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Purification of crude selenium by vacuum distillation and analysis

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ABSTRACT

In this study, metallurgical grade crude selenium (99.4%), comprehensively recovered from copper electrolysis anode slime, was purified to 99.992% through triple consecutive vacuum distillation (TCVD) on a laboratory scale. The actual evaporation rate and accommodation coefficient α of crude selenium were found to be 0.0231 g cm−2 min and 0.3236, respectively, at 523 K and approximately 4 Pa by a vacuum thermogravimetric furnace. Internal heat vacuum distillation equipment was employed in the purification experiments with a dynamic vacuum level of approximately 4 Pa. Detailed analysis of the initial and purified selenium was performed using inductively coupled plasma mass spectrometry (ICP-MS) to identify the 15 most common impurity elements. The analysis confirmed the reduction in the total impurity content from 2997.38 ppmw to <79.08 ppmw. The microscopic impurity elemental distribution was analyzed using an electron probe microanalyzer (EPMA), and it shows that the impurities were relatively concentrated and gathered in crude selenium. The results enrich the database of selenium evaporation kinetics and lay a foundation for the industrial purification of selenium.

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1. Introduction

Selenium (Se) is a relatively rare element in the Earth’s crust. Since it was discovered by Jöns Jacob Berzelius [1], a Swedish chemist, in 1817, Se has been widely used in various high-tech fields as a strategic metal and is an essential trace element in living organisms [2]. In industrial production, most selenium is comprehensively recovered from copper electrolysis anode slime [3–5]. The extracted selenium is generally metallurgical grade (MG-Se, 90–99.5%), but a slightly higher purity of 99.9% is preferred [6]. This has become an urgent need

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due to recent developments in the semiconductor and medical health industries [7–10], such as ZnSe single crystals, Cu(In, Ga)Se₂ thin films, and anticancer drugs. A number of chemical methods that can be used for refining selenium have already been developed, including oxidation-reduction [11], selective leaching-precipitation [12] and the thermal decomposition of hydrogen selenide gas [13,14], which all prepare an intermediate compound by adding chemical reagents and then separate the impurities. While a satisfactory purity can be obtained, the techniques require the disposal of hazardous waste as well as the need to treat any emissions [15,16]. The zone refining process involves physical processes to remove impurities in crude selenium [17–19]. According to the concentration, differences exist between the liquid and solid phases that are in contact during the melting or solidification of a solid solution; however, this process is very time-consuming with a low output [20]. In contrast, there is growing interest in vacuum distillation techniques. A metallurgical process carried out in a confined system below atmospheric pressure with a low energy consumption as well as higher output, which has been widely applied in the fields of the sustainable clean recovery of secondary resources, preparation of high-purity metals and harmless disposal of hazardous wastes [21–25].

Based on the large gap in the saturated vapor pressure between Se and other impurities, when selenium is exposed to a vacuum at a certain temperature, the majority of impurities can be effectively removed. Some studies [26,27] have presented the concept that vacuum distillation can easily purify selenium; however, none of the studies provide any details concerning the process parameters, especially the evaporation rate of selenium by vacuum distillation [28–31]. In the present work, the purification of MG-Se to reach 99.992% was explored by vacuum distillation. The saturated vapor pressure \( p^* \), actual evaporation rate \( \omega \), and accommodation coefficient \( \alpha \) in vacuum distillation were investigated in detail.

2. Materials and methods

2.1. Theoretical analysis of the saturated vapor pressure

The solid and liquid forms of any substance have the tendency to volatilize into a gaseous form and vice versa. Under certain temperature and pressure conditions, a dynamic equilibrium exists between gas and condensed phases, and the number of molecules mutually converted from a condensed state and gaseous state in a unit of time is equal. This pressure is the saturated vapor pressure \( (p^*) \) of the substance at this temperature. The vapor pressure \( p \) is often nonlinearly related to the absolute temperature \( T \), and their relationship can be expressed by the Clausius–Clapeyron equation as follows [32]:

\[
\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m}
\]

where \( \Delta H_m \) is the heat of vaporization, \( \Delta V_m \) is the corresponding increase in volume upon converting a liquid to vapor, and \( T \) is the phase equilibrium temperature. Combining the Clapeyron–Mendeleev equation \((pV = mRT/M)\) and integrating it can produce the relationship between the saturated vapor pressure and temperature [33].

\[
lgp^* = AT^{-1} + BlgT + CT + D
\]

where \( p^* \) is the saturation vapor pressure in Pa, \( T \) is the temperature in K, and \( A, B, C, \) and \( D \) are the evaporation constants obtained from the literature [34,35].

