

## STUDY OF SULFIDES MINERAL FLOTATION WITH XANTHATES: CONTROL PARAMETRES OF FLOTATION

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**Abstract:** The flotation of sulphide minerals and their modulation has been a subject of investigation for many years. The influence of pH,  $D_p$ ,  $D_b$  and xanthate concentration on the sulfide minerals floatability of is well known and it is usually used as one of the flotation control parameters.

In this study, we propose to make a theoretical and experimental study concerning the use of xanthate in the sulfides flotation processes (PbS-ZnS-FeS<sub>2</sub>). Sphalerite ( $D_p$ = 0,4443mm,  $D_b$ =0,1530mm) floted in pH range from 7-10.5 but galena ( $D_p$ = 0,3705mm,  $D_b$ =0.2000 mm) floted better only from pH 8 to 9.5.

Keywords: Flotation, Sulphide Minerals, Xanthate, Pulp

## Introduction

Flotation is a process of separation the mineral species which makes profitable the differences in their surfaces hydrophobia. The fundamental separation mechanism depends on the adsorption of an aqueous solution having properties on surfactant.

Flotation uses properties of minerals surface in order to return some of them selectively either hydrophobic subjects or absorbent. The ore, crushed is put in the form of pulp (mixture of particles and water) and contact with bubbles of air in agitated tanks known as: flotation cells. [1-2]

A large variety of chemical reagents is used, mainly to modify surface qualities of the particles. A significant amount of water is also necessary; the concentrated ore pulp is thickened, dried and sent in the metallurgical circuit of transformation (metal case of ore).

The interaction enters the metal sulphurized with xanthate is done by:

Chemical adsorption for the xanthic ion X

 $X^- \rightarrow X_{ads} + \acute{e}$ 

Xanthate reaction with sulphurized metal (MS) to produce metal xanthate  $(MX_n)$ 

$$MS + nX^{-} \rightarrow MX_{n} + S^{0} + n\acute{e}$$
  
$$MS + nX^{-} + 4H_{2}O \rightarrow MX_{n} + SO_{4}^{2-} + 8H^{+} + (6+n)\acute{e}$$

Xanthate oxidation to the dixantogene  $(X_2)$  on mineral surface

$$2X^- \rightarrow X_2 + 2\acute{e}$$



We choice the diagrams of flotation of oxidized and mixed ores lead-zinc depend on the report/ratio and the character of the ores lead-zinc and the existence of iron sulfide.

The ultimate goal of the regulation is not only to stabilize a process but also to optimize it and to increase economic efficiency by it. We could reach a regulation of an elevated level in the case of some concentrators, but success is still limited, because optimization can be realized only in factories that circuits reached a real balance [3-4].

## Equilibrium equation particle -air bubble under the flotation conditions:

The analysis of the forces acting during the fixing of the particle on the air bubble shows that the particles density is considerably different (water - particles).

In flotation foams about it the acting forces are:

- The flotation.force.
- The centrifugal force.

$$F_f = P_m \cdot \gamma_{\lg} \cdot \sin\theta \tag{1}$$

$$F_c = \rho_s \cdot V_m \cdot \gamma_c \tag{2}$$

*P*<sub>m</sub> : absorptivity Perimeter (cm);

 $\gamma_{lg}$ : Surface tension (liquid - gas) (dyn/cm);

 $V_m$ : maximum Volume of the particle (liquid volume to move) (Cm<sup>3</sup>);

 $\rho_s$  : particle Density (g/cm<sup>3</sup>);

- $\gamma_c$ : Acceleration (cm/s<sup>2</sup>);
- $\theta$  : The contact angle (degree).

