TWO-STAGE LEACHING OF GERMANIUM FROM COPPER CAKE UNDER SUBSEQUENT NON-OXIDIZING AND OXIDIZING CONDITIONS

M. Drzazga *, S. Kozłowicz, I. Maj, S. Orda, A. Radoń, M. Ciszewski

Łukasiewicz Research Network – Institute of Non-Ferrous Metals, Gliwice, Poland

Abstract

Many world economies, such as the EU and the USA, consider germanium to be a critical raw material. Therefore, the development of its recovery from new sources is becoming increasingly important. The leaching of copper cake, produced during the purification of zinc electrolytes, in sulfuric acid solution is presented in the paper. The cake contained 24.7% Cu, 21.2% Cd, 16.3% Zn, 4.50% Pb, 3.96% Ni, 3.22% Co and 231 ppm Ge. The leaching of wet and dried material was examined. It was found that the highest germanium recovery was obtained in a two-stage process consisting of leaching under non-oxidizing conditions followed by pH adjustment with sodium carbonate and by oxidizing leaching of the residue from the first stage. In the first stage of leaching in 12.5% sulfuric acid and subsequent pH adjustment to >2.0 reduced germanium leaching yield to <10%. During oxidizing leaching of remaining residue in 15% sulfuric acid >99% of germanium was leached. The final solution contained 30 mg/dm³ Ge and 72.4 g/dm³ Cu. Germanium can later be recovered from the solution by precipitation with tannic acid or solvent extraction.

Keywords: Germanium recovery; Zinc metallurgy; Zinc electrolyte purification; Leaching

1. Introduction

Germanium is considered an important element for various emerging high-tech applications, including optical fibers, night-vision equipment, semiconductors, and solar panels. Its global refinery production over the last decade is estimated at 120-150 tonnes per annum, with China accounting for over 75% of the total amount [1-3]. Due to its limited availability and significant economic importance germanium is considered a critical raw material by many of the world's leading economies, including the USA and the European Union.

Nowadays zinc concentrates are the main germanium source and it is estimated that only 3% of the germanium contained is recovered from zinc-based materials. So, there is still a lot of room for improvement in recovery technologies. Nowadays, the majority of zinc (over 80%) is produced by hydrometallurgical techniques, while some plants still use pyrometallurgical technologies, including the Imperial Smelting Process. Typical germanium-bearing materials from zinc hydrometallurgy contain up to 0.36% Ge [4].

The first step in germanium recovery is the leaching of the zinc production by-products. Depending on the material composition, different inorganic and organic acids as well as their mixtures can be used in this step [5]. Most often applied leaching media include aqueous solutions of: sulfuric [6-10], hydrochloric [9, 11], oxalic [12] acids, or sodium hydroxide [13]. Oxidizing agents such as air [14], oxygen [15], nitrates [16], persulfate [17], chlorates [11, 18], and permanganate [19] are also used to enhance germanium leaching yield. Reduction leaching with hydrazine sulfate has also been investigated [20]. Then, germanium can be recovered from the solution by precipitation with tannic acid [21-23], cementation using iron [24] or zinc [25] dust, solvent extraction [26-29] as well as membrane techniques [30-32].

Mixtures of mineral and organic acids also seem to be effective in germanium extraction. Song et al. [33] investigated the leaching of zinc-smelting residue (0.5% Ge, 18.3% Cu, 17,7% Zn, 15,2% Si, 8,5% Pb, 6,5% Al, 4,1% Fe, 3,3% As, 0,4% Ga). Leaching efficiencies of germanium for pure solutions of sulfuric or tartaric acid were ca. 65% and <30%, respectively. Application of their mixture allowed to achieve >90% yield.

In some cases, one-step leaching may not be efficiently applied for germanium recovery due to the complex material composition. Then, the sequence of leaching-filtration unit operations should be used. To

process zinc refinery residue (0.47% Ge, 12.6% Si, 6.30% Fe, 5.93% Zn, 4.18% Pb, 0.15% Ga) Rao et al. [34] applied subsequent leaching with H_2SO_4, HCl and NaOH aqueous solutions to leave ca. 92% and 98% Ge in the leaching residues from the first two steps and to leach all the remaining Ge in the last alkaline step. Sulfuric acid leaching was used to extract zinc and gallium, while hydrochloric acid leaching removed lead from the solids. A two-step method, excluding HCl leaching, for processing the similar Ge source was described earlier [35].

Li et al. [18] applied a two-step process for atmospheric leaching of zinc distillation slag (0.2626% Ge, 35.26% Fe, 22.85% Zn, 15.68% Pb, 1.55% Cu, 0.1757% In). In the first step, sulfuric acid with $KMnO_4$ was used to extract zinc, while in the second step, $NaClO_3$ was added to the sulfuric acid. Germanium leaching yields in both steps were 1.8% and 90.7%, respectively.

Liu et al. [36] investigated the subsequent leaching of zinc refinery residue (0.36% Ge, 24% Zn, 9.1% SiO_2, 7.9% Fe, 5.6% Cu, 0.46% Pb, 0.36% Ge, 0.27% Ga) with the sulfuric-tannic acid mixture and oxalic acid solutions. Firstly, most of the zinc, copper, and iron were extracted from the residue. The addition of tannic acid during the initial step reduced the Ge leaching yield to 2.7% and allowed it to reach 99% in oxalic acid leaching.

Despite the limited resources, the range of germanium-bearing materials is quite broad. These sources can be characterized by different compositions, resulting from different technologies of zinc production as well as diverse compositions of the zinc concentrates. One of the streams in which germanium accumulation is observed is the residue obtained during the purification of zinc electrolyte. During the production of electrolytic zinc some impurities, including germanium, need to be removed before zinc electrolysis as they have a negative impact on process efficiency and final product quality. This is done by adding zinc powder and other compounds (As, Sb, Cu), increasing purification efficiency. The process is usually composed of two or more steps.

In the past, the possibility of germanium recovery from various streams of the Çinkur zinc plant (Turkey) was evaluated [37]. Kul and Topkaya [6] investigated the leaching of stockpiled copper cake (700 ppm Ge, 15.33% Cu, 15.63% Zn, 12.6% As, 3.42% SiO_2, 2.62% Pb, 1.66% Cd, 1.33% Ni, 0.64% Co, 0.35% Fe, 0.18% Sb) using a sulfuric acid solution. They found that two approaches can be used:

selective leaching without an oxidant at 40-60°C with 100 g/L H_2SO_4 or collective leaching with air pumping at 85°C with 150 g/L H_2SO_4. Germanium leaching yields for these approaches were 78% and 92,7% respectively.

