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Fundamental Study on Extraction of Sodium Tungstate from Wolframite through Pyrometallurgical Smelting

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Abstract: Tungsten is a high-value resource with a wide range of applications. The end-products of tungsten industry are tungsten metal and alloys that are produced through many steps from high-grade concentrates. Pyrometallurgical extraction of tungsten from complex and low-grade ores has great potential to overcome the problems associated with the hydrometallurgical process. In this study, sodium carbonate and silica were used to extract tungsten from wolframite at high temperatures. Sodium tungstate can be obtained directly from the smelting reaction between 1100 and 1300 oC. The smelting slag is further water-leached to recover sodium tungstate in the solution. The 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, which provides a theoretical basis for the pyrometallurgical smelting process of tungsten extraction.

Keywords: wolframite; smelting; sodium tungstate; recovery

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1. Introduction

Tungsten is one of the strategical minerals due to its special properties, wide applications, a 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 ($CaWO_4$) and wolframite ($(Fe,Mn)WO_4$) are abundant and easy to be concentrated for extraction [4,6–8]. In the 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 goes through a purification and a conversion process to obtain pure ammonium paratungstate (APT) which is the important intermediate compound to produce tungsten metal and alloys [4,6,9,10]. Tungsten metal is produced by decomposition of APT and reduction of WO_3 by hydrogen. Carburization of fine tungsten powder at high temperature 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 a conversion of sodium tungstate solution, a large amount of effluents are generated which needs to be treated with high-cost [18]. As a hydrometallurgical process, 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 H_2O-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 Na_2SiO_3 at 1050 to 1100 °C for 2h. More than 99% of the tungsten was recovered in the halide-tungstate phase which contained 29.8% WO_3, 0.24% FeO and 0.30% MnO. Using the similar conditions, Malyshev et al [20] studied the effects of NaCl and Na_2SiO_3 concentrations on recovery of tungsten into the halide-tungstate phase. 99% recovery was achieved by combination of 45 wt% NaCl and 20 wt% Na_2SiO_3. Gostishchev V.V. and Boiko V. F. [21] used a mixture of NaCl–NaF–$NaCO_3$ to decomposite a scheelite concentrate containing 55 wt% WO_3. Up to 93 wt% tungsten was recovered in the halide-tungstate phase after reaction at 850-900 °C for 1h. If a mixture of NaCl–$NaCO_3$–Na_3AlF_6 was used at 900-947 °C, 95 wt% recovery could be achieved. Phase equilibrium studies in the system Na_2O-SiO_2-WO_3 shown 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 $NaCO_3$ and SiO_2 can decomposite wolframite completely at 1050-1200 °C. Over 99% tungsten can be recovered in the sodium tungstate solution. High $NaCO_3$ and low SiO_2 concentrations are beneficial for the decomposition and recovery of tungsten. Although the formation of two liquids was observed but it was not attempted to obtain the sodium tungstate directly from the melt. In the present study, experimental results on high-temperature preparation of sodium tungstate are reported. Effects of $NaCO_3$, SiO_2, temperature and reaction time on recovery of tungsten and purity of the sodium tungsten are discussed.

2. Experimental procedure

A commercial wolframite concentrate was used in the present study and its dry composition is shown in Table 1. Analytical grade of sodium carbonate and silica were used for decomposition of the wolframite. WO_3, FeO and MnO are the major components of the wolframite.

Table 1. Composition of wolframite used in this study.

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. 10 g 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 35mm, ID 30mm，H 60mm). A muffle furnace was used for all experiments in air. The sample was heated to the required temperature with a heating rate of 10 °C/min. The heated sample was cooled down in the furnace after the reaction at certain time. The crucible was broken carefully to remove the sample inside. High-density sodium tungstate was covered by the low-density silicate 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 WO_3-containing leachate was separated from the residue by filtration. The compositions of the sodium tungstate, slag and leaching residue were analyzed by XRF (PANalytical Axios XRF spectrometer).

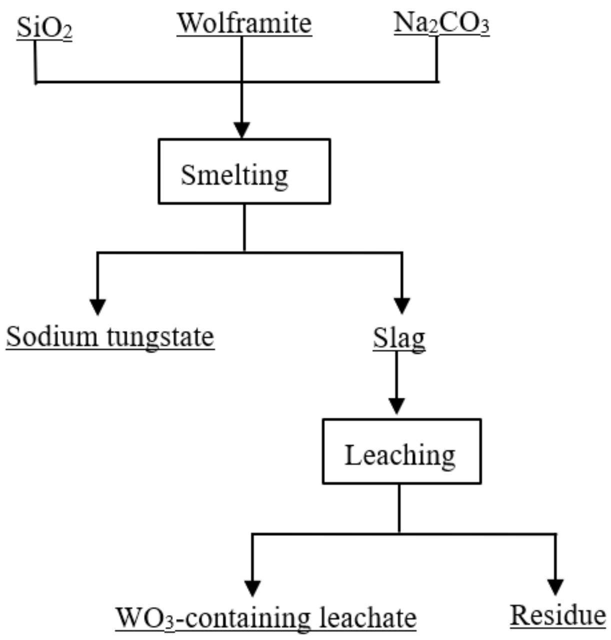


Figure 1. Experimental procedure in the present study.

