≫總 說《

http://dx.doi.org/10.7844/kirr.2013.22.2.3 pISSN: 1225-8326 eISSN: 2287-4380

2次 資源으로부터 濕式方法에 의한 인듐의 回收

王凌云・中李晩承

木浦大學校 工科大學 新素材工學科

Recovery of Indium from Secondary Resources by Hydrometallurgical Method

Lingyun Wang and *Manseung Lee

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Korea

요 약

인듐은 회유금속으로 주로 ITO제조에 사용된다. 본 총설에서는 인듐을 함유한 2차자원을 침출한 용액으로부터 인듐을 분리하기 위한 용매추출, 이온교환 및 석출법에 대한 공정 조건 및 장단점을 조사했다. 보통 정도의 산성용액에서 인듐의 추출제로 D2EHPA가 가장 많이 사용되고 있으며, 매우 강한 염산용액에서는 아민계 추출제가 사용된다. 일반적으로 이온교환수지의 인듐 흡착량이 낮으므로, 인듐의 농도가 낮은 경우에 한해 이온교환은 용매추출보다 장점이 있다.

주제어 : 인듐, 2차 자원, 회수, 용매추출, 이온교환

Abstract

Indium is one of the rare metals, and it has been used mainly for preparation of indium tin oxide (ITO). This review investigated the process parameters and the merits and demerits of several methods to recover indium from the leaching solution of secondary resources, such as solvent extraction, ion exchange, and precipitation. D2EHPA has been used mostly as a cationic extractant for indium extraction in moderate acid solutions, while amine extractants are used in strong hydrochloric acid solution. Since the loading capacity of resins for indium is generally small, ion exchange has some advantage over solvent extraction only when the concentration of indium is low.

Key words: Indium, Secondary resources, Recovery, Solvent extraction, Ion exchange

1. Introduction

Indium is scarce in the nature, and is estimated to be only 50 to 200 parts per billion in the earth's crust.¹⁾ It is not mined for itself and has to be recovered as a byproduct from other metallurgical processes or from

secondary materials. Initially, indium was discovered in zinc ores at 1863 and the reason for the proposed name for "indium" is due to the fact that the spectrum line of indium is shown at indigo blue places.²⁾ Indium has a silvery-white color and good ductile and malleable properties. The chemical properties of indium are

^{*} Received: October 4, 2012 · Revised: November 16, 2012 · Accepted: November 29, 2012

^{*}Corresponding Author: Man-Seung Lee (E-mail: mslee@mokpo.ac.kr)

Department of Advanced Materials Science & Engineering, Mokpo National University, 61 Dorim-ri, Chungkye-myun, Muangun, Chonnam, 534-729, Korea

Tel: +82-62-450-2492 / Fax: +82-62-450-2498

[©] The Korean Institute of Resources Recycling. All rights reserved. This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/), which permits unrestricted non-commercial use, distribution and reproduction in any medium, provided the original work is properly cited.

generally between the gallium and thallium properties. It is well known that the existence of most stable indium valence is trivalent.³⁾

Major uses of indium are flat display panels and thin-film coatings (indium tin oxide, ITO) (90%), solders and alloys (4%), electrical components and semiconductors (3%), intermetallic compounds (2%), and other research (1%). Indium tin oxide (ITO) thin film, alloys of low-melting-temperature and solders are the leading application of indium. Thin film of indium tin oxide (ITO) is widely used in various optoelectronic devices for transparent conducting layers, such as liquid crystal displays (LCD), flat display panels and solar cells. Production of ITO is the leading end use of indium, accounting for the majority of global indium consumption. In the leading end use of indium, accounting for the majority of global indium consumption.

Since the production of ITO is growing, the demand of indium metal is increasing sharply. However, the primary resources of indium are limited. Thus, the development of technology for recovery of indium from waste material becomes urgent to meet the demand from the industry. The most important secondary resource is ITO because sputtering process is highly inefficient. In this process, approximately 30% ITO target is utilized, leaving 70% waste ITO. Recycling of ITO has been developed in the countries with large production of ITO by sputtering, such as China, Japan, and Korea.⁵⁾

In developing a hydrometallurgical technology for metal recovery and separation operations, methods such as solvent extraction, ion exchange, and precipitation have been employed to separate the target metal ion from the leaching solution. In this review, the processes to recover indium from secondary sources are discussed. Especially, several separation methods to obtain indium with high purity are compared.

