

Recovery of value metals from copper smelter slag by ammonium chloride treatment



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ABSTRACT

Processing possibility of copper smelter slag produced by Balkhash copper plant (Kazakhstan) was investigated. The effect of temperature and treatment duration on the metal recovery to water-soluble form was studied. A technique of copper, zinc, and iron recovery from the slag of the plant was proposed. The mixture of the slag and ammonium chloride (wt ratio 1:2) was treated at 320 °C for 120 min and subjected to water leaching. After separation the solid residue was treated with ammonium chloride (wt ratio 1:2) for 160 min. Recovery of zinc, copper, and iron into solution is, respectively, 91.5, 89.7, and 88.3%. Apparent activation energy, pre-exponential factor and Gibbs free energy of activation for processes of Zn, Cu, and Fe recovery to water-soluble form have been calculated. By adding an ammonia water into solution hydroxides of zinc, copper, iron, calcium and magnesium is selectively precipitated. Process flowsheet for the value metal recovery from copper smelter slag of the copper plant was proposed.

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1. Introduction

The vast majority of copper extraction from copper minerals is pyrometallurgical (Davenport et al., 2002). These processes generate slags, which generally contain some significant metals of value. Copper slags are produced in thousands of tons per year. Components of slag eventually contaminate the environment (Parsons et al., 2001). Besides significant amount of copper, zinc, and other valuable metals can be obtained from copper slag. This fact stimulates the researches worldwide to development of methods for the recovery of above mentioned metals from metallurgical wastes such as copper smelter slag. There were some hydrometallurgical methods for the slag processing because they have much advantages. Research has focused on atmospheric leaching, using lixivants such as acids, bases, and salts (Sukla et al., 1986; Herreros et al., 1998; Banza et al., 2002; Altundogan and Tumen, 1997; Arslan and Arslan, 2002; Altundogan et al., 2004; Carranza et al., 2009; Zhang Yang et al., 2010); and on high pressure oxidative acid leaching (Curlook et al., 2004; Baghalha et al., 2007; Li et al., 2008, 2009).

Recently, it was found that ammonium chloride (NH₄Cl) as an alternate agent can be used for extracting value metals from the raw

materials, such as copper ores (D'yachenko and Kraidenko, 2010) and nickel ores (Andreev et al., 2011).

At room temperature, ammonium chloride is safe, non-volatile and an environmentally benign crystalline substance. At 338 °C ammonium chloride decomposes to NH₃ and HCl.

Authors (Borisov et al., 2011, 2012) showed that the reaction of oxides and sulfides of some metals (CaO, ZnO, CuS, FeS, ZnS, Fe₂O₃) takes place via the formation of chloro-metallate complexes, such as (NH₄)₂ZnCl₄, (NH₄)₄CuCl₃ et al. These complexes at 280–320 °C further decomposed to the relevant chlorides. Oxides of silicon (SiO₂) and aluminum (Al₂O₃) do not react with ammonium chloride.

In this study processing possibility of copper smelter slag produced by Balkhash copper plant (Kazakhstan) was investigated. Mining production at Balkhash started in 1938. At the copper plant copper concentrates processed by autogenous smelting to produce copper matte which is further processed to produce copper. Byproducts of this technology are slag and gasses containing mainly sulfur dioxide. Smelting slag mainly consists of oxides, such as fayalite (2FeO * SiO₂), silicon dioxide, iron (II), iron (III), zinc, calcium, and magnesium oxides. Besides that, slag consists of zinc and copper sulfides. At the plant slag is utilized in several ways, such as flotation to produce a copper concentrate, additive to melting as a flux and other. But this methods of slag using are not effective, therefore millions of tons of this product accumulated at the plant in more than 70 years. This fact promoted us to find new ways to copper smelting slag processing.

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2. Materials and methods

2.1. Materials

Mineralogical analysis, performed using DRON-3M model X-ray diffractometer, indicated the presence of the following components in the slag sample: SiO_2 , Fe_2O_3 , FeO , ZnO , CaO , MgO , CuS , Cu_5FeS_4 , CuFeS_2 , ZnS , and Al_2O_3 . Chemical analysis of the slag sample determined by X-ray fluorescence (Spectroscan) is presented in Table 1.

