A clean and efficient method for purifying crude selenium based on a selective leaching - directed decomposition purification process

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Abstract

The rare element selenium is a key material in supporting the development of high-tech and new products. This research has led to the development of a method of purifying crude selenium based on a selective leaching-directed decomposition purification process. The influence of factors such as the concentration of the leaching solution, leaching temperature, solid-liquid ratio, and leaching time on the leaching rate of Se were investigated in detail. The experimental results show that the optimal conditions for selective leaching of selenium were as follows: the concentration of leaching solution (solute: Na$_2$SO$_3$) was 260 g l$^{-1}$, the stirring speed was 300 rpm, the ratio of liquid to solid was 0.10 g ml$^{-1}$, the reaction temperature was 90 $^\circ$C, the reaction time was 180 min, and the leaching rate of selenium on one run was $>$95%. The products of selenium after two runs meet the requirements of Se99.9 in YS 223–2007, the Chinese nonferrous metal industry standard. The direct yield of Se is greater than 90%, and precious metals such as gold, silver and platinum are enriched in the residue. No waste is produced during the whole purification process, and all products can be recycled. This study provides an efficient and environmentally friendly method for the purification of crude selenium, which has important industrial applications.

1. Introduction

The rare element selenium is widely used in metallurgy, materials, the chemical industry, agriculture and medical treatment [1–5]. With the development of selenium-containing advanced materials and the increasing demand for selenium in the fields of electronic semiconductors, solar energy and healthcare, high-quality selenium has become a key material for supporting the development of new high-tech products [6–8]. The preparation of high-quality selenium by efficient and sustainable separation and purification has become a focus of attention [9]. A copper plant in Yunnan uses oxygen pressure removal of copper - extraction selenium by chlorination - sulfur dioxide reduction to extract crude selenium from copper anode mud. The average annual output of crude selenium is approximately 400 t (calculated as metallic Se). However, the grade of crude selenium products is low, only approximately 90% (mass percentage), the composition of crude selenium is complex, there are many kinds of impurities, and purification is difficult. The clean and efficient purification of crude selenium and increasing the added value of the products has become a key issue in need of urgent resolution.

At present, publicly reported selenium purification methods mainly include chemical methods and physical methods [10, 11]. The use of these methods must be determined according to the characteristics of the raw materials and product requirements. Purification of selenium by physical methods, such as vacuum distillation and zone smelting, is based on the difference in the distribution of impurity elements between the gas-liquid-solid three phases to achieve the purification of selenium [12–15]. Although the physical method can increase
the purity of selenium to more than 99.998%, it has high requirements on the quality of raw materials and is only suitable for the purification of crude selenium materials above 3N, and of its ability to separate selenium and tellurium is very small. Chemical purification of selenium, such as oxidative volatilization and $\text{H}_2\text{Se}$ thermal decomposition, converts elemental selenium $\text{Se}$ into compounds containing $\text{Se}^{4+}$, $\text{Se}^{6+}$ or $\text{Se}^{2-}$ through oxidation or reduction. Then, according to their differences in physical and chemical properties, volatilization, selective precipitation, coordinated extraction, ion exchange and other methods are used to separate impurities from selenium [16–22]. Finally, after reduction or oxidation, $\text{Se}^{4+}$, $\text{Se}^{6+}$ or $\text{Se}^{2-}$ is converted into elemental selenium, and after repeated purification, high-quality selenium that meets the quality requirements is obtained.

S. Nielsen et al [23] heated selenium to 650 °C and reacted with $\text{H}_2$ to generate $\text{H}_2\text{Se}$ gas, which was then pumped into the reactor at 1000 °C to dissociate $\text{H}_2\text{Se}$ into $\text{Se}$ and $\text{H}_2$ and successfully removed the impurity tellurium. However, as $\text{H}_2\text{Se}$ is a highly toxic gas, this method can only be used to produce a small amount of ultra-high purity selenium. Song et al [24] used potassium bisulfate to oxidize crude selenium. Selenium and tellurium are oxidized to selenium dioxide and tellurium dioxide respectively. Selenium dioxide is volatilized and absorbed by water to generate selenite solution, which is then reduced to elemental selenium through sulfur dioxide. Tellurium dioxide remains in the slag due to its high melting and boiling point, thus achieving the separation of selenium and tellurium. Gao et al [25] prepared high purity selenium by the method of oxidation combustion. Deep oxidation of selenium was carried out to remove the impurity tellurium. Finally, high purity selenium with a purity of more than 6N was prepared by vacuum distillation. Dutton et al [26] purified selenium by multiple oxidation method, studied the process of selenium vapor oxidation to $\text{SeO}_2$, and carried out complete or partial selenium oxidation experiments. Unfortunately, these methods have disadvantages such as long processes, repeated changes in the valence of selenium, and easy production of toxic and harmful byproducts.