2. Sources of indium

World production of indium was 640 tons in 2011(340 from China, 100 from Korea, 70 from Japan, 65 from Canada, 30 from Belgium, 35 from other countries). In addition, it has been estimated that world reserves of recoverable indium are 2500 tons. It should be mentioned here that in the United States annual

average price for 1 kg of indium was 720 dollars in 2011, which value was increased by 27% from that of 2010.⁵⁻⁶⁾ Indium appears as a chalcophile elemental state of sulfide mineral form.⁴⁾ It is found in trace amount in many minerals, particularly in sphalerite (ZnS) and associated with sulfides of copper, lead, iron and tin.⁷⁾ Because of its relatively low average level of occurrence, indium is classified as a rare metal and can only be economically extracted as a byproduct under the appropriate conditions.⁸⁻¹⁰⁾

The concentration of indium in these ores is 1-50 ppm. Even in the most common commercial source -- sulphur-bearing zinc ore, the proportion of indium is low at 70-200 ppm.⁴⁾ Cook et al. found that indium-sphalerite (up to 6.7 wt.% In) co-exists with Sn-sphalerite (up to 2.3 wt.%) in sphalerite.¹¹⁻¹⁴⁾ Indium is recovered as a by-product from zinc ore industry.^{1,8)} Native indium and indium minerals, such as indit (FeIn₂S₄) and roquesit (CuInS₂) are rare.⁴⁾ The highest known concentrations of indium are found in veins and sulphide ore bodies associated with tin-bearing minerals.¹⁾

3. Secondary resources

A significant proportion of global indium consumption comes from the recycling of production residues or scrap. The strong demand in recent years has led to investment in recycling capacity in major indium producing countries. Already up to 50% of global indium demand will be supplied by the recycling of scrap. Many countries, such as Korea, China, Canada, United Kingdom, Taiwan, Philippines and Japan have tried to develop a process to recover indium from secondary sources. For example, Japan had an annual production capacity of about 350 tons of indium recycling from ITO production waste in 2007.⁴⁾

Indium can also be recovered from CIGS (copperindium-gallium-diselenide) solar cells which are used in the manufacture of new CIGS solar cells. Moreover, indium can be reclaimed from old liquid crystal display (LCD) panels directly. The panels are crushed to millimeter-sized particles and then dissolved in an acid solution from which the indium is recovered.⁵⁾ Indium recovery from tailings (such as lead and zinc mine tailing) was thought to have been insignificant, as tailings contain small percentages of the metal. However, owing to the high price of indium, improvements in process technology have made indium recovery from these wastes feasible.⁵⁾

The greatest portion of global secondary indium is produced from indium-tin oxide (ITO) recycling. ¹⁵⁾ Indium is one of the most important materials in ITO for various optoelectronic devices for transparent conducting layers—most commonly liquid crystal displays (LCDs). Production of ITO thin-film coatings is the leading end use of indium and account for approximately 84% of global indium consumption. ¹⁶⁾ ITO is a mixture of indium (III) oxide (In₂O₃) and tin (IV) oxide (SnO₂), with 80-90% of In₂O₃ and 10-20% of SnO₂ by weight. ^{17,18)} Except the elements of In, Sn and O in the spent ITO, the contents of other elements are less than 20 ppm. Therefore, recovery of indium from spent ITO is not complicated and important for economical and environmental aspects. ¹⁹⁾

The recovery of indium from ITO may include the following steps. First, indium is dissolved from the spent ITO/ITO scrap by leaching with different lixiviants, and then metals (indium or tin or both of them) are recovered by employing solvent extraction, ion exchange and precipitation from the resulting leach liquor. Purity of indium metal has been increased to four or even five nine (99.99% - 99.999%) by employing cementation or electrolytic refining. 19-21)

