

Article

# Germanium and Indium Recovery from Zinc Metallurgy by-Products—Dross Leaching in Sulphuric and Oxalic Acids

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**Abstract:** Leaching of the dross containing 28.7% Sn, 18.0 Pb, 10.6% Cu, 8.9% Ge, 8.1% Zn, and 2.7% In in sulphuric and oxalic acid solution was investigated. The dross was obtained from thermal oxidation of by-product alloy generated during a New Jersey (NJ) zinc rectification process. The influence of different process conditions (temperature, time, acid concentration, and solid to liquid ratio) on leaching yield of the main components was determined. Additionally, the impact of oxidant (hydrogen peroxide, sodium hypochlorite, manganese (IV) oxide) addition on leachabilities was investigated. Germanium leaching yields exceeding 80% were observed for both sulphuric and oxalic acid solutions. Indium leachability in  $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$  was found at the level of 20%, while in  $\text{H}_2\text{SO}_4(\text{aq})$ , it strongly depends on process temperature, and reached 80% at 80 °C.

**Keywords:** germanium recovery; indium recovery; tin recovery; New Jersey process; leaching; hydrometallurgy

## 1. Introduction

Germanium is an important and rare metalloid. Its abundance in the earth's crust is estimated at 1.6 ppm [1]. Germanium is used in many applications like optic fibres (40% of global Ge consumption), infrared optics (30%), electronics and photovoltaics (20%), as well as other applications (10%) [2], e.g., PET (polyethylene terephthalate) production catalysts [3]. It is a dispersed element and is not present in economically-mineable ores, but rather as an accompanying constituent in the ores of other elements. The main sources of germanium are coal ash (56% of Ge production in 2013 [4]), by-products of zinc production (33% in 2013 [4]), and recycling (ca. 30% [5]).

Typical concentrations of germanium in processed materials are not high. Coal ash from Chinese and far-east Russian power plants contain 0.3–0.5% Ge [6], while European ones contain up to 400 ppm Ge [7]. Ash containing <15 ppm Ge are not currently considered as a potential germanium source [8]. Zinc plant residues contain usually 0.01–0.60% Ge [9–12].

There are several different ways to recover germanium from its sources. In the first step, material is usually leached in aqueous solutions of sulphuric [9,10,13], oxalic acid [12,14], or alkalis [15]. Then, germanium may be recovered from solutions by precipitation with tannic acid [10,16,17], sulphide [18], catechol-cetyltrimethylammonium [18],  $\text{GeCl}_4$  distillation [4,19,20], solvent extraction [15,21–23], ion-exchange techniques [24–27]. Pyrometallurgical methods like vacuum metallurgical process [28,29] may be also applied.

Indium is a rarer metal than germanium. Its concentration in earth's crust ranges between 0.05–0.20 ppm [30]. Despite this fact, it is not so dispersed; therefore its annual production is higher—ca. 720 tonnes in 2017.

About 90% of In is used as indium-tin oxide (ITO) in LCD (liquid-crystal display) flat panel displays. It is also applied in solders and alloys, electrical components, semiconductors, as well as in intermetallic compounds [31]. Indium is almost entirely (~95%) obtained as a by-product of zinc production. Minor amounts are produced from copper and tin refinery residues [32]. Usually, materials used for indium recovery contain up to 800 ppm In [33–35].

Generally, the processing of indium-bearing material comprises leaching in hydrochloric [35,36] or sulphuric acid [34,36,37], followed by precipitation of concentrate [35–38] or solvent extraction [33,39]. Ion-exchange resins, electrolytic separation, as well as pyrometallurgical methods may be also applied [40].

Germanium and indium are considered as critical raw materials by the European Union [41]. Therefore, substrates containing significant concentrations of both elements are of great interest. One of the examples is a by-product polymetallic alloy obtained during rectification of zinc by the New Jersey (NJ) method [35]. It contains quite large concentrations of germanium (~10%) as well as a significant indium content (~2%). However, critical elements are not currently recovered from the alloy. So, it is necessary to find appropriate methods for Ge and In recovery.

There are several publications concerning the leaching of Ge and In materials. However, these are mainly focused on the recovery of one of these elements only. Additionally, information about Ge recovery from industrially-available, tin-bearing material is limited.

In this study, GeIn dross obtained by pyrometallurgical oxidation of by-product alloy from NJ process was used as initial material. The alloy was pyrometallurgically drossed to make it suitable for hydrometallurgical processing. This material contained mainly tin, copper, lead, zinc, germanium, and indium.

The aim of the present work was to analyse leaching of the dross in sulphuric and oxalic acid solutions in the context of germanium and indium recovery. Leachabilities of germanium, indium, and accompanying elements were determined. Obtained results were analysed, taking into account the next steps of germanium and indium recovery from aqueous solutions.

