applied sciences

MDPI

Article

Sintering with Sodium Carbonate and Leaching of Wolframite Cakes

Bolotpay Baimbetov [1], Yeleussiz Tazhiyev [1,*], Akmaral Yeleuliyeva [1], Gulnara Moldabayeva [1,*], Adelya Dauletbakova [1], Yelena Yakob [2] and Akbota Taimassova [1]

[1] Department of Metallurgy and Mineral Processing, Non-Profit Joint Stock Company (NJSC) Kazakh National Research Technical University Named K.I. Satbayev, Almaty 050013, Kazakhstan; b.baimbetov@satbayev.university (B.B.); yeleuli.a@gmail.com (A.Y.); a.dauletbakova@satbayev.university (A.D.); a.taimassova@satbayev.university (A.T.)

[2] "KSPSteel" LLP, Pavlodar 140000, Kazakhstan; yakob_ev@ksp-steel.kz

* Correspondence: y.tazhiyev@satbayev.university (Y.T.); gulnara.moldabayeva@satbayev.university (G.M.)

Abstract: Focuses on the processing of tungsten raw materials through various operations, including sintering, leaching, purification, and the production of technical tungstic acid. Modern research aims to enhance these processes, particularly the sintering of wolframite concentrates with alkali metal compounds and the leaching of concentrates and cakes. Experiments revealed that reactions between tungsten minerals and sodium carbonate from Akchatau ores commence at temperatures above 520–550 °C, intensifying between 750 and 850 °C. The concentrates were sintered at 750, 800, and 850 °C with a sodium carbonate excess coefficient of 1.05 to 1.2 to evaluate the effect on sodium tungstate extraction. Water leaching was conducted under a probabilistic–deterministic experimental design, analyzing five factors at four levels. Tungsten extraction was assessed based on solution density and the composition of the insoluble residue. Data processing established polynomial trends for tungsten trioxide extraction, and a material balance for sinter leaching was calculated from experiments using 100 g samples with a liquid-to-solid ratio of 2:1. The findings can be applied to improve tungsten processing technologies.

Keywords: wolframite; scheelite; sodium carbonate; sintering; leaching; electro dialysis

Citation: Baimbetov, B.; Tazhiyev, Y.; Yeleuliyeva, A.; Moldabayeva, G.; Dauletbakova, A.; Yakob, Y.; Taimassova, A. Sintering with Sodium Carbonate and Leaching of Wolframite Cakes. *Appl. Sci.* **2024**, *14*, 12031. https://doi.org/10.3390/app142412031

Academic Editor: Jorge Bañuelos Prieto

Received: 7 November 2024
Revised: 10 December 2024
Accepted: 19 December 2024
Published: 23 December 2024

1. Introduction

The Akchatau molybdenum–tungsten ore deposit [1–3] was developed until the 1990s of the 20th century but is still represented by the remains of tungsten, molybdenum, and beryllium reserves in categories C1, C2, and off-balance ores. The resumption of mining, processing, and metallurgical production of tungsten from the ores of this deposit requires geological exploration and mining work to confirm reserves, as well as the choice of technology for the beneficiation and processing of concentrates, taking into account modern advancements.

The average tungsten content in the Akchatau deposit ore is in tenths of a percent (0.1 to 0.3%). Beneficiation of ore samples from this deposit by gravity and flotation has made it possible to obtain rich concentrates containing 60–62% WO_3 [3–6].

Well-known industrial technologies intended to process tungsten raw materials include the following operations: sintering of concentrates with alkaline reagents; leaching of alloy or sinter; purification of sodium tungstate solutions from impurities; obtaining technical tungsten acid; precipitation of $CaWO_4$ or ammonium paratungstate; and finally, obtaining tungsten trioxide, metallic tungsten, or tungsten carbide [7–13].

Belskiy S.S., in [14], presented the results of research on the processing of wolframite concentrate by sintering it with sodium carbonate, nitrate, and potassium carbonate. The resulting cake was crushed and sent for leaching to obtain a solution of sodium tungstate. "Artificial scheelite" was precipitated from the solution and decomposed with hydrochloric

acid to produce tungstic acid. During the processing of the wolframite concentrate, it was found that the charge must be sintered at 450–500 °C, with the following ratio of components: wolframite concentrate, sodium carbonate, potassium carbonate, and nitrate in the proportion of 1:0.45:0.9:1.

The results of the assessment of the mechanism and kinetics of the thermochemical interaction of wolframite and concentrates with sodium and potassium carbonates were presented in the works of Selivanov E.N. et al. [15]. It has been shown, using the methods of differential thermal and phase analysis of sintering products, that the interaction of wolframite with sodium and potassium carbonates begins above 723–743 K and is accompanied by the formation of alkali metal tungstates and ferrites.

