

# Physicochemical Investigations of Scheelite Concentrate Decomposition

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## Abstract

In the article results of kinetic studies of autoclave-carbonate decomposition of scheelite concentrates are presented. Studies are carried out in temperature range of 368–523 K, at mixing with a speed of 100–400 revolutions per minute. Solutions of sodium carbonate, mol/dm<sup>3</sup>: 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 was used to determine the dependence of the degree of tungsten leaching from scheelite on concentration. It was established, that with increase of concentration of sodium carbonate leaching degree increases and at the concentration of 1.5–2.0 mol/dm<sup>3</sup> it is reached rapid, within 45–60 min, 80–90% of leaching, and the almost complete leaching of tungsten (95.2–99.3%) achieved in 2 h. For interaction of WO<sub>3</sub> with Na<sub>2</sub>CO<sub>3</sub> solution it was obtained the kinetic mode. In this case there is practically no concentration gradient of sodium carbonate at an oxide surface. It is obvious, that increase of the hydrolysis takes place due to the fact that to oxides reaction with a reagent-solvent precedes hydration of their surface. In the adsorbed water molecules due to their interaction with the oxide surface intramolecular bonds are weakened, thereby hydrolysis of oxide ions coming to the hydrated surface flows more fully.

## 1. Introduction

According to remark of representative from analyst firm Metal China at Forum on the Problems of Tungsten, Molybdenum and Vanadium Industry held in China, annual global consumption of tungsten increased on average by 10% [1]. Data obtained in research conducted by Vital Metals suggest that global production should increase from the current 81.2 million kg 10<sup>3</sup> up to 109.328 in three years [2]. Existing at present production is limited and unable to meet the growing demand. In this regard, research and development of technology for production of tungsten taking into account the specific features of the deposit is an urgent problem. The widespread in factories of United States, Japan, Britain, Germany, Austria, Russia and other countries method for processing of tungsten concentrates is autoclave-carbonate process [3–8]. Autoclave soda decomposition of tungsten material in comparison with the method of sintering has several advantages, which consist in the elimination of furnace heating process foregoing to leaching and smaller impurity content (especially phosphorus and arsenic) in the tungstate solutions. Tungsten recovery into final product is 90–94%.

Furthermore, the method is applicable not only for development of standard concentrates but also for low grade industrial by-products and slimes containing 4–5% of WO<sub>3</sub> [9–10].

Purpose of this work is investigation and correction of the kinetic characteristics of the autoclave-carbonate decomposition of scheelite produced from North Katpar ore.

## 2. Experimental

Initial concentrate previously was crushed in a planetary mill «Activator 4M». Weighed sample of concentrate – 0.2 kg was previously washed off by water from fine fraction on the sieve with a mesh size of 18 mesh, through which the concentrate particles not larger than 0.853 mm were passed. Washed fraction and sands were dried at 378 K and weighed. Dried sands were size grading into five classes and each of them was weighed and analyzed for main components content. The research results are presented in Table 1, which data show that medium classes (0.152 ÷ 0.066 mm) yield is ~ 30% and the content of the tungsten trioxide therein is 55%, the rest of components are distributed fairly evenly over

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all size classes. Materials' particles with grain size  $0.152 \div 0.066$  mm were used to study the kinetics.

Leaching was conducted in a laboratory autoclave installation which sketch is shown in Fig. 1. The temperature was regulated by a potentiometer KSP – 4 with an accuracy of  $\pm 1$  K. The mixing was carried out with a mechanical stirrer with magnetic drive at speeds of 100–400 r/min. Research was conducted in the temperature range of 368–523 K. In all experiments sample weight was 0.02 kg, volume of sodium carbonate was 100 ml. Using Concentrations of sodium carbonate solutions varied in range, mol/dm<sup>3</sup>: 0.5, 0.75, 1.0, 1.25, 1.5, 2.0.

### 3. Results and Discussion

To determine dependence of the degree of tungsten leaching from scheelite by sodium carbonate on the temperature 1.5 mol/dm<sup>3</sup> sodium carbonate solution was used. Duration of leaching was 90 min. The obtained results show (Fig. 2) that at low temperatures, the reaction proceeds very slowly and in the beginning is determined by chemical act:

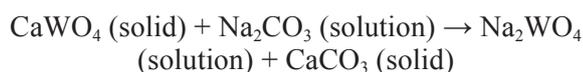


Figure 2 is required in order to show the common pattern that is characteristic for this dependence. The kinetics of heterogeneous reactions of this type comprises a number of successive stages: transfer of the reagent from volume of solution to a solid phase surface through the boundary fluid layer; the diffusion of the reagent through layer of the solid reaction product (layer of CaCO<sub>3</sub> on scheelite particles) chemical reaction on the surface of scheelite;

chemical reaction on scheelite surface; transfer of the reaction product (Na<sub>2</sub>WO<sub>4</sub>) into volume of solution. Research of the kinetics of scheelite interaction with soda solutions in the range of 423–473 K showed that CaCO<sub>3</sub> films are porous and up to a thickness of 110 microns does not affect the speed of the process. The porosity of the film is explained by the fact that the molar volume of CaCO<sub>3</sub> is lesser than the molar volume of CaWO<sub>4</sub> (molar ratio of volumes is 0.75). With intensive stirring, 350–400 rev/min, the reaction flows in the kinetic zone.