3. Results and discussion

The variable parameters used in the extraction of the wolframite included Na_2CO_3/Ore ratio, SiO_2/Ore ratio, temperature and reaction time. The detailed experimental plan is shown in Table 2. The Na_2CO_3/Ore and SiO_2/Ore ratios are in the range of 0.3 to 1.1. Temperature is in the range of 1100 to 1300 ^{o}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 (^{o}C)	Time (min)	Na_2CO_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

Wolframite reacts with sodium carbonate and silica at high temperature:

$$(Fe,Mn)WO_4 + Na_2CO_3 + SiO_2 + O_2 \rightarrow Na_2WO_4 + slag \quad + CO_2 \qquad (1)$$

Tungsten oxide forms liquid sodium tungstate with sodium oxide, oxides of iron and manganese from the wolframite form slag with silica and sodium oxide. Immiscible slat (sodium tungsten) and slag are all liquid and separated in two layers due to different densities. Low-density slag is on the 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:

Recovery of WO_3 in sodium tungstate = (mass of WO_3 in sodium tungstate/mass of WO_3 in the ore)*100 (2)

Total recovery of WO_3 = (1-(mass of WO_3 in residue/mass of WO_3 in the ore))*100 (3)

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

The compositions of the slag, sodium tungstate and leaching residue analysed 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 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%. 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 Na_2CO_3/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 shows that WO_3 in the sodium tungstate is in the range of 70.2-79.8% that are close to that in the Na_2WO_4 (78.9 wt%). Up to 2.7 and 0.9 wt% SiO_2 and sulfur are present in the sodium tungstate as Na_2SiO_3 and Na_2SO_4 have the similar properties as the Na_2WO_4. Presence of Fe_2O_3 and MnO in the sodium tungstate indicates that undecomposed wolframite can form solid solution with Na_2WO_4. The purity of Na_2WO_4 in the sodium tungstate depends on the decomposition of wolframite and dissolution of Na_2SiO_3 and Na_2SO_4. The weights of the sodium tungstate is relatively constant, between 8.2 and 8.9 grams.

Table 4. Weights and compositions of sodium tungstate and direct recovery of WO_3.

Exp No	Weight (g)	Composition (wt%)						Direct recovery of WO_3 (%)
		Fe_2O_3	SiO_2	MnO	SO_3	WO_3	Na_2O	
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

WO_3 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. Fe_2O_3, MnO, SiO_2 and Na_2O are the major components of the leaching residue. The lowest WO_3 in the leaching residue is 0.2 wt% which is much lower than that in the conventional processes [11–15].

Table 5. Weights and compositions of leaching residue and total recovery of WO_3.

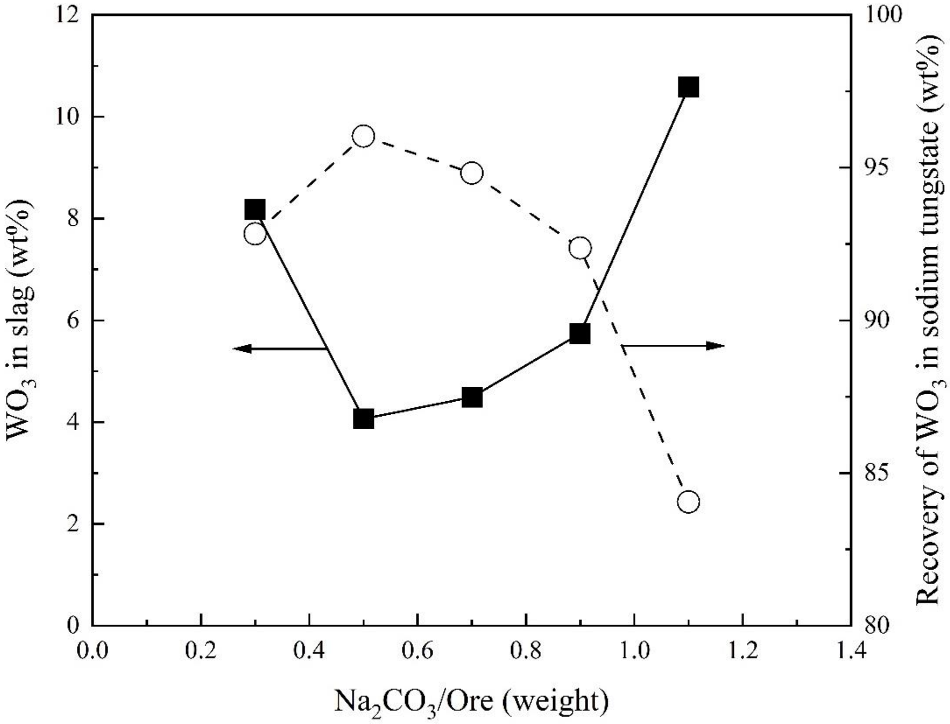
Exp No	Weight (g)	Composition (wt%)						Total recovery of WO_3 (%)
		Fe_2O_3	SiO_2	MnO	SO_3	WO_3	Na_2O	
W1	**8.1**	18.9	41.4	11.2	0.0	2.2	26.2	97.5
W2	8.6	18.2	37.2	10.7	0.0	0.9	32.9	98.9
W3	6.9	31.1	30.5	17.6	0.0	0.3	20.5	99.7
W4	12.4	12.0	42.6	7.1	0.1	4.5	33.7	92.3
W5	14.9	10.0	49.5	5.9	0.1	4.6	29.9	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

In the conventional extraction process of tungsten from the concentrate, the intermediate product is 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, 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 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 the sodium tungstate are discussed in the following sections.

