



## Флотационное обогащение свинцово-флюоритовой руды: влияние характеристик руды и кинетики флотации

### Upgrading of a lead-fluorspar ore by flotation: effects of ore characteristics and kinetics of flotation

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Компания British Fluorspar Ltd. (BFL) разрабатывает свинец-флюорит-баритовое месторождение в районе Peak Lake (Великобритания), где флюорит – главный продукт, а свинец и барит – попутные продукты. Недавно проведённый анализ концентрата  $\text{CaF}_2$  показал высокие содержания вредных примесей (например, Pb, P, S и As), которые влияют на качество продукта. Исследования измельчаемости выявили, что сырьё чрезмерно измельчается до стадии флотации, причём отмечается значительное выщелачивание  $\text{P}_2\text{O}_5$  в основном из-за присутствия флюоритового концентрата.

Данные, полученные в ходе опытной чанной флотации, показали, что при этом извлечение свинца возрастает с 2,33 до 15,03 %, содержание  $\text{Na}_2\text{S}$  снижается до 100 г/т и pH – до 9 в схеме обогащения окисленной свинцовой руды, а также имеет место изменение концентрации  $\text{P}_2\text{O}_5$  на стадии флотации флюорита с 87 до 91 %, который извлекается в хвосты с использованием 200 г/т  $\text{CaCl}_2\text{-CuSO}_4$  в качестве «депрессора» фосфатных минералов.

Ключевые слова: флотация флюорита, свинцово-флюоритовое сырьё, барит, фосфор.

British Fluorspar Ltd (BFL) operates a lead-fluorite-barite deposit located in the Peak Lake District (Derbyshire, UK) with fluorspar as the main product and lead and barite as by-products. Recent analysis of the  $\text{CaF}_2$  concentrate showed high values of deleterious elements such as Pb, P, S and As, which affect the quality of the product. Grindability studies showed an overgrinding of material prior to the flotation stage with high liberation of  $\text{P}_2\text{O}_5$  mainly to the fluorspar concentrate.

Data obtained from bath flotation test indicated an improvement of lead recovery from 2.33% to 15.03%, decreasing  $\text{Na}_2\text{S}$  to 100g/t and pH to 9 in the lead oxide circuit and a depression of  $\text{P}_2\text{O}_5$  in the fluorspar flotation stage from 87% to 91% recovered in the tailings using 200 g/t of  $\text{CaCl}_2\text{-CuSO}_4$  as “depressant” of phosphates related minerals.

Keywords: fluorspar flotation; lead-fluorite; barite; phosphorus.

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\* Our close friend and colleague Dr. Chris Broadbent coordinated this manuscript to its final stage but sadly passed away prior to its publication. We dedicate this work to him.

Наш близкий друг и коллега доктор Крис Бродбент координировал эту рукопись до последней стадии, но, к сожалению, скончался до ее публикации. Мы посвящаем эту работу ему.

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## 1. INTRODUCTION

Recently, Europe has become increasingly reliant on the import of non-energy solid raw materials although historically Europe has been in front of many innovative projects in mining and mineral processing especially those ones focusing on improvement of competitiveness in the raw materials' sector.

The EU has created a list of raw materials (CRMs) critical to Europe's economy. The CRM's are materials of high importance with a high risk associated with their supply.<sup>1</sup> Fluorspar was included in the list of critical raw materials (CRM) in 2010–2011 due to the risks of supply shortage and their impacts on the economy are higher compared with most of the other raw materials. A high share of the worldwide production mainly comes from a handful of countries; in the fluorspar case China and Mexico<sup>2</sup>. Fluorspar remains on the EU CRM list issued in September 2017<sup>3</sup> Asia Pacific accounted for over 60% of the market share in 2014 and is projected to be the fastest growing market in coming years, due to rising demand for fluorspar in steel and aluminium industries. Furthermore, demand of hydrofluoric acid and its derivatives for usage in electronic appliances such as refrigerator, air-conditioners, and other cooling equipment is estimated to boost the consumption of fluorspar in Asia Pacific. Demand for fluorspar in North America and Europe is expected to be sluggish owing to slower growth rate in steel production and aluminium production industries. Each one these industries requiring an ever-higher quality of the final product.

Growing demands on high quality of fluorspar products specifically with lower contents of contaminant elements creates a need for -

a better mineralogical and metallurgical understanding of the ore (s).

The processing of fluorite ores especially those that contain calcite minerals is challenging due to the fact that flotation properties of fluorite, calcite, and other gangue minerals are similar. (Filipova, et al., 2014)

Typically, in the commercial operations, fatty acid collectors (Fuerstenau et al., 2006) are used in fluorspar flotation and water glass as a depressant (Zhou et al., 2013) of silicate gangues; the ore pulps are heated to 35–85 °C in the system (Crozier, 1992). Normally fatty acids are saponified in alkaline medium (i.e. NaOH). Most recently fatty acids are emulsified with the use of a surfactant plus fuel oil. (Baldwin & Wittcoff, 1955)

The type of fatty acid plays an important role in both selectivity and recovery of fluorspar. The activation of fluorspar is (Zhang & Song, 2003) affected by the reaction of an unsaturated fatty acid with the calcium atom of calcium fluoride to form an insoluble film of calcium oleate on the surface of the fluorspar particles. (Rao & Forssberg, 1991)