## 2. Materials and Methods

GeIn dross, prepared in the IMN (Instytut Metali Nieżelaznych, Gliwice, Poland) by thermal oxidation of by-product alloy from New Jersey zinc rectification process was used for experiments. The alloy containing ca. 36% Sn, 21% Cu, 19% Pb, 9% Zn, 7% Ge, and 1.7% In was heated to 600–700 °C in open air with addition of NaNO<sub>3</sub> and vigorously mixed for 40 h. The dross was collected, while a copper- and tin-enriched alloy was casted. Crude dross was sieved through 0.32 mm sieve prior to experiments in order to separate metallic droplets. The oversize fraction was recycled in the thermal oxidation step. The dross was leached using aqueous solution of sulphuric (98%, Avantor, Gliwice, Poland) and oxalic (dihydrate, p.a., Chempur, Piekary Śląskie, Poland) acids. The oxidants used in the investigation were aqueous solutions of hydrogen peroxide (30%, Avantor, Gliwice, Poland) and sodium hypochlorite (min. 12.5% active Cl—150 g/dm<sup>3</sup>, Stanlab, Lublin, Poland) as well as manganese (IV) oxide (88%, electrolytically precipitated, Acros Organics, Geel, Belgium). Post-leaching solution pH was adjusted using aqueous solution of sodium hydroxide (30%, PCC Rokita, Brzeg Dolny, Poland). Distilled water (<2 µS/cm) was used in the experiments.

The dross was leached under different conditions—temperature (25–90 °C), time (0.5–4 h), acid concentration (5–30%) and solid to liquid ratio (S/L, 1/30–1/5 kg/dm<sup>3</sup>). Experiments were performed in 2 dm<sup>3</sup> beakers, using mechanical stirrer (500 rpm) and thermostatic heating plates equipped with thermometers. In the first step, 1 dm<sup>3</sup> of leaching solution was poured into a beaker. Then, the solution was heated to the desired temperature while mixing. When the selected temperature was achieved, an appropriate amount of the dross was added (e.g., 0.1 kg for S/L = 1/10 kg/dm<sup>3</sup>).

The suspension was mixed for the chosen period of time. Then, heating and mixing were turned off, and the suspension was cooled to room temperature and filtered using a Buchner funnel and vacuum pump (0.5 bar underpressure).

Filtrates and dross were analysed at the IMN's Department of Analytical Chemistry. The concentration of elements was measured using ICP MS (Inductively Coupled Plasma—Mass Spectroscopy; Nexion, PerkinElmer, Waltham, MA, USA). Filtrates were diluted and acidified using hydrochloric acid (35%, Avantor, Gliwice, Poland) prior to analysis. In the case of the dross, a 0.2 g portion of the material was first melted with 1 g  $\text{Na}_2\text{O}_2$  (p.a., Avantor, Gliwice, Poland) at 600 °C for 30 min in a corundum crucible. The crucible containing the resulting alloy was placed in a polypropylene vessel where 10 cm<sup>3</sup> of 1:1 mixture of concentrated nitric (65%, Avantor, Gliwice, Poland) and hydrofluoric (40%, VWR, Lutterworth, UK) acid was added. The vessel was heated to 110 °C until complete dissolution of the alloy. The crucible was washed with water, and the resulting solution was filled with water to 100 cm<sup>3</sup> and analysed.

X-ray diffraction (XRD) analysis was performed using Co  $K\alpha$  radiation and an Fe filter (XRD 7, Seifert-FPM, Freiberg, Germany). Analyses were performed in the range of  $2\Theta$  angles from 10° to 100°, which corresponds to  $d_{hkl}$  spacings between 1.027 and 0.1168 nm. The measurements were taken with a step of  $0.04^\circ 2\Theta$  and time 2 s per step. The identification was performed with the use of Seifert and Match! Software and PDF-2 database (ICDD, International Centre for Diffraction Data). The samples were prepared by placing the finely ground powder in a hollow sample holder and levelling the surface with a sharp glass blade.

### 3. Results

#### 3.1. Dross Analysis

Chemical analysis of the fine dross fraction is shown in Table 1, while its XRD pattern is presented in Figure 1. The dross was the mixture of oxide and metallic phases—mainly cassiterite ( $\text{SnO}_2$ ) and metallic lead. It contained also metallic tin as well as mixture of other oxides— $\text{ZnGeO}_4$ ,  $\text{In}_2\text{Ge}_2\text{O}_7$  and smaller amounts of  $\text{Pb}_2\text{O}_3$ ,  $\text{SnPb}_2\text{O}_4$ .

