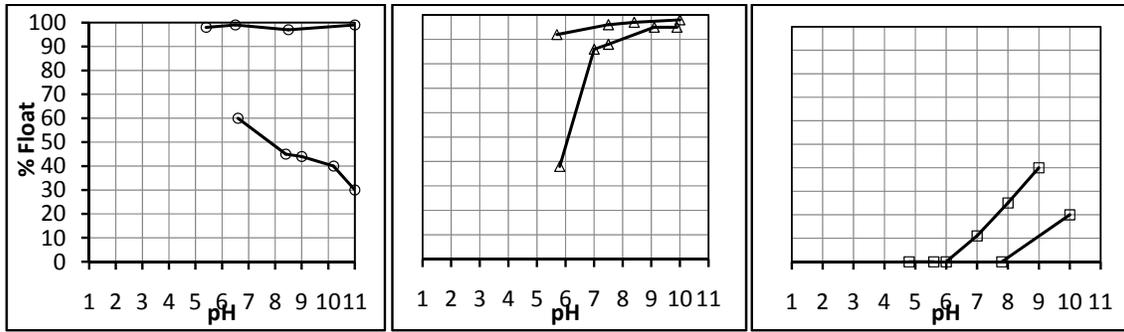
**Figure 1.** Flotation of barite (1), calcite (2) and quartz (3) with sodium dodecylsulfate (• 200g/t, o 100g/t) - Influence of pH.



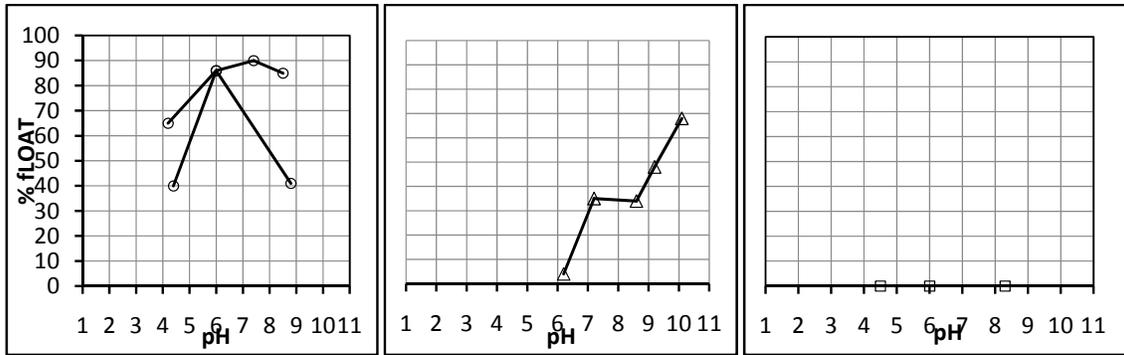
**Figure 2.** Flotation of barite (1), calcite (2) and quartz (3) with Petronate L (• 1000g/t, o 500g/t) - Influence of pH.



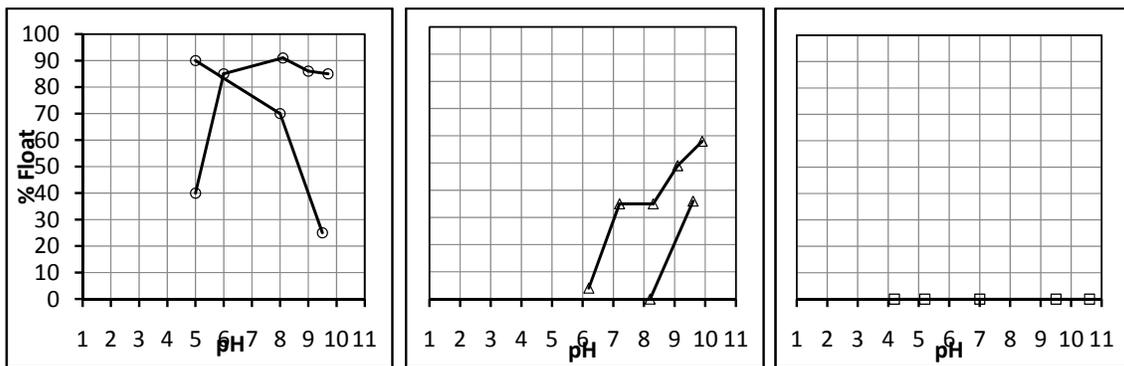
**Figure 3.** Flotation of barite (1), calcite (2) and quartz (3) with Armacflote MFA 18 (• 1000g/t, o 500g/t, Δ 250g/t) - Influence of pH.



**Figure 4.** Flotation of barite (1), calcite (2) and quartz (3) with Petronate L and BaCl<sub>2</sub> - Influence of pH (A: Petronate L (500); B: Petronate L (500) + BaCl<sub>2</sub> (500).



**Figure 5.** Flotation of barite (1), calcite (2) and quartz (3) with Sodium dodecylsulfate and citric acid - Influence of pH. (A: NaDS (100); B: NaDS (100) + citric acid )



**Figure 6.** Flotation of barite (1), calcite (2) and quartz (3) with Sodium dodecylsulfate and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> - Influence of pH. (A: NaDS (100); B: NaDS (100) + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (500))