Unsaturated fatty acids high in oleic and linoleic acids of both vegetable and animal tallow origin are used. The fatty acids of vegetable origin have a typical oleic acid content of about 55%, linoleic 40% and resin acids 1–5%. Fatty acids of tallow origin have an oleic content of 70–80% with 5–8% linoleic and other unsaturated acids. Fatty acids high in oleic acid tend to be a little weak, and those of a resin content of more than 4% tend to make a strong froth of low selectivity. Worldwide, there is a tendency to adapt the flotation process to the fatty acid most readily available. Fluorspar flotation requires the crowding out of gangue minerals from the froth, with a minimum use of frothers. MIBC or similar alcohol frothers are sometimes used to liven up a heavy dead froth to facilitate its removal from the flotation cells. Collectors containing 1–3% of resin acids generally produce optimum froth conditions and no supplemental frothers are necessary. (Weiss, 1985; Bulatovic, 2015)

The pH is varied over a wide range in fluorspar flotation from 8.5–10, with most mills operating in the range of 9.0–9.3. A stronger float results at a

<sup>1</sup> Report on critical raw materials for the EU (European commission document, May 2014)

<sup>2</sup> Communication from the Commission to The European Parliament, The Council, The European Economic and Social Committee and The Committee of the regions, Final Report, 2011

<sup>3</sup> Communication from the Commission to The European Parliament, The Council, The European Economic and Social Committee and the Committee of the regions on the 2017 list of Critical Raw Materials for the EU 13.09.17

high pH, but with a coarse grind can still be selective. Once the reagent combination is established it is necessary to hold to a closely controlled pH. Soda ash is used for pH control, although sodium silicate when used also contributes to alkalinity. (Weiss, 1985)

Caustic soda has been used on siliceous ores and as a supplement to soda ash.

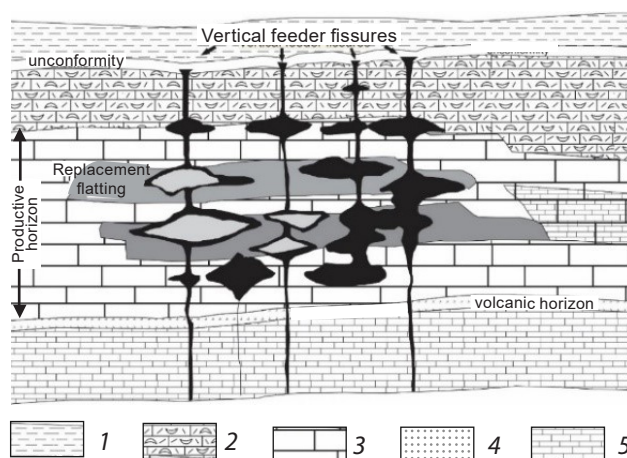
Temperature is an important tool in fluor spar flotation. Temperatures in the range of 25–90°C are used. Below a temperature of 24°C the fluor spar float is slow and less selective than a higher temperature (Gao et al., 2021). Live steam is injected into the mineral slurry in the conditions and at various points in the flotation circuits. Temperatures above 82°C are used in the boiling process. In this process, live steam is injected into the conditioner, with fatty acid, which results in a strong, selective activation of fluor spar. A heavy, matted froth is produced from which gangue minerals are selectively rejected.

Fluor spar flotation feed receives preliminary treatment in conditioners where reagents are added for pH regulation and gangue depression and dispersion. Live steam is injected for maintaining optimum temperature. Two conditioners in series are sometimes used ahead of the rougher float. Reagents for pH control and dispersion are added to the first conditioner and gangue depressing reagents are added to the second. The flotation feed is then ready for the addition of fatty acid collector at the flotation cells. Conditioning time is generally in the range of 8–15 minutes. (Weiss, 1985)

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

### 2.1 Ore samples

Samples from mineral processing streams from Cavendish Mill (BFL) processing plant in the UK were used during this investigation. 10kg from the Pb flotation feed stream and 15kg from the CaF<sub>2</sub> flotation feed were taken in a period of 3hr, the shortest time possible was used to reduce the variability in the plant feed. These samples were sThe plant feed consists of material from mineral deposits in the South Pennine Orefield (SPO). These have been deposited in dilatant fractures,



**Fig. 1. Fissure vein fill structures and replacement scheme for BFL Mine, UK:**

1 – Shale Gint (Kinderscout Group); 2 – Limestone (Eyam Group); 3 – Upper limestone (Monsal Dale Group); 4 – Tuff (Monsal Dale Group); 5 – Lower limestone (Monsal Dale Group)

Рис. 1. Структура жильного выполнения трещин и схема замещения для рудника BFL:

1 – Шале Гинт (Kinderscout Group); 2 – Известняк (Eyam Group); 3 – Верхний известняк (Monsal Dale Group); 4 – Туф (Monsal Dale Group); 5 – Нижний известняк (Monsal Dale Group)

dissolution cavities and zones of metasomatic replacement (Fig. 1). The host rock consists almost exclusively of shallow water carbonates of Asbian-Brigantian (late Dinantian) age (Ford, 2000). The primary mineralization comprises only fluorite, barite, calcite, galena, and sphalerite. Iron sulphides such as pyrite, chalcopyrite and bravoite, are found in microscopic amounts within the main minerals. Nearly all other mineral types described from the SPO are secondary in origin, having resulted from oxidation of the primary minerals. (Quirk, 1993)

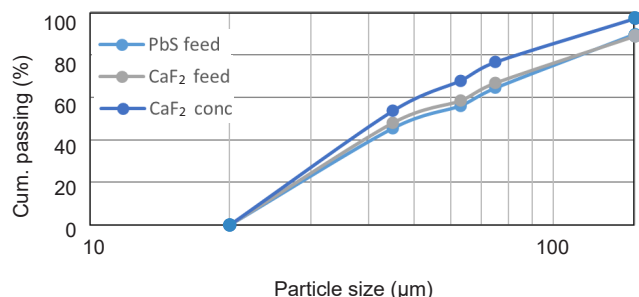
### 2.2 Current plant conditions

Bulk concentrate recoveries in the plant for lead and fluorite varies from 85 to 90%. The lead recovery is 90% and around 6% is lost in the CaF<sub>2</sub> concentrate and 4% in the BaSO<sub>4</sub> concen-

trate. The Pb content in the  $\text{CaF}_2$  concentrate represents a contaminant. The  $\text{CaF}_2$  recovery varies between 80 to 85%.

