

Selective recovery of indium from lead-smelting dust

著者	Sawai Hikaru, Rahman Ismail M.M., Tsukagoshi Yoshinori, Wakabayashi Tomoya, Maki Teruya, Mizutanai Satoshi, Hasegawa Hiroshi
journal or publication title	Chemical Engineering Journal
volume	277
page range	219-228
year	2015-10-01
URL	http://hdl.handle.net/2297/42182

doi: 10.1016/j.cej.2015.04.112

Selective Recovery of Indium from Lead-Smelting Dust

Hikaru Sawai ^{a,*}, Ismail M. M. Rahman ^{a,b,*}, Yoshinori Tsukagoshi ^a, Tomoya Wakabayashi ^a,
Teruya Maki ^c, Satoshi Mizutani ^d, Hiroshi Hasegawa ^{c,*}

^a Graduate School of Natural Science and Technology, Kanazawa University, Kakuma,
Kanazawa 920-1192, Japan

^b Department of Applied and Environmental Chemistry, Faculty of Science, University of
Chittagong, Chittagong 4331, Bangladesh

^c Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192,
Japan

^d Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-Ku,
Osaka 558-8585, Japan

*Author(s) for correspondence

E-mail: hikaru.sawai@gmail.com (HS); I.M.M.Rahman@gmail.com, I.M.M.Rahman@cu.ac.bd
(IMMR); hhiroshi@se.kanazawa-u.ac.jp (HH)

TEL/Fax: +81-76-234-4792

ABSTRACT

Non-ferrous smelting dust, especially lead-smelting dust (LSD), contains percent levels of indium and thus constitutes a novel indium resource. The main difficulty in recovering indium from LSD is the coexisting presence of lead and zinc. In this study, a unique indium separation process was designed, combining techniques that involve washing with a chelant, leaching with acid and precipitation as hydroxide. The majority of the Pb in the LSD was selectively separated during chelant-assisted washing with ethylenediaminedisuccinate (EDDS), while the residual Pb was diminished through an acid leaching treatment with a mixed solution of sulfuric acid and hydrochloric acid. The chelant washing step also ensures a decrease in the raw LSD weight at a ratio of approximately 82 % due to the removal of lead and counterions such as sulfate, and the washing step also minimizes the consumption of corrosive acids in the subsequent step. Selective indium separation from LSD is further complicated by the similarity of the behavior of zinc during the acid leaching step. Therefore, hydroxide precipitation at pH 5 has been introduced as the final step, ensuring the maintenance of zinc as a soluble species in the supernatant and the selective separation of indium (~ 88 %) as a hydroxide precipitate.

Keywords

Indium recovery; Selective separation; Lead-smelting dust; Chelant-assisted washing; Acid leaching, Hydroxide precipitation

1.0 Introduction

The metal indium, particularly as ITO (indium-tin-oxide) thin film, is an industrially important component because ITO is necessary for building electronic devices [1]. ITO is widely utilized for manufacturing liquid crystal displays, plasma displays and solar energy cells [2], which consume approximately two-thirds of the global indium production [1]. One of the resource materials for raw indium is non-ferrous metal ore [3], which is obtained as a by-product of the smelting process of the non-ferrous metal ore [4]. Raw indium deposits are region-specific (i.e., China, Korea, and Russia) [5]. Discrepancies in demand, supply and price are therefore observed. The search for alternate sources of raw indium is vital from the point of view of resource strategy, and this search is focused mostly on the processing of indium-laden waste materials, e.g., ITO scrap [2, 6-8], end-of-life liquid crystal displays [6, 9-11] and etching waste [12-14].

The residue and flue dust from the smelting of non-ferrous metals, such as lead, termed lead smelting dust or LSD hereafter, also includes indium [15] and is expected to be a novel indium resource. Acid leaching is commonly employed for metal smelting from waste resources [16-18]. Indium recovery from waste material has been reported through the use of acid leaching and hydroxide or sulfide precipitation [2, 6, 7, 19-21]. This approach is frequently criticized both in terms of overall efficiency due to the lack of selectivity in separation and in terms of the hazardous impact on the environment. Therefore, a reduction in the use of acid or other corrosive extractants is desirable [22]. As alternative extractants for indium recovery, chelants [10, 11, 23], other solvents, such as carboxylic acid or phosphoric acid derivatives (e.g., di-2-ethylhexylphosphoric acid), chelating compounds (e.g., hydroxyoximes and azoles), and solvating extractants (e.g., tributyl phosphate, trioctylphosphine oxide and methyl isobutyl ketone) have been proposed [6, 24]. Although alternative extractants possess unique leaching behavior (i.e., selectivity, re-usability, etc.), the leaching efficiency of these alternative extractants is not comparable with the leaching efficiency of even acids or bases.

Indium reclamation from waste resources is further complicated by the simultaneous presence of metal components having chemical similarities [25, 26]. For example, tin is the major impurity in the recovery process of indium from ITO waste [2]. The issue of chemical similarities is more of a concern during the recovery of indium from LSD using acids or bases because the acid leaching process consumes a higher quantity of solvents due to the coexistence of base metals (e.g., lead, zinc, etc.) other than the indium, increasing the total operating cost.

The objective of the current work was to develop a unique technique for the quantitative reclamation of indium from LSD. The separation scheme combines chelant-assisted washing, acid leaching and hydroxide precipitation techniques, minimizing the competing effect of coexisting metals.

2.0 Experimental

2.1 Materials

Analytical grade reagents were used during all experiments. Ethylenediaminetetraacetate, (EDTA, Kanto Chemical, Tokyo, Japan), 3-hydroxy-2,2'-iminodisuccinate (HIDS, Nippon Shokubai, Osaka, Japan) and ethylenediaminedisuccinate (EDDS, Chelest, Osaka, Japan) were used as the chelating extractants (Table 1). As buffer reagents, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Nacalai Tesque, Kyoto, Japan), N-tris(hydroxymethyl)-3-aminopropanesulfonate (TAPS) and 3-cyclohexylaminopropane sulfonate (CAPS, MP Biomedicals, Santa Ana, CA) were used. The ICP multi-element standard solution IV containing 1000 mg L⁻¹ of 23 elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn) in diluted nitric acid (Merck KgaA, Darmstadt, Germany) was used as the standard during metal analysis. Purified water (resistivity > 18.2 MΩ·cm) was obtained from an Arium Pro water purification system (Sartorius Stedim Biotech GmbH, Göttingen, Germany) and was used for the preparation of all reagents.

Low-density polyethylene bottles, polyethylene test tubes (Nalge Nunc, Rochester, NY), DigiTUBEs (SCP Science, Quebec, Canada), perfluoroalkoxy tubes and micropipette tips (Nichiryo, Tokyo, Japan) were used as laboratory ware. The laboratory ware was cleaned via overnight soaking in Scat 20X-PF alkaline detergent (Nacalai Tesque, Kyoto, Japan) and then in HCl (3 mol dm⁻³), followed by rinsing with purified water after each of the previous steps.

2.2 Analytical techniques

Concentrations of metals in solution were measured by using the iCAP6300 inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fisher Scientific, Waltham, MA). The ICP-OES was operated under the following conditions: the radio frequency power at the torch was 1.15 kW, the plasma gas flow was 12 dm³ min⁻¹, the auxiliary gas flow was 1 dm³ min⁻¹, the nebulizer gas flow was 0.5 dm³ min⁻¹, and the integration time was 30 s. The Epsilon3 X-ray fluorescence (XRF) spectrometer (PANalytical, Almelo, The Netherlands), JSM-7100F field-emission scanning electron microscope (FE-SEM) (JEOL Co., Tokyo, Japan) combined with the INCA energy dispersive X-ray (EDX) spectrometer (Oxford Instruments, Oxfordshire, UK), and MiniFlex 600 X-ray diffractometer (XRD) (Rigaku Corporation, Tokyo, Japan) were used for the elemental characterization of the LSD solids. Each of the instrumental measurements and treatment procedures was performed in three replicates, and an averaged value is reported.

2.3 Collection and characterization of the LSD samples

The LSD samples were provided from the non-ferrous metal smelting process of a Japanese mining company, who preferred to be introduced as ‘anonymous’ to avoid the violation of intellectual proprietary rights.

