

Prediction of efficiency of preliminary mechanical activation of scheelite concentrate by X-ray analysis

UDC 669.273+66.061.34

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This work demonstrates the possibility of forecasting of efficient mechanical activation conditions for scheelite concentrate from X-ray diffraction (XRD) data with the aim of accelerating subsequent soda leaching. There is presented the XRD data for unmilled and milled low-grade scheelite concentrate. From the XRD data, there were evaluated the contributions of ΔE_d , ΔE_s , and ΔE_e to ΔE_Σ (where ΔE_Σ is the energy stored during mechanical activation (MA), ΔE_d is the energy spent for changing of interplanar spacings in the crystal lattice, ΔE_s is the energy stored in the form of freshly formed crystallite surfaces, and ΔE_e is the energy stored in the form of micro-strain). This approach is unique because it offers the possibility of evaluating of energy stored in the system and, accordingly, predicting the reactivity of materials from XRD data, without chemical or physical characterization, which typically leads to disintegration of the sample and requires significant amounts of activated material. The activation energy change is shown to depend on the type of energy stored during MA. Process tests confirmed the foregoing that the degree of extraction depended not on the total stored energy but on the kind of energy. Our results confirm that the energy stored during mechanical activation in the form of surface energy makes an influence on leaching behavior of the concentrate. There was studied the effect of the surface energy stored in the scheelite phase during mechanical activation on the tungsten extraction into solution through low temperature soda leaching. Evaluation of the reactivity of milled scheelite concentrate from XRD data made it possible us to optimize MA conditions and reach tungsten extraction into solution at a level of 99%.

Key words: scheelite concentrate, mechanical activation, soda leaching, X-ray analysis.

A sharp increase of the role of rare and rare-earth metals, which are used in leading fields of industry that provide economic and defense security for any state, has been noted worldwide.

Metallurgical processing costs for the raw materials of rare metals depend on raw materials (50%), energy, materials and reagents consumption. In connection with this and depletion of natural resources, the rare metals technologies processing should provide the resource and power saving, and maximum possible recovery of all valuable components into final products.

Decrease of the process temperature provides power saving. If the same time resource saving is provided by involving low-grade raw materials into processing. However this requires process intensification. Mechanical activation (MA) is one of the most perspective methods for intensification.

Structural changes, accumulated during MA, are more favorable first of all for the processes limited by kinetics of interphase interaction and diffusion in solid phase. Preliminary MA contributes to lowering of energy barrier due to release of energy, stored at mechanical activation [1]. As a result, the mineral reactivity increases considerably.

However, development and use of this mighty process for intensification of chemical and metallurgical processes is limited by the absence of a method for optimization and prediction of materials' properties after MA.

Criteria to estimation of the degree of mechanical influence and efficiency of MA are necessary in order to choose an activator and the effective conditions of MA, applied for different materials.

Use of the method for estimation of the quantity of energy stored by activated materials can not only reduce research volume, but also provide control on the activation degree of already developed processes. The direct method for evaluation of the energy of the mechanically activated system (W – C) by X-ray diffraction (XRD) data [2] was devised in

National University of Science and Technology "MISIS", using the equation (1):

$$\Delta E_\Sigma = \underbrace{KE_{\text{latt}}}_{\Delta E_d} + \underbrace{6E_{\text{surf}}V_{\text{mol}}((1/D_i) - (1/D_0))}_{\Delta E_s} + \underbrace{(3/2)E_Y(\varepsilon_i^2 - \varepsilon_0^2)V_{\text{mol}}}_{\Delta E_e} \quad (1)$$

where: ΔE_Σ – the energy, stored during MA, kJ/mol; K – the coefficient of relative change of the unit cell volume,

$$K = \left| \frac{V_i - V_0}{V_0} \right|;$$

V_0, V_i – the unit cell volumes before and after MA, respectively, (Å)³; E_{latt} – the crystal lattice energy of the initial material, kJ/mol; E_{surf} – the surface energy of the initial material, kJ/mol; D_i and D_0 – sizes of the coherent scattering regions of activated and initial materials, m; V_{mol} – the molar volume of initial material, m³/mol; E_Y – Young's modulus of the initial material, HPa; $\varepsilon_i, \varepsilon_0$ – the mean-square micro-deformations for activated and initial materials; ΔE_d – the energy spent on the changes of the interplanar spaces in the crystal lattice, kJ/mol; ΔE_s – the energy stored in the form of newly generated surface of coherent scattering region (CSR), kJ/mol; ΔE_e – the energy stored in the form of microstrain.