In contrast, selenium is often leached by sodium sulfite [27–29]. The principle of this method is to use sodium sulfite to selectively leach elemental selenium to generate sodium selenium sulfite ($\text{Se} + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{SeSO}_3$). The impurity is insoluble, so the selenium and the impurities are separated. This process prevents easy to operate, uses simple devices and is free of pollution.

In this work, the crude selenium produced by the wet method of copper anode mud was selected as the research object. According to the thermodynamic characteristics of selenium and impurities, a selective leaching - directed decomposition purification process for crude selenium is proposed to realize the clean and efficient separation and purification of selenium and to realize a high concentration of high-value-added metals such as silver and gold.

2. Materials and methods

2.1. Materials

The initial material (average particle size: 24.24 μm) was produced by a copper electrolytic refining company in Yunnan, PRC. The reagents $\text{Na}_2\text{SO}_3$ and $\text{H}_2\text{SO}_4$ are of analytical grade. Deionized water was used in all experiments.

2.2. Experimental procedure

The research framework for this study is shown in figure 1. Na in the raw material were removed by weak acid washing (liquid-solid ratio 4:1, sulfuric acid concentration of 50 g l$^{-1}$, washing for one hour, drying at 80 °C for 24 h) to avoid affecting the subsequent selective leaching. Then, pretreated crude selenium was used as a raw material for selective leaching experiments under normal pressure. The influence of factors such as the concentration of the leaching solution, leaching temperature, solid-liquid ratio, and leaching time on the leaching rate of Se were investigated, and the optimal process parameters were determined. The leaching rate of Se was calculated by the following equation: leaching rate of Se = 1 - ($m_f / m_i$)? × 100%, where $m_i$ is the mass (g) of the initial material (100g), $m_f$ is the mass (g) of leaching residue, $w_i$ is the content (%) of element Se in the initial material, and $w_f$ is the content (%) of element Se in the leaching residue. After that, at a temperature of 50 °C, concentrated sulfuric acid was added dropwise to the leaching solution at a constant speed until pH = 1.5, and finally, the selenium product was obtained by filtering and washing.

2.3. Characterization

Inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 8000, PerkinElmer Corporation, America) was used for the quantitative determination of the low element contents in the obtained samples. Furthermore, the purity of the obtained selenium was quantitatively determined using chemical titration according to the standards for Nonferrous Metals Industry of the People’s Republic of China (YS/T 226.12e2009), which is suitable for determining 98%–99% selenium. The phases of the obtained samples were examined by x-ray diffraction (XRD) employing a scan speed of 0.02°/s in the 2-theta range and using a
Rigaku/D-Mac-3c x-ray diffractometer with Cu Kα radiation. A Winner 2000 (Jinan Winner Instruments Co., Ltd) laser particle size analyzer was used for particle size analysis of the samples. The elemental distribution of the samples was analyzed using an electron probe microanalyzer (EPMA, JXA8230, JEOL, Japan) at an accelerating voltage of 20 kV and a beam current of $2 \times 10^{-9}$ A.

### 3. Results and discussion

#### 3.1. Materials characterization

The raw material composition after pretreatment is shown in Table 1. The main component of crude selenium is metallic selenium, and it also contains a small amount of the precious metals gold, silver and the base metals lead, bismuth, and copper and so on. The XRD results are shown in Figure 2(a). Due to the small impurity content, the XRD pattern did not show obvious characteristic peaks of impurity. Figures 2(b)–(d) shows the XPS analysis results of Se, Te, and Pb in the raw material. The calibration of the binding energy scale was done by taking the reference of the C1s peak at 284.8 eV. For the XPS analysis results of Se, the Se 3d$_{5/2}$ peak is decomposed to three peaks at 54.78, 55.64 and 54.05 eV, corresponding to Se and PbSe, respectively [33, 34]. As shown in Figure 2(d), the energy band at 571.71 and 582.21 eV corresponds to 3d$_{5/2}$ and 3d$_{3/2}$ peaks of PbTe respectively [35], the energy band at 573.29 and 583.69 eV corresponds to 3d$_{5/2}$ and 3d$_{3/2}$ peaks of elemental state Te respectively [36], the energy band at 574.45 and 584.85 eV corresponds to 3d$_{5/2}$ and 3d$_{3/2}$ peaks of elemental state Te-O respectively [37], while the other doublet at 576.55 and 586.95 eV is assigned to 3d$_{5/2}$ and 3d$_{3/2}$ of TeO$_2$ respectively [38].

Figure 3 shows the EPMA elemental mapping of the pretreated crude selenium in several typical impurity-rich areas. This mapping indicated that the impurity phases aggregated and were easily recognized by electron microscopy. Except for some impurity phase aggregation regions, tellurium is uniformly distributed in the selenium matrix and the typical impurity enrichment regions are mainly composed of Pb-Se, Pb-Se-Te, Pb and other phases, which was consistent with XPS and XRD analysis results.

