

Article

Recovery of Germanium from Sulphate Solutions Containing Indium and Tin Using Cementation with Zinc Powder

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Received: 14 March 2020; Accepted: 14 April 2020; Published: 17 April 2020



Abstract: Cementation of germanium from sulphate solution obtained after the leaching of GeIn dross using zinc dust was investigated. The composition of the examined solution was 5.15 Ge, 1.52 In, and 5.81 g/dm³ Zn. In order to resemble the solution before detinning, Sn concentration between 2–10 g/dm³ was also investigated. It was found that >99% of germanium may be precipitated from the solution. In order to achieve high selectivity, a detinned solution should be used because the precipitation yields of germanium and tin from the solution containing Sn were similar. For cementation with Zn powder at 75 °C for 2 h with a final pH of 2.0, over 99% of the germanium was removed from the solution, while the indium precipitation yield was 12%. The obtained cementate contained 50% Ge, mainly in elementary form.

Keywords: zinc metallurgy; germanium recovery; indium recovery; hydrometallurgy; cementation; zinc dust

1. Introduction

Germanium is a rare metalloid which is important to several sectors of the global industry. It is applied in optical fibers, used for high-speed telecommunication, infrared optics for military applications, solar cells (mainly in artificial satellites), polymerization catalysts for the production of polyethylene terephthalate (PET), in plastic bottles and synthetic textiles, high brightness light emitting diodes (LEDs), transistors for high speed wireless telecommunication, γ -ray detectors, and phosphors [1]. Over 100 tons of refined germanium is produced each year, and over 60% of the world's production comes from China [2]. Germanium does not occur in nature in the form of economically-mineable ores, but is recovered as a by-product. Its main sources are ashes generated after the combustion of Ge-rich coals found in China and far-east Russia [3,4] and residues of zinc metallurgy [4–9]. However, there is still huge room for the improvement of germanium recovery. It is estimated that no more than 3% of Ge contained in zinc concentrates is recovered worldwide [2,10].

Typical methods of germanium-bearing material processing to obtain suitable Ge-enriched products consist of its leaching in a mineral acid solution, mostly sulphate solution, followed by precipitation, usually with tannic acid [8,11–15]. However, this process is expensive, mainly due to the large amounts of tannin required for precipitation—at least 8–10 g per 1 g of dissolved Ge [15,16], or even >300 g [17], depending on the germanium concentration and chemical composition of solutions. A promising method of sulphate solution processing is also solvent extraction [18–20]. However, the production of LIX 63, one of the most promising agents, has been discontinued, according to

information obtained from its supplier. Therefore, it is necessary to investigate other methods of germanium recovery from sulphate solutions.

In zinc, hydrometallurgy cementation processes are mainly used to purify leachates prior to zinc electrowinning operations. The application of zinc powder allows undesirable elements to be removed from solutions, including Ge [11]. However, the cementation technique using iron powder is also considered as a possible method for germanium recovery from sulphate solutions [21].

The objective of the research was to determine the parameters of Ge cementation using zinc dust from an industrial solution also containing zinc, indium, and tin. The investigated solution originated from the processing of zinc metallurgy by-products [5,14]. The influence of temperature, time, the amount of zinc powder added, and final pH on germanium recovery was examined. The reduction potentials of the investigated elements are presented in Table 1. Based on the data, it is expected that germanium cementation with zinc is favoured over Sn and In.

Table 1. Standard reaction potentials of germanium, tin, indium, and zinc [22].

Half-Reaction	Reduction Potential [V]
$\text{Ge}^{4+} + 4\text{e}^- \rightarrow \text{Ge}(\text{s})$	0.12
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	−0.14
$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}(\text{s})$,	−0.34
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	−0.76

2. Materials and Methods

The investigated detinned solution was obtained by leaching GeIn dross with sulphuric acid in accordance with the procedure described in the previous paper [14]. Its composition is presented in Table 2. In each test, 500 dm³ of the solution was poured into the flask, except in the last tests, in which 2.5 dm³ solution was investigated. In the first test series, the original solution was enriched with tin to 6 g/dm³ to resemble leachate before detinning by adding 5.43 g SnSO₄. In order to obtain other Sn concentrations, a proportional amount of tin(II) sulphate was added. Tin(II) sulphate (min. 95.5%, Alfa Aesar, Kandel, Germany) was used as the tin source. Cementation was done by adding the proper amount of zinc powder (superfine 3.0–4.5 µm, NorZinco, Goslar, Germany) to the solution while mixing (300 rpm) with a mechanical stirrer equipped with a propeller. Zinc was added in portions due to intensive gas formation. Tests were performed at initial temperatures of 60 °C for the solution containing tin, and at 75 °C for the detinned solution. It was found that at these temperatures, cementation reactions start to occur: gas formation is noticeable. During the addition of zinc dust, the temperature increased by up to 10 °C. The suspensions obtained after adding the set Zn powder amount were mixed for 2 h to allow for a complete reaction. In order to maintain the final pH at a set level (0.25, 0.5, 0.75, 1.0 and 2.0 were investigated), 30% H₂SO₄ solution obtained by the dissolution of concentrated sulphuric acid (98%, Avantor, Gliwice, Poland) in deionised water was added. The temperature was kept at its initial level. The obtained suspension was filtered using a Buchner funnel and washed with deionised water. The precipitates were dried for 10 h at 50 °C.