However, applicability of this method for prediction of behavior of the components of simple or complex mechanically activated systems during subsequent hydrometallurgical processing requires experimental verification.

A non-standard scheelite concentrate was used as object for research. Traditional methods for processing of scheelite concentrates, sintering with soda at 800–900 °C and autoclave leaching with soda solutions at 200–225 °C, are used for concentrates of various grades. However they are characterized by high energy consumption. Acid

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Table 1
MA regimes and XRD data for the initial and activated samples of the concentrate

Sample	MA regimes	Lattice parameters	Crystallite size	Microstrain, %	ΔE_d	ΔE_s	ΔE_e	ΔE_Σ	$\Delta E_{d, \text{exper}}$	$\Delta E_{d, \text{calc}}$
		Å			kJ/mol					
0	Initial	$a = 5.224$ $c = 11.361$	806 ± 5	0.007 ± 0.005	–	–	–	–	–	–
1	$M_k:M_b = 10:200$; $Z_b = 0.15$; $\tau_a = 0.5$ min	$a = 5.239$ $c = 11.361$	643 ± 4	0.033 ± 0.006	168.22	1.63	0.03	169.88	14.16	18.07
2	$M_k:M_b = 10:200$; $Z_b = 0.15$; $\tau_a = 2.5$ min	$a = 5.224$ $c = 11.306$	174 ± 2	0.183 ± 0.015	141.62	23.41	0.68	165.71	27.30	20.89
3	$M_k:M_b = 10:800$; $Z_b = 0.60$; $\tau_a = 0.5$ min	$a = 5.228$ $c = 11.327$	366 ± 3	0.204 ± 0.005	42.93	7.75	0.83	51.51	27.46	25.58
4	$M_k:M_b = 10:800$; $Z_b = 0.60$; $\tau_a = 2.5$ min	$a = 5.324$ $c = 11.338$	144 ± 1	0.321 ± 0.016	52.65	29.63	2.05	84.33	32.58	37.16
5	$M_k:M_b = 40:200$; $Z_b = 0.15$; $\tau_a = 0.5$ min	$a = 5.239$ $c = 11.361$	683 ± 4	0 ± 0.006	168.22	1.16	0	169.38	14.29	18.01
6	$M_k:M_b = 40:200$; $Z_b = 0.15$; $\tau_a = 2.5$ min	$a = 5.239$ $c = 11.359$	409 ± 3	0.109 ± 0.005	163.03	6.26	0.24	169.53	27.30	19.22
7	$M_k:M_b = 40:800$; $Z_b = 0.60$; $\tau_a = 0.5$ min	$a = 5.245$ $c = 11.374$	590 ± 4	0.044 ± 0.005	269.36	2.38	0.04	271.78	7.60	8.33
8	$M_k:M_b = 40:800$; $Z_b = 0.60$; $\tau_a = 2.5$ min	$a = 5.243$ $c = 11.367$	362 ± 3	0.150 ± 0.005	228.70	7.95	0.45	237.10	13.37	11.98
9	$M_k:M_b = 10:800$; $Z_b = 0.60$; $\tau_a = 2.0$ min	$a = 5.235$ $c = 11.338$	156.7 ± 1.2	0.340 ± 0.012	63.78	26.71	2.30	92.79	39.15	35.65

The scheelite concentrate has $E_{\text{latt}} = 29,251.95$ kJ/mol (valuated by the Fersman method), $E_{\text{surf}} = 1.74$ J/m², $E_y = 266.82$ GPa [5], $V_{\text{mol}} = 49.66$ cm³/mol.

leaching allows to decrease processing temperature down to 100 °C. The acidic methods for scheelite processing differ from the alkaline methods in that they have fewer stages in flowsheet. Nevertheless, tungsten acid, produced by those methods for low-grade scheelite concentrates (<55% WO₃), requires 2–3 ammonium cleaning stages, which is not economic. Therefore acid leaching is often applied for high-grade and pure scheelite concentrates.

