Metallurgical and Materials Data 1, no. 2 (2023): 65-70

Publisher: Association of Metallurgical Engineers of Serbia

Metallurgical and Materials Data

www.metall-mater-data.com

Thermodynamics study for selective leaching of copper and zinc from complex secondary raw materials using oxidative sulfuric acid leaching

Nataša Gajić[1,*], Milisav Ranitović[1], Miloš Marković[2], Željko Kamberović[2]

[1] *Innovation Center of the Faculty of Technology and Metallurgy in Belgrade Ltd. University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*
[2] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

ARTICLE INFORMATION:

https://doi.org/10.30544/MMD10

Received: 25 June 2023

Accepted: 30 June 2023

Type of paper: Research paper

ABSTRACT

This study focuses on the evaluation of optimal process conditions for selective leaching of copper and zinc from complex secondary raw materials using the oxidative sulfuric acid leaching process. The research included a physical and chemical characterization of the materials, and a comprehensive thermodynamic analysis to evaluate the thermodynamic properties and behaviors of the investigated system.

The physical characterization involved the determination of parameters such as bulk density, moisture content, and granulometric composition of the samples. Elemental composition analysis was carried out using X-ray fluorescence spectrometry (XRF) and energy dispersion spectroscopy (EDX), while the phase composition was determined through X-ray diffraction (XRD) analysis. Additionally, the morphology of the materials was examined using scanning electron microscopy (SEM).

The species distribution diagrams and Pourbaix's diagrams were created using Hydra/Medusa software to assess the phase distributions of zinc and copper during the leaching process. The calculations of Gibbs energy change for various reactions occurring during the oxidative sulfuric acid leaching process within a defined temperature range using the reaction module of HSC 9 Chemistry Software were done.

Based on the thermodynamic analysis conducted, it was determined that effective leaching of copper and zinc from the complex secondary raw materials is feasible. Furthermore, the results indicated that the leaching process is relatively insensitive to temperature variations. The optimization of the leaching process should primarily focus on achieving optimized consumption of the oxidizing agent.

Keywords: thermodynamics, secondary raw materials, leaching, copper, zinc.

1. Introduction

Hydrometallurgical recovery of metals from secondary sources has emerged as a crucial pathway, presenting advantages for both environmental preservation and economic advancement. In industrial practice, sulfuric acid is the most commonly employed leaching system due to its availability, price, and solubility (Nozhati & Asghar 2020). Furthermore, leaching is usually conducted with the addition of various oxidizing agents for improving the leaching process, often oxygen or hydrogen peroxide (H2O2).

In the literature, many authors have studied the recovery of copper and zinc from different secondary raw materials. Thus, for example, for the valorization of copper and zinc from the tailings sample obtained after flotation, Antonijević, and Asadi et al. used sulfuric acid as a leaching agent and iron sulfate as an oxidant (Antonijević et al. 2008, Asadi et al. 2017). Santos and others used the same leaching agents to treat sphalerite concentrates (Santos et al. 2010), Chen et al. for sulfide tailings (Chen et al. 2014), and Cao and others for zinc refinery process residues [Cao et al. 2019]. According to Ahmed et al., 95% and 99% of copper were derived from secondary brass slag resources (Ahmed et al. 2016). Karimov et al. reported that by using sulfuric acid during two-phase atmospheric and autoclave oxidation leaching, about 93% of copper and 96% of zinc can be leached from fine dust obtained during copper production (Karimov at al. 2019).

Although a lot of research has conducted on the efficient extraction of copper and zinc from many secondary raw materials such as waste slags, tailings, printed circuit boards, and others, there is still little data on the extraction of zinc and copper from so-called complex secondary raw materials used in low-temperature catalytic processes (Nozhati & Asghar 2020).

---

* Corresponding author.
E-mail address: ngajic@tmf.bg.ac.rs (Nataša Gajić).

Due to their proprietary nature, there is a lack of information related to the processing of this specific type of secondary raw material. It is mainly limited to two patents, which describe their production through hydrometallurgical processes (Zhang Xiaoyang et al. 2010, Wang Ben and Meng Yun, 1998). In patent CN102125851B, the process consists of several steps: calcination at a temperature between 400 and 800 °C, followed by leaching with a nitric acid concentration (Zhang Xiaoyang et al. 2010). Further filtration of the solution through a nanofiltration membrane removes impurities and gives a solution rich in Cu and Zn ions. Finally, the regeneration process follows, where after the analysis of the sample, an adequate component (Cu, Zn, or Al nitrate) is selected to precipitate copper and zinc (Zhang Xiaoyang et al. 2010). Patent CN1258752A also explains the method of obtaining copper and zinc from complex secondary raw materials, and the procedure is based on the dissolution of zinc and copper oxides with ammonia powder to obtain a stable, high-purity copper-zinc ammonia complex (Wang Ben and Meng Yun, 1998).