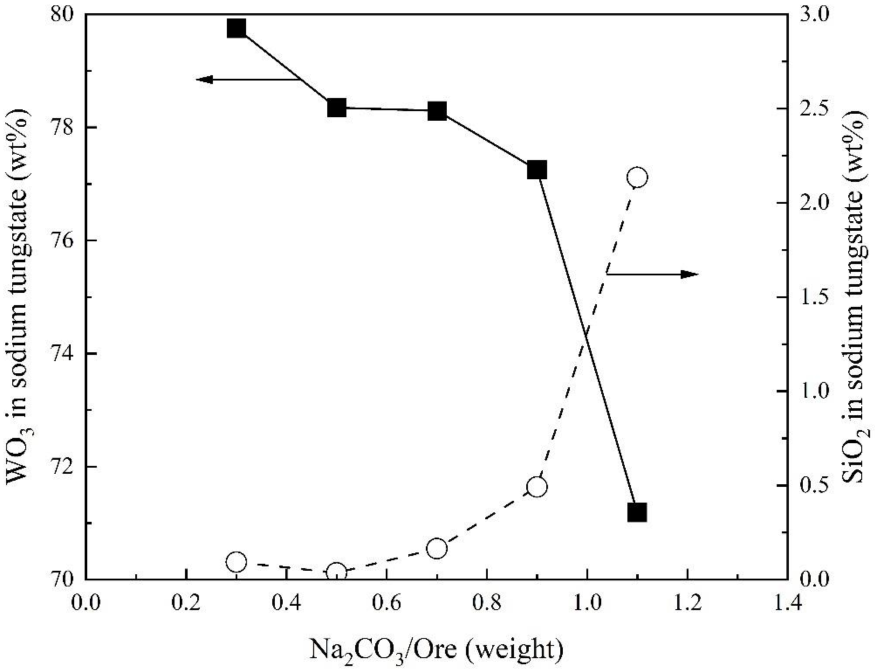
3.1. Effect of Na_2CO_3/Ore on recovery of WO_3 and composition of sodium tungstate

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 Na_2CO_3/Ore ratio. It can be seen from Figure 2(a) that initially the direct recovery of WO_3 increases with increasing Na_2CO_3/Ore ratio. The maximum recovery 96% reached at a Na_2CO_3/Ore ratio of 0.5 and then the direct recovery of WO_3 decreases with increasing Na_2CO_3/Ore ratio. This trend can be explained by Figure 2(b). As 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 2 (b) that WO_3 content in the sodium tungstate decreases with increasing Na_2CO_3/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 (Na_2CO_3/Ore ratio of 0.3), the weight of the salt is lower than W10 (Na_2CO_3/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 Na_2CO_3/Ore ratio of 0.3 is not enough to fully decompose the wolframite. High WO_3 in the salt does not guaranty 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 2(b) shows that SiO_2

content in the sodium tungstate increases with increasing Na_2CO_3/Ore ratio resulting in a decreased WO_3 content.



WO_3 in slag and recovery of WO_3 in sodium tungatate.



(b) WO_3 and SiO_2 contents in sodium tungstate.

Figure 2. Effect of Na_2CO_3/Ore on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, SiO_2/Ore=0.3, 1200 °C, 60min.

Figure 3 shows the WO_3 content in the leaching residue and total recovery of WO_3 as a function of Na_2CO_3/Ore ratio. Low WO_3 in the residue indicates a high recovery of tungsten according to Eq.

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 increasing Na_2CO_3/Ore ratio. A maximum total recovery of 99.7% is achieved at the Na_2CO_3/Ore ratio of 1.1.

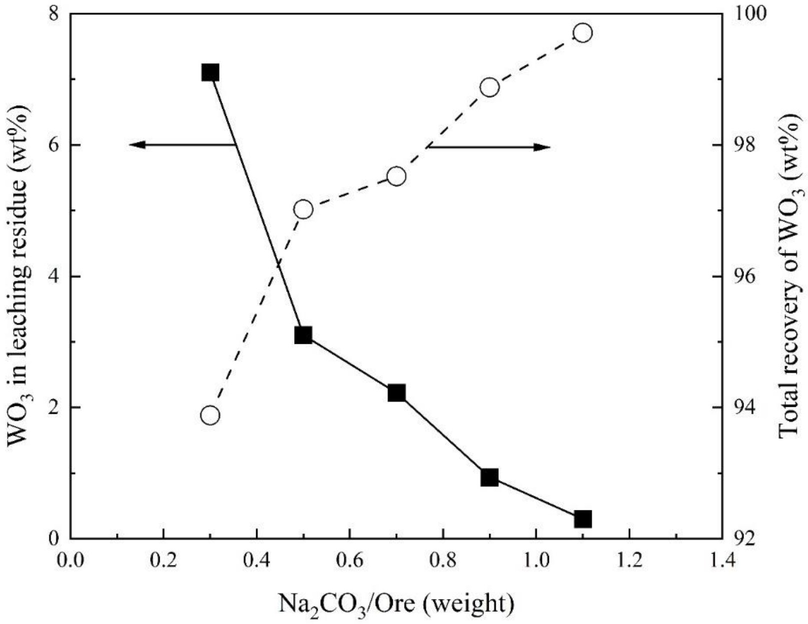


Figure 3. Effect of Na_2CO_3/Ore on total recovery of WO_3, SiO_2/Ore=0.3, 1200 °C, 60min.

Figure 4 shows that the effect of Na_2CO_3/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 Na_2CO_3/Ore ratio of 0.5. The total recovery is only 97% at this Na_2CO_3/Ore ratio. If the Na_2CO_3/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 Na_2CO_3/Ore ratio of 1.1. Figures 2-4 provide options for the industry to decide the operating parameter according to their requirements.