According to Eq. (1) and the values of \( A, B, C, \) and \( D, \) the saturated vapor pressure can be calculated. Fig. 1 shows the saturated vapor pressures for Se and the 15 main impurities at 473 K, 523 K, 623 K and 723 K. It is generally believed that materials with higher vapor pressures have greater volatility [33,36–38]. The vapor pressures of Hg and S are higher than those of Se, which preferentially volatilizes during the distillation process. Other elements with a low vapor pressure are easily removed as a residue. The impurities that are more difficult to remove have vapor pressures close to that of Se. Hence, in this work, triple consecutive vacuum distillation (TCVD) was performed to refine crude selenium. In the first step, the initial crude selenium is vacuum distilled at a low temperature of 453 K to remove Hg and S. The second vacuum distillation at 523 K with the residue of the first distillation removes impurities with lower saturated vapor pressures than Se. Finally, a third vacuum distillation at 503 K is carried out on the second distillation volatiles to achieve the excellent removal of impurities.

2.2. Evaporation rate of selenium

The thermodynamic properties of the saturated vapor pressure can indicate the possibility of the separation of Se and impurities, while the kinetic factors of evaporation rate play a major role in determining the purification efficiency of vacuum distillation. By knowing the evaporation rate of crude selenium, the time required for distillation can be calculated to reduce unnecessary energy consumption and increase the production efficiency. During the vacuum distillation of crude selenium, the Se molecules break away from the evaporat-
ing surface and enter the gas space, forming a metal vapor flow that diffuses and migrates to the condenser in the vapor phase. The distillation type is ‘viscous’ distillation on account of \( \lambda < L \) [39]. The distance (L) between the initial evaporation surface and collector is 8.0 cm, and \( \lambda \) is the mean free path, which was calculated as 0.76 cm for Se using the Sutherland formula:

\[
\lambda = \frac{3.11 \times 10^{-18} T}{d^2 \rho_0}
\]

where \( \rho_0 \) is the system pressure of approximately 4 Pa, \( d \) is the diameter of the selenium vapor molecule (2.32 \( \times \) 10^{-8} cm [35]), and \( T \) is the distillation temperature of 523 K.

The theoretical maximum evaporation rate \( \omega_{\text{cal}} \) of Se at the distillation temperature (523 K) is calculated to be 0.07138 g cm^{-2} min^{-1} by the Langmuir–Knudsen equation as follows [33]:

\[
\omega_{\text{cal}} = 2.624 \times 10^{-2} \alpha \rho_s^0 \sqrt{\frac{M}{T}} (g \cdot \text{cm}^{-2} \text{min}^{-1})
\]

where \( \omega_{\text{cal}} \) is the theoretical evaporation rate in g cm^{-2} min^{-1}; \( \alpha \) is the accommodation coefficient, i.e., the probability of a distilled atom leaving the surface of the melt, which is taken as approaching unity; \( \rho_s^0 \) is the saturated vapor pressure of 5.01 Pa; \( M \) is the molecular weight of 78.96 g; and \( T \) is the melt surface temperature of 523 K. However, the theoretical value of the maximum evaporation rate is several orders of magnitude greater than the experimental values in the actual process, because of the metal evaporates and reaches the condenser directly without colliding with the evaporated molecules or residual gas [40,41]. The reason for this difference is the influence of the molecular size, intermolecular forces, molecular collisions, etc. The detailed factors are analyzed by Ali et al., Gopala et al. and Zhang et al. [40–42]. From Ref. [33], we refer to some studies in the former Soviet Union to obtain the accommodation coefficients of some metals at different temperatures. Among them, the value of \( \alpha \) is rarely unity. Hence, it is critical to study the actual evaporation rate of crude selenium in the vacuum distillation process.