However, since the optimal conditions for the extraction of these metals from complex secondary raw materials depend significantly on their chemical and mineralogical composition, it is necessary to define the appropriate and selective parameters employed in the leaching process to determine an adequate technological scheme for their recovery.

The main objective of this work is the performance of the thermodynamic predictions through the construction and analysis of speciation and Pourbaix's diagrams under defined conditions in the leaching system. By considering the stability of various chemical species of Cu and Zn and their distribution as a function of pH and redox potential, the optimum leaching parameters are assessed. Additionally, the optimal concentration of sulfuric acid for leaching was determined. Thus, in-depth analysis and discussion concerning the thermodynamic aspects included in the oxidative sulfuric acid leaching process of copper and zinc from complex secondary raw materials are presented.

2. Materials and Methods

2.1. Materials

The sample of complex secondary raw materials used for the analysis was subjected to sample preparation methods to obtain a representative sample. To prepare material adequate for hydrometallurgical testing, several procedures were conducted, including milling, drying, and homogenization.

3. Methods

The physical characterization of the sample included the determination of moisture, bulk density, and particle size distribution. Material drying was performed using a Memmert UNE 500 laboratory dryer. Moisture content was determined from the loss in weight of the samples upon drying at a temperature of 105 °C for 24 h in accordance with the ISO 11465:1993 standard. The determination of the bulk density of the sample was done by measuring the mass of three different known volumes of a freely packed layer of material according to ASTM B527 standard. The determination of the particle size analysis of the sample was done by the ISO 3310-1 standard using the Retsch Vibratory Sieve Shaker AS 200.

Mineralogical composition was determined by X-ray diffraction (XRD) analyses using a Rigaku Miniflex600 with CuKα radiation (= 1.54 Å). Measurements were carried out in the 2θ range from 10° to 65° in steps of 0.02. The elemental composition of the sample was determined via X-ray fluorescence (XRF) using an Olympus Vanta C Series Handheld XRF analyzer, in a specific Geochem mode.

A JOEL JSM-7001F scanning electron microscopy (SEM) equipped with an Oxford Instruments Xplore 15 operating at an acceleration voltage of 20 kV was used for characterizing the morphology and elemental composition of the sample.

A comprehensive theoretical examination was conducted to analyze the thermodynamic properties of specific leaching reactions. This effort was aimed at providing a more in-depth understanding of the complex reaction system and establishing the optimal process parameters. Therefore, analysis of the phase stability of the metals, their possible chemical reactions, and their relative order was performed using Hydra/Medusa software and HSC Chemistry software v. 9 (Puigdomenech I. Hydra & Medusa 2006, Roine, A., and P. Lamberg, 2020).

4. Results and Discussion

4.1. Materials Characterization

The size distribution of dried samples obtained by sieve analysis is plotted as a particle and cumulative size distribution and shown in Figure 1.

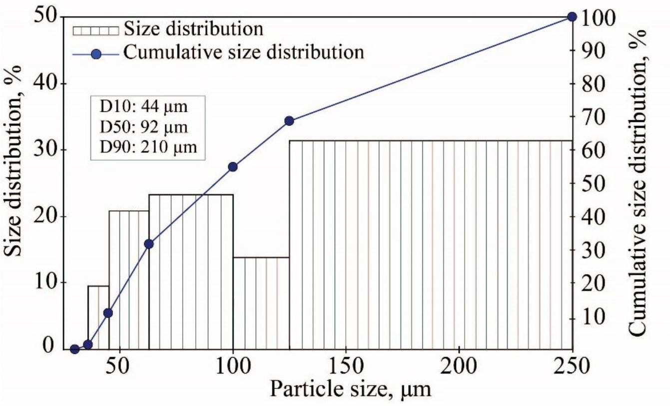

Fig. 1. Particle size distribution and the cumulative size distribution

The results obtained by sieve analysis show that particles smaller than 210 μm sieve are 90 %, whereas less than 10 % are particles smaller than 44 μm (dusty fraction).

The moisture content determined by calculating the mean value of the differences between the wet and dried masses (until constant mass was achieved) of three different samples was 3.07 wt. %.

The results of the bulk density of the individual particle size fractions are presented graphically in Figure 2. The smaller the particle size fraction, the smaller its bulk density.