LSD samples (0.05 g) were transferred into a pre-cleaned PTFE vessel of a Multiwave 3000 microwave digestion system (PerkinElmer, Waltham, MA), which was loaded with HNO₃ (13.2 mol dm⁻³; 1 cm³), HCl (12 mol dm⁻³; 3 cm³) and HF (27 mol dm⁻³; 1 cm³). The microwave

digestion process was conducted under the following conditions: microwave power (max) – 1400 W; ramp time – 15 min; heating time at the maximum temperature – 120 min; and vent time – 30 min. After completion of the primary digestion step, a 5% H₃BO₃ solution (10 cm³) was added to the digested solution to mask the residual hydrofluoric acid as fluoroborate (BF₄⁻). The mixture was heated further under the following conditions: microwave power (max) – 1400 W; ramp time – 15 min; heating time at the maximum temperature – 30 min; and vent time – 30 min. The dissolved samples were transferred to 50 cm³ polypropylene tubes (DigiTUBEs) and were diluted to 50 cm³ with purified water. The content of metal in the samples was determined by ICP-OES.

2.4 Chelant-assisted washing treatment of LSD

LSD samples (0.05 g) were added to 5 mmol g⁻¹ of chelant (EDTA, EDDS, or HIDS) and 0.02 mol g⁻¹ of NaOH mixed solution (5 cm³) in 50 cm³ polypropylene test tubes and were shaken at 180 rpm and 25 °C for 5 h. The mixed solution was centrifuged at 1820 × g for 30 min, and the supernatant was filtered with a 1.0 μm pore size mixed cellulose ester membrane filter (Advantec, Tokyo, Japan). The metal extraction yield (%) was defined using the following equation:

$$\text{Extraction yield (\%)} = \frac{C_{\text{sol}} \times v}{m \times C_{\text{LSD}}} \times 100 \quad (1)$$

In Eq. 1, the symbols are defined as follows: C_{sol} , metal concentration in the solution (mg dm⁻³); v , volume of the given solution (dm³); m , weight of the LSD (kg); and C_{LSD} , metal content in the LSD (mg kg⁻¹).

2.5 Acid leaching treatment of LSD

The LSD sample (0.05 g) was leached by using 5 cm³ of mineral acid (0.1 mol g⁻¹ of HNO₃, HCl and H₂SO₄). The mixture was shaken at 180 rpm and 25°C for 24 h. The mixed solution was centrifuged, and the supernatant was filtered.

2.6 Hydroxide precipitation treatment of LSD

The solution leached from the LSD using the mixed acid solution ($0.02 \text{ mol g}^{-1} \text{ HCl}/0.04 \text{ mol g}^{-1} \text{ H}_2\text{SO}_4$) in accordance with section 2.5 was adjusted to pH 5 with 10 mol dm^{-3} of NaOH solution. The hydroxide precipitate was collected on a membrane filter (pore size $0.45 \text{ }\mu\text{m}$) and dissolved with 1.0 cm^3 of aqua regia (a mixture of $12 \text{ mol dm}^{-3} \text{ HCl}$ and $13.2 \text{ mol dm}^{-3} \text{ HNO}_3$ at a ratio of 1:3 based on volume).

3.0 Results and Discussion

3.1 Chemical composition of LSD

The LSD was composed mainly of lead, zinc and indium, while the auxiliary components were cadmium, calcium, copper, bismuth, and thallium (Table 2). Main and auxiliary metal components in the LSD were calculated as 2.86 mmol g^{-1} . Furthermore, XRF analysis indicated the presence of bromine (23 %) and sulfur (3 %) as non-metallic components of the LSD. The metals in the LSD were estimated to be in the chemical forms of bromide, oxide, sulfide or sulfate, as the LSD was generated from the combustion of sulfide or sulfate ores (e.g., galena, anglesite and sphalerite). The FE-SEM and EDX observation supplied the micro-scale surface image of the LSD sample (Figure 1), which indicated a highly homogenous elemental composition throughout. The analysis also confirmed that LSD is a complex mixture of several metal compounds. The XRD pattern of the LSD sample also had a complex structure with weak peak intensity (Figure 2a). Based on the comparison with the XRD patterns of standard Pb species, PbBr_2 was identified as a major species in the LSD with a possible minor quantity of PbO (Figure 2b–2d). The assumption is sustained because the EDX and XRF analysis also confirmed a high concentration of bromine in the LSD solids, while oxygen was not detected at a significant level. However, it was difficult to identify the In and Zn species in the LSD even after comparison with the XRD patterns of corresponding standard reagents.

3.2 *Chelant-assisted washing treatment of the LSD*

3.2.1 *Effect of chelant concentration*

The effects of chelant application and the corresponding concentrations in solution from the extraction of the main metal components of the LSD (Pb, Zn and In) are illustrated in [Figure 3a](#). Quantitative Pb extraction was observed with the chelant solutions, whereas Zn and In extraction was limited to less than 26% and 8%, respectively. To achieve the maximum Pb extraction yield, the concentration of chelant in solution is required to be greater than 5 mmol g⁻¹. As shown in section 3.1, the content of total metals in the LSD was 2.86 mmol g⁻¹. Hence, the calculated simulation indicated that 2.86 mmol g⁻¹ of chelant is required for the formation of 1:1 metal (M)-chelant (Y) [27-29] complexes (Eq. 2), considering a chelant-LSD mixing ratio of 100 cm³ g⁻¹. The simulation calculation, therefore, further supports the experimental observations and confirms that more than 5 mmol g⁻¹ of chelant should be required to remove the lead from the LSD.



3.2.2 *Effect of extraction time*

Chelant-assisted washing treatment was performed at 25°C, and temporal changes in the extraction behavior are shown in [Figure 3b](#). The Pb and Zn extraction patterns indicated that equilibrium was attained within 5 h, irrespective of the type of chelant, whereas the reaction rate was slower for indium. The extractive In leaching rate with the chelants was minimal compared to the leaching rate of Pb and Zn, thus becoming an issue of secondary concern. Hence, in terms of the efficiency of Pb extraction, an extraction period of 5 h was maintained for the chelant-assisted treatment step.

3.2.3 *Effect of solution pH*

The effect of extractant pH on the chelant-assisted metal leaching rate from LSD was examined with simultaneous control runs. The extraction yields obtained in the absence of

chelants were higher at an acidic pH than under basic conditions (Figure 4a). This behavior is attributable to the interaction of the hydrogen ions (H^+) in solution [30]. The hydrogen ions may react with metal compounds on the surface of the LSD and dissolve or desorb [31] these metal compounds (Eq. 3).



The presence of chelant in solution increased the metal extraction yields throughout the pH range from 3 to 11. In addition, an increase in the metal extraction yields under both acidic (e.g., Zn: 32 % at pH 3, EDTA) and basic (e.g., Zn: 24 % at pH 11, EDTA) pH was observed. The increased yield at lower pH may be due to the higher release rate of metals (M) from the solid phase (Eq. 3). The higher extraction yield at basic pH is attributable to the high conditional formation constant of the chelant-metal complex ($K_f'_{MY}$) due to acid dissociation of the chelant (Eq. 4), which designates the increment in metal-chelate complexation (Eq. 2). The extraction yield of metals in the acidic region has been higher than the extraction yield in the basic region, indicating that the chemical form of the metal constituents in the LSD solids has a significant role during the chelant-assisted leaching of metals under the influence of solution pH [32].

The difference in the extraction efficiencies among the chelants (EDTA, EDDS, or HIDS) was found to be prominent at an acidic pH (pH ~ 3). The Pb and Zn extraction rates were lower with the HIDS and EDDS chelants than with EDTA and commonly occurred in the following order: EDTA > HIDS > EDDS. This ordering can be attributed to protonation of the chelant, which can be described as the back reaction of Eq. 4. The complexation ability of the chelant, as denoted by $K_f'_{MY}$, tends to be lower after protonation. The calculated $\log K_f'_{MY}$ at pH 3 is as follows: EDTA-Pb (7.40) > HIDS-Pb (2.14) > EDDS-Pb (0.68) and EDTA-Zn (5.90) > HIDS-Zn (1.69) > EDDS-Zn (1.38). Hence, the extraction yield of metals was found to be dependent on the

conditional formation constant at an acidic pH causing a decrease in the complex formation ability of the chelant.