The particle size distribution for the flotation feed is shown in the Fig. 2. There is a slight difference between the PbS feed flotation curve and the floated product curves, this difference could be related with kinetics of flotation and the liberation degree of targeted minerals. The sulphides which should float in the first flotation stage due to its properties are more brittle than gangue minerals and it is believed to be finer than the gangue minerals which considering that optimum flotation can be related with mineral density, fine particles of galena should float very well. However, as it is possible to observe in the PSD curve, tailings of PbO flotation ( $\text{CaF}_2$  feed) conserve the same distribution and the initial flotation feed and the fine particles are floating better in the fluorite flotation stage. It could mean that fine particles of galena are interlocked with fluorite as suggested in the MLA study done previously (29% of lead floated in the fluorite concentrated was  $< 10 \mu\text{m}$ ).

It was not possible to sample the tailing stream so the effect of particle size in flotation could not be evaluated.



**Fig. 2. Particle size distribution curves for PbS feed,  $\text{CaF}_2$  feed and  $\text{CaF}_2$  concentrate**

Рис. 2. Кривые распределения размера частиц для сырья PbS,  $\text{CaF}_2$  и концентрата  $\text{CaF}_2$

### 2.3 Chemical reagents

Sodium Isopropyl Xanthate (SIPX), sodium sulphide ( $\text{Na}_2\text{S}$ ), MIBC, sodium carbonate, causticized dextrin, sodium metasilicate, tan-X, oleic acid and sodium carbonate were all high-grade chemical reagents.

### 2.4 Experimental procedures

A 2000 ml Denver sub-aeration flotation cell was used for carrying out the flotation tests of samples. A pulp with 30% solids of samples were added to the cell. The pH of the pulp was adjusted for 3 minutes at pH value of 10.5 for most of the test and varied according to the parameters needed and at temperature value of  $20^\circ\text{C}$  during conditioning and flotation by continuously adding the lead and fluor spar reagents. After 3 minutes of mixing the required amount of collector (SIPX) and frother (MIBC) was added, and conditioning continued for three more minutes in absence of air flow. Air was then introduced into the cell and flotation continued until barren froth was observed (2–3 min). The flotation products were collected, filtered, washed, dried, weighed and analysed by XRF.

## 3. RESULTS AND DISCUSSION

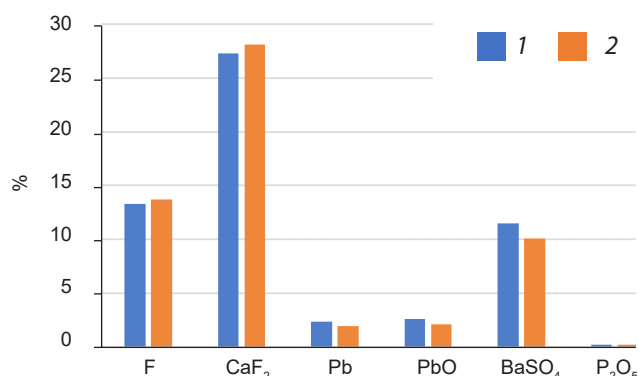
### 3.1 Lead sulphide and lead oxide flotation

When parameters as the mass flow and the material in feed are fixed, the relation between them can be estimated from the grade vs. recovery curves. The performance of the flotation process will move along these curves when the different parameters vary in the tests.

Test FT1 is a downscale of the current process in flowsheet used at Cavendish Mill and is the starting point for the comparison of the tests. Chemical analysis results from products were used to compare the head grade from the sample with the back calculated grade (Fig. 3.). Relative error was calculated (Table 1) as an indicator of how good back calculated results are relative to the head grade of the sample. Back calculated results and head grade of sample do not present a big difference between them, and its similarity indicates that there was no significant experimental error during the flotation procedure.

#### 3.1.1 Effect of different reagent's dosage

Tests FT1 to FT3 (Table 2) on PbS flotation sample, showed that the current conditions of the plant are the more suitable dosage for the PbS/PbO flotation in terms of high grade and high recovery.

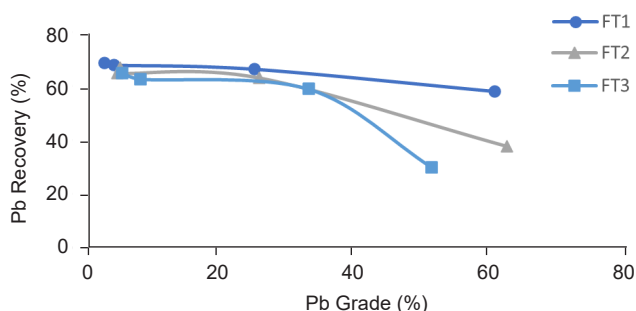


**Fig. 3. Head grade sample vs Head grade from products BC = back calculated in lead flotation:**  
1 – Head Grade Sample (F); 2 – Head Grade from product (BC)

