ARSENOPYRITE ENRICHMENT BY COLUMN FLOTATION

P. MAVROS, K.A. KYDROS and K.A. MATIS

Department of Chemistry, Aristotle University, GR-540 06 Thessaloniki, Greece
(Received 4 February 1993; accepted 2 July 1993)

ABSTRACT

Arsenic-rich, gold-bearing pyrite concentrates may be further enriched in arsenic to assist subsequent Au beneficiation. Among several amines tested in refloating a local Chalkidiki pyrite concentrate, 2-coco 2-methyl ammonium chloride proved successful by raising the grade from 9% to 22%, although total solids recovery was low. The use of a froth-stabilizing frother was also beneficial to the process. Optimum hydrodynamic conditions were: intermediate pulp flowrate, low wash water and gas flowrate; the latter abated the mixing/dispersion process in the collection zone.

Keywords
Column flotation; arsenopyrite; amines

INTRODUCTION

Pyrite concentrates sometimes contain considerable amounts of arsenic. Since they are usually used for the production of sulphuric acid, this is undesirable. However, gold is often associated with arsenopyrite, often exhibiting a direct relationship between Au content and As grade [1]. There is, therefore, some scope for concentrating arsenopyrite, since the ore itself is otherwise of little value.

Previous work on pyrites has usually concentrated on the problem of floating pyrite. Xanthates are the most common collectors; these are used in conjunction with some arsenic-depressing reagent, e.g. KMnO₄, H₂O₂, NaOCl, among others [2] - at a limited dosage, otherwise pyrite is depressed, too. Other collectors are used, too, e.g. mercaptobenzothiazole [3] or dithiophosphates [4].

Arsenopyrite itself may be floated using a variety of reagents, e.g. dithiophosphates and dithiocarbamates [5], sodium dodecyl sulphonate [6] and other cationic collectors [7]. It was also found, through electrophoretic studies, that ferric iron (Fe³⁺) ions confer a positive surface charge to pyrite particles; in contrast, arsenopyrite remains negative. This surface alteration becomes important in the acidic region around pH 4.

Cetyl-trimethyl ammonium bromide has also been used as collector at acidic pH values, with ferric iron added to the dispersion [7]; it proved effective in raising - albeit moderately, from 7.5% to 14% - the arsenic content of the concentrate.

The presence of xanthates, however, may cause problems in the subsequent cyanidation of pyrites when recovering their Au value [3,8]; this justifies the need to find alternative collectors. In a previous study with Cu, Zn and Pb sulphides [9], a C₁₂-amine acetate collector was compared to two common xanthate collectors - potassium amyl (KAX) and potassium ethyl (KEX) xanthate. The experimental results indicated that the amine exhibited a behaviour similar to that of the xanthates, with galena requiring a higher dosage of some frother and the use of an activator, prior to flotation by the amine. The benefit of the amine was in its lower consumption, as compared to the xanthate systems.
Several amines have been tested with various sulphides (a selection is shown in Table 1) as well as other ores, e.g. siliceous material [8] or Co-bearing lead ore [10]. Some reagents, e.g. Na$_2$S and K$_2$Cr$_2$O$_7$, have also been found [8] to affect the adsorption of the amines on the sulphide particles, hence these amines may be beneficial to the process by altering the optimum pH for pyrite flotation, achieving possibly some selectivity.

**TABLE 1 Amines used or studied in relation to flotation [8].**

<table>
<thead>
<tr>
<th>Amine</th>
<th>Ore</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armeen 12*</td>
<td>chalcopyrite</td>
<td>---</td>
<td>11</td>
</tr>
<tr>
<td>Arquad 12**</td>
<td>chalcopyrite</td>
<td>---</td>
<td>11</td>
</tr>
<tr>
<td>α-naphthylamine</td>
<td>sulphides</td>
<td>---</td>
<td>12</td>
</tr>
<tr>
<td>butylamine</td>
<td>chalcopyrite, pyrite</td>
<td>---</td>
<td>11,13</td>
</tr>
<tr>
<td>coco-amine acetate</td>
<td>pyrite/mica</td>
<td>8-9</td>
<td>14</td>
</tr>
<tr>
<td>dibutylamine</td>
<td>chalcopyrite</td>
<td>---</td>
<td>11</td>
</tr>
<tr>
<td>dodecylamine</td>
<td>galena</td>
<td>2-12</td>
<td>15</td>
</tr>
<tr>
<td>iso-amylamine</td>
<td>sphalerite</td>
<td>7-12</td>
<td>16</td>
</tr>
<tr>
<td>laurylamine hydrochloride</td>
<td>sphalerite/galena</td>
<td>max. 9.5</td>
<td>17</td>
</tr>
<tr>
<td>long-chained amine</td>
<td>pyrite</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>tallow diamine acetate</td>
<td>silica/calcite</td>
<td>8-9</td>
<td>14</td>
</tr>
<tr>
<td>tetradecyl pyridinium bromide</td>
<td>pyrite, galena</td>
<td>2-12</td>
<td>19</td>
</tr>
<tr>
<td>tridecylamine</td>
<td>var. sulphides</td>
<td>---</td>
<td>17</td>
</tr>
<tr>
<td>tri-isoamylamine</td>
<td>sphalerite</td>
<td>6.5-11</td>
<td>16</td>
</tr>
</tbody>
</table>