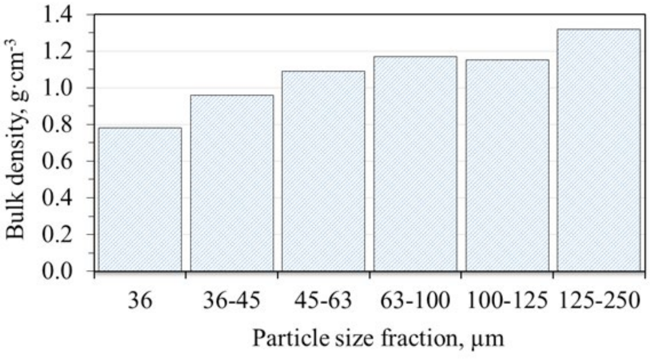

Fig. 2. Results of bulk density for different particle size fraction

Prior to XRF analysis, complex secondary raw materials were milled and pressed using the vertical hydraulic press to produce a homogeneous sample pellet. The results, as the average value of three different measurements, are presented in Table 1.

Table 1. Chemical composition.

Element	Cu	Zn	S	Ca	Si	Fe	Al	Other*
Concentration, wt. %	30.15	5.32	7.68	1.19	0.73	0.54	0.40	<0.5

*Other: Co, Ni, Mn, Cr, Bi, Sn, Sb, Ti, Pb

The results of XRD analysis presented in Figure 3 revealed that the main components of the sample are: CuS (JCPDS no. 96-900-8389), CuSO4·5H2O (JCPDS no. 96-900-8254), ZnO (JCPDS no. 96-210-7060), ZnS (JCPDS no. 96-153-8618) and 2CaO·SiO2 (JCPDS no. 96-210-3317). The copper phases with the highest match were CuS. Elements with content below 1% are under the detection limit of the XRD method, and therefore their phase composition is unknown.

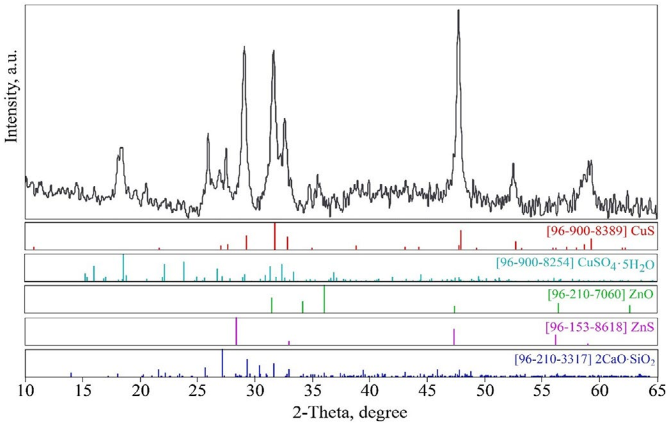

Fig. 3. XRD pattern of copper-zinc complex secondary raw material

Figure 4 shows representative SEM micrographs of the sample. Both the irregular-shaped particles with an average size of 0.1 µm that aggregate (Figure 4a) and the triclinic prismatic particles with an average size of about 0.1 µm in diameter and 1 µm in length (Figure 4b) are observed.

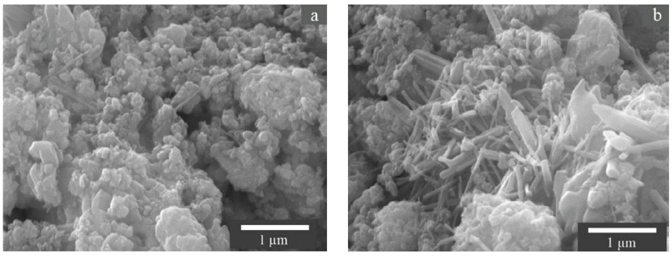

Fig. 4. SEM microphotographs of copper-zinc complex secondary raw material

The results of SEM-EDX analysis and mapping are shown in Figure 5. According to EDX mapping (Fig.5b), it is noticeable that Cu and S are evenly distributed on the particle surface and follow each other. The EDX spectra (Figure 5c) demonstrated that the sample mainly comprised Cu and S elements, which were attributed to the $CuSO_4·5H_2O$ (Spectrum 1) and CuS (Spectrum 2) phases, which is in accordance with morphology determinate in Figure 4.

4.2. Thermodynamic analysis

The diagrams illustrated in Figure 6, created using Hydra/Medusa software, represent the distribution of Cu and Zn species as a function of SO_4^{2-} concentration and pH values in the leaching solution under predefined conditions. The leaching factors, such as acid concentration and molal concentration, were aligned with findings from prior research by various authors (Željko Kamberović et al. 2018).

According to the diagram for copper (Figure 6a), at pH=1, the dominant Cu species that exist in the SO_4^{2-} concentration below 0.7 in the leaching solution are Cu^{2+} ions. As the concentration of SO_4^{2-} increases, the distribution of $CuSO_4$ increases, indicating that more copper ions bind with sulfate ions to form $CuSO_4$. At the same time, the distribution of Cu^{2+} ions decreases. The $CuSO_4$ is achieving its maximum distribution at a SO_4^{2-} concentration higher than 2.5 mol·dm^{-3}. These thermodynamic restrictions are represented in the diagrams of Figure 6 by the blue area.