Table 2. Composition of detinned solution used in cementation tests.

Ge	Composition (g/dm ³)			pH
	In	Zn	Sn	
5.15	1.52	5.81	0.02	0.21

Filtrates and solids were analysed at the Łukasiewicz-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) prior to analysis. In the case of the solids, a 0.2 g portion of the material was first melted with 1 g Na_2O_2 (p.a., Avantor) at 600 °C for 30 min in a corundum crucible. The crucible containing the resulting alloy was placed in a polypropylene vessel into which 10 cm³ of 1:1 mixture of concentrated nitric (65%, Avantor) and hydrofluoric (40%, VWR, Lutterworth, UK) acid was added. The vessel was heated to 110 °C, until the alloy was completely dissolved. The crucible was washed with water, and the resulting solution was filled with water to 100 cm³ and analysed.

X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer Rigaku MiniFlex 600 (Rigaku, Tokyo, Japan) with a copper tube $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm), a tube voltage of 40 kV, and a current of 15 mA, using a D/teX Ultra silicon strip detector.

3. Results

3.1. Ge Cementation from Solution Containing Tin

In the first step, germanium cementation from the solution containing tin was investigated. This solution resembled the solution obtained after leaching GeIn dross, which was described in the previous paper [14]. The solution was enriched in Sn using solid tin(II) sulphate directly before the tests. This was due to the instability of the solution containing Sn caused by the oxidation of Sn(II) to Sn(IV) and precipitation of tin(IV) oxide.

During the first test, the amount of zinc dust required for the precipitation of germanium, tin, and indium was determined. Tests were done at 60 °C for 2 h. The initial tin concentration was 6 g/dm³. Precipitation yields of the investigated elements are presented in Figure 1.

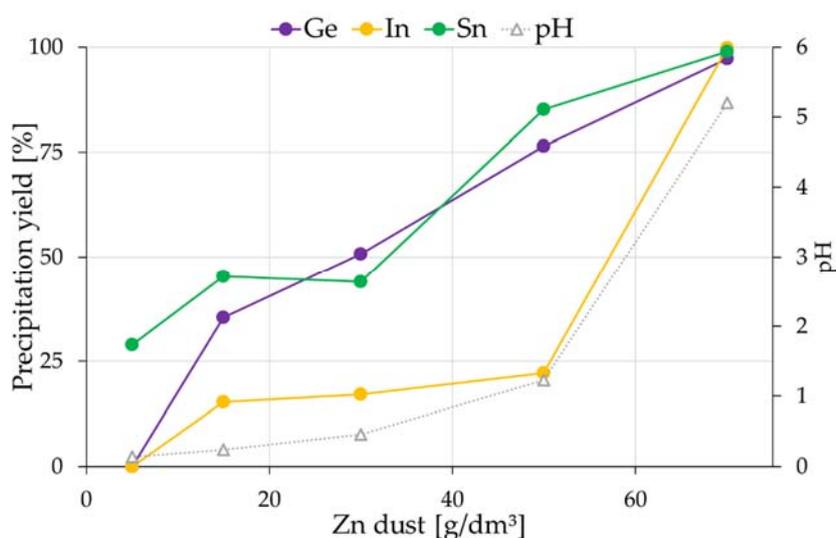


Figure 1. Influence of Zn dust amount on precipitation yields of Ge, In, and Sn, and final pH (60 °C, 2 h, 6 g/dm³ Sn in initial solution).

The precipitation yields of germanium and tin increased as the amount of zinc dust added was increased. Moreover, the levels of precipitated Sn and Ge were comparable for different masses of the reducing agent. Only for the smallest investigated amount of Zn added (5 g per 1 dm³ solution) was the Sn precipitation yield significantly larger than that of Ge (29% vs. 1%). For the highest investigated amount of zinc dust (70 g/dm³), the complete precipitation of all investigated elements was achieved.

It was observed that the complete separation of germanium could not be achieved when the final pH of the cementation was not kept below 2.0. Therefore, in the next experimental series, the investigation of the final pH on Ge, In, and Sn precipitation yields was examined. Tests were performed at 60 °C for 2 h, and 100 g/dm³ of zinc dust was added. A final cementation pH in the range

0.25–2.0 was maintained by adding sulphuric acid. The influence of the final pH on the precipitation yield is presented in Figure 2.