It should be noted that increase in reactivity of mechanically activated standard scheelite concentrate in autoclave leaching with soda solutions ($\tau_{\text{MA}} > 9$ min) was demonstrated in the references [3]. However, information about effective low temperature leaching of scheelite concentrates with soda solutions is not available. In connection with this, an improvement of the low temperature pressurized leaching with soda solutions is of current importance.

The aim of this work is to find the interrelation between quantity of the energy stored by scheelite phase during MA, reactivity of scheelite and XRD data of the activated material.

Experimental part, calculation techniques and discussion of results

The scheelite concentrate with particle size of predominantly 90% less than (–0.071) mm and a chemical composition (35.6% W; 22.3% Ca; 1.23% Si; 1.19% P; 0.46% S; 0.16% Cu¹) was subjected to mechanical activation.

MA was carried out in dry regime in a centrifugal planetary mill LAIR-0.015 with an acceleration of 25 g, using steel grinding balls with a diameter of 5–8 mm.

The structural parameters of the scheelite phase of activated concentrate were examined by XRD on diffractom-

eter system DRON-4 using XRD data analysis software and ASTM data [4].

MA regimes for scheelite concentrate, XRD data for the initial and activated samples of the concentrate and calculation results of the quantity of energy stored during MA (ΔE_Σ) are presented in Table 1.

In the Table 1 it can be seen that samples 7 and 8 have the maximum energy (ΔE_Σ) and only sample 4 has the maximum value of ΔE_s . Based on previous researches on tungstate concentrate [6] it can be proposed that sample 4 will have the maximum reactivity.

In order to verify the prediction and establish the interrelation between calculated and experimental values of quantity of the energy, stored during MA, kinetic and technological investigations were conducted.

Kinetic investigations for leaching of initial and activated samples of scheelite concentrate were carried out in accordance to technique [7]. Based on experimental data, kinetic dependences of the degree of leaching (α) on time (τ) were constructed and dependences of $\ln(d\alpha/d\tau)$ on $(1/T_i) \cdot 10^{-3}$ were calculated from initial portions of the kinetic curves (Fig. 1). The quantities of energy stored by scheelite were determined from the change in activation energy of initial and activated samples ($\Delta E_a = E_a^0 - E_a^*$) (Table 1).

On the basis of calculation results on equation (1) and kinetic investigations, semi-empirical dependence (2) and response surface of change in activation energy of soda leaching process of scheelite ΔE_a on structural changes observed by XRD in mineral after mechanical activation in dry regime (ΔE_d and $(\Delta E_s + \Delta E_e)$) were obtained (Fig. 2):

$$\Delta E_a = \Delta E_\Sigma / (1.1877 \exp(0.0123 \Delta E_d)) \quad (2)$$

¹ Chemical analysis was carried out in spectrometer SPECTRO CYROS VISION.

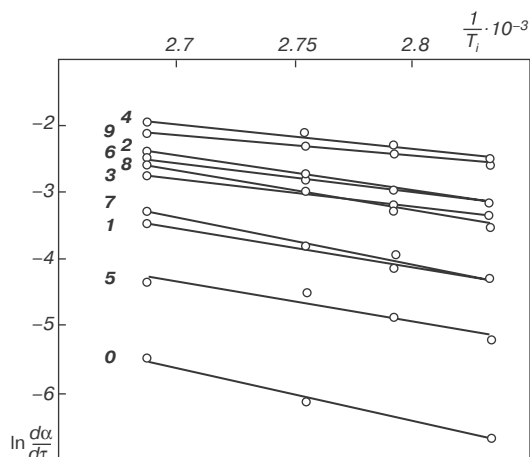


Fig. 1. Relationship between $\ln da/dt$ and $(1/T_i) \cdot 10^{-3}$ for the scheelite phase in initial and activated samples of the concentrate (samples 1–9)

Dependence of ΔE_a of soda leaching process before and after MA on energy of structural changes has a character of graphs with extremal points. The area in which ΔE_a has maximum values corresponds to the area, where values of ΔE_d are equal to 30–100 kJ/mol and $(\Delta E_s + \Delta E_e)$ is more than 16.7 kJ/mol (Fig. 2).