In the recovery of indium from spent ITO, hydrochloric, nitric and sulfuric acid solutions are usually used in the leaching step. Sami et al. reported that 6 hours leaching time is enough for complete dissolution of ITO sample in 1 M H₂SO₄ and HCl solutions at L/S ratio of 1000:1 with the rotation speed of 545 rpm, whereas the dissolution rate of ITO in the nitric acid solution was slow. Since H2SO4 is less corrosive to process equipment than HCl, sulfuric acid solution has a slight advantage over the latter.²²⁾ Li et al. reported that the leaching rate of indium was faster in sulfuric acid solution than in hydrochloric acid solution but the leaching percentage of indium was the same in both leaching systems at 90°C for 2 h. Since sulfuric acid is cheaper than hydrochloric acid and less corrosive, sulfuric acid solution is recommended as a leaching agent for ITO at high temperature. 19)

4. Recovery of indium from the leaching solutions

Indium and tin coexist in the leaching solution of spent ITO. Therefore, separation of indium from the leaching solution is necessary to produce pure indium. In hydrometallurgy, solvent extraction, ion exchange, and precipitation are normally employed to separate metal ions. In these three methods, solvent extraction and ion exchange can result in high separation factor while it is difficult to get pure solution by precipitation.

4.1. Solvent extraction

Solvent extraction is one of the techniques for the separation of metals from solution. In general, solvent extraction involves two immiscible liquid phases contacting each other to provide the selective transfer of some ionic or molecular species from aqueous phase to organic phase.²³⁾ Many works have been done on the solvent extraction of indium from different solutions since 1960.²⁴⁾ Some patents and papers have appeared on the development of hydrometallurgical technology including solvent extraction for indium from 1980s.²⁵⁻²⁷⁾ Diverse extractants have been used in the extraction of indium, such as acidic extractants, solvating extractants and basic extractants.

4.1.1. Acidic extractants

Among the extractants available for indium, acidic compounds will be discussed first.

4.1.1.1. D2EHPA

Di-2-ethylhexylphosphoric acid (D2EHPA) is the most popular extractant since last decades, and it has high loading capacity and good selectivity for indium over many other metal ions, for example, Zn(II), Fe(II), Cd(II), As(III) and Cu(II). ²⁶⁻²⁸ Sato et al. investigated the distribution of indium (III) from sulphuric, nitric and hydrochloric acid solution by D2EHPA in kerosene under various conditions. They found that the extraction of indium was in the order HNO₃ > H₂SO₄ > HCl at low acid concentrations, but this order became reversed in concentrated acids. ^{28,29)} According to Sato et al., In(III) ion took part in the solvent extraction from sulfuric acid solution, while indium form complexes with nitrate ion when the

concentration of nitric acid was higher than 0.1 M, and these indium complexes were not extracted by D2EHPA. The equation for the extraction of indium from sulfuric and nitrate medium can be written as follows:^{28,29)}

$$\begin{split} &mIn^{3+} + (2m+1)(HA)_{2,org} \\ &= In_m A_{2(2m+1)} H_{(m+2),org} + 3mH^+ \end{split} \tag{1}$$

In chloride media the corresponding reaction is

$$mInCl^{2+} + (m+1)(HA)_{2,org}$$

= $In_mCl_mA_{2(m+1)}H_{2,org} + 2mH^+$ (2)

When the concentration of hydrochloric acid is higher than 1M, indium ion can form neutral complexes with chloride ion and these neutral species can be extracted by the following reaction:^{28,29)}

$$InCl3 + (HA)2,org = InCl3·2HAorg$$
 (3)

In the solvent extraction of indium from the leaching solution of ITO, Nikov et al. found that tin was coextracted with indium by D2EHPA and TBP was necessary to separate indium and tin.30) Tomii and Tsuchida mentioned in their patent that a mixture of D2EHPA and TBP had some selectivity for indium over tin.²⁵⁾ Sami et al. reported that D2EHPA could extract both indium and tin from sulfuric acid leaching solution of ITO but indium could be selectively stripped with HCl from the loaded D2EHPA. They did the continuous experiments by using the mixture of D2EHPA and TBP, and reported that only tin was selectively extracted from 1.5M HCl solution by using the mixture of 2 M D2EHPA and 0.8 M of TBP. Thus by separating tin from the hydrochloric acid solution of ITO, indium was recovered. A scheme for the recovery of indium from 1M of H2SO4 containing tin as an impurity by solven extraction is shown in Fig. 1.22)

4.1.1.2. Cyanex272

Cyanex272 has low aqueous solubility, good recycling capacity and miscibility with the commonly used diluents. Bina et al. studied on the use of Cyanex272 for the extraction of indium. They reported that from hydrochloric, nitric and sulfuric acid medium, the extraction of In was quantitative up to 0.1

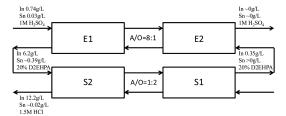


Fig. 1. Suggested flow sheet for solvent extraction recovery of indium from 1 M H2SO4 containing tin as an impurity. Phase ratios are for extraction (E1 and E2) A/O = 8:1 and for stripping (S1 and S2) A/O = 1:2.

