Recovering selenium from a selenium-bearing pyrite smelting dust by collectorless flotation

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Abstract. In order to recover the valuable selenium in a pyrite smalter which contain 2.18% selenium, 0.18% copper, 0.75% zinc and 45.87% iron, contains this paper many tests were conducted and finally determined flotation as a suitable method. Satisfying results were obtained under the following flotation conditions: grinding fineness was 95% of -0.037mm and the flowsheet including one stage roughing, one stage cleaning and two stage scavenging. In addition, sulfuric acid was used as pH modifier, sodium silicate and sodium hexametaphosphate were used as depressants. According the test results, the flotation concentrate contains 7.254% selenium with recovery 80.60%, only 0.409% selenium contain in tailings, meanwhile mercury and silver are recovered as by-products, the bulk concentrate contain 987.35g/t mercury, 1025.10g/t siliver.

1. Introduction
Selenium is a rare element that there is no independent ore deposit. The main resources which are used for recovering selenium are: anode slime in electroanalysis plant, smelter dust and slags in metallurgical plant or chemical plant. Amount of methods were investigated to recycle selenium, such as precipitation-flocculation, solvent extraction, filtration using microemulsion liquid membranes and sorption by activated carbon or ion exchange resins[1], leaching, roasting-leaching. Some of these methods suffer from inconveniences such as: lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi stage, lower enrichment factors and consumption of organic harmful solvents[2]. Among these methods, flotation still plays an important role because obvious results, environmental test using, simple flowsheet and so on. Undoubtedly, flotation is a prospective technique to enrich the selenium in a certain mineral, then it will be gained in the metallurgy step.

Selenium is a semi-metallic element[3] and it can be used in food stuff, semiconductor industrial, medical areas, etc. It is an essential element for humans at trace level, but it is toxic at higher concentration[4,5]. In order to enrich or preconcentrate the trace elements, recover the minerals associated with them is a feasible method, and many beneficiation methods can be employed, such as flotation, density separation, etc.

In this paper, it was investigate in detail that recoving selenium from a pyrite acidic residue in Yunnan province China, which contains 2.18% Se, 337.5% Ag. The selenium in this residue has great value if it is recoverd reasonably. In addition, Ag could also be recovered as a by-product. In this paper, flotation technique is first employed to recover trace amout of Se form.
2. Another section of your paper Materials and methods

2.1. Materials
The ore was prepared according to the prescribed procedure. Chemical compositions and phase analysis of the sample were determined by X-ray fluorescence analyser (XRF) and X-ray diffraction (XRD), respectively. And the Results of chemical analysis, sample phase are shown in table 1, 2.

| Element | Se  | Cu  | Zn  | Fe  | Te  | Pb  | SiO₂ | Al₂O₃ |
|---------|-----|-----|-----|-----|-----|-----|------|-------|
| Content (%) | 2.18 | 0.18 | 0.75 | 45.87 | 0.26 | 6.28 | 7.02 | <0.3 |

| Element | MgO | CaO | Al₂O₃ | Ag* | Hg* |
|---------|-----|-----|-------|-----|-----|
| Content (%) | <0.3 | <0.3 | <0.3 | 337.5 | 37004.43 |

*: g/t

| phase | Fe₂O₃ | PbSO₄ | Pb₂(SO₄)₂(SeO₄) | HgS* | HgTe* | ZnS |
|-------|-------|-------|------------------|------|-------|-----|
| Content (%) | 45.87 | 6.28 | 0.09 | 34401.00 | 2603.03 | 0.75 |

| phase | Cu₉S₅ | HgSe | CaSO₄·2H₂O | S | AgCl* | others |
|-------|-------|------|------------|---|-------|--------|
| Content (%) | 0.24 | 5.59 | 1.65 | 2.10 | 330.5 | 5.00 |

2.2. Flotation tests
During flotation process, sulfuric acid was used as pH modifier, sodium silicate and sodium hexametaphosphate were used as depressants. Tap water is used in the whole flotation tests.

Flotation tests were carried out in the laboratory flotation cells (Type XFD-0.5L, 1L and 1.5L in volumes) according to the different purposes of roughing, cleaning, and scavenging operations. The order of reagent addition was modifier, depressant. The conditioning times for them were 3min and 1min, respectively. Flotation tests were carried out at the normal temperature of 23℃.

3. Results and discussion

3.1. Mineralogy
As presented in table 1, the sample contains 2.18% Se, 5.80% Hg, and 337.5g/t Ag, these elements are targeted elements being recovered. Meanwhile it contains 45.87% Fe, which should be carefully removed. The total contents of Al₂O₃, CaO and MgO are less than 0.3%, it’s profitable for selenium recover, because high contents of these elements always deteriorate beneficiation and metallurgy.

As shown in table 2, the selenium is mainly in form of HgSe, and mercury is mainly in form of HgS. The sulphide phase is favorable for mercury recover, and selenium can also be recovered as a by-product. But lead is mainly in form of lead sulfate, the oxide phase may cause difficult when recover the valuable elements by flotation.