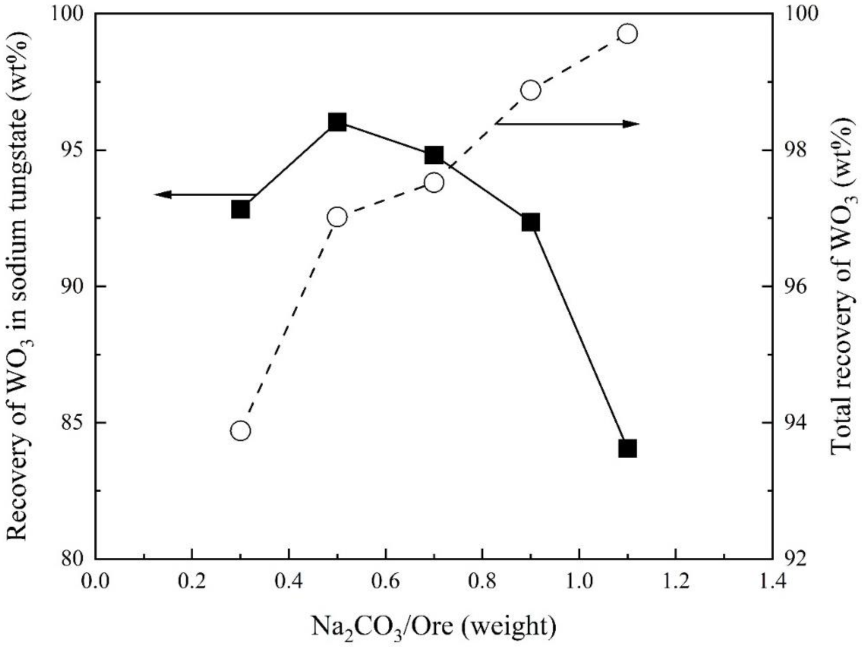
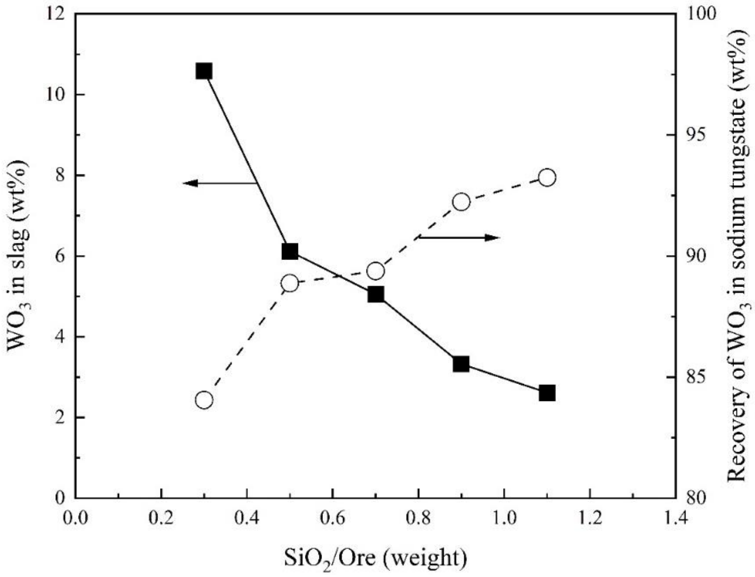


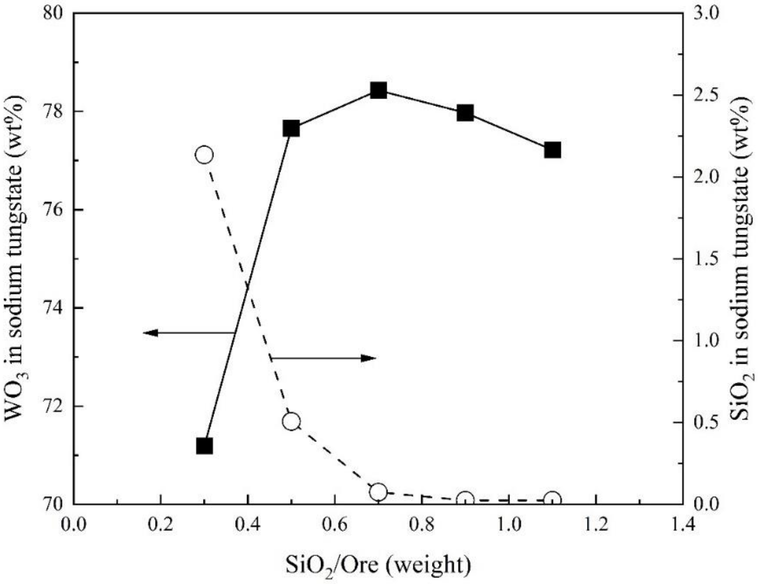
Figure 4. Effect of Na_2CO_3/Ore on direct recovery and total recovery of WO_3, SiO_2/Ore=0.3, 1200 °C, 60min.

3.2. *Effect of SiO_2/Ore on recovery of WO_3 and composition of sodium tungstate*

When Na_2CO_3/Ore ratio is fixed, effect of 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 5(a) that the direct recovery of WO_3 increases continuously with increasing SiO_2/Ore ratio. Increase of the SiO_2/Ore ratio from 0.3 to 1.1 resulted a increase of the direct recovery from 84.1 to 93.2%. Figure 5(b) 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.



(a) WO_3 in slag and recovery of WO_3 in sodium tungatate



(b) WO_3 and SiO_2 contents in sodium tungstate

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, Na_2CO_3/Ore=1.1, 1200 °C, 60min.

Figure 6 shows the WO_3 content in the leaching residue and 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%.

