

Two-stage leaching of germanium from copper cake under subsequent non-oxidizing and oxidizing conditions

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Abstract

Many world economies, like the EU and USA, consider germanium as a critical raw material. Therefore, the development of its recovery from new sources is becoming more and more important. The leaching of copper cake, originating from the purification of zinc electrolyte, 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 achieved for a two-stage process composed of leaching under non-oxidizing conditions followed by pH adjustment with sodium carbonate followed by oxidizing leaching of residue from the first stage. In the first stage leaching in 12.5% sulfuric acid and later 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 may be later 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 by many leading world economies, including USA and European Union, as a critical raw material.

Nowadays zinc concentrates are the main germanium source and it is estimated that only 3% of germanium contained is recovered from zinc-based materials. So, there is still huge room for improvement in its recovery technologies. Nowadays, the majority of the 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 of germanium recovery is leaching of the zinc production by-products. Depending on material composition, different inorganic and organic acids as well as their mixtures may 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 like 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 was also investigated [20]. Then, germanium may 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 for 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 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 H₂SO₄, 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 remaining Ge in the last alkaline step. Sulfuric acid leaching was used to extract zinc and gallium, while hydrochloric acid leaching removed lead from solid. 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 KMnO₄ was used to extract zinc, while in the second one, NaClO₃ was added to sulfuric acid. Germanium leaching yields in both steps were 1.8% and 90.7%, respectively.

Liu et al. [36] investigated subsequent leaching of zinc refinery residue (0.36% Ge, 24% Zn, 9.1% SiO₂, 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 may 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. It 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 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% SiO₂, 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 may be used: selective leaching without oxidant at 40-60°C with 100 g/L H₂SO₄ or collective leaching with air pumping at 85°C with 150 g/L H₂SO₄. Germanium leaching yields for these approaches were 78% and 92.7% respectively.

Data concerning germanium recovery from zinc electrolyte purification residues is limited and focused on ones with quite significant Ge content. There are no reports on germanium recovery from sources containing <400 ppm Ge. Moreover, more attention to the difference between fresh and stockpiled materials should be paid as oxidation may 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

leaching yields of the copper cake both in fresh and dried form. To enhance germanium recovery 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

Copper cake from the second stage of crude zinc electrolyte purification with zinc dust was collected from a Polish zinc smelter. More detailed description of the cake origin is provided in our previous work [38]. Its chemical and phase composition is 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 may also resemble stockpiled cake.

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

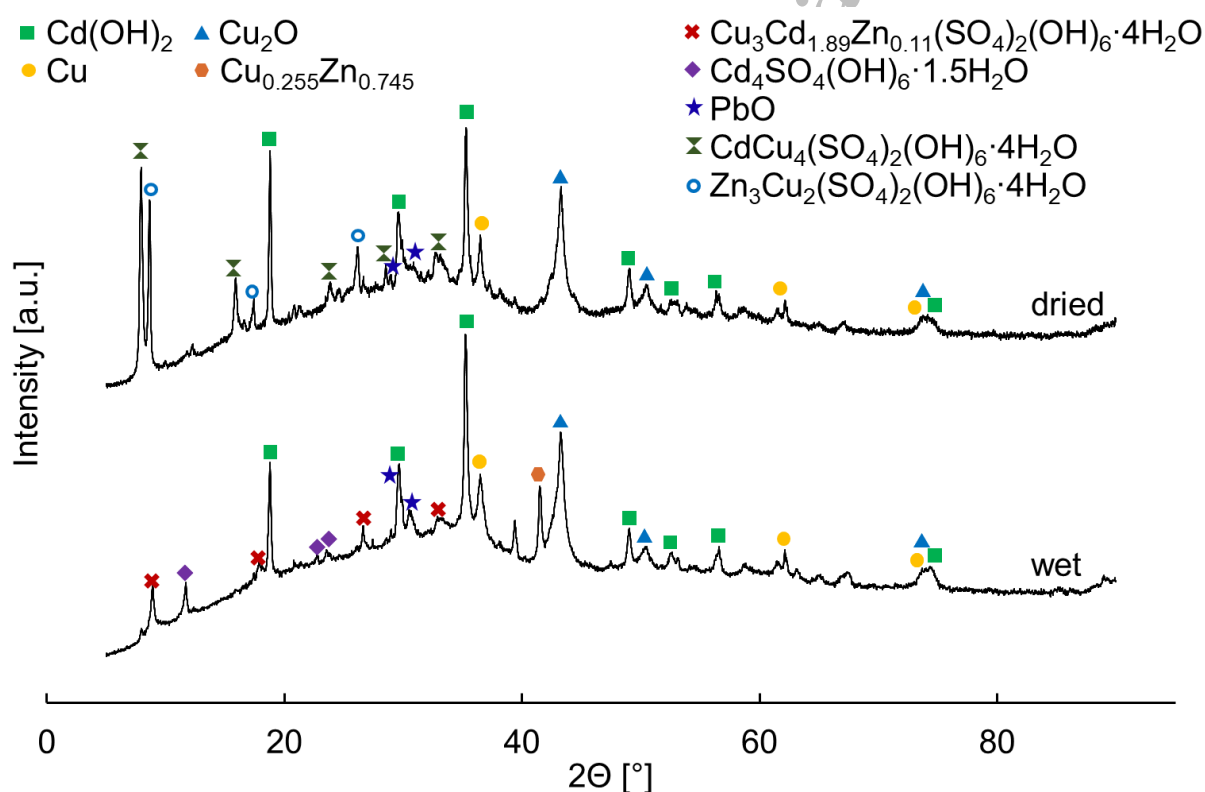
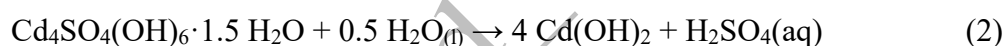
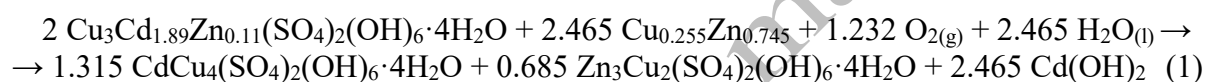