\* 90% dodecylamine, 9% tetradecylamine, 1% octadecylamine quaternary amine, largely dodecyl trimethyl ammonium chloride

In this work, an industrial pyrite concentrate\(^1\) has been reprocessed in a laboratory-scale flotation column; this constitutes the final concentrate obtained after removing PbS and ZnS by flotation, using xanthates at alkaline pH values. The choice of this particular pyrite was based on the following points:

- primarily, its relatively important Au content - 21 g/ton - makes this material attractive from the Au-recovering point of view; however, for this to be realised, further re-processing of the concentrate would be necessary and flotation could possibly be the process used.

- the fact that the pyrite was a xanthate-floated concentrate was also considered; however, this pyrite is stock piled (sulphuric acid plants now tend to obtain sulphur from the oil industry) and it is thus subjected to long-term weathering. Preliminary work [21] indicated that even if traces of xanthates persisted, they were unable to float it beyond a total solids recovery of just 10%. On the other hand, it was planned to investigate the pyrite flotation using several amines in the acidic pH region, in which xanthates have no effect.

---

1. Kindly supplied by the Hellenic Chemical Products & Fertilizers Co., operators of the Olympias Pb-Zn-Fe sulphide mines of Chalkidiki, Northern Greece
The parameters studied in particular were the effects of the column hydrodynamics (superficial pulp, gas and wash water velocities) and of the physicochemical parameters - collector and frother type - in order to determine suitable conditions for the enrichment of the concentrate in arsenic and hence also in Au.

EXPERIMENTAL APPARATUS AND PROCEDURE

The arsenic content of the pyrite was approximately 9% (from an initial 3.5% of the mixed sulphide ore). The material was sieved and the -75 μm fraction was used for all experiments. The pulp density in all experiments was kept low, i.e. 0.5%.

A cylindrical laboratory-scale flotation column was used for the beneficitation experiments, with an internal diameter of 4 cm. Its total height was 200 cm; the collection zone-froth interface was always kept at a height of 150 cm - by manually adjusting the tailings flowrate - thus allowing for a 50 cm deep froth. The feed point was 10 cm below the froth-collector zone interface.

Air was introduced through a cylindrical gas sparger at the bottom of the column; the sparger was made of porous ceramic material, with pores ranging from 16 to 40 μm.

In some experiments, wash water was added at the top of the column, through a sprinkler located 1 cm below the top of the froth. The gas and wash water flowrates were measured using calibrated rotameters.

Conditioning was performed in an agitated vessel. The pulp pH was adjusted to about 4 (with H₂SO₄); in a previous study [8], it had been found that pyrites float best either at acidic (pH < 5) or highly alkaline (pH > 11) regions. The conditioning was done in two stages: 10 min after the addition of Fe₂(SO₄)₃, and another 10 min after the addition of a suitable amount of collector. An appropriate amount of frother was also added at the same time as the collector. The pulp was then fed at a steady flowrate into the column, using a peristaltic pump.

The column was initially filled with plain tap water; in some experiments, frother was also added to the water, with the frother concentration the same as that in the pulp. However, this did not significantly affect the time necessary for the column to attain the hydrodynamic conditions - in terms mainly of bubble size and gas/slurry mixing - that would be maintained throughout the experiment.

Samples taken from both concentrate and tailings were weighed, dried and assayed by spectrophotometry for As; using these results the column mass balance was checked (in terms of flowrates and arsenic content of both concentrate and tailings) and the time necessary for the column to attain steady-state conditions was also determined. The recoveries - total and in terms of arsenic - were calculated using the following formulae:

\[ R_{\text{tot}} = \frac{C_x C}{F_x F} \times 100 \ (\%) \]  

(1)

and

\[ R_{\text{As}} = \frac{C_x g_C}{F_x g_F} \times 100 \ (\%) \]  

(2)

where C and F are the concentrate and (pulp) feed flowrates, \( x_C \) and \( x_F \) are the corresponding densities and \( g_C \) and \( g_F \) the corresponding grades.