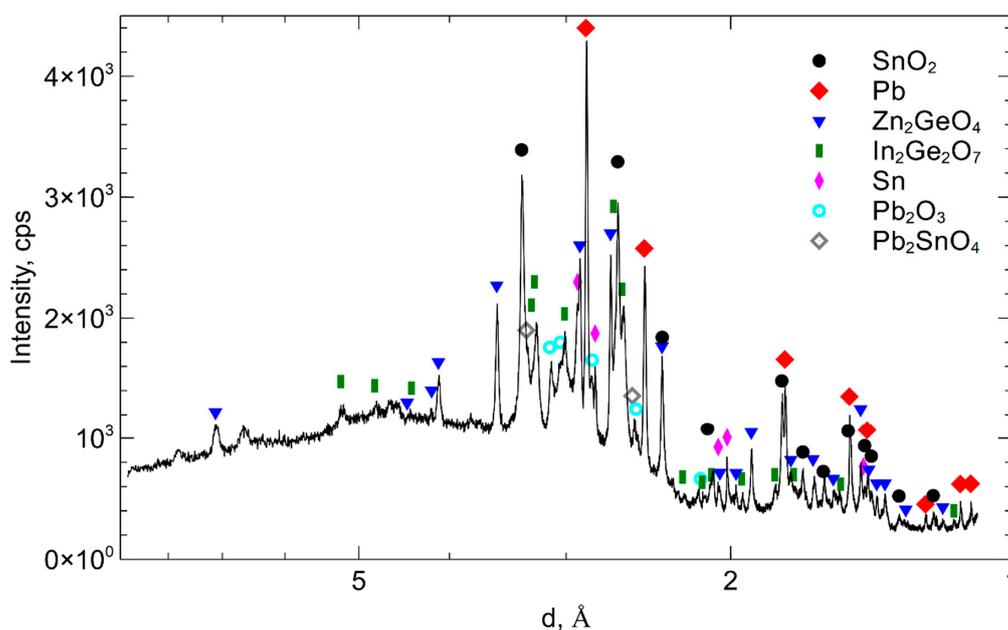


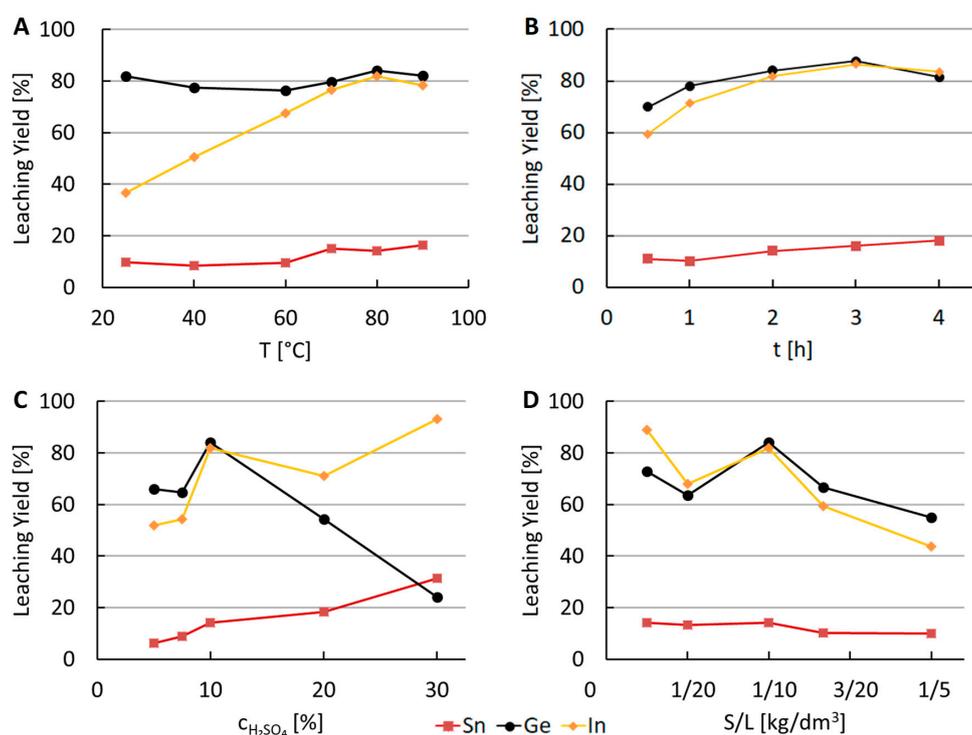
Figure 1. X-ray powder diffraction (XRD) pattern of GeIn dross.

**Table 1.** Composition of GeIn dross used in experiments.

Element	Sn	Pb	Cu	Ge	Zn	In
[wt. %]	28.7	18.0	10.6	8.90	8.12	2.74

### 3.2. Leaching—Sulphuric Acid

In the first step, GeIn dross was leached using an aqueous solutions of sulphuric acid. The influence of four different process parameters was investigated—temperature, time, acid concentration, and dross mass to leaching solution volume ratio. Leachabilities of germanium, indium, and tin are shown in the Figure 2A–D. It was found that in each case copper, lead and silver were not leached, and their concentrations in the post-leaching solutions did not exceed  $0.025 \text{ g/dm}^3$  (Table 2), while over 95% of zinc was leached.



**Figure 2.** Leachabilities of tin, germanium and indium in sulphuric acid solution. Influence of: (A) temperature ( $t = 2 \text{ h}$ ,  $C_{\text{H}_2\text{SO}_4} = 10\%$ ,  $S/L = 1/10$ ); (B) time ( $T = 80 \text{ }^\circ\text{C}$ ,  $C_{\text{H}_2\text{SO}_4} = 10\%$ ,  $S/L = 1/10$ ); (C)  $\text{H}_2\text{SO}_4$  concentration ( $T = 80 \text{ }^\circ\text{C}$ ,  $t = 2 \text{ h}$ ,  $S/L = 1/10$ ); (D) S/L ratio ( $T = 80 \text{ }^\circ\text{C}$ ,  $t = 2 \text{ h}$ ,  $C_{\text{H}_2\text{SO}_4} = 10\%$ ).

