

Article

A Fundamental Study on the Preparation of Sodium Tungstate from Wolframite via the Smelting Process

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Abstract: Tungsten is a high-value resource with a wide range of applications. The tungsten metal is produced via ammonium paratungstate, which is a multi-stage process including leaching, conversion, precipitation, calcination, and reduction. A short process to produce tungsten metal from the electrolysis of molten sodium tungstate has been demonstrated. However, sodium tungstate cannot be directly produced from wolframite in the conventional hydrometallurgical process. There was no information reported in the literature on producing sodium tungstate directly from tungsten concentrates. The present study proposed a simple and low-cost process to produce sodium tungstate by high-temperature processing of wolframite. The mixtures of wolframite, sodium carbonate, and silica were melted in air between 1100 and 1300 °C. High-density sodium tungstate was easily separated from the immiscible slag, which contained all impurities from wolframite, flux, excess sodium oxide, and dissolved tungsten oxide. The slag was further water leached to recover sodium tungstate in the solution. Effects of Na₂CO₃/Ore and SiO₂/Ore ratios, temperature, and reaction time on the recovery of tungstate and the purity of sodium tungstate were systematically studied. Sodium tungstate containing over 78% WO₃ was produced in the smelting process, which is suitable for the electrolysis process. The experimental results will provide a theoretical basis for the direct production of sodium tungstate from wolframite. The compositions of the WO₃-containing slags and sodium tungstate reported in the present study fill the knowledge gap of the tungsten-containing thermodynamic database. Further studies to use complex and low-grade tungsten concentrates to produce sodium tungstate are underway.

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Keywords: wolframite; smelting process; sodium tungstate; immiscible; slag

1. Introduction

Tungsten is one of the most strategical minerals due to its special properties, wide applications, lack of potential substitutes, and geographically concentrated production [1–3]. Tungsten and alloys are widely used in metalworking, cutting tools, automotive and aircraft production, electronics manufacturing, oil and gas drilling, and defense [4–6]. Many tungsten-bearing minerals have been discovered. However, only scheelite (CaWO₄) and wolframite ((Fe,Mn)WO₄) are abundant and easy to concentrate for extraction [4,6–8]. In current industry practices, the concentrates of scheelite, wolframite, or their mixtures are decomposed in a leaching process by soda or/and caustic soda to produce soluble sodium tungstate. Then, the sodium tungstate solution undergoes a purification and a conversion process to obtain pure ammonium paratungstate (APT), which is an important intermediate compound for producing tungsten metal and alloys [4,6,9,10]. Tungsten metal is produced by the decomposition of APT and the reduction of WO₃ by hydrogen. Carburization of fine tungsten powder at high temperatures will obtain tungsten carbide. The leaching residue containing valuable elements needs to be further treated to maximize the value of the resource [11–15]. If arsenic-containing ore is used, the leaching residue requires proper

harmless treatment to fix the arsenic [16,17]. In the processes of purification and conversion of sodium tungstate solution, a large number of effluents are generated, which need to be treated at a high cost [18]. As a hydrometallurgical process, the digestion of tungsten minerals requires high-grade and fine particle concentrates, which results in a low recovery rate in the mineral processing stage.

To improve the efficient utilization of the limited tungsten resource and overcome the disadvantages of the hydrometallurgical process, a high-temperature-solvent extraction technique has been proposed [19–21]. In the H₂O-free process, wolframite or scheelite concentrate, sodium carbonate, sodium metasilicate, and/or sodium chloride are melted at temperatures above 1100 °C to obtain two immiscible liquids. The sodium chloride–sodium tungstate phase is used directly for producing tungsten metal or alloys by reduction or electrolysis. The silicate phase containing the oxides of calcium, iron, manganese, and sodium can be further treated to recover valuable elements. Gomes et al. [19] melted a mixture of high-grade wolframite, NaCl, and Na₂SiO₃ at 1050 to 1100 °C for 2 h. More than 99% of the tungsten was recovered in the halide–tungstate phase, which contained 29.8% WO₃, 0.24% FeO, and 0.30% MnO. The rest of the components are NaCl and Na₂O. Using similar conditions, Malyshev et al. [20] studied the effects of NaCl and Na₂SiO₃ concentrations on the recovery of tungsten into the halide–tungstate phase. A 99% recovery rate was achieved by a combination of 45 wt% NaCl and 20 wt% Na₂SiO₃. The produced halide–tungstate phase contained 31.2% WO₃, 0.21% FeO, and 0.33% MnO. Gostishchev V.V. and Boiko V. F. [21] used a mixture of NaCl–NaF–NaCO₃ to decompose a scheelite concentrate containing 55 wt% WO₃. Up to 93 wt% tungsten was recovered in the halide–tungstate phase after reaction at 850–900 °C for 1 h. If a mixture of NaCl–NaCO₃–Na₃AlF₆ was used at 900–947 °C, 95 wt% recovery could be achieved. The compositions of the produced halide–tungstate phase were not given [21]. In these studies [19–21], sodium halides were used as one of the raw materials, which resulted in a halide–tungstate phase to collect tungsten. The halide–tungstate phase contained only 30% WO₃, which is much lower than that in sodium tungsten (78.8%) and not suitable for the electrolysis process. Phase equilibrium studies in the system Na₂O–SiO₂–WO₃ show that two immiscible liquids, sodium tungstate and sodium silicate, can be obtained [22,23]. The phase diagrams reported in these studies indicated that the high-temperature-solvent extraction technique can be applied without sodium halides. In a recent study, Xu and Zhao [24] demonstrated by thermodynamic calculations and high-temperature experiments that NaCO₃ and SiO₂ can decompose wolframite completely at 1050–1200 °C. Over 99% of tungsten can be recovered in the sodium tungstate solution. High NaCO₃ and low SiO₂ concentrations are beneficial for the decomposition and recovery of tungsten. Although the formation of two liquids was observed, it was not attempted to obtain the sodium tungstate directly from the melt [24]. No information was found in the literature to produce sodium tungstate directly from tungsten concentrates. In the present study, experimental results on high-temperature preparation of sodium tungstate are reported. Effects of NaCO₃, SiO₂, temperature, and reaction time on recovery of tungsten and purity of the sodium tungsten are discussed.

2. Experimental Procedure

A commercial wolframite concentrate (particle size less than 0.075 mm) was used in the present study, and its dry composition is shown in Table 1. Analytical grades of sodium carbonate and silica were used for the decomposition of the wolframite. WO₃, FeO, and MnO are the major components of wolframite.

Table 1. Composition of wolframite used in this study (wt%).

WO ₃	CaO	FeO	MnO	SiO ₂	S
78.0	1.1	10.7	7.9	1.7	0.6

The experimental procedure used in the present study is shown in Figure 1. The underline words indicate the raw materials, intermediate and final products. An amount of 10 g of wolframite concentrate was well mixed with the required sodium carbonate and silica in an agate mortar. The mixture was pelletized and placed in an alumina crucible (OD 35 mm, ID 30 mm, H 60 mm). A muffle furnace was used for all experiments in the air. The sample was heated to the required temperature with a heating rate of 10 °C/min. After the high-temperature reaction, the sample was cooled to room temperature in the furnace. The crucible was broken carefully to remove the sample inside. High-density sodium tungstate on the bottom of the crucible was covered by the low-density smelting slag. The sodium tungstate was carefully separated from the slag for further analysis. The slag was ground and leached in water at 50 °C for 120 min. The water-to-slag ratio was 5:1, and the WO₃-containing leachate was separated from the residue by filtration. The compositions of the sodium tungstate, smelting slag, and leaching residue were analyzed by XRF (PANalytical Axios XRF spectrometer, PANalytical B.V., Almelo, Netherlands).