In this way XRD data of initial and activated scheelite allows to control the energy state of activated material.

However, the results of technological investigations (Table 2) have shown that the sum of energies $(\Delta E_s + \Delta E_e)$ has a greater influence on the reactivity of scheelite after MA in following low-temperature leaching by soda solutions. Corresponding dependences are shown at Fig. 3. It indicates that

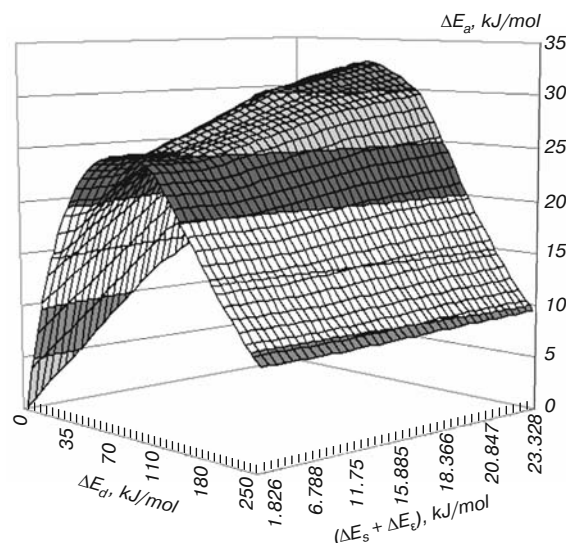


Fig. 2. Relationship between 3D response surface for ΔE_a of soda leaching process and structural changes in scheelite by XRD data (ΔE_d and $(\Delta E_s + \Delta E_e)$) after MA in dry regime

diffusion had more effect on process of low-temperature soda leaching of scheelite concentrate.

It's found that tungsten extraction in solutions acceptable for industry can be obtained at low-temperature leaching (with ratio S:L = 1:12; $[\text{Na}_2\text{CO}_3] = 250 \text{ g/l}$; $t = 90^\circ\text{C}$; $\tau = 6 \text{ h}$) of scheelite concentrate which is activated for 2 min [8].

Thus, possibility to predict the change in activation energy of leaching and the reactivity of scheelite concentrate by XRD data was shown, it doesn't use any chemical or physical methods, which lead to sample disintegration and require a significant amount of the activated material. Moreover, the effective processing of non-standard scheelite concentrate at 100°C allows to decrease the power consumption of process by 2–3 times and set up the processing of materials directly at ore mining and processing enterprises. This decreases transports expenditures in costs of tungsten products.

Table 2 Leaching results for the scheelite concentrate						
Sample	Leaching conditions				Tungsten extraction into solution, wt %	
	S:L	$t, ^\circ\text{C}$	τ, h	$[\text{Na}_2\text{CO}_3], \text{g/l}$		
Initial	1:6	99	3	200	18.11	
	1:12	99	6	250	46.19	
	1:10	99	6	250	35.95	
1	1:6	99	3	200	30.55	
	1:12	99	6	250	54.48	
	1:10	99	6	250	49.21	
2	1:6	99	3	200	47.83	
	1:12	99	6	250	83.13	
	1:10	99	6	250	83.73	
3	1:6	99	3	200	39.32	
	1:12	99	6	250	77.18	
	1:10	99	6	250	75.79	
4	1:6	99	3	200	58.98	
	1:12	99	6	250	92.03	
	1:10	99	6	250	86.73	
5	1:6	99	3	200	25.58	
	1:12	99	6	250	60.97	
	1:10	99	6	250	55.37	
6	1:12	99	6	250	85.22	
	1:10	99	6	250	70.13	
	1:6	99	3	200	34.48	
7	1:12	99	6	250	67.27	
	1:10	99	6	250	58.77	
	1:6	99	3	200	37.26	
8	1:12	99	6	250	80.75	
	1:10	99	6	250	99.18	
	1:6	99	3	200	37.26	
9	1:12	99	6	250	80.75	
	1:10	99	6	250	99.18	
	1:6	99	3	200	37.26	