Data concerning germanium recovery from zinc electrolyte purification residues are limited and focus on residues with a quite significant Ge content. There are no reports on germanium recovery from sources containing <400 ppm Ge. Moreover, more attention should be paid to the difference between fresh and stockpiled materials as oxidation can cause significant differences in phase composition and leaching behavior. Therefore, the leaching of copper cake obtained during zinc electrolyte purification was investigated. The objective of the study was to compare the leaching yields of the copper cake in both fresh and dried form. To enhance germanium recovery, a two-stage process including sulfuric acid leaching with subsequent pH adjustment without oxidant addition followed by leaching under oxidizing conditions was examined.

2. Experimental
2.1. Materials

The copper cake from the second stage of crude zinc electrolyte purification with zinc dust was collected from a Polish zinc smelter. A more detailed description of the cake origin is provided in our previous work [38]. Its chemical and phase composition are presented in Table 1 and Fig. 1, respectively. Part of the material was dried at 70°C for 8 hours before investigation. Dried material due to partial oxidation can also resemble stockpiled cake.

The main components of the cake were copper, cadmium, zinc, lead, nickel, and cobalt. Cadmium was mostly present as hydroxide – $[Cd(OH)_2]$, however, it was also found as hydrated cadmium hydroxide sulfate $[Cd_4SO_4(OH)_6 \cdot 1.5H_2O]$ and edwardsite $[Cu_3Cd_{1.89}Zn_{0.11}(SO_4)_2(OH)_6 \cdot 4H_2O]$ in the wet material and as niedermayrite $[CdCu_4(SO_4)_2(OH)_6 \cdot 4H_2O]$ in the dried material. Copper was found mainly in the form of metallic Cu and copper(I) oxide $[Cu_2O]$. Moreover, it was also present in the wet cake as intermetallic $Cu_{0.255}Zn_{0.745}$ and edwardsite, while after dying as niedermayrite and christelite $[Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4H_2O]$. Zinc was found in $Cu_{0.255}Zn_{0.745}$ and edwardsite before drying, whereas in christelite after thermal treatment. In both cases, the main lead phase was massicot [PbO]. Due

Table 1. Composition of the wet copper cake

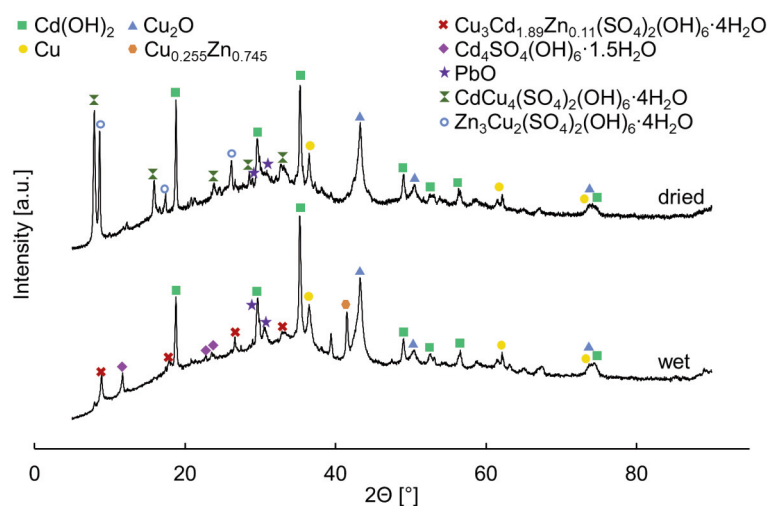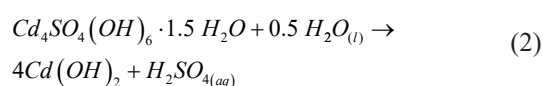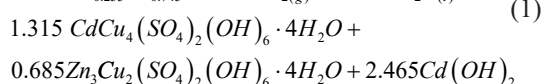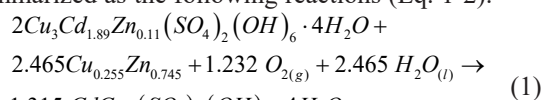| Element	Cu	Cd	Zn	Pb	Ni	Co	Ge	Dry loss
Content [% wt.]	24.7	21.2	16.3	4.50	3.96	3.22	231 ppm	38.7

Figure 1. *XRD patterns of wet and dried copper cake*

to the low content, it was not possible to determine in which phases nickel, cobalt, and germanium (231 ppm) were present. However, as the copper cake is a product of the cementation process with zinc dust, based on previous germanium cementation tests [24,39], it might be expected that Ge would be present as a mixed metallic (Ge) and oxide (GeO$_2$) form. Dry loss factor resembles, both, mass loss due to moisture evaporation and mass gain due to oxidation - Cu$_{0.255}$Zn$_{0.745}$ peak is present only for the wet cake, while niedermayrite and christelite are only present for the dried cake. Due to its low content (231 ppm), it was not possible to determine the form in which germanium was present in the cake.

It could be that the oxidation of the cake took place during the drying process. Intermetallic Cu$_{0.255}$Zn$_{0.745}$ was present only in the dried cake, while the edwardiste phase was transformed to niedermayrite and christelite ones. It was also observed that the intensity of the Cd(OH)$_2$ phase with respect to other intensities of other phases (e.g. Cu, Cu$_2$O) increased, suggesting that the mass share of cadmium hydroxide increased. This could be related to the thermal decomposition of hydrated cadmium hydroxide sulfate, associated with the formation of sulfuric acid catalysing oxidation reactions, as well as with the abovementioned phase transitions. The most important phase transition reactions can be summarized as the following reactions (Eq. 1-2):

$$2Cu_3Cd_{1.89}Zn_{0.11}(SO_4)_2(OH)_6 \cdot 4H_2O +$$
$$2.465Cu_{0.255}Zn_{0.745} + 1.232\ O_{2(g)} + 2.465\ H_2O_{(l)} \rightarrow \quad (1)$$
$$1.315\ CdCu_4(SO_4)_2(OH)_6 \cdot 4H_2O +$$
$$0.685Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4H_2O + 2.465Cd(OH)_2$$

$$Cd_4SO_4(OH)_6 \cdot 1.5\ H_2O + 0.5\ H_2O_{(l)} \rightarrow \quad (2)$$
$$4Cd(OH)_2 + H_2SO_{4(aq)}$$