The amines tested as collectors in this work were:

Armoflot 43 (manufactured by Akzo);
Arquad C-50 (Akzo);
Arquad-2C (di-coco di-methyl ammonium chloride; Akzo); benzyl tri-methyl ammonium chloride (Akzo); and hexadecylamine (Fluka).

All chemicals used in these experiments were (unless otherwise stated) of technical grade.

The use of a frother was warranted by the need, on the one hand, to reduce the bubble size (checked by visual inspection) to the sizes usually required in flotation systems, and on the other hand to provide a froth with an appropriate texture, capable of carrying the solid particles. Several frothers (0.15 % w/v) were used: ethanol (absol.), pine oil (1.0% w/v, dissolved in ethanol), and two commercial ones, Acetofroth 88 (American Cyanamid) and Dowfroth 1012 (Dow Chemicals). The amount of frother used was chosen to obtain a stable froth structure but also to avoid too much frothing.

RESULTS AND DISCUSSION

Preliminary experiments indicated that some of the amines, e.g. 2-coco 2-methyl ammonium chloride (2C2MACl), hexadecylamine (HDA) and Armoflot 43 yielded satisfactory recoveries, whereas the others, e.g. benzyl tri-methyl ammonium chloride and Arquad C50, gave very poor recoveries. The first three amines were then selected for further experimental work, which involved:

- the study of the way changes in the superficial gas, pulp and wash velocities affected the metallurgical results (grade and recovery); the results and the discussion of the effects of the various flowrates is done in terms of superficial velocities - uL, uG, uW - which is customary in flotation columns, since it makes scaling-up of the experimental results more straightforward; and
- the modifying action of ferric sulphate, in conjunction with the various collectors.

The time required for the column to attain steady-state operating conditions (in terms of total solids recovery) is illustrated in Figure 1; for example, for pulp and gas flowrates of 385 and 830 cm³/min respectively (corresponding to superficial pulp and gas velocities of uL = 0.51 cm/s and uG = 1.1 cm/s), steady-state conditions were reached in approximately 10 min. The time scale in this Figure is also presented in terms of dimensionless time (Θ), which is the ratio of the (actual) time (t) divided by the mean residence time (τ); the latter may be roughly calculated from the collection zone height (h_L) and the superficial pulp velocity (u_L):

$$\tau = \frac{h_L}{u_L}$$

Thus, for a collection zone height h_L = 150 cm and a superficial liquid velocity of u_L = 0.51 cm/s, the mean residence time (τ) is 294 s or 4.9 min; the steady-state time of 10 min therefore corresponds to approximately twice the mean residence time.

From Figure 1 it is obvious that the steady-state time depends upon the pertaining operating conditions, and on the gas flowrate in particular; an increase in u_G (from 0.5 to 0.8 and then to 1.1 cm/s) caused a slight shortening of the steady-state time (from 4τ - i.e., four times the mean residence time - to 3τ and then to 2τ). It seems however that some limit was reached: increasing u_G to 1.3 cm/s proved deleterious to the column performance, with a considerable lengthening of the time required for steady-state and also possibly a lower total recovery. This probably corresponds to a worsening of mixing conditions inside the column, as has been determined recently in residence time distribution studies in flotation columns [20].

The gas flowrate also affected the metallurgical results, but the effect also depended upon the pulp flowrate (Figure 2). As u_G increased, total recovery went through a maximum, which obviously depended upon the particular pulp velocity, u_L; the concentrate grade, however, tended to diminish. On the other hand, an increase in pulp velocity caused an increase in grade but a drop in recovery. Therefore, an intermediate point has to be chosen in order to achieve the objective of enriching the concentrate in arsenic without rejecting too much of the material.
Wash water is often added at the top of the column, so that the separation and selectivity of the process may be enhanced. This was tested with two different reagent systems, hexadecylamine with pine oil in ethanol as frother, and 2-coco 2-methyl ammonium chloride with Acetofroth 88 as a frother (Figure 3). The former reagent system exhibited no selectivity, hence the grade of the concentrate was not affected by the increase in wash water flowrate and remained practically the same. However, when $u_w$ increased above 0.9 cm/s, an inversion of the process was noticed: the particles were entrained towards the bottom of the column, instead of the top, and a sharp drop in both grade and As recovery were observed. The second reagent system was more selective and here the effects of the wash water addition were more pronounced. An increase in $u_w$ caused a significant increase in grade, as well as a slight increase in recovery. Overall, it seems that the wash water flowrate has to be adjusted according to the particular reagent system used.