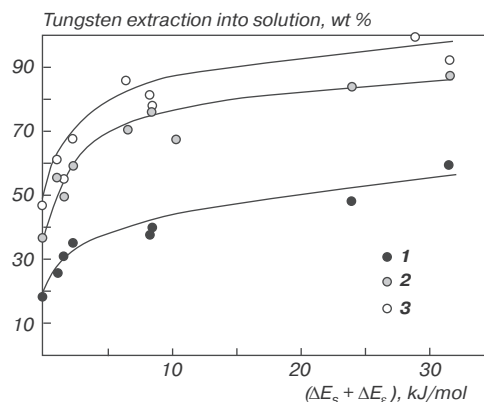


Fig. 3. Relationship between tungsten extraction into solution and $(\Delta E_s + \Delta E_e)$: 1 – S:L = 1:6, $[\text{Na}_2\text{CO}_3] = 200 \text{ g/l}$, $\tau = 3 \text{ h}$; 2 – S:L = 1:10, $[\text{Na}_2\text{CO}_3] = 250 \text{ g/l}$, $\tau = 6 \text{ h}$; 3 – S:L = 1:12, $[\text{Na}_2\text{CO}_3] = 250 \text{ g/l}$, $\tau = 6 \text{ h}$

Displayed results of work point out to possibility of selective extraction of required component without dissolution of all material and allow to devise criteria for estimation of efficiency of MA for rare metal concentrates and to apply MA for improvement of available technologies purposefully.

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NFM

Tsvetnye Metally
2013, No. 1, pp. 55–59

Rhenium and platinum extraction from dead-catalysts of oil processing with the use of electrochemical hydrochlorination

UDC [669.849+669.231]:66.097.3

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The behaviors of platinum, rhenium and dead catalysts KR-108 (TS 2177-019-04610600-99) in hydrochloric solutions have been investigated.

The unique construction of an electrochemical set for the processing of dead reforming catalysts, permitting to produce the chlorinating agent "in situ" (directly in technological process) and extract platinum and rhenium simultaneously, have been developed and introduced into the research process.

Experiments with use of the burnt and not burnt catalysts, and also in addition subjected to crushing have been conducted.

The degree of extraction of valuable components for the burnt and not burnt catalyst are practically equal (platinum – 87.2%, rhenium – 84.1% and platinum – 89.1%, rhenium – 87.5% accordingly), however for processing of the burnt catalysts are necessary more long time of their finding in a reactionary zone on 8-10 hours.

Dependence of degree of extraction on time of process of electrochemical hydrochlorination has been received.

It has been established, that crushing of the catalyst till the size of particles of an order of 0.1 mm allows to raise extraction degree: platinum – 98.2%, rhenium – 91.4%.

Solubility of a basis of the crushed catalyst at electrochemical hydrochlorination has been investigated.

It has been shown, that use of the cathode with the developed surface on the basis of graphite materials allows reaching residual concentration of platinum and rhenium to concentration in some milligramme and less. The technological scheme of processing of the dead reforming catalyst via electrochemical hydrochlorination, by which metal concentrate containing rhenium and platinum is formed, has been suggested.

Key words: catalysts, platinum, rhenium, processing, electrochemical hydrochlorination, electrochemical allocation.

Recently rhenium recycling issue is quite actual. This is related to many factors but mostly to the rise of metal prices because of recently occurred demand-supply disbalance on rhenium market. Special interest of Russian Federation in this problem is connected with the lost of the basic industrial facilities and raw rhenium materials at the end of XX century. These facilities and materials have been remained in union republics (Kazakhstan, Armenia, Uzbekistan) after USSR disintegration. This led to the almost total dependence of domestic

machine engineering on the rhenium import. A significant amount of rhenium and its compounds is utilized in catalyst production (14% of rhenium application), which have high activity and selectivity in various organic and hetero-organic synthesis reactions [1–5]. Therefore dead catalysts represent a promising rhenium resource.

The results of the investigation of platinum, rhenium and dead catalyst CP-108 (Standard 2177-019-04610600–99) behavior in hydrochloric-acid solutions are given within this paper. The central technological

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