2.2. Experimental method

The leaching tests were performed using sulfuric acid (98%, Avantor) and hydrogen peroxide (30%, Avantor). The volume of the acid solution was 600 cm^3 for all trials. The influence of temperature, time, initial acid concentration, solid-to-liquid phase ratio (S:L), and the amount of oxidant was examined. The initial sulfuric acid solutions (5-20 % wt.) were prepared by diluting concentrated acid in deionized water (<0.1 µS/cm). Then, a pure acid solution was heated to the desired temperature (25-90°C) and a weighted portion of copper cake (120 g for S:L=1:5 and 200 g for S:L=1:3 based on the mass after drying) was added. In the case of oxidant addition, H$_2$O$_2$ was added in portions – 2.5 cm^3 portion every 3 minutes. In oxidative leaching tests of the wet cake pure oxygen gas (≥99.5%, Siad) was added at constant flow rate. The suspension obtained after each test was mixed for a set time and then vacuum-filtered using a Buchner funnel.

In selected tests, the pH of the suspension was adjusted with solid sodium carbonate (99.8%, Eurochem) before filtration. Na$_2$CO$_3$ was selected as the potentially cheapest industrial option for pH control. For the second stage leaching of the residue from the first stage with the addition of oxygen gas (Siad) was performed.

The dry loss was determined by drying a sample of ca. 10g at 70°C until constant weight using a moisture analyzer - the procedure was repeated 3 times.

The Gibbs free energies (ΔG^0_{298}) of possible reactions were estimated using HSC Chemistry 9.6.1 software (Metso, Finland) Reaction Equations module and the built-in database.

2.3. Analysis and Characterisation

X-ray diffraction (XRD) was used for the analysis of the copper cakes and residues. XRD patterns were collected using an X-ray diffractometer Rigaku MiniFlex 600 (Rigaku, Tokyo, Japan) with a copper tube Cu Kα (λ = 0.15406 nm), a tube voltage of 40 kV, and a current of 15 mA, using a D/teX Ultra silicon strip detector.

The concentrations of elements in solutions were analyzed using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry; Optima 5300 V, PerkinElmer). Solid samples were chemically dissolved before analysis.

3. Results and discussion
3.1. Leaching of dried cake

In the first part, the leaching of dried copper cake in sulfuric acid was investigated. The influence of process temperature, time, and initial acid concentration was examined. The results are presented in Figure 2.

It should be noted that temperature influenced the leaching yield of germanium – it increased from 53% at 25°C to 92% at 90°C. There was no significant impact of temperature on the leaching yield of other investigated elements – the leaching yield of Cd, Co,

and Ni was 95-99%, Zn – 88-96%, and Cu – 75-81%. The analysis of process time impact on leaching yield led to the conclusion that the leaching process reached equilibrium in less than 30 minutes as the yield for longer processes remained almost stable.

It was also clear that the initial acid concentration influenced Cu, Zn, and Ge. Germanium leaching yield increased from 6% at 5% H_2SO_4 to 98% at 20% acid. Zinc leaching yield reached 95% at 15% sulfuric acid and all other investigated concentrations were lower, whereas copper yield increased to 77-80% at H_2SO_4 concentrations lower than 12,5%. Leaching tests performed at a solid-liquid ratio of 1:3 also showed that Cd, Ni, Co, and Zn leaching yields increased similarly as initial acid concentration increased, whereas Cu and Ge leaching was noticed for sulfuric acid concentrations higher than 12.5%.

Under the conditions investigated, the highest germanium leaching yield was 98%. The acid concentration and the S:L had the most significant impact on the yield. The process temperature also influenced the germanium leaching. However, it should be noted that almost all the main elements present in the copper cake were leached. This can lead to additional problems later on during the separation of elements. The maximum copper leaching yield was 80%. This was due to only partial Cu oxidation during the drying process. Part of the copper in the dried
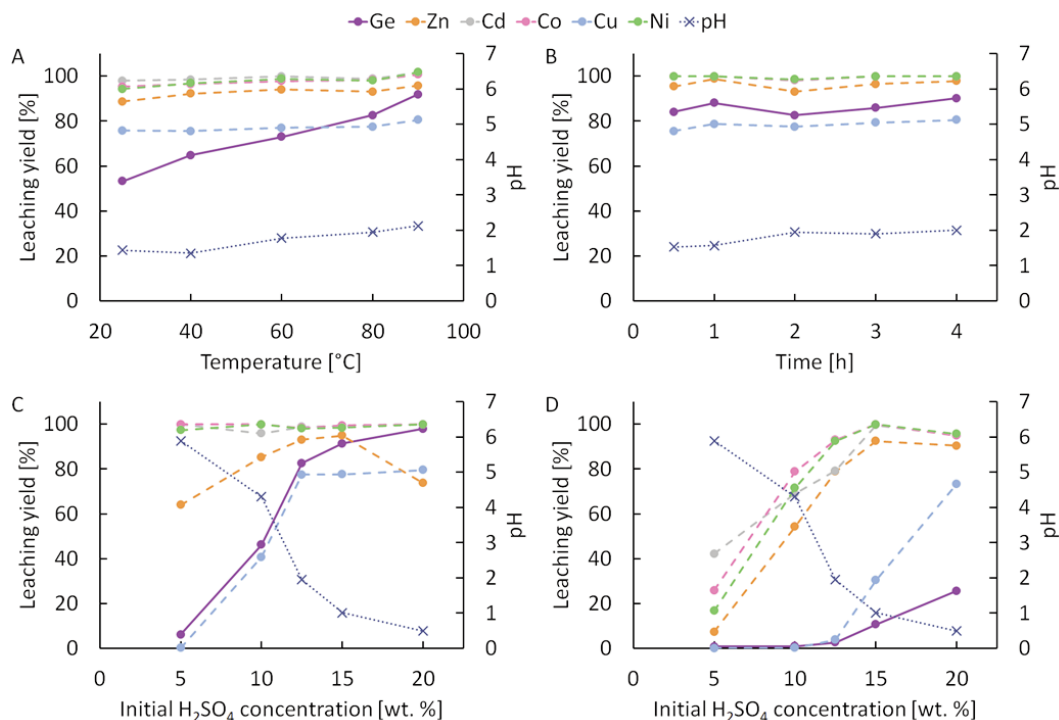