Рис. 3. Образец головного продукта в сравнении с содержанием в головном продукте, BC = обратный расчёт при флотации свинца:

1 – Head Grade Sample (F); 2 – Head Grade from product (BC)

However, as the process simulated two different flotation stages for lead sulphide and lead oxide the selectivity of rougher flotation for lead was examined on grade-recovery curves with cumulative values of 2 to 10 minutes. Following the concept of selective concentration, test FT3 represents more selectivity for lead recovery in the process as shown in the Fig. 4. At industrial scale in Cavendish mill, it is important to achieve higher and selective recovery than higher grades. The



**Fig. 4. Grade vs Recovery curve – PbS/PbO flotation different reagent's dosage**

Рис. 4. Кривая содержания/извлечения – различное количество реагента для флотации PbS/PbO

**Table 1. Head grade sample vs head grade from products – back calculated in lead flotation (%)**

Табл. 1. Образец головного продукта в сравнении с содержанием в головном продукте – обратный расчёт при флотации свинца, %

|                              | F     | CaF <sub>2</sub> | Pb    | PbO   | BaSO <sub>4</sub> | P <sub>2</sub> O <sub>5</sub> |
|------------------------------|-------|------------------|-------|-------|-------------------|-------------------------------|
| Head grade sample (F)        | 13.32 | 27.34            | 2.39  | 2.58  | 11.52             | 0.19                          |
| Head grade from product (BC) | 13.7  | 28.11            | 1.95  | 2.1   | 10.06             | 0.18                          |
| Relative error (BC-F)/F      | 0.03  | 0.03             | -0.18 | -0.19 | -0.13             | -0.05                         |

curve for FT1 seems to be constant but non-selective for sulphides.

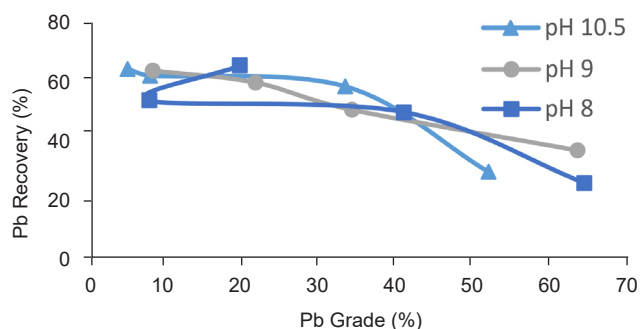
### 3.1.2 Effect of the pH

It is known that galena (main sulphide mineral in the ore) can float at pH 6.5 and higher. Altering pH from that used currently in the plant was tested to achieve a high recovery of lead and lower contaminants in the concentrate. The flotation tests (FT3, FT4 and FT6) were designed in a way that if successful it did not affect subsequent flotation stages.

**Table 2. Reagent's dosage (g/t) for different flotation tests**

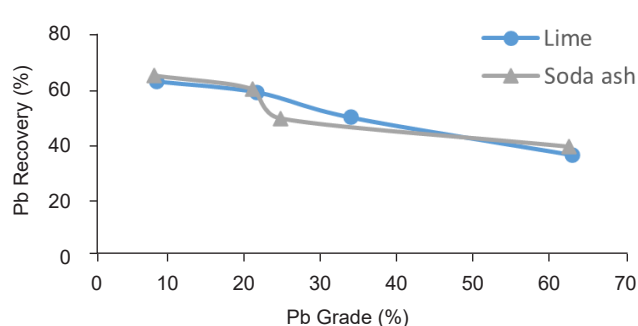
Табл. 2. Количество реагента (г/т) для различных опытных флотаций

| Test | pH   | Lime | SIPX | MIBC | Na <sub>2</sub> S |
|------|------|------|------|------|-------------------|
| FT1  | 10.5 | 310  | 350  | 30   | 200               |
| FT2  | 10.5 | 310  | 150  | 25   | 550               |
| FT3  | 10.5 | 240  | 150  | 25   | 100               |



**Fig 5. Grade vs Recovery curve – PbS/PbO flotation at different pH**

Рис. 5. Кривая содержания/извлечения – флотация PbS/PbO при различном pH



**Fig 6. Grade vs Recovery curve – PbS/PbO flotation with different pH regulators**

Рис. 6. Кривая содержания/извлечения – флотация PbS/PbO с различными регуляторами pH

Tests FT3, FT4 and FT6 were performed at pH 10.5 (slightly above galena critical pH), 9 and 8 respectively and with the same reagent's dosage as the FT1 (current conditions of the plant).

The negative effect on the lead sulphide flotation at pH 8 is observed, where the recovery is significantly lower and the lower grade of Pb decrease from the lead sulphide to the lead oxide flotation concentrate. There is a slight difference in recovery between pH 10.5 and 9 with 63.76% and 63.20% respectively. In terms of grade, as shown in the Fig. 5 it is possible to achieve a higher grade of Pb at pH 9 positioning this parameter as the most suitable for the flotation of lead sulphides and lead oxides present in the Milldam ore.

However, maintaining a pulp at a particular pH value does not necessarily provide information regarding the chemistry changes occurring within the plant.

### 3.1.3 Effect of different pH regulator

Currently, Cavendish Mill uses soda ash as the pH regulator due to its effectiveness in fluorite flotation, however, the lead flotation tests were performed with lime as the most common pH regulator in sulphide flotation. In order to estimate if there are any effect in the flotation process changing the pH regulators test FT4 and FT7 were performed.

