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RESEARCH OF KINETICS OF ZINC LEACHING WITH SULFURIC ACID FROM SMITHSONITE

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The study investigates the kinetics of zinc leaching from smithsonite with sulfuric acid in order to expand the zinc production feedstocks. The recovery rate of zinc from smithsonite into water-soluble zinc sulfate was found at different leaching time and temperature. Sulfuric acid concentration, its consumption and smithsonite particles size selected in this work for leaching of zinc from this mineral using the indicated solution allowed to determine the magnitude of "apparent" activation energy of the smithsonite reaction with the indicated acid, equal to 2,633 kJ / mol. The calculated value of E, shows that the process investigated is accompanied by diffusion phenomena.

Keywords: zinc sulfate, smithsonite, sulfuric acid, leaching, activation energy

INTRODUCTION

The continuously growing world consumption of zinc is about 13 million tons per year [1].

Zinc consumption is constrained by the high cost of this metal, which currently stands at USD 2 745 per ton [2]. Therefore, the urgent task is to reduce costs in hydrometallurgical zinc production. Another factor constraining the consumption of zinc is the limited mineral resource base with practically the only mineral - sphalerite (ZnS) [3,4]. A decrease in sphalerite reserves and a continuously growing demand for zinc require the involvement of new minerals of this metal in zinc hydrometallurgy.

An important source of mineral raw materials for zinc production is smithsonite ($ZnCO_3$) [3,4]. An example of a smithsonite deposit is Shaimerden deposit located in the north of Kazakhstan [5-7], where ore is mined by the open-cut mining.

The attractiveness of smithsonite for zinc production lies in the fact that, unlike sphalerite, smithsonite does not require its expensive oxidative roasting prior to sulfuric acid leaching of zinc from it [6]. But, zinc-rich smithsonite ore of Shaimerden deposit is not used today for sulphate leaching of zinc. This ore is currently used in the expensive Waelz process [7-9] in the classical processing of sphalerite using sulfuric acid technology, which is largely due to the lack of knowledge of the kinetics of sulfuric acid leaching of zinc from smithsonite.

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The lack of studies on the kinetics of sulfuric acid leaching of zinc from smithsonite is evidenced by the lack of publications on this problem. Only the kinetics of hydrochloric acid leaching of zinc from smithsonite has been studied [10].

So in work [10] the value of the «apparent» activation energy of the chemical reaction of smithsonite with hydrochloric acid at a temperature of 25÷45 °C was determined, equal to 59,58 kJ / mol. This value of the activation energy of the reaction suggests that the specified chemical reaction proceeds in the kinetic region.

The results of work [10] ensure the extraction of zinc into a hydrochloric acid solution of 95 % with the following parameters of the process of leaching zinc from smithsonite: size of smithsonite particles –0,18 + 0,15 mm, leaching duration 30 min, concentration of hydrochloric acid in the solution for leaching 1,5 M, solid:liquid ratio is 25 g / dm^3, the stirring frequency of the pulp leaching with a stirrer is 500 rpm.

The given model of hydrochloric acid leaching of zinc from smithsonite [10] cannot be used in operating hydrometallurgical zinc plants, since these industries use sulfuric acid leaching of zinc from mineral raw materials.

The lack of published data on the kinetics of the reaction of smithsonite with sulfuric acid does not allow scientifically sound recommendation of this mineral for its sulfuric acid leaching in zinc production. The work below aims to fill this gap.

EXPERIMENTAL PART AND RESULTS

To understand the process of reaction of smithsonite with sulfuric acid, the following reaction equation can be used:

$$ZnCO_3 + H_2SO_4 = ZnSO_4 + CO_2\uparrow + H_2O$$

In carrying out the studies below, the ore of the indicated deposit with a size of –20 mm was used, in which smithsonite was contained in the form of crystals several millimeters in size. Smithsonite crystals extracted from the ore were ground in a ball mill to a size of –1 mm and then analyzed for zinc content by a spectral method on ICP-MS 7500cx inductively coupled plasma mass spectrometer "Agilent Technologies", USA. The results of the analysis of smithsonite showed that it contained 52,11 % of zinc by mass. Then, weighed portions of crushed smithsonite, weighing 25 g, were lowered into a glass beaker with a volume of 0,5 dm^3, into which a solution of sulfuric acid with a concentration of 150 g / dm^3 in an amount of 0,1 dm^3 was poured. The glass with the obtained pulp was placed on an electric stove and the pulp was stirred for 20 min with a magnetic stirrer at different temperatures (in these experiments, the rotation speed of the mixer was 220 rpm, the pulp temperature was determined with an alcohol thermometer, the measurement error of which was ± 1,0 °C). After leaching zinc from smithsonite, the pulp was filtered through a red ribbon filter on a funnel with a diameter of 13 cm. The filtered insoluble residue (cake) was dried in an oven at 105 °C to a constant weight, and then analyzed for zinc content on the mentioned mass spectrometer.