Figure 2. *Leaching yields of the main components from dried copper cake under different conditions: a) varying temperature (2h, 12.5% wt. H_2SO_4, S:L 1:5), b) varying process time (80°C, 12.5% wt. H_2SO_4, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5), d) varying initial acid concentration (2h, 80°C, S:L 1:3)*

cake was still present in the metallic or Cu_2O phases, which were not prone to leaching without an oxidant. The amount of Cu_2O phase could have been partially reduced by a disproportionation reaction in a slightly acidic solution. However, the rate of this reaction was limited due to a very low solubility of Cu^+ ions. The leachability of germanium and copper was found to be correlated – especially during tests with different initial acid concentrations (Figure 2cd). It suggested that germanium is bonded with copper. As the copper in the dried cake was not fully oxidized it was predicted that the addition of oxidant would increase the Cu leachability and, therefore, the Ge leaching yield. In the next step, the leaching of the dried cake under oxidative conditions was examined. Hydrogen peroxide was used as an oxidant. The results of the tests are presented in Figure 3. The compositions of solution and residues obtained after non-oxidative and oxidative leaching of the dried copper cake are presented in Table 2.

The addition of hydrogen peroxide during the leaching process increased the leaching yield of copper, however, it had a negative (for 12.5% H_2SO_4) or no impact on germanium leaching - at lower acid concentration H_2O_2 addition reduced the yield to 68% for the highest investigated oxidant dose. Therefore, it seems that the leaching of the dried cake under

oxidative conditions was not germanium selective and even led to only partial Ge leaching. Higher oxidant doses reduced the germanium yield. It might be explained by the formation of GeO_2, which has very limited solubility, especially for pH>2.

3.2. Leaching of wet cake

The second part of the investigation covered the leaching of wet copper cake in sulfuric acid. The impact of process temperature, time, and initial acid concentration was examined. The results are presented in Figure 4.

It can be observed that copper was not leached from the wet cake. Copper in metallic or Cu_2O phase is not prone to leaching under non-oxidizing conditions. Therefore, it can be clearly stated that drying caused copper oxidation, which is also confirmed by XRD analysis (Fig. 1). Germanium is only partially leached from the wet cake. The highest leaching yield under the conditions investigated was 51%. This is an undesirable situation as germanium should be potentially later recovered from both the solution and the residue. In the case of other investigated elements, it is possible to achieve almost complete (zinc, cadmium) or > 80% (nickel, cobalt) leaching yield.
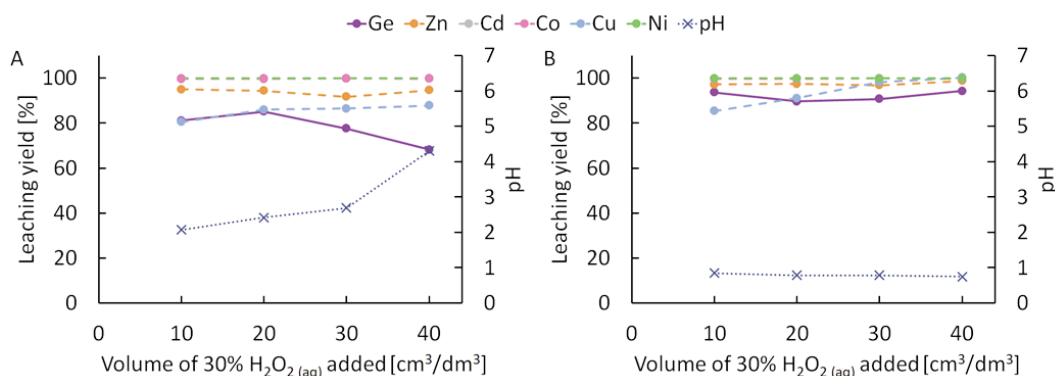

Figure 3. *Leaching yields of the main components from dried copper cake under oxidative conditions – different H_2O_2 doses a) (80°C, 2h, 12.5% wt. H_2SO_4, S:L 1:5), b) (80°C, 2h, 15% wt. H_2SO_4, S:L 1:5)*

Table 2. *Composition of the residue and solutions obtained after leaching of dried copper cake under non-oxidative and oxidative conditions (80°C, 2h, 12.5% H_2SO_4, S:L 1:5, 40 cm³/dm³ for oxidative leaching)*

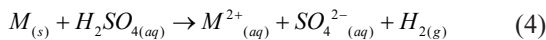| Element	Cu	Cd	Zn	Pb	Ni	Co	Ge*	Dry loss	Mass/volume
non-oxidative leaching									
Concentration in residue [% wt.]	27.0	2.15	3.58	20.4	0.22	0.16	617	54.9	16.98 g
Concentration in solution [g/dm³]	31.0	35.0	17.8	0.02	2.70	4.00	46.4	-	570 cm³
oxidative leaching									
Concentration in residue [% wt.]	2.39	2.09	3.86	24.5	0.18	0.13	679	54.2	14.97 g
Concentration in solution [g/dm³]	33.4	34.8	17.2	0.02	2.74	4.00	36.4	-	600 cm³