During flotation we have:  $F_f = Fc$ 

$$P_m \cdot \gamma_{\rm lg} \cdot \sin \theta = \rho_s \cdot V_m \cdot \gamma_c \tag{3}$$

Let 's consider the cubic particle:  $V_{\text{max}} = d_{\text{max}}^3$  and  $P_m = 4d_m$ 

$$d_{m} = \sqrt[3]{\frac{4\gamma_{\text{lg}}\sin\theta}{\rho_{s}\gamma_{c}}} \tag{4}$$



The calculation of maximum diameter  $D_m$  introduced the concept of proportionality factor K (K < 1):

$$d_m = \sqrt[3]{\frac{4k\gamma_{\rm lg}\sin\theta}{\rho_s\,\gamma_c}} \tag{5}$$

## Dimension of the air bubble necessary to flotation:

The critical diameter of the air bubble is given by the following relation:

$$D_{critique} = \frac{6 \cdot \alpha \cdot d \cdot \rho_s}{\rho_l} \tag{6}$$

 $\alpha$ : Coefficient of mineralization of the air bubble characterizing the relation of the section of the surface of the mineral air bubble charged with particles (0.03-0.3).

 $\rho_s$ : mineral particles Density (=3.5-17.5g/cm<sup>3</sup>);

 $\rho_l$ : pulp Density (g/cm<sup>3</sup>);

d: the diameter (mm).

## Methods and Characterization of Minerals:

#### Sphalerite (ZnS):

System: cubic Density: d=3.5-4.2 Properties: fairly lasts, heavy, very fragile Cleavage: perfect (12faces) Colors: yellow with brown reddish Glare: hard or resinous Transparency: transparency with translucent Use: principal mineral of zinc. Galena (PbS): System: cubic Density: d=7.5-7.6 Properties: to tend, very door Cleavage: very perfect Colors: lead gray Glare: metal sharp



Transparency: opaque

Use: principal lead ores.

## Pyrite (FeS<sub>2</sub>):

System: cubic Density: d=5-5.2 Properties: last, very heavy, very fragile Cleavage: not Colors: yellow brass blade Glare: metal very sharp Transparency: opaque Use: sulphuric acid. [5-11]

## **Flotation Study** Calculation of the parameters influencing the sulfides flotation:

#### **1. Acceleration Influences:**

To carry out the reactions in heterogeneous medium require usually a device of agitation (according to the equation (5)). Its aime is to ensure the best possible contact between the components of a mixture and, if required, to regularize the temperature.

- the case of three minerals:





The figure (1) shows the particle diameter variation according to acceleration with

various minerals and it is noticed that the increase in acceleration supports the reduction in the flotable maximum galenite diameter, the sphalerite and the pyrite.

- For the galena (PbS):  $g = 400 \text{ cm/sec}^2$ ;  $D_m = 0.4103 \text{ mm}$ .
- For the sphalerite (ZnS):  $g = 400 \text{ cm/sec}^2$ ;  $D_m = 0.4909 \text{ mm}$ .
- For the pyrite (FeS<sub>2</sub>):  $g = 400 \text{ cm/sec}^2$ ;  $D_m = 0.4564 \text{ mm}$ .

#### 2. Contact angle Influences:

The diameter of the air bubble plays a very important part in the limitation of the contact angle, we note that the contact angle decreases considerably with the reduction of the contacts surface diameter of air bubble.

- The case of three minerals:



Figure 2. Particle diameter variation according to the contact angle to different minerals.

According to the figure (2) we can note that the increase in the contact angle teta supports the increase in the maximum flotable diameter for the three minerals, sphalerite and the pyrite with g=400 cm/sec<sup>2</sup>.

The calculation results show that:

- For galena (PbS): teta = $40^{\circ}$ ; D<sub>m</sub> = 0.3705mm.
- For the sphalerite (ZnS): teta =40°;  $D_m = 0.4443$ mm.
- For the pyrite (FeS<sub>2</sub>): teta = $40^{\circ}$ ; D<sub>m</sub> = 0.4132mm.

Under the industrial conditions; the time of contacts between the air bubbles and the solid is relatively short for the turbulent mode  $(10^{-3}sec)$ ; what supposes a minimum with the value of the angle contact necessary to preserve favorable kinetics of flotation (we take the contact angle between 30° and 40°). [12-17]

## 3. Density Influence on the air bubbles diameter:



Figure 3. Variation of the critical air bubble diameter according to the density.