Three different collector/frother systems were compared, to determine their respective capability to enrich arsenopyrite: 2-coco 2-methyl ammonium chloride with Dowfroth 1012, and hexadecylamine and Armoflot, both with pine oil in ethanol (Figure 4). The best total recovery was achieved with hexadecylamine - with a maximum for a concentration of approximately 50 ppm - but with a very slight increase only in As grade, from 9% to 10.5%. Armoflot 43 exhibited similar behaviour, with a slightly better enrichment but a lower total recovery. The third amine, 2-coco 2-methyl ammonium chloride, however, proved very promising in terms of concentrate enrichment, raising the As grade from 9% to 14%, although the total recovery was still very low. Further experiments with the same amine but a different frother (Acetofroth 88) showed similar results (Figure 3) indicating a possibility for substantial enrichment.

The effect on metallurgical characteristics of the concentrate of varying the amount of ferric sulphate added to the pulp was also studied; the same three collectors as before were used and their performance is compared in Figure 5. Both hexadecylamine and Armoflot 43 exhibit an increased recovery but a very low enrichment, whereas 2-coco 2-methyl ammonium chloride shows a considerable enrichment; a compromise has to be made, therefore, between a high grade and a low recovery, hence a concentration of 15 ppm of ferric sulphate was used in all other experiments.
Fig. 2 Effect of superficial pulp and gas velocities on metallurgical results; $u_w = 0$.

[2-coco 2-methyl ammonium chloride] 42 ppm, [EtOH] 0.15% (v/v), [$\text{Fe}_2(\text{SO}_4)_3$] 15 ppm.

Plotting the As grade against the As recovery results (Figure 6; top) for the 2-coco 2-methyl ammonium chloride amine shows the usual trend: a high grade is achieved at the expense of recovery; however, it also shows that it is possible to improve the process by gradual parameter adjustment. The use of a "simple" frother, i.e. ethanol - which in fact just reduces the size of the bubbles but does not yield a thick-texture froth - leads to results that form an "envelope" which includes the other amine results (not displayed on the Figure for clarity reasons). An improvement is achieved first by adding wash water, seen in the Figure by a gradual shift towards increased As grades, and then by adding an appropriate surface active agent too (Acetofroth), which is capable not only of reducing the size of the bubbles (like ethanol) but also of supporting the emerging mineralised froth, thus producing concentrates with even higher...
grades. This may also be seen in the parity plot between total recovery and arsenic recovery (Figure 6; bottom), where the best reagent system (2-coco 2-methyl ammonium chloride plus Acetofroth) shows a net trend towards arsenic enrichment, with the corresponding points lying above the parity line. The few high-grade points of Figure 6 (top) do not permit quantitative conclusions, but they are indicative of the effect that the gradual changes made to the process have on the arsenic enrichment, this being the scope of the work.

Fig. 3 Effect of wash water on recovery and grade. (a) [2-coco 2-methyl ammonium chloride] 42 ppm, [Acetofroth 88] 10 ppm, $u_L = 1.00 \text{ cm/s}$, $u_G = 0.51 \text{ cm/s}$. (b) [hexadecylamine] 45 ppm, [pine oil] 50 ppm, [EtOH] 0.025% (v/v), $u_L = 0.84 \text{ cm/s}$, $u_G = 0.72 \text{ cm/s}$. (c) [2-coco 2-methyl ammonium chloride] 42 ppm, [EtOH] 0.15% (v/v), $u_L = 1.02 \text{ cm/s}$, $u_G = 0.65 \text{ cm/s}$ (no wash water).

In all cases: $[\text{Fe}_2(\text{SO}_4)_3] 15 \text{ ppm}$. 
Fig. 4 Effect of collector concentration on As grade and recovery. (a) 2C2MACI; [Dowfroth 1012] 85 ppm, \( u_L = 0.75 \text{ cm/s} \), \( u_Q = 0.83 \text{ cm/s} \), \( u_W = 0.60 \text{ cm/s} \); \( [\text{Fe}_2(\text{SO}_4)_3] 50 \text{ ppm} \). (b) HDA; [pine oil] 50 ppm, [EtOH] 0.025\%, \( u_L = 0.84 \text{ cm/s} \), \( u_Q = 0.72 \text{ cm/s} \), \( u_W = 0.66 \text{ cm/s} \); \( [\text{Fe}_2(\text{SO}_4)_3] 15 \text{ ppm} \). (c) Armoflot 43; [pine oil] 50 ppm, [EtOH] 0.15\% (v/v), \( u_L = 0.84 \text{ cm/s} \), \( u_Q = 0.72 \text{ cm/s} \), \( u_W = 0.66 \text{ cm/s} \); \( [\text{Fe}_2(\text{SO}_4)_3] 15 \text{ ppm} \).