Even when the grade-recovery curves (Fig. 6) present a similar trend, it was found that soda ash

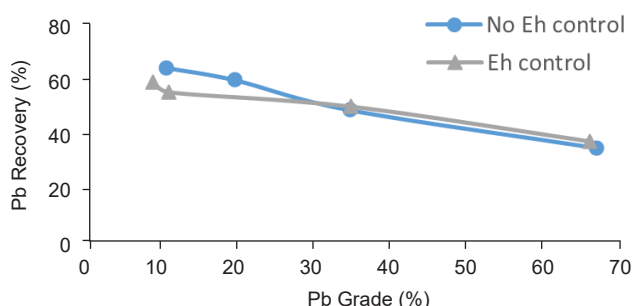
affects the Pb oxide flotation with a decrease in both lead grade and recovery.

### 3.1.4 Effect of Eh control in PbO flotation

The measurement and control of other pulp physical chemistry parameters (Eh, dissolved oxygen and temperature) in base metal flotation plants is somewhat limited.

Greet et al. (2006) suggested that it has been recognized for some time that Eh may impart considerable information about sulphide mineral system under investigation. Authors have dedicated their work to prove the relationship between sulphide minerals surfaces and electrochemical nature (Woods, 1976). Several works demonstrated the possibility of using Eh as a tool to identify mineral oxidation and adsorption of collectors (Winter and Woods, 1973; Woods et al., 1990; Woods et al., 1992). Nevertheless, it is important to mention that Eh readings are better to use in laboratory scale but not in flotation plants, considering that those readings obtained correspond to a mixed potential (Woods, 1976).

It was possible to observe during lab scale that adding sodium silicate to the pulp keep values of Eh stable. The Eh was then monitored adding sodium silicate until a value of -50 was stabilized in the pulp during conditioning time of PbO flotation. However, it is possible to observe that when Eh was controlled the grades and recoveries of lead decreased (Fig. 7).



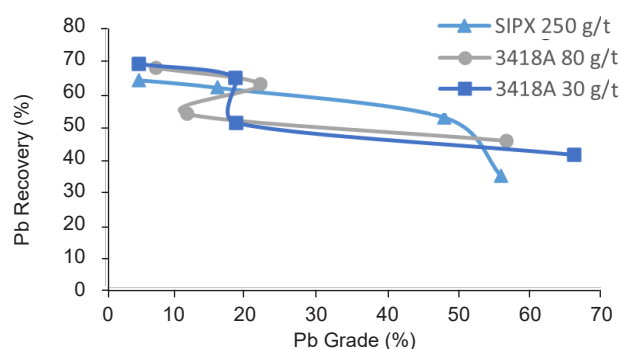
**Fig 7. Grade vs Recovery curve – PbS/PbO flotation controlling Eh/mV**

Рис. 7. Кривая содержания/извлечения – флотация PbS/PbO с контролем Eh/mV

### 3.1.5 Effect of combination of reagents

As mentioned previously, the reagents for the lead sulphide flotation are added in the ball mill which means that the sample used for FT5, FT9 and FT10, collected in the flotation feed tank already contains SIPX and MIBC so, Aerophine 3418A promoter was used to increase the selectivity of galena in the presence of arsenic, iron and some non-activated zinc minerals.

Aerophine 3418A promoter is an effective primary collector in the selective flotation of lead, gold silver minerals and complex lead minerals with high silver content or lead minerals where the head grade of lead does not exceed 1.50 percent (product data sheet CYTEC).



**Fig 8. Grade vs Recovery curve – PbS/PbO flotation using different sulphide collector**

Рис. 8. Кривая содержания/извлечения – флотация PbS/PbO с использованием различных флотационных собирателей сульфидов

Even when the results (Fig. 8) show a similar behaviour during the sulphide flotation, it is possible to observe the big changes produced in the oxide flotation increasing mainly the lead recovery. For a lower concentration of promoter both recovery and grade increased significantly compared with test undertaken with no promoter added, making these parameters more efficient than current ones used in the plant.

The results indicate that even when the recoveries are higher when promoter 3418A is used the final grade of the concentrate obtained is better when SIPX used.

### 3.2 Fluorspar flotation

For the  $\text{CaF}_2$  flotation stage as in the previous analysis, different parameters were combined in order to find the more suitable conditions for depressing  $\text{P}_2\text{O}_5$  without affecting  $\text{CaF}_2$  grade and recovery.

Chemical analysis results from products were used to compare the head grade from the sample with the back calculated grade (BC). Relative error was calculated as an indicator of how good back calculated results are relative to the head grade of the sample (Table 3). Back calculated results and head grade of sample do not present a big difference between them, and its similarity could

**Table 3. Head grade sample vs head grade from products – back calculated in fluorspar flotation (%)**

Табл. 3. Образец головного продукта в сравнении с содержанием в головном продукте – обратный расчёт при флотации флюорита, %

|                               | F     | Pb   | $\text{CaF}_2$ | PbO  | $\text{BaSO}_4$ | $\text{P}_2\text{O}_5$ |
|-------------------------------|-------|------|----------------|------|-----------------|------------------------|
| Head grade sample (F)         | 14.58 | 0.45 | 29.93          | 0.49 | 11.23           | 0.19                   |
| Head grade from products (BC) | 16.04 | 0.54 | 32.93          | 0.58 | 12.40           | 0.20                   |
| Relative error (BC-F)/F       | 0.10  | 0.19 | 0.10           | 0.19 | 0.10            | 0.05                   |

be related with the same analytical method used in both cases as lead flotation.

