Recovery and separation of gallium(III) and germanium(IV) from zinc refinery residues: Part I: Leaching and iron(III) removal

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Abstract: In this research, gallium and germanium were separated and recovered from zinc refinery residues by a two-stage leaching. In the first leaching stage with sulfuric acid media, 92% of zinc and 94% of copper were leached resulting in significant gallium and germanium enrichment up to ca. 300%. In the second leaching stage with oxalic acid media, the effects of $\text{H}_2\text{C}_2\text{O}_4$ concentration, leaching time, liquid-to-solid(L/S) ratio and temperature on the recovery of gallium and germanium were investigated. More than 96% of gallium and 99% of germanium were leached out using 70 g/L $\text{H}_2\text{C}_2\text{O}_4$ with a L/S ratio of 10 at 90 °C for 2 h. The removal of iron in the $\text{H}_2\text{C}_2\text{O}_4$ leach solution was carried out using an ultrasound-assisted ferrous iron precipitation method in which more than 96% of Fe(III) was removed in the form of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with minor losses of Ga(III) and Ge(IV) (1.4% and 1.3%). The results indicated that high recoveries of gallium and germanium from the zinc refinery residues could be achieved with two-stage leaching method.

Keywords: Zinc refinery residue; Gallium; Germanium; Oxalic acid leaching; Iron removal

1 Introduction

Gallium and germanium are important strategic resources that have been used extensively in a variety of high-technology fields, such as

semiconductors, infrared optics, optical fibers, medicine and catalysis (Schimmel et al., 2001; Tyszczyk et al., 2007; Depuydt et al., 2006; Fujiwara et al., 2002). So far, no independent germanium and gallium ore deposits have been found in nature, but these metals are recovered as a side product from the metallurgical processes of nonferrous metals, such as zinc, lead and aluminum.

Zinc refinery residues, which are the typical by-products of hydrometallurgical zinc processes, usually contain between 0.20 - 0.50 wt.% Ge and 0.30 - 0.40 wt.% Ga with Zn, SiO₂, Cu, Fe and Pb as the main components (Liu et al., 2016^{a,b}). Both Ga and Ge exist as their dissociative or combined oxides with iron and silica. As Ga and Ge are difficult to recover and separate from such compounds, currently there is no industrial process for Ga and Ge recovery from these types of residue.

In order to effectively recover Ga and Ge from the by-products of hydrometallurgical zinc processes, several studies have been conducted on the behavior of Ga, Ge and related elements such as Fe and Si (Harbuck, 1993; Torma, 1991; Nishihama et al., 1999; Kul and Topkaya, 2008; Nusen et al., 2015; Zhang et al., 2016). Torma (1991) and Lee et al. (1994) used an alkaline leaching process to treat zinc refinery residues. Although good leaching of related elements was achieved, the leach solution contained high concentrations of Si, Pb and Al, which made the metal recovery and solution purification difficult. Wardell and Davidson (1987) investigated a reductive SO₂ leaching process as an alternative for Ga and Ge recovery from zinc leaching residue. It was found that under optimal conditions approximately 90% of Ga, but only 57% of Ge were leached. The low recovery of Ge was mainly attributed to the formation of silica-germanium gel because H₄GeO₄ and H₄SiO₄ were shown to hydrolyze the mixed polymers (Dutrizac et al., 1996; Efremov et al., 2002; Liang et al., 2009). Several efforts have been made to eliminate the

negative influence of silicon on the recovery of Ga and Ge in sulfuric acid leaching including the use of leaching assistant agents (Liu et al., 2016^a), pressure sulfuric acid leaching (Liu et al., 2016^b) and stepwise leaching (using sulfuric acid and hydrofluoric acid leaching sequentially) (Harbuck et al., 1989; Harbuck, 1993). The results showed that the recovery of Ga and Ge as well as the filterability of the leaching residues can be improved significantly. Nevertheless, some challenges still remain to the use of these processes on the industrial scale: for example, the large consumption and difficult subsequent separation of the leaching assistant reagents, high capital and operational costs of pressure acid leaching and the highly corrosive nature of hydrofluoric acid. As a result, the processing methods for high silicon materials rich in Ga and Ge still need to be further developed.

