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Intensification of the Process of Extracting Non-Ferrous Metals from Kazakhstani Technogenic Raw Materials

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The article proposes an environmentally friendly method for processing industrial waste by the example of slags from the Balkhash copper smelting plant (Kazakhstan). The first stage involved copper extraction. The second stage is gold recovery. For a more complete extraction of copper, microwave activation was used at various stages of the process. As a result, the recovery of copper using microwave radiation was 91 %, zinc 87.2 % and iron 94 % and without copper 65.7 %, zinc 84.6 % and iron 93.4 %, respectively. Such efficiency of copper recovery allows using thiourea as a reagent for gold recovery and avoiding the use of cyanides.

1. Introduction

To date, Kazakhstan has accumulated a large amount of Technogenic waste (≈ 31.6 $\cdot 10^9$t). Technogenicwaste creates environmental risks, while being a source of valuable metals and building materials. About $1\cdot 10^9$t is formed annually. These are mainly Technogenic mineral formations (TMF), including overburden and ash slags (70 % of the total), waste from the manufacturing industry (10 % of the total) and other activities (20 %). The share of recycled and disposed industrial waste for the 3rd quarter of 2020 is 29.7 % Egov.kz (2021). Among other industrial waste, copper smelting slags are of particular interest, since they can be a source for the extraction of such valuable components as copper, iron Kaksonen et al. (2017), silver and gold Echeverry-Vargas et al. (2016). The raw materials remaining after the extraction of useful components can be used to produce building materials Lemougna et al. (2020).
Depending on the composition of the slags, there are different approaches to their processing. Hydrometallurgical methods are the most acceptable in terms of efficiency and environmental friendliness, although there are some issues with the disposal of waste solutions, for example, when using cyanides Eisler et al. (2004). Hydrometallurgical methods for processing man-made waste differ in the used reagents and the conditions of the leaching process, which depend on the extracted components. In a study by Lee et al. (2015), the copper smelter slag was preliminarily reduced to an Fe alloy containing 1.04 wt% Cu and 0.46 wt% Si by fusion reduction. The Fe alloy was completely dissolved in a concentrated HNO_3 solution for the electrochemical reduction of Fe at constant cathodic potentials. NaOH and NH_4Cl were added to control the pH of the solution and suppress the precipitation of α-FeO(OH). The Cu and Si levels in the resulting Fe-precipitate are undetectable. The lowest O/Fe mass ratio in the Fe precipitate was 0.011 when 0.561 mol/L NH_4Cl was added to the HNO_3-based solution, which indicates an oxygen content of 1.09 wt%.
In the work of Nadirov et al. (2013), the possibility of processing slags from the Balkhash copper smelting factory (BCSF) is investigated. The slag contains copper 2.2 %, iron 36 % and zinc ≈ 6 %. Technology for the extraction of copper, zinc and iron from the plant slags has been proposed. A mixture of slag and ammonium chloride (weight ratio 1/2) was treated at 320 °C for 120 min and leached with water. After separation, the solid residue was treated with ammonium chloride (weight ratio 1/2) for 160 min. The extraction of zinc, copper and iron into the solution is 91.5 %, 89.7 % and 88.3 %. In the work of Aracena et al. (2020), the converter slag with a high copper content (36 wt%) was treated with ammonium hydroxide at room temperature. Increasing

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the temperature and NH_4OH concentration with decreasing particle size leads to higher copper recovery, reaching values of 84.8 %. Under the same conditions, the main impurity (iron) was minimal (<2 %). The pH of the solution also affects slag leaching. Stirring the solution has a positive effect on the rate of copper recovery. The authors of Echeverry-Vargas et al. (2016) propose the processing of copper slag using hydrometallurgical methods (using cyanides) to extract gold and silver.