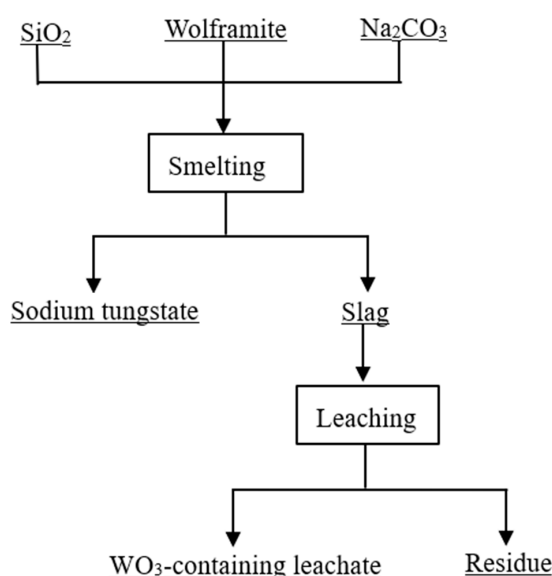


Figure 1. Experimental procedure in the present study.

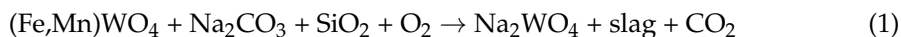
The variable parameters used in the extraction of the wolframite included Na₂CO₃/Ore ratio, SiO₂/Ore ratio, temperature, and reaction time. The detailed experimental plan is shown in Table 2. The Na₂CO₃/Ore and SiO₂/Ore ratios are in the range of 0.3 to 1.1. The temperature is in the range of 1100 to 1300 °C and the reaction time is between 30 and 120 min.

Table 2. Experimental conditions of wolframite smelting in air.

Exp No	Ore (g)	Temp (°C)	Time (min)	Na ₂ CO ₃ (g)	SiO ₂ (g)
W1	10	1200	60	7	3
W2	10	1200	60	9	3
W3	10	1200	60	11	3
W4	10	1200	60	11	5
W5	10	1200	60	11	7
W6	10	1200	30	11	3
W7	10	1200	120	11	3
W8	10	1100	60	11	3
W9	10	1300	60	11	3
W10	10	1200	60	5	3
W11	10	1200	60	3	3
W12	10	1200	60	11	9
W13	10	1200	60	11	11

3. Results and Discussion

Wolframite reacts with sodium carbonate and silica at high temperatures:



Tungsten oxide forms liquid sodium tungstate with sodium oxide, and oxides of iron and manganese from the wolframite form slag with silica and sodium oxide. Immiscible slag (sodium tungsten) and slag are all liquid and separated into two layers due to different densities. Low-density slag is on top of the high-density salt. From the compositions of the reactants listed in Table 2 and the compositions of the sodium tungstate, slag, and leaching residue, mass balance calculations can give the weights of the generated sodium tungstate, slag, and leaching residue. The recovery of WO_3 in sodium tungstate and total recovery of WO_3 can be calculated from the following equations:

$$\text{Recovery of } \text{WO}_3 \text{ in sodium tungstate} = \frac{\text{mass of } \text{WO}_3 \text{ in sodium tungstate}}{\text{mass of } \text{WO}_3 \text{ in the ore}} \times 100 \quad (2)$$

$$\text{Total recovery of } \text{WO}_3 = \frac{1 - \text{mass of } \text{WO}_3 \text{ in leaching residue}}{\text{mass of } \text{WO}_3 \text{ in the ore}} \times 100 \quad (3)$$

The total recovery of WO_3 calculated from Equation (3) includes the WO_3 present in the sodium tungstate and leachate.

The compositions of the slag, sodium tungstate, and leaching residue analyzed by XRF are given in Tables 3, 4, and 5, respectively. The weights of the slag, sodium tungstate, and leaching residue obtained from mass balance are also given in the tables. It can be seen from Table 3 that the loss of WO_3 in the slag is in the range of 4–16.9%, indicating that direct recovery of WO_3 in the sodium tungsten is in the range of 83.1–96%. FactSage is a powerful thermodynamic model to predict the high temperature reactions of slag and salt [25]. However, tungsten oxides are not included in the slag phase of the current FactSage database. The slag compositions given in Table 3 will provide useful information for the development of a WO_3 -containing thermodynamic database. In addition to Fe_2O_3 , MnO , and SiO_2 , 10.3–39.6% Na_2O is also present in the slag. The weights of the slag increase with increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ and SiO_2/Ore ratios.

Table 3. Weights and compositions of smelting slag and WO_3 loss in the slag.

Exp No	Weight (g)	Composition (wt%)						WO_3 Loss in Slag (%)
		Fe_2O_3	SiO_2	MnO	SO_3	WO_3	Na_2O	
W1	8.3	18.2	40.1	10.7	0.0	4.5	26.4	5.2
W2	9.6	15.7	34.4	9.2	0.1	5.7	34.9	7.6
W3	10.9	13.7	28.9	7.7	0.1	10.6	38.9	15.9
W4	13.2	11.3	40.3	6.7	0.1	6.1	35.5	11.1
W5	15.2	9.9	48.3	5.8	0.1	5.1	30.8	10.6
W6	10.9	13.6	28.8	7.9	0.2	11.3	38.3	16.9
W7	11.0	13.9	29.7	7.4	0.2	10.2	38.5	15.5
W8	10.9	14.0	29.2	7.8	0.1	11.0	37.9	16.6
W9	11.0	13.7	29.2	7.3	0.2	9.9	39.6	15.0
W10	7.1	20.8	46.7	11.0	0.3	4.1	17.1	4.0
W11	6.3	20.2	53.6	7.7	0.0	8.2	10.3	7.2
W12	16.9	9.1	54.8	5.1	0.1	3.3	27.6	7.8
W13	18.7	8.2	59.6	4.6	0.1	2.6	25.0	6.8

Table 4. Weights and compositions of sodium tungstate and direct recovery of WO₃.

Exp No	Weight (g)	Composition (wt%)						Direct Recovery of WO ₃ (%)
		Fe ₂ O ₃	SiO ₂	MnO	SO ₃	WO ₃	Na ₂ O	
W1	8.8	0.0	0.2	0.0	0.9	78.3	20.6	94.8
W2	8.6	0.0	0.5	0.0	0.9	77.3	21.4	92.4
W3	8.5	0.2	2.1	0.3	0.8	71.2	25.4	84.1
W4	8.3	0.0	0.5	0.0	0.8	77.7	21.0	88.9
W5	8.2	0.0	0.1	0.0	0.9	78.4	20.6	89.4
W6	8.6	0.3	2.7	0.4	0.8	70.2	25.6	83.1
W7	8.4	0.1	1.6	0.4	0.8	72.5	24.6	84.5
W8	8.5	0.1	1.2	0.1	0.7	70.9	27.0	83.4
W9	8.5	0.2	2.2	0.6	0.8	72.5	23.6	85.0
W10	8.9	0.4	0.0	0.8	0.7	78.3	19.7	96.0
W11	8.4	2.1	0.1	3.6	0.4	79.8	14.0	92.8
W12	8.6	0.0	0.0	0.0	0.5	78.0	21.4	92.2
W13	8.7	0.0	0.0	0.0	0.6	77.2	22.1	93.2

Table 5. Weights and compositions of leaching residue and total recovery of WO₃.