2.2. Thermal treatment of “slag- NH_4Cl ” mixture

Sample of slag (10 g; – 200 mesh) was thoroughly mixed with analytical grade NH_4Cl at NH_4Cl /slag weight ratio equals 2 in an alumina crucible. The mixture was placed in a sealed aluminum container fitted with a tube for gas removing. The container was placed in a muffle furnace with exhaust. The furnace was preheated to the required temperature. Bottom of the tube was removed through the exhaust and was immersed in a water bottle with a rubber stopper. Mixture was heated at temperatures ranged from 280 to 320 °C. Separated gas basically contained NH_3 and water vapor was absorbed by water and used for solution pH adjusting.

2.3. Water leaching of heated mixtures and components separation

Based on solubility differences of products obtained by “slag- NH_4Cl ” mixture thermal treatment and differences of metals pH hydration in water at room temperature, the product mixture was subjected to water leaching. Solution pH was regulated by ammonia water. Concentration of metal ions in solution was determined by atomic adsorption spectrometer Shimadzu (AA-6200). Solid residues were analyzed by X-ray fluorescence (Spectroscan).

3. Results and discussion

3.1. Influence of temperature and thermal treatment time on metal recovery to water-soluble form

The effect of temperature and heat treatment duration on the metal recovery to water-soluble form was investigated. For this after the thermal processing a mixture was treated by water. Then the content of metal ions in solution and the degree of metal recovery to water-soluble form was determined.

Fig. 1 shows the effect of temperature and thermal treatment time on weight loss of residue obtained after leaching of water-soluble components from thermal treated mixture; weight of initial slag is taken as 100%. It can be seen that an increase of reaction time and temperature increases slag components recovery to water-soluble form.

Figs. 2–4 show the effect of temperature on zinc, copper, and iron recovery to water-soluble form. It can be seen that zinc and copper recovered to water-soluble form almost completely at 320 °C for 120 min. However iron recovery at abovementioned conditions is about 35% and increases to 42% for 140 min.

To increase the completeness of iron recovery to water-soluble form, experiments at higher duration of thermal processing were conducted. Further higher treatment time favors the increase in iron recovery (Fig. 5). As can be seen at Fig. 5 iron almost completely recovered to water-soluble form at 320 °C for 300 min. This fact can be used for selective recovery of zinc, copper, and iron from copper smelter slag.

Table 1
Chemical analysis of slag sample.

Component (%)							
Si	Fe	Zn	Ca	Mg	Cu	S	Al
15.30	36.41	5.92	2.94	0.21	2.20	1.34	0.74

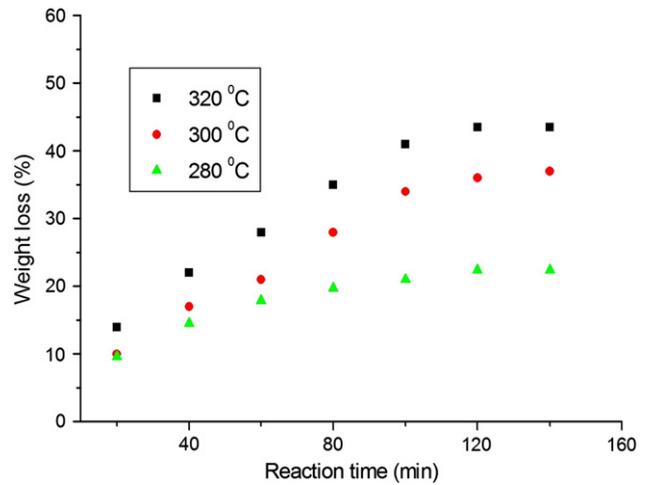


Fig. 1. Effect of temperature and thermal treatment time on weight loss of mixture after water leaching.

To investigate the possibility of a two-stage thermal processing of furnace slag the following experiment was performed. Heating of the slag with ammonium chloride according to the abovementioned methodology for 120 min was carried out. The product of thermal processing

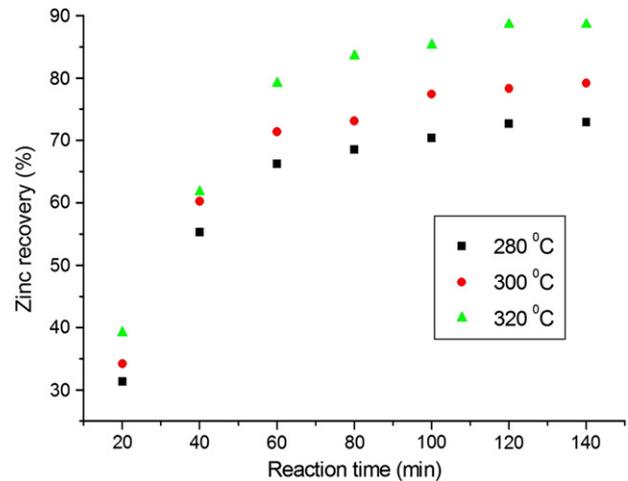


Fig. 2. Effect of temperature and thermal treatment time on zinc recovery to water-soluble form.