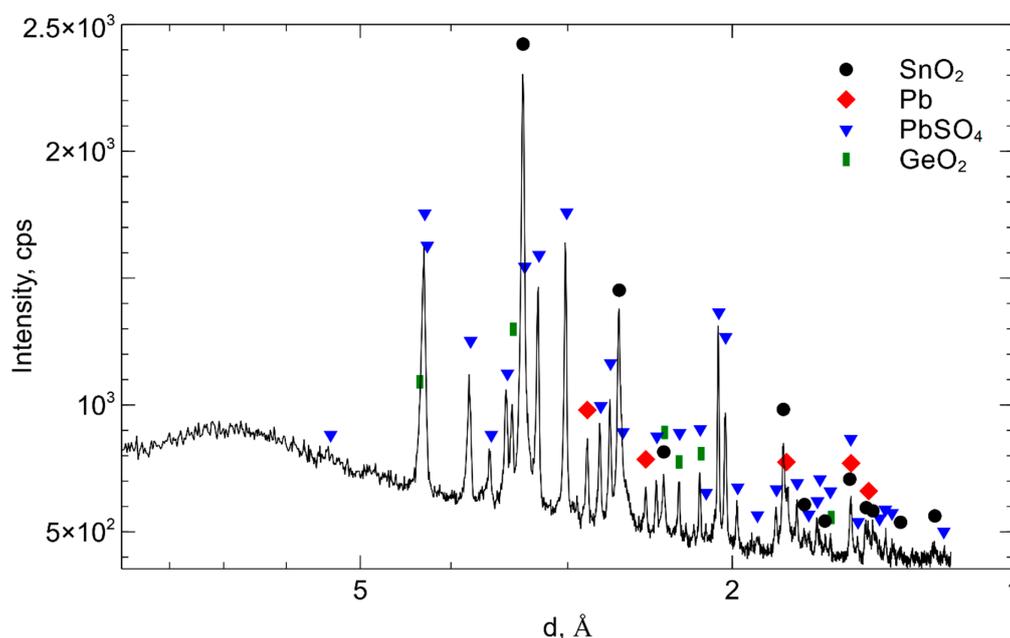
Temperature has almost no influence on Ge leachability, which is between 77–82%. A significant increase of indium leachability is observed, while temperature is increased—it changes from 37% at  $25 \text{ }^\circ\text{C}$  to 82% at  $80 \text{ }^\circ\text{C}$ . Tin leaching yield is low, and slightly increases from 8% at  $25 \text{ }^\circ\text{C}$  to almost 16% at  $90 \text{ }^\circ\text{C}$ .

It may be noted that leachabilities of Ge and In increased with time, reaching a maximum (85%) after 2–3 h. The leaching rate of tin was also slightly increased with time.

The concentration of sulphuric acid had significant influence on germanium leachability. It was found that it reached its maximum (82%) for 10%  $\text{H}_2\text{SO}_4$ . In the case of indium and tin, higher acid concentration leads to higher leaching efficiency.

The ratio of the dross mass to acid solution volume also had an impact on the leaching yield of germanium and indium, which reaches the maximum value for  $S/L = 1/10$ . The leachability of tin slightly decreases with increasing S/L.

Figure 3 presents the XRD pattern of leaching residue. It was mainly composed of lead sulphate ( $\text{PbSO}_4$ ) and cassiterite ( $\text{SnO}_2$ ); however, germanium oxide ( $\text{GeO}_2$ ) and metallic lead were also detected.