M acid and thereafter decreased, except in the case of HCl solution where a slight increase was observed beyond 1 M HCl. Stripping of In from loaded organic phase was possible by 1M HCl. The extracted species have been identified as $In(OH)A_2$ and the extraction reaction can be expressed³¹⁾

$$In(OH)^{2+} + (HA)_{2,org} = In(OH)A_{2,org} + 2H^{+}$$
 (4)

The above equation was obtained from low acidity condition whereas the extraction percentage of In was negligible at high acidity.

4.1.1.3. PC88A

The extraction behavior of indium by PC88A has been investigated by Kang et al. They found that indium was extracted efficiently in an acidity range of 0.1 to 0.5 M. PC88A extracts In, Al, Mo and Fe from the HCl medium, but In could be selectively stripped by 2 M acid solution from the loaded solvent.²⁰⁾

4.1.1.4. Chelating extractants

Alguacil et al. performed solvent extraction experiments of indium by using LIX 973N. LIX 973N is a mixture of 5-dodecyl-salicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime. They reported that LIX 973N can be used as an extractant for indium from sulphate media at moderate acidic pH values and low aqueous ionic strength. The reaction equation of indium extraction by chelating extractants can be described by the following reaction³²⁾

$$In^{3+} + 3HA_{org} = InA_{3,org} + 3H^{+}$$
 (5)

4.1.2. Solvating extractants

TBP, TOPO, and MIBK are solvating extractants which have been frequently used for extraction of several metal ions, including In.^{33,34)} It has been known that indium could be extracted by TBP.³⁵⁻³⁷⁾ In hydrochloric acid medium, indium has a strong tendency to form complexes with chloride ion and thus the distribution coefficient of indium is increased with the increase of HCl concentration.²⁴⁾ The nature of the extracted species was found to be InCl₃·nTBP at HCl concentration below 2M and H(InCl₄) ·nTBP at higher HCl concentrations. The following extraction reaction was proposed³⁶⁾

$$In^{3+} + 3H^{+} + 3CI^{-} + nTBP_{org}$$

= $InCl_{3} \cdot nTBP_{org} + 3H^{+}$ (6)

$$In^{3+} + 4H^{+} + 4CI^{-} + nTBP_{org}$$

= $H(InCl_4) \cdot nTBP_{org} + 3H^{+}$ (7)
where n = 2 or 3.

In the extraction of indium by TOPO from chloride acid medium, the composition of the extracted species was found to be InCl₃·2TOPO and HInCl₄·2TOPO.^{33,35,38,39)}

Although several solvating reagents can be used to extract indium, these reagents have been employed to extract other metal ions. Compared to cationic extractants, the selectivity of solvating extractants for indium over other metal ions is not good and solvating extractants are not used commercially to separate indium.

4.1.3. Basic extractants

In weak to moderately concentrated hydrochloric acid solution, indium exists as ${\rm In}^{3+}$, ${\rm InCl}^{2+}$, ${\rm InCl}^{2+}$, and ${\rm InCl}_3$ and indium can be extracted by cationic or solvating extractants. However, solvent extraction studies on the extraction of In from concentrated chloride solutions by amines suggested that anionic indium complexes, such as to ${\rm InCl}_4^-$, ${\rm InCl}_5^{2-}$, and ${\rm InCl}_6^{3-}$ moieties exist in chloride solution and these species can be well extracted by basic extractants. $^{40-42)}$

