**R. A. RAMAZANOVA, V. I. SAMOILOV, N. V. SERAYA, G. K. DAUMOVA, E. M. AZBANBAYEV, R. A. AUBAKIROVA**

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# INVESTIGATION OF THE KINETICS OF SULPHURIC ACID LEACHING OF ZINC FROM CALAMINE

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This article aims at the research of kinetics of the sulphuric acid leaching of zinc from calamine (hemimorphite) of Shaimerden deposits. The ratio of zinc extraction from calamine to water-soluble zinc sulphate was determined at various leaching durations and its temperatures. The concentration of the sulfuric acid solution, the flow rate of this solution and the size of the calamine particles, selected in the course of this work for leaching zinc from this mineral with the specified solution, made it possible to establish the value of the "apparent" activation energy of the reaction of calamine with sulfuric acid, amounting to 3,075 kJ / mol.

*Keywords*: zinc, calamine, sulphuric acid, leaching, activation energy

## INTRODUCTION

World usage of zinc is constantly growing, currently amounting to about 14 million tons per year [1].

Zinc usage is constrained by its high cost, which today is estimated at 2 286 USD per ton [2]. Thus, reducing costs in hydrometallurgical zinc production is an urgent task. Another factor constraining zinc usage is the limited mineral resource base of almost the only mineral - sphalerite (ZnS) [3,4]. Reduction of the sphalerite ores deposits and continuous zinc consumption worldwide demands the involvement of new minerals of this metal into zinc hydrometallurgy.

Reduction of the sphalerite ores deposits and continuous zinc consumption worldwide demands the involvement of new minerals of this metal into zinc hydrometallurgy calamine (hemimorphite) – $Zn_4[Si_2O_7](OH)_2 \cdot H_2O$ [5-7]. One of the well-known examples of calamine deposits is the Shaimerden deposit in the northern Kazakhstan [8, 9], where ore is mined by open-pit mining.

The attractiveness of calamine for zinc hydrometallurgy lies in the fact that, unlike sphalerite, calamine does not allow using its expensive oxidative calcination until leaching zinc from sulphuric acid. However, zinc-rich calamine-containing ore of the Schaimerden deposit is not actually used to leach zinc to sulphuric acid from it. Today, the ore is used in the costly Waelz process [10-12] in the classical sphalerite processing with sulphuric acid. This is largely due to insufficient knowledge of the kinetics of sulfuric acid leaching of zinc from calamine, as evidenced by a very limited number of publications on this issue [13, 14].

In [13], the value of the "apparent" activation energy of the chemical reaction of calamine with sulfuric acid, carried out in a laboratory autoclave at a temperature of 100–140 °C, was established, which amounted to 44,9 kJ / mol. This value of the activation energy suggests that the specified chemical reaction takes place in the kinetic region.

The authors of [13], referring to the paper [14], also noted that the interaction of calamine with sulfuric acid at atmospheric pressure (at a leaching temperature of 20 ÷ 80 °C) is characterized by the activation energy of this interaction of 13,4 kJ / mol [14]. This value of the activation energy indicates that at a leaching temperature of 20 ÷ 80 °C, the interaction of calamine with sulfuric acid occurs in the diffusion region.

The lack of data on the kinetics of the interaction of calamine with sulfuric acid that is attractive for zinc hydrometallurgy does not allow scientifically soundly recommending this mineral for its sulfuric acid leaching in zinc production. The work below aims to fill this gap.