It was found that gold was dispersed in the grains of copper ferrite, while silver was dissolved in the Cu-S matrix in amounts ranging from 1 % to 50 %. Cyanidation tests have shown that 95 % gold recovery can be obtained at a concentration of 0.06 g/L KCN, pH 10.5, room temperature and a leaching time of 80 h. When the temperature was raised to 75 °C and the other cyanidation parameters remained unchanged, the same recovery was obtained, but with a shorter leach time. Silver recovery was less than 30 % at a concentration of 1.2 g/L KCN, a pH of 10.5, a temperature of 45 °C and a leaching time of more than 72 h. Other authors Xing and Lee, 2017, leached gold and silver from anode sludge with a mixture of hydrochloric acid and oxidising agents. The influence of the concentration of oxidants, reaction temperature and time, pulp density and stirring rate on the leaching of metals in the anode sludge (Au, Ag, Cu, Sn, Ni and Zn) was investigated. According to the results, all metals, except for silver, were completely dissolved in the mixture of HCl and oxidising agents used in this work. However, the Ag leaching percentage was only 10 % with a mixture of HCl and H_2O_2 or NaClO, while 28 % Ag was dissolved in a mixture of HCl and HNO_3. Complete dissolution of silver was difficult in the presence of chloride ion.

All the above methods are characterised by a relatively long leaching time (90 h. Echeverry-Vargas et al. (2016), or a low percentage of recovery of valuable components Ag 10 % - 28 % Xing and Lee (2017) and high process temperatures 320 °C Nadirov et al. (2013). The cyanides used in gold extraction are toxic and require special handling. Consequently, increasing the efficiency of hydrometallurgical methods for processing copper-smelting slag in terms of the completeness of extraction of useful components, reducing the process time and increasing the environmental friendliness of the process is relevant.

Thiourea can be used to recover gold from copper slags. Compared to traditional leaching methods, thiourea $CS(NH_2)_2$ is less toxic, does not harm the environment, and has high gold leaching rates Li et al. (2018). However, thiourea decomposes in the presence of copper Rao et al. (2020). Therefore, at the first stage, it is necessary to extract copper as fully as possible and then use thiourea to extract gold. To maximise the extraction of copper, it is necessary to increase the efficiency of the applied reagents. Some researchers have tried to increase the efficiency of hydrometallurgical processing processes using various force fields. For example, there are known works with the effect of vibration fields on hydrometallurgical processes, which enhanced the effect of an aqueous solution of HCl Sapinov et al. (2020), and ultrasonic fields Beşe (2007), which enhanced the effect of an aqueous solution of H_2SO_4 (with an increase in Cu extraction by 9 %, according to compared to normal conditions). Exposure to microwave radiation is also quite effective in extracting useful components from industrial waste. This can be pre-treatment of the material before leaching Amaya et al. (2015), as well as the effect of microwave radiation directly on the leaching process Turan et al. (2017), both mineral Yang et al. (2017) and technogenic raw Sadeghi et al. (2017) materials. Sabzezari et al. (2019) compared conventional leaching to microwave leaching based on kinetic modelling. The optimum conditions for obtaining maximum copper recovery were as follows: 250 g/L H_2SO_4, 5 % solids, 1000 W microwave power, 10 g/L HNO_3 and 10 min leach time. The final copper recovery with conventional heating and microwave irradiation was 80.88 % and 69.83 %. Kinetic studies have shown that leaching reactions follow diffusion through the product bed. Based on powder X-ray diffraction (XRD) analysis during routine sulphate experiments; the components are formed with high intensity in the form of an ash layer, which prevents the access of reagents to the solid surface and reduces the dissolution of Cu. While sulphate components are not found in microwave leach residues, this means that microwave irradiation has helped to reduce ash layer formation. Considering all the above results it can be concluded that microwave leaching can be considered as an effective method for recovering valuable metals from waste.

In the course of the analysis, it was found that the proposed methods of processing technogenic raw materials are characterised by high energy costs due to the duration of the processes in the extraction of copper, and the use of toxic cyanides in the extraction of gold. Therefore, there is a need for an environmentally friendly and energy-efficient method.