Figure 1 XRD patterns of wet and dried copper cake

The main components of the cake were copper, cadmium, zinc, lead, nickel, and cobalt. Cadmium was mostly present as hydroxide – $[\text{Cd}(\text{OH})_2]$, however, it was also found as hydrated cadmium hydroxide sulfate $[\text{Cd}_4\text{SO}_4(\text{OH})_6 \cdot 1.5\text{H}_2\text{O}]$ and edwardsite $[\text{Cu}_3\text{Cd}_{1.89}\text{Zn}_{0.11}(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}]$ in wet material and as niedermayrite $[\text{CdCu}_4(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}]$ in dried one. Copper was found mainly as a metallic Cu and copper(I) oxide $[\text{Cu}_2\text{O}]$. Moreover, it was also present in wet cake as intermetallic $\text{Cu}_{0.255}\text{Zn}_{0.745}$ and edwardsite, while after drying as niedermayrite and christelite $[\text{Zn}_3\text{Cu}_2(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}]$.

Zinc was found in $\text{Cu}_{0.255}\text{Zn}_{0.745}$ and edwardsite before drying, whereas in christelite after thermal treatment. In both cases, the main lead phase was massicot $[\text{PbO}]$. Due to 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 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 - $\text{Cu}_{0.255}\text{Zn}_{0.745}$ peak is present only for the wet cake, while niedermayrite and christelite only for the dried one. Due to its low content (231 ppm) it was not possible to determine the form in which germanium was present in the cake.

It might have been noticed that the oxidation of the cake took place during drying process. Intermetallic $\text{Cu}_{0.255}\text{Zn}_{0.745}$ was present only in dried cake, while edwardite phase was transformed to niedermayrite and christelite ones. It was also observed that intensity of $\text{Cd}(\text{OH})_2$ phase with respect to other intensities of other phases (e.g. Cu, Cu_2O) increased suggesting that mass share of cadmium hydroxide increased. It might have been associated with thermal decomposition of hydrated cadmium hydroxide sulfate, associated with formation of sulfuric acid catalysing oxidation reactions, as well as with abovementioned phase transitions. The most important phase transitions reactions might be summarized as the following reactions (Eq. 1-2):



2.2. Experimental method

Leaching tests were performed using sulfuric acid (98%, Avantor) and hydrogen peroxide (30%, Avantor). The volume of 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 amount of oxidant was examined. The initial sulfuric acid solutions (5-20 % wt.) were prepared diluting concentrated acid in deionized water ($<0.1 \mu\text{S}/\text{cm}$). 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_2O_2 was added in portions – 2.5 cm^3 portion every 3 minutes. In oxidative leaching tests of the wet cake pure oxygen gas ($\geq 99.5\%$, 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 before filtration pH of the suspension was adjusted using solid sodium carbonate (99.8%, Eurochem). Na_2CO_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.

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

2.3. Analysis and Characterisation

X-ray diffraction (XRD) was used for 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 K α ($\lambda = 0.15406$ nm), a tube voltage of 40 kV, and a current of 15 mA, using a D/teX Ultra silicon strip detector.

