

REAGENTS CHOICE FOR AN OPTIMAL FLOTATION OF INDUSTRIAL MINERALS

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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 work and valorize its out hydrocarbons resources, especially mineral ones, among which barite and fluorite, two industrial minerals of great importance. The former plays a leading role in the oil industry, where it's as a major ingredient in drilling muds and the latter is essentially used as flux in metallurgy.

To meet these purposes, their ores have to undergo an appropriate processing.

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% BaSO₄ grade and a fluorite concentrate with 93,6% CaF₂, both answering the users' requirements.

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

I. 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 it's out-hydrocarbons resources, especially the 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 used in this study is flotation.

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.

II. 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.

II.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 copper 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% SiO₂). 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.

II.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.

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

Reagents	Composition
<u>Collectors</u>	
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	$\text{ROOC-CH}_2\text{-CH.COO}^-\text{M}^+$ $\quad \quad \quad $ $\quad \quad \quad \text{SO}_3^- \text{M}^+$
Sulfopon T35	Sodium Alkylsulfate
Sodium dodecylsulfate	C ₁₂ H ₂₅ SO ₄ Na
Flotbel R 159 A1	Sodium sulfate ester type
Flotbel R 171 A	Sodium salt of a phosphate ester
Armac 18	C18 primary amine acetate with formula : R-NH ₃ ⁺ CH ₃ COO ⁻
Armacflote MFA 18	Cationic collector
<u>Modulating agents</u>	
Barium chloride	BaCl ₂
Citric acid	C ₆ H ₈ O ₇
Potassium dichromate	K ₂ Cr ₂ O ₇
Sodium silicate	Na ₂ SiO ₃
Aluminium chloride	AlCl ₃ .6H ₂ O
Quebracho	Tanins group compound

II.3 The experiments

II.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 :
 - o the solid content of the pulp was set at 20% ;
 - o the water used was distilled water ;
 - o pH was adjusted by addition of sulfuric acid or whitewash, followed by a 5 minutes conditioning ;
 - o after adding a possible modulating agent, if any, the collector is allowed to act during 10 minutes ;
 - o when necessary, oil pine is added as frother.

II.3.2 Results

II.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 Sulfofon 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 Mokrousov [7].

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.

II.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 modifiers, 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.

III. Artificial mixtures flotation

III.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 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.

III.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.

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

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

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.

IV. 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.

IV.1 The samples

IV.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.

IV.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.

IV.2 Experimental conditions in cell flotation and results

IV.2.1 Barite ore

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

IV.2.1 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, 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 out a 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.

Table 3. Barite ore cell flotation results

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

The sinking product of fluorite roughing operation contained 31,6 % of BaSO₄ 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.

Table 4. Fluorite-Barite ore cell flotation results

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	05.6	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

IV.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 BaSO₄ content of the roughing concentrate, which is 95,1 % for the barite ore and the CaF₂ content (93,6%) obtained during fluorite concentrate cleaning (for the fluorite-barite ore).

These products answer the users' requirements.