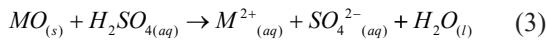** Ge concentrations in [ppm] and [mg/dm³]*
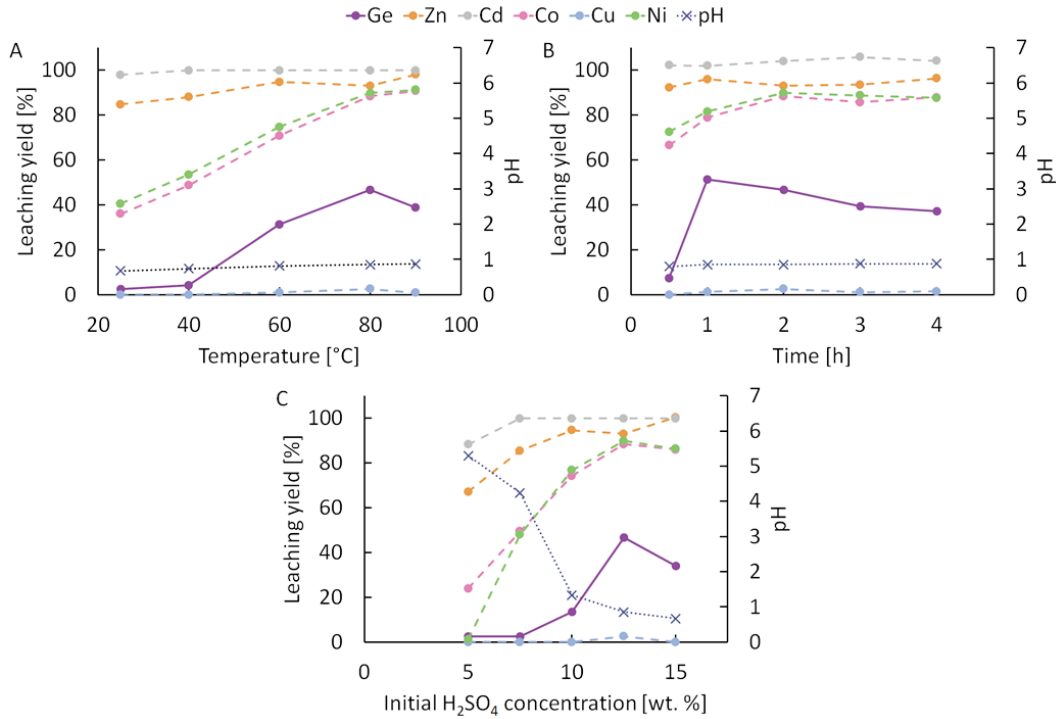
Figure 4. *Leaching yields of the main components from wet copper cake under different conditions: a) varying temperature (2h, 12.5% wt. H_2SO_4, S:L 1:5), b) varying process time (80°C, 12.5% wt. H_2SO_4, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5)*

Zinc, cadmium, nickel and cobalt, no matter if they are metallic or bivalent, would be dissolved in sulfuric acid as they form soluble sulfates (Eq. 3). Moreover, their reduction potentials were negative, and therefore their metallic forms reacted with acids to form respective bivalent sulfates and hydrogen gas (Eq. 4). Therefore, regardless of the form of the cake (wet or dried) they were leached in the first non-oxidative step and to achieve high leaching yields without the addition of an oxidant.

$$MO_{(s)} + H_2SO_{4(aq)} \rightarrow M^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + H_2O_{(l)} \quad (3)$$

$$M_{(s)} + H_2SO_{4(aq)} \rightarrow M^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + H_{2(g)} \quad (4)$$
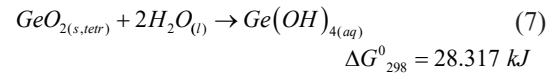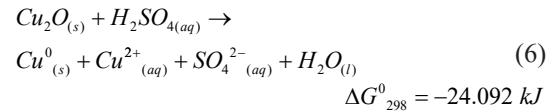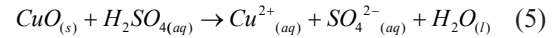
where M is Zn, Cd, Ni, Co.

Similarly, lead would also react with sulfuric acid according to aforementioned reaction, but to form insoluble $PbSO_4$. Therefore, the lead was accumulated in the solid phase at all leaching stages.
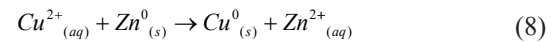
In the case of copper and germanium only fully oxidized forms, i.e. Cu(II) and Ge(IV), would be dissolved in sulfuric acid (Eq.5). Metallic Cu and Ge as well as monovalent copper would accumulate in the solid phase unless an oxidant was added. In highly acidic conditions Cu_2O would disproportionate to form metallic and bivalent forms (Eq.6) [40]. In acidic and neutral solutions (pH 1.0-8.0) germanium is present as neutral species of germanic acid – $Ge(OH)_4$ (Eq.7) [41].
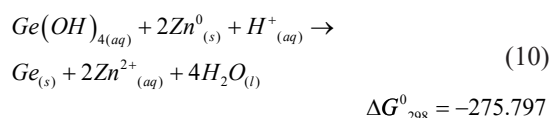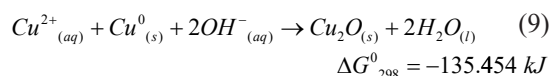
$$CuO_{(s)} + H_2SO_{4(aq)} \rightarrow Cu^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + H_2O_{(l)} \quad (5)$$

$$Cu_2O_{(s)} + H_2SO_{4(aq)} \rightarrow$$
$$Cu^0_{(s)} + Cu^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + H_2O_{(l)} \quad (6)$$
$$\Delta G^0_{298} = -24.092 \; kJ$$

$$GeO_{2(s,tetr)} + 2H_2O_{(l)} \rightarrow Ge(OH)_{4(aq)} \quad (7)$$
$$\Delta G^0_{298} = 28.317 \; kJ$$

Germanium dioxide solubility in aqueous solution depends on its crystal structure. Hexagonal GeO_2 is more soluble, while tetragonal one is more stable [42]. Moreover, it was found that the solubility of tetravalent germanium in acidic solutions is non-linearly associated with acid concentrations [43] and lowering of acid concentration may reduce the solubility of Ge(IV).

Moreover, the wet cake contained also significant amount of the intermetallic $Cu_{0.255}Zn_{0.745}$ phase. Therefore, copper and germanium leached during the process was reduced by metallic zinc to insoluble form, depending on the process conditions (Eq. 8-10):

$$Cu^{2+}_{(aq)} + Zn^0_{(s)} \rightarrow Cu^0_{(s)} + Zn^{2+}_{(aq)} \quad (8)$$

$$Cu^{2+}_{(aq)} + Cu^{0}_{(s)} + 2OH^{-}_{(aq)} \rightarrow Cu_2O_{(s)} + 2H_2O_{(l)} \quad (9)$$

$$\Delta G^{0}_{298} = -135.454 \; kJ$$

$$Ge(OH)_{4(aq)} + 2Zn^{0}_{(s)} + H^{+}_{(aq)} \rightarrow$$
$$Ge_{(s)} + 2Zn^{2+}_{(aq)} + 4H_2O_{(l)} \quad (10)$$

$$\Delta G^{0}_{298} = -275.797$$

Therefore, to achieve a better separation of the germanium between the phases, an adjustment of the final suspension pH was investigated. This was done by the addition of sodium carbonate to a suspension obtained after cake leaching at 80°C, for 2h, with 12.5% H_2SO_4, S:L 1:5. After pH adjustment, the suspension was mixed for an additional 30 min. The results are presented in Tables 3 and 4.