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

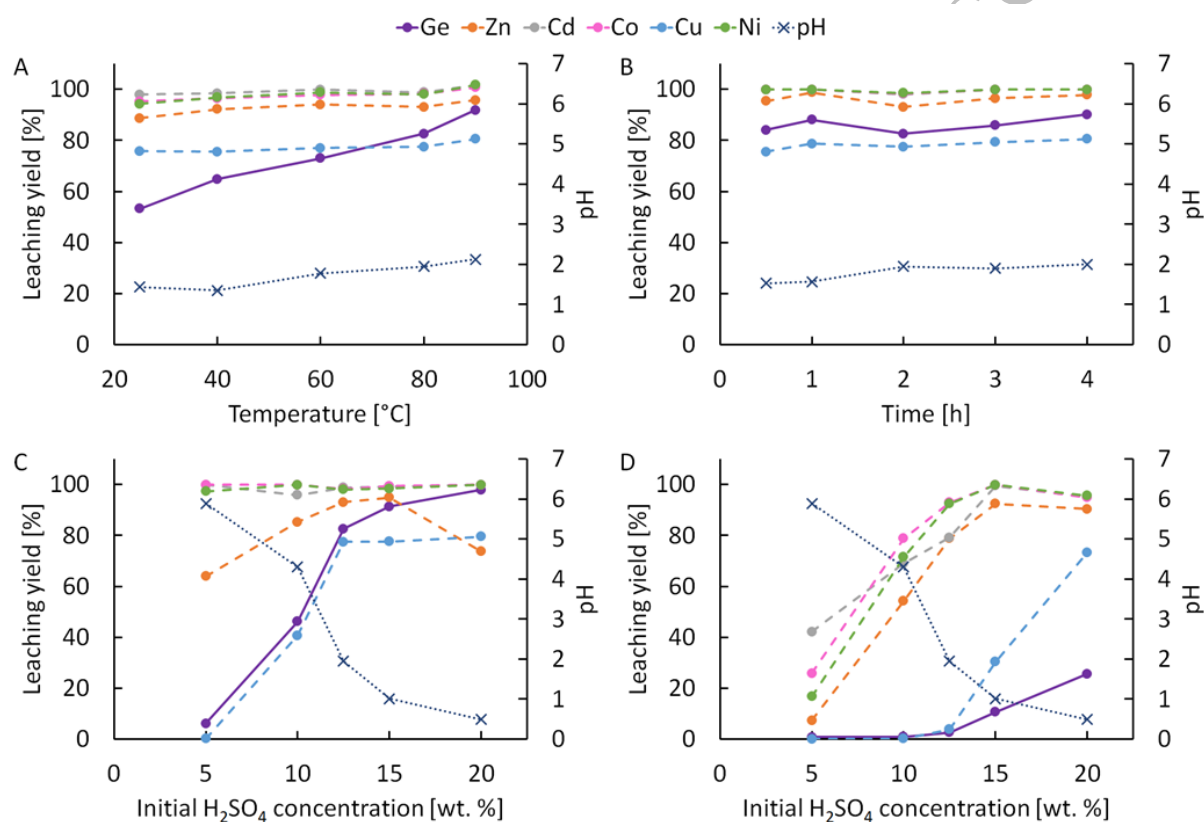


Figure 2 Leaching yields of the main components from dried copper cake under different conditions: a) varying temperature (2h, 12.5% wt. H₂SO₄, S:L 1:5), b) varying process time (80°C, 12.5% wt. H₂SO₄, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5), d) varying initial acid concentration (2h, 80°C, S:L 1:3).

It may 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 were 95-99%, Zn – 88-96%, and Cu – 75-81%. 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 initial acid concentration influenced Cu, Zn, and Ge. Germanium leaching yield increased from 6% for 5% H₂SO₄ to 98% for 20% acid. Zinc leaching yield reached 95% for 15% sulfuric acid and all other investigated concentrations were lower, whereas copper yield increased to 77-80% for H₂SO₄ concentrations lower than 12,5%. Leaching tests performed at a solid-liquid ratio 1:3 also showed that Cd, Ni, Co, and Zn leaching yields increased similarly as initial acid concentration increased, whereas Cu and Ge leaching might have been noticed for sulfuric acid concentrations higher than 12.5%.

Under investigated conditions, the highest germanium leaching yield was 98%. Acid concentration and S:L had the most significant impact on the yield. Also, process temperature influenced germanium leaching. However, it should be noted that almost all the main elements present in the copper cake were leached. It may lead to additional problems later during the separation of elements. Maximum copper leaching yield was 80%. It was due to only partial Cu oxidation during the drying process. Part of the copper in a dried cake was still present in the metallic or Cu₂O phases, which were not prone to leaching without an oxidant. The amount of Cu₂O phase might have been partially reduced by disproportionation reaction in a slightly acidic solution. However, the rate of this reaction was limited due to a very low solubility of Cu⁺ ions. It could be noted that germanium and copper leachabilities were correlated – especially during tests with different initial acid concentrations (Figure 2cd). It suggested that germanium is bonded with copper. As copper in the dried cake was not fully oxidized it was predicted that the addition of oxidant would increase Cu leachability and, therefore, also Ge leaching yield. In the next step leaching of dried cake under oxidative conditions was examined. Hydrogen peroxide was used as an oxidant. The results of the tests are presented in Figure 3. Compositions of solution and residues obtained after non-oxidative and oxidative leaching of dried copper cake are presented in Table 2.