References

- [1] COUNET, J. La mine de barytine de Fleurus en Belgique, *Ind. Min. – Mines et Carrières*, vol. 72, N° 4, Avr. 1990, pg. 52-54.
- [2] EIGELES, M.A. Selective flotation of non-sulfide minerals, Progress in Mineral Dressing, *Trans. 4th Intern. Min. Dress. Congr.*, Stockholm 1957, pg. 591-609.
- [3] GAUDIN, A.M. *Flotation*, 2 ed. Mc Graw Hill, Book Cy, New York, 1957, 573 pgs.
- [4] GHIANI, M., MASSACCI, P. Contributo alla conoscenza del potere collettore delle aminine alifatiche primarie nelle flottazione di alcuni minerali non metallici, *Res. Associazione Mineraria Sarda*, N° 4, Aprile 1968.
- [5] HANNA, H.S. and SOMASUNDARAN, P. *Flotation of salt-type minerals – in Flotation*, A.M. Gaudin Mem. vol., A.I.M.E., New York, 1976, pg. 196-272.
- [6] HOUOT, R., SAVE, M., FROMIGUE, B. et VIGOUREUX, P. *Industrial sulphonates and barite flotation*, *Trans. I.M.M.*, vol. 94, N° 12, Dec. 1985, pg. C195-C200.
- [7] KLASSEN, V.J. and MOKROUSOV, V.A. *An introduction to the theory of flotation*, London, Butterworths, 1973.
- [8] LOVELL, V.M. *Industrial flotation reagents – in principles of flotation*, Ed. R.P. King, Johannesburg, 1982, pg. 73-89.
- [9] MARINAKIS, K.I. and SHERGOLD, H.L. Influence of sodium silicate addition on the adsorption of oleic acid by fluorite, calcite and barite, *Intern. J. of Min. Process.*, vol. 14, 1985, pg. 177-193.
- [10] PRYOR, E.J. *Mineral processing*, 3rd ed., Elsevier, Amsterdam – London – New York, 1965, 844 pgs.
- [11] ROBERT, D. Concentration de fluorine utilisant des réactifs cationiques, *Ind. Min. – Minéralurgie*, vol. 57, N° 1, Fév. 1975, pg. 25-32.
- [12] VAN LIERDE, A. Valorisation par flottation de minerais de barytine à gangue calcaire, *Ind. Min. Section Minéralurgie*, vol. 57, N° 1, Fév. 1975, pg. 34-42.

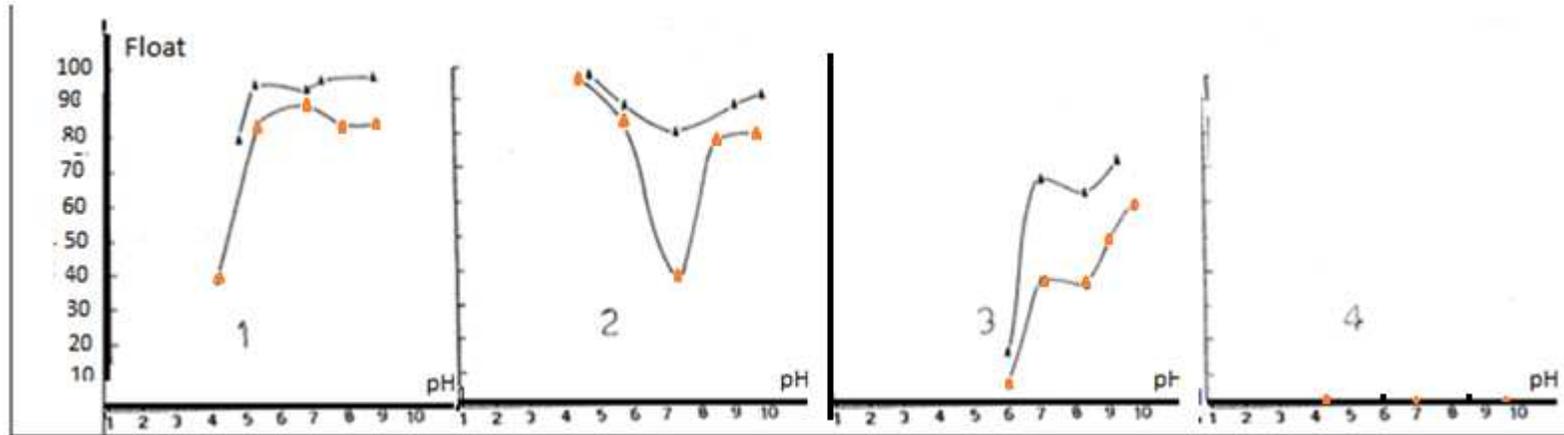


Figure 1. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Na dodecylsulfate (▲ 200 g/t ; △ 100 g/t) – Influence of pH