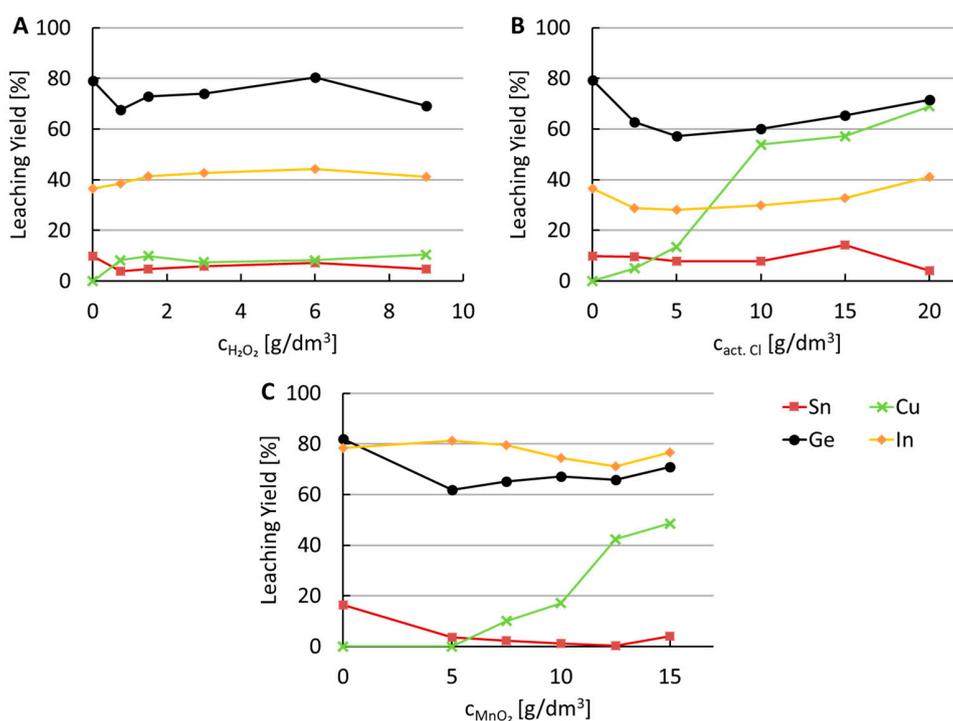
**Figure 3.** X-ray powder diffraction (XRD) pattern of the residue obtained from leaching of GeIn dross in sulphuric acid solution.

### 3.3. Leaching—Sulphuric Acid + Oxidant

The influence of three different oxidants (hydrogen peroxide, sodium hypochlorite, manganese dioxide) on leachabilities of selected elements was also investigated. Experiments were performed at 25 °C ( $\text{MnO}_2$  addition was investigated at 90 °C due to no effect at lower temperature) for 2 h, using 10% aqueous solution of sulphuric acid and  $S/L = 1/10$ . The results of the tests are shown in the Figure 4A–C.

**Table 2.** Concentration of investigated elements in filtrates under selected process conditions ( $S/L = 1/10$  in all cases).

Conditions		c [g/dm <sup>3</sup> ]							
Acid	Oxidant	T [°C]	t [h]	Pb	Sn	Zn	Ge	Cu	In
10% $\text{H}_2\text{SO}_4$	-	80	2	0.015	2.8	8.1	6.4	0.002	3.4
10% $\text{H}_2\text{SO}_4$	-	25	2	0.013	1.9	7.7	6.0	0.006	1.5
10% $\text{H}_2\text{SO}_4$	9.0 g/dm <sup>3</sup> $\text{H}_2\text{O}_2$	25	2	0.006	0.9	7.8	4.8	0.54	1.6
10% $\text{H}_2\text{SO}_4$	20 g/dm <sup>3</sup> act. Cl ( $\text{NaClO}$ )	25	2	0.12	4.1	6.3	4.8	3.4	1.5
10% $\text{H}_2\text{SO}_4$	15.0 g/dm <sup>3</sup> $\text{MnO}_2$	90	2	0.011	0.05	7.7	4.8	2.4	2.8
10% $\text{H}_2\text{C}_2\text{O}_4$	-	90	2.5	0.025	1.5	0.033	6.1	0.006	0.37



**Figure 4.** Leachabilities of tin, copper, germanium and indium in 10% sulphuric acid with addition of different oxidants: (A) H<sub>2</sub>O<sub>2</sub> (25 °C, 2 h, S/L = 1/10); (B) HClO (25 °C, 2 h, S/L = 1/10); (C) MnO<sub>2</sub> (90 °C, 2 h, S/L = 1/10).

It was found that the application of oxidants had no positive impact on leaching yield of germanium. For all investigated concentrations, Ge leachabilities did not exceed 80%, and were lower than that when an oxidant was not used. In the case of indium and tin, oxidant addition also had no positive influence on leaching yields.

On the other hand, the application of an oxidant improved the leachability of copper. While for hydrogen peroxide the improvement was slight (up to 10%), for two other oxidising agents, leaching yields increased significantly—for the highest applied concentrations of hypochlorous acid and manganese dioxide, leachabilities were 69% and 49%, respectively.