Publication [16] presents the rationale for the technology intended to process low-quality wolframite concentrates based on sintering with Na_2CO_3 and K_2CO_3 and conducted model experiments with the use of the mathematical planning method. The authors determined particular dependencies linking the degree of extraction (γ) of tungsten into the solution during leaching with the amount (Q) of introduced alkali metal carbonates at the sintering stage, temperature (T), and process duration (τ).

The composition of the initial concentrates and literature data confirm that for Akchatau tungsten concentrates, the most appropriate technology is sintering with sodium carbonate, leaching of the cake with water, and separation of tungsten acid with the subsequent production of tungsten trioxide and tungsten carbide.

2. Materials and Methods

The interaction reactions of tungsten minerals with Na_2CO_3 for concentrates from Akchatau ores begin at temperatures above 520–550 °C and proceed intensively in the range of 750–850 °C, as we have found.

To study the temperature conditions of sintering concentrates with sodium carbonate and the influence of leaching factors on the extraction of sodium tungstate into aqueous solutions, the batch was sintered in a muffle furnace using carborundum crucibles at temperatures of 750, 800, and 850 °C, with an excess of sodium carbonate ranging from 1.05 to 1.2. The chemical and phase composition of the wolframite concentrate was analyzed using an SPM-35 X-ray spectrometer (CJSC "Nauchpribor", Orel, Russia) and an Empyrean multichannel diffractometer (Malvern Panalytical Company, Almelo, The Netherlands) at the "Research Center KSP Steel" LLP. The data obtained are presented in Tables 1 and 2 [3].

Table 1. Chemical composition of wolframite concentrate, % (wt.).

Content, wt.%											
WO_3	Fe_2O_3	SiO_2	Al_2O_3	P_2O_5	S	CaO	MnO	MgO	MoO_3	Re	C
68.8	6.52	2.96	2.51	0.037	1.94	5.51	7.31	2.65	0.35	0.06	0.73

Table 2. Phase (structural) analysis of wolframite concentrate, % (wt.).

Quantum Distribution, %											
WO_3	$FeWO_4$	$MnWO_4$	SiO_2	CaO	Al_2O_3	MgO	MoO_3	S	C	Fe_2O_3	MoO_3
25	27	31	3	6	3	3	-	14	-	-	-

As a result of structural analysis, the minerals $FeWO_4$ (Ferberite), $MnWO_4$ (Manganese Wolframate), and tungsten oxides WO_2, WO_3, $WO_2 \cdot H_2O$ were identified.

As a result of sintering, black-colored cakes were obtained. The cakes were crushed and ground in a laboratory rod vibrating mill, followed by classification on sieves and allocation into classes with average particle size in microns: 815, 635, 365, 100.

Cakes were leached with distilled water in laboratory thermostats at temperatures from 65 to 95 °C and stirred with a paddle-type stirrer at a rotation speed of 240 to 420 rpm.

Reference [17] (according to E.P. Bogomilskaya and Sh.I. Matusevich) shows the composition and specific gravity of sodium tungstate solutions in the form of Table 3.

Table 3. Composition of sodium tungstate solutions by leaching stages.

Leaching Stage	Specific Gravity of Solution	WO_3, g/L	SiO_2, g/L	SiO_2/WO_3,%
1	1.26	230	0.18	0.08
1 + 2	1.19	172	0.17	0.1
1 + 2 + 3	1.12	104	0.14	0.13
4	1.014	15	0.08	0.5
Process waters	1	4	0.03	0.8

According to the data in Table 3, a linear dependence of the content of sodium tungstate in the solution was obtained in terms of WO_3, g/L.

$$Y = 0.88 \times X - 875.87; R^2 = 1.00, \quad (1)$$

where Y is the content of sodium tungstate and metal in the solution in terms of WO_3, g/L; X is the density of the sodium tungstate solution, g/L.

The density of the resulting solutions was measured at 20 °C with the use of a standard set of hydrometers and the pycnometric method [18] to calculate the extraction of sodium tungstate into solution, and optical and adsorption density measurements were also used by the photocalorimetric method with a Jenway 6300 spectrophotometer (Jenway Company, Stone, UK).

The content of WO_3 in solutions was calculated based on the measured density of the solution. Leaching was carried out at a ratio of L:S = 5:1 with 20 g of cake. Filtration of the pulp was carried out on paper filters; the pulp settles and filters relatively easily.

Experiments with cakes obtained at temperatures of 750–850 °C were performed, taking into account 5 factors at 4 levels according to probabilistic design of experiments [19].

The conditions for leaching experiments of cakes obtained at different firing temperatures and the extraction of WO_3 into solution are specified in Table 4.