The experimental results (Table 1) showed that the maximum extraction of zinc from smithsonite is achieved in 20 min of leaching it at 80 ºC and is more than 73,5 % (experiment 1).

Table 1 **The relationship of zinc extraction into solution with the selective dissolution temperature of smithsonite (leaching duration - 20 min)**

№ experi-ment	Tempera-ture/ °C	Cake (dry)		Zn extraction into solution/ %
		mass/ g	Zn content/ mass. %	
1	80	6,65	51,87	73,52
2	60	7,08	51,89	71,80
3	40	7,66	51,99	69,43
4	20	8,06	52,04	67,80

Reextraction of zinc from cakes (Table 1) is possible via Waelz process, which is used in the classical sulfuric acid processing of sphalerite. However, in order to exclude the expensive Waelz process from the processing of smithsonite, it was of interest to study whether the rate of zinc leaching from smithsonite is limited by the rate of the chemical reaction (1) or the rate of diffusion of sulfuric acid molecules to the reaction surface through the layer of the products of this reaction, or both.

For this purpose, at the next stage of the work, the kinetic relationships were investigated and the value of the "apparent" activation energy of the reaction of smithsonite with sulfuric acid was calculated using the procedure described in [11]. This technique was previously used by us in the study of the kinetics of sulfuric acid leaching of zinc from calamine [12].

At the beginning of this work, guided by the Woldman-Zelikman method [11], zinc recovery rate from

Table 2 **Relationship of zinc extraction into solution with the duration and temperature of leaching of smithsonite**

№ experi-ment	τ/ min	Cake (dry)		Zn extraction into solution/ %
		mass/ g	Zn content/ mass. %	
Extraction temperature 80 °C				
1	5	14,99	52,08	40,07
2	10	11,25	52,06	55,04
3	15	8,34	51,94	66,75
4	20	6,65	51,87	73,52
Extraction temperature 60 °C				
5	5	15,27	52,10	38,93
6	10	11,65	52,08	53,43
7	15	8,97	52,02	64,18
8	20	7,08	51,89	71,80
Extraction temperature 40 °C				
9	5	15,55	52,09	37,82
10	10	12,04	52,08	51,86
11	15	9,59	52,03	61,70
12	20	7,66	51,99	69,43
Extraction temperature 20 °C				
13	5	15,80	52,08	36,83
14	10	12,39	52,08	50,47
15	15	10,06	52,05	59,81
16	20	8,06	52,04	67,80

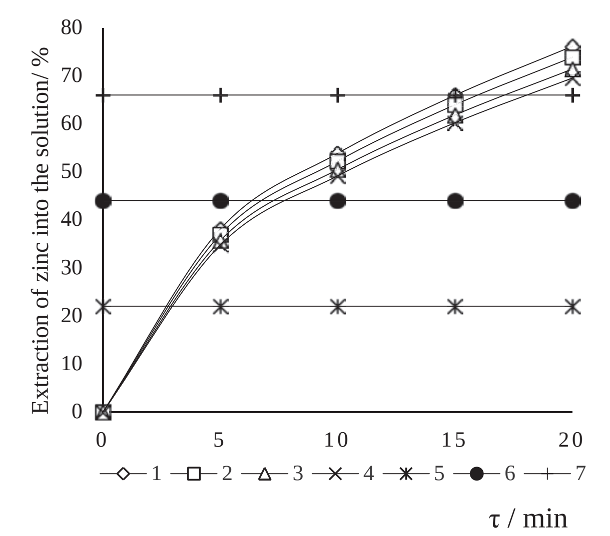
smithsonite into water-soluble zinc sulfate was determined at different leaching times (τ) and different leaching temperatures (T). The results are shown in Table 2 and graphically shown in Figure 1 using an Excel spreadsheet processor.

Then, using the abovementioned method [11], using the four obtained experimental curves (Figure 1), the leaching durations were determined, providing the same zinc recovery into solution (22, 44 and 66 %) at different leaching temperatures. For this, through 4 experimental curves, 3 auxiliary straight lines equidistant by 22 % were drawn, intersecting the indicated curves (Figure 1). The values obtained in the course of this work and the results of their processing using an Excel spreadsheet processor are presented in Table 3 and further are used to estimate the "apparent" activation energy of the interaction of smithsonite with sulfuric acid.

For this, guided by the Woldman-Zelikman method [11], the dependences of the logarithm of the time required to achieve the same degree of zinc extraction into solution at different temperatures of its leaching on the inverse temperature were determined (Figure 2).