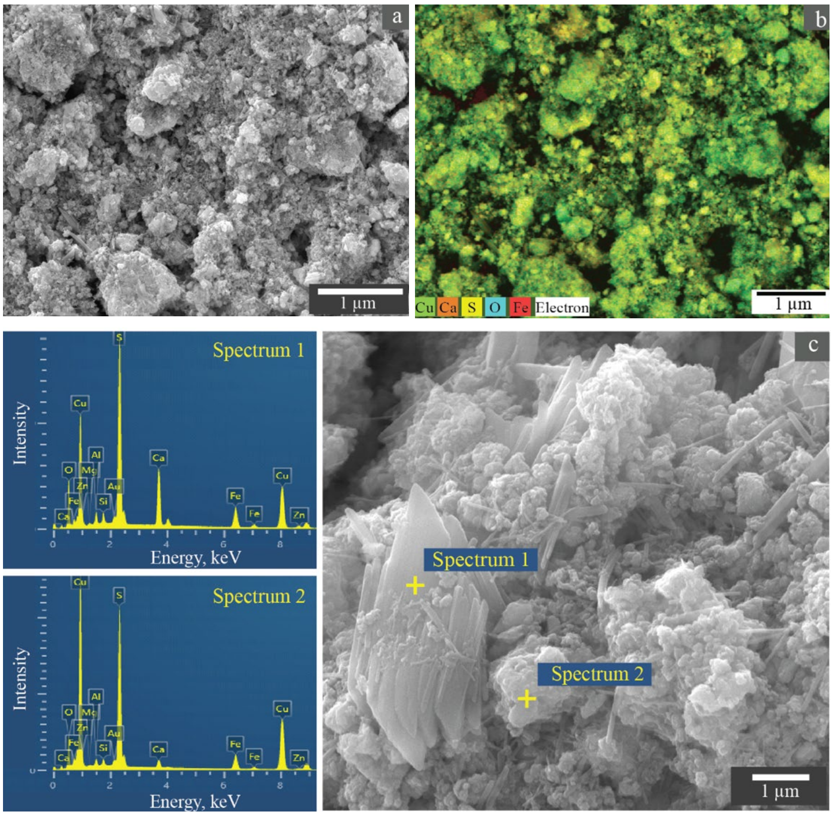

Fig. 5. SEM microphotograph of copper-zinc complex secondary raw material: (a), EDX mapping (b) and EDX spectra (c)

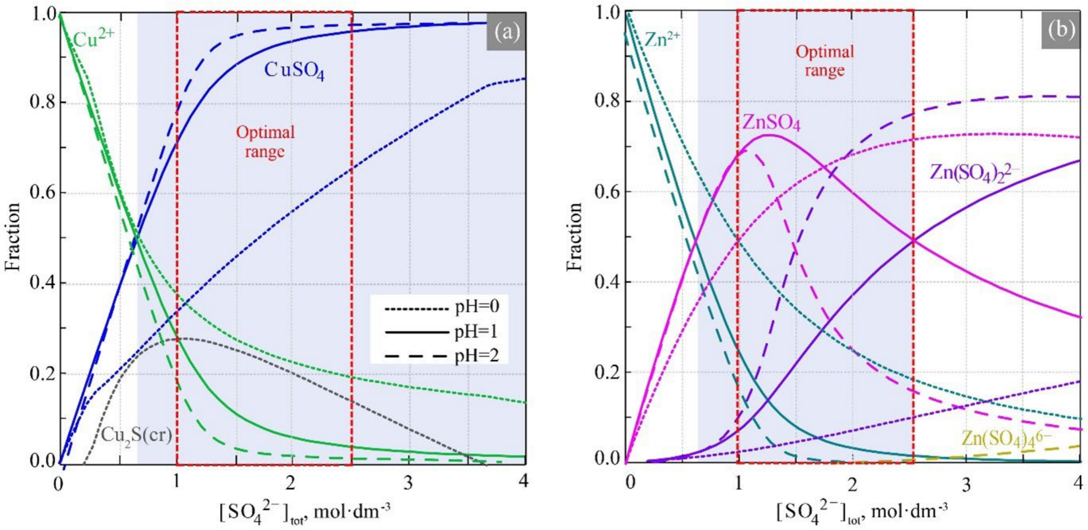

Fig. 6. Species distribution of Cu (a) and Zn (b) with over a range of SO$_4^{2-}$ concentrations at 50 °C. Conditions: $[Zn^{2+}]_{tot}$=0.2 mol·dm^{-3}, $[Cu^{2+}]_{tot}$=1.0 mol·dm^{-3}, $[H_2O_2]_{tot}$=0.8 mol·dm^{-3}, Eh=0.5 V