With temperature increasing the rate of chemical reactions increases and becomes greater than the diffusion rate, i.e. determining stage is diffusion. Reactions mechanism changing from chemical to diffusion with temperature increase is induced by precipitation of calcium carbonate on the surface of scheelite and hydroxide – ions produced at hydrolysis of carbonate – ions.

Determination of dependence of scheelite leaching rate on the concentration of sodium carbonate was conducted at T = 368 K, leaching duration 15–120 min and concentration of sodium carbonate, mol/dm<sup>3</sup>: 0.5, 0.75, 1.0, 1.25, 1.5; and 2.0. Analysis of the kinetic curves shown (Fig. 3) that at concentration of sodium carbonate: 0.5, 0.75, 1.0, 1.25 mol/dm<sup>3</sup>, leaching process flows insufficiently fully. Within 120 min at low concentrations of sodium carbonate (0.5–1.25 mol/dm<sup>3</sup>) and at T = 368 K about 70–90% of tungsten, leached under these conditions, has reacted. With rise of concentration of sodium carbonate leaching degree increases and at its concentration 1.5–2.0 mol/dm<sup>3</sup> it is reached rapid, within 45–60 min, 80–90% leaching, and the almost complete leaching of tungsten (95.2–99.3%) achieved in 2 h.

**Table 1**

Fractional composition, determined by sieving method on the sieves with various perforation and the results of chemical analyzes of scheelite concentrate

#	Grain-size class, mm	Mesh size, mesh	Class yield, %	Content of components, %					
				WO <sub>3</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	P	As
1	Initial concentrate $\leq 0.853$	18	100.0	48.7	4.2	27.0	1.3	0.53	0.29
2	$< 0.853 \div 0.152$	100	2.27	49.1	7.1	20.28	1.26	0.20	0.15
3	$3 < 0.152 \div 0.104$	150	6.11	55.0	5.3	22.5	1.51	0.61	0.21
4	$< 0.104 \div 0.076$	200	14.1	55.0	4.8	22.1	1.32	0.70	0.25
5	$< 0.076 \div 0.066$	240	7.24	54.5	4.0	25.6	0.96	0.56	0.30
6	$< 0.066 \div 0.044$	350	11.2	54.2	3.8	30.4	1.1	0.60	0.25
7	Fine dispersed fraction $< 0.044$	-	58.42	47.0	4.15	27.88	1.9	0.49	0.34
8	Losses	-	0.66	-	-	-	-	-	-
9	Total (calculation)	-	100.0	48.9	4.3	26.5	1.26	0.52	0.3

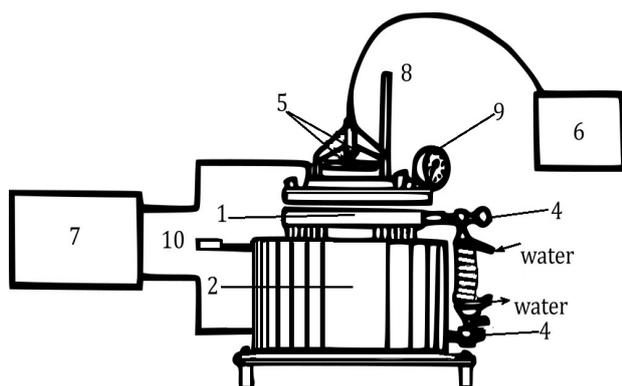


Fig. 1. Laboratory autoclave installation: 1 – reactor; 2 – heater; 3 – cooled sampling instrument; 4 – valves; 5 – magnetic system and mechanical stirrer with flexible shaft; 6 – actuator to mechanical stirrer; 7 – heating control block with a potentiometer KSP-4; 8 – thermometer; 9 – manometer; 10 – safety valve.

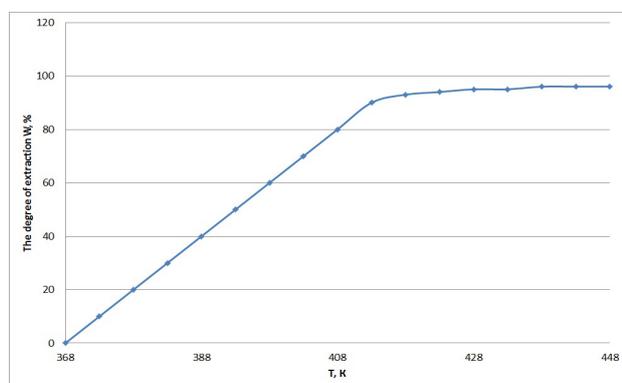


Fig. 2. Dependence of scheelite leaching degree on process temperature.