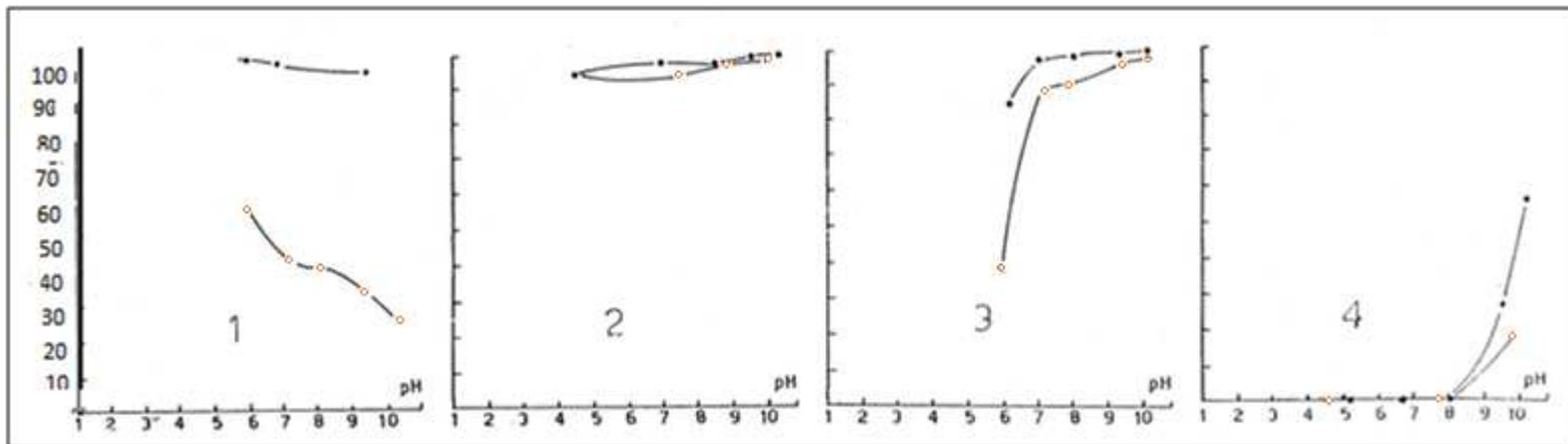


Figure 2. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Petronate L (● 1000 g/t; ○ 500 g/t) – Influence of pH