In this study, a novel stepwise leaching process has been investigated. In the first stage, which uses low sulfuric acid leaching, Zn and Cu were selectively leached from zinc refinery residues, whilst Ga and Ge effectively enriched and are obtained as part of the high silicon residues. In the second-stage, the oxalic acid leaching of these high silicon residue was carried out for Ga and Ge.

In order to recover Ga and Ge, another challenge is the removal of iron from the solution. The ultrasound-assisted ferrous iron precipitation method was proposed for iron removal from oxalate solution, when compared to both a solvent extraction process (Demopoulos et al., 1993; Principe et al., 2005; Sun et al., 2016; Mishra et al., 2010; Principe et al., 2004) and the neutralization precipitation process for iron removal. This ferrous iron precipitation method also has the added advantage of reducing the losses of Ga and Ge due to co-extraction / precipitation / occlusion. In the purified oxalate solution, the stable complexes of Ga and Ge can subsequently be effectively extracted by tri(octyl-decyl)

amine (N235) which is widely used in complexes extraction due to its low cost, widespread availability and high extraction efficiency (Fang et al., 2014; Yang et al., 2015; Chen et al., 2016).

In order to verify the applicability of the proposed processes of stepwise leaching and iron removal, the recovery of Ga and Ge and the behavior of the other elements of interest in each step was investigated in the current study.

2 Experimental

2.1 Experimental procedure

The low sulfuric acid leaching experiments and oxalic acid leaching experiments were conducted in 500 mL and 300 mL round-bottom flasks, with magnetic stirring at 300 rpm, respectively. Temperature was set and controlled by a water bath (DF-101S, Gongyi Yuhua Instrument Co., China). Iron removal experiments were initially performed for 100 mL of the resulting leachate in 250 mL conical flasks, and the ultrasound time was set and controlled by an ultrasonic cleaner at 30 °C (KQ-2550E, Jiangsu Kunshan Ultrasonic Cleaning Instrument Co., China, 40 kHz, 200 W), then the sonification solution was heated at desired temperature by a water bath with mechanical stirring at 300 rpm. The amount of iron powder required is mainly determined by the content of Fe(III) concentration present in leachate after leaching. After each experiment, both residue and filtrate were subsequently analyzed. The investigated parameters utilized are displayed in Table 1. In the experiment, The chemical reagents used were of analytical grade, and deionized water was used throughout the experiments.

2.2 Analytical methods

The phases of the samples were identified by a Rigaku-TTRIII X-ray diffractometer (Cu target, $K_{\alpha 1}$, $\lambda = 0.15406$ nm). The compositions of the sample phases were measured by Electron-Probe X-ray Microanalysis (EPMA), and the analysis was performed by a JEOL JXA-8230 instrument operated at 15 kV with a 10 nA beam current. The phase compositions of Ga and Ge in the samples were examined by chemical selective dissolution method; the zinc concentrations in leach solutions were analyzed by the ethylene diamine tetraacetic acid titration; the concentrations of Si and Ge in leach residues or solutions were analyzed by silicon molybdenum blue spectrophotometry method and extraction separation-benzfluorenone spectrophotometry method respectively (Yu et al., 2004); the concentrations of Ga, Fe and Cu in leach residues or solutions were determined by a Thermo Electron IRIS Intrepid II XSP Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) spectrometer. The specific surface area of iron powder was measured by a SSA-4200 specific surface area and pore size analyzer. The leach slurry was poured into a $\Phi 100$ Buchner funnel and filtered by vacuum suction using a SHZ-D(III) water-ring pump with a vacuum degree of 0.07 MPa in order to observe the filtration performance according to the filtration rate.

3 Results and discussion

3.1 Materials

The zinc refinery residue investigated was obtained from a Danxia smelter in southern China and it was used in the experiments as received, without further pre-treatment. The particle size of the residue was determined by a wet screen analysis, which showed that ca.76 wt% of the particles in the residue were $< 45 \mu\text{m}$ (Table 2).

