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Kinetic Features of Technogenic Raw Material Leaching in Aqueous Sulphuric Acid Solution with Microwave Intensification

Zhanserik Shoshay[a], Ruslan Viktorovich Sapinov[a,*], Marzhan A. Sadenova[b], Petar Sabev Varbanov[c], Assel Bakytovna Bayeva[d]

[a]NPJSC "Toraigyhrov University", 64 Lomov str. 140008, Pavlodar, Kazakhstan
[b]Center of Excellence «Veritas», D. Serikbayev East Kazakhstan Technical University, 19 Serikbayev str. 070000, Ust-Kamenogorsk, Kazakhstan
[c]Sustainable process integration laboratory, researcher NETME CENTRE Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2,616 00 Brno, Czech Republic
[d]RGF on PCB "National Centre for Expertise" sanitary-hygienic laboratory in Pavlodar region SCEC MH RK, Kazakhstan
sapinov.r@tou.edu.kz

In this article, the effect of temperature and microwave irradiation on the apparent activation energy of sulphuric acid leaching of copper slag from Balkhash copper smelter (Kazakhstan) was studied. Leaching was carried out under normal conditions and with microwave irradiation of the raw materials, before and during leaching. Leaching in both cases was carried out at 298, 318 K, 333 K and 358 K. It was found that using microwave irradiation, at 358 K, copper recovery into the productive solution increased from 65.7 % (without irradiation) to 91 %. Apparent activation energy with the use of microwave irradiation decreases from 19.108 kJ/mol (without activation) to 15.517 kJ/mol.

1. Introduction

Today, the issue of processing of technogenic waste is acute in Kazakhstan. It is known that technogenic waste can be a source of various metals (Habib et al., 2020). Both pyrometallurgical and hydrometallurgical methods are applicable for processing of technogenic raw materials in order to extract metals. Hydrometallurgical methods are known to have several advantages over pyrometallurgical methods in terms of lower energy and resource consumption and the release of various harmful reaction products (Fathi et al., 2017). However, hydrometallurgical methods are not without disadvantages, such as time-consuming leaching processes, or incomplete recovery of useful components from different raw materials (Lee et al., 2015), or reagent toxicity (Neag et al., 2020). To improve the efficiency of hydrometallurgical processes in terms of reduced process time and energy consumption, various ways of intensifying hydrometallurgical processes have been applied. These can be the use of vibration (Sapinov et al., 2020), ultrasound (Guo et al., 2019) and microwave radiation (Roy et al., 2020). The authors have previously studied the effect of microwave exposure on the leaching of copper from technogenic copper smelter waste for further thiourea gold extraction (Shoshay et al., 2021). It was noted that exposure to microwaves significantly increased the recovery of copper and other metals. This finding correlates with works in which in the leaching of gold (Amaya et al., 2015) and copper (Sabzezari et al., 2017), exposure to microwaves was found to significantly improve process performance in terms of reduced leaching time and increased metal recovery. It was observed that microwave irradiation contributed to the reduction of ash layer formation, preventing the access of reagents to the solid surface and reducing metal dissolution. A next study of chalcopyrite leaching using microwave irradiation also noted the positive effect of microwaves on copper recovery. Superior mineral leachability was associated with excess covellite intermediates, while the microwaves promoted the conversion of chalcopyrite to covellite. Furthermore, the microwave can increase the active centres by removing the passivation layer and increasing

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the effective reaction surface. In this work, the relationship between high copper recovery and modification of the chalcopyrite surface structure has been systematically summarised (Wen et al., 2020).