Table 4. Conditions of experiments on cake leaching for 4 levels and 5 factors.

Experiment No.	1. Leaching Temperature, °C	2. Duration, min	3. Particle Size, μm	4. Stirrer Speed, rpm	5. Coefficient of Excess Sodium Carbonate, Units	Yec, % (Sinter 750 °C)	Yec, % (Sinter 800 °C)	Yec, % (Sinter 850 °C)
1	65	30	815	240	1.05	85.77	86.83	89.49
2	65	45	635	300	1.1	91.08	92.95	93.38
3	65	60	365	360	1.15	94.35	96.19	95.17
4	65	75	100	420	1.2	96.45	97.72	95.68
5	75	30	635	360	1.2	94.98	97.36	94.61
6	75	45	365	420	1.05	95.69	96.75	95.45
7	75	60	100	240	1.1	94.18	92.57	97.00
8	75	75	815	300	1.15	95.88	95.55	95.27
9	85	30	635	360	1.2	95.9	95.88	97.23
10	85	45	365	420	1.05	95.61	95.93	98.18
11	85	60	100	240	1.1	96.25	99.65	96.59
12	85	75	815	300	1.15	95.86	96.93	97.79
13	95	30	635	360	1.2	96.82	97.98	99.44
14	95	45	365	420	1.05	96.53	99.03	97.48
15	95	60	100	240	1.1	97.02	98.02	98.56
16	95	75	815	300	1.15	95.32	98.03	98.75

The assessment of the extraction degree of tungsten into the solution was controlled by the composition and weight of the insoluble residue; the effect of the transfer of silicon impurities into the solution, etc., is insignificant due to their low content in the cake.

3. Results and Discussion

The decomposition of wolframite concentrate by sintering it with sodium carbonate in the presence of oxygen proceeds according to reactions [3,7,8,14,15].

$$2FeWO_4 + 2Na_2CO_3 + 0.5O_2 = 2Na_2WO_4 + Fe_2O_3 + 2CO_2 \quad (2)$$

$$3MnWO_4 + 3Na_2CO_3 + 0.5O_2 = 3Na_2WO_4 + Mn_3O_4 + 3CO_2 \quad (3)$$

$$WO_3 + Na_2CO_3 = Na_2WO_4 + CO_2 \quad (4)$$

$$WO_3 \times H_2O + Na_2CO_3 = Na_2WO_4 + CO_2 + H_2O \quad (5)$$

$$WO_2 + Na_2CO_3 + ½O_2 = Na_2WO_4 + CO_2 \quad (6)$$

$$WO_2 \cdot H_2O + Na_2CO_3 + ½O_2 = Na_2WO_4 + CO_2 + H_2O \quad (7)$$

An increase in the coefficient of excess sodium carbonate during sintering of the charge in the range from 1.05 to 1.2 leads to a greater completion of the formation reactions of Na_2WO_4, and at the stage of sinter leaching, the extraction of sodium tungstate into the solution increases from 87.4 to 98.6% and is described by the dependence:

$$y = -0.5115x^2 + 5.8247x + 82.914; R^2 = 0.9707$$

where y is the degree of extraction of sodium tungstate into solution, %, x = 1, 2, 3, 4-coded values of the excess coefficient values (1.05, 1.10, 1.15, 1.20).

An increase in the sintering temperature of the charge within 700–800 °C leads to an increase in the extraction of sodium tungstate into the solution from 83.1 to 97.8%:

$$y = -0.9244x^2 + 9.1753x + 75.35; R^2 = 0.9822$$

where y is the degree of extraction of sodium tungstate into solution, %, x= 1, 2, 3-coded values of sintering temperatures (700 °C, 750 °C, 800 °C).