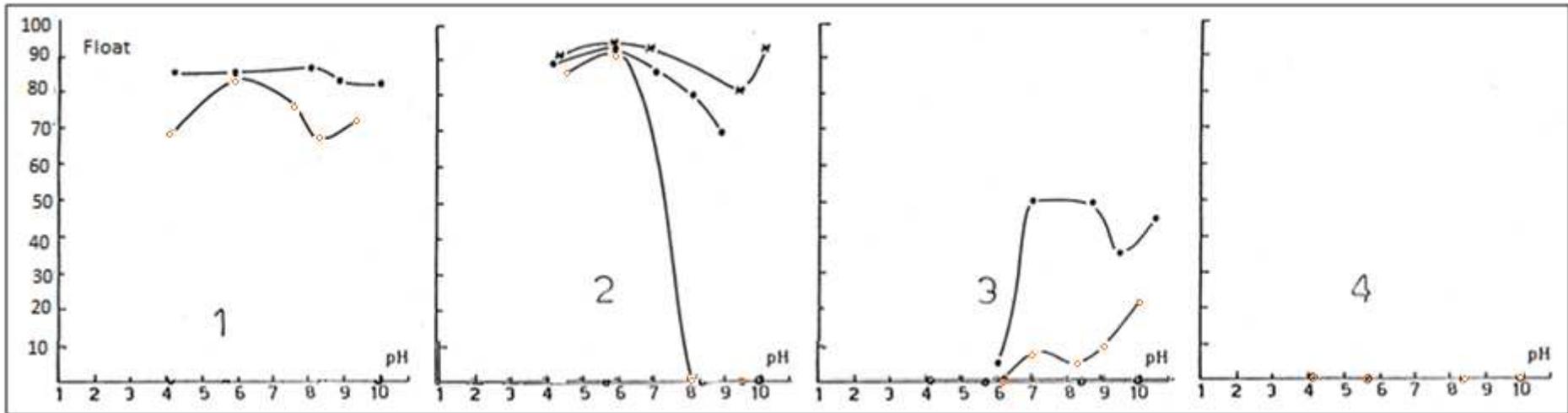


Figure 3. Flotation of barite (1), fluorite (2), calcite (3) and quartz (4) with Sulfofon T35 (* 2000 g/t ● 1000 g/t ;○ 500 g/t) – Influence of pH

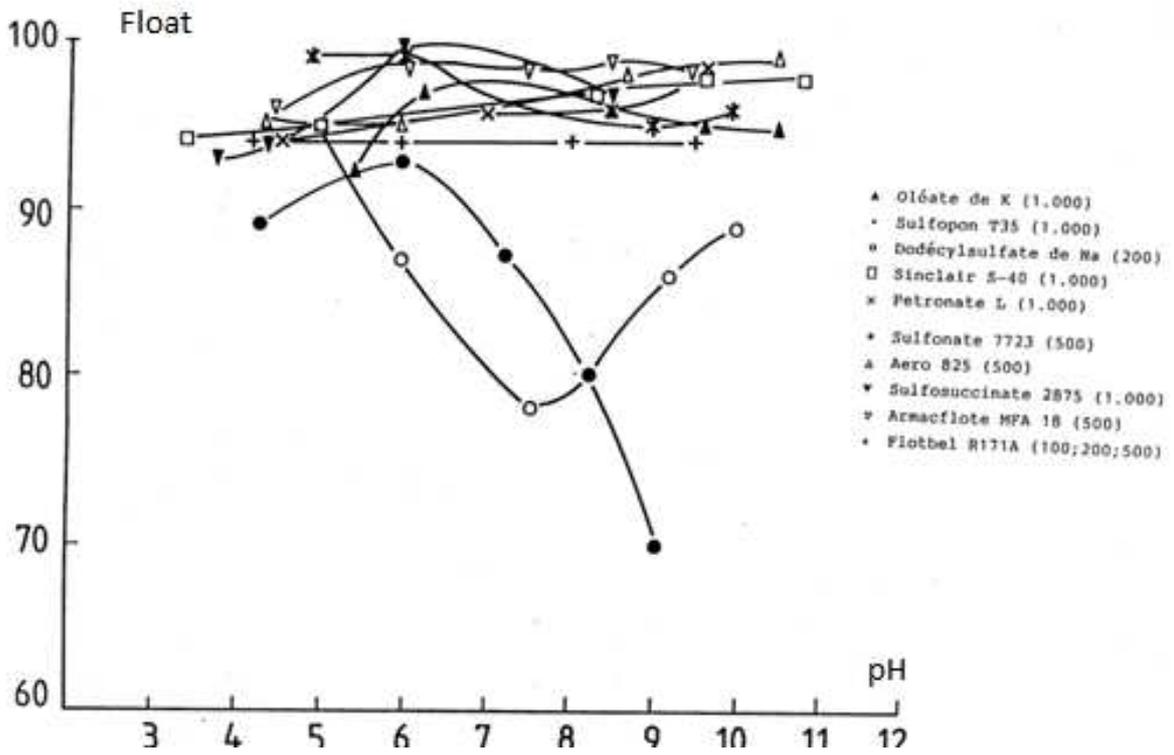


Figure 4. Flotation of fluorite in presence of various collectors – Influence of pH
 (the number between parenthesis indicate the consumption in g/t)