2. Materials and methods

All experiments were carried at the premises of the D. Serikbayev East Kazakhstan Technical University. The elemental composition of the materials was determined using an ICP-MS 7500 cx inductively coupled plasma mass spectrometer from AgilentTechnologies (USA) (Table 1). The phase composition of the slags was determined using an X'Pert PRO X-ray diffractometer manufactured by PANalitical (Table 2). All reagents were of analytical grade. For leaching, heat-resistant chemical dishes were used. To activate the processes, a microwave oven with a power of 1 kW, 2.45 GHz was used. Leaching was carried out with stirring on a magnetic stirrer. Ball and vibration mills were used to grind the materials. Copper slags of the Balkhash copper smelter were used as raw materials. Element distribution profiles in the selected area (Table 3) were made using a JSM-6390LV scanning microscope manufactured by JEOLLtd. (Japan). The solid and liquid phases were separated by filtration, and the filtrates were analysed for gold and other valuable components. The residues were dried and analysed to determine the content of gold and other valuable components.

2.1 Experiment description. Leaching stage

In our study, we compared the complex leaching of slags from the Balkhash copper smelter (KZ) under normal conditions and using microwave radiation at various stages. Leaching was carried out in two stages. At the first stage, copper and iron, zinc was extracted using an aqueous solution of sulfuric acid and nitric acid. At the second stage, gold was extracted using an aqueous solution of thiourea (Figure 1).
Based on the foregoing, it can be assumed that at the first stage, intensification of the leaching process with microwaves will allow a more complete recovery of copper and other components. This, in turn, will allow the second stage to use thiourea to extract gold from slags. The proposed technology can be effective in terms of complex extraction of valuable components, and more environmentally friendly due to the use of less toxic reagents.

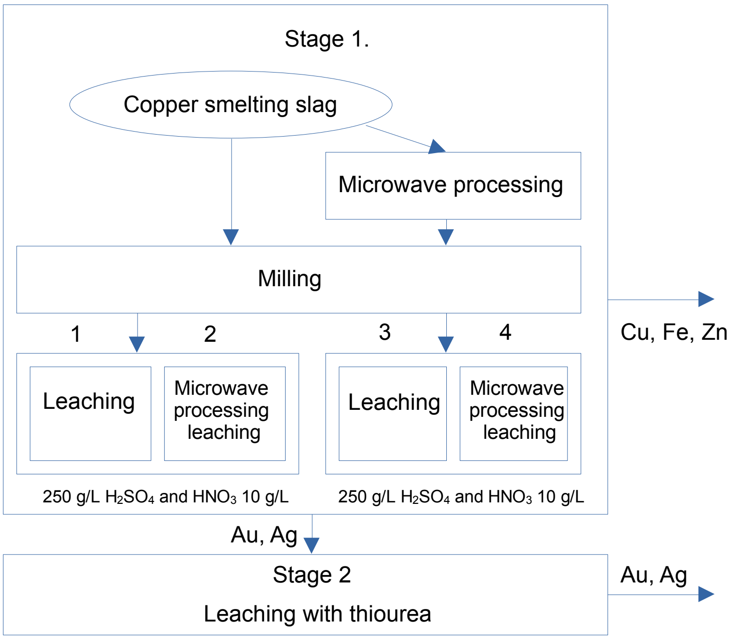

Figure 1: The suggested scheme of the experiment

During the study, samples of industrial waste were leached in 4 ways. This will test the effect of microwave radiation on the material itself and the leaching process.
Method 1 (Figure1). The raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, without microwave activation, with stirring on a magnetic stirrer.
Method 2 (Figure1). The raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, stirring for 30 min, while subjected to microwave activation every 10 min for 5 min.
Method 3 (Figure1). The raw materials were placed in a microwave oven and processed for various periods of time (60, 120, 180, 240 s). Power 1 kW. Then the resulting raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, without microwave activation, with stirring on a magnetic stirrer.
Method4 (Figure1). The raw materials were placed in a microwave oven and processed for various periods of time (60, 120, 180, 240 s). Power 1 kW. Then the resulting raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, with stirring and simultaneously subjected to microwave activation, every 10 min for 5 min.