Exp No	Weight (g)	Composition (wt%)						Total Recovery of WO ₃ (%)
		Fe ₂ O ₃	SiO ₂	MnO	SO ₃	WO ₃	Na ₂ O	
W1	8.1	18.9	41.4	11.2	0.0	2.2	26.2	97.5
W2	8.6	18.2	37.2	10.7	0.0	0.9	32.9	98.9
W3	6.9	31.1	30.5	17.6	0.0	0.3	20.5	99.7
W4	12.4	12.0	42.6	7.1	0.1	4.5	33.7	92.3
W5	14.9	10.0	49.5	5.9	0.1	4.6	29.9	90.6
W6	6.6	36.6	24.7	22.1	0.0	0.3	16.2	99.7
W7	7.5	29.6	27.8	18.0	0.0	0.2	24.3	99.7
W8	7.3	29.8	28.7	18.5	0.0	0.2	22.8	99.8
W9	7.2	30.5	30.6	15.4	0.0	0.5	23.0	99.5
W10	6.9	21.4	47.3	11.3	0.1	3.1	16.7	97.0
W11	6.2	20.8	54.2	7.9	0.0	7.1	9.9	93.9
W12	16.8	8.9	55.3	5.1	0.1	3.1	27.5	92.7
W13	18.5	8.1	60.2	4.7	0.1	2.6	24.3	93.2

Table 4 shows that WO₃ in the sodium tungstate is in the range of 70.2–79.8%, which is close to that in the pure Na₂WO₄ (78.9 wt%). The WO₃ content in the salt of the present study is much higher than those obtained in the previous works [19–21]. Most of the NaCl used in these studies [19–21] was present in the halide–tungstate phase, resulting in a low WO₃ content (≈30%). Up to 2.7 and 0.9 wt% SiO₂ and sulfur are present in the sodium tungstate as Na₂SiO₃ and Na₂SO₄ have similar properties as Na₂WO₄. The presence of Fe₂O₃ and MnO in the sodium tungstate indicates that undecomposed wolframite can form a solid solution with Na₂WO₄. No solid solution information is available for the sodium tungstate in the current database of FactSage 8.3 [25]. It is difficult to accurately predict high-temperature reactions with only pure compounds. The compositions of the sodium tungstate given in Table 4 will support the development of a WO₃-containing thermodynamic database. The purity of Na₂WO₄ in the sodium tungstate depends on the decomposition of wolframite and the dissolution of Na₂SiO₃ and Na₂SO₄. The weights of the sodium tungstate are relatively constant, between 8.2 and 8.9 g.

WO₃ in the leaching residue determines the total recovery of tungsten. It can be seen from Table 5 that up to 99.8% total recovery can be achieved at the optimum conditions. Fe₂O₃, MnO, SiO₂, and Na₂O are the major components of the leaching residue. The lowest WO₃ in the leaching residue is 0.2 wt%, which is much lower than that in the conventional processes [11–15].

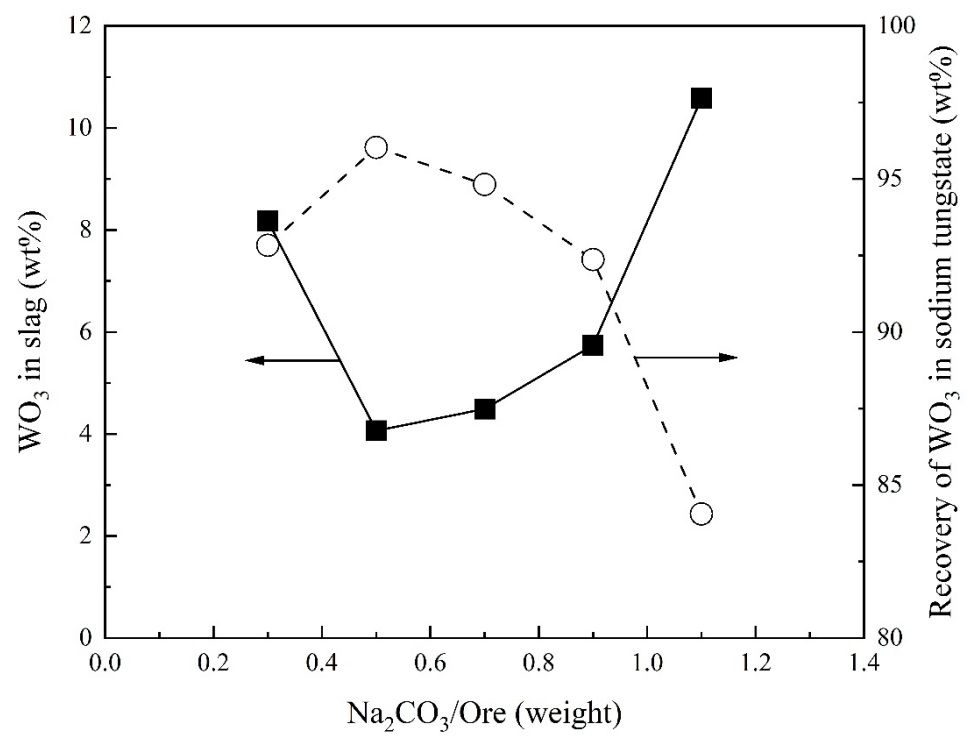
In the conventional extraction process of tungsten from the concentrate, the intermediate product is a water solution of sodium tungstate and sodium hydroxide, which has limited applications. The product of the smelting extraction proposed in the present study is sodium tungstate, which has more direct applications. Direct recovery of tungsten in the form of sodium tungstate can be as high as 96%. However, the total recovery of tungsten is also important because it is a high-value element. High- WO_3 in the sodium tungstate indicates a low level of impurities. Effects of the reaction parameters such as $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio, SiO_2/Ore ratio, temperature, and reaction time on the direct and total recovery of tungsten and WO_3 in the sodium tungstate are discussed in the following sections.

3.1. Effect of $\text{Na}_2\text{CO}_3/\text{Ore}$ on Recovery of WO_3 and Composition of Sodium Tungstate

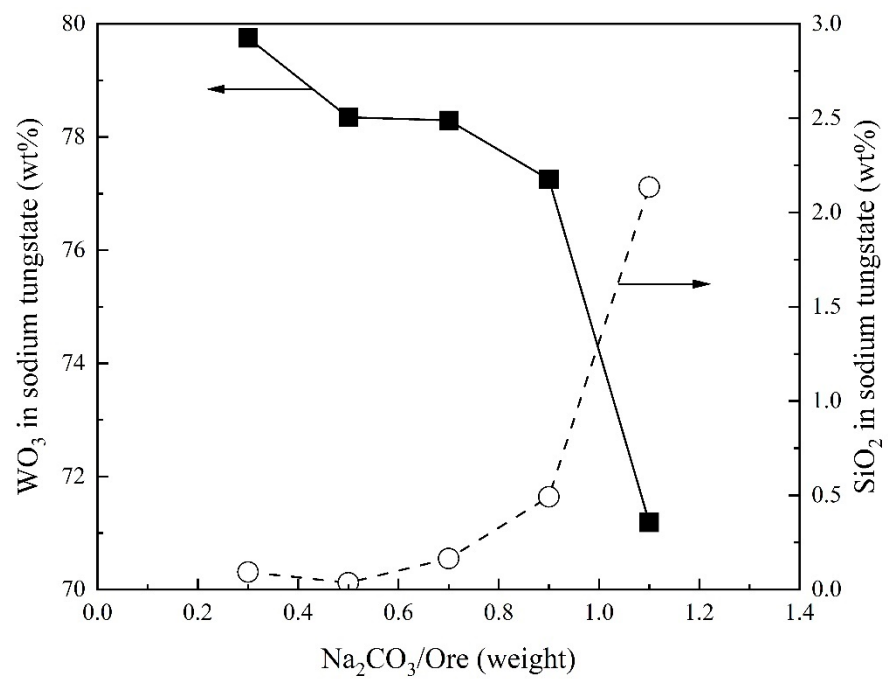
Figure 2 shows the direct recovery of WO_3 in the form of sodium tungstate and WO_3 content in the sodium tungstate as a function of $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. It can be seen from Figure 2a that initially, the direct recovery of WO_3 increases with increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. The maximum recovery of 96% was reached at a $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 0.5 and then the direct recovery of WO_3 decreases with increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. This trend can be explained by Figure 2b. It is shown in Table 4 that the weights of the sodium tungstate are relatively constant. The direct recovery of WO_3 is a function of WO_3 content in the sodium tungstate. It can be seen from Figure 2b that WO_3 content in the sodium tungstate decreases with increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. However, it can be seen from Table 4 that although the WO_3 content in the sodium tungstate is 79.8% in W11 ($\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 0.3), the weight of the salt is lower than W10 ($\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 0.5). The direct recovery of WO_3 in W11 is lower than that in W10. High Fe_2O_3 and MnO contents in the salt of W11 indicate that the $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 0.3 is not enough to fully decompose the wolframite. High WO_3 in the salt does not guarantee a high purity Na_2WO_4 . The salt in W10 contains lower WO_3 (78.3%) than that in W11 (79.8%). However, the content of the Na_2WO_4 in W10 is higher than that in W11. Figure 2b shows that SiO_2 content in the sodium tungstate increases with increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio, resulting in a decreased WO_3 content.