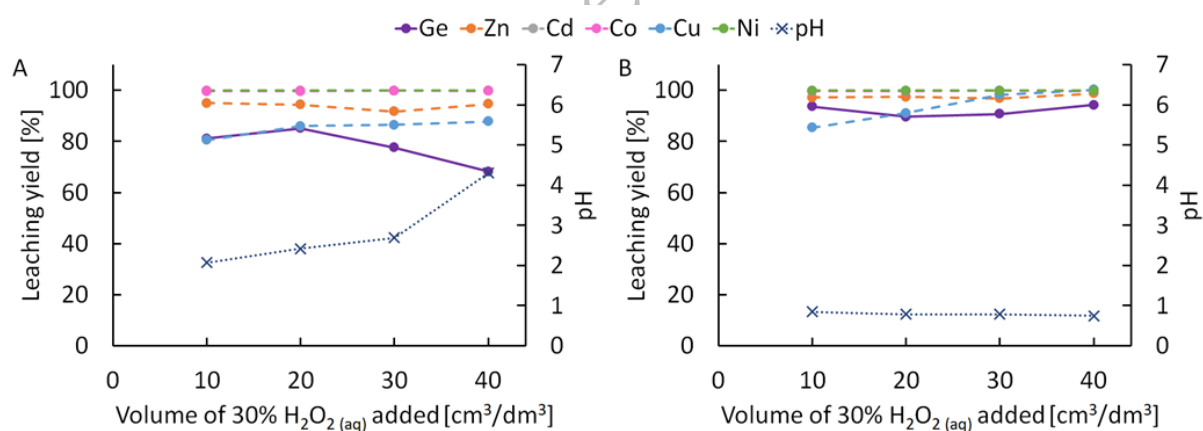


Figure 3 Leaching yields of the main components from dried copper cake under oxidative conditions – different H₂O₂ doses a) (80°C, 2h, 12.5% wt. H₂SO₄, S:L 1:5), b) (80°C, 2h, 15% wt. H₂SO₄, S:L 1:5).

The addition of hydrogen peroxide during the leaching process increased the leaching yield of copper, however, it had a negative (for 12.5% H₂SO₄) or no impact on germanium leaching - at lower acid concentration H₂O₂ addition reduced the yield to 68% for the highest investigated oxidant dose. Therefore, it seems that the leaching of dried cake under oxidative conditions was not germanium selective and even led to only partial Ge leaching. Higher oxidant doses reduced germanium yield. It might be explained by the formation of GeO₂, which had very limited solubility, especially for pH>2.

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% H₂SO₄, S:L 1:5, 40 cm³/dm³ for oxidative leaching)

Element	Cu	Cd	Zn	Pb	Ni	Co	Ge*	Dry loss	Mass/volume
<i>non-oxidative leaching</i>									
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/dm ³]	31.0	35.0	17.8	0.02	2.70	4.00	46.4	-	570 cm ³
<i>oxidative leaching</i>									
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/dm ³]	33.4	34.8	17.2	0.02	2.74	4.00	36.4	-	600 cm ³

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

3.2. Leaching of wet cake

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

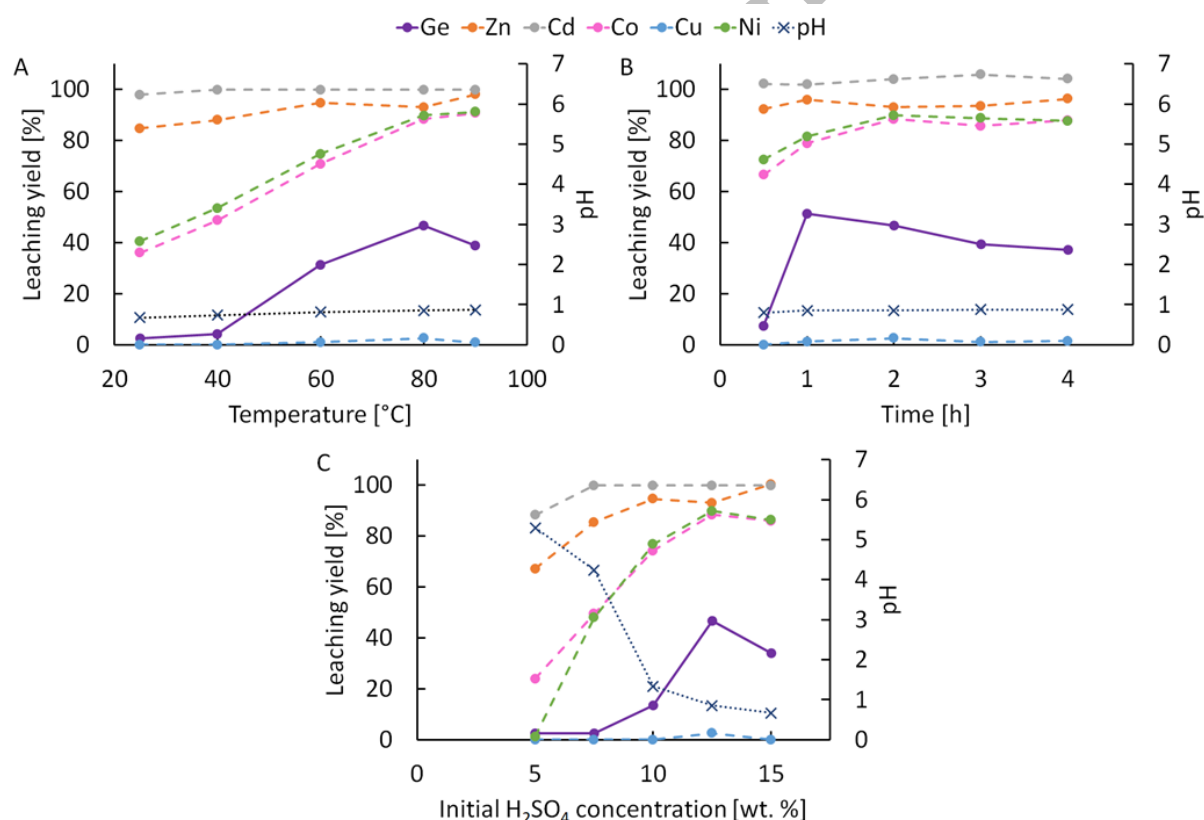
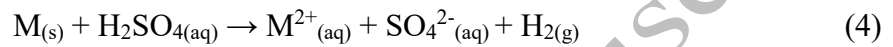
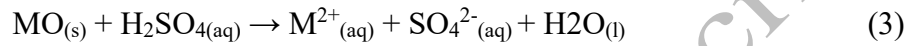