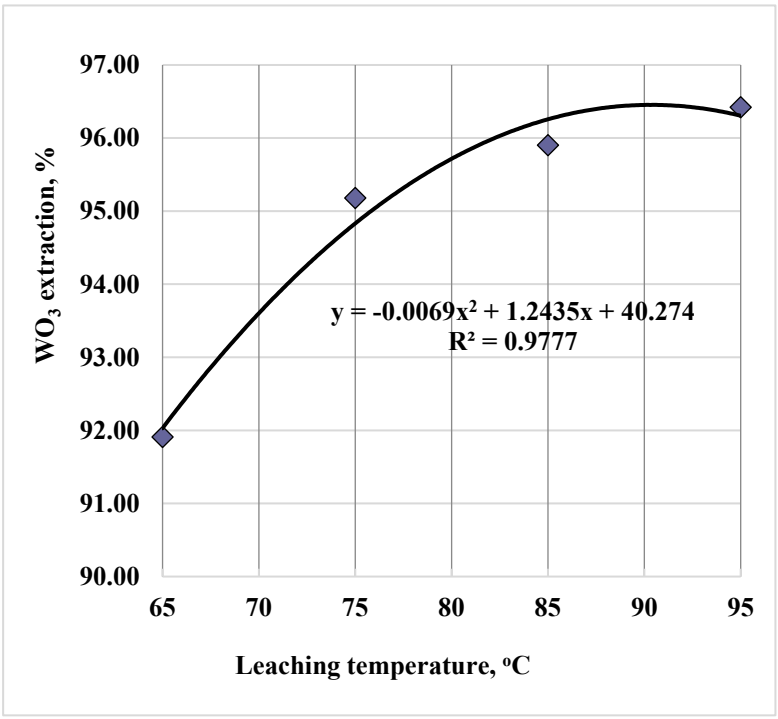
During leaching of the cake [3,7,8,14], sodium tungstate and soluble impurities pass into the solution (Na_2SiO_3, Na_2HPO_4, Na_2HasO_4, Na_2MoO_4, Na_2SO_4), as well as excess of Na_2CO_3.

The density of the resulting sodium tungstate solutions was in the range of 1105–1128 g/L, and the content of the extracted component in terms of WO_3 was 93–110 g/L; the cake yield after leaching was 4.1–6.1 g. Composition of the cake obtained at 750 °C and sodium carbonate excess coefficient Kc = 1.2, as well as the mass and composition of the cake obtained during leaching, are given in Table 5.

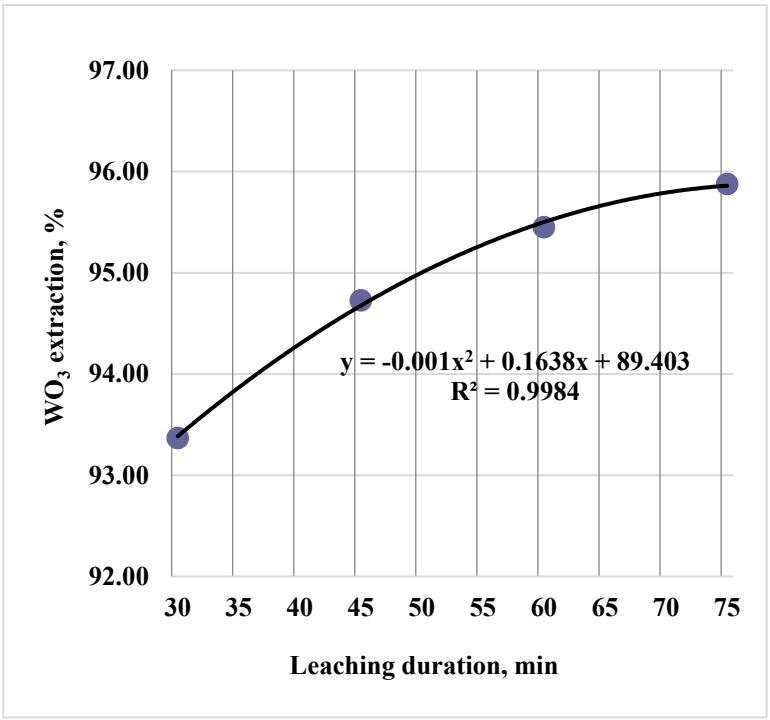
Table 5. Composition of cake obtained at 750 °C and water leaching cake.

	Weight, g	Content of Chemical Elements, %								
		WO_3	Fe_2O_3	SiO_2	Al_2O_3	P_2O_5	S	CaO	MnO	MgO
1. Sinter	20	54.67	5.18	2.35	1.99	0.03	1.54	4.38	5.81	2.11
2. Cake	5.19	11.31	19.96	9.06	7.68	0.11	5.94	16.86	22.37	8.11

Processing of experimental data made it possible to identify the dependences of tungsten trioxide leaching into solution and the trend equations presented for the sinter obtained at 750 °C in Figure 1a–e.