### 3.2.1 Effect of the temperature

Solubility of oleic acid in higher temperature and basic pH is increased therefore its performance as collector for floatation is more selective and better; current conditions in the plant perform floatation in temperatures around 9–18°C. Considering the valuable effect that temperature can produce in fluorite floatation test FT1, FT3, FT4 and FT5 at 19, 30, 40 and 50°C respectively were performed.

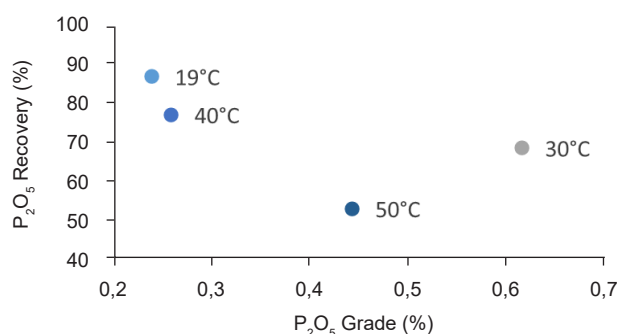
Increasing the solubility in the reagents and their selectivity should increase recovery in the floatation cell. As shown in Table 4 the optimum and highest recovery for the  $\text{CaF}_2$  floatation is achieved at a temperature = 30°C. Further test at temperatures higher than 50°C should be studied considering that recoveries started to increase again at this point of the graphic.

On the other hand, the aim of our study comprises the behaviour and the recovery of the  $\text{P}_2\text{O}_5$  in the tails and the decreasing of grade in the concentrate compare with the current conditions of the plant. The graphic in the Fig. 9 shows the effect of temperature in the depression of  $\text{P}_2\text{O}_5$  during floatation translated into the grade and recovery in the floatation tailings.

**Table 4. Grades and recoveries results at different temperatures in  $\text{CaF}_2$  floatation**

Табл. 4. Содержания и результаты извлечения при различных температурах при флотации  $\text{CaF}_2$

| Test | Temperature °C | Grade $\text{CaF}_2$ (%) | Recovery $\text{CaF}_2$ (%) |
|------|----------------|--------------------------|-----------------------------|
| FT1  | 19             | 84.65                    | 90.74                       |
| FT3  | 30             | 76.03                    | 97.14                       |
| FT4  | 40             | 63.32                    | 94.00                       |
| FT5  | 50             | 36.48                    | 94.84                       |



**Fig 9. Grade vs Recovery curve –  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  floatation at different temperature**

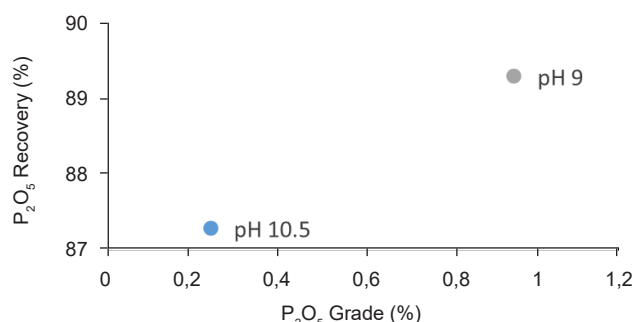
Рис. 9. Кривая содержания/извлечения – флотация  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  при различной температуре

### 3.2.2 Effect of pH

As mentioned before the current conditions in the plant are adjusted to work at pH 10.5. Considering that the main gangue of the material is calcite, quartz and phosphates FT1 and FT2 were performed to analyse the effect in the depression of  $\text{P}_2\text{O}_5$ .

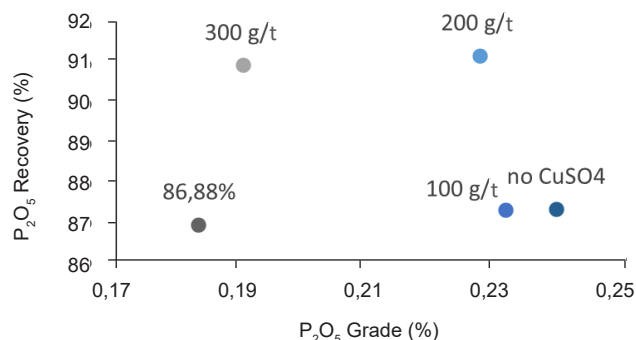
Song et al. (2006) mentioned in their study about improving fluorite floatation that according to the DLVO theory (Verwey and Overbeek, 1947), aggregative stability of colloidal suspensions is due to the existence of a potential energy barrier between particles preventing the proximity of the particles, and the potential energy barrier arises as a result of interaction energies of electrical double layer and van der Waals. For the systems of fluorite-quartz and calcite-quartz in aqueous solutions, the van der Waals interaction between the particles is always attractive and the electrical double layer interaction is also attractive at pH 9.0 because the interacted particles are charged reversely. Therefore, at pH 9.0, the total potential energy of interaction between fluorite and quartz particles or calcite and quartz particles is attractive at every distance.

It was found that the recovery of  $\text{P}_2\text{O}_5$  in the tailings increases at lower pH as shown in the Figure 10, but when performing the test, it was observed that the froth was not stable at pH 9 and most of the material stayed in the cell. The Table 5



**Fig. 10. Grade vs Recovery curve –  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  flotation at different pH**

Рис. 10. Кривая содержания/извлечения – флотация  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  при различном pH



**Fig. 11. Grade vs Recovery curve –  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  flotation with  $\text{CuSO}_4$  as depressant**

Рис. 11. Кривая содержания/извлечения – флотация  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  с использованием  $\text{CuSO}_4$  в качестве депрессора

supports these observations as just a 10.74%  $\text{CaF}_2$  recovery was achieved in the test at pH 9 against 90.74% recovery at pH 10.5 where the froth was strong and stable.