## EXPERIMENTAL PART

The basic understanding of calamine interaction with sulphuric acid gives the following equation of reaction:

$$Zn_4[Si_2O_7](OH)_2 \cdot H_2O + 4H_2SO_4 = 4ZnSO_4 + 2SiO_2\downarrow + 6H_2O$$

The studies below used ore from the Schaimerden deposit with a grain size of – 20 mm, in which a few millime-

R. A. Ramazanova (raigul_77_33@mail.ru), N. V. Seraya.
G. K. Daumova, D. Serikbayev East Kazakhstan Technical university, Ust-Kamenogorsk, Kazakhstan
V. I. Samoilov, R.A. Aubakirova, S. Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan
E. M. Azbanbayev, «Kazakhstan Paramount Engineering» LLP, Nur-Sultan, Kazakhstan

tres of crystals represented calamine. Calamine crystals extracted from ore were crushed in a ball mill to a grain size of – 1 mm, and then analysed for zinc content by a spectral method on an inductively coupled plasma mass spectrometer ICP-MS 7500cx by the US company Agilent technologies. According to the report, calamine contained 54,64 wt.% of zinc. Weighed portions of the crushed mineral weighing 25 g were then put in a 0,5 $dm^3$ beaker to which 0,1 $dm^3$ of a 150 g / $dm^3$ concentration sulphuric acid solution was added. A glass containing the obtained pulp was mounted on an electric stove and the pulp was mixed with a magnetic stirrer at various temperatures for 20 minutes (in our experiments the stirrer rotated at 220 rpm, the temperature of the pulp was set with an alcohol thermometer with a measuring error of ± 1.0 ° C). Upon zinc leaching from calamine, the pulp was filtered through a red ribbon filter in a funnel with a diameter of 13 cm. The filtered insoluble residue (cake) was dried in an oven at a temperature of 105 °C to constant weight, which required 20–25 min depending on the cake moisture content. The dry cake was analyzed for zinc content by a spectral method.

The experimental results (Table 1) indicate that the highest zinc extraction from calamine is achieved in 20 minutes of leaching at 80 ºC and is almost 65 % (experiment 1).

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

| № experiment | Temperature / °C | Cake (dry) | | Extraction of Zn into the solution/ % |
|---|---|---|---|---|
| | | weight/g | Zn content/ wt.% | |
| 1 | 80 | 14,9 | 32,13 | 64,95 |
| 2 | 60 | 15,4 | 32,60 | 63,25 |
| 3 | 40 | 16,1 | 33,21 | 60,86 |
| 4 | 20 | 16,6 | 33,53 | 59,25 |

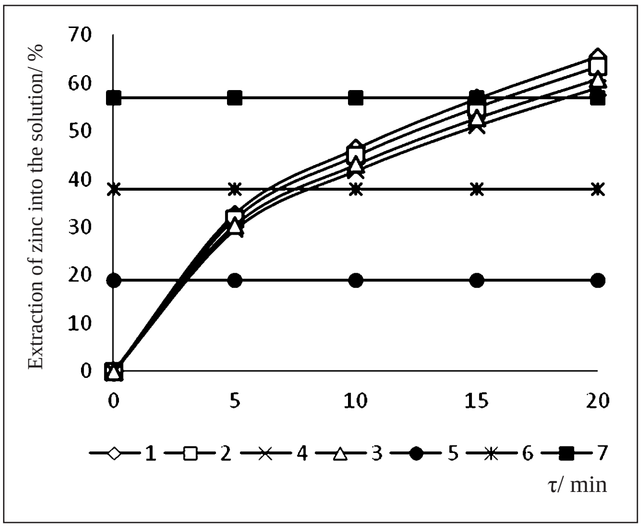


**Figure 1** Extraction of zinc from calamine into the solution at 80 ºC (line 1), 60 ºC (line 2), 40 ºC (line 3), 20 ºC (line 4), lines 5, 6 and 7 correspond to the extraction of zinc into the solution 19, 38 and 57 % respectively

For zinc extraction from cakes (Table 1), their Waelz process, used in the classical sulphuric acid processing of sphalerite, can be recommended.

However, in order to exclude the expensive Waelz stage from the processing of calamine, it was of interest to study what limits the rate of zinc leaching from calamine - the rate of the chemical reaction or the rate of diffusion of sulfuric acid molecules to the reaction surface through the layer of the products of this reaction, or both.