### 3.4. Leaching—Oxalic Acid

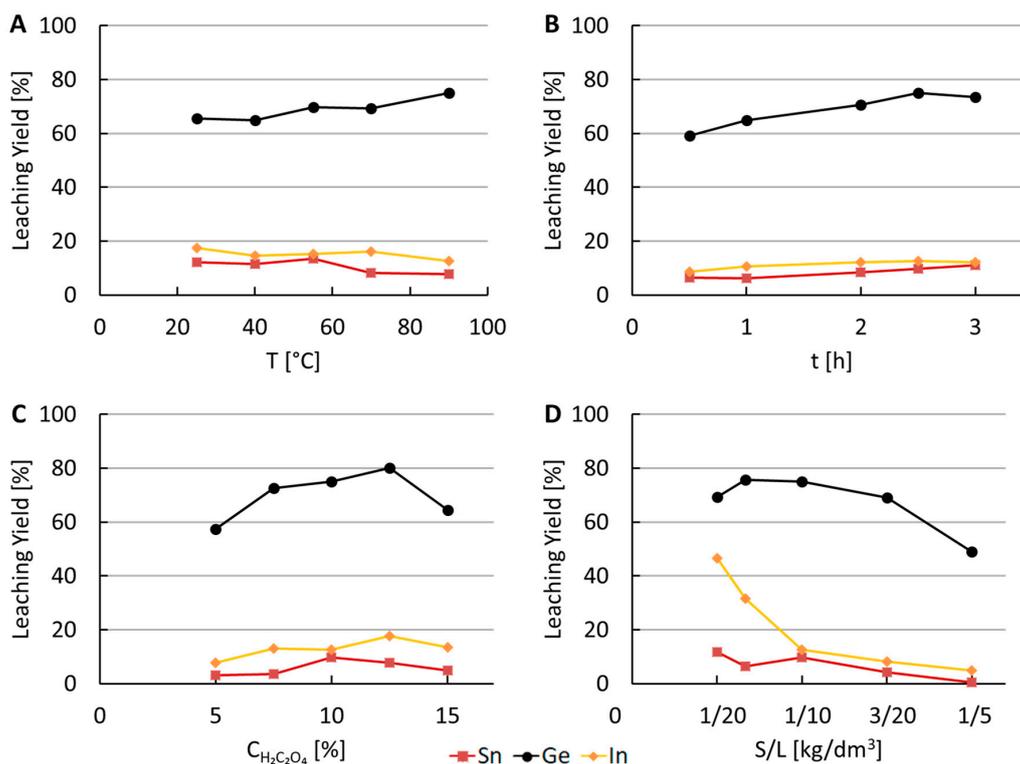
Leaching of the dross in aqueous solutions of oxalic acid was investigated. The influence of four parameters (temperature, time, acid concentration, and dross mass to leaching solution volume ratio) on leachabilities of metals of interest was determined. The results of the tests are presented in Figure 5A–D.

It was found that in each case, copper, lead, silver, and zinc were not leached (<0.1%), and their concentrations in the post-leaching solutions did not exceed 0.03 g/dm<sup>3</sup> (Table 2).

Germanium leachability slightly increased with temperature, and reached 75% for 90 °C. In the case of indium and tin, no significant impact was observed, and their leaching yields were between 13–17%.

The maximum leaching yield of germanium was achieved after 2.5 h of leaching. Leachabilities of the other investigated elements increased slightly with time, but did not exceed 15% after 3 h.

It may be noted that the highest Ge leachability (80%) was obtained for 12.5% aqueous solution of oxalic acid. The leaching yields of indium and tin were not significantly affected by the change of acid concentration.



**Figure 5.** Leachabilities of tin, germanium and indium in oxalic acid solution. Influence of: (A) temperature ( $t = 2.5$  h,  $C_{H_2C_2O_4} = 1$  M,  $S/L = 1/10$ ); (B) time ( $T = 90$  °C,  $C_{H_2SO_4} = 1$  M,  $S/L = 1/10$ ); (C)  $H_2C_2O_4$  concentration ( $T = 90$  °C,  $t = 2.5$  h,  $S/L = 1/10$ ); (D) S/L ratio ( $T = 90$  °C,  $t = 2.5$  h,  $C_{H_2C_2O_4} = 1$  M).

The ratio of the dross mass to solution volume significantly influenced on Ge and In leaching yields. Germanium leachability reached maximum for S/L between 1/15–1/10. In the case of indium, a decrease of leaching yield with increasing S/L ratio was observed—from 47% for 1/20 to 5% for 1/5.

#### 4. Discussion

Zinc was almost fully leached in sulphuric acid, forming soluble zinc sulphate. In the case of germanium and indium, a maximum leaching yield of 85% was achieved. One of the reasons of the incomplete leaching might have been the adsorption of Ge and In containing species on the surface of SnO<sub>2</sub> particles formed during leaching.

It may be also noted that the reaction rate of germanium dissolution was higher than for indium. Ge and In leaching yields are similar after 3 h, while for shorter times, Ge leachability is higher (Figure 2B). Also, temperature dependence (Figure 2A) suggested similar conclusions—at higher temperatures, a shorter time was needed to achieve maximum leaching yield.

The leaching yield of germanium reached its maximum for 10% H<sub>2</sub>SO<sub>4</sub>. This observation was also proved by other authors [10,42]. Sulphuric acid was required to decompose mixed germanium-zinc and germanium-indium oxides present in the dross. On the other hand, the solubility of GeO<sub>2</sub>, which was one of the decomposition products, decreased as the H<sub>2</sub>SO<sub>4</sub> concentration increased [43,44]. This form of germanium was present in the residue.

Only a small part of tin present in the dross was leached in sulphuric acid. Most of the tin contained in the initial material was in the form of cassiterite (SnO<sub>2</sub>), which was insoluble in water and weak acids. Tin leachability rose significantly when acid concentration was increased (Figure 2C). It was connected with the higher solubility of tin(IV) oxide in concentrated H<sub>2</sub>SO<sub>4</sub>.