2.3. Experimental procedure

The initial material was produced by a copper electrolytic refining company in Yunnan, China. In this research work, we employed a vacuum thermogravimetric furnace (Fig. 2) developed by ourselves to accurately and quickly measure the actual evaporation rate of selenium at the experimental temperature (523 K). From Fig. 2, it can be clearly seen that the crucible and the analytical balance are connected by insulating material. When the material is vacuum distilled, the slight changes in mass, pressure, and temperature in the system can be recorded by the balance, vacuum gauge and thermocouple respectively, and the signal is transmitted to the computer terminal. The actual experimental evaporation rate will be found by measuring the change in the mass of selenium per unit time and area in the actual distillation process.

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An inner resistance-heated vacuum distillation equipment (Fig. 3) was used in the purification experiments. The distillation chamber of the stainless-steel furnace contains a thermocouple, refractory, heater, graphite crucible and condenser. Then, 10 g of initial input material was added into a high-purity graphite crucible for the TCVD experiment at the conditions of 453 K, 523 K, and 503 K. A dynamic vacuum level of approximately 4 Pa in the distillation chamber was obtained by a mechanical vacuum pump. The heating rate was controlled at 3 K/min, and the temperature was controlled by an automatic temperature control system when the target distillation temperature was reached. The furnace was evacuated for approximately 3 h at 673 K to remove any moisture. As the temperature inside the crucible reached the target temperature, the material started evaporating. After the end of distillation, as the temperature in the chamber dropped to room temperature, the condenser was cleaned off and weighed. The vacuum pump continued running during the cooling process, ensuring that the system was always in a vacuum state, thus preventing gas leakage and the oxidation of the metal.

2.4. Characterization

The purity of the initial selenium was directly determined by chemical titration. The concentrations of the 15 main impurities (copper, mercury, arsenic, antimony, tellurium, ferrous, lead, nickel, bismuth, magnesium, aluminum, silicon, boron, sulfur, and tin) were determined using inductively coupled plasma mass spectrometry (ICP-MS, 7700x, Agilent, America) according to the Standards for the Nonferrous Metals Industry of the People’s Republic of China (YS/T 223-2007 and YS/T 226.13-2009) issued by the National Development and Reform Commission. Then, the purity of distilled selenium was calculated by (100% – total impurities). The sample for analysis was taken from the condenser by random selection from five places and mixed to obtain an average impurity result. The surface morphology and elemental distribution of the crude selenium were analyzed by an electron probe microanalyzer (EPMA, JXA8230, JEOL, Japan) under an accelerating voltage of 20 kV and a beam current of 2 × 10⁻⁹ A.

3. Results and discussion

3.1. Actual evaporation rate and accommodation coefficient

The variation curves for the instantaneous mass \(m_{\text{selenium}}\), system pressure \(p_0\) and temperature \(T\) in the distillation process of crude selenium were obtained, as shown in Fig. 4(a).

It was observed that with the temperature raised continuously, the mass change curve is horizontal, while the system pressure has a significant fluctuation at a certain rate in the first 80 min, which is caused by the rapid evaporation of a small amount of water in the equipment. At 80 min, the mass decreases, the temperature is 485 K, and selenium begins to evaporate. Upon raising the temperature to 523 K and holding, selenium begins to lose weight at a certain rate until it is completely evaporated. Therefore, the temperature stability range of 120–150 min can be linearly fit to obtain \(k_{\text{exp}}\), and the experimental evaporation rate at 523 K was directly calculated to be 0.0231 g cm⁻² min using the following formula:

\[
\omega_{\text{exp}} = \frac{\Delta m}{\Delta t \cdot S} = \frac{k_{\text{exp}}}{S}
\]

