A LABORATORY STUDY OF REMOVING ARSENIC FROM A SYNTHETIC COPPER CONCENTRATE

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Abstract Arsenic is the 20th most abundant element in the earth's crust at a level of about 2 ppm. It is a constituent of over 300 minerals and is commonly found in non-ferrous ores such as copper, lead, zinc, gold and uranium. Efficient separation of arsenic minerals from other sulphide minerals is of great importance for the metallurgical performance of flotation processes. This work was undertaken to study the separation of enargite, an arsenic-bearing mineral from chalcopyrite in copper concentrates. To achieve this aim the possible depression of enargite using some sulphide depressants was studied.

Key Words Arsenic, Sulphide Minerals, Flotation, Depression

چکیده آرسنیک بیستمین عنصر فراوان پوسته زمین با مقدار متوسط ۲ پی پی ام می باشد. این عنصر یکی از اجزاء تشکیل دهنده بیش از سیصد کانی بوده و بطور معمول در کانه های غیرآهنی نظیر مس ، سرب، روی ، طلا و اورانیوم وجود دارد. جدایی مؤثر کانیهای آر سنیک دار از دیگر کانیهای سولفوره دارای اهمیت زیادی در فرایندهای فلوتاسیون سولفورها می باشد. این تحقیق به منظور مطالعه جدایی انارژیت که یک کانی محتوی آرسنیک است، از کالکوپیریت در یک کنسانتره مس انجام گر دید. بر ای دستیابی به این هدف امکان بازداشت آنارژیت توسط تعدادی از بازداشت کننده های سولفورها مور د مطالعه قرار گرفت.

INTRODUCTION

Copper sulphide minerals occur occasionally with arsenic minerals, particularly enargite (Cu_3AsS_4) and tennantite ($(CuFe)_{12}As_4S_{13}$). In sulphide mineral flotation, a copper concentrate containing up to 10% arsenic may be produced [1]. The arsenic bearing concentrates cannot be smelted as they exist because arsenic would pollute the environment and contaminate the smelter products [2]. Concentrates containing a high percentage of arsenic are penalized by many smelters. The main reason that penalties are applied is the additional costs incurred by the smelters to remove arsenic from the refined metal in order to comply with international standards. Smelters can also attract extra environmental control costs because of the arsenic impurity.

Pyrometallurgical and hydrometallurgical processes provide a means of removing arsenic from the concentrates. In pyrometallurgical methods conventional roasting of copper concentrates, or alternatives to this method (i.e., nonoxidative techniques such as electric furnaces, rotary kilns) for arsenic removal is used. The roasting and smelting of arsenical concentrates have always involved problems in handling the arsenic compounds [3]. Arsenic is normally produced in a roasting operation in the form of an oxide (As_2O_3), known in the trade as white arsenic. White arsenic is soluble in water and is quite toxic. Because of its solubility and toxicity, the disposal of the waste containing arsenic, where market for the oxide are limited, has caused considerable problems. In nonoxidative techniques, a possible way to solve the arsenic problem, which has never been practiced commercially, would be to dispose of it as arsenic sulphide, which occurs in nature as the minerals orpiment (As_2S_3) and realgar (As_2S_5). The arsenic sulphide is more than one hundred times less soluble than the oxide form [3]. Hydrometallurgical techniques for removing arsenic from copper concentrates are alternatives to the pyrometallurgical techniques. These techniques are discussed in detail by Nadkarni and Kusik [4]. However, the stability of waste materials produced from removing arsenic by existing hydrometallurgical techniques will not meet the regulatory requirements of the future for long term disposal [5]. Due to these limitations, it is necessary to find an alternative to current processes. In this regard the present work was undertaken. Since the specific gravity of enargite is close to the specific gravity of chalcopyrite, gravity concentration is not applicable. However, the froth flotation technique seems to be a suitable method of reducing the arsenic content of copper concentrates.

The previous investigations [6] have identified the conditions in which each mineral can be floated with Potassium Amyl Xanthate (PAX). This work [6], which focused on a detailed physicochemical characterization of the surface composition of these minerals in relation to flotation, provides a basis for the separation of these minerals under controlled conditions. It appears that this information could lead to the development of strategies for selective flotation.

SEPARATION BY FLOTATION

The appropriate conditions for the separation of enargite and chalcopyrite were used. These conditions gave the highest differences in the floatability of enargite and chalcopyrite in the single mineral flotation [7]. Therefore, they were used in the separation of a mixture of minerals.