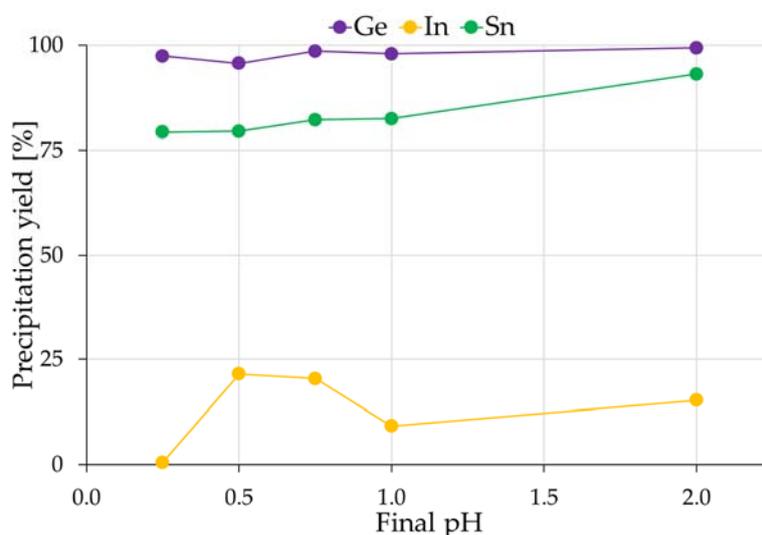


Figure 2. Influence of final pH on precipitation yields of Ge, In, and Sn (60 °C, 2 h, 100 g/dm³ Zn used, 6 g/dm³ Sn in initial solution).

It was observed that for the investigated dose of zinc powder, almost complete precipitation of germanium (>96%) was achieved for all of the investigated final pH values. Tin precipitation yields increased with higher final pH values—from 79% at 0.25 to 93% at 2.0. Indium precipitation yields were below 25%, but varied in the final pH. The most In (20%–22%) precipitated at 0.5–0.75. No indium cementation was observed for pH 0.25.

Due to the observed co-cementation of tin and germanium in the first tests, in the third test, the influence of tin concentration on Ge and In precipitation yields was investigated. This was done by adding different amounts of the tin source to the investigated solution. All tests were done at 60 °C for 2 h. In all tests, 50 g/dm³ Zn dust was added. The results of the tests are shown in Figure 3.

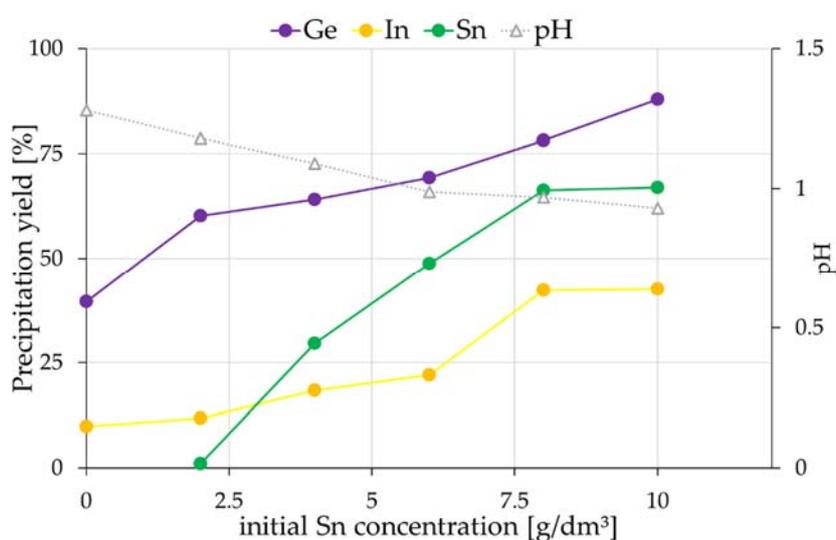


Figure 3. Influence of Sn concentration in the solution on precipitation yields of Ge, In, and Sn, and final pH (60 °C, 2 h, 50 g/dm³ Zn used).

It was observed that the increase of tin concentration in the initial solution improved the germanium precipitation yield. For the solution without tin, the Ge precipitation yield was 39%, while for the one with $10 \text{ g/dm}^3 \text{ Sn}$, it was 88%. The final pH of the solution after cementation was lower for higher tin concentrations—1.28 for the initial solution without tin and 0.93 when the initial Sn concentration was 10 g/dm^3 . The precipitation yield of tin also increased for its higher initial amounts. For the smallest investigated Sn concentration, less than 1% of tin was precipitated, while when $8\text{--}10 \text{ g/dm}^3$ tin was in the initial solution, 67% of tin was precipitated. The indium precipitation yield was also affected by the change of Sn concentration—the lowest (10%) was in the detinned solution, while the highest (42%) was observed for the highest investigated tin concentrations ($8\text{--}10 \text{ g/dm}^3$).