where \(\omega_{\text{exp}}\) is the experimental actual evaporation rate of selenium in g cm⁻² min, which represents the mass change \(\Delta m, g\) of selenium in a certain time \(\Delta t, s\) and area of evaporation \(R, 1.5 \text{ cm}; S, 7.065 \text{ cm}^2\) during the distillation process. The theoretical value of \(k_{\text{cal}}\) was calculated by \(k_{\text{cal}} = \omega_{\text{cal}} \times S\) and is shown in Fig. 4(b). There is a gap between the theoretical value and actual value, and the reasons are primarily as follows: (1) the selenium vapor collides with residual gas molecules in the distillation chamber, as the distillation process is the viscous type, which will ensure maximum intercollisions and changes in the movement trajectory of the selenium vapor molecules; (2) the evaporation surface is partially occupied by other nonvolatile impurities; and (3) the decrease of the vapor pressure of the selenium melt resulting from the influence of...
the impurities. These factors will all contribute to the value of \( \alpha \). Furthermore, the actual value of \( \alpha \) at 523 K is found to be 0.3236 according to the ratio of \( \omega_{\text{exp}} \) to \( \omega_{\text{cal}} \). Consequently, the distillation time can be determined according to the value of the actual evaporation rate. Table 1 indicates the distillation time required under different selenium volatilizations.

### 3.2. Results of ICP-MS

The TCVD experiments were carried out under the conditions of 453 K, 30 min; 523 K, 60 min; and 503 K, 60 min; respectively. The 15 most prominent impurities in the initial and vacuum distilled selenium are given in Table 2. The purity of the initial crude selenium is 99.4%, and S, As, Bi, Fe, and Si account for >84.95% of the total impurities. Most impurities were removed effectively by TCVD, and the total content of impurities decreased from 2997.38 ppmw to <79.08 ppmw; in other words, MG-Se (99.4%) was purified to >99.992%. The removal efficiency of the impurity elements is expressed by Eq. (2):

\[
Re = \frac{C_i - C_p}{C_i} \times 100\% \tag{2}
\]

where \( Re \) (%) is the removal efficiency of the impurity elements, \( C_i \) is the initial selenium component content of the impurity elements, and \( C_p \) is the purified selenium component content.

The removal results for Hg and S after the 1st distillation show that Hg decreases to below the detection limit, which is consistent with the expected results. However, after the 1st distillation, the content of S increased, and a portion of S did not volatilize completely and is therefore enriched in the residue, similar to other low volatility impurities. Meanwhile, 10% of the material has volatilized, leading to increases in the contents of other impurities. After the 2nd distillation, Se volatilizes, yet most of the impurities are enriched in the residues. The impurities can be effectively removed, especially S, which is obviously reduced. This result also shows that S not only exists as a simple substance but also as a sulfide phase with a lower volatility than Se. The 3rd distillation strengthens the 2nd distillation, and we can observe a significant reduction in the concentrations of the major nonvolatile impurities, such as Si. The level was below the detection limit, achieving separation from the selenium matrix. S, As and Te are difficult to further remove because they are elements adjacent to Se and their saturated vapor pressures are similar to that of Se. These impurities are evaporated in the condenser in the distillation process. Overall, the removal efficiency of all of the impurities is above 97.36%, and the volatilization of selenium is greater than 90%.

### 3.3. Elemental distributions of typical impurities

Fig. 5 displays the EPMA elemental EDS and mapping of typical impurities in a microscopic area (Cu, Pb, S, Si and Te) that are difficult to remove from selenium in the 2nd distillation step, as shown in Table 1. From Fig. 5f(k), it can be clearly seen that the impurities aggregate; this area is smaller than others, which is easily recognized by electron microscopy. We can easily identify the distribution areas of the impurity elements that are relatively concentrated and gathered by elemental EDS. Moreover, it can be seen from Fig. 5f(k) that these impurities appear in the same region and are independent of Se. The sources of these impurities can be traced back to the copper anode slime, existing in the form of Cu_{2}Te, Cu_{2}Se, PbSe, CuSO_{4}, PbSO_{4}, etc. [43,44]. In the extraction process of selenium, incomplete decomposition of this phase is inevitable.
Table 2 – Concentrations of impurities in the initial and purified selenium by TCVD (ppmw).