Figure 3 shows the WO_3 content in the leaching residue and the total recovery of WO_3 as a function of $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. Low WO_3 in the residue indicates a high recovery of tungsten, according to Equation (3). It can be seen from Figure 3 that the WO_3 content in the leaching residue decreases, and the total recovery of tungsten increases with the increasing $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. A maximum total recovery of 99.7% is achieved at the $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 1.1.

Figure 4 shows that the effect of the $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio on the direct recovery of WO_3 is different from the total recovery. The direct recovery of WO_3 in the form of sodium tungstate has a maximum (96%) at $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 0.5. The total recovery is only 97% at this $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio. If the $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio is increased to 1.1, the total recovery of WO_3 is increased to 99.7%. However, the direct recovery of WO_3 in the form of sodium tungstate is only 84.1% at a $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio of 1.1. It has been explained in Figure 2 that a minimum amount of Na_2CO_3 is required to fully decompose the wolframite. However, excess Na_2CO_3 can cause competitive dissolution of Na_2SiO_3 and Na_2SO_4 into the sodium tungstate, resulting in a lower recovery of WO_3 in the sodium tungstate. On the other hand, more Na_2O in the smelting slag increases the basicity of the smelting slag which enables more Na_2WO_4 to be formed and leached into water. Figures 2–4 provide options for the industry to decide the operating parameters according to their requirements.



(a) WO_3 in slag and recovery of WO_3 in sodium tungstate.



(b) WO_3 and SiO_2 contents in sodium tungstate.

Figure 2. Effect of $\text{Na}_2\text{CO}_3/\text{Ore}$ on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, $\text{SiO}_2/\text{Ore} = 0.3$, 1200 °C, 60 min.

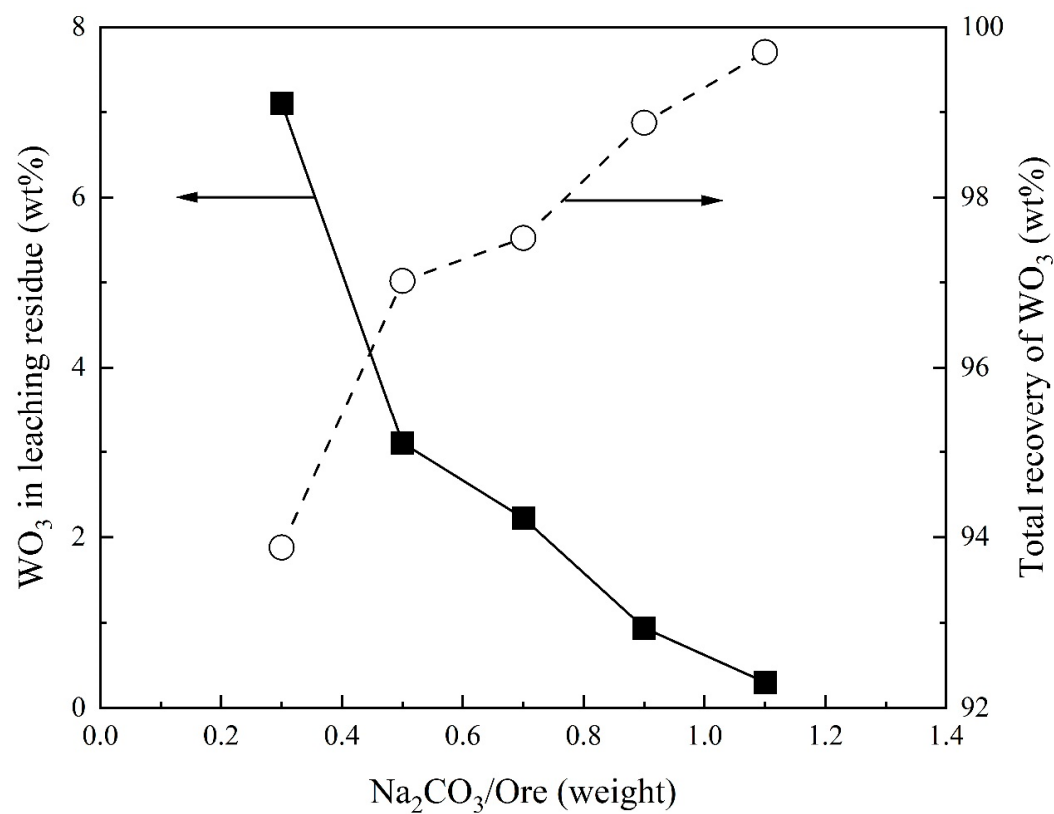


Figure 3. Effect of $\text{Na}_2\text{CO}_3/\text{Ore}$ on total recovery of WO_3 , $\text{SiO}_2/\text{Ore} = 0.3$, $1200\text{ }^\circ\text{C}$, 60 min.

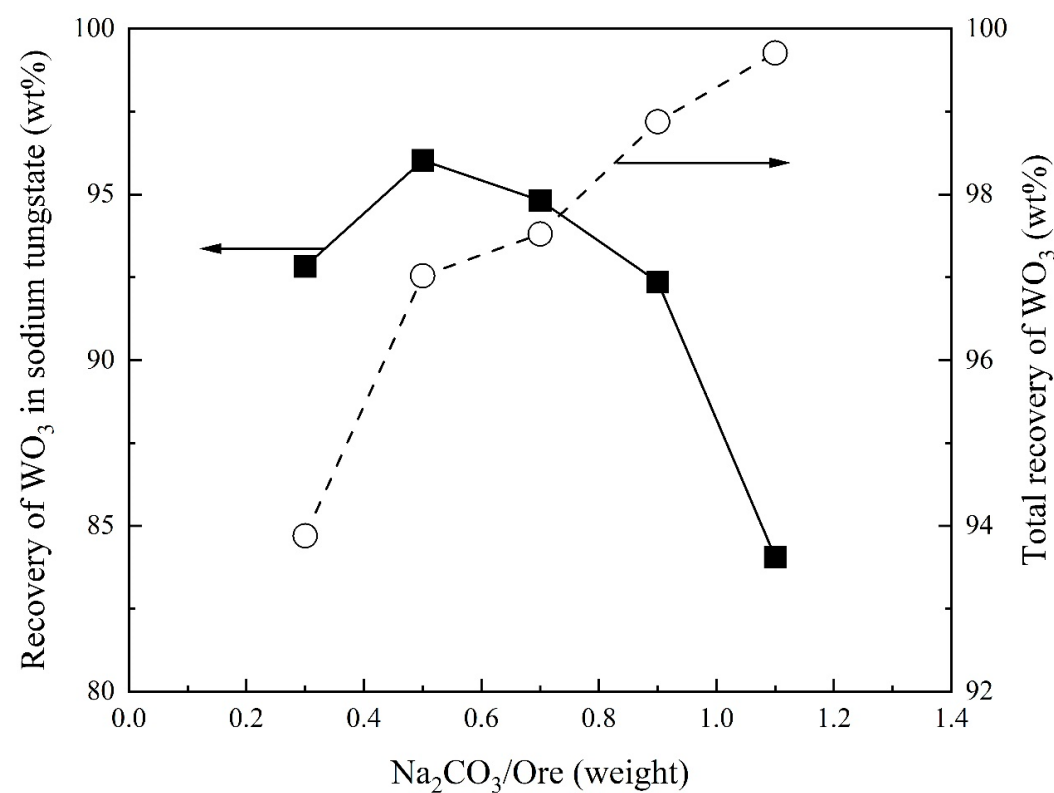


Figure 4. Effect of $\text{Na}_2\text{CO}_3/\text{Ore}$ on direct recovery and total recovery of WO_3 , $\text{SiO}_2/\text{Ore} = 0.3$, $1200\text{ }^\circ\text{C}$, 60 min.