3.2. Ge Cementation from Detinned Solution

Although the tin contained in the solution improved the Ge precipitation yield, in the next series of tests germanium cementation from a detinned solution was investigated. This was done in order to obtain a tin-free precipitate, which might be better a product from an industrial point of view.

In the first test, the influence of zinc dust mass on precipitation yields of germanium and indium was determined. Tests were performed at $75 \text{ }^\circ\text{C}$ for 2 h. The results of the tests are shown in Figure 4.

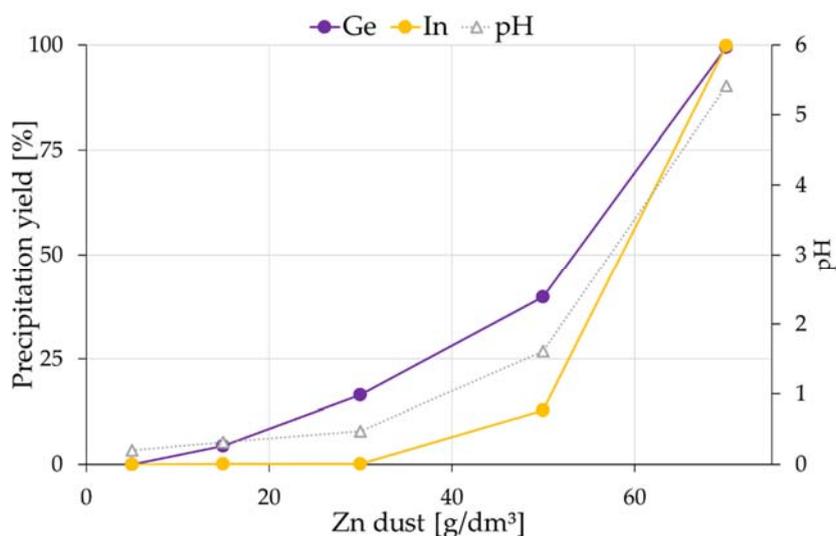


Figure 4. Influence of Zn dust amount on precipitation yields of Ge and In, and final pH ($75 \text{ }^\circ\text{C}$, 2 h, detinned solution).

It was observed that, as in the case of the solution containing tin, a higher amount of zinc dust increased the precipitation yields of germanium and indium. However, only for the highest investigated zinc dose (80 g/dm^3) were precipitation yields the same for both solutions ($>99\%$). When a lower mass of Zn dust was added, Ge and In precipitation yields from the detinned solution were lower. On the other hand, the pH of the solution after adding zinc to the detinned solution was higher than that of the solution containing tin.

It was found that without control of the final pH, it was not possible to separate Ge and In. Therefore, in the next experimental series, the final pH was kept at 1.0 by adding sulphuric acid. The influence of the amount of Zn powder on germanium and indium cementation is demonstrated in Figure 5.

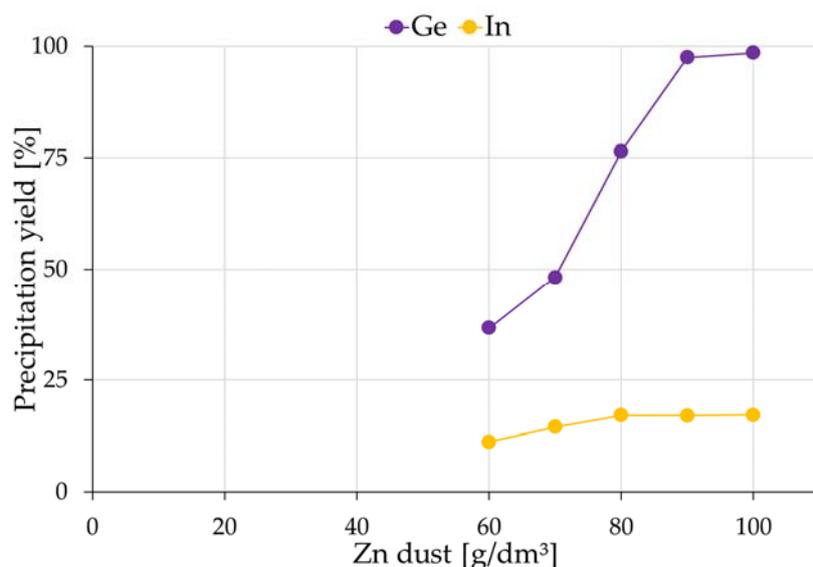


Figure 5. Influence of Zn dust amount on precipitation yields of Ge and In (75 °C, 2 h, detinned solution, final pH 1.0).