When studying the process of leaching zinc from ore, it was found that microwave heating has a significant effect on phase transformation and leaching. Thus, with microwave radiation, the rate of zinc leaching in an ammonium chloride solution with a total ammonium concentration of 7.5 mol/L can reach 82.06% within 1 hour. In contrast, the zinc leaching rate for ore samples fired in a conventional resistance electric furnace is only 30.62% (Yang et al., 2016). Thus, many researchers agree that the application of microwaves significantly affects the leaching kinetics of metals from different raw materials. It is known that the leaching process involves three main stages: 1) transport of reactants and solution to the reaction surface; 2) chemical reaction; and 3) transport of soluble products from the surface to the solution volume. Each of these stages may consist of several stages. Since the leaching rate increases when exposed to microwave radiation, therefore, there is an impact at one of the above stages, or at several stages in different sequences. In this article, the authors set a goal to consider in more detail the effect of microwave radiation on the kinetics of the process of leaching copper from technogenic raw materials - copper slag of the Balkhash copper smelter. For this purpose, the activation energy of the leaching process was determined under normal conditions and with microwave exposure. The activation energy is the energy level (kJ/mol) (www.chem.fsu.edu) that the reactant molecules must overcome before a reaction can take place. Then, using the known activation energies, the limiting stages of the leaching process were determined. Experiment 1 was carried out under normal conditions and experiment 2 under microwave exposure. A schematic of the experiment is shown in Figure 1.

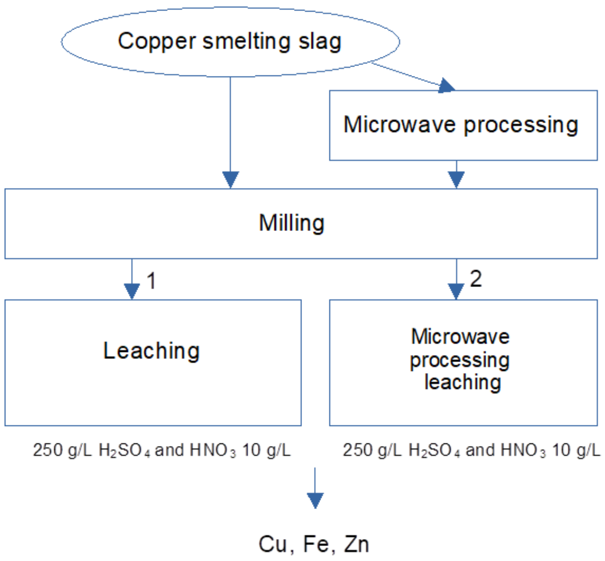

Figure 1: The scheme of the experiment

2. Materials and methods

All experiments were carried out in D. Serikbaev EKTU laboratory (https://www.ektu.kz). Copper slag from the Balkhash copper smelter was used as raw material. Ball and vibrating mills were used for grinding the materials. The elemental composition of the materials was determined using an ICP-MS 7500 cx inductively coupled plasma mass spectrometer from Agilenttechnologies (USA) (Table 1). A JSM-6390LV scanning microscope manufactured by JEOL Ltd. (Japan) was used to show the distribution of element profiles. All reagents were of analytical purity. Chemical heat resistant glassware was used for leaching. A microwave oven with a power of 1 kW, 2.45 GHz was used to activate the processes. Leaching was carried out with stirring on a magnetic stirrer, the solid and liquid phases were separated by filtration, and the filtrates were analysed for the content of valuable components. The residues were dried and also analysed to determine the content of valuable components in them. All tests were conducted twice, and if the results differed by more than 1%, the test was redone.

2.1 Leaching stage

During the study, the samples of technogenic waste were leached in 2 ways.

Method 1. Raw materials were crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and $HNO_3$10 g/L, at temperatures of 298, 318 K, 333 K and 358 K. The ratio of solid and liquid phases (S/L) = 1/20, with stirring on a magnetic stirrer, for 60 min. Samples were taken after 5, 10, 15, 30, 45 and 60 min. Method 2. The raw material was placed in a microwave oven and treated for a time of 240 sec. The power was 1 kW. Then the obtained raw material was ground and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, at temperatures of 298, 318 K, 333 K and 358 K. The ratio of solid and liquid phases (S/L) = 1/20, with stirring on a magnetic stirrer, for 60 min. The dish with the solution was placed in the microwave oven at the beginning of leaching and then every 15 min for 60 sec. Samples were taken after 5, 10, 15, 30, 45 and 60 min.