Figure (3) shows variation of the critical diameter of the air bubble according to the density of various minerals, and we can note that the diameter of the air bubble increases according to the density.



## 4. Density Influence on the air bubbles diameter with different mineralization coefficients:

Figure 4. Variation of the critical air bubble diameter according to the density with different mineralization coefficients.

Figure (4) shows variation of the critical diameter of the air bubble according to the density with different mineralization coefficients, and we can notice that the increase in the mineralization coefficients supports the increase in the air bubble diameter and the density.

The calculation results show that the minimal critical diameter of the air bubble should not be lower a:

- 0.2000 mm for the flotation of PbS to a maximum diameter of 0.3705 mm
- 0.1530 mm for the flotation of ZnS to a maximum diameter of 0.4443 mm
- 0.1910 mm for the flotation of FeS<sub>2</sub> to a maximum diameter of 0.4132 mm



5. Maximum size of various galenite particles (PbS):



Figure 5. Maximum size of various galenite particles.



6. Maximum size of various sphalerite particles (ZnS):



Figure 6. Maximum size of various sphalerite particles.



7. Maximum size of various pyrite particles (FeS<sub>2</sub>):



Figure 7. Maximum Dimension of various pyrite particules.

According to figures (5), (6) and (7) it is noted that the increase in acceleration causes the maximum reduction in the diameter of the various flotable mineral particles on bubbles identical (even dimension) under different flow condition ; under all the conditions the maximum size of the particles inversely proportional to the density of floted mineral.

The results of calculates show:

- For galenite (PbS): teta =40°; Dm=0.3705mm.
- For the sphalerite (ZnS): teta = $40^{\circ}$ ; Dm=0.4443mm.
- For the pyrite (FeS<sub>2</sub>): teta =40°; Dm=0.4132mm. [18-21]



# Physicochemical modeling of the pH pulp action on the xanthate concentration necessary in sulphuretted minerals flotation:

The regulation of the pulp pH is one of the essential selectivity parameters of the process of extraction by flotation of the polymetallic ores. The value of the xanthate concentration necessary is important for the regulation of the flotation process and also for the development and the adjustment of a regulation automatic system of the reagent consumption.

**Table 1.** Concentrations values of ion xanthates in solution necessary to the appearance of lead xanthate on the galenite surface.

рН	Ethyl xanthate		Isopropyl xanthate		Butyl xanthate	
	mol/l	mg/l	mol/l	mg/l	mol/l	mg/l
7	1,4.10-6	0,2	<i>4,3.10</i> <sup>-7</sup>	0,06	1,2.10-7	0,02
8	4,5.10-6	0,5	1,4.10-6	0,2	4,0.10-7	0,06
9	1,4.10-5	1,7	4,3.10-6	0,6	1,2.10-6	0,2
10	<i>9,5.10</i> -5	11,5	2,9.10-5	3,9	8,5.10-6	1,3
11	3,2.10-4	38.6	<i>9,8.10</i> -5	13,2	2,9.10-5	4,3
12	1,5.10 <sup>-3</sup>	181,0	4,6.10-4	62,0	1,3.10-4	19,3

Calculation is made on the basis of solubility of ethyl xanthate of K lead equalizes to 1,  $7.10^{-7}$ , isopropyl xanthate equalizes to 1,  $58.10^{-18}$ , on the other hand the butylic xanthate of lead equalizes to 1,  $35.10^{-19}$ .



Figure 8. pH variation according to different xanthate types.

#### Flotation and repair mode of sulphuretted minerals:

The selective flotation of sulphuretted lead minerals starting from the sulphuretted and mixed ores lead-zinc (Zavar Factory in India, Boubekkeur in Morocco, Bouguerou in Italy, Almaliskaya in Russia) with use in quality of depressing for sulfides of zinc and iron: the cyanide (2-100gr/tonne) and the zinc sulfate  $ZnSO_4$  (30-700gr/tonne) in the mode cheridane.