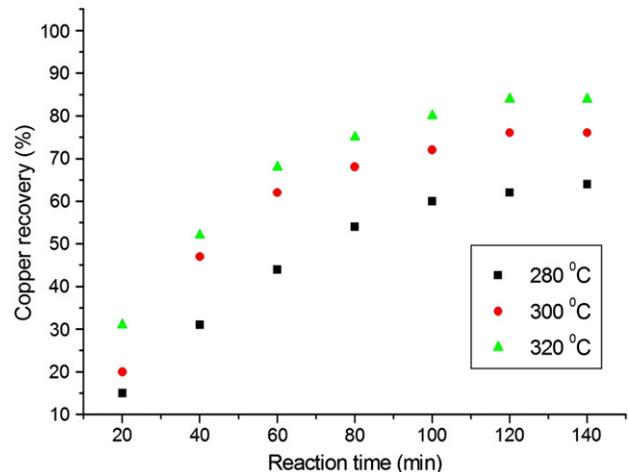


Fig. 3. Effect of temperature and thermal treatment time on copper recovery to water-soluble form.

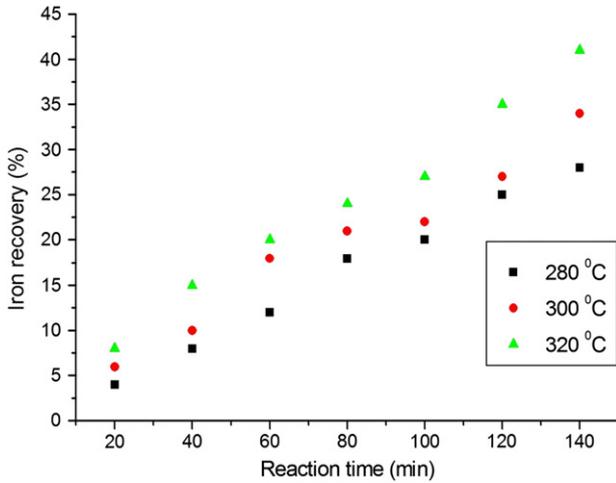


Fig. 4. Effect of temperature and thermal treatment time on iron recovery to water-soluble form.

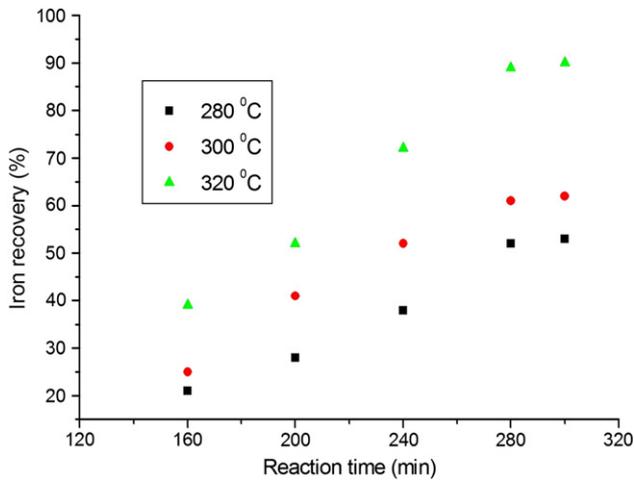


Fig. 5. Effect of temperature and thermal treatment time on iron recovery to water-soluble form.

was leached by water, and the solid residue was analyzed; results of the analysis are presented in Table 2.

This residue was then subjected to heat treatment with ammonium chloride; the effect of temperature and treatment duration on the iron recovery to water-soluble form is shown in Fig. 6. It can be seen that iron is recovered to water-soluble form on 82% when treatment is at 320 °C for 160 min. Analysis of solid residue after leaching is shown in Table 3.