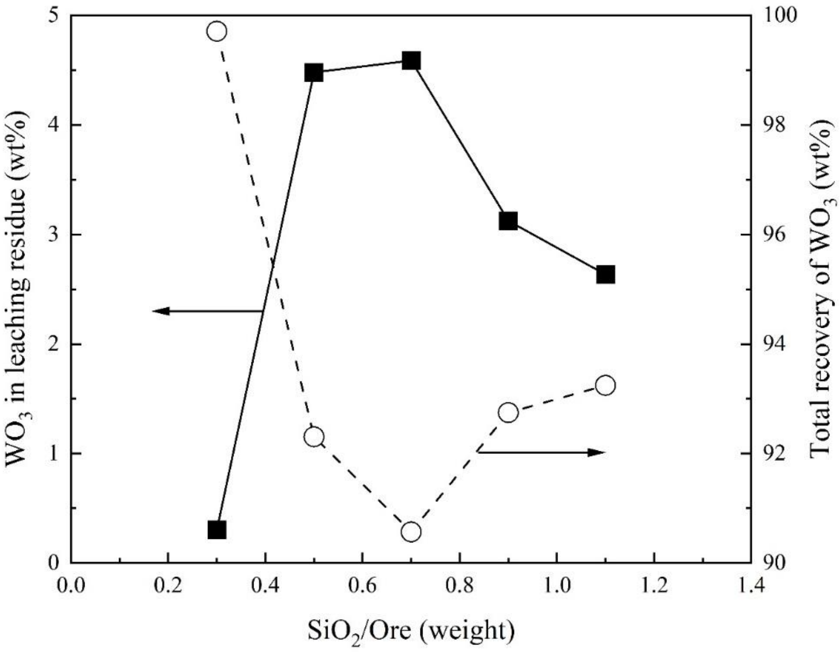


Figure 6. Effect of SiO_2/Ore on total recovery of WO_3, Na_2CO_3/Ore=1.1, 1200 °C, 60min.

Figure 7 shows the effect of SiO_2/Ore ratio on the direct recovery and total recovery of WO_3. It is clear that 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 high recovery and purity of Na_2WO_4 is 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.

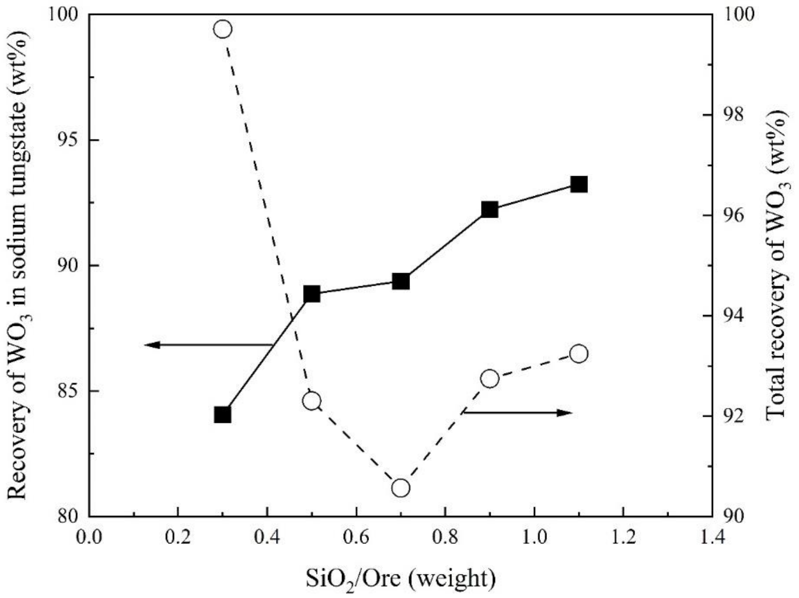
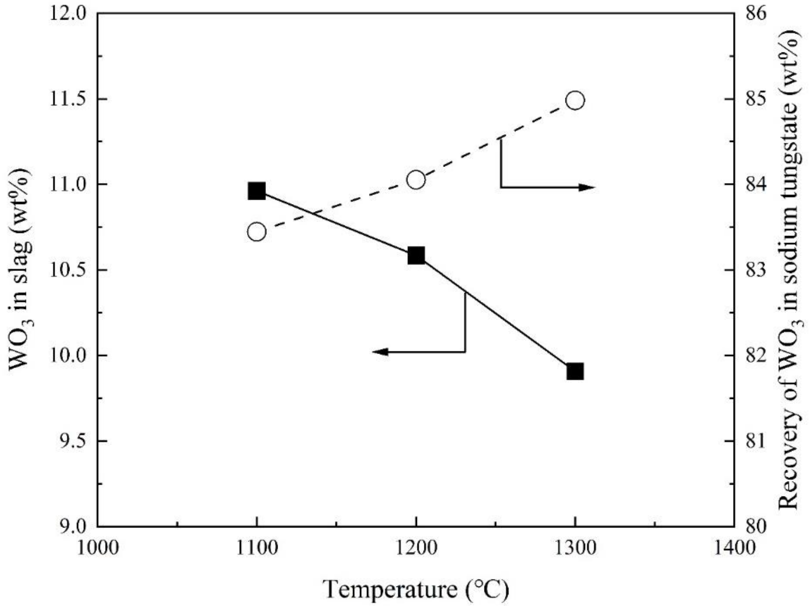