3.2. Effect of SiO_2/Ore on Recovery of WO_3 and Composition of Sodium Tungstate

When the $\text{Na}_2\text{CO}_3/\text{Ore}$ ratio is fixed, the effect of the SiO_2/Ore ratio on the direct recovery of WO_3 and WO_3 content in the sodium tungstate is shown in Figure 5. It can be seen from Figure 5a that the direct recovery of WO_3 increases continuously with increasing SiO_2/Ore ratio. An increase in the SiO_2/Ore ratio from 0.3 to 1.1 resulted in an increase in the direct recovery from 84.1 to 93.2%. Figure 5b shows that the WO_3 content in the sodium tungstate initially increases and then decreases with increasing SiO_2/Ore ratio. The maximum WO_3 content in the sodium tungstate is obtained at the SiO_2/Ore ratio of 0.7. It can be seen from Table 4 that the SiO_2 and sulfur contents in the sodium tungstate also decrease with increasing SiO_2/Ore ratio. Therefore, both high recovery and purity of Na_2WO_4 can be obtained by high SiO_2/Ore ratio. However, the total recovery of tungsten must be considered to determine the optimum parameters.

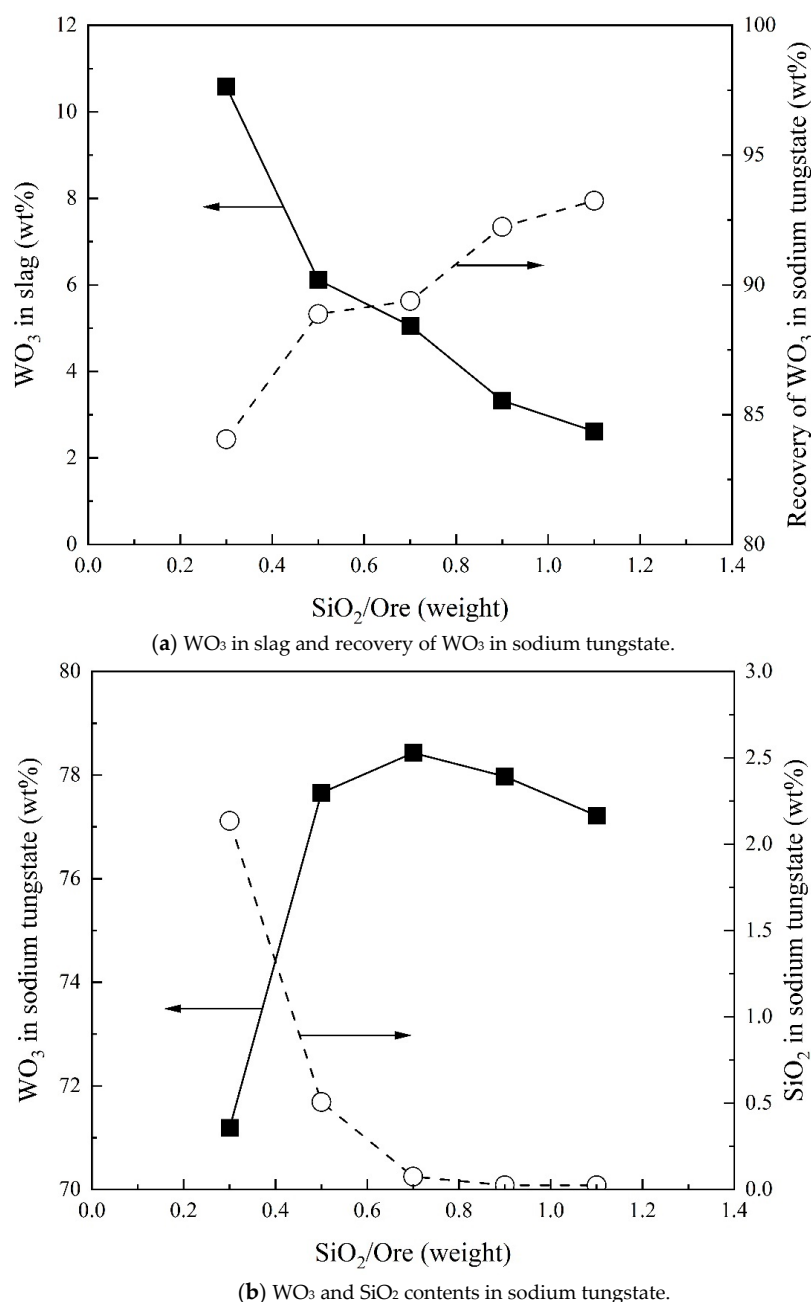


Figure 5. Effect of SiO_2/Ore on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, 1200°C , 60 min.

Figure 6 shows the WO_3 content in the leaching residue and the total recovery of WO_3 as a function of SiO_2/Ore ratio. As expected, the trend of total recovery of WO_3 is opposite to that for the WO_3 content in the leaching residue. It can be seen from Figure 6 that the total recovery of tungsten initially decreases and then increases with increasing SiO_2/Ore ratio. However, at higher SiO_2/Ore ratios (0.9 and 1.1), the total recovery of WO_3 is still below 94%.

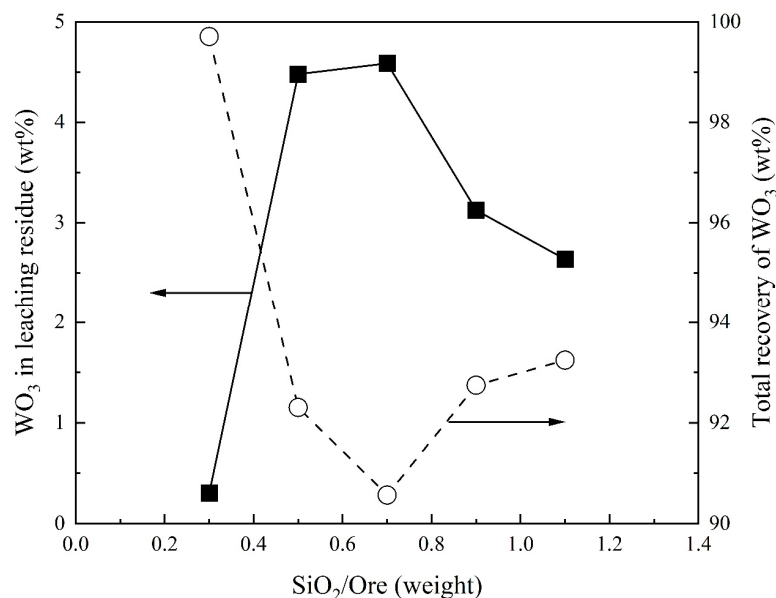


Figure 6. Effect of SiO_2/Ore on total recovery of WO_3 , $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, 1200°C , 60 min.

Figure 7 shows the effect of SiO_2/Ore ratio on the direct recovery and total recovery of WO_3 . Although both direct recovery and total recovery of WO_3 increase with increasing SiO_2/Ore ratio at higher SiO_2/Ore ratios (above 0.7), the total recovery of WO_3 is too low. Unless the high recovery and purity of Na_2WO_4 are more important than the total recovery of WO_3 , the SiO_2/Ore ratio is better to be controlled at a lower level. A low SiO_2/Ore ratio can also reduce the slag and residue weights.