As seen from Figure 6b, below a SO$_4^{2-}$ concentration of 2.5 mol·dm^{-3} to 0.6 mol·dm^{-3} at pH=1, most Zn^{2+} ions are bonded to sulfate ions in the form of ZnSO$_4$. When the SO$_4^{2-}$ concentration is 2.5, the distribution of Zn(SO$_4$)$_2^{2-}$ complex and ZnSO$_4$ is equal. However, when SO$_4^{2-}$ concentration becomes higher than 2.5, Zn(SO$_4$)$_2^{2-}$ complex becomes the dominant species in the solution.

Under the analyzed range of SO$_4^{2-}$ concentrations, satisfactory leaching of both metals is not possible at pH values 0 and 2. Therefore, the optimal SO$_4^{2-}$ concentration range of 1–2.5 mol·dm^{-3} (marked by a dotted red line) at pH=1 is optimal for leaching of both metals.

To further investigate the existing species in leaching solution under the defined conditions, Pourbaix's diagrams (potential vs. pH) calculated by Hydra/Medusa software are illustrated in Figure 7.

The thermodynamic parameters, pH and potential, at which the metals (Cu and Zn) would be leached by 2 mol·dm^{-3} H$_2$SO$_4$, are deducted from Figure 7. It is noticeable in the Pourbaix diagram depicted in Figure 7a that to achieve the complete dissolution of copper, the solution potential must be higher than 0.5 V, suggesting that leaching requires highly oxidative conditions. On the other hand, a pH value above 3.5 is the value at which leached copper could precipitate as Cu$_3$SO$_4$(OH)$_4$, Cu$_4$SO$_4$(OH)$_6$, or CuO. Therefore, the copper leaching process must be implemented at a pH below 3.5 to ensure the complete copper dissolution process and avoid any precipitation reaction. This thermodynamic restriction is represented in the Pourbaix diagram of Figure 7a by the blue area.

For zinc (Figure 7b), in the region of a thermodynamic restriction for copper leaching shown in Figure 7a (potential greater than 0.5 V and a pH below 3.5), three chemical species are present, Zn^{2+}, ZnSO$_4$, and complex Zn(SO$_4$)$_2^{2-}$.

Thus, to leach both metals, the potential restriction for copper should be modified to pH below 1.2 so that zinc can be leached, while the restriction for potential could be maintained. The pH value below 1.2 and a potential greater than 0.5 V, as shown in Figure 5 by the doted red line, predict the complete leaching of not only copper but also zinc.

The diagrams in Figure 8 show the fractional presence of copper and zinc species in the leachate solution determined by the pH values under the defined conditions (calculated by Hydra/Medusa software).

According to the diagram (Figure 8a), the presence of Cu^{2+} ions and CuSO$_4$ at pH ranges from 0 to 3 (blue area) is evident when copper ions start to precipitate out as Cu$_3$SO$_4$(OH)$_4$.

The fraction diagram for zinc (Figure 8b) shows the presence of Zn^{2+} ions, Zn(SO$_4$)$_2^{2-}$ complex, and ZnSO$_4$ at pH ranges from 0 to 1.2 (blue area). With further increases in pH, the presence of Zn(SO$_4$)$_4^{6-}$ and Zn(SO$_4$)$_3^{4-}$, as well as Zn(SO$_4$)$_2^{2-}$ complex and ZnSO$_4$ is evident. Further increases in pH to values above 7.5 lead to the precipitation of Zn$_4$(OH)$_6$SO$_4$.

Therefore, the optimal pH range to leach both metals is from -1 to 1.2, marked in Figure 8 by a dotted red line.

The speciation diagram of the leaching solution (Figure 9) was constructed using the Hydra/Medusa software to evaluate the formed

