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Study on selenium extraction from anode slime

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Abstract: Taking a copper anode slime as the raw material, a novel process for selenium extraction was studied. The primary selenium recovery can reach above 88.5% and the quality index of selenium product can be up to 99.5%. The economic benefit resulted is remarkable and environment has been protected.

Key words: copper anode slime; extraction; selenium

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1 Intrduction

Selenium is a rare and scattered metallic element, its average concentration in earth's crust is 0.05×10^{-6}, it generally cannot form a separate mineral and is patchily distributed in some minerals such as copper ore, lead ore and Hg (S,Se). Selenium is widely used due to its unique property in some areas such as electronics, glass, metallurgy, chemicals, agriculture and medicine. It was reported that the amount of selenium application had been up to 2100－200 t/a[1], and its demands will grow in the future with the progress of technology.

Anode slime is the major source for selenium extraction as the selenium content in it can be up to 20%－50%. The main extraction methods include sulphating roasting, soda roasting, oxidative high pressure leaching in caustic alkali, acid oxidative leaching, etc. While selenium reduction is conducted mostly with sulphur dioxide (or sodium sulphite) and copper. For all these processes, apart from the special advantages each, shortcomings which cannot be overcome also exist: severe environmental pollution, complexity and sever corrosion to equipment, lower recovery. In order to improve working conditions, reduce production cost and increase economic benefit. The technology study of selenium extraction from anode slime is of an important realistic meaning.

2 Experimental

2.1 Materials

The employed copper anode slime is from some plant at abroad, its main compositions are shown in Table 1.

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Table 1 Analytical results for main elements of anode slime

Element	Se	Te	Cu	Pb	Ag	Ni	Fe	SiO_2	Al	Ca	Sb
Mass fraction/%	45.8	1.2	25.9	5.2	0.015	1.02	2.8	3.5	1.05	1.85	2.3

2.2 Experimental methods

This process composed of three parts: leaching, precipitation of Se and purification. For which, conditional experimental studies has been conducted to determine the optimum process. First, during alkaline leaching, the effects of temperatures, sodium hydroxide concentrations and solid-liquid ratios on Se leaching rate were mainly investigated. Second, during Se precipitation process the effects of the pH values of solutions and reductants on Se recovery and purity were mainly investigated. Third, during the purification of Se the effects of the temperatures, oxidizing agent on Se recovery and purity were mainly investigated.

Pilot experiment: leaching and Se precipitation process was controlled by means of a thermostat water bath, electric stirrer and vacuum filter. A small smelter furnace was applied for the purification.

The Se contained in raw materials, leaching solutions, metallic products, leaching slags, Se precipitation solutions and smelter slags was analyzed by using chemical volumetric method. As for the calculation of leaching rate, the average value between the metal leaching rate calculated according to leaching solution and that calculated according to solid phase, the recovery calculation is the same.

2.3 Experiment flowsheet

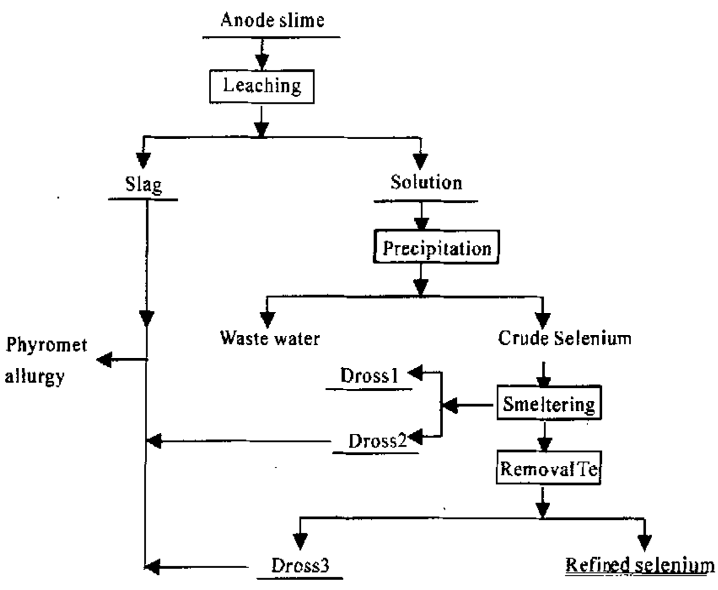

Fig. 1 Experiment flowsheet

3 Experimental results and discussions

3.1 Conditions for leaching

3.1.1 Influence of alkali concentration on selenium leaching rate

An experiment for evaluating the effects of sodium hydroxide concentrations on the leaching rates of Se with solid-liquid ratio 1 : 4 at temperature 80—85℃ was conducted, its results are shown in Fig. 2.

Fig. 2 reveals that the leaching rate of Se improves with the increase of sodium hydroxide concentrations, but when after up to 250 g/L the leaching rate has not much change, the curve tends to get flat, the leaching rate of Se is 92.3%. The chosen sodium hydroxide concentration was 250 g/L.

The alkali concentration is an important factor affecting Se leaching rate. The main reaction process for leaching is as follows:

$$3Se + 6NaOH \longrightarrow 2Na_2Se + Na_2SeO_3 + 3H_2O$$

The increase of alkali concentration contributes to the proceeding of above reaction, resulted in the improvement of leaching rate.