Chelant-assisted washing was also carried out under stronger basic conditions ($> \text{pH } 11$), and the results are shown in [Figure 4b](#). The indium extraction yield was below the limit of detection at $0.02 < [\text{NaOH}] < 0.2 \text{ mol g}^{-1}$ ([Figure 4b](#), In) for EDTA and EDDS-assisted washing. The increased concentration of hydroxide ions in the solution results in the precipitation of indium as indium hydroxide (e.g., $\text{In}(\text{OH})_3$, $K_{\text{sp}} = 1.26 \times 10^{-37}$) (Eq. 5), and the magnitude of this chemical reaction was larger than the rate of In-chelant complex formation (e.g., In-EDTA^- , $K_f = 8.91 \times 10^{24}$).



In the presence of 0.01 mol g^{-1} of NaOH in solution ([Figure 4b](#)), the extraction yields of Pb and Zn were comparable to a great extent, indicating a larger solubility range for hydroxide precipitation of the corresponding metals. Furthermore, an increase in the reactive species Y^{n-} occurred under alkaline conditions, resulting in a higher formation rate for soluble chelant coordination compounds and increased metal extraction rates [33]. These observations indicate that the physicochemical form of the metals and their interaction with the hydroxide ions are important and make a strong contribution to chelant-assisted washing at a basic pH. Based on these experimental findings, we concluded that chelant-assisted washing with 0.02 mol g^{-1} NaOH in chelant solution will be advantageous for the separation of indium from other coexisting metals.

Although there are differences in the rate of metal extraction with EDTA, EDDS and HIDS, the differences are not significant except under highly acidic and strongly basic conditions. In spite of the higher efficiency of EDTA, its poor photo-, chemo- and biodegradability evoke environmental concerns [34-37], and the biodegradable alternatives (EDDS or HIDS) deserve consideration [38-40]. The extraction of Pb and Zn from solids with EDDS was observed to be

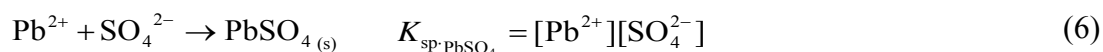
superior to extraction with HIDS under basic conditions [40], and EDDS has been selected for subsequent studies.

3.3 Acid leaching

The chelant-assisted washing treatment facilitated the quantitative removal of lead and concentrated the indium and zinc in the LSD. However, the selective leaching of indium is difficult with chelants. Therefore, an acid-leaching step was employed with the aim of reallocating solid-phase indium in the LSD to the aqueous phase.

3.3.1 Effects of acid concentration

The effects of various acids and their corresponding concentrations on the leaching efficiency of indium from LSD were studied (Figure 5). HNO₃-assisted leaching was successful for the quantitative recovery of indium and the other coexisting metals (Pb and Zn) at ≥ 0.5 mol g⁻¹ acid, while HCl and H₂SO₄ were able to recover the same amounts at ~ 0.1 mol g⁻¹ acid. Furthermore, Pb extraction was not observed at ~ 0.1 mol g⁻¹ H₂SO₄ due to the formation of PbSO₄ precipitate ($K_{sp} = 7.2 \times 10^{-8}$) (Eq. 6), making this set of conditions more efficient than the other alternatives for isolating indium from residual lead.



3.3.2 Effects of a mixed acid solution

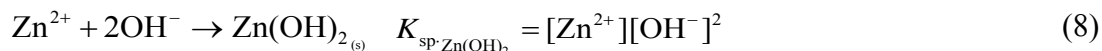
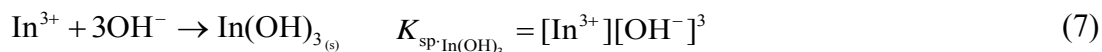
The metal leaching efficiency of a mixture of HCl and H₂SO₄ was examined to determine moderate separation conditions, and the composite concentration ratio was varied within 0.1 mol g⁻¹. Increasing the H₂SO₄ concentration in the mixture was observed to decrease the lead extraction yield (Figure 6a) due to the common ion effect. Optimum separation performance, as represented by Pb leaching of < 1%, was achieved with a mixture of 0.04 mol g⁻¹ H₂SO₄ and 0.02 mol g⁻¹ HCl. However, the leaching behavior of Zn with these acids is similar to the leaching behavior of indium. Hence, the desired selectivity toward indium in LSD is not completely achievable during the acid-assisted leaching step.

3.3.3 Effects of leaching time

The effects of leaching time on the acid-assisted recovery of indium and zinc using the 0.04 mol g⁻¹ H₂SO₄ plus 0.02 mol g⁻¹ HCl mixture were examined (Figure 6b). A period of 24 h was required to achieve an indium yield of up to 94%, and solution equilibrium (yield: 97%) for zinc was achieved within 12 h. Hence, a leaching time of 24 h was selected to ensure complete indium leaching from the LSD.

3.4 Hydroxide precipitation

Separation of indium from zinc in LSD is difficult because of their similar behavior. The hydroxide precipitation technique was therefore examined to separate indium from zinc. The hydroxides of indium and zinc are known as weakly soluble salts in water, and the corresponding solubility products (K_{sp}) are $1.26 \times 10^{-37} \text{ mol}^4 \text{ dm}^{-12}$ (Eq. 7) and $2.0 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9}$ (Eq. 8), respectively. The K_{sp} values of indium and zinc are significantly different, and this difference is useful for separating indium from zinc by adjusting the solution pH.



A calculated simulation of hydroxide solubility indicates that indium precipitates at pH > 4, while zinc remains as a soluble species in the supernatant at pH values < 7 (Figure 7a). Thus, the pH adjustment of an acid-leached solution is expected to separate indium as a hydroxide precipitate in the following pH range: 4 < pH < 7.

Experimental observations showing indium and zinc species in the aqueous and solid phases with changes in the pH of an acid-leached solution are shown in Figure 7b. The total indium content was observed to exist in the aqueous phase at pH 0.2 to 2, and its precipitation as indium hydroxide started at pH > 2 and approached completion at pH 5. By contrast, zinc precipitation as hydroxide was initiated at pH > 5.4. Therefore, the separation of indium and zinc from the aqueous phase is achievable by adjusting the solution pH to 5.

3.5 Sequential separation scheme for selective indium separation from the LSD

A sequential separation scheme was designed for the selective recovery of indium from LSD according to the optimized conditions identified in the previous sections during evaluation of the chelant-assisted washing, acid leaching and hydroxide precipitation techniques (Figure 8). The scheme was experimentally verified using 9.9968 g of LSD as a starting sample. The sample was subjected to the chelant-assisted washing treatment using 5 mmol g⁻¹ EDDS and 0.02 mol g⁻¹ NaOH at 25 °C, resulting in the almost quantitative separation of lead and separation of approximately 22 % of the zinc from the raw LSD. The subsequent step was the acid leaching of the chelant-treated LSD with a mixed acid solution (0.02 mol g⁻¹ HCl and 0.04 mol g⁻¹ H₂SO₄) at 25 °C, and the acid-leached eluate included mostly indium (1.1 g dm⁻³) and zinc (2.1 g dm⁻³). The acid-leached eluate was then subjected to separation by hydroxide precipitation by adjusting the solution pH to 5. The precipitated solid obtained (1.0463 g) included 0.23 g of indium and 0.03 g of zinc. Overall, a total of 88.2 % of the indium was selectively recovered from the LSD by the proposed sequential separation scheme.

The mass distribution of indium, lead and zinc in the LSD during application of the sequential separation scheme is summarized in Figure 9, calculated using the following relation:

$$\text{Mass distribution (\%)} = \frac{m}{m_{\text{CAW}} + m_{\text{ALR}} + m_{\text{HP,sup}} + m_{\text{HP,ppt}}} \times 100 \quad (9)$$

where the symbols in the equation indicate the following: m (%), each distribution of metal; m_{CAW} (%), metals in the chelant-assisted washing eluate; m_{ALR} (%), metals in the acid leaching residue; $m_{\text{HP,sup}}$ (%), metals in the hydroxide precipitation supernatant; and $m_{\text{HP,ppt}}$ (%), metals in the hydroxide precipitate. The total recovery of indium from the 9.9968 g LSD sample with the sequential separation process was 96%, while the contribution of indium hydroxide was 88% in that total.