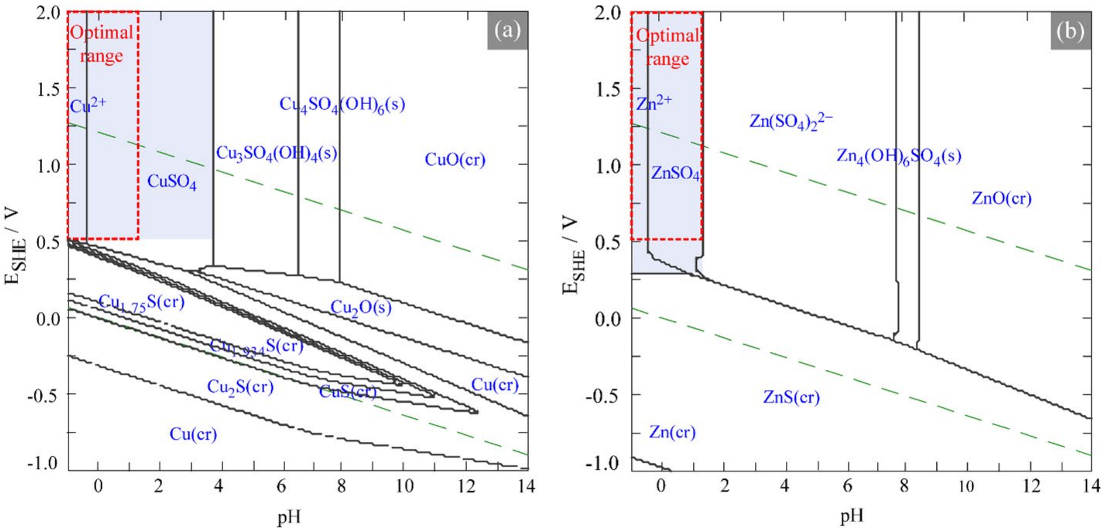

Fig. 7. Pourbaix's diagram of Cu (a) and Zn (b) in the leaching system. Conditions: $[Zn^{2+}]_{tot}$ =0.2 mol·dm^{-3}, $[Cu^{2+}]_{tot}$ = 1.0 mol·dm^{-3}, $[SO_4^{2-}]_{tot}$ = 2.0 mol·dm^{-3}, $[H_2O_2]_{tot}$ = 0.8 mol·dm^{-3}, T=50 °C.

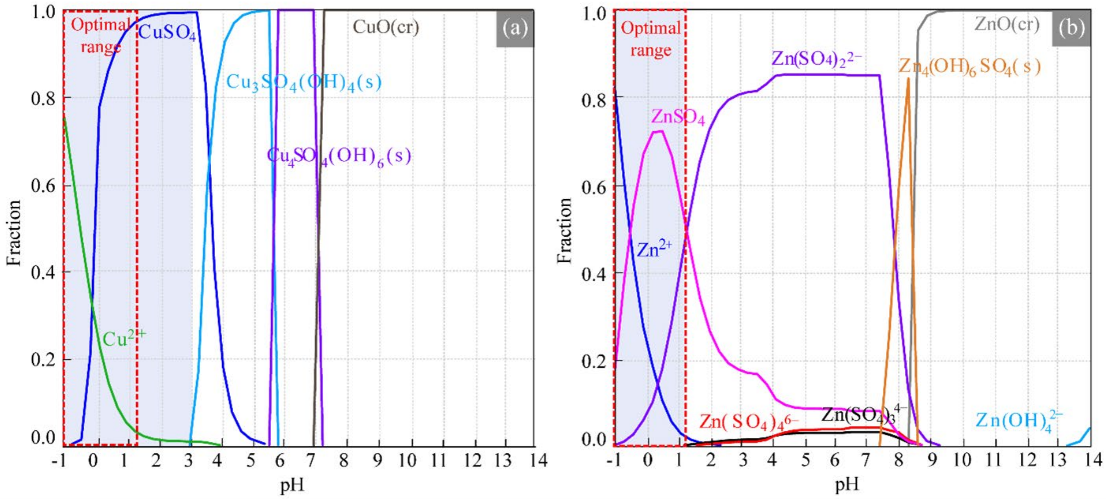

Fig. 8. Speciation fraction of Cu (a) and Zn (b) at various pH from -1 to 14 under the conditions: $[Zn^{2+}]_{tot}$ =0.2 mol·dm^{-3}, $[Cu^{2+}]_{tot}$ = 1.0 mol·dm^{-3}, $[SO_4^{2-}]_{tot}$ = 2.0 mol·dm^{-3}, $[H_2O_2]_{tot}$ = 0.8 mol·dm^{-3}, Eh=0.5 V, T=50 °C.

species. Additionally, based on the information given in the following figure, thermodynamically favored reactions in the system were determined.

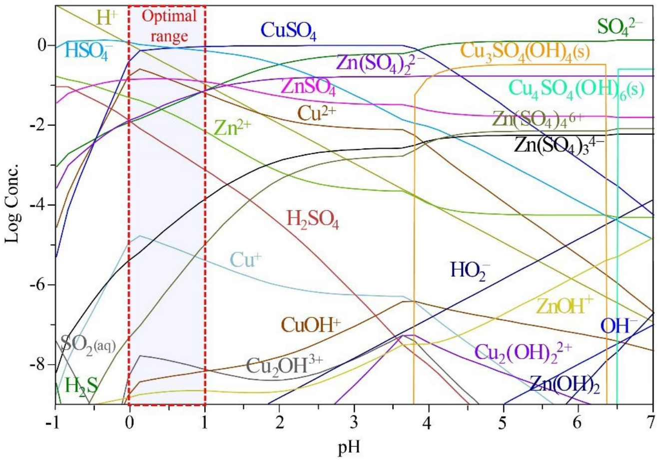

Fig. 9. Speciation diagram for the leaching system. Conditions: $[Zn^{2+}]_{tot}$ =0.2 mol·dm^{-3}, $[Cu^{2+}]_{tot}$ = 1.0 mol·dm^{-3}, $[SO_4^{2-}]_{tot}$ = 2.0 mol·dm^{-3}, $[H_2O_2]_{tot}$ = 0.8 mol·dm^{-3}, Eh=0.5 V, T=50 °C.