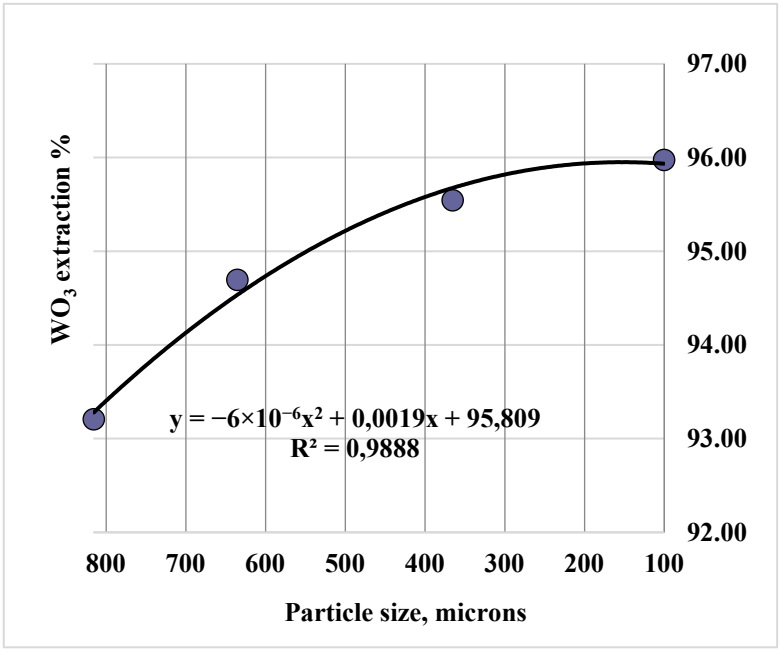


(**a**)

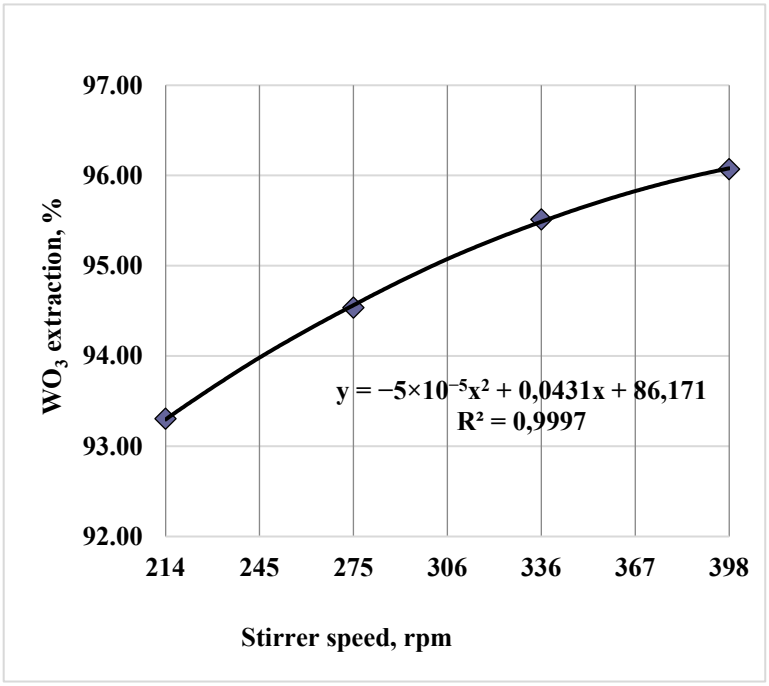


(**b**)

Figure 1. *Cont.*

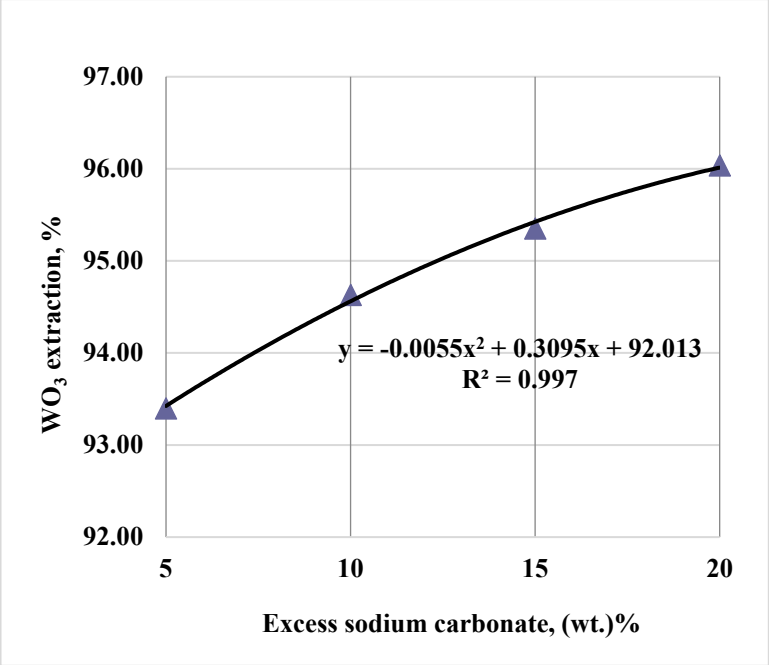


(**c**)



(**d**)

Figure 1. *Cont.*



(**e**)

Figure 1. Paired dependences of solution on factors: temperature (**a**), duration (**b**), particle size (**c**), stirrer speed (**d**), and sodium carbonate excess coefficient (**e**).