Thus, the two-stage heat treatment of the slag is suitable. At the first stage about 90% of zinc and copper, as well as about 35% of iron recovered to water-soluble form. At the second stage iron from the residue after leaching recovered to water-soluble form additionally. The total iron recovery is 88.3%, considering the first stage. At the same time the recovery process of nonferrous metals and iron into solution is more selective than when slag processing at one stage.

Table 2
Chemical analysis of solid residue after heat treated “slag-NH₄Cl” mixture leaching.

Component (%)							
Si	Fe	Zn	Ca	Mg	Cu	S	Al
27.15	41.92	1.23	1.01	0.07	0.61	0.37	1.24

T = 320 °C; τ = 120 min.

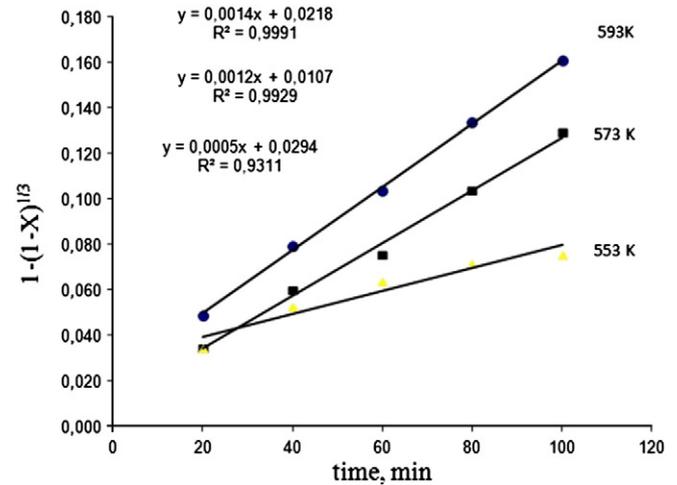


Fig. 6. Plots of $1 - (1 - X)^{1/3}$ vs. time.

3.2. Kinetics study

The considered decomposition of copper smelter slag by NH₄Cl could be analyzed with the shrinking core model (Levenspiel, 1972). By hypothesis, the particle of copper slag is spherical and the reaction between components of copper slag and NH₄Cl is first order for NH₄Cl, the following kinetic equation can be proposed as follows (for chemical reaction controlled process):

$$1 - (1 - X)^{1/3} = kt \tag{1}$$

where X is the slag sample fraction reacted at time t (min), k is the apparent rate constants.

There is a good linear tendency for $1 - (1 - X)^{1/3}$ vs. time dependence for slag sample at each treatment temperature (see Fig. 6).

The apparent rate constants for slag sample were found from the plots of $1 - (1 - X)^{1/3}$ vs. time at three operating temperatures. For the temperatures 280, 300 and 320 °C, the following values of the apparent rate constants were obtained, respectively (min⁻¹): 0.0005; 0.0012 and 0.0014. It can be seen, with increase in temperature the apparent rate constant value also increases. The process activation energy, calculated by Arrhenius equation, was 70.67 kJ/mol.

It was of interest to calculate the apparent rate reaction constants of zinc, copper, and iron recovery to water-soluble form, as well as the apparent activation energy for noted metal recovery (Table 4).

Table 3
Chemical analysis of solid residue after heat treated “residue-NH₄Cl” mixture leaching.

Component (%)							
Si	Fe	Zn	Ca	Mg	Cu	S	Al
40.09	12.28	1.93	1.67	0.12	1.01	0.89	2.02

T = 320 °C; τ = 160 min.

Table 4
Kinetic parameters of zinc, copper, and iron recovery to water-soluble form.

T, K	Zn		Cu		Fe	
	k, min ⁻¹	Apparent activation energy, kJ/mol	k, min ⁻¹	Apparent activation energy, kJ/mol	k, min ⁻¹	Apparent activation energy, kJ/mol
553	0.0026	30.9	0.0023	26.7	0.0007	70.7
573	0.0030		0.0029		0.0009	
593	0.0041		0.0034		0.0017	

Table 5
Leaching experiment results.