Basic extractants are good extractants for recovery of indium. Extractants, such as TOA (tri-n-octylamine),⁴⁰⁻⁴²⁾ Aliquat 336,⁴³⁾ and n-octylaniline⁴⁴⁻⁴⁶⁾ were used for the extraction of In from different types acid medium. In the

solvent extraction of indium from concentrated hydrochloric acid solution by basic extractants, extraction of neutral adduct or exchange of anionic indium species can be occurred depending on the acidity of the aqueous solution⁴¹⁾

$$InCl_3 + R_3NH^+Cl_{org}^- = R_3NH^+InCl_{org}^-$$
 (8)

$$InCl_4^- + R_3NH^+Cl_{org}^- = R_3NH^+InCl_{org}^+ + Cl^-$$
 (9)

4.2. Ion exchange

Ion exchange may be an alternative to solvent extraction processes. The prerequisite for solvent extraction process is that the concentration of the metal in the solutions must be over several hundreds of ppm. Otherwise, its efficiency decreases for the treatment of less concentrated solutions. However, ion exchange has been recognized as an effective method for selective recovery of small amounts of metal ions from solutions.

Marinho et al.⁴⁷⁾ proposed a process by using strong basic anion exchange resins to recover indium, platinum and tin. They reported that the loading percentage of indium was the highest from the solution in the ion exchange by Amberlite IRA–400AR, Amberlite IRA 420, Dowex 1 and Amberjet 4200 CI. Indium was easily eluted from the resin by using 0.1 M EDTA. Indium can be isolated from its eluate by adding 3 mol/L Na₂S at 80°C dropwise and then indium sulfide (In₂S₃) is precipitated as a brown-yellowish solid. The purity of indium is more than 99 wt%.

Fortes et al. 48) investigated the loading of indium onto some ion exchange resins with different organic functional groups. They reported that the chelating resin containing aminophosphonic acid groups - SR950 and the cation exchange resin Amberlite® IR-120P did not show selectivity for indium, while chelating resin containing iminodiacetic acid groups - Ionac® SR-5 provided a similar indium adsorption rate with the resin with diphosphonic acid groups - Ionac® SR-12. However, the former was more selective on indium in the presence of iron and the loading percentage of indium and iron was 40 and 5%, respectively. According to the experimental results, the selection of chelating resin containing iminodiacetic acid groups - Ionac® SR-5 was found to be enough to be used for indium purification from indium sulfate acidic solution.

4.3. Precipitation

Numerous researchers have attempted to separate indium by adjusting pH of the solution since pH is one of the critical parameters. Indium is far more reactive over the wide range of pH in solution compared to tin. Therefore, indium can be successfully recovered from leaching solution of ITO scrap by this method. The EhpH diagram for indium indicates that indium is precipitated to form In_2O_3 as the pH of the solution increases. It is believed that when indium ion is subjected to precipitation by increasing pH of the solution, it will be precipitated as hydrated form of In_2O_3 .

$$2In^{3+} + 3H_2O = In_2O_3 + 6H^+$$
 (10)

Han et al. proposed a method for recovering indium from ITO scrap by chemical precipitation followed by solvent extraction. They reported that in the presence of an oxidant such as sodium nitrite and hydrogen peroxide, tin precipitates completly at pH 3.5. On the other hand, indium does not precipitate easily unless the pH of the solution is raised above 4-5 with an oxidant. They concluded that 99.99% pure indium can be obtained by employing chemical precipitation alone at pH 3-4. After solvent extraction step, the indium purity will be increased to higher than 99.999%. ⁵⁰⁾

Koleini et al. investigated that precipitation of indium could be almost completed at pH 6 with ammonia solution in 90°C, while the recovery of overall iron and zinc was very low at this pH. In addition, they mentioned that ammonia is more effective than sodium and calcium hydroxide in raising the pH of the solution in terms of recovery percentage of indium.⁵¹⁾

Barakat and Jiang et al. proposed phosphide precipitation method to recover indium. The method of Barakat involved precipitation of indium as phosphate by using H₃PO₄ at pH 3.91, converting the phosphate to the oxide by leaching with sodium hydroxide solution.²¹⁾ Jiang et al. found that precipitation percentage of indium with sodium tripolyphosphate (Na₅P₃O₁₀) increased with increasing pH of the solution and most of indium would be precipitated when the pH of the solution exceeded 2.6.⁵²⁾

5. Conclusions

Recycling of indium has increased to the point where indium recycling accounts for a larger portion of the supply of indium than primary refinery production. The greatest portion of secondary resources for indium involves recovery from spent ITO. Based on the literature information, the following separation methods have been investigated and discussed: solvent extraction, ion exchange and precipitation.