Controlling the final pH had a positive impact on the separation of germanium from tin. It was observed that as the amount of zinc dust increased, the Ge precipitation yield also increased. When 90–100 g/dm³ Zn powder was added, over 97% Ge was cemented. On the other hand, the In precipitation yield increase was lower—from 11% for 60 g/dm³ of zinc added to 17% for 100 g/dm³ Zn.

In the next test, the final pH of the process was kept at different constant levels between 0.25 and 2.0 in order to determine maximum possible Ge precipitation yield and possibility of indium separation. The final pH was adjusted using sulphuric acid solution. The obtained precipitation yields are presented in Figure 6.

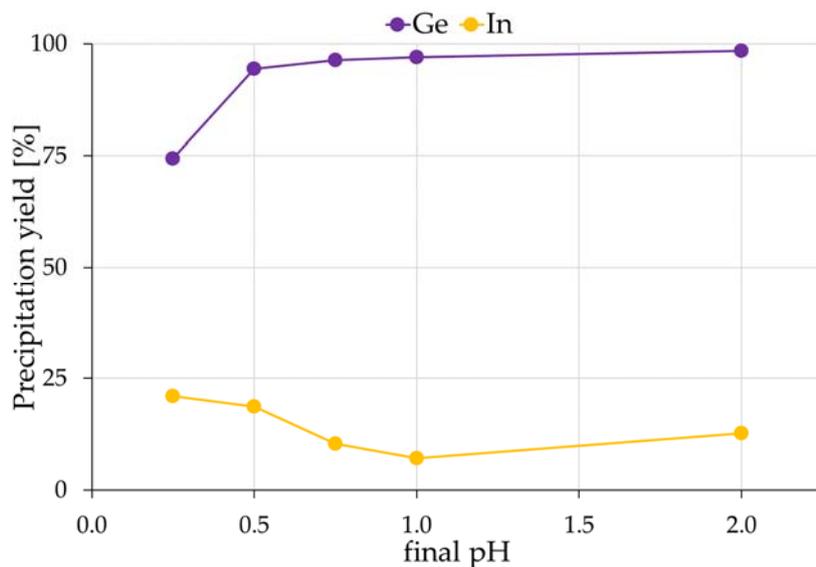


Figure 6. Influence of Zn final pH on precipitation yields of Ge and In (75 °C, 2 h, detinned solution, 100 g/dm³ zinc dust added).

It was observed that at a lower final pH, more indium was cemented. For pH 0.25, 21% of indium was removed from the solution, while at pH 1.0 and 2.0 it was 7% and 12%, respectively. On the other hand, the most germanium (>99%) was removed for the highest investigated final pH (2.0). At a final pH of 0.25 only 74% Ge was precipitated.

The quality of the solid obtained by cementation was verified by cementation at a larger scale, i.e., using a detinned solution with a volume of 2.5 dm³. The cementation process was carried out at 75 °C, 100 g/dm³ Zn dust was added in portions with control of the final pH at 2.0, and the obtained suspension was mixed for 2 h. The results are collected in Table 3. XRD analysis of the cementate is presented in Figure 7.

Table 3. Composition of solution and precipitate obtained after cementation (75 °C, 2 h, 100 g/dm³ Zn dust, final pH 2.0).

	Ge	In	Zn
initial solution [g/dm ³]	5.15	1.52	5.81
final solution [g/dm ³]	0.009	1.09	105
precipitate [%]	50.0	4.7	8.2
precipitation yield [%]	>99%	18%	n/d

Note: n/d—not determined.