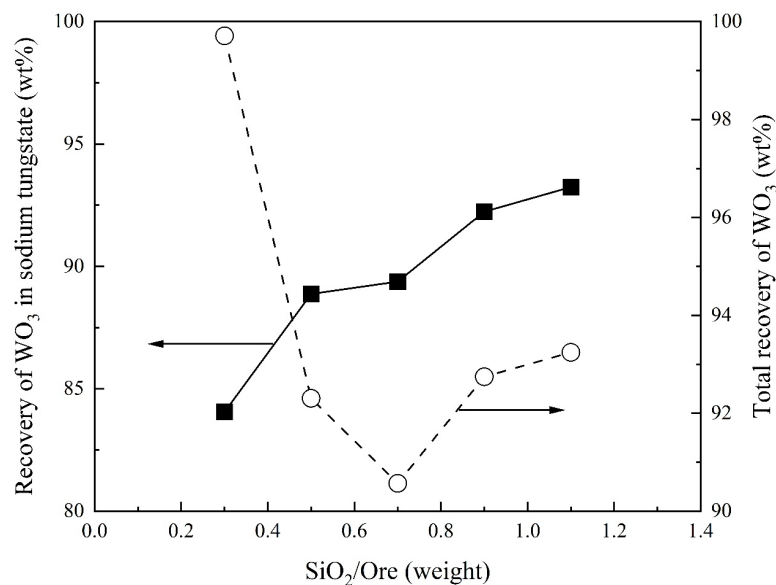


Figure 7. Effect of SiO_2/Ore on direct recovery and total recovery of WO_3 , $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, 1200°C , 60 min.

3.3. Effect of Temperature on Recovery of WO_3 and Composition of Sodium Tungstate

When both $\text{Na}_2\text{CO}_3/\text{Ore}$ and SiO_2/Ore ratios are fixed, the temperature can affect the direct recovery of WO_3 and WO_3 content in the sodium tungstate. It can be seen from Figure 8 that, at $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, $\text{SiO}_2/\text{Ore} = 0.3$, the direct recovery of WO_3 and WO_3 content in the sodium tungstate increases with increasing temperature. The direct recovery of WO_3 increases from 83.4 to 85%, and WO_3 content in the sodium tungstate increases from 70.9 to 72.5% when the temperature is increased from 1100 to 1300 °C. It seems that the direct recovery of WO_3 and WO_3 content in the sodium tungstate are not very sensitive to the temperature. On the other hand, it can be seen from Table 4 that the SiO_2 and MnO contents also increase with increasing temperature. Therefore, high-temperature operation can cost high energy and reduce the purity of the Na_2WO_4 .

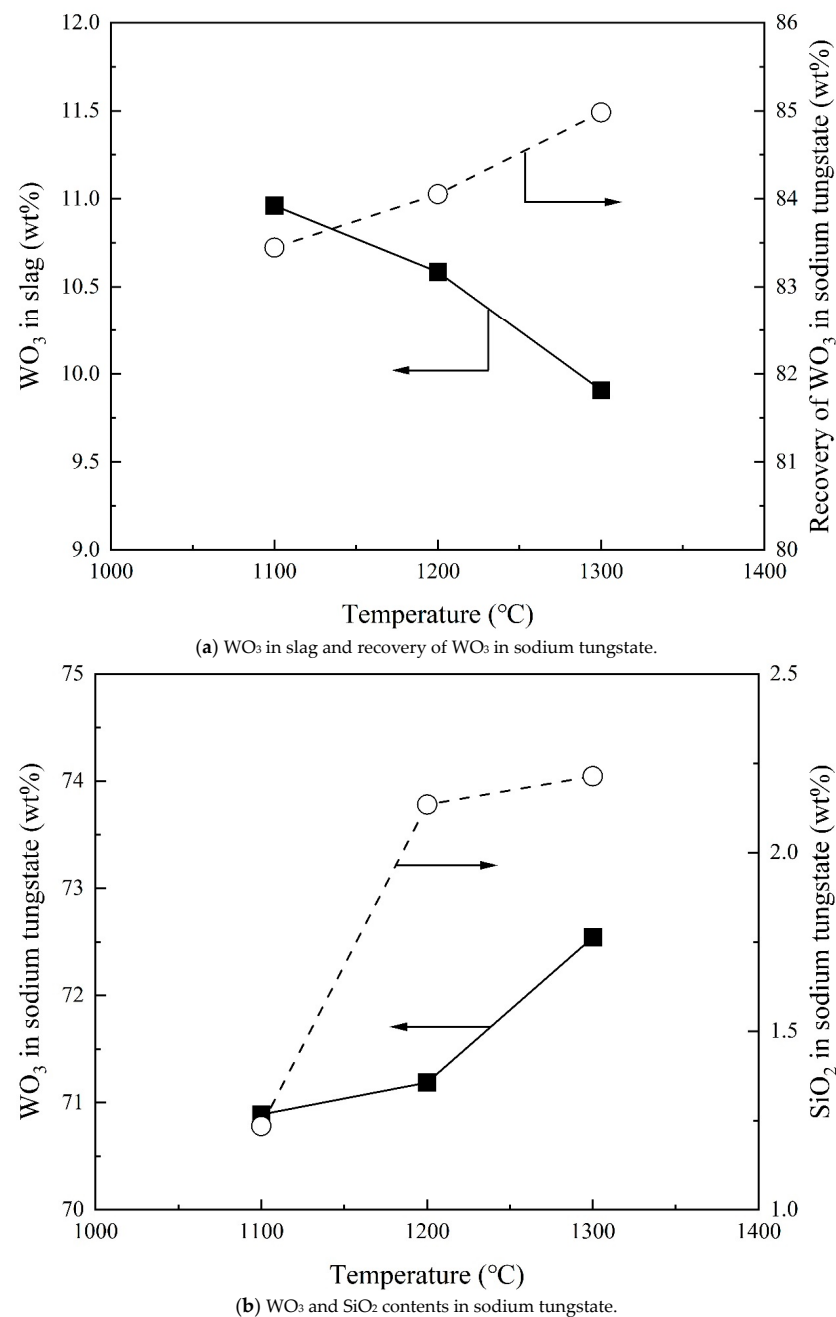


Figure 8. Effect of temperature on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, $\text{SiO}_2/\text{Ore} = 0.3$, 60 min.

Figure 9 shows a clear but not significant effect of temperature on the WO_3 content in the leaching residue and total recovery of WO_3 . The WO_3 content in the leaching residue increases, and the total recovery of WO_3 decreases with increasing temperature. It can be seen that the total recovery of WO_3 decreases from 99.8 to 99.5% when the temperature is increased from 1100 to 1300 °C. Low-temperature smelting seems to be more efficient in recovering tungsten from the wolframite. The WO_3 content in the leaching residue is below 0.2 wt% at 1100 °C.

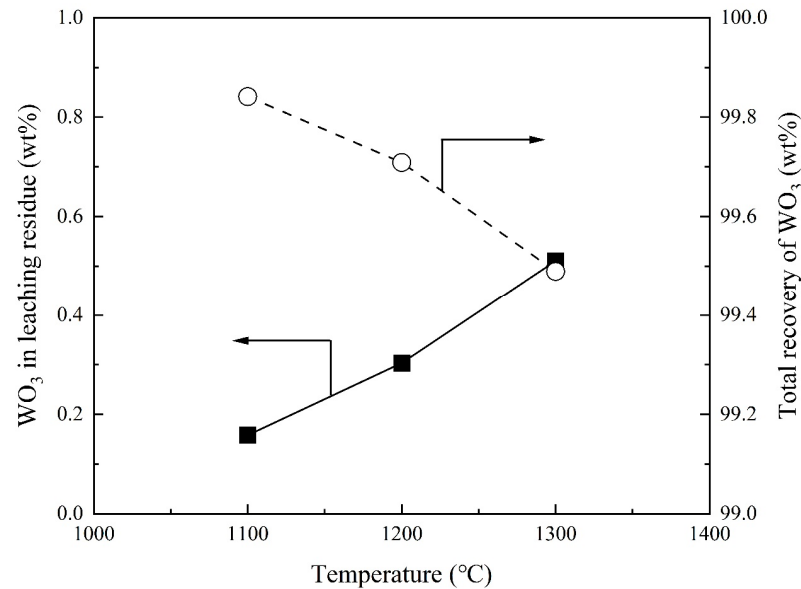


Figure 9. Effect of temperature on total recovery of WO_3 , $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, $\text{SiO}_2/\text{Ore} = 0.3$, 60 min.