It is important to mention that both tests were performed at natural temperature as the current plant conditions at around 18°C. In order to ob-

serve the effect of the combined parameters pH and temperature and additional flotation test was performed at pH 9 and 40°C temperature, finding an increasing in recovery for  $\text{P}_2\text{O}_5$  in the tailings with a value of 88.13% and a recovery of  $\text{CaF}_2$  of 82.99% which is not convenient for the objectives of this study.

**Table 5. Grades and recoveries for  $\text{CaF}_2$  at different pH**

Табл. 5. Содержания и извлечение  $\text{CaF}_2$  при различном pH

| Test | pH   | Grade $\text{CaF}_2$ (%) | Recovery $\text{CaF}_2$ (%) |
|------|------|--------------------------|-----------------------------|
| FT1  | 10.5 | 84.65                    | 90.74                       |
| FT2  | 9    | 69.24                    | 10.74                       |

### 3.2.3 Effect of $\text{CuSO}_4$ for removal of phosphates

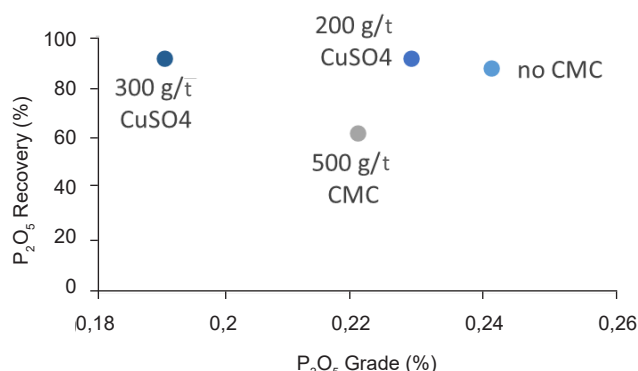
Test FT7, FT8, FT9 and FT10 were performed using a copper sulphate as possible removal of  $\text{P}_2\text{O}_5$  in the rougher flotation without affecting the flotation of  $\text{CaF}_2$  (Zhang and Zong, 2003).

According to the results, as shown in the Fig. 11 a significant reduction of the content of  $\text{P}_2\text{O}_5$  in the concentrate translated in a high recovery of  $\text{P}_2\text{O}_5$  in the tailings was achieved using 200g/t of  $\text{CuSO}_4$  at pH 10.5.  $\text{P}_2\text{O}_5$  recovery increases by 4% com-

**Table 6. Grades and recoveries of  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  with different dosages of  $\text{CuSO}_4$  (g/t)**

Табл. 6. Содержания и извлечение  $\text{CaF}_2$  и  $\text{P}_2\text{O}_5$  при различном количестве  $\text{CuSO}_4$  (г/т)

| test | pH   | Grade $\text{CaF}_2$ (%) | Recovery $\text{CaF}_2$ (%) | Grade $\text{P}_2\text{O}_5$ (%) | Recovery $\text{P}_2\text{O}_5$ (%) | $\text{CuSO}_4$ concentration (g/t) |
|------|------|--------------------------|-----------------------------|----------------------------------|-------------------------------------|-------------------------------------|
| FT1  | 10.5 | 84.65                    | 90.74                       | 0.239                            | 87.27                               | 0                                   |
| FT8  | 10.5 | 85.31                    | 31.43                       | 0.190                            | 90.89                               | 300                                 |
| FT7  | 10.5 | 87.57                    | 74.10                       | 0.227                            | 91.13                               | 200                                 |
| FT9  | 10.5 | 83.77                    | 83.25                       | 0.231                            | 87.25                               | 100                                 |
| FT10 | 9    | 72.48                    | 28.33                       | 0.183                            | 86.88                               | 200                                 |



**Fig.12. Grade vs Recovery curve – CaF<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> flotation with CMC as depressant**

Рис. 12. Кривая содержания/извлечения – флотация CaF<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> с использованием CMC в качестве депрессора

pared to current conditions in the plant. Table 6 shows the recovery of CaF<sub>2</sub> decreases but the grade resulted with a slightly higher difference with the current conditions.

### 3.2.4 Effect of CMC as depressant

Song et al. (2006) found that the dispersion processing with CMC as dispersant could effectively improve the fluorite flotation, increasing the fluorite recovery from 72% to 78.5% at the same concentrate grade of 98% CaF<sub>2</sub>. The idea using CMC as depressant has an advantage of elimination of the heterocoagulation considering its flocculation effect between calcite and fluorite particles, in order to improve the beneficiation of the fluorite ore by froth flotation. As mentioned previously the used of different reagent as disperser

**Table 7. Grade and recoveries of CaF<sub>2</sub> with CMC as depressant (%)**

Табл. 7. Содержания и извлечение CaF<sub>2</sub> с использованием CMC в качестве депрессора (%)

| Test | Grade CaF <sub>2</sub> | Recovery CaF <sub>2</sub> |
|------|------------------------|---------------------------|
| FT1  | 84.65                  | 90.74                     |
| FT11 | 56.6                   | 89.62                     |

and depressor was succesful for the authors (Li, 2015), but a different effect was found in the Mill-dam sample.

As shown in Table 7 and Fig. 12, both grade and recovery of CaF<sub>2</sub> decreased with the use of CMC and the addition of CuSO<sub>4</sub> keeps being more effective than other depressants. This negative effect in the process could be related with the high dosage of CMC during the flotation test and also to the mineral associations in the ore.