At the time of the existence in the sphalerite and pyrite ore of with a weak activity with respect to flotation (Factory Broken Hill), it is necessary to introduce into the floatation cycle of zinc sulfate or a small quantity of cyanide, soda is to float the lead minerals with low fuel consumption of flotation reagent. The suppression of the natural buoyancy of zinc at the time of the cycle of lead-zinc flotation can be reached by addition of a mixture of cyanide and ferrous sulfate. [22]

In the majority of the cases the lead flotation is carried out in medium slightly basic (optimum condition for buoyancy suppression of zinc and iron per cyanide); pH=7-9, creates by soda (100-300gr/tonne), to exclude the suppression from galenite flotation on oxidized surface.

The addition of collector in the crushers supports the buoyancy activation of the galenite and decreases the sphalerite buoyancy.

For the process optimization can be used the automation system illustrated on shape:



Figure 9. Autoimmunisation systems control and regulation of reagents consummation in the flotation.



- 1- Detector;
- 2- Sodium sulfide batcher;
- 3- Sodium sulphite batcher;
- 4- Zinc sulfate batcher;
- 5- Sulfate batcher of ammonia;
- 6- Xanthate batcher;
- 7- Crushing;
- 8- Flotation;
- 9- Regulation;
- 10- Detector or sensor of concentration of the sulphuretted ions;
- 11- Sensor of pH;
- 12- Sensor of concentration of ions KX-;
- 13- Building block working with the function:
- 14- Building block working with the function:
- 15- Lime dosage;
- 16- Temperature regulator;
- 17- Sensor of concentration of the calcium ions;
- 18- Building block working with the function:

The use of cyanide and zinc sulfate in ore enriching is not in favor of a sufficient selectivity and at the termination end of the lead floatation operation, an activity of sphalerite flotation is noticed. The researchers [40] deduce that most stable zinc sulfide depression is reached by sodium sulfide addition with sodium sulphite in the crushing or flotation cycle. [23-26]

#### Conclusion

The results of calculate of the physicochemical parameters influence on the sulfides flotation:

- 1- acceleration Influence (g = 400 cm/sec2):
  - $D_m$  (PbS) =0.2628 mm
  - $D_m$  (FeS<sub>2</sub>) =0.3083 mm
  - $D_m$  (ZnS) =0.3439 mm.
- 2- contact angle Influence (teta =  $40^{\circ}$ ):
  - D<sub>m</sub> (PbS) =0.2255 mm
  - $D_m$  (FeS<sub>2</sub>) =0.2656 mm
  - $D_m(ZnS) = 0.2962 \text{ mm.}$

Under the industrial conditions, the particle - bubble contact time is relatively short for the turbulent mode ( $10^{-3}$  dryness).

- 3- density Influence on the critical diameter of the air bubbles (N = 0.15):
- 0.2000 mm for the flotation of PbS to a maximum diameter of 0.2255 mm
- 0.1910 mm for the flotation of  $FeS_2$  to a maximum diameter of 0.2656 mm
- 0.1530 mm for the flotation of ZnS to a maximum diameter of 0.2962 mm

- 4- The addition of foaming on the other hand causes the reduction of the rise speed of the air bubbles in pure water the speed of rise increases abruptly.
- 5- Xanthate concentration necessary for the galenite flotation:
  - equalize at least necessary [KX<sup>-</sup>], guaranteeing the appearance of lead xanthate on the galenite surface for a given value of pH;
  - it is the same one for galenite of the various layers;
  - can be calculated for each value of pH according to the equation (4) or (5). •

On the technological level the elimination of salts and shlamms up to 6% supports the stabilization of the enrichment operations succession with reduction in the concentration of reagents, increase in the quality of concentrated and of metals extraction degrees.

The choice of the flotation diagrams of the oxidized and mixed ores lead-zinc depends on the report/ratio and the ores lead-zinc character and the existence of iron sulfide.

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## REFERENCES

[1]: AbramovA.A., Ribakov, V.V, Enrichissement des minerais des métaux nobles et rares dans le pays d'asie, d'afrique et d'amerique latine, Moscou ; p.108-140,1991.

[2] : Abramov.A.A, Modélisation physico-chimique des systèmes de flottation; Moscou, p.6-14,1977.