Experimental data are described by polynomials of the 2nd degree (the x-values correspond to the levels of factors in codes 1, 2, 3, 4 in the equations). During water leaching of cakes for firing temperatures of 800 and 850 °C, similar dependences of the degree of tungsten extraction into solution (in terms of WO_3) are obtained, shown in Table 6.

Table 6. Paired dependences of tungsten extraction into solution.

No.	Factor Influencing Leaching, Interval	Function Type	Approximation Coefficient
	Leaching dependences for sinter obtained at 800 °C		
1	Temperature, 75–95 °C	$y = -0.0024x^2 + 0.5477x + 68.054$	$R^2 = 0.9998$
2	Duration, 30–75 min	$y = -0.0013x^2 + 0.1941x + 89.952$	$R^2 = 0.98$
3	Particle size, 100–815 microns	$y = -9 \times 10^{-6}x^2 + 0.0047x + 96.578$	$R^2 = 0.9927$
4	Stirrer speed, 240–420 rpm	$y = -8 \times 10^{-5}x^2 + 0.0672x + 82.523$	$R^2 = 0.9999$
5	Excess sodium carbonate in the charge, 5–20% (wt.)	$y = -0.0060x^2 + 0.3242x + 93.1631$	$R^2 = 1.0000$
	Leaching dependences for sinter obtained at 800 °C		
1	Temperature, 75–95 °C	$y = -0.0026x^2 + 0.5895x + 66.102$	$R^2 = 0.9993$
2	Duration, 30–75 min	$y = -0.001x^2 + 0.1419x + 91.802$	$R^2 = 0.9947$
3	Particle size, 100–815 microns	$y = -3 \times 10^{-6}x^2 + 0.0003x + 96.918$	$R^2 = 0.9772$
4	Stirrer speed, 240–420 rpm	$y = -6 \times 10^{-5}x^2 + 0.0437x + 88.139$	$R^2 = 0.9944$
5	Excess sodium carbonate in the charge, 5–20% (wt.)	$y = -0.0124x^2 + 0.412x + 93.424$	$R^2 = 0.9926$

Balance experiments for cake leaching. Experiments were performed with 100 g weighed cake samples and an L:S ratio of 2:1 to assess the material balance of cake leaching.

An approximate calculated balance of leaching of cake obtained at a charge firing temperature of 750 °C is specified in Table 7.

Table 7. Calculated balance of leaching of cake.

Materials Received	Total, g	WO_3, g	Products Received	Total, g	WO_3, g
1. Sinter	100	55.47	1. Cake	32,313	3.023
2. Water	400	0	2. Productive solution	242,077	47.47
			3. Process water	225,525	4.966
Total, g	500	55.47	Total, g	499,915	55.459
			Residual, g	−0.085	−0.011

According to the balance, the extraction of WO_3 into leaching products was, in cake, 5.45%; in the productive solution, 85.58%; in wash water, 8.95%.

In the traditional industrial scheme, the concentrate is mixed with a screw mixer with recycled materials from cake leaching, air separator dust, and sodium carbonate

The WO_3 content in the charge is reduced to 20–22% due to the turnover of leaching tailings to avoid melting of the charge and the formation of deposits in the drum furnace [3,7,8].

The proposal is to sinter the granulated charge in a vertical shaft-type reactor with the supply of hot air from a heater instead of roasting in a rotary kiln. No recycled materials are added to the charge, and the leaching cake is processed in a separate scheme.

The possibility of electrodialysis of sodium tungstate solutions was reported in [20–22]. The process intended to remove sodium ions from sodium tungstate solutions with the use of membrane electrodialysis processes allows one to reduce the use of mineral acids, as well as prevent the formation of salt waste.

The productive solution is purified from impurities using known reagents, with the exception of the consumption of inorganic acids for neutralization operations and the precipitation of tungstic acid. In this work, preliminary experiments demonstrated the feasibility of using electrodialysis in a two-chamber apparatus, which separates the anode and cathode spaces with a cation exchange membrane, for purifying sodium tungstate solutions from impurities and isolating commercial sodium tungstate at the final stage.

The processes of electrodialysis of sodium tungstate solutions were studied under conditions of continuous supply of initial solutions and removal of electrodialysis products. The current efficiency indices were calculated, and the total energy consumption for electrodialysis of one weight unit of sodium tungstate was determined at different current densities on the cathode. The energy consumption for electrochemical processes in an electrodialysis cell, at current densities on the cathode ranging from 130 to 524 A/m^2, is 3.32 to 3.48 kWh per 1 kg of Na_2WO_4. However, the total energy consumption during electrodialysis also depends on losses in the contact network, losses due to heat release in the electrolyte, and under laboratory setup conditions, amounting to 5.72 to 13.40 kWh per 1 kg of Na_2WO_4.