Figure 4 Leaching yields of the main components from wet copper cake under different conditions: a) varying temperature (2h, 12.5% wt. H₂SO₄, S:L 1:5), b) varying process time (80°C, 12.5% wt. H₂SO₄, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5), c) varying initial acid concentration (2h, 80°C, S:L 1:5).

It may be observed that copper was not leached from wet cake. Copper in metallic or Cu₂O phase is not prone to leaching under non-oxidizing conditions. Therefore, it may 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 investigated conditions was 51%. It is an undesirable situation as germanium should be potentially later recovered from both solution and residue. In the case of other investigated elements, it is possible to achieve almost complete (zinc, cadmium) or > 80% (nickel, cobalt) leaching yield.

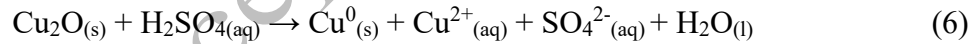
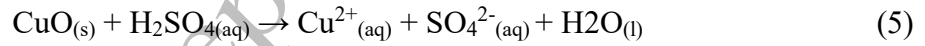
Zinc, cadmium, nickel and cobalt, no matter if they were metallic or bivalent, would be dissolved in sulfuric acid as they form soluble sulfates (Eq. 3). Moreover, their reduction potentials were negative, and therefore their metallic forms reacted with acids to form respective bivalent sulfates and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



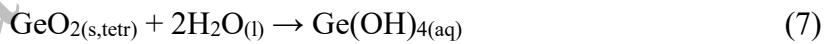
where M is Zn, Cd, Ni, Co.

Similarly, lead would also react with sulfuric acid according to aforementioned reaction, but to form insoluble $PbSO_4$. Therefore, 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].



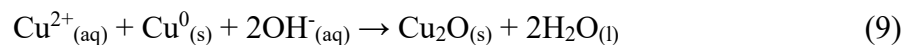
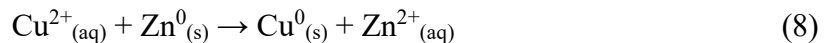
$$\Delta G^0_{298} = -24.092 \text{ kJ}$$



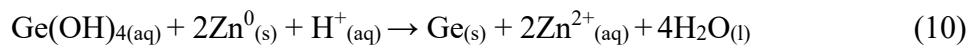
$$\Delta G^0_{298} = 28.317 \text{ kJ}$$

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 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 process conditions (Eq. 8-10):



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



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

Therefore, to achieve better separation of germanium between phases, adjustment of the final suspension pH was investigated. It was done by the addition of sodium carbonate to a suspension obtained after cake leaching at 80°C, for 2h, with 12.5% H₂SO₄, S:L 1:5. After pH adjustment suspension was mixed for an additional 30 min. Results are presented in Tables 3 and 4.

Table 3 Influence of final pH on germanium leaching yield

Final pH	Mass of NaCO ₃ added [g/dm ³]	Final Ge concentration in solution [mg/dm ³]	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

Table 4 Leaching yields of selected elements from copper cake (80°C, 2h, 12.5% H₂SO₄, S:L 1:5, final pH 3.12)

Element	Zn	Cd	Co	Cu	Ni	Ge*
Concentration [g/dm ³]	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]

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 other investigated elements did not change significantly. Therefore, the addition of sodium carbonate to the suspension obtained after leaching of the wet copper cake may be used as a method for increasing the selectivity of germanium recovery. In the next step, 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 copper would be shared between two different material streams.