DISCUSSIONS

The slope coefficients [d(lgτ)/d(1/T)] of the functional lines logτ = f (1/T) (Figure 2) are related to the value of the «apparent» activation energy by the equation $d(\log\tau)/d(1/T) = E_{app}/ (2,3R)$ [11], where R = 8,31 kJ / mol is the universal gas constant. When zinc is extracted into a solution of 22, 44 and 66 %, the indicated coefficients, determined using the Excel processor, are, respectively, 137,7407, 137,7407 and 137,7402 (Figure



Lines: 1 – 80 ° C, 2 – 60 °C, 3 – 40 °C,
4 – 20 °C, 5, 6 и 7 – auxiliary lines, corresponding to Zn extraction into solution 22, 44 and 66 %

Figure 1 Relationship of zinc extraction from smithsonite with the duration and temperature of its leaching

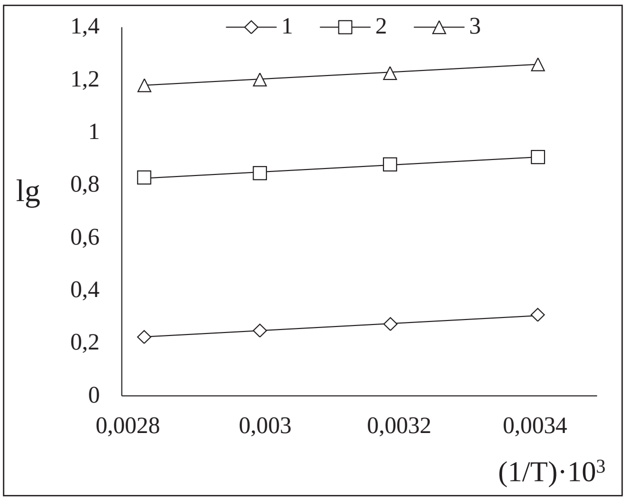


Figure 2 Relationship of the logarithm of the leaching duration with its reverse temperature at zinc extraction of 22 % (line 1: lg τ = 137,7407/T – 0,1656), 44 % (line 2: lg τ = 137,7407/T + 0,436463) и 66 % (line 3: lg τ = 137,7402/T + 0,788647)

Table 3 **Duration of leaching of smithsonite (τ), providing a given extraction of zinc into solution at different temperatures of leaching (T)**

№ experiment	T		1/T/ K^{-1}	τ/ min	lg τ
	/ °C	/ K			
Extraction into solution 66 %					
1	80	353	0,002833	15,02508	1,176817
2	60	333	0,003003	15,96234	1,203097
3	40	313	0,003195	17,08607	1,232642
4	20	293	0,003413	18,03317	1,256072
Extraction into solution 44 %					
5	80	353	0,002833	6,677815	0,824634
6	60	333	0,003003	7,094371	0,850914
7	40	313	0,003195	7,593810	0,880460
8	20	293	0,003413	8,014741	0,903889
Extraction into solution 22 %					
9	80	353	0,002833	1,669454	0,222574
10	60	333	0,003003	1,773593	0,248854
11	40	313	0,003195	1,898452	0,2784
12	20	293	0,003413	2,003685	0,301829

caption on Figure 2); The “apparent” activation energy was determined from the mean slope values equal to 137,7405.

Thus, the value of the “apparent” activation energy of the reaction of smithsonite with sulfuric acid, calculated from the expression $d(\log\tau)/d(1/T) = E_{app}/(2,3R)$ [11], was 2,633 kJ / mol, which indicates on the diffusion nature of the specified interaction and requires renewal of the reaction surface of Smithsonite in the process of leaching zinc from it.

CONCLUSION

Investigation of the effect of the leaching temperature of smithsonite on zinc recovery rate showed that zinc extraction naturally increases with increasing leaching temperature (Figure 1).

The completeness of zinc extraction from smithsonite also naturally increases with an increase in the duration of leaching of smithsonite (Figure 1).

The determined value of E_{app} (2,633 kJ / mol) indicates that the reaction of smithsonite with sulfuric acid occurs in the diffusion region. It can be assumed that this reaction is limited by the diffusion rate of acid molecules into the reaction surface through a layer of the resulting reaction products - soluble zinc sulfate and carbon dioxide.

Based on the above results of kinetic studies, it seems possible to increase the degree of zinc extraction from smithsonite by renewing the reaction surface of this mineral in the process of leaching zinc from it, i.e., by intensively removing reaction products from the reaction surface. In order to further extract zinc from this mineral into a solution above 73,52 %, in further work it is advisable to check the process of leaching zinc from smithsonite in several stages with sulphate solutions free of zinc sulfate.

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