<table>
<thead>
<tr>
<th>Impurity elements</th>
<th>Initial selenium</th>
<th>After 1st distillation</th>
<th>After 2nd distillation</th>
<th>After 3rd distillation</th>
<th>Removal efficiency in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>6.20</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>~100</td>
</tr>
<tr>
<td>S</td>
<td>940.00</td>
<td>960.00</td>
<td>43.6</td>
<td>15.50</td>
<td>98.35</td>
</tr>
<tr>
<td>As</td>
<td>724.00</td>
<td>808.44</td>
<td>95.57</td>
<td>22.18</td>
<td>96.94</td>
</tr>
<tr>
<td>Te</td>
<td>85.00</td>
<td>80.98</td>
<td>40.89</td>
<td>26.99</td>
<td>68.24</td>
</tr>
<tr>
<td>Mg</td>
<td>5.68</td>
<td>13.19</td>
<td>/</td>
<td>/</td>
<td>~100</td>
</tr>
<tr>
<td>Sb</td>
<td>53.30</td>
<td>111.14</td>
<td>6.65</td>
<td>2.81</td>
<td>94.73</td>
</tr>
<tr>
<td>Pb</td>
<td>84.81</td>
<td>122.82</td>
<td>22.38</td>
<td>3.02</td>
<td>96.44</td>
</tr>
<tr>
<td>Bi</td>
<td>750.00</td>
<td>930</td>
<td>24.2</td>
<td>3.50</td>
<td>99.53</td>
</tr>
<tr>
<td>Sn</td>
<td>11.93</td>
<td>39.41</td>
<td>1.36</td>
<td>0.52</td>
<td>95.64</td>
</tr>
<tr>
<td>Al</td>
<td>16.40</td>
<td>40.06</td>
<td>2.89</td>
<td>0.72</td>
<td>95.61</td>
</tr>
<tr>
<td>Cu</td>
<td>69.92</td>
<td>151.81</td>
<td>6.82</td>
<td>1.18</td>
<td>98.31</td>
</tr>
<tr>
<td>Fe</td>
<td>132.10</td>
<td>196.87</td>
<td>4.88</td>
<td>2.54</td>
<td>98.08</td>
</tr>
<tr>
<td>Si</td>
<td>96.00</td>
<td>130</td>
<td>9.5</td>
<td>/</td>
<td>~100</td>
</tr>
<tr>
<td>Ni</td>
<td>16.12</td>
<td>27.30</td>
<td>1.45</td>
<td>0.12</td>
<td>99.25</td>
</tr>
<tr>
<td>B</td>
<td>5.71</td>
<td>8.30</td>
<td>/</td>
<td>/</td>
<td>~100</td>
</tr>
<tr>
<td>Total</td>
<td>2997.17</td>
<td>3620.32</td>
<td>260.19</td>
<td>&lt;79.08</td>
<td>&gt;97.36</td>
</tr>
<tr>
<td>Purity of Se (%)</td>
<td>99.4</td>
<td>&gt;99.97</td>
<td>&gt;99.992</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

/ represents below the detection limit.

Fig. 5 – EPMA elemental EDS and mapping of typical impurities. (a) (b) Microscopic scanning; (c)–(e) elemental EDS of pt1–pt3; (f)–(k) elements mapping of Se, Te, Pb, S, Cu and Si.
and will enter the crude elemental selenium. All of these impurities can be removed by multiple distillation steps to meet the application requirements. However, it is difficult to achieve excellent separation of Se and Te by distillation for the following two reasons: (1) Se and Te are completely miscible in each other in the liquid and solid states and form an isomorphous system [45] and (2) there are azeotropic phenomena in the Se-Te system [46].

4. Conclusions

Crude selenium (99.4%) comprehensively recovered from copper electrolisis anode slime was purified to 99.992% through three consecutive vacuum distillation steps. The actual evaporation rate and accommodation coefficient α of crude selenium were found to be 0.0231 g cm⁻² min⁻¹ and 0.3236, respectively, at 523 K and approximately 4 Pa using a vacuum thermogravimetric furnace. The detailed analysis confirmed the reduction in the total impurity content from 2997.38 ppmw to <79.08 ppmw by using ICP-MS analysis for the 15 most common impurity elements. The impurities were relatively concentrated and gathered in crude selenium.

Conflict of interest

The authors declare no conflicts of interest.

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