Table 3. *Influence of final pH on germanium leaching yield*

Final pH	Mass of Na_2CO_3 added [g/dm³]	Final Ge concentration in solution [mg/dm³]	Ge leaching yield [%]
0.86 (no adjustment)	-	18.9	46.6
2.06	12.21	3.3	7.7
2.54	18.45	3.1	7.0
3.12	22.30	3.9	9.1
3.70	25.11	3.6	8.9

It was noticed that pH adjustment to >2 reduced germanium leaching yield to 7.7%. Further pH increase did not have a significant impact on Ge yield. Moreover, the leaching yield of the other investigated elements did not change significantly. Therefore, the addition of sodium carbonate to the suspension

Table 4. *Leaching yields of selected elements from copper cake (80°C, 2h, 12.5% H_2SO_4, S:L 1:5, final pH 3.12)*

Element	Zn	Cd	Co	Cu	Ni	Ge*
Concentration [g/dm³]	27.4	39.9	5.06	0.002	6.24	3.9
Leaching yield [%]	91.0	99.8	85.1	~0	85.3	9.1

* *Ge concentration in [mg/dm³]*

obtained after leaching of the wet copper cake can be used as a method for increasing the selectivity of germanium recovery. In the next step, the germanium-enriched residue was leached under oxidative conditions. The composition of the residue is presented in Table 5, while its phase composition is in Figure 5. The final pH adjustment procedure was not investigated for the dried cake, because due to partial oxidation of copper it is not possible to achieve proper selectivity of the process – in the case of a two-stage process, the copper would be shared between two different material streams.

More than twofold enrichment in copper and lead as well as almost twofold enrichment in germanium, comparing their levels in the cake and residue, was achieved. The content of other elements was significantly reduced. Copper was present mainly as a

Table 5. *Composition of residue obtained after leaching of wet copper cake under non-oxidative conditions (80°C, 2h, 12.5% H_2SO_4, S:L 1:5, final pH 3.12)*

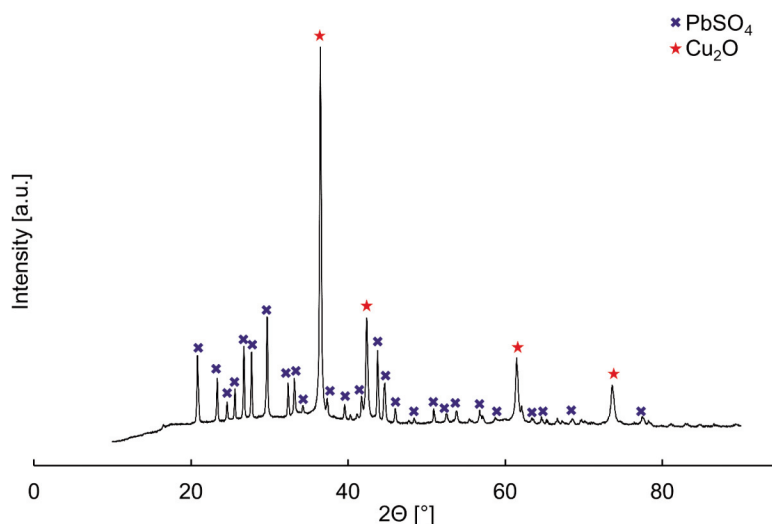| Element	Cu	Cd	Zn	Pb	Ni	Co	Ge	Dry loss
Concentration [% wt.]	57.5	2.50	3.24	9.70	2.15	1.73	420 ppm	46.6

Figure 5. *XRD pattern of the residue obtained after leaching of wet copper cake under non-oxidative conditions (80°C, 2h, 12.5% H_2SO_4, S:L 1:5, final pH 3.12)*

cuprite (Cu_2O), which was not prone to leaching under non-oxidative conditions, while lead was converted during leaching to insoluble anglesite ($PbSO_4$). The content of other elements was too low to determine their phases.

In the next step, the leaching of the residue under oxidizing conditions was investigated. Oxygen gas dosed at 50 dm^3/h was used as an oxidant. The influence of reaction time, temperature, initial acid concentration, and solid-liquid ratio was investigated. The results are presented in Figure 6.

The highest Ge leaching yield was >99% and was observed for 15% H_2SO_4 and S:L 1:10. For higher and lower acid concentrations at the same S:L less germanium was leached. On the other hand, maximum Cu leaching yield >95% was reached for 12.5% and higher acid concentration and S:L 1:7.5 and 1:10. The maximum Ge leaching yield was achieved after 1.5 h of leaching and then started to decrease, while for Cu 0.5 h was enough to achieve >99% yield. There was also a significant temperature

impact on leaching yields – almost all of the germanium was leached after 2h at 60°C, while the highest Ge yield was obtained for the highest investigated temperature - 80°C. Time had no significant influence on leachabilities – copper was almost completely leached after 30 minutes, while the maximum germanium leaching yield (81%) was achieved after 90 minutes. For the longer tests, germanium leaching yield decreased – to 74% after 3 hours. This could be connected with the formation of GeO_2 during longer processes, which is almost insoluble in acidic solutions.

The composition of a solution and residue obtained after oxidative leaching is presented in Table 6. XRD analysis of the residue is shown in Figure 7. The solution contained mostly copper (>70 g/dm^3), and lower concentrations (< 3g/dm^3) of zinc, nickel, cadmium, and cobalt were also determined. The concentration of germanium was 30 mg/dm^3.