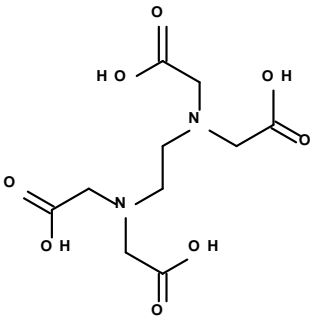
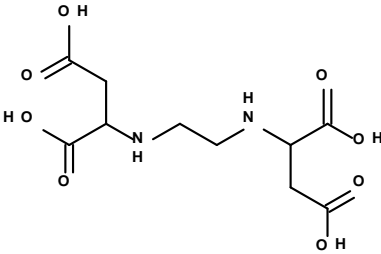
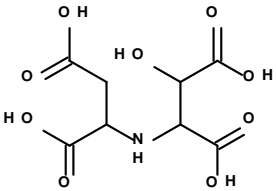
4.0 Conclusion

The present study was aimed at the development of a selective technique for the recovery of indium from LSD. The extraction yield of metals from LSD was found to be strongly influenced by solution pH and interactions between the metals and hydrogen ions or hydroxide ions. Indium and zinc remained fixed in the LSD while lead was extracted with a solution containing 5 mmol g^{-1} EDDS and 0.02 mol g^{-1} NaOH. A subsequent acid leaching step induced the release of indium and zinc from the LSD. Hydroxide precipitation by adjusting the solution pH to 5 ensured the separation of indium as indium hydroxide precipitate, while the total zinc content remained in the supernatant. The proposed multiple step treatment selectively separated and concentrated indium as a hydroxide precipitate from the matrix component of the LSD, and the total separated indium was 88 % as the precipitate. The present technique is expected to be able to refine indium quantitatively with little harm to the environment because of its minimal consumption of acids and bases.

Acknowledgments

This research was partially supported by the Grants-in-Aid for Scientific Research (15H05118 and 25·5863) from the Japan Society for the Promotion of Science. One of the authors, I.M.M. Rahman, acknowledges the financial grant from ‘The Public Foundation of Chubu Science and Technology Center, Japan’ to support his research at the Kanazawa University, Japan.

Table 1. Chemical structures and acid dissociation constants (pK_a) of chelants

Chelant	Structure	pK_a
EDTA ^a , Ethylenediaminetetraacetate		pK_{a1} 2.00 pK_{a2} 2.69 pK_{a3} 6.13 pK_{a4} 10.37
EDDS ^a , Ethylenediaminedisuccinate		pK_{a1} 2.95 pK_{a2} 3.86 pK_{a3} 6.84 pK_{a4} 10.01
HIDS ^b , 3-Hydroxy-2,2'-iminodisuccinate		pK_{a1} 2.14 pK_{a2} 3.08 pK_{a3} 4.07 pK_{a4} 9.61

^a At 25 °C ($\mu = 0.1$ M) [41], ^b At 25 °C ($\mu = 0.1$ M) [28, 29, 39].

Table 2. Metal concentrations in LSD by microwave-assisted digestion/ICP-OES detection

Metal	Concentration [%]
Bi	0.195 ± 0.005
Ca	0.59 ± 0.01
Cd	0.62 ± 0.01
Cu	0.234 ± 0.005
In	2.64 ± 0.06
Pb	40.6 ± 0.7
Tl	0.13 ± 0.01
Zn	5.7 ± 0.2

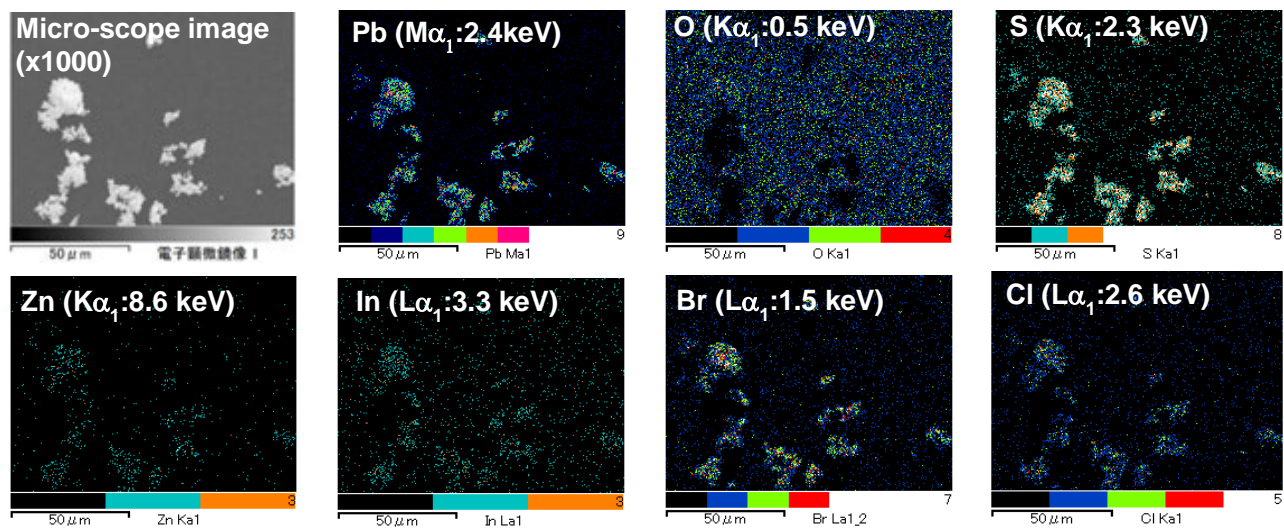


Figure 1. FE-SEM/EDX observation and element mapping image

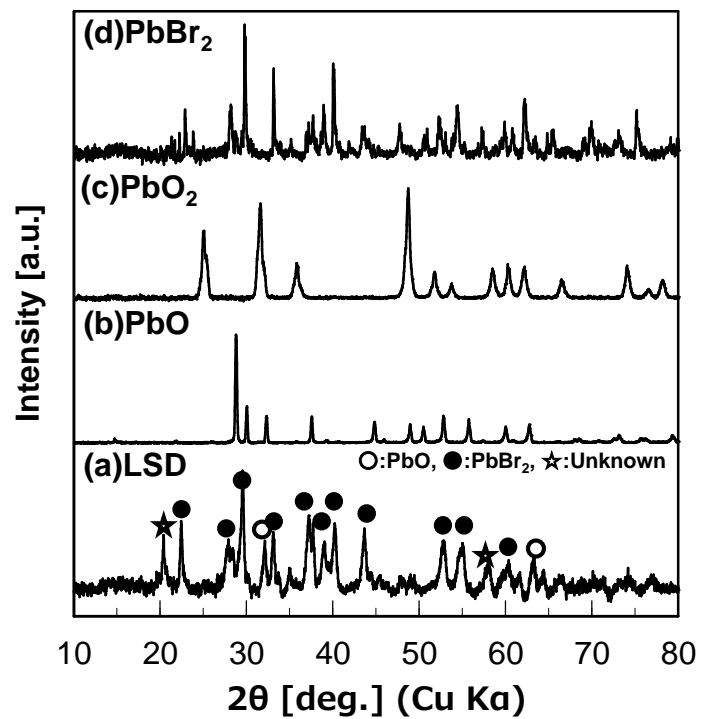


Figure 2. XRD pattern comparison of (a) LSD sample with (b~d) Pb salts, which are (b) PbO, (c) PbO₂ and (d) PbBr₂.