Solvent extraction is an efficient operation on separate indium from leaching solutions by using different types of extractants. Among all the cationic extractants, D2EHPA has been used mostly since it has a high loading capacity and good selectivity for indium over many other metals. However, this extractant suffers mainly from difficult stripping and emulsion formation. Solvating extractants also showed a possibility to extract indium. On the other hand, amine extractants can extract indium from the strong hydrochloric acid solution where anionic indium species exist. The main drawback of the solvent extraction process is related to the loss of the extractant resulting from its partial dissolution in the aqueous phase, which may cause environmental hazards and economic limitation.

Compared with solvent extraction, ion exchange is attractive because of its compact process circuit, fast reaction kinetics and high separation factor. Nonetheless, the limitation of this method lies in the facts that ion exchange is only efficient when the concentration of indium is low, because the loading capacity of resins is low. Precipitation also shows a possibility to separate indium from acid solutions. However, this method has been employed to enrich indium from the solution rather than to separate.

감사의 글

본 논문은 환경부 "환경융합신기술개발사업"의 연구비 지원에 의해 수행되었습니다.

References

- 1. Alfantazi, A.M., Moskalyk, R.R., 2003: Processing of indium: a review, Minerals Engineering, 16, pp. 687-694.
- 2. Ullmann, et al., 2001: Ullmann's Encyclopaedia of

- Industrial Chemistry 6th ed, Volume 19 Indium and Indium Compounds, pp. 65-74, Wiley-VCH, Weinheim, Germany.
- Wikipedia, General internet address, General internet address: http://en.wikipedia.org/wiki/Indium (accessed on September 2012).
- Fact sheet: Indium, Polinares working paper n.39, March 2012, pp.1-6. General internet address: http://www.polinares. eu/docs/d2-1/polinares_wp2_annex2_factsheet5_v1_10.pdf (accessed on September 2012).
- Tolcin, A.C., 2012: Mineral Commodity Summaries, U.S.Geological Survey, January 2012, pp. 74-75.
- Micheal, W. G., 2005: Mineral Commodity Summaries, U.S.Geological Survey, January 2005, pp. 80-81.
- Schampera, U.S., Herzig, P.M., Indium: Geology, Mineralogy, and Economics, Springer, Berlin, 2002, p2.
- Li, C.X., Chang, W., Xu, H.S., Deng, Z.G, Liao, J.Q., Li, X.B., Li, M.T., 2010: Kinetics of indium dissolution from sphalerite concentrate in pressure acid leaching, Hydrometallurgy, 105(2010), pp. 172-175.
- Li, S.Q., Tang, M.T., He, J., Yang, S.H., Tang, C.B., Chen, Y.M., 2006: Extraction of indium from indium-zinc concentrates, Trans. Nonferrous Met. SOC. China, 16(2006), pp. 1448-1454.
- Li, C.X., Wei, C., Xu, H.S., Li, M.T., Li, X.B., Deng, Z.G., Fan, G., 2012: Oxidative pressure leaching of sphalerite concentrate with high indium and iron content in sulfuric acid medium, Hydrometallurgy, 102(2010), pp. 91-94.
- Sinclair, W.D., Kooiman, G.J.A., Martin, D.A., Kjarsgaard, I.M., 2006: Geology, geochemistry and mineralogy of indium resources at Mount Pleasant, New Brunswick, Canada. Ore Geology Reviews 28, pp. 123-145.
- Seifert, T., Sandmann, D., 2006: Mineralogy and geochemistry of indium-bearing polymetallic vein-type deposits: implications for host minerals from the Freiberg district, Eastern Erzgebirge, Germany. Ore Geology Reviews 28, pp. 1-31.
- Murao, S., Deb, M., Furuno, M., 2008: Mineralogical evolution of indium in high grade tinpolymetallic hydrothermal veins - a comparative study from Tosham, Haryana state, India and Goka, Naegi district, Japan. Ore Geology Reviews 33, pp. 490-504.
- Cook, N.J., Ciobanu, C.L., Pring, A., Skinner, W., Shimizu, M., Danyushevsky, L., Saini-Eidukat, B., Melcher, F., 2009: Trace and minor elements in sphalerite: a LA-ICPMS study, Geochimica et Cosmochimi ca Acta 73, pp. 4761-4791.
- Goonan, T.G., 2012: Materials flow of indium in the United States in 2008 and 2009: U.S. Geological Survey Circular 1377, 12 p. http://pubs.usgs.gov/circ/1377/ (accessed on September 2012).
- Tolcin, A.C., 2008: Mineral Commodity Summaries, U.S. Geological Survey, January 2008, pp. 80-81.
- Hammarberg, E., Prodi-Schwab, A., Feldmann, C., 2008: Microwave-assisted synthesis of indium tin oxide nanocrystals in polyol media and transparent, conductive layers