Copper and lead were not leached under the investigated conditions. Most of the lead present in the dross formed lead (II) sulphate, which was insoluble in water and sulphuric acid solutions. Copper was not dissolved, because it was present in the metallic form, which did not react with acid under non-oxidising conditions.

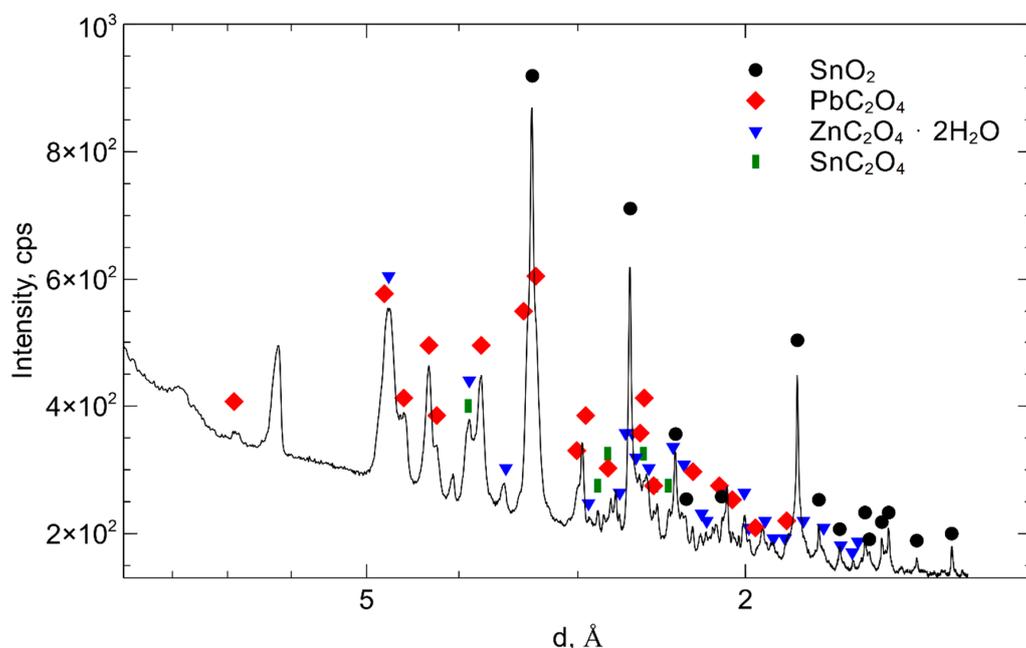
The oxidants were added in order to dissolve the metallic matrix, which might have contained entrapped Ge and In species. However, it was found that leachabilities of germanium and indium were not higher.

The addition of an oxidising agent increased the conversion rate of germanium to  $\text{GeO}_2$ , which is sparingly soluble in sulphate solutions [43]. Therefore, Ge leaching yield was not improved. In the case of  $\text{HClO}$ , it was noticed that the lowest germanium leachability (58%) was achieved for  $5 \text{ g/dm}^3$  of added active Cl. For higher levels of active chlorine, Ge leaching yields were higher. This effect was connected with increasing the concentration of chlorides in the solution. The solubility of germanium (IV) oxide in  $\text{HCl}$  solutions is higher than in  $\text{H}_2\text{SO}_4$  [43].

Tin oxidation led to the formation of  $\text{SnO}_2$ , which is insoluble in diluted  $\text{H}_2\text{SO}_4$  solution. Therefore, any additional tin transferred to the solution was precipitated as an oxide. A decrease of tin leaching yield was noticed, especially when  $\text{H}_2\text{O}_2$  and  $\text{MnO}_2$  was used; this was a result of  $\text{Sn(II)}$  oxidation and formation of insoluble  $\text{SnO}_2$ . In the case of  $\text{NaClO}$ , it was not so noticeable due to formation of water-soluble tin chlorides. Additionally, the formation of  $\text{SnO}_2$  might have led to adsorption of other elements like indium, which reduced their leaching yields.

It was noted that the addition of oxidants increased the leaching yields of copper. Copper in the dross was present in metallic form, which was not susceptible to leaching in sulphuric acid solution. After addition of oxidants copper was oxidized and formed soluble  $\text{CuSO}_4$ .

It was found that  $\text{Pb}$ ,  $\text{Zn}$ ,  $\text{Cu}$ , and  $\text{Ag}$  are not leached by oxalic acid solutions. Zinc and lead were converted to water insoluble oxalates. Therefore,  $\text{Zn}$  and  $\text{Pb}$  were present only in residue (Figure 6). Copper and silver in the dross were present in metallic form and did not react with oxalic acid, which is a weak acid.



**Figure 6.** X-ray powder diffraction (XRD) pattern of the residue obtained after leaching of GeIn dross in oxalic acid solution.