Finally, it is also possible to examine whether the hydrodynamic conditions inside the collection zone affect - and to what extent - its performance. The experimental results showed that an increase in gas flowrate resulted in a loss of performance, especially in terms of grade. However, the gas flowrate is also related to the mixing process inside the collection zone [20], especially the axial dispersion coefficient, which may be used to characterize the extent of mixing inside a system. In Figure 7, the experimental As grades are plotted against the corresponding axial dispersion coefficients, calculated using the relevant equation for this column size [20]:

\[
D = 7.1 \ u_G^{0.603} \]  
(4)
The scattering of the data, due mainly to the grouping of all results, irrespective of reagent system and/or hydrodynamic conditions, somewhat conceals the decreasing trend which these display, corroborating the conjecture that, as the mixing process becomes more intense inside the collection zone, the poorer is the grade of the concentrate. It seems, therefore, that in order to enrich the pyrite concentrate in arsenic, hydrodynamic conditions of low mixing and dispersion should be adjusted in relation to the collector/frother system. It would also be interesting to determine whether a change in hydrodynamic conditions may further enhance the performance of a flotation column, once the reagent system has been somehow "optimized".

![Graph](image)

**Fig. 5** Effect of Fe$_2$(SO$_4$)$_3$ on grade and recovery. (a) [2-coco 2-methyl ammonium chloride] 42 ppm; [EtOH] 0.15% (v/v); $u_L = 1.02$ cm/s, $u_G = 0.65$ cm/s, $u_W = 0.53$ cm/s. (b) [hexadecylamine] 45 ppm, [pine oil] 50 ppm, [EtOH] 0.025%, $u_L = 0.84$ cm/s, $u_G = 0.72$ cm/s, $u_W = 0.66$ cm/s. (c) [Armoflot 43] 50 ppm, [pine oil] 50 ppm, [EtOH] 0.025%; $u_L = 0.84$ cm/s, $u_G = 0.71$ cm/s, $u_W = 0.66$ cm/s.
Fig. 6 (Top) Arsenic recovery vs. arsenic grade for the 2-coco 2-methyl ammonium chloride amine. (Bottom) Parity plot between total and As recovery.
Arsenopyrite enrichment by column flotation

CONCLUSIONS

Pyrite concentrates often have a high percentage of arsenic, which is often associated with the pyrite gold value. Hence, an arsenic enrichment of the concentrate by further reprocessing, e.g. by flotation, would be beneficial to the Au-recovering process. This has been performed in a laboratory-scale flotation column, using a locally-produced pyrite concentrate.

Several amines have been tested, as alternative reagent to the commonly used xanthates, since the latter have been found to be deleterious to the subsequent pyrite cyanidation. Of these, the 2-coco 2-methyl ammonium chloride amine in acidic pH has been found to produce the highest enrichment, although at a low recovery. Experiments were performed in low pulp densities, but the results obtained were helpful in determining the particular amine/frother system yielding the best metallurgical results.

The experimental results indicate, so far, that:

- a suitable frother should also be used to obtain a stabilized froth and enhance the As grade;
- wash water is, as expected, beneficial, since it enhances the process selectivity;
- the optimum hydrodynamic conditions for the flotation column operation correspond to an intermediate pulp flowrate and a rather low gas flowrate, so as to keep the dispersion and mixing process inside the collection zone of the column low.

ACKNOWLEDGEMENTS

The financial assistance of the General Secretariat for Research and Technology of the Greek Ministry for Energy and Technology and the help of Messrs. P. Xanthopoulos and G. Savvopoulos in the experimental part of this work is gratefully acknowledged.
NOMENCLATURE

D : axial dispersion coefficient
d_C : column (inside) diameter
C : concentrate flowrate
F : pulp (feed) flowrate
\( \varepsilon_C \) : concentrate grade
\( \varepsilon_F \) : feed grade
h_L : collection zone height
R_AAs : arsenic recovery
R_tot : total recovery
u_G : superficial gas velocity
u_L : superficial liquid velocity
u_W : superficial wash water velocity
x_C : concentrate density
x_F : pulp density

Greek letters

\( \Theta \) : dimensionless time
\( \tau \) : mean residence time

REFERENCES