The residue obtained after the second leaching under oxidative conditions contained about 33%
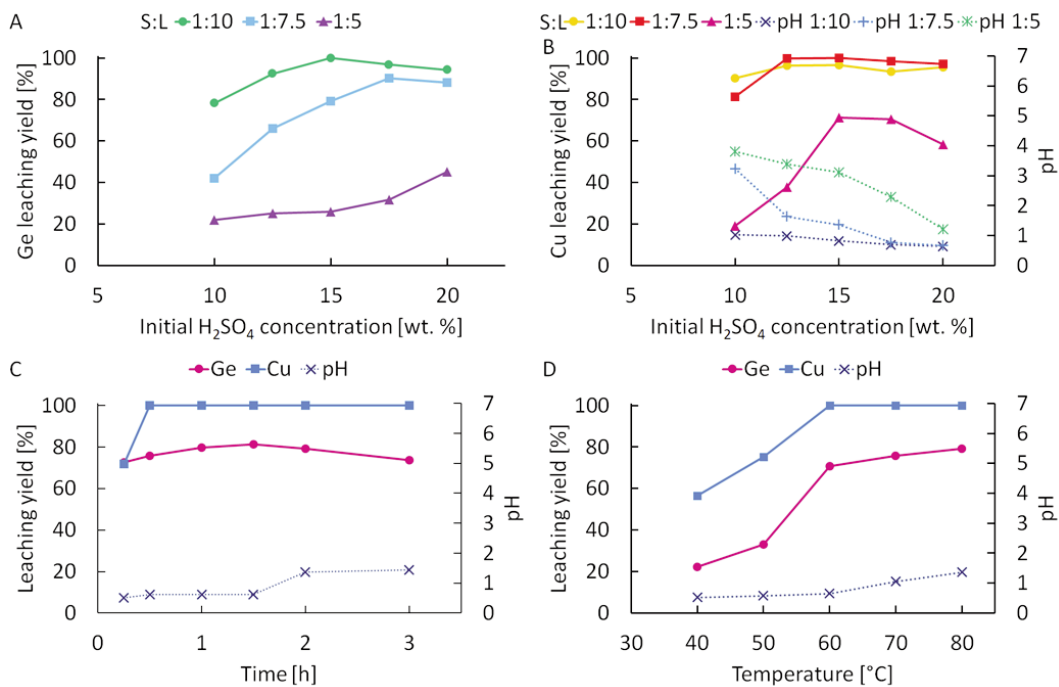

Figure 6. *Ge and Cu leaching yields from the residue under oxidative conditions (50 dm³/h O₂) – a,b) different initial acid concentration and solid-liquid ratio (80°C, 2h), c) different process time (80°C, 15% wt. H₂SO₄, S:L 1:7.5), d) different temperature (2h, 15% wt. H₂SO₄, S:L 1:7.5)*

Table 6. *Composition of the residue and solution obtained after oxidative leaching of the residue from the first non-oxidative stage (80°C, 2h, 15% H₂SO₄, S:L 1:7.5, 50 dm³/h O₂)*

Element	Cu	Cd	Zn	Pb	Ni	Co	Ge*	Dry loss	Mass/volume
Concentration in residue [% wt.]	2.60	0.06	1.86	33.3	0.05	0.01	410	40.8	23.42 g
Concentration in solution [g/dm³]	72.4	1.86	2.57	n/d	1.88	1.47	30	-	580 cm³

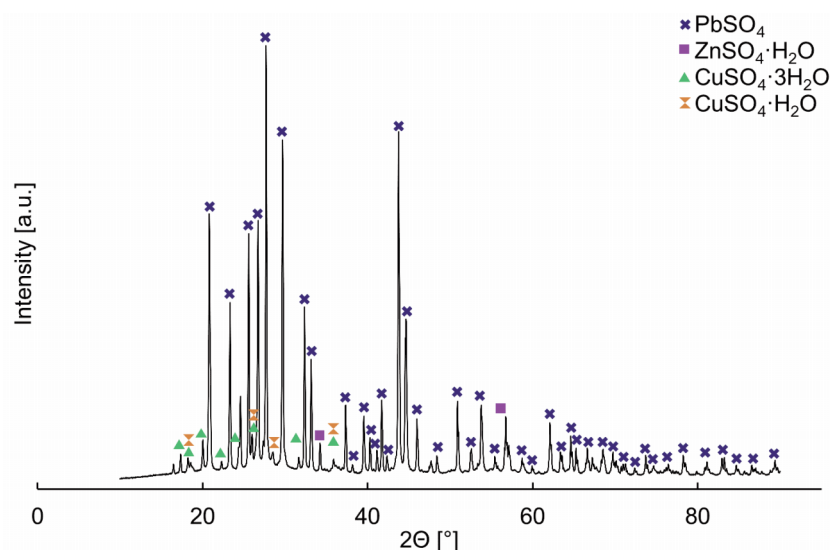** Ge concentrations in [ppm] and [mg/dm³]*

Figure 7. XRD pattern of the residue obtained after oxidative leaching of the residue (80°C, 2h, 15% H_2SO_4, S:L 1:7.75, 50 dm^3/h O_2)

lead, in the form of insoluble anglesite ($PbSO_4$). Minor amounts of copper (2.60%) and zinc (1.86%) were also detected. Copper was present as hydrated copper sulfates – bonattite ($CuSO_4 \cdot 3H_2O$) and poitevinite ($CuSO_4 \cdot H_2O$), which are soluble, however, may be entrapped in the residue structure due to high copper concentration in the water phase (>70 g/dm^3). Zinc was present in the zinc sulfate monohydrate phase ($ZnSO_4 \cdot H_2O$). The presence of both the copper and zinc phases resulted from the non-complete washing of the final residue, which was not achievable in standard filtration procedure. Pulping of the residue would have reduced the Cu and Zn levels.