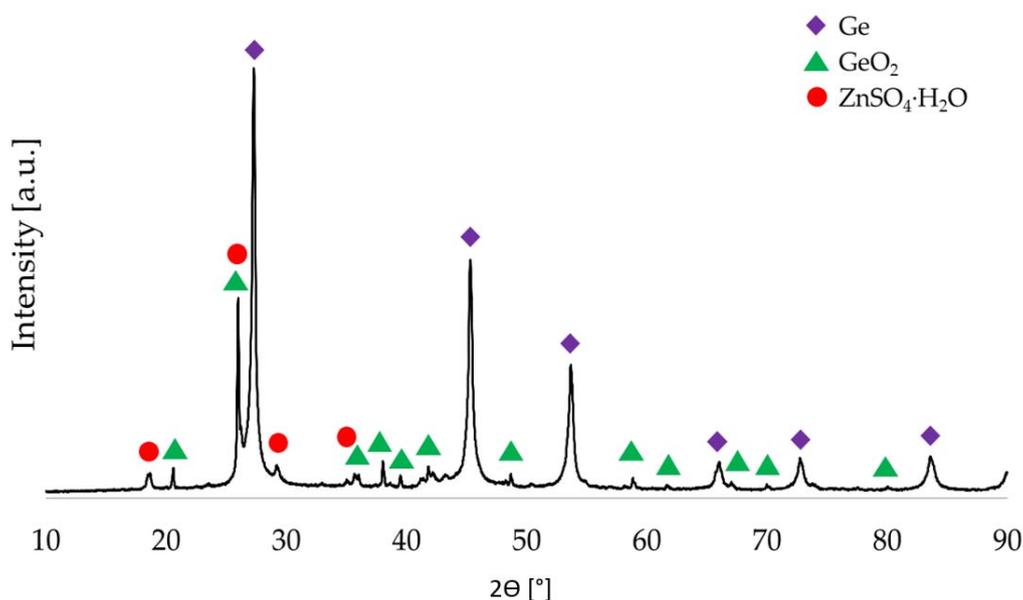


Figure 7. XRD pattern of precipitate obtained after cementation of detinned solution with zinc dust (75 °C, 2 h, 100 g/dm³ Zn dust); a.u.—arbitrary units.

The main precipitate component was germanium, which constituted half of the dry mass. According to XRD analysis, most of the germanium was present in metallic form. Part of the germanium was also present as GeO₂. The cementate also contained 8.2% Zn, present mainly as sulphate monohydrate and 4.7% indium. Minor identified metallic components were copper, gallium, and iron (1.5%–2.5%).

4. Discussion

The final pH of cementation should be kept below 2.0. For higher pH values, the complete precipitation of germanium, tin, and indium was observed. In this situation, it was not possible to separate these elements and obtain a valuable solid. The amount of zinc powder used was higher than required to achieve pH 2.0. Therefore, pH adjustment by sulphuric acid addition was required.

The mechanisms of the cementation in the presence of tin and in detinned solutions seemed to be different. In Figure 3, it may be observed that the precipitation yields of germanium and indium are higher when tin concentration is high. Additionally, the final pH of the process was lower, which suggests that less hydrogen was evolved at a higher tin concentration. The comparison of Figures 1

and 4 may also lead to a similar conclusion. For zinc doses at which the final pH was below 2, lower Ge and In precipitation yields, as well as a higher pH, were observed for detinned solutions.

As can be seen in Table 1, the standard reduction potential difference of germanium is slightly higher than that of hydrogen (0.12 V), and much higher than that of indium (0.46 V). Therefore, germanium cementation should be more favourable than hydrogen emission and indium cementation. However, all of these reactions took place simultaneously and were driven by the oxidation of zinc powder. The reduction potentials for these reactions were 0.88 for Ge, 0.76 for H, and 0.42 V for In. A relatively low concentration of germanium in the initial solution (5.15 g/dm³) also had an influence on hydrogen evolution during the process, especially at the beginning of the process. In the case wherein tin was present in the solution, it might act as an intermediate, i.e., tin was reduced with zinc dust, and later germanium was cemented with metallic tin. The relative difference between the reduction potential of hydrogen evolution and tin cementation with zinc was not very high (0.76 for H₂, 0.62 V for Sn); therefore, both reactions may have occurred in parallel. However, the relative difference between the reduction potential of germanium and hydrogen with tin was much more significant (0.26 and 0.14 V, respectively). This may have had influence on the lower hydrogen evolution and lower final pH of the suspension (Figure 3).

It may be noted that the amount of zinc dust consumed for complete Ge cementation was much higher than expected. According to stoichiometry, 1.8 g Zn should be used to precipitate 1 g Ge. In the test it was found that 100 g of zinc powder was required to achieve >99% germanium precipitation, which corresponds to almost 20 g Zn required to cement 1 g Ge. During the experiment, high amounts of evolving gas (hydrogen) were observed right after the addition of each zinc portion. Therefore, most of the zinc was consumed for solution neutralisation and the reduction of hydronium ions. This conclusion was also supported by the results of tests without final pH control, in which a significant increase of the final pH, even >5.0, was observed.

In future research, more attention should be paid to the control of reaction kinetics, which may be an effective way to reduce hydrogen formation during cementation. Slower Zn addition does not seem to be a suitable solution. During experiments it was observed that temperatures of 60 °C (for solution containing Sn) and 75 °C (for detinned solution) were important limits, and for lower values no reaction was observed—when zinc dust was added below those temperatures, gas evolution, precipitate formation, and temperature increase were not observed. The addition of zinc powder also caused a rapid increase in temperature, up to >10 °C. The reduction of the reaction area, e.g., by applying larger zinc particles, might limit reaction kinetics.