The highest leaching yield for oxalic acid was noticed in the case of germanium. This was due to formation of water soluble  $[\text{Ge}(\text{OH})_2(\text{C}_2\text{O}_4)_2]^{2-}$  complex. Indium- and tin-oxalate compounds are

only sparingly soluble in acidic aqueous solutions, e.g. solubility of indium oxalate in 10% H<sub>2</sub>SO<sub>4</sub> solution is 0.3 g/dm<sup>3</sup> [45]. Therefore, In and Sn leachabilities were significantly smaller. Additionally, part of the tin present in the form of tin(IV) oxide was not leached, because it is insoluble in slightly acidic solutions.

For the highest investigated concentration of oxalic acid, decrease of Ge leaching yield was noticed. A saturated H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution at 20 °C has a concentration of ca. 10%. For the solution leached in 12.5% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution, precipitation of the acid during cooling was not an issue, because it formed insoluble Pb and Zn salts. However, for higher concentrations, an excess of oxalic acid precipitated during cooling, and Ge might have been adsorbed on the precipitate particles.

Leachabilities of germanium in sulphuric and oxalic acids were similar. However, a significant difference in indium and zinc leaching yields was noticed. The reason for this was that their sulphates are water soluble, while oxalates are not. In both cases lead, copper and silver were not leached. Lead formed insoluble salts of respective acids, while metallic form of copper and silver was present in the dross.

The addition of an oxidant during leaching in sulphuric acid solution was not favourable. It did not improve leachabilities of germanium and indium. Moreover, it increased copper leaching yields, which had to be removed at later stages.

In cases where high leaching yields of germanium and indium are desired, leaching in a H<sub>2</sub>SO<sub>4</sub> solution at 80 °C might be applied. Leaching in oxalic acid or sulphuric acid at 25 °C may be applied for recovery of Ge only.

Based on the obtained results, the highest possible leachabilities of germanium and indium were obtained for the process carried out using 10% H<sub>2</sub>SO<sub>4</sub> solution, at 80 °C for 2 h and the dross mass to leaching solution ratio—1:10 kg/dm<sup>3</sup>. After filtration, the obtained solution contained 8.1 g/dm<sup>3</sup> Zn, 6.4 g/dm<sup>3</sup> Ge, 3.4 g/dm<sup>3</sup> In and 2.4 g/dm<sup>3</sup> Sn. In order to achieve selective recovery of the elements, different techniques may be applied. One is the selective precipitation of germanium using tannic acid followed by raising pH to obtain tin-indium concentrate. Alternatively, solvent extraction techniques might be also applied for separation of the elements.

In the case of oxalic acid application, the highest leachability of germanium was achieved for tests performed using 12.5% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution, at 90 °C for 2.5 h, and the dross mass to leaching solution ratio—1:10 kg/dm<sup>3</sup>. The solution obtained after a filtration was composed of 6.1 g/dm<sup>3</sup> Ge, 1.5 g/dm<sup>3</sup> Sn and 0.37 g/dm<sup>3</sup> In. In the next step, solvent extraction might be used to selectively recover elements from the solution.

The dross contained significant amounts of valuable copper and silver. These metals were not leached in sulphuric and oxalic acids and remained in a residue. As the residue contained also significant amounts of other elements like lead and tin, it might be recycled in the pyrometallurgical process. An additional advantage of this solution is that the germanium and indium that remained in the residue may be recovered in a dross.

## 5. Conclusions

The leaching of the dross containing 28.7% Sn, 18.0 Pb, 10.6% Cu, 8.9% Ge, 8.1% Zn and 2.7% In, obtained by thermal oxidation of by-product alloy from NJ process was analysed. Leachability of the element in sulphuric and oxalic acid solutions under different conditions was determined. The following conclusions were derived:

- (1) the highest leaching yield of germanium in H<sub>2</sub>SO<sub>4(aq)</sub> was 85%. It was achieved for T = 80 °C, t = 3 h, C<sub>H<sub>2</sub>SO<sub>4</sub></sub> = 10%, S/L = 1/10.
- (2) germanium leachability in sulphuric acid strongly depends on acid concentration and S/L ratio—there was a maximum observed for C<sub>H<sub>2</sub>SO<sub>4</sub></sub> = 10% and S/L = 1/10.
- (3) indium leaching yield in sulphuric acid strongly depends on temperature—for 2 h process In leachability increased from 37% at 40 °C to ca. 82% at 80 °C.

- (4) the addition of an oxidant to sulphuric acid during leaching increased copper leachability—by up to 69% when sodium hypochlorite was used. However, it did not have a positive impact on Ge, In, and Sn leaching yields.
- (5) leaching in H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> allowed us to achieve an 80% leaching yield of germanium. Leaching yields of indium and tin for S/L ≥ 1/10 were below 20%.
- (6) high germanium leachability may be achieved in both sulphuric and oxalic acids. However, when a high leaching yield of indium is also desired, sulphuric acid at >80 °C should be used.

Solutions obtained after leaching contain germanium, indium, zinc, and tin. In order to selectively recover germanium, precipitation with tannic acid may be applied. Then, tin and indium may be precipitated by solution pH increase. Alternatively, solvent extraction techniques may be applied during later stages.

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