From analysis of the residue XRD pattern shown in Fig. 1, it can be clearly seen that there are several diffraction peaks that are related to metallic zinc, zinc sulfate heptahydrate, zinc ferrite and zinc silicate. In contrast, diffraction peaks associated with the other components within the residue are not observed due to their low concentrations or amorphous states.

The EPMA results are shown in Fig. 2 and Table 3. The analysis confirms the presence of zinc sulfate with a small quantity of Ga and Ge (point analysis 1); slightly increased Ga and Ge contents present in the ferrite phase and zinc silicate phase individually (point analysis 6, 11, 13 and 3, 8) whilst the other points with increased contents of Ga and Ge are observed for the mixtures of iron, silica gels with zinc, lead, copper, calcium sulfates and metallic zinc, respectively.

Using the data listed in Table 3, the contents of Ga and Ge in the residue were determined as a function of the contents of analogous Fe and Si utilizing the regression analyses presented in Eqs. (1) – (4):

$$\text{pct Ge} = 0.1132 + 0.0534 \text{ pct Si} \quad R = 0.842 \quad (1)$$

$$\text{pct Ge} = 0.3061 + 0.0245 \text{ pct Fe} \quad R = 0.597 \quad (2)$$

$$\text{pct Ga} = 0.2114 + 0.0321 \text{ pct Si} \quad R = 0.298 \quad (3)$$

$$\text{pct Ga} = 0.1156 + 0.0061 \text{ pct Fe} \quad R = 0.078 \quad (4)$$

From the analysis it can be seen that there is a moderately strong positive correlation between Ge and Si and also between Ge and Fe. In contrast, the same analysis only shows a relatively weak positive correlation between Ga and Si and between Ga and Fe. From these results, it can be suggested that Ge is mainly co-precipitated with iron gel and silica gel in the form of $\text{MeO} \cdot \text{GeO}_2$, while Ga is mainly replaced by zinc powder into metallic form and then oxidized to Ga_2O_3 .

The phases of gallium and germanium outlined in Table 4 provide further confirmation of the results from EPMA that showed that gallium and germanium primarily exist in the form of dissociative or combined oxides.

The concentrations of Ga, Ge and other main elements of interest present in the residue are shown in Table 5. As can be seen, the residue contains 0.27 wt.% Ga and 0.36 wt.% Ge respectively, whereas the total iron and Fe(II) content are 7.9 wt.% and 3.7 wt.% respectively. The silica content is as high as 9.1 wt.%, indicating that the leaching of gallium and germanium can be challenging.

The particle size of the reduced iron powder used in the experiments was 80 microns, and the specific surface area was 0.36 g/m².

3.2 First leaching stage - Low acid leaching

The purpose of the low acid leaching for the zinc refinery residue was to dissolve zinc, copper and iron from the residue, whilst further enriching the Ga and Ge. This also has the added benefit of reducing the consumption of oxalic acid in the subsequent oxalic acid leaching of Ga and Ge. In order to reduce the leaching of Ge in the first-stage, the tannic acid was introduced because Ge can form insoluble solids with tannic acid in the leach solutions containing very low concentration of germanium (Kul and Topkaya, 2008). The most suitable conditions were determined to be as follows: temperature of 60 °C, sulfuric acid concentration of 60 g/L, tannic acid (TA) concentration of 2 g/L, L/S ratio of 10 and leaching time of 2 h.

The components of the residue before and after low acid leaching, and the leaching efficiencies of the metals, are shown in Table 5. The leaching efficiencies of Zn, Cu, Fe, Ga and Ge attained were 92%, 94%, 70%, 0.62% and 2.7% respectively. Fig. 3 shows the distributions of Ge,

Ga, Fe and SiO₂ in the residue, indicating that Ge and Ga mainly co-exist with SiO₂ in the residue after low acid leaching.