Figure 10 shows that temperature has the opposite effect on the direct recovery and total recovery of WO_3 . However, the extent of the effect is different in the direct recovery and total recovery of WO_3 . When the temperature is increased from 1100 to 1300 °C, the total recovery of WO_3 only decreases from 99.8 to 99.5%. The same increment of the temperature increases the direct recovery of WO_3 increases from 83.4 to 85%.

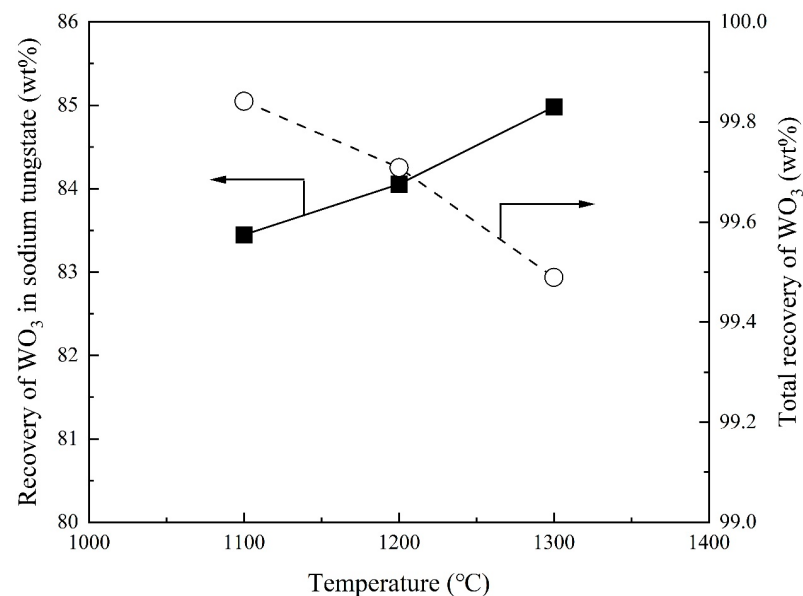
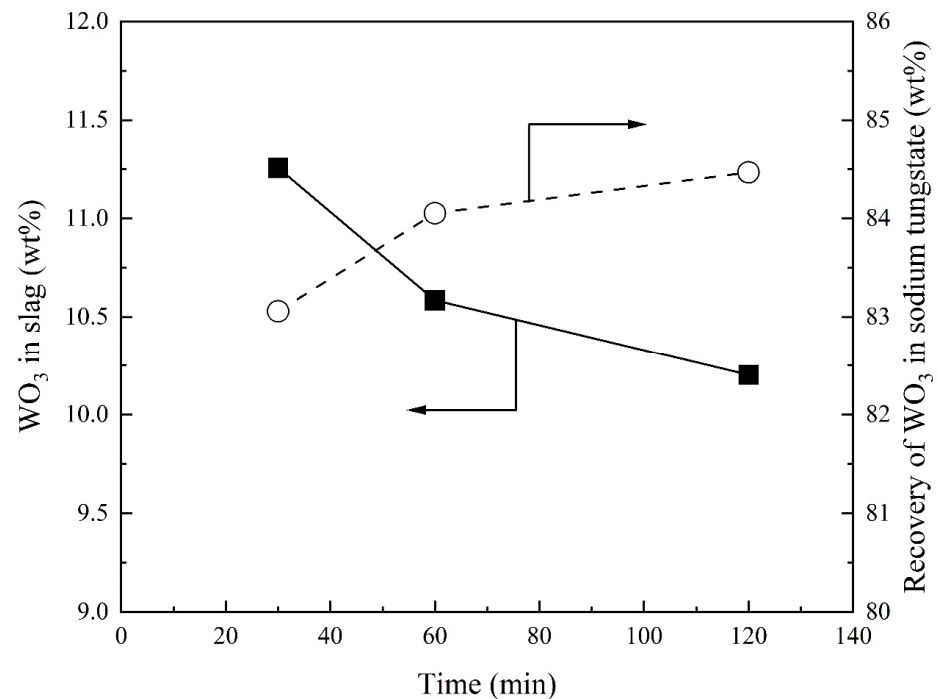


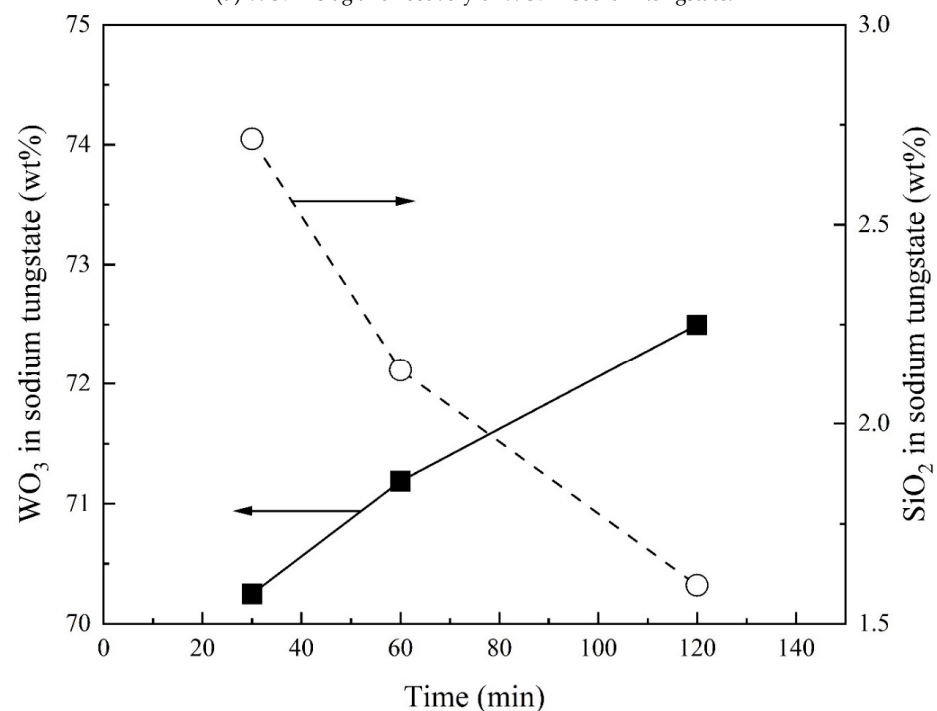
Figure 10. Effect of temperature on direct recovery and total recovery of WO_3 , $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, $\text{SiO}_2/\text{Ore} = 0.3$, 60 min.

3.4. Effect of Reaction Time on Recovery of WO_3 and Composition of Sodium Tungstate

When other parameters are fixed, the effect of reaction time on the recovery of WO_3 and the composition of the sodium tungstate are shown in Figures 11–13. It can be seen from Figure 11 that extending the reaction time from 30 to 120 min decreases the WO_3 content in the slag from 11.3 to 10.2 and increases the direct recovery of WO_3 from 83.1 to 84.5%. The WO_3 content in the sodium tungstate increases from 70.2 to 72.5% when the reaction time is increased from 30 to 120 min.



(a) WO_3 in slag and recovery of WO_3 in sodium tungstate.



(b) WO_3 and SiO_2 contents in sodium tungstate.

Figure 11. Effect of reaction time on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, $\text{Na}_2\text{CO}_3/\text{Ore} = 1.1$, $\text{SiO}_2/\text{Ore} = 0.3$, 1200°C .