3 Results and discussion

The data obtained from the chemical analysis of the slag of the Balkhash copper-smelting plant are shown in Table 1. The presence of iron 30.9 %, copper 0.4 %, zinc 1.5 % and other elements is shown. The gold content is 0.000045 % (0.45 g/t).

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

Fe	Cu	Zn	Ag	Sn	Sb	Au	Pb	S
30-31.8	0.3-0.5	1.3-1.4	0.000082-0.000084	0.00080-0.00082	0.17-0.19	0.000044-0.000046	0.08-0.10	1.3-1.5

XRD analysis showed the presence of tic compounds such as fayalite 30.1 %, ferrosilite 24.5 %, clinoferrite 2.9 %, zinc ferrite 16.2 %, copper sulfide 0.7 %, borite 0.6 %, sphalerite 1.1 % (Table 2).

Table 2: Phase composition of BCSF slag (wt. %)

Phases	Fe_2SiO_4 fayalite	$FeSiO_3$ ferrosilite	Fe (Ca)SiO_3 clinoferrite	$ZnFe_2O_4$ Zinc ferrite	Cu_2S Copper sulfide	Cu_5FeS_4 Borite	$CuFeS_2$ sphalerite
Content (%)	30-30.2	24.4-24.6	2.8-2.10	16.1-16.3	0.6-0.8	0.5-0.7	1.0-1.2

Figure 2 shows the images of the profiles of the distribution of elements in the selected area. It also shows the presence of iron, zinc, and copper (Table 3).

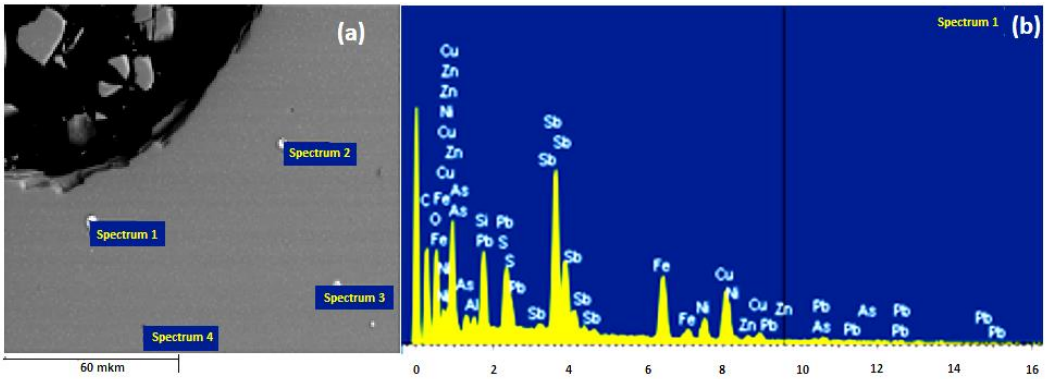

Figure 2: Electronic image a, images of distribution profiles of elements in a selected area b

As shown in Tables 1, 2 and 3, there is sulphur in the slag, which will affect the leaching process Sabzezari et al., (2019).

Table 3: Distribution of elements in the selected area

Spectra	O	Si	S	Fe	Cu	As	Ba
Max.	29.39-29.41	0.11-0.13	47.41-47.43	41.21-41.23	1.05-1.07	1.17-1.19	45.97-45.99
Min.	7.07-7.09	0.11-0.13	18.91-18.93	8.25-8.27	0.86-0.88	1.17-1.19	2.41-2.43

Leaching of copper

After the slag of the Balkhash copper smelter (Figure 3a) was subjected to ball milling (Figure 3b), the study of the effect of microwave radiation on the process of leaching of copper and other components from copper smelting slags was carried out according to the experimental design. The experiment is described below.