Zinc and copper were almost completely leached in the first leaching stage, with the main phases present in the residue found to be PbSO₄, SiO₂ and ZnFe₂O₄ (Fig. 4). The contents of Ga and Ge were shown to increase from 0.27% to 0.66% and 0.32% to 0.94%, respectively, suggesting enrichment of ca. 300% for these elements.

3.3 Second leaching stage - Oxalic acid leaching

3.3.1 Effect of oxalic acid concentration

The effect of H₂C₂O₄ concentration was examined by varying the H₂C₂O₄ concentration from 20 g/L to 115 g/L, as shown in Fig. 5. The results indicate that the extraction of Ga, Ge and Fe increases substantially as the H₂C₂O₄ concentration increased from 20 g/L to 70 g/L, with a change from 77% to 96% and from 56% to 99% for Ga and Ge, respectively. In contrast, with further increase in the acid concentration between 70 g/L to 115 g/L, the extraction of Ga and Ge is only slightly increased, the leaching of Ga and Ge can reach 98% and 99%, respectively, with 85 g/L H₂C₂O₄. On the other hand, the leaching of iron was also increased from 62% to 72% when H₂C₂O₄ concentration changed from 70 g/L to 85 g/L, thus the amount of oxalic acid used in the leaching can have a detrimental effect on the subsequent solution purification. Under the same conditions, the extraction of Cu and Zn decreased gradually from 5.5% to 0.46% and 6.1% to 0.85% with an increase in the H₂C₂O₄ concentration from 20 g/L to 115 g/L, and the leaching of Cu and Zn were 0.91% and 1.4%, respectively, when the H₂C₂O₄ concentration was 70 g/L. The reason for the observed decrease is that Zn(II) and Cu(II) form precipitates with oxalic acid (Eqs. (5) – (6)) as the concentration is increased (Chenakin et al., 2016; Ni et al., 2011).

Nevertheless, the leaching of Si decreased only slightly from 0.75% to 0.54 % when $\text{H}_2\text{C}_2\text{O}_4$ concentration was increased from 20 g/L to 115 g/L. Ga(III), Ge(IV) and iron(III) are known to form stable complexes with the dicarboxylic acids (Eqs. (7) – (9)) thus increased oxalic acid concentrations support leaching, whereas for Si complex formation (Eq. (10)) is inhibited and is thus not so dependent on the oxalic acid concentration (Taxiarchou et al., 1997; Pokrovski et al., 1998; Veglio et al., 1999), and the main reactions and the corresponding stability constants derived are listed in Table 6.

3.3.2 Effect of leaching time

The effects of leaching time on the recovery of metals during the second leaching stage are presented in Fig. 6. It can be seen that the leaching of Ga and Ge were efficient and fast with 85% of the Ga and 88% of the Ge extracted within 30 min from the commencement of leaching. Thereafter, the leaching of Ga and Ge reached a maximum recovery of 96% and 99%, respectively, after 2 h. The leaching of iron increased from 40 to 65% when the leaching time was increased from 0.5 h to 4 h. The leaching of Zn and Cu increased with increasing leaching time up to 1 h with measured recovery of 2.0% and 2.5% to the solution. Further increase in the leaching time resulted in a gradual decrease in the levels of Zn and Cu leaching observed. The reason for the decrease is attributed to the increased formation of CuC_2O_4 and $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with leaching times longer than approximately one hour. In contrast, the leaching of silica remained nearly constant at approximately 0.59% for all leaching times investigated due to the weak interaction of silica with the organic functional groups in oxalic acid.

3.3.3 Effect of L/S ratio

Fig. 7 shows the effects of the liquid-to-solid (L/S) ratio on the leaching of Ga, Ge, Fe, Cu, Zn and Si. These results indicate that the leaching of Ga, Ge and Fe increased gradually as L/S increased from 4 to 10, but that the leaching of Cu and Zn tends to decrease after an initial rise in the leaching percentage. The leaching of Ga, Ge, Fe, Cu and Zn at L/S ratio of 10 reached yields of 96%, 99%, 62%, 0.91% and 1.4%, respectively. Further increase in L/S ratio was found to have no remarkable effect on the leaching of Ga and Ge. Under the same conditions, the leaching of Si increased from 0.53% to 0.81% with an increase in the L/S ratio from 4 to 12, resulting in a decrease in the filtration rate of the leach slurry from $688 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $566 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. The formation of silica gel, which results in a decreased filterability of the slurry, is more likely at higher L/S ratios due to the higher Si content (Hua et al., 2002; Harbuck, 1993; Bodas, 1996).