The presence of tin improved cementation efficiency; however, co-cementation of germanium and tin was not favourable when a Ge-enriched product is desired. Cementation using Zn dust from the solution containing Ge, Sn, and In allowed us to only obtain a solid enriched in germanium and tin. It was not possible to separate germanium and tin. Therefore, it was necessary to remove tin before the cementation step.

In the case of the detinned solution, it was not possible to achieve high separation of germanium from indium when the final pH was kept below 1.0. For pH 1.0 and 2.0, precipitation yields of germanium and indium were 97% and 99%, respectively. For the same pH values, 7% and 12% In was cemented. Based on the Ge precipitation yields and sulphuric acid consumption, a pH of 2.0 should be preferred for an industrial process.

The cementate was composed mainly of germanium, which was mainly in the elementary form. Part of the germanium was present as dioxide. It is not clear if GeO₂ was formed during cementation, or later during drying, despite a drying temperature of 50 °C being applied. Zinc was in the form of sulphate. Monohydrate was formed during drying as the hexa- and heptahydrate were more favourable forms of ZnSO₄ precipitate from aqueous solutions. The presence of the zinc in sulphate form suggests that washing the cementate with water was not sufficient, and pulping techniques should be applied for the purification of final product. The application of an additional washing step for precipitation and control of the drying process may improve the quality of the final product.

The solution obtained after germanium cementation contained significant amounts of indium, which might be suitable for recovery. Moreover, high zinc levels were present in the solution. Therefore, there is a possibility of indium and zinc recovery, but further cementation or precipitation using other agents should also be considered before application in an industrial scale.

5. Conclusions

The cementation of germanium from sulphate solution containing 5.15 Ge, 1.52 In, 5.81 g/dm³ Zn with and without Sn using zinc dust was investigated. Precipitation yields of the analyzed elements under different conditions were determined. The following conclusions were derived:

1. The final pH of the cementation process should be controlled and kept at ≤ 2.0 ; with a higher pH, precipitation yields of Ge, Sn, and In were close to 100%; therefore, Ge in the solid was not separated from Sn and In;
2. the presence of Sn in the solution reduced the Zn consumption required to achieve Ge cementation; however, Sn was co-precipitated with Ge, and therefore only separation from In was achieved—20% of the indium present in the solution was precipitated;
3. the almost complete cementation of Ge (>99%) from the investigated solution was achieved with the following parameters: 75 °C, 2 h, Zn dust consumption: 100 g/dm³ solution, final pH: 2.0; under these conditions, ca. 12% of In was precipitated from the solution;
4. the solid obtained after cementation contained 50% Ge, 8.2% Zn, and 4.7% In; germanium was present mainly in the elementary form, and also partially as GeO₂; zinc was present mainly as sulphate;
5. the solution obtained after cementation contained 1.09 In and 105 g/dm³ Zn; therefore, it may be a source for indium and zinc recovery.

Author Contributions: Conceptualization, M.D.; investigation, M.D., M.C., M.K., A.R., S.K., K.G., and P.K.; methodology, M.D. and G.B.; supervision, M.D. and K.L.-S.; visualization, M.D.; writing—original draft, M.D. and M.C.; writing—review and editing, G.B. and K.L.-S. All authors have read and agreed to the published version of the manuscript.

Funding: The study was funded by the Polish Ministry of Science and Higher Education under the project ST/33/2019/G “Investigation on germanium recovery from post-leaching solutions”.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. European Commission. *Study on the Review of the List of Critical Raw Materials—Critical Raw Materials Factsheets*; Publications Office of the European Union: Luxembourg, 2017. [[CrossRef](#)]
2. U.S. Geological Survey. *Mineral Commodity Summaries: Germanium*; U.S. Geological Survey: Reston, VA, USA, 2020.
3. Dai, S.F.; Seredin, V.V.; Ward, C.R.; Jiang, J.H.; Hower, J.C.; Song, X.L.; Jiang, Y.F.; Wang, X.B.; Gornostaeva, T.; Li, X.; et al. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int. J. Coal Geol.* **2014**, *121*, 79–97. [[CrossRef](#)]
4. Robertz, B.; Verhelle, J.; Schurmans, M. The Primary and Secondary Production of Germanium: A Life-Cycle Assessment of Different Process Alternatives. *JOM* **2015**, *67*, 412–424. [[CrossRef](#)]
5. Kulawik, S.; Prajsnar, R.; Chmielarz, A.; Cybulski, A.; Michalski, R.; Klejnowska, K.; Drzazga, M.; Krawiec, G. Thermal Oxidation of Indium, Germanium, and Tin from Lead-Bearing Alloys Generated in Zinc Refinement. *Metals* **2019**, *9*, 166. [[CrossRef](#)]
6. Topkaya, Y.A.; Karakaya, I.; Özbayoglu, G. Potential Recovery of Germanium from Leach Residues and Electrolyte Purification Precipitates of Turkish Zinc Plant. *Miner. Process. Extr. Metall. Rev.* **1992**, *10*, 281–289. [[CrossRef](#)]