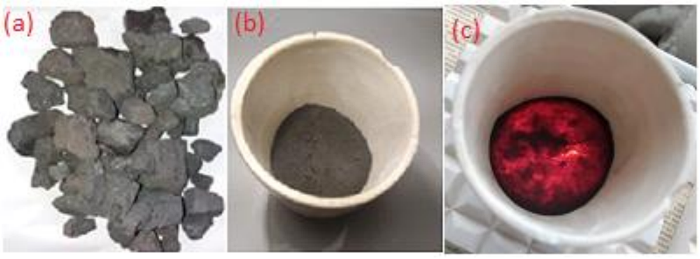

Figure3: Copper slag (a) before and (b) after grinding, copper slag after removing the microwave (c)

Method 1. The raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, without microwave activation, with stirring on a magnetic stirrer.
Method 2. The raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, stirring for 30 min, while subjected to microwave activation every 10 min for 5 min.
Method 3. The raw materials were placed in a microwave oven and processed for various periods of time (60, 120, 180, 240 s). Power 1 kW. Then the resulting raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, without microwave activation, with stirring on a magnetic stirrer.
Method 4. The raw materials were placed in a microwave oven and processed for various periods of time (60, 120, 180, 240 s). Power 1 kW. Then the resulting raw material was crushed and subjected to leaching in an aqueous solution of 250 g/L H_2SO_4 and HNO_3 10 g/L, solids content 5 %, for 30 min, with stirring, and simultaneously subjected to microwave activation, every 10 min for 5 min.
After leaching, the productive solution was passed through a filter. Then the productive solution and cake were sent for analysis of the content of valuable components. After the first method, the extraction of copper was 65.7 %, zinc 84.6 % and iron 93.4 %. After the second method, the extraction of copper was 79.7 %, zinc 85.3 % and iron 96.4 %. After the third method, the recovery of copper was 73.2 %, zinc 85.7 % and iron 94 %. After the fourth method, the recovery of copper was 91 %, zinc 87.2 % and iron 94 %. Table 4 shows the percentage of recovery of elements in the productive solution. The impact on raw materials before leaching and on the leaching process itself by microwave (Figure 3c) radiation gives the highest copper recovery (91 %).

Table4: Extraction of valuable components into a productive solution (%)

Fe	Cu	Zn	Ag	Sn	Sb	Au	Pb	S
92-96	90-92	87.1-87.3	0	88-90	92-94	0	93-95	98.1-98.3

This is apparently since microwave radiation destroys the material, facilitating the extraction of copper Amaya et al. (2015), and at the leaching stage, microwave irradiation helped to reduce the formation of an ash layer, which facilitates diffusion of the reagent to the leached component Sabzezari et al. (2019). This makes it possible to use thiourea as a reagent for leaching gold from raw materials. At the next stage, gold was leached with thiourea. The material remaining after copper leaching is placed in an aqueous solution of thiourea with a concentration of 12 g/L. S/W ratio = 1/10 (solid / liquid). The material is leached for 240 min at 25 °C, 45 °C and 60 °C with stirring on a magnetic stirrer. The pH of the process is 1.5. Samples were taken every 60 min to study the kinetics of the process. To maintain the pH of the process, $Fe_{2(}SO_4)_3$ was added. The most effective temperature for gold recovery was 60 °C (Au 88.6 %). The lowest recovery was at 25 °C. An increase in temperature to 85 °C did not give a noticeable increase.

4. Conclusions

Studies have shown the effectiveness of microwave radiation in terms of increasing copper recovery compared to conventional methods. The recovery of copper without microwave activation was 65.7 %, all other things being equal. The highest copper recovery was 91 % when processing raw materials in a microwave oven before leaching (4 min) and then leaching with microwave activation (45 min). Such efficiency of extraction of copper with microwave activation made it possible to use an aqueous solution of thiourea for the extraction of gold, in an amount of 88.6 % without using cyanides. domestic) to extract copper, zinc, iron, and precious metals. The team of authors will work towards developing of an integrated method for processing various types of waste (technogenic, electronic, domestic) to extract copper, zinc, iron, and precious metals.

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