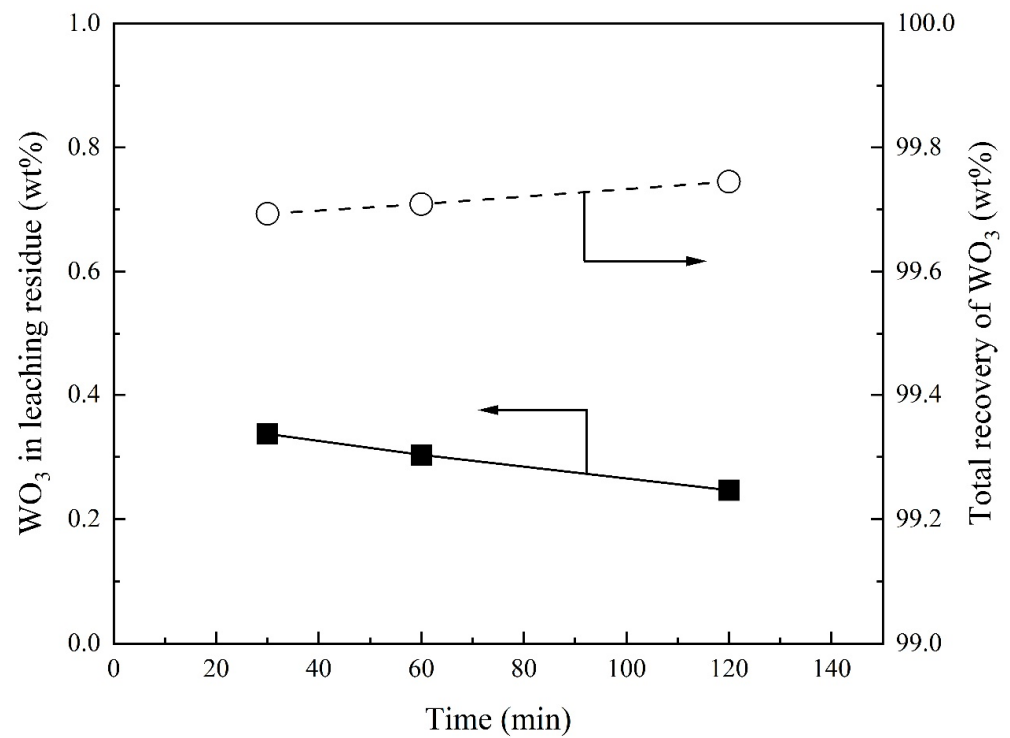


Figure 12. Effect of reaction time on total recovery of WO₃, Na₂CO₃/Ore = 1.1, SiO₂/Ore = 0.3, 1200 °C.

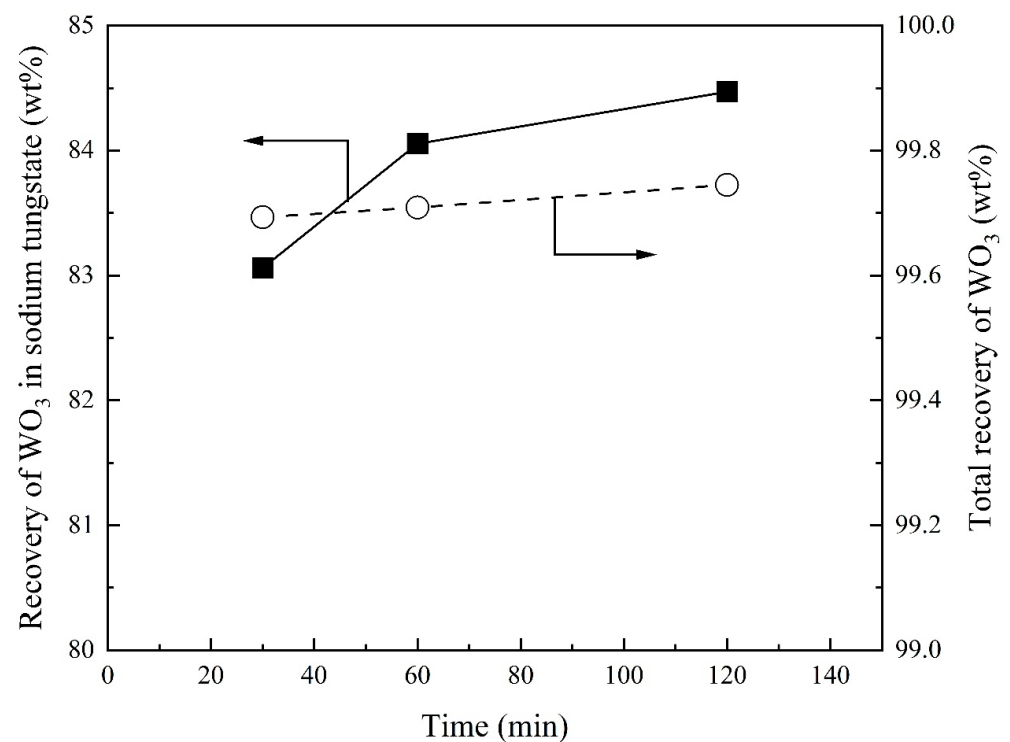


Figure 13. Effect of reaction time on direct recovery and total recovery of WO₃ and WO₃ content in sodium tungstate, Na₂CO₃/Ore = 1.1, SiO₂/Ore = 0.3, 1200 °C.

The reaction time has little effect on the WO₃ content in the leaching residue and the total recovery of WO₃. It can be seen from Figure 12 that the WO₃ content in the leaching residue decreases, and the total recovery of WO₃ increases slightly with increasing reaction

time. Considering the productivity and energy consumption, 60 min is enough to complete the smelting reaction of wolframite.

Figure 13 shows the effect of reaction time on the direct recovery and total recovery of WO_3 . The total recovery is around 99.7% when the reaction time is between 30 and 120 min. The direct recovery of WO_3 is increased from 84.1 to 84.5% when the reaction time is extended from 60 to 120 min.

4. Conclusions

Sodium tungstate is a potential raw material to produce tungsten metal via electrolysis. Direct production of sodium tungstate from wolframite has not been reported. The present study demonstrated that high-purity sodium tungstate can be directly produced from wolframite with a high recovery. Effects of Na_2CO_3 /Ore ratio, SiO_2 /Ore ratio, temperature, and reaction time on the direct and total recovery of tungsten and WO_3 in sodium tungstate were investigated systematically. The compositions of the WO_3 -containing slags and sodium tungstate reported in the present study fill the knowledge gap of the tungsten-containing thermodynamic database. The important findings include the following:

1. Direct recovery of tungsten can be achieved in the form of Na_2WO_4 initially increasing and then decreasing with increasing Na_2CO_3 /Ore ratio. The SiO_2 /Ore ratio increases the direct recovery of tungsten continuously. Temperature and reaction time slightly increase the direct recovery of tungsten. At a Na_2CO_3 /Ore ratio of 0.5 and SiO_2 /Ore ratio of 0.3, 96% tungsten can be directly recovered as sodium tungstate.
2. The WO_3 content in sodium tungstate decreases with increasing Na_2CO_3 /Ore ratio and has a maximum with SiO_2 /Ore ratio. Temperature and reaction time can slightly increase the WO_3 content in sodium tungstate. A percentage of 78% WO_3 in sodium tungstate ($\approx 99\%$ sodium tungstate) can be obtained at a range of Na_2CO_3 /Ore and SiO_2 /Ore ratios.
3. Total recovery of tungsten increases with increasing Na_2CO_3 /Ore ratio. The SiO_2 /Ore ratio initially decreases and then increases the total recovery of tungsten. The total recovery of tungsten decreases slightly with increasing temperature and is almost independent of the reaction time above 30 min.
4. Up to 11.3 wt% WO_3 was reported in the silicate slag. Up to 2.7% SiO_2 , 0.9 wt% SO_3 , 2.1 wt% Fe_2O_3 , and 3.6 wt% MnO were reported in the sodium tungstate. These experimental data will support the development of a WO_3 -containing thermodynamic database.

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