Table 5 Composition of residue obtained after leaching of wet copper cake under non-oxidative conditions (80°C, 2h, 12.5% H₂SO₄, 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

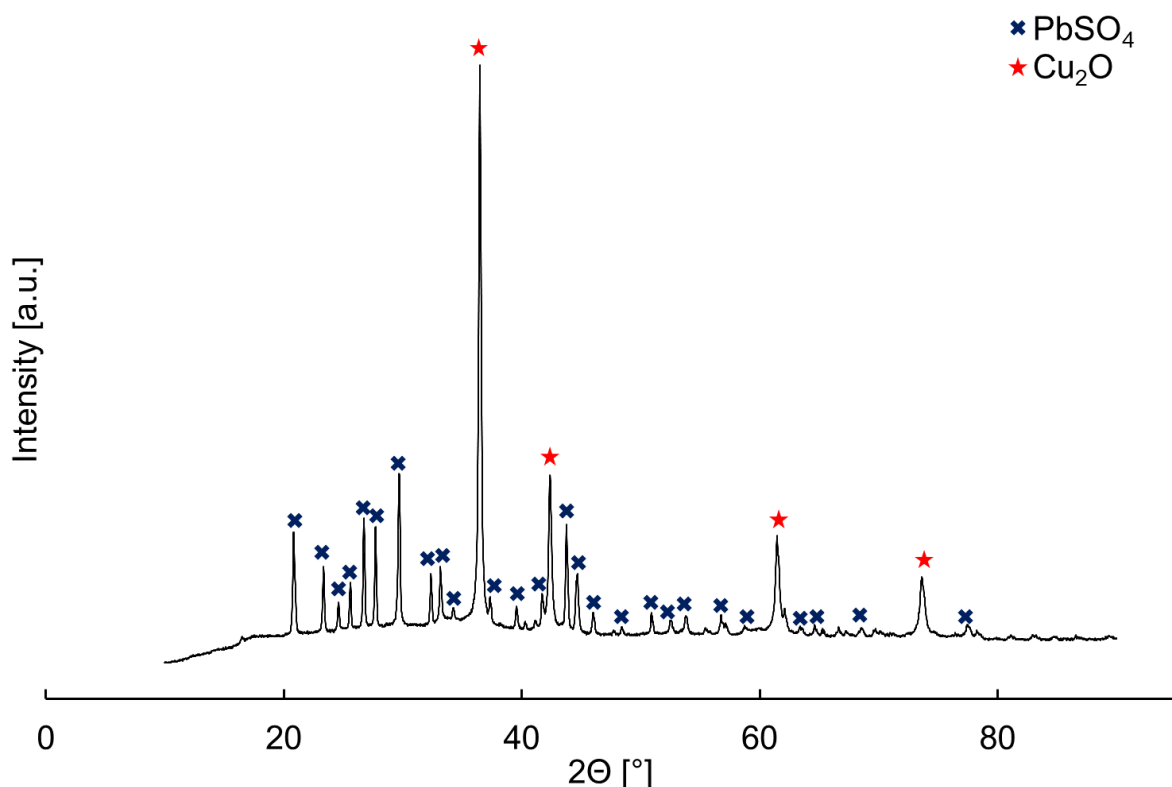


Figure 5 XRD pattern of the residue obtained after leaching of wet copper cake under non-oxidative conditions (80°C, 2h, 12.5% H₂SO₄, S:L 1:5, final pH 3.12)

More than two-fold enrichment in copper and lead as well as almost two-fold 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 cuprite (Cu₂O), which was not prone to leaching under non-oxidative conditions, while lead was converted during leaching to insoluble anglesite (PbSO₄). 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 dm³/h was used as an oxidant. The influence of reaction time, temperature, initial acid concentration, and solid-liquid ratio was investigated. Results are presented in Figure 6.