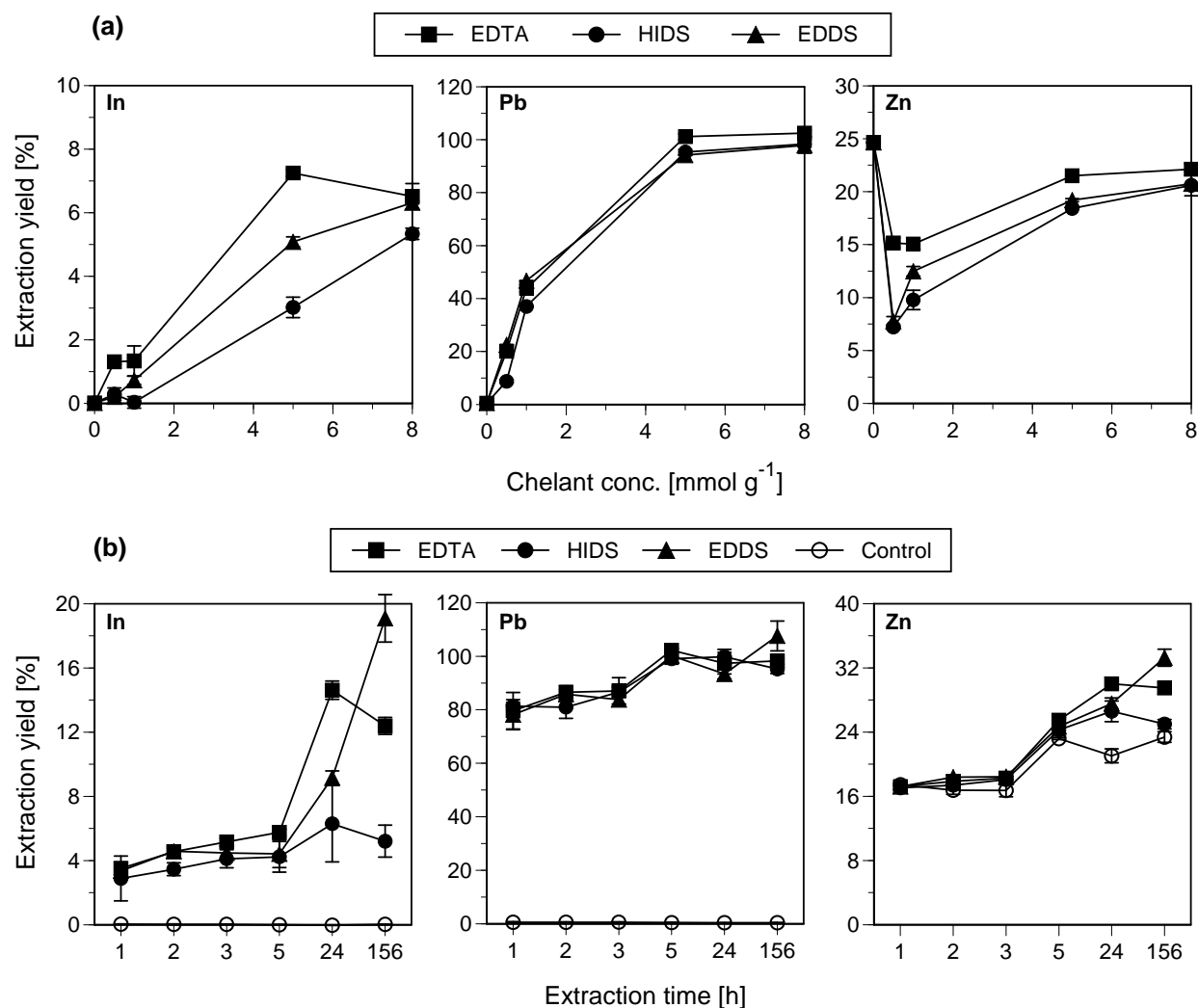


Figure 3. Effect of (a) chelant concentration (extraction time: 24 h) and (b) extraction time (chelant concentration: 5 mmol g⁻¹) on extraction yield (%) during chelant-assisted washing treatment of LSD. Solution pH, 7; liquid solid ratio, 100 cm³ g⁻¹; temperature, 25°C.

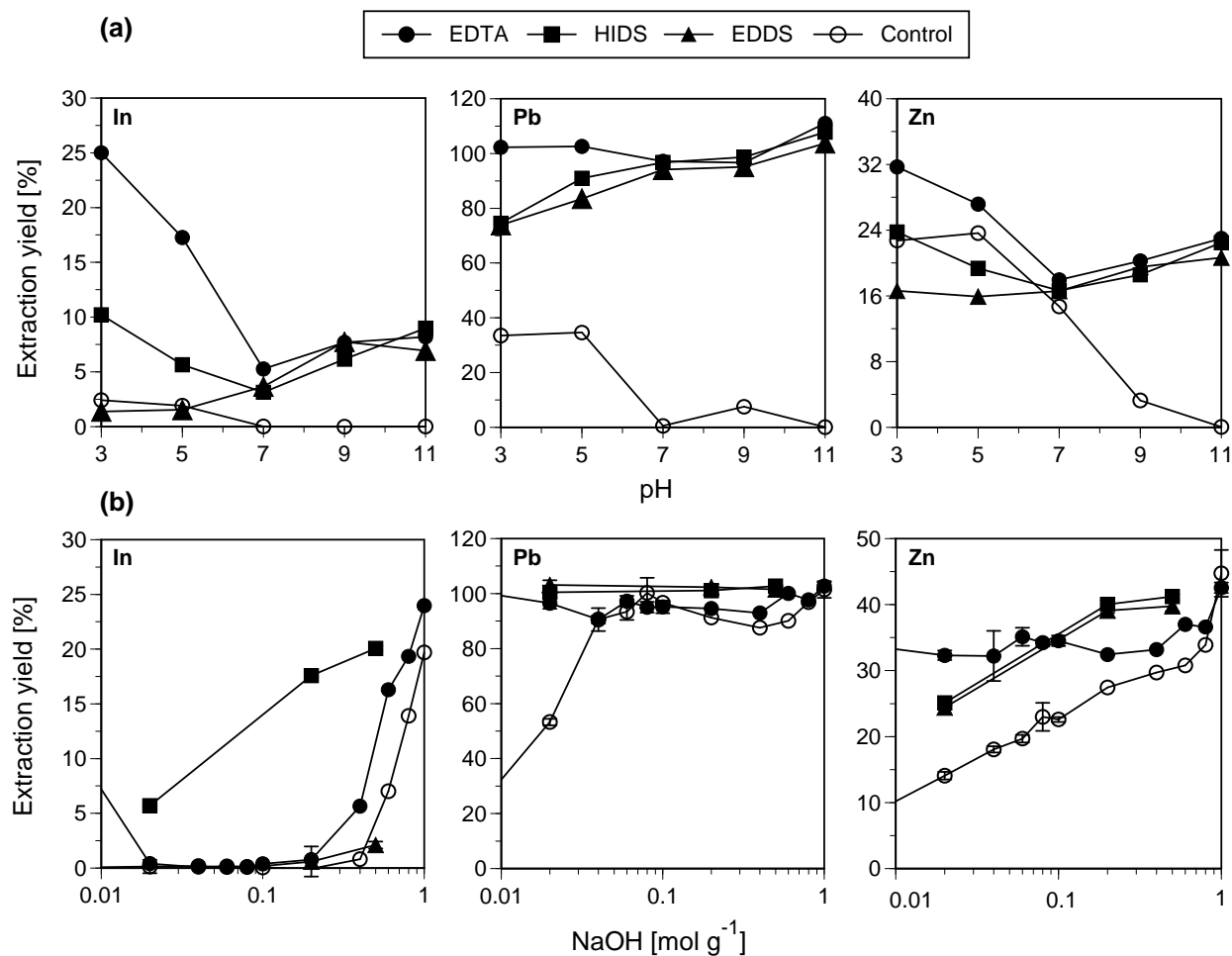


Figure 4. Effect of (a) solution pH (3 to 11) and (b) NaOH addition (0.01 to 1 mol g⁻¹) on extraction yield (%) during chelant-assisted washing treatment of LSD. Chelant concentration, 5 mmol g⁻¹; liquid solid ratio, 100 cm³ g⁻¹; extraction time, 24 h; temperature, 25°C.