2.2 Determination of apparent activation energy

Using the obtained copper extraction data, graphs of copper leaching processes under normal conditions and with microwave activation were constructed and optimized by the least squares method. The leaching durations were then determined to ensure the same copper recovery into solution (40, 60, 80 %) at different temperatures of the sulphuric acid leaching process. To estimate the apparent activation energy, the dependences of the logarithm of the time required to achieve the same degree of copper extraction into the solution at different temperatures of its hydrochloric acid leaching under normal conditions were determined from the reverse temperature. The slope coefficients of the straight lines $\lg\tau=f(1/T)$ are related to the value of apparent activation energy by the relation $d(\lg\tau)/d(1/T) = E/(2.3R)$ (Voldman et al. 2003).

3. Results and discussion

The obtained data of chemical analysis of Balkhash copper smelter slag are shown in Table 1. Presence of iron 31 %, copper 0.4 %, zinc 1.5 % and other elements is shown. The content of gold is 0.00005 % (0.5 g/t).

Table 1: Average concentration of metals in slag mixture samples (wt. %)

Element	Fe	Ni	Cu	Zn	Ag	Sn	Sb	Au	Pb	S
%	31	0.1	0.4	1.5	0.00008	0.0008	0.2	0.00005	0.1	1.4

Figure 2 shows images of the element distribution profiles at a selected sample site. It shows that Fe, Ni, Cu, Zn, Si, Sb, Pb, and S are present in the raw material. After microwaving, the pre-milled raw material melted and formed a monolithic structure. After the raw material had cooled down, it was regrind in the mill (Figure 3).

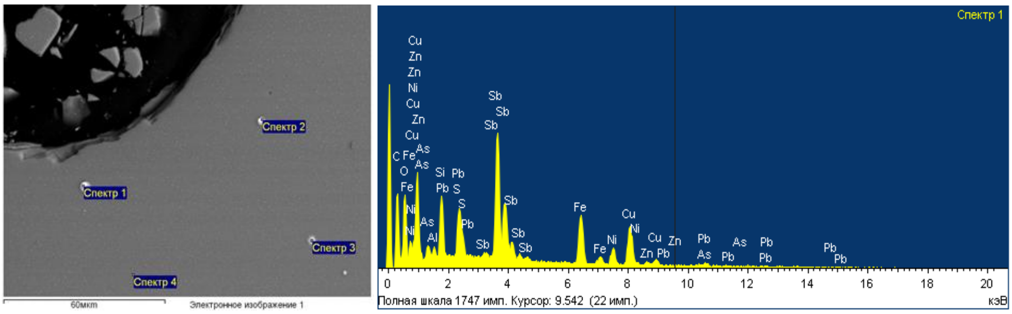

Figure 2: Images of element distribution profiles in the selected area

Figure 3: Images of raw materials after processing in a microwave oven (a) and after grinding (b)

Using the copper recovery data obtained at leaching stage, graphs of copper leaching processes under conventional conditions (Figure 4a) and with microwave activation (Figure 4b) were plotted and optimized using the least squares method. Then the leaching process durations were determined to ensure the same copper recovery into solution (40, 60, 80 %) at different temperatures of sulphuric acid leaching process.