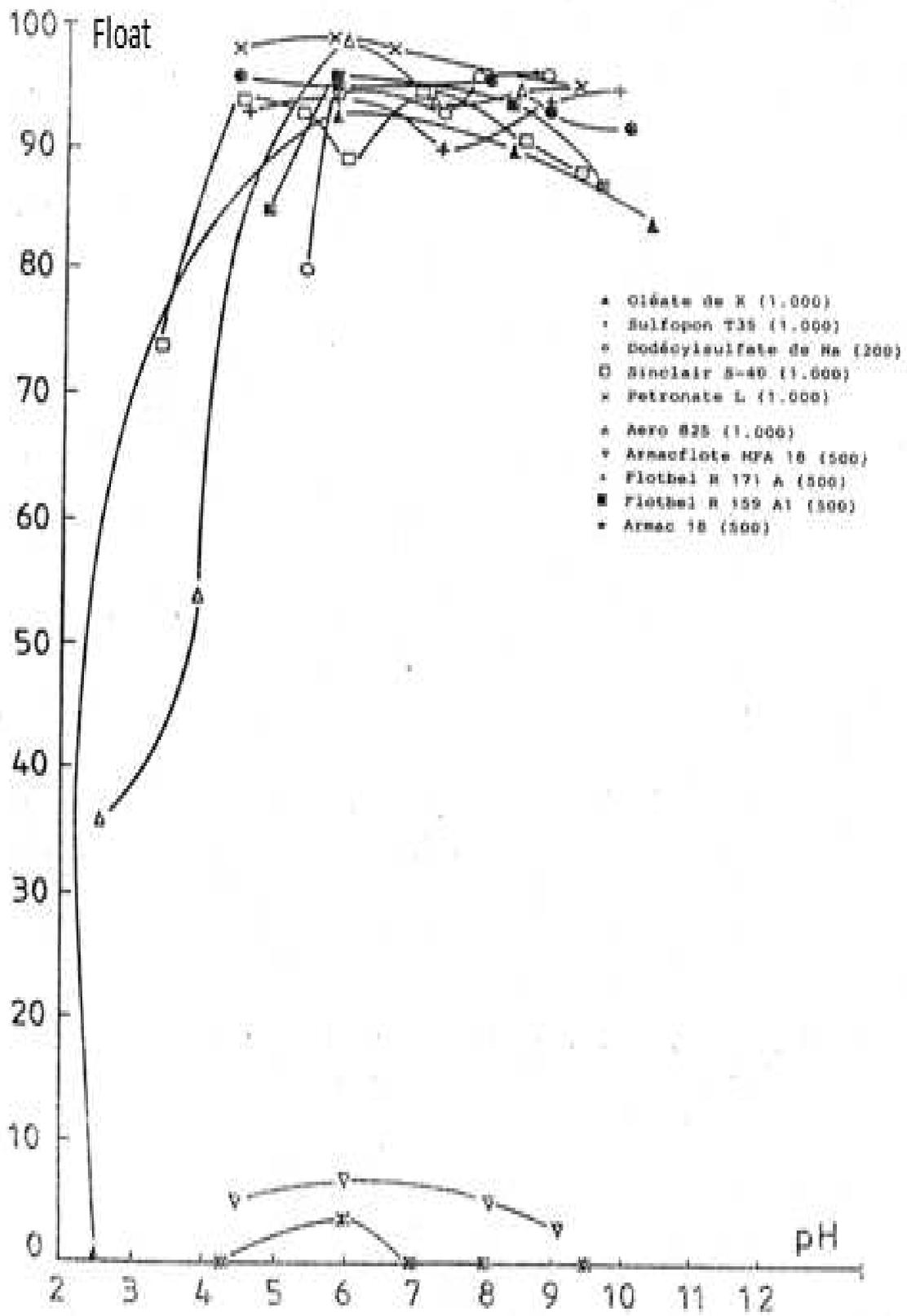


Figure 5. Flotation of barite in presence of various collectors – Influence of pH
 (the number between parenthesis indicate the consumption in g/t)