3.3.4 Effect of temperature

The yields of Ga, Ge, Fe, Cu, Zn and Si into the leach solution were investigated over a temperature range between $30\text{ }^{\circ}\text{C}$ – $90\text{ }^{\circ}\text{C}$ and the results are shown in Fig. 8. Temperature was observed to have a significant effect on the leaching of Ga, Ge and Fe, but only a minor effect on the dissolution of Cu, Zn and Si under the same conditions. The dissolution of Ga and Ge increased from 71% to 96% and 70% to 99%, respectively, when the temperature was increased from $30\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$, whereas only 62% of Fe was leached at $90\text{ }^{\circ}\text{C}$. This iron leaching phenomenon can be attributed to the simultaneous precipitation reaction of ferrous ions and oxalic acid (Eq. (11)), that leads to the formation of $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (Fig. 9). Ferrous ions in the solution can originate from the first-stage leaching residues or from the reduction of Fe(III) by $\text{H}_2\text{C}_2\text{O}_4$ (Taxiarchou et al., 1997; Veglio et al., 1999).

By comparison, the dissolution of Cu, Zn and Si was found to be only minor (0.5% to 2.0%) over the same temperature range.

3.3.5 Most suitable operating conditions

Based on the above results, the most suitable second stage leaching conditions were determined to be a $\text{H}_2\text{C}_2\text{O}_4$ concentration of 70 g/L with an L/S ratio of 10 at 90 °C for 2 h. Under these conditions, 96% Ga, 99 % Ge were extracted to give a leach solution with a composition of 0.65 g/L Ga(III), 0.93 g/L Ge(IV), 5.4 g/L Fe(III), 0.052 g/L Zn(II), 0.011 g/L Cu(II) and 0.17 g/L Si(IV). The XRD of leaching residues showed that the main phase in the leach residues were $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 and PbSO_4 .

It is noteworthy that ca. 60% of the iron was leached in the form of a complex (ferric oxalate) during the oxalic acid leaching. This can have a detrimental impact on the extraction of Ga(III) and Ge(IV) and the recycling efficiency of the extractant in the subsequent Ga(III) and Ge(IV) extraction processes. As a result, the following iron removal step was included as a necessary part of the overall extraction process.

3.4 Removal of iron

In this study, the process of ultrasound-assisted ferrous iron precipitation was adopted in order to remove iron through reduction of the ferric iron in solution to the ferrous form, which subsequently precipitates in the form of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and the main reaction is expressed in Eq. (12).

The most suitable conditions for the maximum removal of 96% of the iron were determined as follows: Fe(iron powder)/Fe(III) molar ratio of 5,

ultrasound time of 10 min, reaction temperature of 50 °C; stirring speed of 300 rpm; reaction time of 1 h. The results are shown in Table 7 and it can be seen that during this stage that 1.4% Ga(III) and 1.3% Ge(IV) present in the solution also precipitated along with the iron product, and the pH of the solution increased slightly from 0.50 to 0.63.

4 Conclusions

In this paper, a hydrometallurgical process for treating zinc refinery residues was investigated. In the first low sulfuric acid leaching stage, Zn and Cu could be dissolved selectively into the solution, with yields found to be 92% and 94%, respectively, resulting in the enrichment of Ga and Ge in the residue up to ca. 300 %.

In the second leaching stage by oxalic acid, it was shown that $\text{H}_2\text{C}_2\text{O}_4$ concentration and temperature strongly influenced the leaching of Ga and Ge. Under the most suitable conditions, 96% Ga and 99% Ge were leached, whilst the leaching of Zn, Cu and Si were all observed to be less than 2%.