Therefore, at the next stage of research, the kinetic dependences were studied and the value of the «apparent» activation energy of the interaction of calamine with sulfuric acid was determined using the Woldman-Zelikman method described in [15]. This technique was reviously used by us in the study of the process of sulfuric acid extraction of lithium from its silicate minerals. The results of these studies have been repeatedly published by us in international peer-reviewed journals such as [16] and others.

At the beginning of this work, guided by the Woldman-Zelikman method [15], the rate of zinc extraction from calamine to water-soluble zinc sulfate was determined at various temperatures (T) of leaching and its duration (τ). The data obtained are shown in Table 2 and using an Excel spreadsheet processor are graphically presented in Figure 1.

Then, using the method [15] above, using the four obtained experimental curves (Figure 1), the leaching durations were determined, providing the same zinc recovery into solution (19, 38 and 57 %) at different leaching temperatures. For this, through 4 experimental curves, 3 auxiliary straight lines equidistant by 19 %

Table 2 **The relationship of the extraction of zinc into the solution with the duration and temperature of leaching of calamine**

| № experiment | τ/ min | Cake (dry) | | Extraction of Zn into the solution / % |
|---|---|---|---|---|
| | | weight / g | Zn content / wt. % | |
| Lixiviation temperature 80 ° C | | | | |
| 1 | 5 | 17,5 | 53,38 | 31,62 |
| 2 | 10 | 16,4 | 44,57 | 46,49 |
| 3 | 15 | 15,6 | 36,51 | 58,30 |
| 4 | 20 | 14,9 | 32,13 | 64,95 |
| Lixiviation temperature 60 ° C | | | | |
| 5 | 5 | 17,7 | 53,65 | 30,48 |
| 6 | 10 | 16,7 | 45,10 | 44,86 |
| 7 | 15 | 15,8 | 38,26 | 55,75 |
| 8 | 20 | 15,4 | 32,60 | 63,25 |
| Lixiviation temperature 40 ° C | | | | |
| 9 | 5 | 17,8 | 54,20 | 29,37 |
| 10 | 10 | 17,0 | 45,57 | 43,29 |
| 11 | 15 | 16,5 | 38,70 | 53,25 |
| 12 | 20 | 16,1 | 33,21 | 60,86 |
| Lixiviation temperature 20 ºC | | | | |
| 13 | 5 | 18,0 | 54,35 | 28,38 |
| 14 | 10 | 17,1 | 46,41 | 41,90 |
| 15 | 15 | 16,9 | 39,30 | 51,38 |
| 16 | 20 | 16,6 | 33,53 | 59,25 |

Table 3 **The duration of the leaching of calamine, providing a given extraction of zinc into the solution at various temperatures of leaching**

| № experi ment | T |  | 1/T/ $K^{-1}$ | τ/ min | lg τ |
|---|---|---|---|---|---|
|  | / °C | / K |  |  |  |
| Extraction into the solution 57 % |  |  |  |  |  |
| 1 | 80 | 353 | 0,002833 | 15,07162 | 1,178160 |
| 2 | 60 | 333 | 0,003003 | 16,16406 | 1,208550 |
| 3 | 40 | 313 | 0,003195 | 17,51270 | 1,243353 |
| 4 | 20 | 293 | 0,003413 | 18,64776 | 1,270627 |
| Extraction into the solution 38 % |  |  |  |  |  |
| 5 | 80 | 353 | 0,002833 | 6,698498 | 0,825977 |
| 6 | 60 | 333 | 0,003003 | 7,184026 | 0,856368 |
| 7 | 40 | 313 | 0,003195 | 7,783422 | 0,891171 |
| 8 | 20 | 293 | 0,003413 | 8,287895 | 0,918444 |
| Extraction into the solution 19 % |  |  |  |  |  |
| 9 | 80 | 353 | 0,002833 | 1,674625 | 0,223918 |
| 10 | 60 | 333 | 0,003003 | 1,796006 | 0,254308 |
| 11 | 40 | 313 | 0,003195 | 1,945856 | 0,289111 |
| 12 | 20 | 293 | 0,003413 | 2,071974 | 0,316384 |