EXPERIMENTAL TECHNIQUES

Synthetic enargite and pure chalcopyrite were used for all the tests and the micro-flotation method described elsewhere [6] was used for this purpose. The sample was conditioned for 20 minutes with the collector solution in the flotation cell and then with depressant for a desired time period followed by one minute of flotation. The sample used for the Hallimond tube test was a 2 g artificial mixture: 0.5 g enargite and 1.5 g chalcopyrite. This composition was chosen (4.75% As) because enargite containing concentrates from copper mines often contain up to 10% arsenic. An aqueous solution of the required pH value, collector and depressant were used for flotation (Table 1). Elemental chemical analyses of the minerals showed that the enargite contained of 48.42% Cu, 19.02% As and 32.56% S and the chalcopyrite contained of 33.2% Cu, 29.9% Fe and 35.6% S. Since arsenic only exists in enargite and iron only exists in chalcopyrite, the recovery of enargite in the concentrate can be calculated using the content of arsenic in the concentrate (i.e., the percentage of As in the concentrate), and the recovery of chalcopyrite can be calculated using the content of Fe in the concentrate .

Because the unwanted mineral is enargite, which is also a Cu-containing mineral, the loss of copper in the tailings is unavoidable. Theoretically, the Cu/As weight ratio in enargite is 2.54 and, therefore, 32.7% of the copper in the sample is contained in enargite. If an extremely high selectivity is wanted (i.e., no As in the concentrate) the theoretical Cu recovery cannot exceed 67.3% for this sample.

RESULTS

The variables investigated in the laboratory study of enargite/chalcopyrite flotation separation are summarized in Tables 1 and 2.

With an increase in the collector concentration from 10 mg/l to 30 mg/l there was an increase in the copper/arsenic separation efficiency (defined as the copper recovery minus the arsenic recovery [8]), from 3.47 percent to 7.32 percent. Based on the above mentioned results the concentration of xanthate was therefore selected as 30 mg/l for the other tests. The type of pH modifier was tested at various pH values. When NaOH was used the copper/arsenic separation efficiency was maximum at pH 9. The separation efficiency was higher using lime at the same pH. Using lime as a pH modifier resulted in a better rejection of arsenic; however, the arsenic recovery was still very high and the percentage of arsenic in the concentrate was 4.31. The effect of NaCN was tested for 5 and 20 minutes conditioning with NaCN at 15 mg/l concentration. After 5 minutes NaCN contact time the copper/arsenic separation efficiency was 13.93 percent, but the copper recovery was very low. For 20 minutes contact time the copper/arsenic separation efficiency was maximum and the copper recovery was 55.21 percent. The percentage of arsenic in this test was also minimum. The concentration of CN^- was critical, and the excess concentration of 20 mg/l resulted in chalcopyrite depression (i.e., 61% chalcopyrite recovery).

Test results show that using $KMnO_4$ as a depressant for enargite leads to a maximum copper/arsenic separation efficiency of 17.39 percent with an arsenic recovery of 48.54 percent for 10 minutes contact at 25 mg/l $KMnO_4$ concentration. Aeration conditioning, on the other hand, increased the copper/arsenic separation efficiency along with decreasing the arsenic recovery and a decrease in the copper recovery. This is because aeration preferentially depresses enargite and therefore there is an improvement in the separation efficiency. When sodium sulphide was used as the chalcopyrite depressor, the floated product contained high arsenic and the nonfloated product contained low arsenic. The results show that copper/arsenic separation efficiency was 22.12 percent and 24.15 percent for Na_2S contact times of 5 and 20 minutes, respectively. Therefore the maximum separation efficiency or minimum arsenic grade of 3.30 percent could be obtained for 20 minutes sodium sulphide contact time at a concentration of 10 mg/l.

TABLE 1. Separation Flotation Tests for the Mixture of Enargite and Chalcopyrite at 4.75% As in Feed Sample.