![Figure 1. New process flow chart of 'selective leaching - directional decomposition' for selenium purification.](image)

| Elements sample | As  | Cu  | Fe  | Pb  | Se  | Sb  | Te  | Na  | Ni  | Au (g/t) | Ag (g/t) |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----------|----------|
| Initial material| 0.09| 0.77| 0.074| 5.35| 82.04| 0.03| 1.55| 0.73| 0.01| 110.78   | 3118.80  |
| Pretreated crude selenium | 0.05| 0.54| 0.071| 5.23| 87.52| 0.02| 1.66| 0.01| 0.01| 119.09   | 3353.80  |
3.2. Factors influencing the selective leaching of selenium

3.2.1. Influence of leaching solution concentration on the selective leaching of selenium

Under the conditions of a stirring speed of 300 rpm, a liquid-to-solid ratio of 0.10 g ml\(^{-1}\), a reaction temperature of 90 °C and a leaching time of 180 min, the effects of different leaching solution concentrations (200 g l\(^{-1}\), 220 g l\(^{-1}\), 240 g l\(^{-1}\), 260 g l\(^{-1}\), 280 g l\(^{-1}\), 300 g l\(^{-1}\)) on the leaching rate of selenium were studied. The experimental results are shown in figure 4.

When the concentration of the leaching solution was low, the leaching effect of selenium was not satisfactory. At low concentrations, it is difficult for selenium to fully contact Na\(_2\)SO\(_3\) and the slow leaching rate.
prevented the selenium from being completely leached within the reaction time. When the concentration reached 260 g l$^{-1}$, the leaching of selenium was relatively complete, and as the concentration continued to increase, the leaching rate of selenium remained basically unchanged. Therefore, 260 g l$^{-1}$ is considered to be the most suitable concentration of the leachate.

### 3.2.2. Influence of leaching temperature on selective leaching of selenium

Under the conditions of stirring speed, liquid-solid ratio, leaching solution concentration, and leaching time controlled to 300 rpm, 0.10 g ml$^{-1}$, 260 g l$^{-1}$, and 180 min, the effects of different leaching temperatures (50 °C, 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C) on the leaching rate of selenium were studied. The experimental results are shown in figure 5.

With the continuous increase in leaching temperature, the rate of the leaching reaction increased, and the leaching rate of selenium continued to increase and remained mostly unchanged above 90 °C. When the leaching temperature is low, the selenium particles accumulate together in a certain form, and the reaction surface area is relatively small. In addition, the reaction rate coefficient is small under the condition of low temperature. Therefore, the leaching reaction speed is relatively slow at low temperature. Therefore, 90 °C is considered the best leaching temperature.

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Figure 4. Influence of leaching solution concentration on the leaching rate of selenium.

Figure 5. Influence of leaching temperature on the leaching rate of selenium.
3.2.3. Influence of the solid-to-liquid ratio on the selective leaching of selenium

Under the conditions of a leaching solution concentration of 260 g l\(^{-1}\), a reaction temperature of 90 °C, a stirring speed of 300 rpm, and a leaching time of 180 min, the effect of different solid-liquid ratios (0.25 g ml\(^{-1}\), 0.20 g ml\(^{-1}\), 0.16 g ml\(^{-1}\), 0.14 g ml\(^{-1}\), 0.10 g ml\(^{-1}\), and 0.01 g ml\(^{-1}\)) on the leaching rate of selenium was explored. The experimental results are shown in figure 6.

As the solid-to-liquid ratio increased, the viscosity of the solution increased, hindering the diffusion of the components, and the leaching rate of Se gradually decreased. The solid-to-liquid ratio of 0.10 g ml\(^{-1}\) had the best leaching effect, reaching 95.1%. Therefore, the most appropriate solid-liquid ratio was 0.10 g ml\(^{-1}\).

3.2.4. Influence of leaching time on the selective leaching of selenium

Under the conditions of a leaching solution concentration of 260 g l\(^{-1}\), a reaction temperature of 90 °C, a stirring speed of 300 rpm, liquid-to-solid ratio of 0.10 g ml\(^{-1}\), and reaction temperature of 90 °C, the effects of different leaching times (60 min, 90 min, 120 min, 160 min, 180 min, and 270 min) on the leaching rate of selenium were studied. The experimental results are shown in figure 7.