3.3. Flowsheet of Ge recovery process including two-stage leaching

Based on the experimental results, the flowsheet of the Ge recovery process from copper cake was proposed. It is shown in Figure 8. It is composed of two-stage leaching – firstly under non-oxidative conditions, then under oxidative conditions. Firstly, a copper cake is leached in 12.5% wt. H_2SO_4, at 80°C, for 2h with S:L 1:5. After that time sodium carbonate is added to the suspension to increase pH >2.0. Then, the suspension is mixed for an additional 30 minutes and filtered. In the second leaching stage, the residue from the first stage is added to 15% wt. H_2SO_4 and mixed for 2h, at 80°C with S:L 1:7.5 and the addition of oxygen gas. Then, the suspension is filtered. The solution obtained after oxidative leaching can be used for germanium separation, e.g. using precipitation with tannic acid. It is supposed

that selective Ge precipitation may result in concentrate containing ca. 1% germanium, which after burning may be further refined to get pure Ge compounds. Alternatively, solvent extraction or ion-exchange techniques can be also applied. Solvent extraction approach using chelating and tertiary amine extractants was presented in our recent publication [38].
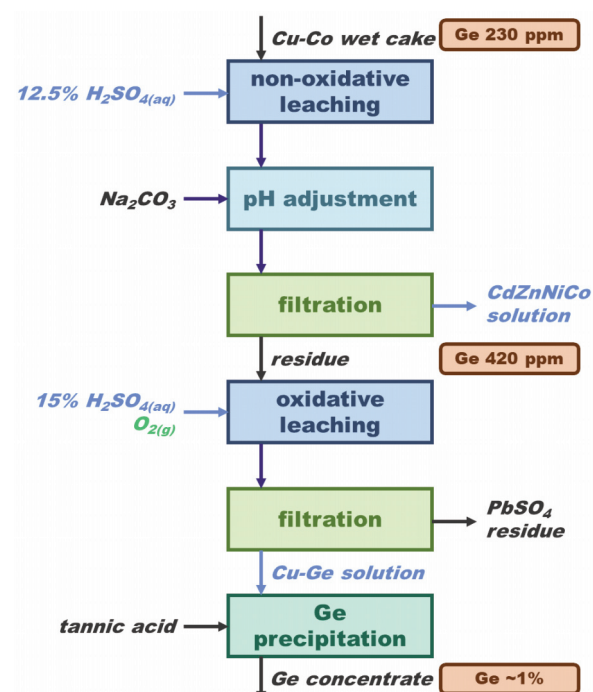

Figure 8. Proposed flowsheet of Ge recovery from copper cake including two-stage leaching

4. Conclusions

The leaching process for germanium recovery from copper cake using sulfuric acid solution was investigated. The process is composed of two stages – non-oxidative and oxidative. After the first stage, the pH of the obtained suspension is adjusted before filtration to reduce germanium loss.

It was found that the best selectivity and germanium recovery rate was obtained for the leaching of the wet cake. The dried cake, which could resemble stockpiled material, was partially oxidized, and leaching all main components, including copper, was noticed. Then, during non-oxidative leaching of the wet cake, copper remained in a solid phase, while germanium was partially leached (up to 51%). Other components (cadmium, zinc, nickel, and cobalt) were mostly recovered to the aqueous phase. The highest leaching yield of these metals was reached for leaching at 80°C, for 2h, with 12.5% H_2SO_4, S:L 1:5. To reduce germanium losses at this stage, the pH adjustment by sodium carbonate addition was applied. For pH > 2.0 less than 8% germanium was leached.

In the second stage, oxidative leaching using oxygen gas was investigated. It was found that using 15% H_2SO_4, at 80°C for 2h and S:L 1:10, over 99% of the copper and germanium was leached. The remaining residue contained mainly lead and a minor amount of copper. The obtained solution, containing ~30 mg/dm^3 Ge, can be used for germanium recovery, e.g., by its precipitation with tannic acid.

It was found that the dissolution behavior of the dried and wet form of the cake after were significantly different in terms of Cu and Ge. In the case of non-oxidative leaching stage, it was determined that the Cu and Ge leachability was lower for the wet form. These metals were kept in the solid phase after the non-oxidative stage and a subsequent oxidative leaching process was applied to the solid material again to transfer Cu and Ge into an aqueous solution. In this way, it was demonstrated that the two-stage leaching process could be suitable for Ge and Cu recovery.

Acknowledgment

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Michał DRZAZGA: Investigation, Supervision, Funding acquisition, Writing - Original Draft, Writing - Review & Editing; Sylwia KOZŁOWICZ: Investigation; Writing - Original Draft Izabela MAJ: Investigation; Szymon ORDA: Investigation; Adrian RADOŃ: Investigation, Writing - Original Draft; Mateusz CISZEWSKI: Investigation, Writing - Review & Editing.

Data availability

Data availability will be provided on request.

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DVOFAZNO LUŽENJE GERMANIJUMA IZ BAKARNOG TALOGA POD UZASTOPNIM NEOKSIDACIONIM I OKSIDACIONIM USLOVIMA

M. Drzazga [*], S. Kozłowicz, I. Maj, S. Orda, A. Radoń, M. Ciszewski

Istraživačka mreža Łukasjevič – Institut za nemetale, Gljivice, Poljska

Apstrakt

Mnoge svetske ekonomije, kao što su EU i SAD, smatraju germanijum kritičnom sirovinom. Zbog toga razvoj metoda za njegovo izdvajanje iz novih izvora postaje sve značajniji. U ovom radu prikazano je luženje bakarnog taloga, koji nastaje tokom prečišćavanja cinkovih elektrolita, u rastvoru sumporne kiseline. Talog je sadržao 24,7% Cu, 21,2% Cd, 16,3% Zn, 4,50% Pb, 3,96% Ni, 3,22% Co i 231 ppm Ge. Ispitivano je luženje vlažnog i osušenog materijala. Utvrđeno je da se najveći prinos izdvajanja germanijuma postiže u dvostepenom procesu koji se sastoji iz luženja u neoksidacionim uslovima, zatim podešavanja pH natrijum-karbonatom, i oksidacionog luženja ostatka iz prve faze. U prvoj fazi luženja u 12,5% sumpornoj kiselini i naknadnim podešavanjem pH na > 2,0, prinos luženja germanijuma opao je na manje od 10%. Tokom oksidacionog luženja preostalog ostatka u 15% sumpornoj kiselini, izluženo je više od 99% germanijuma. Konačni rastvor sadržao je 30 mg/dm³ Ge i 72,4 g/dm³ Cu. Germanijum se kasnije može izdvojiti iz rastvora taloženjem pomoću taninske kiseline ili solventnom ekstrakcijom.

Ključne reči: Izdvajanje germanijuma; Metalurgija cinka; Prečišćavanje cinkovih elektrolita; Luženje