According to these figures, the most stable products of sulfuric acid dissociation were H^+ and HSO_4^-. In addition, under leaching conditions, the primary product formed from ZnS and CuS leaching was $ZnSO_4$ and $CuSO_4$ aqueous.

Considering thermodynamics predictions, the following equations are proposed:

CuS(s) + H2SO4(ia) + 3 H2O2(l) = CuSO4(ia) + 4H2O(l) + SO2(g) (1)

CuS(s) + H2SO4(ia) + H2O2(l) = CuSO4(ia) + 2H2O(l) + S(s) (2)

ZnS(s) + H2SO4(ia) + 3H2O2(l) = ZnSO4(ia) + 4H2O(l) + SO2(g) (3)

ZnS(s) + H2SO4(ia) + H2O2(l) = ZnSO4(ia) + 2H2O(l) + S(s) (4)

1.25ZnS(s) + H2SO4(ia) + H2O2(l) = 1.25ZnSO4(ia) +H2O(l) + H2S(a) (5)

ZnO(s) + H2SO4(ia) + 2H2O2(l) = ZnSO4(ia) + 3H2O(l) + O2(g) (6)

CuO(s) + H2SO4(ia) + 2H2O2(l) = CuSO4(ia) + 3H2O(l) + O2(g) (7)

$H_2S(a)+H_2O_2(l)=2H_2O(l)+S(s)$ (8)

By calculating the Gibbs free energy change (Δ_rG^θ) using HSC Chemistry software (Table 2), energetically favorable reactions at a given temperature were determinated.

Table 2 shows negative values of the standard Gibbs energies, which indicate that these reactions (Eqs. (1)–(8)) take place in the direction of product formation and should be spontaneous at temperatures from 0 to 100 °C. According to equations (2) and (4), is evident that there is the formation of a non-soluble compound sulfur in the system. Products

Table 2. Δ_rG^θ values of Equations (1) – (8)

T, °C	ΔrGθ, kJ							
	Eq. (1)	**Eq. (2)**	**Eq. (3)**	**Eq. (4)**	**Eq. (5)**	**Eq. (6)**	**Eq. (7)**	**Eq. (8)**
0	-764.77	-234.67	-835.14	-305.04	-269.39	-296.18	-275.98	-327.43
10	-764.96	-233.48	-835.38	-303.90	-268.03	-296.53	-276.37	-326.93
20	-765.22	-232.36	-835.64	-302.78	-266.72	-296.90	-276.83	-326.39
30	-765.54	-231.32	-835.92	-301.70	-265.45	-297.31	-277.37	-325.80
40	-765.93	-230.34	-836.23	-300.64	-264.21	-297.74	-277.97	-325.18
50	-766.39	-229.44	-836.56	-299.62	-263.00	-298.20	-278.64	-324.54
60	-766.91	-228.61	-836.92	-298.61	-261.81	-298.69	-279.39	-323.88
70	-767.51	-227.85	-837.30	-297.64	-260.64	-299.20	-280.20	-323.19
80	-768.17	-227.15	-837.71	-296.69	-259.49	-299.74	-281.08	-322.49
90	-768.89	-226.53	-838.13	-295.77	-258.35	-300.30	-282.03	-321.77
100	-769.69	-225.98	-838.59	-294.88	-257.23	-300.89	-283.05	-321.05

of copper and zinc leaching in sulfuric acid (Eqs. (1)–(6)) are sulfates of these elements. This indicated the involvement of the sulfate ion (or HSO^{4-} anion), which, along with the $ZnSO_4$ and $CuSO_4$ ions (both larger molecules), must diffuse through the sulfur layer. Therefore, the diffusion of these species can be a limiting step in the reaction. Also, dissolution of ZnS follows an indirect reaction of oxidation, which involves acid dissolution (Eq. 5) and the release of H_2S(a) and its further oxidation to elemental S(s) by H_2O_2 from leaching solution (Eq. 8). However, comparing the energies values between equations shows that the reactions with SO_2(g) as product are more thermodynamically possible than those with S(s) as product. Based upon the Gibbs energy (Table 2), values of Equations (1)–(8), and the information given in Figure 9, the leaching of ZnS and CuS was indicated to occur by sulfation of zinc and copper ions and sulfur oxidation.