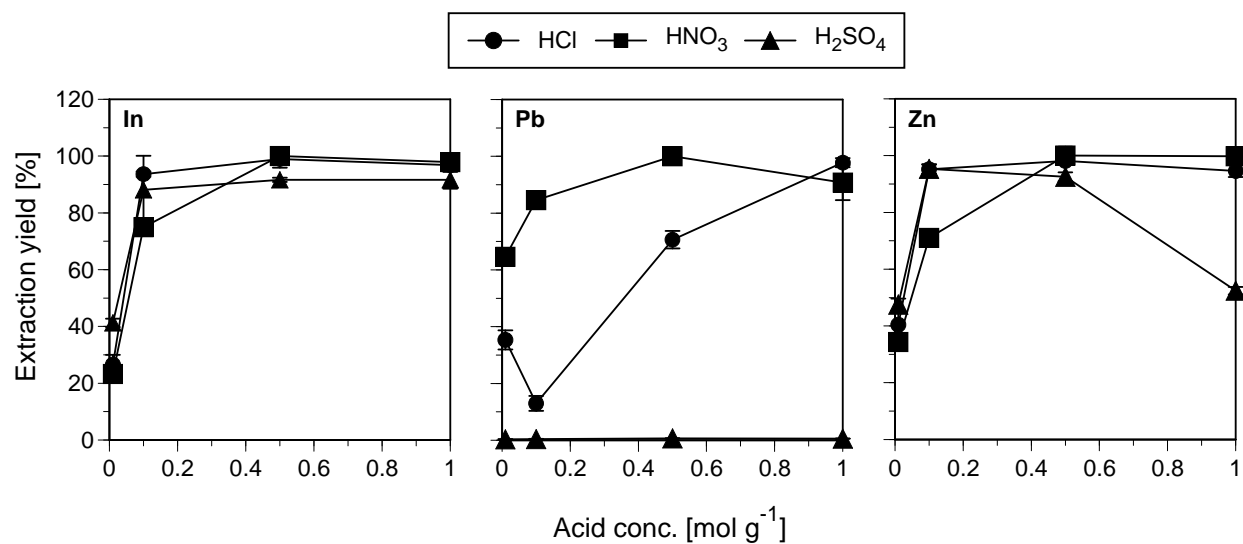


Figure 5. Metal extraction yields during mineral acid leaching treatment of LSD. Liquid solid ratio, 100 cm³ g⁻¹; extraction time, 24 h; temperature, 25°C.

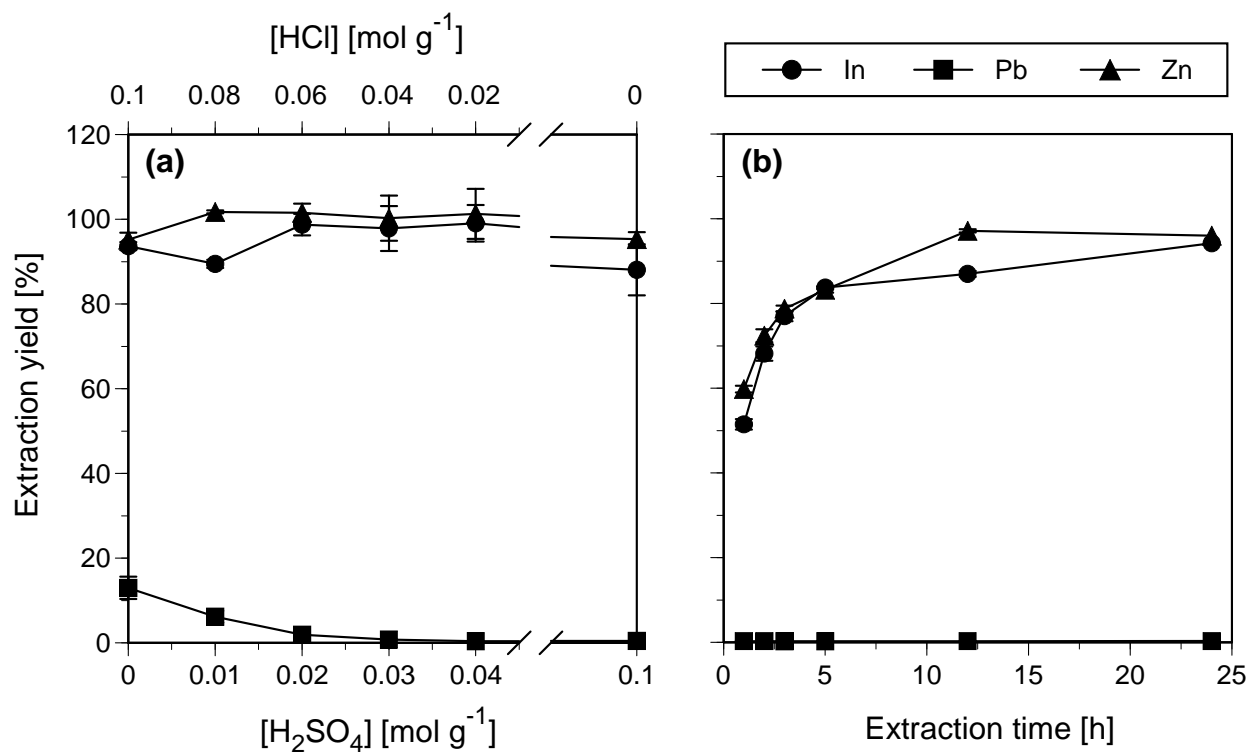


Figure 6. Extraction yields of metals (In, Pb and Zn) during acid-leaching treatments of LSD: (a) Effect of varying HCl/H₂SO₄ ratio (extraction time: 24 h); (b) Effect of extraction time with HCl (0.02 mol g⁻¹) and H₂SO₄ (0.04 mol g⁻¹) mixture. Liquid solid ratio, 100 cm³ g⁻¹; temperature, 25°C.

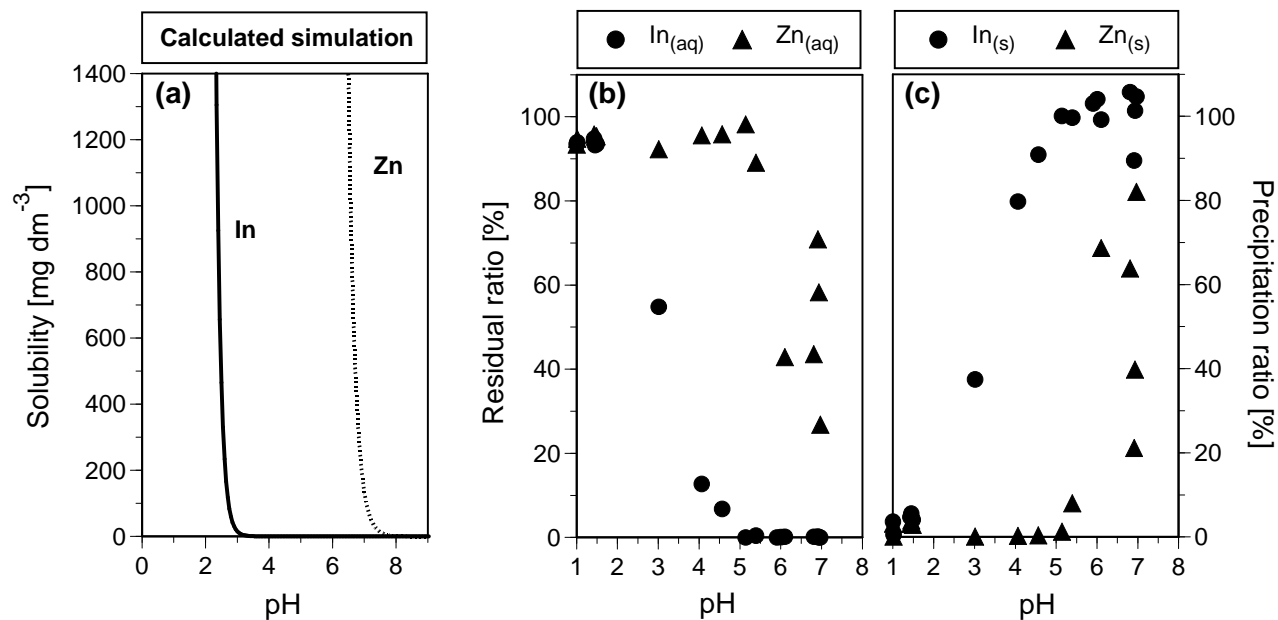


Figure 7. Separation of indium from zinc using the hydroxide-precipitation technique: (a) calculated simulation; (b) residual ratio (%) in the aqueous medium of the supernatant; (c) precipitation ratio (%) during hydroxide precipitation.