- thereof, Thin Solid Films, 516(21), pp. 7437-7442.
- Jeon, M.K., Kang, M., 2008: Synthesis and characterization of indium-tin-oxide particles prepared using sol?gel and solvothermal methods and their conductivities after fixation on polyethyleneterephthalate films, Materials Letters, 62(4-5), pp. 676-682.
- Li, Y.H., Liu, Z.H., Li, Q.H., Liu, Z.Y., Zeng, L., 2011: Recovery of indium from used indium – tin oxide (ITO) targets, Hydrometallurgy, 105, pp. 207-212.
- Kang, H. N., Lee, J.Y., Kim, J.Y., 2011: Recovery of indium from etching waste by solvent extraction and electrolytic refining, Hydrometallurgy, 110(2011), pp. 120-127
- Barakat, M.A., 1998: Recovery of lead, tin and indium from alloy wire scrap, Hydrometallurgy, 49(1998), pp. 63-73
- Sami, V., Don, I., Erkki, P., 2011: Recovery of indium from indium tin oxide by solvent extraction, Hydrometallurgy, 107, pp. 56-61.
- Fortes, M.C.B., Benedetto, J. S., 1998: Technical note separation of indium and iron by solvent extraction, Mincruls Engineering. Vol. II, No. 5, pp. 447-451.
- Paiva, A.P. 2001: Recovery of indium from aqueous solutions by solvent extraction, Separation science and technology, 36(7), pp. 1395-1419.
- Tomii, K., Tsuchida, H., 1981: Solvent extraction recovery process for indium, U.S. Patent 4292284.
- Ke, J., Qiu, R., Chen, C., 1984: Recover y of metal values from copper smelter flue dust, Hydrometallurgy, 12, pp. 217-224.
- Fossi, P., Sambarino, E., 1983: Process for the Recovery of Indium. U.S. Patent 4372922.
- Sato, T., Sato, K., 1992: Liquid-liquidextraction of indium (III) from aqueousacid solutions by acid organophosphorus compounds, Hydrometallurgy, 30(1992), pp. 367-383.
- Sato, T., 1975: The extraction of indium(III), lanthanum(III) and bismuth(III) from sulphuric acid solutions by di-(2-ethylhexyl)-phosphoric acid, J. Inorg. Nucl. Chem., 37, pp. 1485-1488.
- Nikov, B., Stojanov, P., Stojadinovic, T., 1994: Production of indium from imperial smelting process residues. Proceedings of Hydrometallurgy '94. Chapman and Hall, Cambridge, pp. 1153-1164.
- Bina, G., Niti, M., Indu, S., 2007: Separations and recovery of indium and gallium using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), Separation and Purification Technology, 57(2007), pp. 294-303.
- Alguacil, F.J., 1999: Solvent extraction of indium(III) by LIX 973N, Hydrometallurgy, 51, pp. 97-102.
- Navratil, O., Meindl, J., Kos, J., 1981: Extraction of indium(III) and antimony(III) from hydrochloric acid solutions by means of some neutral organophosphorus reagents, Coll. Czech. Chem. Commun., 46, pp. 1906-1912.
- Seo, J.S., Ahn, J.W., Lee, M.S., 2010: Solvent extraction of Sn(IV) from Hydrochloric Acid Solution by Tri-Butyl Phosphate(TBP), J. of Korean Inst. of Resources