Test Conditions						
No.	PAX Conc. (mg/l)	pH	Regulator	Depressant	Depression Time (min.)	Feed Weight (g)
1	10	9	NaOH	-	-	2
2	20	9	NaOH	-	-	2
3	30	9	NaOH	-	-	2
4	30	6	-	-	-	2
5	30	10	NaOH	-	-	2
6	30	9	CaO	-	-	2
7	30	10	CaO	-	-	2
8	30	9	NaOH	15 mg/l NaCN	5	2
9	30	9	NaOH	15 mg/l NaCN	20	2
10	30	9	NaOH	20 mg/l NaCN	20	2
11	30	9	NaOH	10 mg/l $KMnO_4$	10	2
12	30	9	NaOH	25 mg/l $KMnO_4$	10	2
13	30	9	NaOH	Aeration	10	2
14	30	9	NaOH	Aeration	20	2
15	30	9	NaOH	Aeration	30	2
16	30	9	NaOH	10 mg/l Na_2S	5	2
17	30	9	NaOH	10 mg/l Na_2S	20	2

TABLE 2. Separation Flotation Results for the Mixture of Enargite and Chalcopyrite at 4.75% As in Feed Sample.

Results								
No.	Conc. Weight (g)	%As	%Fe	%Cu	$\%R_{Cu}$	$\%R_{En}$ or $\%R_{As}$	$\%R_{Ch}$	%Sep. Eff.
1	1.43	4.54	23.08	37.16	71.81	68.34	73.51	3.47
2	1.60	4.44	23.36	37.22	80.48	74.78	83.24	5.70
3	1.68	4.39	23.66	37.42	84.95	77.63	88.53	7.32
4	1.64	4.46	23.47	37.39	82.86	76.99	85.73	5.87
5	1.47	4.70	22.65	37.09	73.68	72.73	74.16	0.95
6	1.49	4.31	24.30	37.93	76.37	67.60	80.64	8.77
7	1.41	4.48	23.15	37.09	70.67	66.49	72.70	4.18
8	0.90	3.02	24.60	34.98	42.54	28.61	49.31	13.93
9	1.07	2.75	28.11	38.18	55.21	30.97	66.99	24.24
10	0.92	2.18	29.81	38.61	48.00	21.11	61.08	26.89
11	1.47	3.98	25.44	38.36	76.20	61.59	83.29	14.61
12	1.26	3.66	26.50	38.72	65.93	48.54	74.37	17.39
13	1.45	4.22	24.31	37.71	73.89	64.41	78.51	9.48
14	1.22	3.85	26.05	38.70	63.80	49.44	70.78	14.36
15	1.07	3.45	27.44	39.22	56.71	38.86	65.33	17.85
16	1.12*	3.35	29.01	40.71	61.62	39.50	72.36	22.12
17	1.18*	3.30	29.25	40.85	65.14	40.99	76.87	24.15

* Non-floated Weight

DISCUSSION

The arsenic problem in a copper concentrate could be alleviated by the optimization of flotation conditions for separating enargite and chalcopyrite. The implementation of lime as a pH modifier at a PAX concentration of 30 mg/l and pH 9 along with the use of an appropriate amount of sodium cyanide as a depressant represents a good arsenic rejection. As can be seen from the results a 24.24 percent copper/arsenic separation efficiency or an arsenic grade of 2.75 percent was obtained at 15 mg/l NaCN concentration and pH 9 for 20 minutes contact time. With an increase in NaCN concentration to 20 mg/l a maximum of 26.89 percent copper/arsenic separation efficiency, corresponding to 2.18 percent arsenic, was attained.

Note from Table 2 that the flotation results of different flotation conditions are similar. For example there are very similar copper/arsenic separation efficiencies by either 30 minutes aeration or 10 minutes contact with 25 mg/l $KMnO_4$. The arsenic grades are also very similar at these conditions. Similarly, the copper and arsenic recoveries are higher using $KMnO_4$. Using 15 mg/l sodium cyanide at pH 9 and 20 minutes contact time, or 10 mg/l sodium sulphide at pH 9 and 20 minutes contact time, gives very similar copper/arsenic separation efficiencies. The arsenic rejection is higher when sodium cyanide is used but with a lower copper recovery.

Generally speaking, regression analysis of the data, presented in Figure 1, which shows copper recovery versus arsenic recovery, indicates that the increase in arsenic rejection brings about an increase in the rejection of copper.