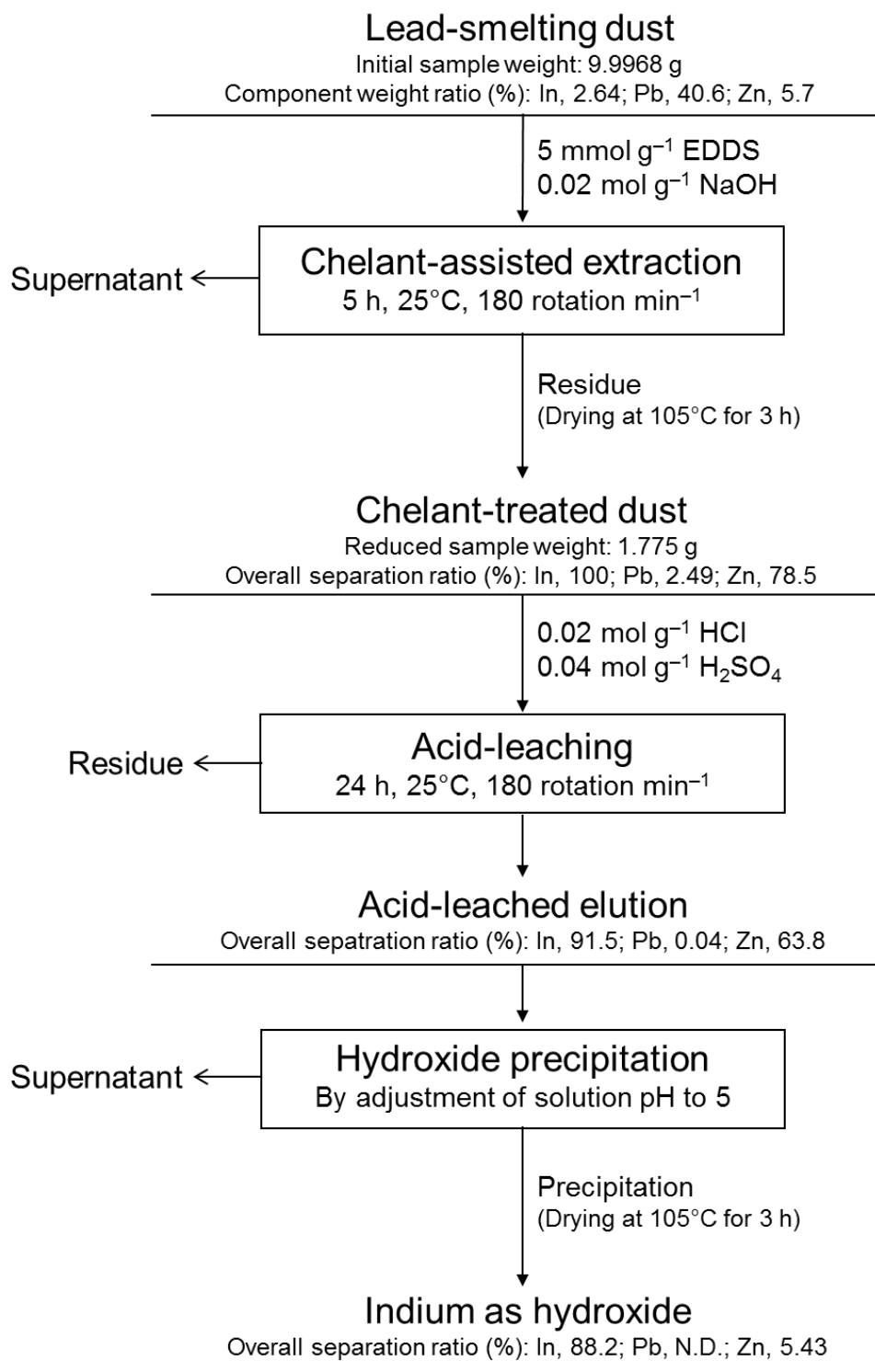


Figure 8. Sequential scheme for selective indium separation from LSD. In the figure, ‘N.D.’ stands for ‘not detected’.

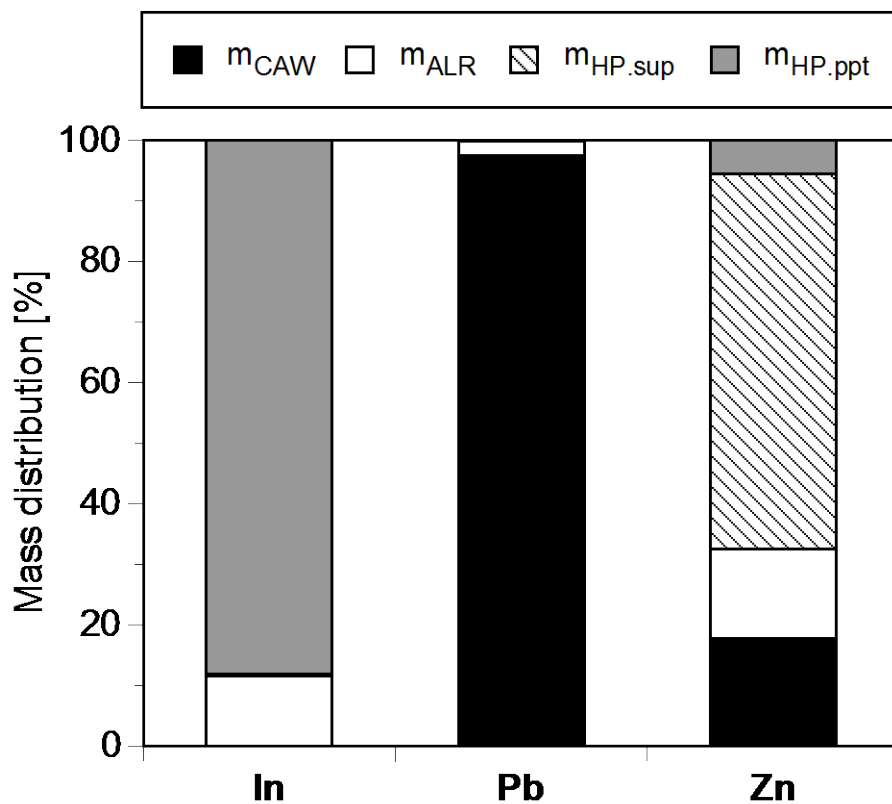


Figure 9. Mass distribution of the major metal components of the LSD during the sequential separation process. The symbols stand for the following: m_{CAW} (%), metal in the chelant-assisted washing eluate; m_{ALR} (%), metal in the acid-leaching residue; $m_{HP.sup}$ (%), metal in the hydroxide-precipitation supernatant; $m_{HP.ppt}$ (%), metal in the hydroxide precipitate.