- Recycling, 19, pp. 45-51.
- 35. Sato, T., Yasumura, H., Mizuno, Y., T. Nishimura, T, 1996: Solvent extraction of trivalent gallium, indium and thallium from hydrochloric acid solutions by TOPO and TB, Proceedings of the International Solvent Extraction Conference, ISEC '96, Shallcross, D. C., Paimin, R., Prvcic, L. M. (Eds.), Univ. Melbourne, Vol. 1, pp. 559-564.
- Golinski, M., 1971: Extraction of tin and indium with tributylphosphate from hydrochloric acid solutions. Proceedings of the International Solvent Extraction Conference, ISEC'71, London, pp. 603-615.
- De, A. K., Sen, A. K., 1967: Solvent extraction and separation of gallium(III), indium(III) and thallium(III) with tributylphosphate, Talanta, 14, pp. 629-635.
- Bao, C.; Li, D.; Chou, J. 1987: Extraction of indium with trioctylphosphine oxide (TOPO). Wuji Huaxue, 1987, 3(1), pp. 16-21.
- Hasegawa, Y.; Shimada, T., 1980: Niitsu, M. Solvent extraction of 3B group metal ions from hydrochloric acid with trioctylphosphine oxide. J. Inorg. Nucl. Chem., 42, pp. 1487-1489.
- Aguilar, M., 1975: Extraction with long-chain amines. XX. Extraction of indium(III) chloride by tri-n-octylammonium chloride dissolved in benzene, Chem. Scripta, 1975 8(1), pp. 37-42.
- Fischer, C., Wagner, H., Bagreev, V. V., Stojanov, E. S, 1977: On the extraction of In(III) with tri-n-octylamine from HCl solutions, J. Inorg. Nucl. Chem., 1977, 39, pp. 513-517.
- Nelson, A.D., Fasching, J.L., Mcdonald, R.L., 1965: Extraction of Fe(III) and In(III) from aqueous HCl by trin-octylamine in nitrobenzene, J. Inorg. Nucl. Chem., 1965, 27, pp. 439-447.
- 43. Karve, Ms. M. A.; Khopkar, S. M., 1992: Solvent extraction

- separation of indium with quaternary ammonium anion exchanger Aliquat 336S from an ascorbate solution, Analytical Science, v. 8, pp. 77-80.
- Kuchekar, S. R., Chavan, M. B., 1988: Separation of gallium, indium and thallium by extraction with noctylaniline in chloroform, Talanta, v. 35, 5, pp. 357-360.
- Mahamuni, S.V., Kolekar, S.S., Wadgaonkar, P.P., Anuse M.A., 2009: Solvent Extraction of Trivalent Indium from Succinate Solution by 2-Octylaminopyridine in Chloroform, J. Iran. Chem. Soc., Vol. 6, No. 1, pp. 200-212.
- Shilmkar, T.N., Kolekar, S.S., Wadgaonkar, P.P., 2008: Rapid extraction and separation of indium(III) with a high molecular weight amine, Indian Journal of Chemical Technology Vol. 15, May 2008, pp. 291-297.
- 47. Marinho, R.S., Silva, C.N., Afonso, J.C., Cunha, J.W., 2011: Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins, Journal of Hazardous Materials, 192 (2011), pp. 1155-1160.
- Fortes, M.C.B., Martins, A.H., Benedetto, J.S., 2003: Indium adsorption onto ion exchange polymeric resins, Minerals Engineering, 16(2003), pp. 659-663.
- Chung, Y.H., Lee, C.W., 2012: Electrochemical behaviors of Indium, Journal of Electrochemical Science and Technology, Vol. 3, pp. 1-13.
- Han, K.N., Siddartha, K., Park, K.W., Kang, H.M., 2002: Recovery of Indium from Indium/Tin Oxides Scrap by Chemical Precipitation, Geosystem Eng., 5(4), pp. 93-98.
- Koleini, S.M., Mehrpouya, H., Saberyan, K., Abdolahi, M., 2010: Extraction of indium from zinc plant residues, Minerals Engineering, 23(2010), pp. 51-53.
- 52. Jiang, J.B., Liang, D.Q., Zhong, Q.D., 2011: Precipitation of indium using sodium tripolyphosphat, Hydrometallurgy, 106(2011), pp. 165-169.





- 중국 연태대학교 응용화학 학사
- 현재 목포대학교 신소재공학과 석사 과정

李 晚 承

- 현재 목포대학교 신소재공학과 교수
- 당 학회지 제11권 1호 참조