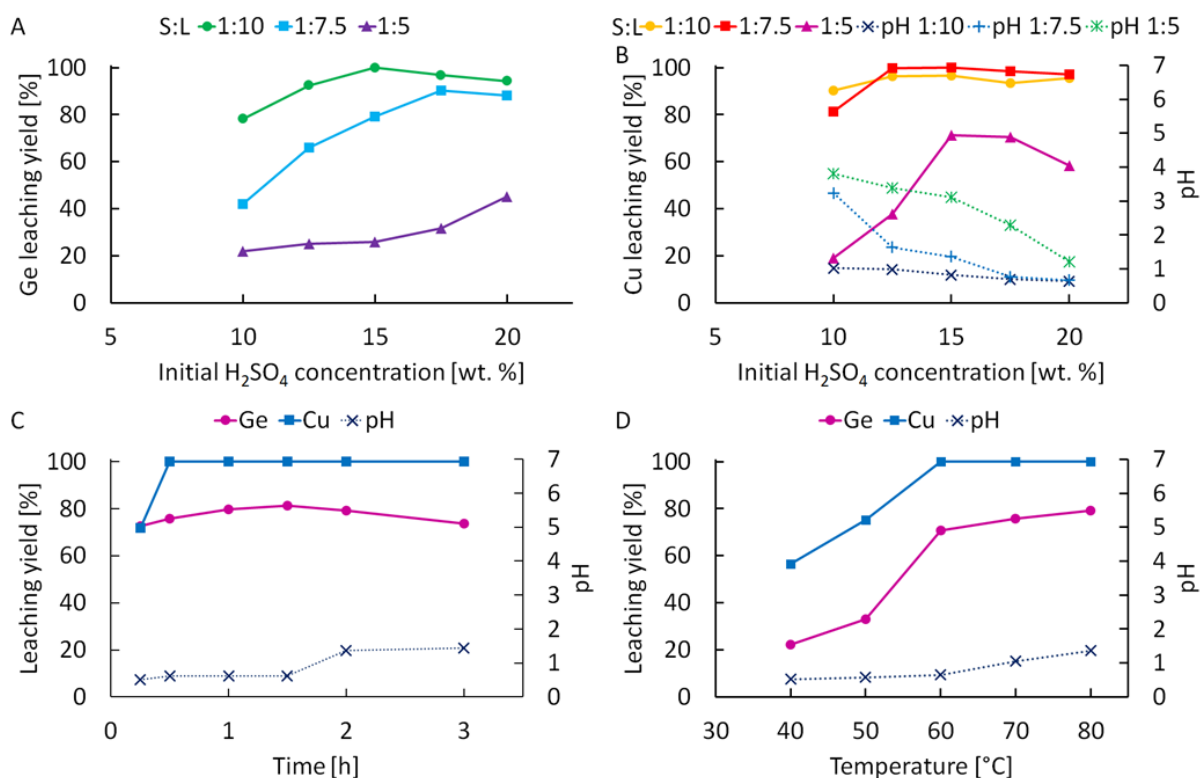


Figure 6 Ge and Cu leaching yields from the residue under oxidative conditions ($50 \text{ dm}^3/\text{h O}_2$) – a,b) different initial acid concentration and solid-liquid ratio (80°C , 2h), c) different process time (80°C , 15% wt. H_2SO_4 , S:L 1:7.5), d) different temperature (2h, 15% wt. H_2SO_4 , S:L 1:7.5)

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. Maximum Ge leaching yield was achieved after 1.5 h 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 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 maximum germanium leaching yield (81%) was achieved after 90 minutes. For the longer tests, germanium leaching yield decreased – to 74% after 3 hours. It might 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 ($>70 \text{ g/dm}^3$), and lower concentrations ($< 3 \text{ g/dm}^3$) of zinc, nickel, cadmium, and cobalt were also determined. The concentration of germanium was 30 mg/dm^3 .

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% H_2SO_4 , S:L 1:7.5, $50 \text{ dm}^3/\text{h O}_2$)

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/dm^3]	72,4	1,86	2,57	n/d	1,88	1,47	30	-	580 cm^3

* Ge concentrations in [ppm] and [mg/dm^3]

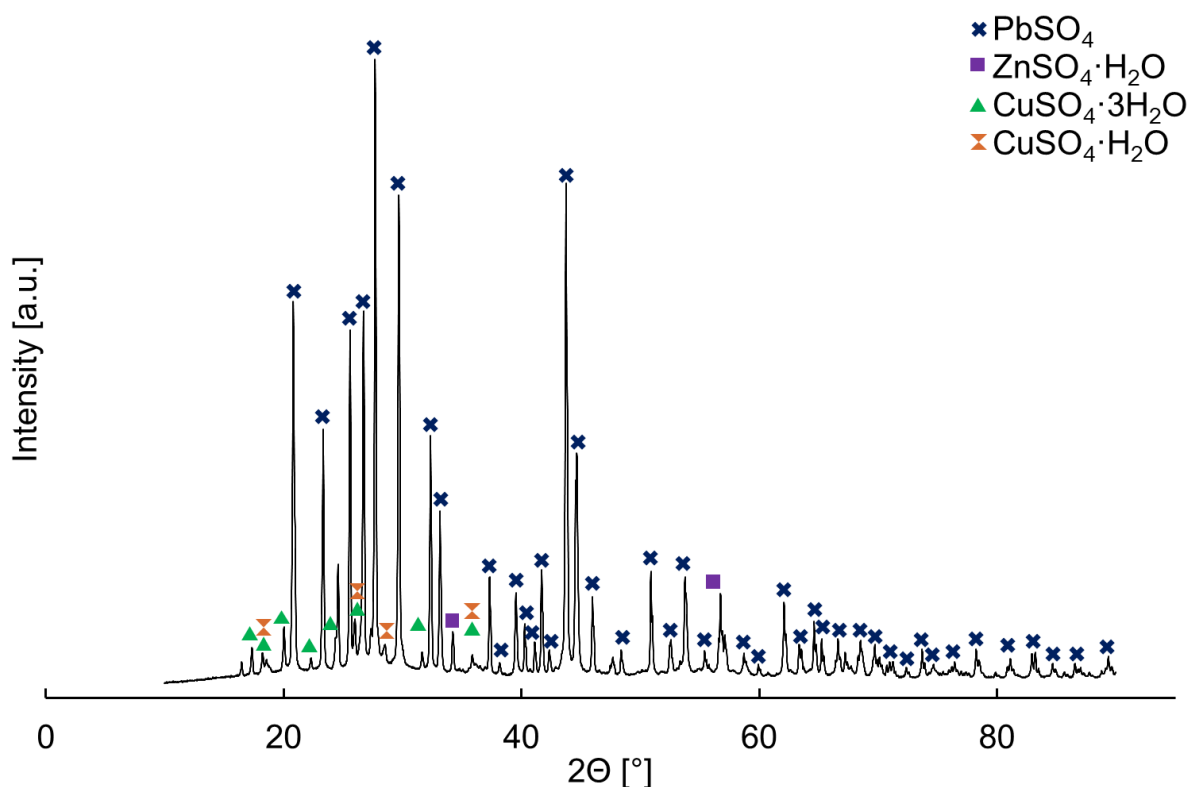


Figure 7 XRD pattern of the residue obtained after oxidative leaching of the residue (80°C, 2h, 15% H₂SO₄, S:L 1:7.75, 50 dm³/h O₂)