Moreover, flotation is a suitable method of reducing the arsenic content of the copper

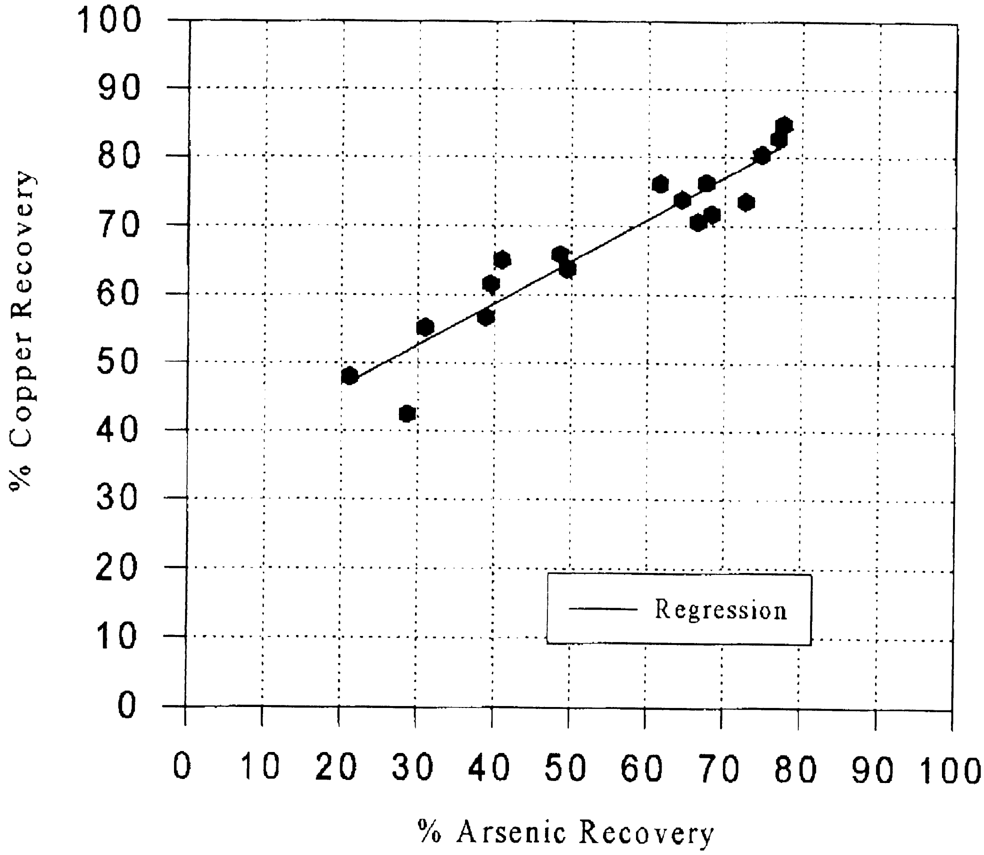

Figure 1. Copper recovery versus arsenic recovery at 4.75% As in feed sample.

concentrates by using sodium cyanide as an enargite depressor. This process consists of isolating chalcopyrite in a high-copper concentrate. It entails physical separation of the chalcopyrite by froth flotation to form a low-arsenic product and an arsenic-rich tailing. The low-arsenic product is destined for smelting. The arsenic-rich product could be discharged since it is a natural sulphide and is less toxic than arsenic oxide produced in pyrometallurgical processes. Or it could be used for hydrometallurgical extraction in which Cu is extracted by direct leaching. Such a hydrometallurgical extraction may be economically feasible due to the lower mass quantity to process. Furthermore, since chalcopyrite is a major mineral and enargite is a minor mineral, it is not logical to depress chalcopyrite using sodium sulphide and float enargite.

CONCLUSIONS

An attempt has been made to study the possibility of arsenic reduction in a copper concentrate containing enargite. From the results obtained, the following conclusions can be made:

- Separation efficiency was a maximum when using 20 mg/l NaCN as a depressant at a contact time of 20 minutes. A separation efficiency of about 24.15 percent was obtained with the use of Na_2S as a chalcopyrite depressor. The same results were obtained when 15 mg/l NaCN was used at the same conditions.

- A minimum copper recovery of 42.54 percent was attained by using 15 mg/l NaCN at a contact time of 5 minutes. However, a copper recovery of 48.00 percent was obtained at 20 minutes contact time by 20 mg/l NaCN.

- Arsenic recovery was a minimum using 20 mg/l NaCN at a contact time of 20 minutes, and the copper recovery was also a minimum.

- The minimum grade of arsenic was 2.18 percent. This is the best result regarding the arsenic reduction in the copper concentrate for the test conditions in this study. This grade corresponds to 48 percent copper recovery.

- The overall conclusion is that using sodium cyanide at a concentration of 20 mg/l with a contact time of 20 minutes gave the best results (the least arsenic grade) for the separation flotation tests performed in this investigation.

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