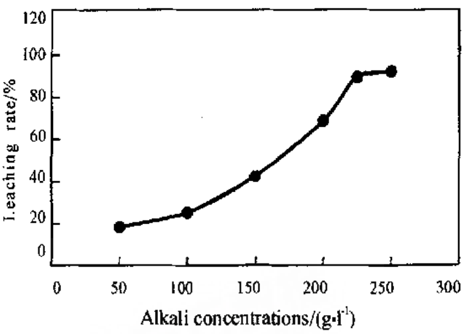

Fig. 2 The effects of alkali concentrations on Se leaching rates

3.1.2 Effects of temperature on Se leaching rate

An experiment for evaluating the effects of different temperatures on the leaching rates of Se with solid-liquid ratio 1∶4 at temperature of 80−85℃ was conducted, its results are shown in Fig. 3.

Fig. 3 shows that the leaching rate improves with the temperature increase. It is seen from the experimental results that Se leaching rates remain mostly unchanged when temperatures above 80℃. The chosen proper temperature for the experiment was 80−85℃.

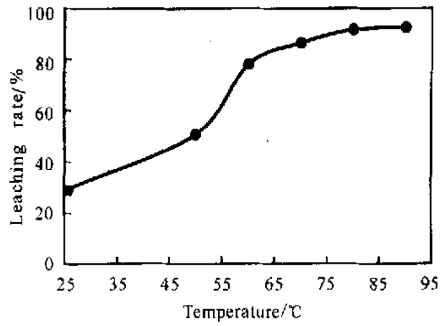

Fig. 3 The effects of temperature on Se leaching rates

3.1.3 Effects of solid-liquid ratios on Se leaching rates

The effects of sodium hydroxide concentrations on Se leaching rates under temperature of 80−85℃ is shown in Table 2.

Table 2 Effects of solid-liquid ratios on Se leaching rates

Solid-liquid ratio	1∶2	1∶3	1∶4	1∶5
Leaching rate/%	60.5	82.5	92.5	93.6

It can be seen from Table 2 that the leaching rate improves with solid-liquid ratio increase. Although the leaching rate of solid-liquid ratio 1∶5 is 1.50% higher than that of solid-liquid ratio 1∶4, considering from the angle of economic benefit, the chosen solid-liquid ratio was 1∶4.

3.2 Conditions for Se precipitation

3.2.1 Effects of acidity and alkalinity on Se recovery and purity

The pH of above leaching solutions were adjusted with sulfuric acid (1∶1), its effects on the recovery and purity of Se are shown in Table 3. From which, it can be known that when pH value within the range of acidity, the Se concentration in effluent solution varies not much, around 3−5 g/L. The Se recovery is 94%−96%. Se purity becomes lower and lower with the pH value decrease. In consideration to the Se contained in the effluent solution needs further recovery, the finally chosen pH value was 4−5.

Table 3 Effects of pH values on Se recoveries and purities

pH value	Se concentration in effluent solution/$(g \cdot L^{-1})$	Se recovery/%	Se purity/%
8.0	8.62	91.36	95.23
6.0	5.13	94.87	95.23
4.0	4.36	95.63	95.05
2.0	3.85	96.13	83.84

Note: The preliminary Se concentration is 100 g/L, the volume is 10000 mL.

3.2.2 Effects of reductants on Se recoveries

Because a certain amount of Se is contained in the effluent solution, recovering should be done so as to ensure the recovery and economic benefit of Se metal. Normally, the reduction with sodium sulphite simply can meet the discharge requirements, Se<0.1 g/L. But the reduction is incomplete and cannot meet the requirements with the above effluent solution of pH value within 4—5. Therefore, through a reductant selective experiment, it was found that the reductant A exhibits better effects, the Se concentration within the discharged waste water is less than 0.1 g/L.

3.3 Purification process

First, the as-prepared crude Se was washed by a multi-stage method, then samples were taken after drying and analyzed. The typical chemical compositions are shown in Table 4. From which it can be known that the main impurities are Te, Sb, Pb, Cu, etc.

Table 4 Chemical compositions of crude Se

Element	Se	Te	Pb	Cu	Sb	Na	Ca	Al
Mass fraction/%	95.2	1.53	0.52	0.12	1.28	0.5	0.15	0.02

3.3.1 Lead removal by pyrometallurgy

First made the above crude Se molten under temperature 300℃, stirred it, then kept the temperature and kept it aside, removed dross 1; Added into lead removing agent, stirred for half an hour, kept it aside and took out dross 2. The metallic impurity contents are shown in Table 5. The Se impurity has arrived to over 98%, and the direct recovery of as-obtained Se has arrived to over 99%.

Table 5 Contents of metallic impurities in crude Se after lead removed

Element	Te	Pb	Cu	Sb	Ca	Al
Mass fraction/%	1.65	0.02	0.01	0.58	0.005	0.01

3.3.2 Te removal by oxidation

Made the crude Se molten under a certain temperature, stirred it, slowly added into oxidant Ya, then kept the temperature and stirred for 3—4 hours, kept it aside and finally took out dross 3, the metal Te was recovered and metal Se was discharge. The oxidant could be recycled and utilized. After this process, the Se purity could reach above 99.5%, and the Se recovery above 98%.

Table 6 Quality analysis of Se product

Element	Se	Te	Cu	Pb	Ag	Ni
Mass fraction/%	≥99.5	≤0.1	≤0.01	≤0.02	≤0.001	≤0.001
Element	Si	Al	Mg	Ca	Sb	Na
Mass fraction/%	≤0.05	≤0.01	≤0.05	≤0.01	≤0.1	≤0.01

4 Conclusions

After having treated the copper anode slime of some plant from abroad by this process, the quality of Se product can reach above 99.5%, the direct recovery of 88.5%−90%. This flow sheet is advanced, the economic benefit obtained is higher, the environment has been protected, and labour intensity has been greatly decreased.

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