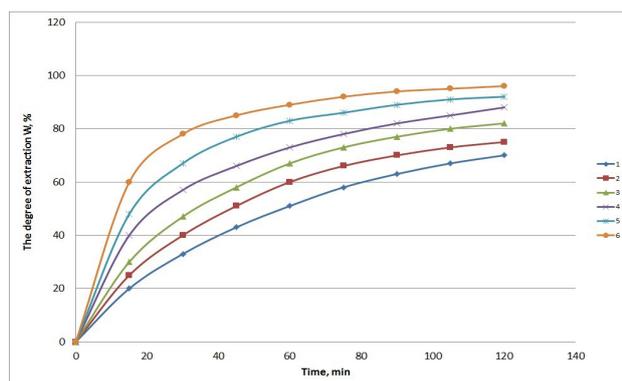


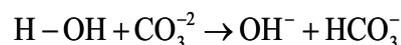
Fig. 3. The kinetic curves of scheelite interaction with solutions of sodium carbonate. Concentration of sodium carbonate, mol/dm<sup>3</sup>: 1 – 0.5; 2 – 0.75; 3 – 1.0; 4 – 1.25; 5 – 1.5 and 6 – 2.0.

Figure 3 shows that starting from 0.75 mol/dm<sup>3</sup> concentration of sodium carbonate and above under the chosen conditions there are fractures on the curves and at that second part of the curves are more

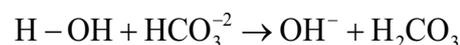
flat. Characteristically that the inflection points correspond to beginning precipitation of calcium carbonate formed at scheelite leaching by sodium carbonate solution. Time to reach tungsten 50% extracting into solution depending on the concentration of sodium carbonate is 45 min for 0.5 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 40 min for 0.75 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 35 min for 1.0 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 28 min for 1.25 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>; 20 min for 1.5 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub> and 15 min for 2.0 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>.

The scheelite dissolution in sodium carbonate solutions is a complicated oxidation-reduction process, which mechanism is determined by concentration of sodium carbonate, temperature and duration of the dissolution process. Changing these factors contributes to flowing of secondary reactions: precipitation of calcium carbonate as well as to formation on the WO<sub>3</sub> surface of high concentrations of sodium carbonate in a solution of the intermediate gelled product.

To explain this phenomenon, when the scheelite dissolution takes place in the mixed mode near to diffusion, one of the reasons for the increase of sodium carbonate hydrolysis may be Na<sub>2</sub>CO<sub>3</sub> concentration decrease in the diffusion boundary layer. However, for interaction WO<sub>3</sub> with a solution of Na<sub>2</sub>CO<sub>3</sub> were found kinetic mode. In this case, there is practically no the concentration gradient of sodium carbonate on the surface of oxide, therefore, increased hydrolysis along with indicated can have other causes, which, in our view is the following. It is known that surface hydration precedes oxides reaction with a reagent-solvent. In the adsorbed water molecules due to their interaction with the oxide surface takes place a weakening of intramolecular bonds, so the hydrolysis of coming to the hydrated surface CO<sub>3</sub><sup>2-</sup> oxide ion proceeds more fully.



HCO<sub>3</sub><sup>2-</sup> – ion reacts by same way:



Subsequent reaction of released at the described interaction OH<sup>-</sup> ions with oxide proceeds without additional difficulties because they are already in the adsorbed state. Thus there are at least two reasons for the increasing of hydrolysis of sodium carbonate at scheelite dissolution. They are reducing the concentration of carbonate-ions because of slow diffusion and reduction of the stability of water molecules during their sorption on the surface of scheelite. From it follows that the dissolution of

scheelite by solutions of sodium carbonate at a temperature of 298–323 K proceeds in the diffusion-kinetic area, and at 323–368 K in the diffusion.

## Conclusions

As result of research of the kinetics of autoclave-carbonate decomposition of scheelite concentrate obtained from ore of North Katpar deposit, it was found that the reaction of scheelite dissolution in sodium carbonate solutions is a complicated oxidation-reduction process, the mechanism of which is determined by the concentration of sodium carbonate, the temperature and duration of the dissolution process. Changing these factors contributes to the occurrence of secondary reactions: calcium carbonate precipitation as well as the formation on the  $WO_3$  surface of high concentrations of sodium carbonate in a solution of the intermediate solid gelled product.

With increase of concentration of sodium carbonate leaching degree increases and at the concentration of 1.5–2.0 mol/dm<sup>3</sup> it is reached rapid, within 45–60 min, 80–90% of leaching, and the almost complete leaching of tungsten (95.2–99.3%) achieved in 2 h. In the case when scheelite dissolution proceeds in a mixed mode close to diffusion, one of the reasons for the increase of sodium carbonate hydrolysis may be decrease of  $Na_2CO_3$  concentration in the diffusion boundary layer. For interaction of  $WO_3$  with  $Na_2CO_3$  solution was found kinetic regime. In this case, almost no concentration gradient of sodium carbonate on the surface of the oxide. Obviously, increase of the hydrolysis takes place due to the fact that to oxides reaction with a reagent-solvent precedes hydration of their surface.

In the adsorbed water molecules due to their interaction with the oxide surface intramolecular bonds are weakened, thereby hydrolysis of oxide ions coming to the hydrated surface flows more fully.

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