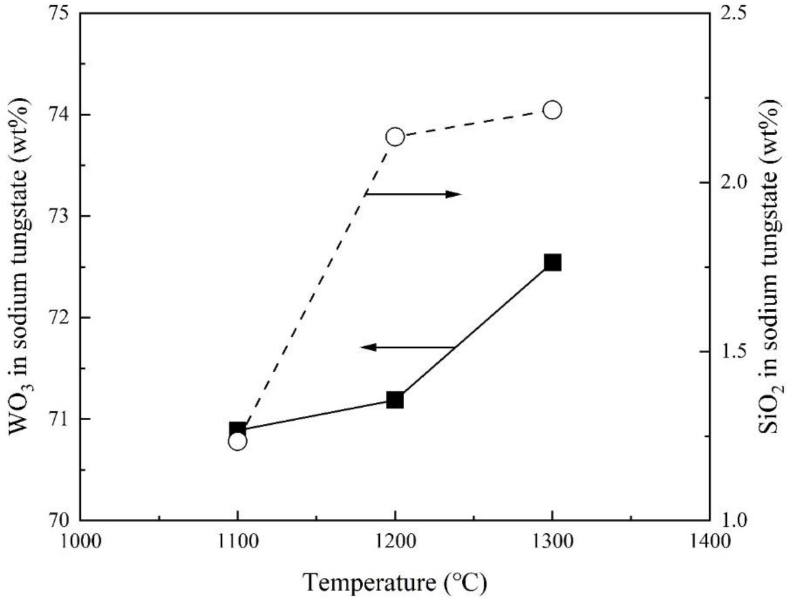
Figure 7. Effect of SiO_2/Ore on direct recovery and total recovery of WO_3, Na_2CO_3/Ore=1.1, 1200 °C, 60min.

3.3. *Effect of temperature on recovery of WO_3 and composition of sodium tungstate*

When both Na_2CO_3/Ore and SiO_2/Ore ratios are fixed, 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 Na_2CO_3/Ore=1.1, SiO_2/Ore=0.3, the direct recovery of WO_3 and WO_3 content in the sodium tungstate increase 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.



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



(b) WO_3 and SiO_2 contents in sodium tungstate

Figure 8. Effect of temperature on (a) direct recovery of WO_3 and (b) WO_3 and SiO_2 contents in sodium tungstate, Na_2CO_3/Ore=1.1, SiO_2/Ore=0.3, 60min.

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 to recover tungsten from the wolframite. The WO_3 content in the leaching residue is below 0.2 wt% at 1100 °C.

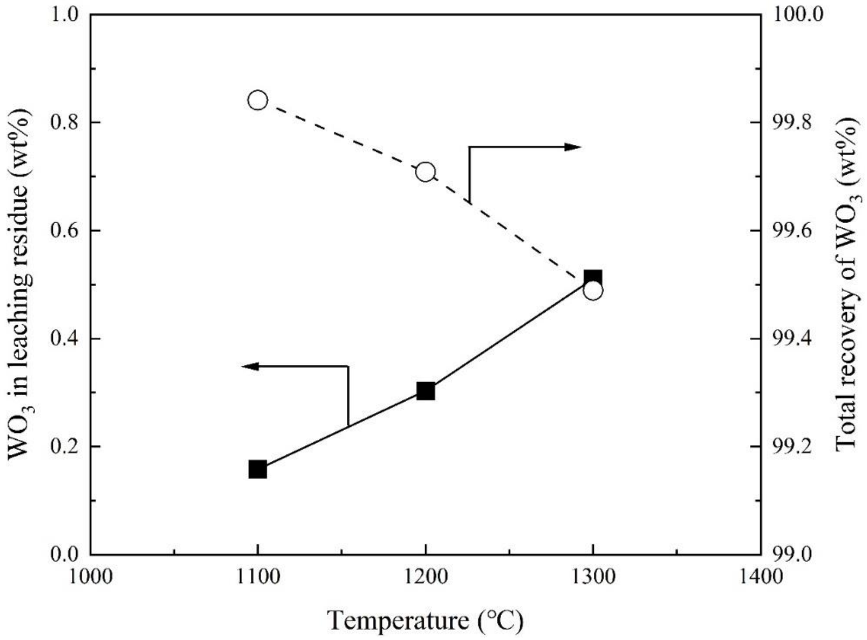


Figure 9. Effect of temperature on total recovery of WO_3, Na_2CO_3/Ore=1.1, SiO_2/Ore =0.3, 60min.

Figure 10 shows that temperature has opposite effect on the direct recovery and total recovery of WO_3. However, the extent of the effect is different on 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 increament of the temperature increases the direct recovery of WO_3 increases from 83.4 to 85%.