REFERENCES

- [1] A.M. Alfantazi, R.R. Moskalyk, Processing of indium: A review, *Miner. Eng.*, 16 (2003) 687–694.
- [2] Y. Li, Z. Liu, Q. Li, Z. Liu, L. Zeng, Recovery of indium from used indium-tin oxide (ITO) targets, *Hydrometallurgy*, 105 (2011) 207–212.
- [3] M. Shimizu, A. Kato, Roquesite-bearing tin ores from the omodai, akenobe, fukoku and ikuno polymetallic vein-type deposits in the inner zone of southwestern japan, *Can. Mineral.*, 29 (1991) 207–215.
- [4] B. Gupta, N. Mudhar, I. Singh, Separations and recovery of indium and gallium using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), *Sep. Purif. Technol.*, 57 (2007) 294–303.
- [5] J.D. Jorgenson, M.W. George, Mineral Commodity Profiles: Indium, in, U.S. Geological Survey, Virginia, 2005.
- [6] S. Virolainen, D. Ibane, E. Paatero, Recovery of indium from indium tin oxide by solvent extraction, *Hydrometallurgy*, 107 (2011) 56–61.
- [7] J.C. Park, The recovery of indium metal from ITO-scrap using hydrothermal reaction in alkaline solution, *B. Korean Chem. Soc.*, 32 (2011) 3796–3798.
- [8] S.J. Hsieh, C.C. Chen, W.C. Say, Process for recovery of indium from ITO scraps and metallurgic microstructures, *Mater. Sci. Eng. B-Adv.*, 158 (2009) 82–87.
- [9] Y.S. Park, W. Sato, G. Grause, T. Kameda, T. Yoshioka, Recovery of indium from In_2O_3 and liquid crystal display powder via a chloride volatilization process using polyvinyl chloride, *Thermochim. Acta*, 493 (2009) 105–108.
- [10] H. Hasegawa, I.M.M. Rahman, Y. Egawa, H. Sawai, Z.A. Begum, T. Maki, S. Mizutani, Recovery of indium from end-of-life liquid-crystal display panels using aminopolycarboxylate chelants with the aid of mechanochemical treatment, *Microchem. J.*, 106 (2013) 289–294.
- [11] H. Hasegawa, I.M.M. Rahman, Y. Egawa, H. Sawai, Z.A. Begum, T. Maki, S. Mizutani, Chelant-induced reclamation of indium from the spent liquid crystal display panels with the aid of microwave irradiation, *J. Hazard. Mater.*, 254–255 (2013) 10–17.
- [12] H.N. Kang, J.Y. Lee, J.Y. Kim, Recovery of indium from etching waste by solvent extraction and electrolytic refining, *Hydrometallurgy*, 110 (2011) 120–127.

- [13] H.M. Liu, C.C. Wu, Y.H. Lin, C.K. Chiang, Recovery of indium from etching wastewater using supercritical carbon dioxide extraction, *J. Hazard. Mater.*, 172 (2009) 744–748.
- [14] H. Hasegawa, I.M.M. Rahman, Y. Umehara, H. Sawai, T. Maki, Y. Furusho, S. Mizutani, Selective recovery of indium from the etching waste solution of the flat-panel display fabrication process, *Microchem. J.*, 110 (2013) 133–139.
- [15] X.H. Li, Y.J. Zhang, Q.L. Qin, J.A. Yang, Y.S. Wei, Indium recovery from zinc oxide flue dust by oxidative pressure leaching, *T. Nonferr. Metal Soc.*, 20 (2010) S141–S145.
- [16] B.R. Conard, The role of hydrometallurgy in achieving sustainable development, *Hydrometallurgy*, 30 (1992) 1–28.
- [17] D.S. Flett, Solution purification, *Hydrometallurgy*, 30 (1992) 327–344.
- [18] H. Xu, C. Wei, C. Li, G. Fan, Z. Deng, M. Li, X. Li, Sulfuric acid leaching of zinc silicate ore under pressure, *Hydrometallurgy*, 105 (2010) 186–190.
- [19] S.M.J. Koleini, H. Mehrpouya, K. Saberyan, M. Abdolahi, Extraction of indium from zinc plant residues, *Miner. Eng.*, 23 (2010) 51–53.
- [20] Y.J. Zhang, X.H. Li, L.P. Pan, X.Y. Liang, X.P. Li, Studies on the kinetics of zinc and indium extraction from indium-bearing zinc ferrite, *Hydrometallurgy*, 100 (2010) 172–176.
- [21] M.A. Barakat, Recovery of lead, tin and indium from alloy wire scrap, *Hydrometallurgy*, 49 (1998) 63–73.
- [22] F.M. Doyle, Teaching and learning environmental hydrometallurgy, *Hydrometallurgy*, 79 (2005) 1–14.
- [23] R.S. Marinho, C.N. da Silva, J.C. Afonso, J.W.S.D. da Cunha, Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins, *J. Hazard. Mater.*, 192 (2011) 1155–1160.
- [24] A.P. Paiva, Recovery of indium from aqueous solutions by solvent extraction, *Separ. Sci. Technol.*, 36 (2001) 1395–1419.
- [25] J.-C. Park, The removal of tin from ITO-scrap via ozonization, *B. Korean Chem. Soc.*, 30 (2009) 3141–3142
- [26] J.-C. Park, The removal of tin from ITO-scrap using molten NaOH, *B. Korean Chem. Soc.*, 29 (2008) 255–256.

- [27] J.-C. Yoo, C.-D. Lee, J.-S. Yang, K. Baek, Extraction characteristics of heavy metals from marine sediments, *Chem. Eng. J.*, 228 (2013) 688–699.
- [28] Z.A. Begum, I.M.M. Rahman, H. Sawai, Y. Tate, T. Maki, H. Hasegawa, Stability constants of Fe(III) and Cr(III) complexes with dl-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2'-iminodisuccinic acid (HIDS) in aqueous solution, *J. Chem. Eng. Data*, 57 (2012) 2723–2732.
- [29] Z.A. Begum, I.M.M. Rahman, Y. Tate, Y. Egawa, T. Maki, H. Hasegawa, Formation and stability of binary complexes of divalent ecotoxic ions (Ni, Cu, Zn, Cd, Pb) with biodegradable aminopolycarboxylate chelants (dl-2-(2-carboxymethyl)nitrilotriacetic acid, GLDA, and 3-hydroxy-2,2'-iminodisuccinic acid, HIDS) in aqueous solutions, *J. Solution Chem.*, 41 (2012) 1713–1728.
- [30] T.T. Lim, J.H. Tay, J.Y. Wang, Chelating-agent-enhanced heavy metal extraction from a contaminated acidic soil, *J. Environ. Eng.-ASCE*, 130 (2004) 59–66.
- [31] Y.-J. Tu, S.-C. Lo, C.-F. You, Selective and fast recovery of neodymium from seawater by magnetic iron oxide Fe₃O₄, *Chem. Eng. J.*, 262 (2015) 966–972.
- [32] A. Barona, I. Aranguiz, A. Elías, Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedures, *Environ. Pollut.*, 113 (2001) 79–85.
- [33] K. Fischer, H.P. Bipp, Removal of heavy metals from soil components and soils by natural chelating agents. Part ii. Soil extraction by sugar acids, *Water Air Soil Poll.*, 138 (2002) 271–288.
- [34] T. Egli, Biodegradation of Metal-Complexing Aminopolycarboxylic Acids, *J. Biosci. Bioeng.*, 92 (2001) 89–97.
- [35] X. Liu, J.H. Fan, Y. Hao, L.M. Ma, The degradation of EDTA by the bimetallic Fe-Cu/O₂ system, *Chem. Eng. J.*, 250 (2014) 354–365.
- [36] A. Vintiloiu, M. Boxriker, A. Lemmer, H. Oechsner, T. Jungbluth, E. Mathies, D. Ramhold, Effect of ethylenediaminetetraacetic acid (EDTA) on the bioavailability of trace elements during anaerobic digestion, *Chem. Eng. J.*, 223 (2013) 436–441.
- [37] H. Hasegawa, I.M.M. Rahman, M. Nakano, Z.A. Begum, Y. Egawa, T. Maki, Y. Furusho, S. Mizutani, Recovery of toxic metal ions from washing effluent containing excess aminopolycarboxylate chelant in solution, *Water Res.*, 45 (2011) 4844–4854.

- [38] I.M.M. Rahman, Z.A. Begum, H. Sawai, M. Ogino, Y. Furusho, S. Mizutani, H. Hasegawa, Chelant-assisted depollution of metal-contaminated Fe-coated sands and subsequent recovery of the chemicals using solid-phase extraction systems, *Water Air Soil Poll.*, 226 (2015) 37.
- [39] Z.A. Begum, I.M.M. Rahman, Y. Tate, H. Sawai, T. Maki, H. Hasegawa, Remediation of toxic metal contaminated soil by washing with biodegradable aminopolycarboxylate chelants, *Chemosphere*, 87 (2012) 1161–1170.
- [40] Z.A. Begum, I.M.M. Rahman, H. Sawai, S. Mizutani, T. Maki, H. Hasegawa, Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soils, *Water Air Soil Poll.*, 224 (2013) 1381.
- [41] A.E. Martell, R.M. Smith, R.J. Matekaitis, NIST Standard Reference Database 46: NIST Critically Selected Stability Constants of Metal Complexes Database (Version 8.0 For Windows), in, Texas A&M University, College Station, TX, 2004.