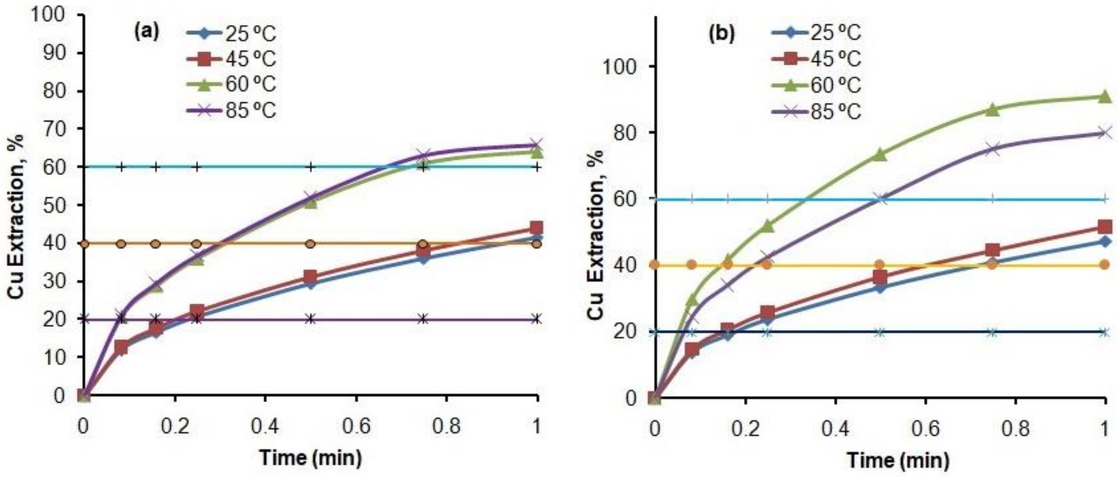

Figure 4: Plots of recovery versus duration and temperature of the copper leaching process (a) under normal conditions, (b) with microwave activation

The obtained values and their results are presented in Table 2 and 3 and further used to estimate the apparent activation energy of slag interaction with aqueous sulphuric acid solution (Nabiyeva et al., 2019). For this purpose, the logarithm of the time required to achieve the same degree of copper recovery in solution at different leaching temperatures was determined as a function of the inverse temperature (Figure 5). Table 2 shows the duration of sulphuric acid leaching of copper smelting slag, without exposure to microwaves

Table 2: Duration of sulphuric acid leaching of copper smelting slags for given copper recovery into a solution at different leaching temperatures

T K	1000/T, K^{-1}	*τ, min*	lg τ
	Extraction in to solution 20 %		
298	3.355704698	13.81230425	1.140266136
318	3.144654088	12.33480375	1.091132244
333	3.003003003	4.645441557	0.667027001
358	2.793296089	4.458469071	0.649185758
	Extraction in to solution 40 %		
298	3.355704698	55.24921698	1.742326127
318	3.144654088	49.33921499	1.693192235
333	3.003003003	18.58176623	1.269086992
358	2.793296089	17.83387628	1.25124575
	Extraction in to solution 60 %		
298	3.355704698	124.3107382	2.094508645
318	3.144654088	111.0132337	2.045374753
333	3.003003003	41.80897401	1.62126951
358	2.793296089	40.12622164	1.603428268

The dependence of the logarithm of the time required to achieve the same degree of copper recovery in solution at different temperatures of its leaching under normal conditions is shown in Figure 5a. Table 3 shows the duration of sulphuric acid leaching of copper smelter slag, with microwave irradiation. The dependence of the logarithm of the time required to achieve the same degree of copper recovery in solution at different leaching temperatures under normal conditions on the inverse temperature is shown in Figure 5b.

Table 3: Duration of sulphuric acid leaching of copper smelting slag providing a given copper recovery into a solution at different temperatures of leaching with microwave radiation

T, K	1000/T, K^{-1}	*τ, min*	lg τ
Extraction in to solution 20 %			
298	3.355704698	10.66737117	1.028057407
318	3.144654088	9.050071348	0.956652003
333	3.003003003	2.226541968	0.347630886
358	2.793296089	3.313319307	0.520263291
Extraction in to solution 40 %			
298	3.355704698	42.66948467	1.630117398
318	3.144654088	36.20028539	1.558711994
333	3.003003003	8.906167871	0.949690877
358	2.793296089	13.25327723	1.122323283
Extraction in to solution 60 %			
298	3.355704698	96.00634051	1.982299916
318	3.144654088	81.45064214	1.910894513
333	3.003003003	20.03887771	1.301873395
358	2.793296089	29.81987376	1.474505801