[3] : AbramovA.A., Avdokhin V.M., Oxydation des Minéraux Sulfurés dans les Procédés d'enrichissement, Moscou, "NEDRA", p.161-167, 1989.

[4]: Avdokhin V.M., Oxydation des minéraux Sulfurés dans les procédés d'enrichissement, p. 123-131; 161-167, Moscou, Nedra, 1989.

[5] : Adamov E.B., Evaluation Technologique des ressources Minérales, Méthodes de Recherches, Moscou, p.76-84, 1990.

[6]: Baranov V.F., Guide de Projection des Fabriques d'enrichissement, Tome 1, Moscou, "NEDRA", p.290-293, 1988.

[7] : Bartton,D.H.R;Mc combie;S;W;J.Chem.Soc,Perkin trans I,1975,1574-1585.p.7-9,2002.

[8]: Bogdanov O.S., Maxinov, Théorie et Technologie de Flottation, Moscou, "NEDRA", p.114-116, 1980.

[9]: Cevher Hazrlama El kitab, Editors; Prof.Dr. Guven Anal, Prof.Dr.Gunduz Ateok, June, p.122-125, 1994.

[10] : Choubov L.Y., Ivankov S.I, Réactifs de flottation dans les procédés d'enrichissement des minerais, Tom 1, p.79-91, Moscou "NEDRA",1990.



[11] : Choubov L.Y., Ivankov S.I, Réactifs de flottation dans les procédés d'enrichissement des minerais, Tom 2, p.180-231., Moscou "NEDRA",1990.

[12] : Eren Cancer ORHAN;Sulfide Flotation; Hacettepe Univercity; Ankara;Turkey, p.1-5, 15 October 1997.

[13]: Full public report .Sodium Ethyl Xanthate. Priority exiting chemical N°5.Australian government publishing service .Canberra, p.1-16, May 1995.

[14]:Gaudin. A.M., Flottation, Memorial Volum, p.110-112, New York, 1976.

[15] :Glembotski V.I., Flottation, p.101-110, Mouscou, "NEDRA", 1973.

[16]: Kelly,E.G, Spottiswood,D.J.Introduction to mineral processing, John Wiley and sons,p.75-79, 1982.

[17]: Keller W.D., Rickett E.E., Absorption Of Infred Radiation By Powdred Silicamineral, "Amer-Mineral", p.174,1952.

[18]: Klarck.S, Mémoire des Constantes Physique des Roches, Mir, p.541, 1969.

[19]: Melik.GayKazyan V.I.,Abramov A.A., Méthodes de recherche dans les procédés de flottation, p.128-138, Moscou."NEDRA", 1990.

[20]: Melik.GayKazyan V.I; Bases physicochimique en théorie de flottation. Moscou, p.22-50, 1983.

[21]: Neeraj K.Mendiratta, Kinetic Studies of Sulfide Mineral Oxidation and Xanthate Adsorption ;Blacksburg, Virginia , p.25-28, May 2000.

[22]: NICNAS, Sodium Ethyl Xanthate, Priority Existing Chemical, Secondary Notification Assessment, Report N° 5S,p. 20-22, February 2000.

[23]: Pierre Blazy; El Aid Jdid, Flottation- Mécanismes et Réactifs; Technique d'ingénieur, France, j3350, p.2-7, 1966.

[24]: Pierre Blazy; El Aid Jdid, Flottation- Mécanismes et Réactifs; Technique d'ingénieur, France, j2<sub>2</sub> [j3350, j3360], p.2-17, 1966.

[25]: RaXtchev A.D., Nouvelles méthodes physico-chimiques d'étude des minéraux, p.220-221, Moscou."NEDRA", 1989.

[26]: Sodium Ethyl Xanthate. Chapitre 6, d'autre technique de précipitation .Fin de support 1110-1-4012., p.116-120, 15 Novembre 2001.

[27]: Zongfu D.and John Ralston, Particule-Bubble attachement in mineral flotation ; J.C.I.S, Elsevier Science 217, p.70-76, 1999.