Over 96% Fe(III) was removed in the form of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by an ultrasound-assisted ferrous iron precipitation method with minor losses of Ga(III) and Ge(IV). After iron removal, Ga(III) and Ge(IV) could be extracted from the iron free solution using an organic system containing N235 and TBP in sulfonated kerosene, which will be focused on Part II of this paper.

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Fig.2. X-ray diffraction pattern of the zinc refinery residue.

Fig. 3. EPMA image of the zinc refinery residue.

Fig.4. Distribution maps of Ge, Si, Ga and Fe in the leaching residues after the first leaching stage ($T=60^{\circ}\text{C}$; $[\text{H}_2\text{SO}_4]=60\text{g/L}$; $L/S=10$; $[\text{TA}]=2\text{g/L}$; $t=2\text{h}$).

Fig.5. X-ray diffraction pattern of the leaching residues after the first leaching stage ($T=60^\circ\text{C}$; $[\text{H}_2\text{SO}_4]=60\text{g/L}$; $L/S=10$; $[\text{TA}]=2\text{g/L}$; $t=2\text{h}$).

Fig.6. Effect of oxalic acid concentration on the recovery of Ga, Ge, Fe, Cu, Zn and Si to the solution during zinc refinery residue leaching ($T=90^{\circ}\text{C}$; $L/S=10$; $t=2\text{h}$).

Fig.7. Effect of leaching time on the recovery of Ga, Ge, Fe, Cu, Zn and Si to the solution during zinc refinery residue leaching ($[\text{H}_2\text{C}_2\text{O}_4]=70 \text{ g/L}$; $T=90^\circ\text{C}$; $L/S=10$).

Fig.8. Effect of L/S on the recovery of Ga, Ge, Fe, Cu, Zn and Si to the solution during zinc refinery residue leaching ($[\text{H}_2\text{C}_2\text{O}_4]=70 \text{ g/L}$; $T=90 \text{ }^\circ\text{C}$; $t=2\text{h}$).

Fig.9. Effect of temperature on the recovery of Ga, Ge, Fe, Cu, Zn and Si to the solution during zinc refinery residue leaching ($[\text{H}_2\text{C}_2\text{O}_4]=70\text{g/L}$; $\text{L/S}=10$; $t=2\text{h}$).

Fig.10. X-ray diffraction pattern of the leaching residue after oxalic acid leaching ($T=90^\circ\text{C}$; $[\text{H}_2\text{C}_2\text{O}_4]=70 \text{ g/L}$; $L/S=10$; $t=2\text{h}$).

Table 1. Main parameters investigated in the experiments.

Experiment	Investigated parameters
First leaching stage	Liquid-to-solid (L/S) (ml/g): 4-12; Temperature (°C): 30-80; H ₂ SO ₄ (g/L): 20-100; Reaction time (h): 1-4; Tannic acid (g/L): 0.5-4
Second leaching stage	L/S (ml/g): 4-12; Temperature (°C): 30-90; H ₂ C ₂ O ₄ (g/L): 20-115; Reaction time (h): 0.5-4
Iron removal	Fe/Fe(III) mole ratio:1-7; Ultrasound (200 W) time (min): 0-15; Temperature (°C): 30-70; Time (h): 0.5-2

Table 2. Particle size distribution of the zinc refinery residue by wet screen analysis.

Particle size/ μm	<45	45-60	60-93	93-150	>150
wt%	76	4.7	4.6	11	3.8

Table 3. EPMA results of the spots shown in Fig.3 (wt.%).