3.2. Effect of depressants
In order to obtain a better flotation results, the open-circuit tests were carried out. The flowsheet was show in fig 1, the dosage of dextrin is 5000g/t in the roughing and scavenging stage, the dosage of sodium sulphide is 1000g/t in the roughing stage while 500 g/t in the scavenging stage. Butylxanthate was utilized as collector with a dosage of 50g/t. The results shown in table 3.
Feed 95% - 0.037% roughing scavenging tailings
concentrating
middling2
middling3
middling1
concentrate

Figure 1. Open-circuit flowsheet

Table 3. The open-circuit flotation results

| depressants                  | product       | yield(%) | grade(%) | recovery(%) |
|------------------------------|---------------|----------|----------|-------------|
| sodium sulphide dextrin      | concentration | 2.00     | 4.46     | 4.42        |
|                              | middling 1    | 4.00     | 3.59     | 7.71        |
|                              | middling 2    | 14.00    | 3.04     | 21.07       |
|                              | middling 3    | 9.50     | 3.20     | 15.05       |
|                              | tailings      | 70.50    | 1.50     | 52.35       |
|                              | raw of the ore| 100.00   | 2.02     | 100.00      |
| Sodium silicate sodium hexametaphosphate | concentration | 5.50     | 6.88     | 17.84       |
|                              | middling 1    | 6.50     | 5.44     | 16.67       |
|                              | middling 2    | 8.00     | 3.77     | 14.22       |
|                              | middling 3    | 18.00    | 4.51     | 23.21       |
|                              | tailings      | 62.00    | 0.96     | 28.06       |
|                              | raw of the ore| 100.00   | 2.21     | 100         |

Dextrin is a well known depressant for both sulfide minerals and non sulfide minerals\[^6\], and in this test it was utilized as combinatorial depressants with sodium sulfide. According to the result in table 3, the results were not approving as the grade of concentrate is 4.46% with recovery 4.42%, the latter reagents show a better effect, because the grade of concentrate increased 2.42%, and recovery increased 13.42% also. The main reason attributes to this phenomenon is: both dextrin and sodium sulfide do not have the ability to disperse the pulp, as the sample was finely grade, it was easily being slimed in the flotation test. Compare with dextrin and sodium sulfide, sodium silicate and sodium hexametaphosphate show a better inhibit effect as well as disperse effect.

3.3. Effect of collectors
In this test, the sodium silicate and sodium hexametaphosphate were utilized as depressants, and their dosage is 1000g/t. The butylxanthate is utilized as collector under dosage 50g/t. The sulphuric acid utilized as pH regulator. The flowsheet was shown in fig 2 and result in table 4.
The table 4 shown that better results were obtained through the collectorless, the grade of the concentrate increased 2.11%. Because the small particles cannot overcome the fluid drag and tend to be carried together with water into the froth [7], so the grade of the concentrate decreased if the fine gangue mineral particles be floated. And the powerful collecting ability of butylxanthate makes a “contribution” to the poor flotation results. Therefore, in order to obtain a satisfying flotation results, non collectors was used.

3.4. Close-circuit flotation test

Single-factor tests were carried out to determine the reagent scheme in rougher flotation. The optimum conditions for the rougher were obtained, i.e., sodium silicate 200g/t in the first rough stage while 600g/t in the second rough stage, sodium hexametaphosphate 1000g/t in the first rough stage while 600g/t in the second rough stage, the pH around 2~4. And the grade and recovery of rough concentrate obtained at the above optimum conditions are as follows: the grade of selenium is 4.45% with recovery 70.50% for residue containing 2.18% selenium.

The expanded flotation flowsheet in close circuit is illustrated in Fig. 3 and the results are shown in Table 5. The dosages of reagents in scavenger were determined by experience, i.e., sodium silicate 400g/t, sodium hexametaphosphate 1000g/t, the pH is controlled around 2~4 by sulfuric acid.
Table 5. The results of close-circuit flotation test

| product       | Yield (%) | Se (g/t) | Hg* (g/t) | Ag* (g/t) | Se (%) | Hg (%) | Ag (%) |
|---------------|-----------|----------|----------|----------|--------|--------|--------|
| Concentrate   | 28.38     | 7.26     | 978.35   | 1025.10  | 80.60  | 85.40  | 86.20  |
| Tailings      | 71.62     | 0.40     | 129.07   | 65.03    | 19.40  | 14.60  | 13.8   |
| raw of ore    | 100.00    | 2.18     | 37004.43 | 337.5    | 100.00 | 100.00 | 100.00 |

As illustrated in table 5, the selenium grade reached 7.26% with recovery 80.60% in the bulk concentrate. Only 0.40% selenium wasted in tailings. Meanwhile the grade of Hg, Ag is 978.35g/t, 1025.1g/t respectively, with recovery 85.4%, 86.2% respectively. Most valuable elements are recovered, obviously the flotation reagents are suitable for Se, Hg and Ag recover.

4. Conclusions

4.1. Mineralogy The pyrite acidic residue contain 2.18% selenium, 5.80g/t mercury and 337.5g/t silver, they are the main valuable elements which should be recovered.

4.2. The sodium silicate not only significantly depressant the gangue minerals but also disperse the pulp, using sodium silicate and sodium hexametaphosphate as combinatorial depressants, the obtained flotation indicators are prominent.

4.3 The valuable elements are easily enriched by flotation, and none collector or frother was utilized in this research, while the obtained results are satisfying, i.e., the grade of se, Hg, Ag is 7.254%, 978.35g/t, 1025.10g/t respectively, all of their recovery achieved more than 80%. The collectorless flotation method is favorable and it is possible to be a good example in comprehensive utilization of the selenium containing ores and residues in China.

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