4. Conclusions

The average tungsten content in the ore of the Akchatau deposit is 0.1–0.3%. Concentrates containing 60–62% WO_3 were obtained by enriching ore samples through gravity and flotation methods. The chemical and mineralogical composition of the concentrates was studied using an SPM-35 X-ray spectrometer and an Empyrean multichannel diffractometer.

It was found that the reactions of tungsten minerals with sodium carbonate proceed intensively in the temperature range of 750–850 °C. To study the effect of sintering temperature and leaching parameters on the extraction of sodium tungstate into solutions, the concentrate was sintered with sodium carbonate at temperatures of 750, 800, and 850 °C, with a sodium carbonate excess factor ranging from 1.05 to 1.2. An increase in the excess coefficient of sodium carbonate during the sintering of the batch, from 1.05 to 1.2, leads to a more complete reaction for the formation of Na_2WO_4. Consequently, at the leaching

stage of the sinter, the extraction of sodium tungstate into the solution increases from 87.4% to 98.6%.

Purification of the productive solution from impurities is carried out using known reagents, excluding the consumption of inorganic acids for neutralization and precipitation of H_2WO_4. In the course of preliminary experiments the efficiency of electrodialysis application in a two-chamber cell with separation of anode and cathode spaces by a cation-exchange membrane was established, which allows to effectively purify Na_2WO_4 solutions from impurities and to extract marketable Na_2WO_4 at the final stage.

The processes of electrodialysis of sodium tungstate solutions were investigated at continuous feeding of initial solutions and removal of electrodialysis products. The total energy costs of electrochemical processes were determined, taking into account losses in the contact network and losses due to heat generation in the electrolyte. On an industrial scale, the energy consumption depends on the plant design and the electrolyte circulation system.

The possibility of using electrodialysis in a two-chamber apparatus, with separation of the anode and cathode spaces by a cation-exchange membrane, has been demonstrated for purifying sodium tungstate solutions from impurities and isolating commercial sodium tungstate at the final stage. Energy costs for electrochemical processes, within the range of current densities on the cathode of 130–524 A/m^2, are estimated to be 3.32–3.48 kWh per 1 kg of Na_2WO_4. The total energy consumption also depends on losses in the contact network, as well as heat release in the electrolyte. Under laboratory setup conditions, the total energy consumption ranges from 5.72 to 13.40 kWh per 1 kg of Na_2WO_4. In an industrial installation, the energy consumption will be determined by the design of the apparatus and the configuration of the electrolyte circulation system.

Author Contributions: Conceptualization, B.B.; Data curation, Y.T.; Formal analysis, A.D.; Investigation, A.T.; Methodology, G.M.; Project administration, B.B.; Resources, Y.Y.; Software, Y.T. and A.Y.; Visualization, A.Y., A.D. and A.T.; Writing—original draft, B.B.; Writing—review and editing, Y.T. and G.M. All authors have read and agreed to the published version of the manuscript.

Funding: The research was carried out within the framework of grant funding of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan for 2023–2025 in the priority area "Rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and structures" project No. AP19677216 "Research and development of technologies, equipment for electrodialysis of solutions of tungstate, sodium sulfate with the regeneration of alkalis, acids".

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Author Yelena Yakob was employed by the company KSPSteel" LLP. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Bogolepov, V.G.; Shirkunov, M.V.; Gulyayeva, N. Structure, composition and distribution of mineralization in the main greisen bodies of the Akchatau rare metal deposit. In *Mineralogy and Geochemistry of Tungsten Deposits*; Saint Petersburg State University: Saint Petersburg, Russia, 1971; pp. 96–104.
2. Bychkov, A.; Matveeva, S. Thermodynamic model of the formation of ore bodies at the Akchatau wolframite greisenvein deposit. *Geochem. Int.* **2008**, *46*, 867–886. [CrossRef]
3. Baimbetov, B.; Moldabayeva, G.; Yeleuliyeva, A.; Jumankulova, S.; Taimassova, A.; Adilzhan, Z.; Baisultanov, R.; Yakob, E.; Serikbayev, V. Prospects of Processing Tungsten Ores from the Akchatau Deposit. *Processes* **2024**, *12*, 77. [CrossRef]
4. Wang, X.; Qin, W.; Jiao, F.; Dong, L.; Guo, J.; Zhang, J.; Yang, C. Review of tungsten resource reserves, tungsten concentrate production and tungsten beneficiation technology in China. *Trans. Nonferrous Met. Soc. China* **2022**, *32*, 2318–2338. [CrossRef]
5. Mountain Encyclopedia. Available online: http://www.mining-enc.ru/v/volframovaya-promyshlennost (accessed on 10 January 2022).
6. Yang, X. Beneficiation studies of tungsten ores—A review. *Miner. Eng.* **2018**, *125*, 111–119. [CrossRef]
7. Zelikman, A.N.; Korshunov, B.G. *Metallurgy of Rare Metals*; Metallurgy: Moscow, Russia, 1991; 432p. Available online: https://reallib.org/reader?file=412937 (accessed on 10 January 2022).