The leaching process of copper and zinc was successfully theoretically optimized by its design based on a thermodynamic study that deduced its optimal parameters: pH=1 and potentials greater than 0.5 V for efficient leaching in sulfuric acid solutions (concentration 2 mol·dm^{-3}) with the addition of H_2O_2.

5. Conclusion

This study examined the complex secondary raw material, including its physical and chemical characteristics. In addition to the material characterization, a detailed thermodynamic analysis of the investigated system was carried out to understand the complex reaction system and establish the optimal process parameters for leaching copper and zinc using oxidative sulfuric acid leaching.

According to the results of the study, hydrometallurgical processes can be used to effectively extract copper and zinc from the complex secondary raw materials under defined conditions (SO_4^{2-} concentrations of the leaching system from 1-2.5 mol·dm^{-3}, pH values less than 1.2, and Eh higher than 0.5 V). The results also showed that the leaching process is relatively insensitive to temperature variations. The oxidizing agent's optimal consumption should be the main goal of the further leaching process's optimization.

References

Ahmed, I.M., A.A. Nayl, and J.A. Daoud. "Leaching and Recovery of Zinc and Copper from Brass Slag by Sulfuric Acid." Journal of Saudi Chemical Society 20 (2016) s280-s285.

Antonijević, M.M., M.D. Dimitrijević, Z.O. Stevanović, S.M. Serbula, and G.D. Bogdanovic. "Investigation of the Possibility of Copper Recovery from the Flotation Tailings by Acid Leaching." Journal of Hazardous Materials 158, no. 1 (2008): 23–34.

Asadi, Tahereh, Asghar Azizi, Jae-chun Lee, and Mohammad Jahani. "Leaching of Zinc from a Lead-Zinc Flotation Tailing Sample Using Ferric Sulphate and Sulfuric Acid Media." Journal of Environmental Chemical Engineering 5, no. 5 (2017): 4769–75.

Cao, Lei, Ya-long Liao, Gong-chu Shi, Yu Zhang, and Mu-yuan Guo. "Leaching Behavior of Zinc and Copper from Zinc Refinery Residue and Filtration Performance of Pulp under the Hydrothermal Process." International Journal of Minerals, Metallurgy, and Materials 26, no. 1 (2019): 21–32.

Chen, Tao, Chang Lei, Bo Yan, and Xianming Xiao. "Metal Recovery from the Copper Sulfide Tailing with Leaching and Fractional Precipitation Technology." Hydrometallurgy 147–148 (2014): 178–82.

Kamberović, Željko, Milisav Ranitović, Marija Korać, Zoran Andjić, Nataša Gajić, Jovana Djokić, and Sanja Jevtić. "Hydrometallurgical Process for Selective Metals Recovery from Waste-Printed Circuit Boards." Metals 8, no. 6 (2018): 441.

Karimov, K. A., S. S. Naboichenko, A. V. Kritskii, M. A. Tret'yak, and A. A. Kovyazin. "Oxidation Sulfuric Acid Autoclave Leaching of Copper Smelting Production Fine Dust." Metallurgist 62, no. 11–12 (2019): 1244–49.

Nozhati, Ramezan Ali, and Asghar Azizi. "Leaching of Copper and Zinc from the Tailings Sample Obtained from a Porcelain Stone Mine: Feasibility, Modeling, and Optimization." Environmental Science and Pollution Research 27, no. 6 (2019): 6239–52.

Puigdomenech, I. HYDRA (Hydrochemical Equilibrium-Constant Database) and MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) Programs. Royal Institute of Technology, Stockholm, 200, http://www.kemi.kth.se/medusa/

Roine, A., and P. Lamberg. "HSC Chemistry, vers. 9." Outotec Pori (2020). https://www.hsc-chemistry.com/

Santos, Sílvia M.C., Remígio M. Machado, M. Joana Correia, M. Teresa Reis, M. Rosinda Ismael, and Jorge M.R. Carvalho. "Ferric Sulphate/Chloride Leaching of Zinc and Minor Elements from a Sphalerite Concentrate." Minerals Engineering 23, no. 8 (2010): 606–15.

Wang Ben, Meng Yun. Recovery method of copper and zinc oxide from waste copper-zinc catalyst, Patent: CN1258752A (1998).

Zhang Xiaoyang, Hu Zhibiao, Ling Hua Zhao, Hu Gaorong, Qiu Chuangui, Liu Jinglin, Li Qian, Huang Hong, Xu Xiaofeng. Application method of waste copper-based catalyst to preparing catalyst for preparing hydrogen from methanol, Patent: CN102125851B (2010).