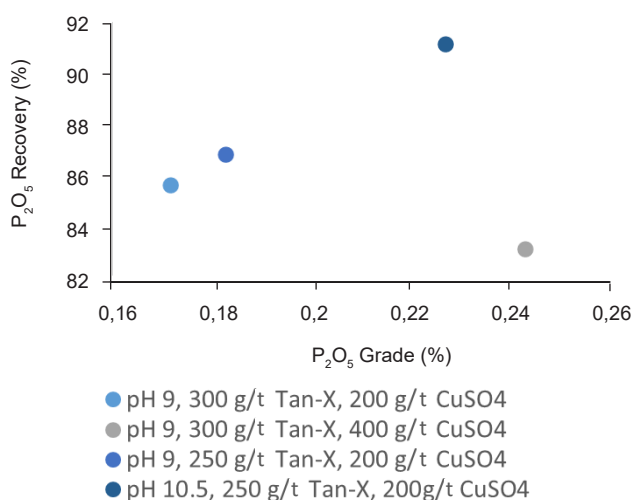
### 3.2.5 Combined effect of pH, reagent's dosage and CuSO<sub>4</sub> as depressant

It is probable that the flotation kinetics is improved when different parameters are combined and not with a change in only one of them. In previous tests was possible to observe how grades and recoveries changes with pH, temperature, reagents and dosages. Tests FT7, FT10, FT12 and FT13 (Table 8) were performed in order to compare the best relation of parameters for the best P<sub>2</sub>O<sub>5</sub> recovery achieved.

**Table 8. pH, reagents dosage and depressants (g/t) in CaF<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> flotation tests**

Табл. 8. pH, количество реагентов и депрессоры (г/т) при опытной флотации CaF<sub>2</sub>/P<sub>2</sub>O<sub>5</sub>

| Test | pH   | Soda Ash | Tan-X | R3-3F | Dextrine | Na <sub>2</sub> SiO <sub>3</sub> | CuSO <sub>4</sub> |
|------|------|----------|-------|-------|----------|----------------------------------|-------------------|
| FT7  | 10.5 | 825      | 250   | 140   | 320      | 160                              | 200               |
| FT10 | 9    | 825      | 250   | 140   | 320      | 160                              | 200               |
| FT12 | 9    | 200      | 300   | 220   | 400      | 160                              | 200               |
| FT13 | 9    | 250      | 300   | 220   | 400      | 160                              | 400               |



**Fig. 13. Grade vs Recovery curve –  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  flotation at different pH and different reagent's dosages**

Рис. 13. Кривая содержания/извлечения – флотация  $\text{CaF}_2$ - $\text{P}_2\text{O}_5$  при различном pH и различных количествах реагента

Fig. 13 shows that the best recovery for  $\text{P}_2\text{O}_5$  is given at pH 10.5, with the current concentration of Tan-X used in the plant (250 g/t) and adding to the process 200 g/t of  $\text{CuSO}_4$  (depressant) with a recovery value of 91.15%, which represents an increase of 3% on current dosage in the plant.

#### 4. DISCUSSION

The fully liberated lead in the fluorspar concentrate can be reduced improving the selectivity and recovery in the PbO flotation stage either (i) adding a promoter (3418A) in the PbS flotation cell by decreasing reagent's dosage (to 100 g/t) and pH (to 9) or (ii) decreasing reagent's dosage (to 100 g/t) and pH (9). Batch flotation test at current conditions in the plant recovered 2.33% Pb in the lead oxide flotation whereas at option (i) recovered 18.03% Pb and at option (ii) recovered 15.71% Pb. It was found that option (i) not only improves the recovery of lead in PbO flotation stage, also improves the recovery of sulphur sulphide in final concentrate which leads to a lower amount of sulphur going to the fluorspar flotation feed. As mentioned previously in this study the company

aims to increase the lead recovery even if the process decreases the lead grade in the concentrate.

The content of calcite and Ca phosphates in the  $\text{CaF}_2$  concentrate can be reduced, by adjusting the reagents in the rougher-cleaner system with the current reagents' dosage and including the use of salted-copper sulphate ( $\text{NaCl-CuSO}_4$ ) as "depressant" (effective removal) of gangue minerals specially those ones associated with phosphates (calcite and quartz). The maximum recovery of  $\text{P}_2\text{O}_5$  (91.13%) in the tailings for fluorspar flotation was achieved with a dosage of 200 g/t in a batch rougher flotation with the current conditions of the plant.

An optimum reduction of the  $\text{P}_2\text{O}_5$  in the concentrate can be achieved either (iii) adding the  $\text{CuSO}_4$  as depressant in the rougher system and cleaner 1 to 3 or (iv) adding the  $\text{CuSO}_4$  as depressant in the cleaners.

The proportions to reduce the  $\text{CuSO}_4$  from rougher to cleaner or in the cleaner system.

#### 5. CONCLUSIONS

Obtained data from bath flotation test in the PbS/PbO system proposed an improvement of lead recovery from 2.33% to 15.03% by decreasing collector dosage ( $\text{Na}_2\text{S}$ ) to 100 g/t and adjusting pH to 9 just in the lead oxide circuit or an improvement from 2.33% to 18.01% adding Aerophine 3418A as a promoter in the lead sulphide flotation.

Results from the fluorspar flotation stage focused on the reduction of  $\text{P}_2\text{O}_5$  content in the concentrate proposed a depression of  $\text{P}_2\text{O}_5$  in the fluorspar flotation stage from 87% to 91% recovered in the tailings using 200 g/t of  $\text{NaCl-CuSO}_4$  as depressant.

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