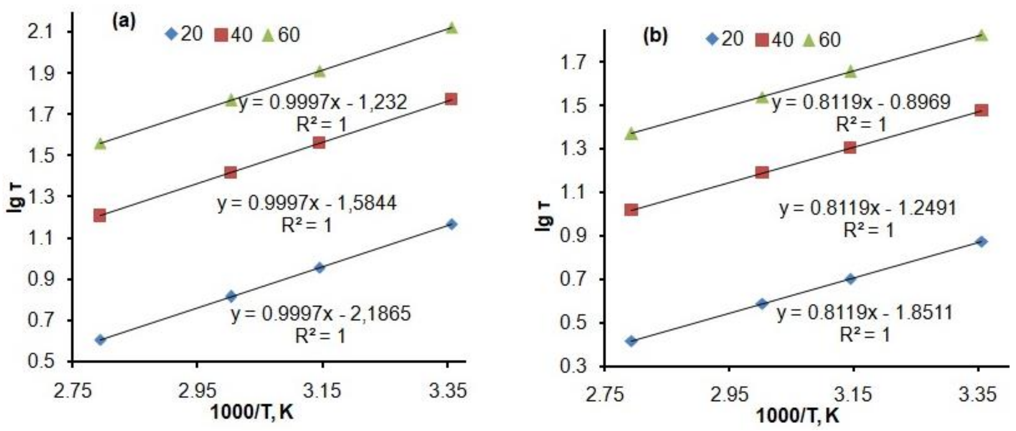

Figure 5: Dependences of the logarithm of the leaching process duration on its inverse temperature under normal conditions (a), with microwave irradiation (b)

The apparent activation energy of the interaction of slag and aqueous sulphuric acid solution without microwave treatment was 19.108 kJ/mol. The apparent activation energy of interaction of slag and aqueous sulphuric acid solution with microwave treatment decreased and was 15.517 kJ/mol. It is known that the activation energy can be lowered in two ways: increasing the energy level Eapp of the starting substances (applying thermal and mechanical activation) and reducing the barrier height E_1 using catalysts. In this case, the decrease of the activation energy from 19.108 kJ/mol to 15.517 kJ/mol can be explained by the following factors. Heating using microwave radiation is much more efficient than traditional, since heating occurs both outside and in the volume of the heated body due to the conversion of electrical energy into thermal energy. Consequently, thermal activation takes place with greater efficiency, since the heating comes from the inside, and not from the surface of the material. The second reason is due to the fact that the raw materials under study contain materials that absorb electromagnetic radiation and can be heated using microwaves. These are metal particles, moisture, etc. They are also materials that are not amenable to heating. As a result of uneven heating, the material opens up and the reagent penetrates better. However, in our case we completely melted the raw material at the beginning of the experiment. Therefore, we then had to grind it again. Perhaps when heating to temperatures lower than melting, the effect of opening the raw material will be greater. Values of apparent activation energy corresponding to diffusion Eapp= 8-20 kJ/mol, and kinetic Eapp= 40-300 kJ/mol (Voldman et al., 2003). Thus, the value of apparent activation energy Eapp= 15.517 kJ/mol means that the process of sulphuric acid leaching of copper slag proceeds in the diffusion region.

4. Conclusions

The study of the kinetics of the sulfuric acid leaching process of copper slags is aimed at finding the activation parameters of the leaching process and establishing the stage mode by determining the dependence of the leaching time and extraction of copper on the main technological parameters – temperature and duration of the process. A kinetic model of sulphuric acid leaching of copper smelter slag was constructed. The experimental data of activation energy without microwave treatment Eapp = 19.108 kJ/mol, and with microwave treatment of raw material Eapp = 15.517 kJ/mol were obtained. Thus, the values of apparent activation energy in both cases Eapp = 15.517 kJ/mol and 19.108 kJ/mol mean that the process of sulfuric acid leaching of copper slag proceeds in the diffusion region. It was also shown that the application of microwave irradiation for sulphuric acid leaching of copper smelter slag significantly increased copper recovery. For example, at a temperature of 358.15 K under normal conditions the Cu extraction was 65.7% and under microwave irradiation 91%. Moreover, the microwave irradiation reduced the activation energy of the leaching process from 19.108 kJ/mol to 15.517 kJ/mol. A fuller study of the effect of microwave irradiation on the reduction of the activation energy is in progress. We consider the effect of microwave radiation on the phase structure of the raw material as the change in phase structure also affects the change in apparent activation energy. To this end, the phase composition of the raw material before and after microwave exposure will be investigated. The effect of microwave irradiation on ash layer on the raw material surface will also be studied. Since in this study an ordinary household cooker with 1 kW power and 2.45 GHz frequency was used, the effect of microwaves of different power and frequency needs to be studied further, for which special equipment will be needed.

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