Spot	O	Ge	S	Ga	Zn	Fe	Cu	Si	Pb	Ca
1	40	0.073	11	0.041	22	1.7	3.1	2.7	0.26	0.061
2	40	0.84	2.7	0.43	21	5.9	5.6	6.5	1.3	ND
3	42	0.81	2.6	0.31	13	6.0	2.7	12	0.28	5.5
4	42	0.41	4.3	0.24	24	5.5	5.5	2.3	0.32	0.47
5	55	0.51	3.2	0.48	14	4.5	5.7	6.2	0.72	10
6	27	0.10	0.49	0.16	17	41	1.2	0.48	0.07	ND
7	47	0.046	11	0.50	23	2.6	3.7	1.2	0.47	14
8	41	0.73	1.4	0.29	14	5.3	1.8	14	0.21	3.1
9	46	0.56	6.2	0.52	24	2.2	5.5	13	0.28	0.90
10	47	0.54	4.2	0.42	23	3.5	4.5	9.8	0.32	3.5
11	29	0.12	0.39	0.16	17	42	0.8	0.45	0.10	0.14
12	50	0.47	4.9	0.45	16	2.6	5.4	6.8	0.11	2.7
13	39	0.14	0.30	0.34	20	38	0.70	0.55	0.069	1.1
14	42	0.86	3.1	0.30	12	5.8	2.7	15	0.24	2.6
15	47	0.61	4.7	0.20	25	5.1	5.4	11	0.32	0.47

ND – not detected at a minimum detection limit of 300 ppm.

Table 4. Phase composition of gallium and germanium in the zinc refinery residue.

Germanium phases	wt. %	Distribution (%)	Gallium phases	wt. %	Distribution (%)
MeO·GeO ₂	0.22	61	MeO·Ga ₂ O ₃	0.076	29
GeO+GeO ₂	0.081	23	Ga ₂ O ₃	0.19	70
Ge+GeS ₂ +GeS	0.059	16	Ga+Ga ₂ S ₃	0.003	1.0
Total	0.36	100	Total	0.27	100

Table 5. Metal contents in the residue before and after the first leaching stage (low acid leaching) and the leaching efficiencies of metals.

Element	Zn	Cu	Fe	Pb	Ga	Ge	SiO ₂
wt. %	24	5.6	7.9	0.46	0.27	0.36	9.1
wt. %	5.2	0.80	8.0	1.3	0.66	0.94	21
Leaching (%)	92	94	70	0.15	0.62	2.7	0.25

Table 6. The main reaction and corresponding equilibrium constants in oxalate leaching stage (298.15 K).

Equation no.	Reaction	logK	References
(5)	$\text{ZnO} + \text{HC}_2\text{O}_4^- + \text{H}^+ + \text{H}_2\text{O} = \text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	15.70	Weast (1976)
(6)	$\text{CuO} + \text{HC}_2\text{O}_4^- + \text{H}^+ = \text{CuC}_2\text{O}_4 + \text{H}_2\text{O}$	8.89	Weast (1976)
(7)	$\text{Ga}_2\text{O}_3 + 6\text{HC}_2\text{O}_4^- = 2\text{Ga}(\text{C}_2\text{O}_4)_3^{3-} + 3\text{H}_2\text{O}$	9.12	Weast (1976) HSC 7.0 software
(8)	$\text{GeO}_2 + 2\text{HC}_2\text{O}_4^- = \text{Ge}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$	2.95	Everest(1955) Pokrovski(1998)
(9)	$\text{Fe}_2\text{O}_3 + 6\text{HC}_2\text{O}_4^- = 2\text{Fe}(\text{C}_2\text{O}_4)_3^{3-} + 3\text{H}_2\text{O}$	30.50	Weast (1976)
(10)	$\text{SiO}_2 + \text{HC}_2\text{O}_4^- + \text{H}^+ = \text{Si}(\text{OH})_2\text{C}_2\text{O}_4$	-16.64	Bennett(1991) Pokrovski(1998)

Table 7. Composition of oxalate solution before and after ferrous iron precipitation and the precipitation ratio of metals.

Element	Fe	Zn	Cu	Ga	Ge	Si	pH
Before (g/L)	5.4	0.052	0.011	0.65	0.93	0.17	0.50
After (g/L)	0.20	0.050	0.001	0.64	0.92	0.064	0.63
Precipitation (%)	96	0.96	91	1.4	1.3	61	