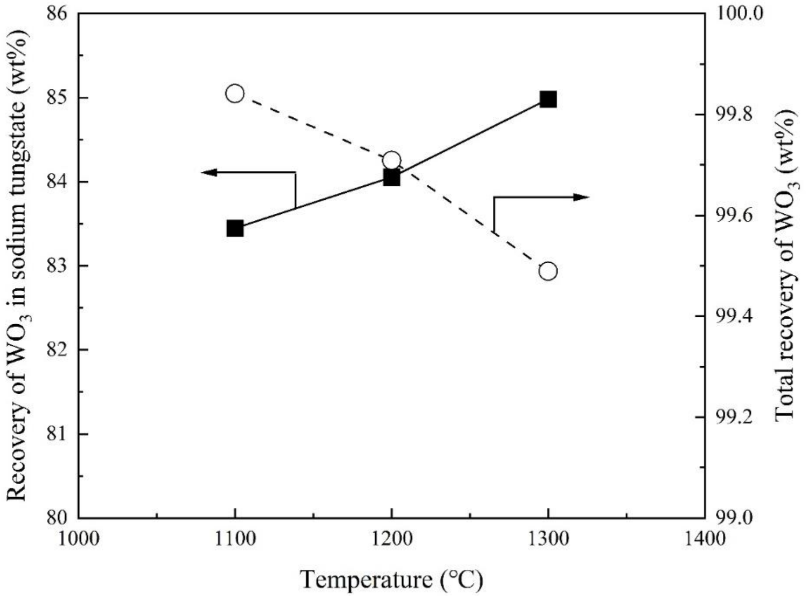
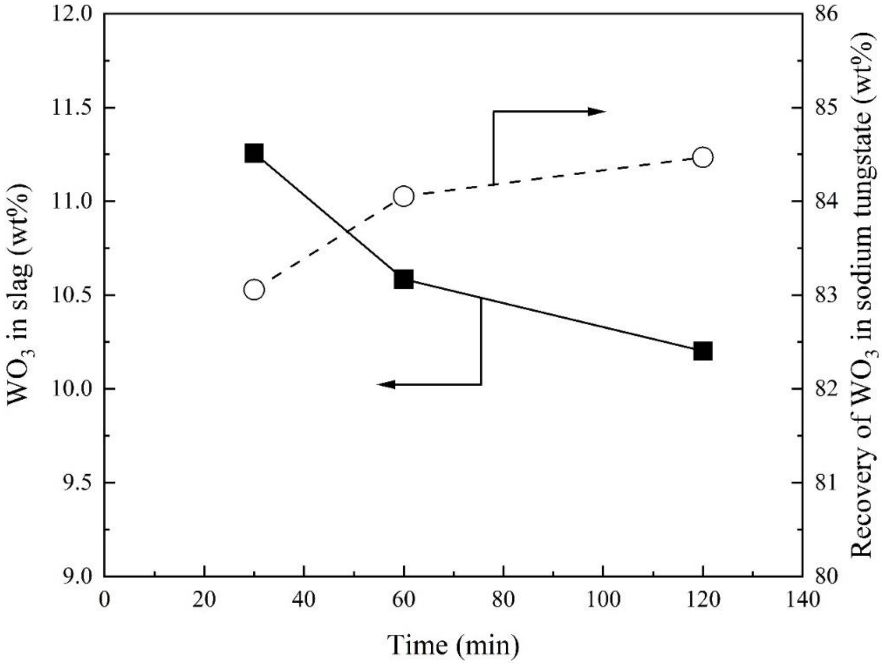


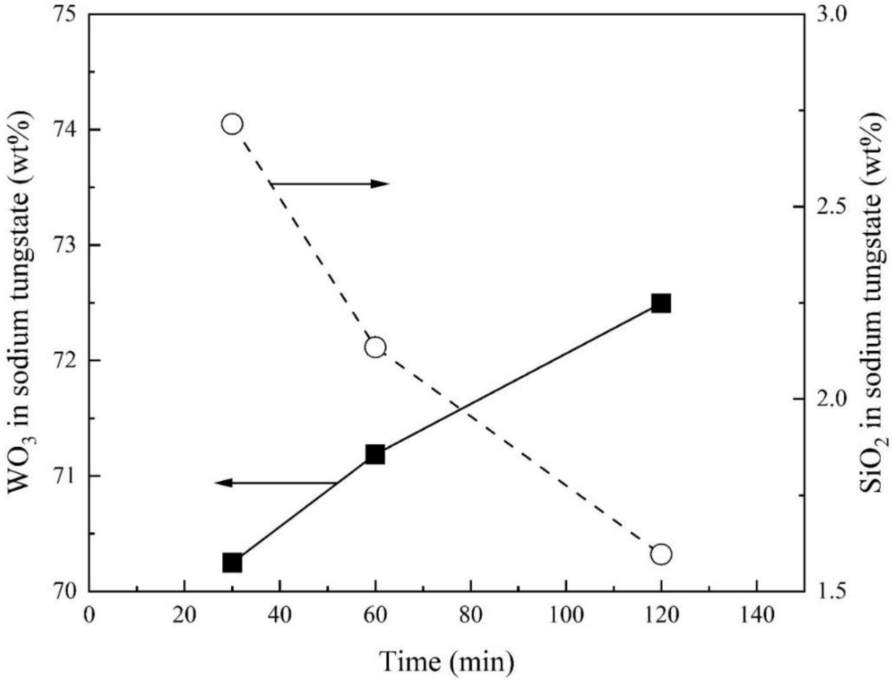
Figure 10. Effect of temperature on direct recovery and total recovery of WO_3, Na_2CO_3/Ore=1.1, SiO_2/Ore =0.3, 60min.

3.4. *Effect of reaction time on recovery of WO_3 and composition of sodium tungstate*

When other parameters are fixed, 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 120min 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 120min.



(a) WO_3 in slag and recovery of WO_3 in sodium tungatate



(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, Na_2CO_3/Ore=1.1, SiO_2/Ore =0.3, 1200 ^{o}C.

The reaction time has a little effect on the WO_3 content in the leaching residue and total recovery of WO_3. It can be seen from Figure 12 that the WO_3 content in the leaching residue decreases and total recovery of WO_3 increases slightly with increasing the reaction time. Considering the productivity and energy consumption, 60min is enough to complete the smelting reaction of wolframite.