8. Plyushcheeva, V.E. *(Translator) Handbook of Rare Metals*; Mir: Moscow, Russia, 1965; p. 922.
9. Zhao, Z.; Li, J.; Wang, S.; Li, H.; Liu, M.; Sun, P.; Li, Y. Extracting tungsten from scheelite concentrate with caustic soda by autoclaving process. *Hydrometallurgy* **2011**, *108*, 152–156. [CrossRef]
10. Sun, P.M.; Li, H.G.; Li, Y.J.; Zhao, Z.W.; Huo, G.S.; Sun, Z.M.; Liu, M.S. Decomposing scheelite and scheelite-wolframite mixed concentrate by caustic soda digestion. *J. Cent. South Univ. Technol.* **2003**, *10*, 297–300. [CrossRef]
11. Queneau, P.; Huggins, D.; Beckstead, L. Autoclave Soda Digestion of Refractory Scheelite Concentrates. U.S. Patent 4320095A, 16 March 1982. Available online: https://patents.google.com/patent/US4320095A/en (accessed on 15 June 2022).
12. Premchand. Processing of low grade tungsten ore concentrates by hydrometallurgical route with particular reference to India. *Bull. Mater. Sci.* **1996**, *19*, 295–312. [CrossRef]
13. Lei, Y.; Sun, F.; Liu, X.; Zhao, Z. Understanding the wet decomposition processes of tungsten ore: Phase, thermodynamics and kinetics. *Hydrometallurgy* **2022**, *213*, 105928. [CrossRef]
14. Belskiy, S.S. Processing of wolframite concentrate. *Bull. Irkutsk. State Tech. Univ.* **2018**, *22*, 186–193. [CrossRef]
15. Selivanov, E.N. Kinetics and mechanism of natural wolframite interactions with sodium carbonate. *Int. J. Miner. Metall. Mater.* **2019**, *26*, 1364–1371. [CrossRef]
16. Sitdikov, F.G. Preparation of calcium tungstate from low-quality concentrates. In Proceedings of the Innovations in the Complex Processing of Mineral Raw Materials, Almaty, Kazakhstan, 21–22 January 2016; pp. 548–553.
17. All About Metallurgy. Available online: https://metal-archive.ru/redkie-metally/4200-razlozhenie-volframitovyh-koncentratov-sposobom-spekaniya-ili-splavleniya-s-sodoy.html (accessed on 22 November 2022).
18. Mettler Toledo. Available online: https://www.mt.com/int/en/home/products/Laboratory_Analytics_Browse/density-meter/densitometer/D6.html (accessed on 22 November 2022).
19. Malyshev, V.P. *Probabilistic and Deterministic Planning of Experiments*; Science: Almaty, Kazakhstan, 1981; 116p. Available online: https://search.rsl.ru/ru/record/01001059848 (accessed on 30 January 2023).
20. Smirnova, N.M.; Glukhova, L.P.; Rusakova, I.S. Method for Decarbonization of Tungstate-Soda Solutions and Regeneration of Sodium Hydroxide by Electrodialysis. SU 1750719 A1, 30 July 1992. Available online: https://patents.su/3-1750719-sposob-dekarbonizacii-volframatno-sodovykh-rastvorov-i-regeneracii-gidroksida-natriya-ehlektrodializom.html (accessed on 20 October 2022).
21. Butukhanov, V.L.; Lebukhova, N.V.; Yershova, T.B. Method for Production of Tungstic Acid. RF Patent 2073644C1, 20 February 1997. Available online: https://patents.google.com/patent/RU2073644C1/ru (accessed on 20 October 2022).
22. Verkhoturov, A.D.; Makienko, V.M.; Butukhanov, V.L. Possibilities of Processing Tungsten Raw Materials in Environmentally Friendly Conditions. Scientific Notes of Komsomolsk-on-Amur State Technical University. No. III-1 (15). 2013, pp. 102–106. Available online: https://www.uzknastu.ru/files/pdf/2013-15-1/102-106.pdf (accessed on 20 October 2022).