With the extension of the leaching time, the concentration of the leaching solution and the amount of remaining selenium gradually decreased, while the selenium leaching rate continued to increase. After 180 min, the selenium leaching rate remained predominantly unchanged. At this time, the leaching reaction reached
Selenium products is shown in table 4. After the second purification, the requirements of Se99.9 in the industry standard of selenium powder is obvious and no other valence state of selenium is identified. XPS results show that the purity of selenium is high, the characteristic peak of the prepared product selenium in this process was a gray powder with uniform particle size, and the average particle size was 59.43 μm. XRD and XPS results show that the purity of selenium is high, the characteristic peak of the prepared product selenium was indexed to Se99.9. The direct yield of selenium was calculated to be 92.6%.

Table 2. Chemical analysis of the main elements of the intermediate products in each process.

| Product                  | Quantity | Se   | Te  | Pb  | Au  | Ag  | Pt  | Pd  |
|--------------------------|----------|------|-----|-----|-----|-----|-----|-----|
| Residue                  | 15.3 g   | 34.78% | 9.96% | 47.51 | 716.00 g/t | 20200.00 g/t | 23.80 g/t | 54.60 g/t |
| Decomposition of liquid  | 1.01     | 0.067 g l⁻¹ | /   | /   | /   | /   | /   | /   |

Note: ‘/’ indicates that the content is lower than the ICP-AES detection limit.

Table 3. Results of chemical analysis of selenium products in one purification (%).

| Elements number | As    | Cu    | Fe    | Pb    | Sb    | Te    | Ni    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| Se999           | 0.003 | 0.001 | 0.005 | 0.002 | 0.001 | 0.007 | 0.002 |
| No. 1           | 0.0098 | 0.0024 | 0.0060 | 0.0053 | 0.021 | 0.0071 | 0.00058 |
| No. 2           | 0.015 | 0.0021 | 0.0050 | 0.0051 | 0.021 | 0.0036 | 0.002 |
| No. 3           | 0.010 | 0.0017 | 0.0043 | 0.0088 | 0.11 | 0.001 | 0.001 |
| No. 4           | 0.008 | 0.0015 | 0.0032 | 0.0056 | 0.14 | 0.001 | 0.0005 |
| No. 5           | 0.040 | 0.0016 | 0.0027 | 0.0076 | 0.056 | 0.001 | 0.0005 |

equilibrium, and the selenium was almost completely leached. Therefore, the most suitable leaching time is 180 min.

Under the experimental conditions, the optimal conditions for selective leaching of selenium were as follows: the concentration of leaching solution was 260 g l⁻¹, the stirring speed was 300 rpm, the ratio of liquid to solid was 0.10 g ml⁻¹, the reaction temperature was 90 °C, the reaction time was 180 min, and the leaching rate of selenium was >95%. Chemical analysis results of leaching residue obtained under optimal conditions are shown in table 2. Almost all of the precious metals were enriched in the leaching residue, which can be used to recover the precious metals.

3.3. Experimental results of directional decomposition

Concentrated sulfuric acid was added dropwise to the leachate obtained under the best experimental conditions at a constant speed until pH = 1.5, and finally, the gray selenium product was obtained. In addition, to verify the stability and reproducibility of the experiment, five sets of parallel experiments were carried out under the optimal experimental conditions. The chemical composition of the selenium products is shown in table 3.

The selective leaching-directed decomposition process for purifying crude selenium has a significant effect, especially for Te in crude selenium, which is removed efficiently, and this process can effectively separate selenium and tellurium. The main grade of fine selenium obtained by one purification of crude selenium was >99.5%. However, the contents of As, Cu, Pb and Sb did not meet the requirements of Se99.9 in YS223–2007, the Chinese nonferrous metal industry standard.

As shown in table 2, the amount of selenium in the decomposition liquid was as low as 0.067 g l⁻¹, which means that Na₂SeSO₃ had almost completely decomposed. The direct yield of selenium was calculated to be 93.5 ~95.1% according to the final dried fine selenium product. The decomposition liquid can be recycled by crystallization through evaporation to obtain anhydrous sodium sulfate powder. The evaporation solution can be recycled. In summary, no waste is produced during the whole purification process, and all the process flow diagram of the selenium purification technology proposed in this paper is shown in figure 9. 3N selenium was prepared by selective leaching - directed decomposition process, while the output of SO₂, residue containing precious metal returned to the processes of sulfuric acid preparation and precious metal recover. And the decomposition solution can be prepared by evaporation and crystallization of Na₂SO₄, and the condensate can be recycled.
products can be recycled. This study provides an efficient and environmentally friendly method for the purification of crude selenium, which has important industrial applications.

4. Conclusions

(1) Through the selective leaching process, the separation of selenium and tellurium is obvious, and the leaching rate of selenium can reach 95.1%.

(2) Throughout the process, Au, Ag, Pt and Pd are enriched in the leaching residue, which can be used to recover the precious metals.

(3) The purity of selenium obtained by twice purification meets the Requirements of the Industry Standard (YST223–2007), and the direct yield of selenium is 92.6%.

(4) No waste is produced during the whole purification process, and all products can be recycled.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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