7. Liu, F.P.; Liu, Z.H.; Li, Y.H.; Wilson, B.P.; Lundstrom, M. Behavior of gallium and germanium associated with zinc sulfide concentrate in oxygen pressure leaching. *Physicochem. Probl. Miner. Process.* **2017**, *53*, 1047–1060. [[CrossRef](#)]
8. Liang, D.; Wang, J.; Wang, Y. Germanium recovery by co-precipitation of germanium and iron in conventional zinc metallurgy. *J. South Afr. Inst. Min. Metall.* **2008**, *108*, 715–718.
9. Fayram, T.S.; Anderson, C.G. The development and implementation of industrial hydrometallurgical gallium and germanium recovery. *J. S. Afr. Inst. Min. Metall.* **2008**, *108*, 261–271.
10. Licht, C.; Peiro, L.T.; Villalba, G. Global Substance Flow Analysis of Gallium, Germanium, and Indium: Quantification of Extraction, Uses, and Dissipative Losses within their Anthropogenic Cycles. *J. Ind. Ecol.* **2015**, *19*, 890–903. [[CrossRef](#)]
11. Kul, A.; Topkaya, Y. Recovery of germanium and other valuable metals from zinc plant residues. *Hydrometallurgy* **2008**, *92*, 87–94. [[CrossRef](#)]
12. Bayat, S.; Aghazadeh, S.; Noaparast, M.; Gharabaghi, M.; Taheri, B. Germanium separation and purification by leaching and precipitation. *J. Cent. South Univ.* **2016**, *23*, 2214–2222. [[CrossRef](#)]
13. Liu, F.P.; Liu, Z.H.; Li, Y.H.; Liu, Z.Y.; Li, Q.H.; Zeng, L. Extraction of gallium and germanium from zinc refinery residues by pressure acid leaching. *Hydrometallurgy* **2016**, *164*, 313–320. [[CrossRef](#)]
14. Drzazga, M.; Prajsnar, R.; Chmielarz, A.; Benke, G.; Leszczyńska-Sejda, K.; Ciszewski, M.; Bilewska, K.; Krawiec, G. Germanium and Indium Recovery from Zinc Metallurgy by-Products—Dross Leaching in Sulphuric and Oxalic Acids. *Metals* **2018**, *8*, 1041. [[CrossRef](#)]
15. Arroyo Torralvo, F.; Fernández-Pereira, C.; García Villard, E.; Luna, Y.; Leiva, C.; Vilches, L.; Villegas, R. Low environmental impact process for germanium recovery from an industrial residue. *Miner. Eng.* **2018**, *128*, 106–114. [[CrossRef](#)]
16. Drzazga, M.; Chmielarz, A.; Benke, G.; Leszczyńska-Sejda, K.; Magdalena, K.; Kowalik, P.; Ciszewski, M. Precipitation of Germanium from Sulphate Solutions Containing Tin and Indium Using Tannic Acid. *Appl. Sci.* **2019**, *9*, 966. [[CrossRef](#)]
17. Liang, D.Q.; Wang, J.K.; Wang, Y.H.; Wang, F.; Jiang, J.B. Behavior of tannins in germanium recovery by tannin process. *Hydrometallurgy* **2008**, *93*, 140–142. [[CrossRef](#)]
18. Nusen, S.; Zhu, Z.W.; Chairuangri, T.; Cheng, C.Y. Recovery of germanium from synthetic leach solution of zinc refinery residues by synergistic solvent extraction using LIX 63 and Ionquest 801. *Hydrometallurgy* **2015**, *151*, 122–132. [[CrossRef](#)]
19. Liang, J.; Xu, K.; Fan, L.J.; Huang, Y. The Synthesized Principle and Property of Several Extraction Agents for Germanium. *Adv. Mater. Res.* **2012**, *455–456*, 624–629. [[CrossRef](#)]
20. Cheng, B.H.; Zhang, T.A.; Zhang, K.F.; Cao, Z.Y.; Zeng, L. Recovery of germanium from acid leach solutions of zinc refinery residue using an oxime extractant of HBL101. *Metall. Res. Technol.* **2018**, *115*, 6. [[CrossRef](#)]
21. Zhou, Z.-A.; Chu, G.; Gan, H.-X.; Yang, T.-Z.; Chen, L. Ge and Cu recovery from precipitating vitriol supernatant in zinc plant. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 1506–1511. [[CrossRef](#)]
22. Haynes, W.M. (Ed.) *CRC Handbook of Chemistry and Physics*, 93rd ed.; CRC Press/Taylor and Francis: Boca Raton, FL, USA, 2012.



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