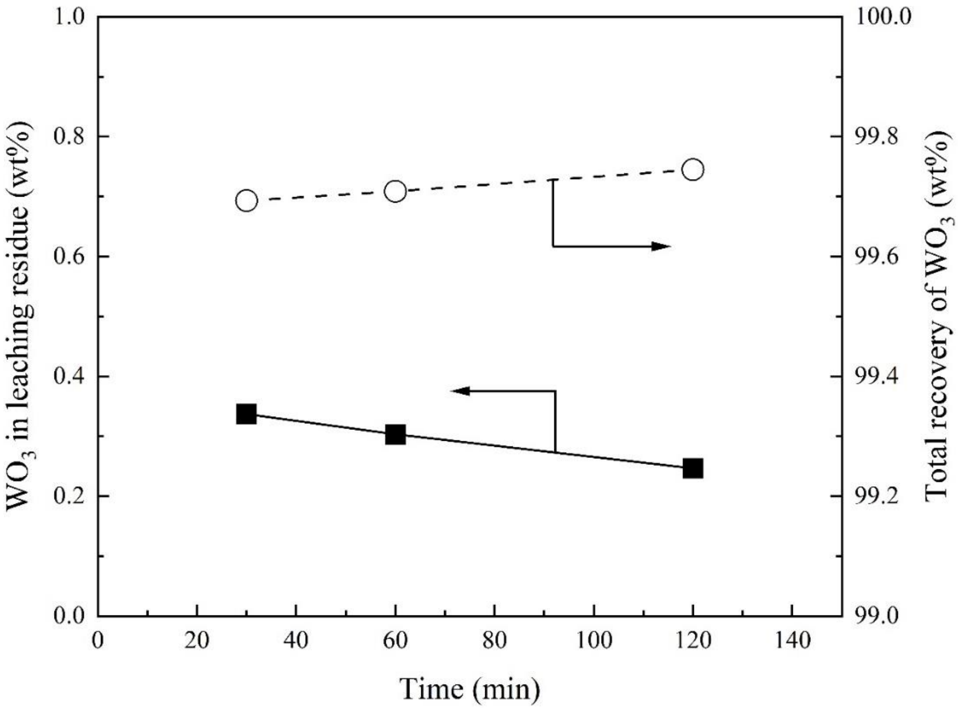


Figure 12. Effect of reaction time on total recovery of WO_3, Na_2CO_3/Ore=1.1, SiO_2/Ore =0.3, 1200 °C.

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 120min. The direct recovery of WO_3 is increased from 84.1 to 84.5% when the reaction time is enetnded from 60 to 120min.

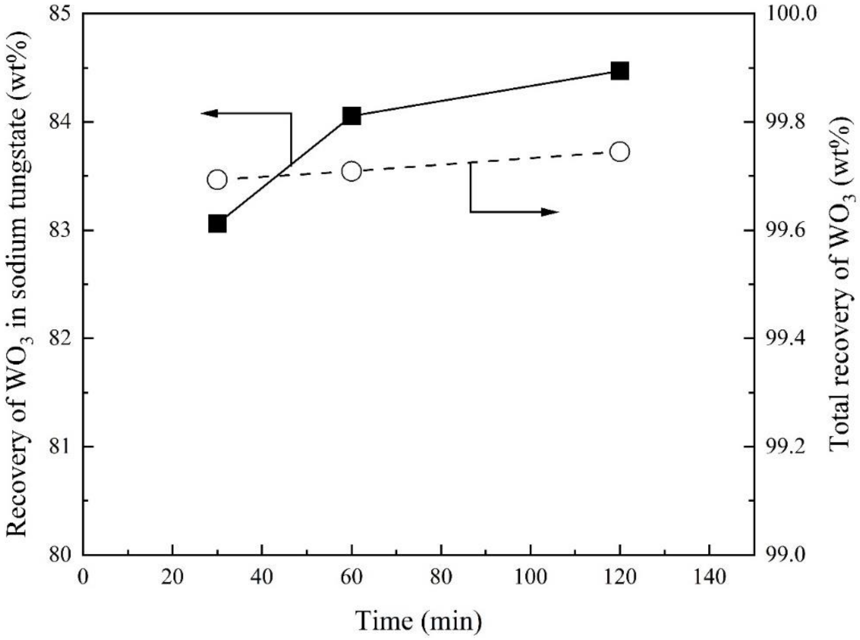


Figure 13. Effect of reaction time on direct recovery and total recovery of WO_3 and WO_3 content in sodium tungstate, Na_2CO_3/Ore=1.1, SiO_2/Ore =0.3, 1200 °C.

4. Conclusions

High temperature experiments have been carried out in air to extrac tungsten from wolframite. 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 the sodium tungstate are investigated systematically. It was found that:

1. Direct recovery of WO_3 in the form of Na_2WO_4 initially increases with increasing Na_2CO_3/Ore ratio. After reaching the maximum recovery 96% at a Na_2CO_3/Ore ratio of 0.5, the direct recovery of WO_3 decreases with increasing Na_2CO_3/Ore ratio. WO_3 content in the sodium tungstate decreases with increasing Na_2CO_3/Ore ratio. The total recovery of tungsten increases with increasing Na_2CO_3/Ore ratio and up to 99.8% can be recovered in two steps.
2. Direct recovery of WO_3 increases continuously with increasing SiO_2/Ore ratio. The WO_3 content in the sodium tungstate initially increases and then decreases with increasing SiO_2/Ore ratio. The total recovery of tungsten initially decreases and then increases with increasing SiO_2/Ore ratio. A high total recovery of tungsten can only be attained at low SiO_2/Ore ratios.
3. Direct recovery of WO_3 and WO_3 content in the sodium tungstate increase with increasing temperature. The total recovery of WO_3 decreases slightly with increasing temperature.
4. The reaction time can slightly increase the direct recovery of WO_3 and the WO_3 content in the sodium tungstate. The total recovery of WO_3 is almost independent of the reaction time above 30min.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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