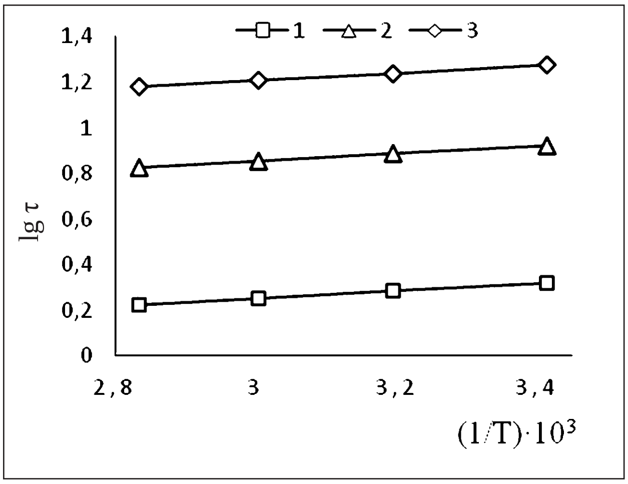


**Figure 2** Relationships of the logarithm of the leaching duration with its reciprocal temperature during zinc extraction 19 % (line 1: lg τ = 160,8843/T – 0,22958), 38 % (line 2: lg τ = 160,8858/T + 0,372474) and 57 % (line 3: lg τ = 160,8859/T + 0,724656)

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 assess the "apparent" activation energy of the interaction of calamine with sulfuric acid. For this, guided by the Woldman-Zelikman method [15], 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 reciprocal temperature were determined (Figure 2).

## RESULTS AND DISCUSSIONS

The angular coefficients [d(lgτ)/d(1/T)] of the lines lgτ = f(1/T) (Figure 2) are related to the value of the "apparent" activation energy by the relation d(lgτ)/d(1/T) = $E_{app}$/(2,3R) [15], where R is the universal gas constant equal to 8,31 kJ / mol. When zinc is extracted into a solution of 19, 38 and 57 %, the slope coefficients determined using an Excel processor are 160,8843; 160,8858 and 160,8859, respectively (Figure 2); The "apparent" activation energy was calculated from the mean slope value equal to 160,8853.

Thus, the value of the "apparent" activation energy of the interaction of calamine with sulfuric acid, calculated from the expression d (logτ)/d(1/T) = Eapp/(2,3R) [15], was 3,075 kJ / mol, which indicates on the diffusion nature of the specified interaction and requires updating the reaction surface of calamine in the process of leaching zinc from it.

The problem of updating the reaction surface of calamine in the process of sulfuric acid leaching of zinc from it was solved by us in [17]. In this work, a four-stage direct-flow sulfuric acid leaching of zinc was carried out from the calamine-smithsonite ore of the Shaimerden deposit, which contains 21,07 % zinc and has a mass ratio of calamine: smithsonite ($ZnCO_3$ [6,7]) 2.3 : 1 in terms of zinc.

As the results of recent studies carried out by us have shown, the process of direct-flow four-stage sulfuric acid leaching of zinc from calamine-bearing ore from the Shaimerden deposit [17] can be improved if this process is performed in a counter-current mode. This countercurrent leaching provides 94,65 % zinc recovery from calamine.

## CONCLUSION

The study of the influence of the leaching temperature on the degree of zinc extraction from calamine showed that the extraction of zinc naturally increases with an increase in the leaching temperature (Figure 1).

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

The calculated value of Eapp., Equal to 3,075 kJ / mol, indicates that the studied process takes place in the diffusion region. Therefore, it can be assumed that this process is limited by the rate of diffusion of acid molecules to the reaction surface through a layer of the resulting reaction products - poorly soluble hydrated silica and soluble zinc sulfate.

This assumption is confirmed by the results of enlarged laboratory studies of the process of four-stage sulfuric acid leaching of calamine-bearing ore from the Shaimerden deposit with a relatively pure sulphate solution in terms of silicon and zinc. This process, organized in a countercurrent flow, can be recommended for industrial processing of the specified ore instead of the expensive Waelz ore used today.

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