The residue obtained after the second leaching under oxidative conditions contained about 33% lead, in the form of insoluble anglesite (PbSO₄). Minor amounts of copper (2.60%) and zinc (1.86%) were also detected. Copper was present as hydrated copper sulfates – bonattite (CuSO₄·3H₂O) and poitevinite (CuSO₄·H₂O), which are soluble, however, might be entrapped in the residue structure due to high copper concentration in the water phase (>70 g/dm³). Zinc was present in the zinc sulfate monohydrate phase (ZnSO₄·H₂O). The presence of both 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 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. H₂SO₄, 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 residue from the first one is added to 15% wt. H₂SO₄ 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 may 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 may be also applied. Solvent extraction approach using chelating and tertiary amine extractants was presented in our recent publication [38].

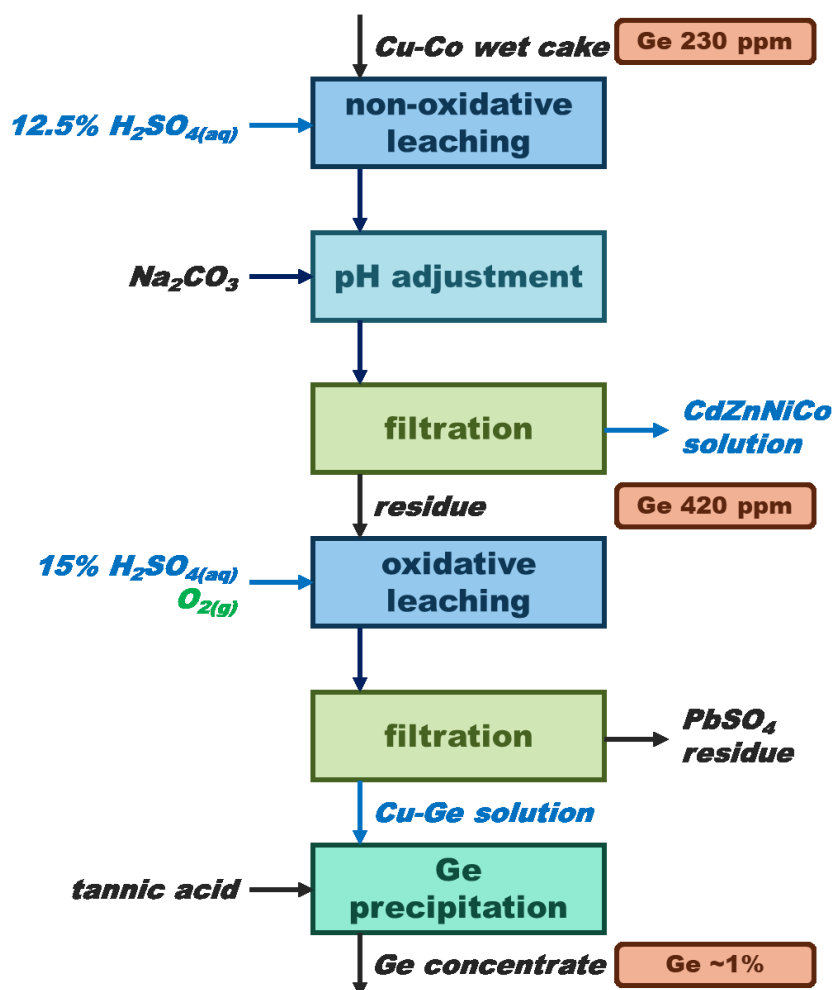


Figure 8 Proposed flowsheet of Ge recovery from copper cake including two-stage leaching

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 one 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 wet cake. Dried cake, which might resemble stockpiled material, was partially oxidized, and leaching all main components, including copper, was noticed. Then, during non-oxidative leaching of 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% H₂SO₄, S:L 1:5. To reduce germanium losses at this stage 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% H₂SO₄, at 80°C for 2h and S:L 1:10 over 99% of copper and germanium was leached. The remaining residue contained mainly lead and a minor amount of copper. The obtained solution, containing ~30 mg/dm³ Ge, may be used for germanium recovery, e.g., by its precipitation with tannic acid.

It was found that the dissolution behaviors 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 Cu and Ge leachability was lower for the wet form. These metals were kept in solid phase after non-oxidative stage and a subsequent oxidative leaching process was applied to the solid material again to transfer Cu and Ge into aqueous solution. In this way, it was demonstrated that the two-stage leaching process may be suitable for Ge and Cu recovery.

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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 DRZAGA: 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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