Number of mixture	Mixture weight after heat treatment, g	V_{H_2O} , mL	$V_{H_2O_2}$, mL	Solid residue weight after leaching, g	Metal ions' concentration in solution, g/L			
					Zn ²⁺	Cu ²⁺	Fe ³⁺	Ca ²⁺ + Mg ²⁺
1	23.71	5	100	5.65	4.98	1.76	12.13	2.36
2	12.46	10	80	3.47	≤0.01	≤0.01	21.51	≤0.01

Analysis of the data from Table 4 allows the following conclusions. Iron proceeds more slowly to the water-soluble form than zinc and copper at temperatures investigated. As the temperature increases from

553 K to 593 K, the rate of iron recovery to water-soluble form increases by 2.43 times; for copper and zinc, these values are 1.58 and 1.48, respectively. That is, the process of iron recovery to water-soluble form

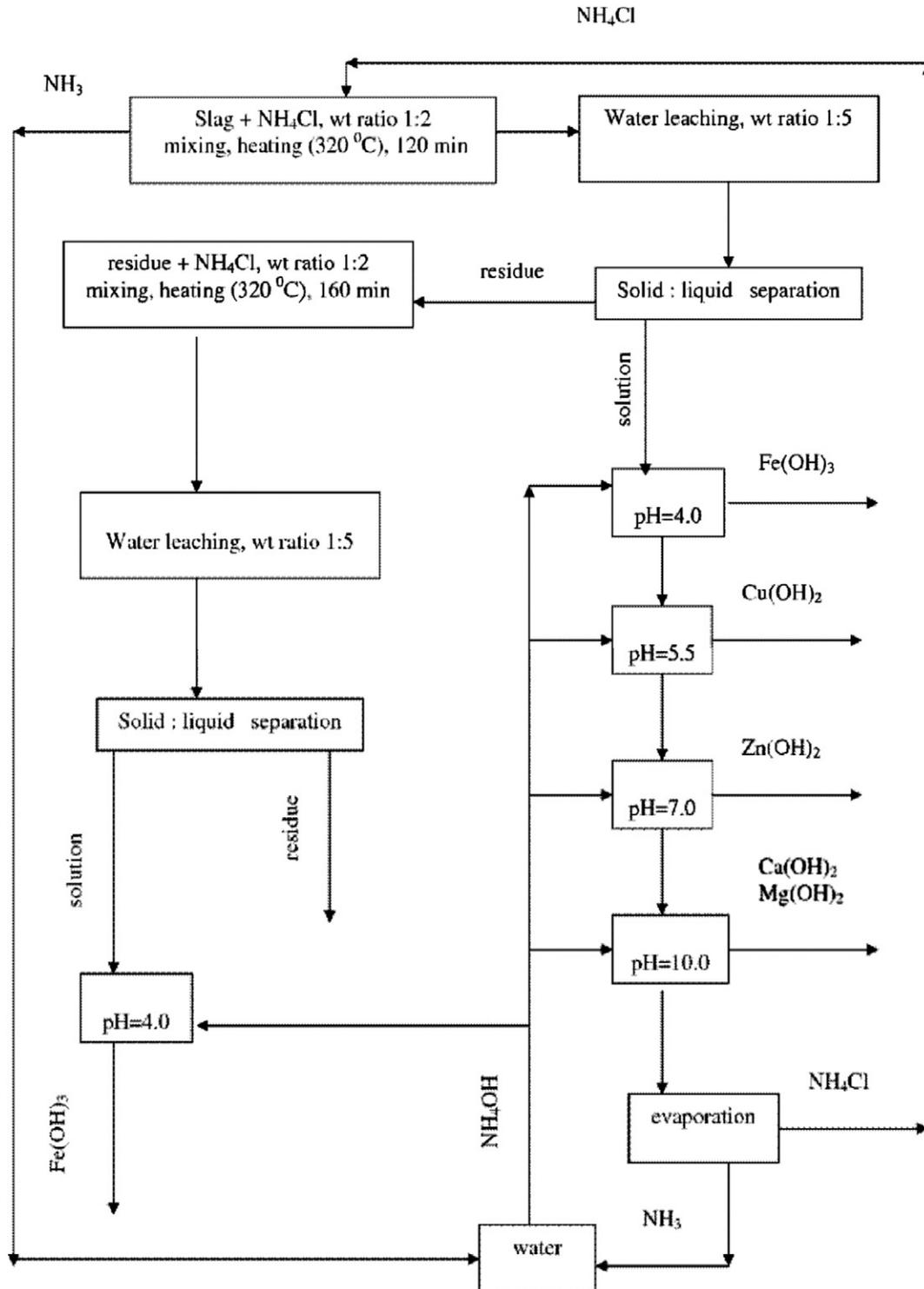


Fig. 7. Proposed flowsheet for the copper, zinc, and iron recovery from copper smelter slag.

is more sensitive to temperature than the processes of zinc and copper recovery.

For metal recovery processes to water soluble form pre-exponential factors were calculated by the Arrhenius equation (Levine, 2005):

$$k = Ae^{-E_a / (RT)} \quad (2)$$

where k is the apparent rate constants, on the absolute temperature T , A is the pre-exponential factor, E_a is the apparent activation energy, and R is the universal gas constant.

Another Arrhenius-like expression appears in the “transition state theory” of chemical reactions, formulated by Wigner, Eyring, Polanyi and Evans (Levine, 2005):

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (3)$$

where k_B is Boltzmann's constant, h is Planck's constant, and ΔG^\ddagger is the Gibbs free energy of activation.

Accurate calculation of the Gibbs free energy of activation by Eq. 3 is impossible, but it can comparatively evaluate the values of ΔG^\ddagger for Zn, Cu and Fe.

For zinc, copper, and iron, the following values of the pre-exponential factor were obtained, respectively (min^{-1}): 2.05; 0.77 and 2870. It can be seen that the pre-exponential factor for iron recovery to water-soluble form exceeds that of pre-exponential factors for copper and zinc more than three orders.

Comparison of right-hand sides of Eqs. 2 and 3 shows that ΔG^\ddagger in the case of iron is much higher than ΔG^\ddagger for zinc and copper at the same temperature. This means that the formation of activated complex of iron significantly hampered than the formation of activated complexes of zinc and copper. This fact is confirmed by a lower iron recovery to water-soluble form during experiments.

3.3. Metal recovery from solution

Mixture obtained by slag heat treatment with ammonium chloride at 320 °C for 120 min (mixture no. 1) was used for water leaching. In addition, the mixture obtained by heat treatment (320 °C, 160 min) of residue after leaching with ammonium chloride (mixture no. 2) was subjected to leaching. After separation of the solids H_2O_2 was rushed into filtrate upon heating for oxidation of Fe^{2+} to Fe^{3+} . Solution pH was adjusted with ammonia water sequentially to values of 4, 5.5, 7, 10. Thus sediments were formed, respectively: $\text{Fe}(\text{OH})_3$; $\text{Cu}(\text{OH})_2$; $\text{Zn}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. Sediments were separately filtered and dried to constant weight. The experimental results are presented in Table 5.

The total recovery of metals from the slag into a solution is, %: zinc—91.5; copper—89.7; iron—88.3.

3.4. Reagents recovery

After metal hydroxides precipitation the solution was evaporated to obtain of ammonium chloride. Ammonium chloride was dried to constant weight and was reused. Ammonia solution, obtained by absorption of gas, used to increase the pH of the solution after mixture leaching and filtration of solid residue. Solution after metal hydroxides precipitation was used to leaching the new portion of the mixture.

3.5. Proposal for a technological implementation of the method

Fig. 7 shows a proposed process flowsheet for the copper, zinc, and iron recovery from copper smelter slag of Balkhash copper plant. In this process, crushed slag, with ammonium chloride in a weight ratio 1:2 is subjected to heat treatment for 120 min at 320 °C. Evolved gas

was absorbed by water. The treated mixture was leached with water; after solid–liquid separation, the leach liquor goes to metal hydroxides sequentially precipitation by varying the pH by ammonia water. The residue after leaching treated with ammonium chloride in a weight ratio 1:2 at 320 °C for 160 min. After solid–liquid separation, the leach liquor goes to $\text{Fe}(\text{OH})_3$ precipitation. The process is closed; NH_4Cl and NH_4OH separated and reused.

4. Conclusions

The process of value metal recovery from copper smelter slag of Balkhash copper plant by heat treatment with ammonium chloride was investigated. The effect of temperature and heat treatment duration on the metal recovery to water-soluble form was studied. It was found that 91.5% of zinc and 89.7% of copper are removed to water-soluble form at 320 °C for 120 min. The process of iron recovery to water-soluble form is more sensitive to temperature than the processes of zinc and copper recovery at the investigated temperatures. Additional heat treatment of the residue after leaching with ammonium chloride is recommended. This allows that the total value recovery of iron to water-soluble form is 88.3%.

Apparent activation energy, pre-exponential factor and Gibbs free energy of activation for processes of Zn, Cu, and Fe recovery to water-soluble form have been calculated.

By changing the pH of the solution metal hydroxides is selectively precipitated from the solution. Process flowsheet for the value metal recovery from copper smelter slag of Balkhash copper plant was proposed.

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