

Recovery of Indium from Scrap

†Kenneth N. Han

*Department of Materials and Metallurgical Engineering South Dakota School of
Mines and Technology Rapid City, SD 57701-3995*

ABSTRACT

Indium frequently associated with the semiconductor industry is becoming an important metal element widely used in industry. In this paper, its properties especially in relation to its recovery from scrap are reviewed and discussed. Also presented in this paper is how best indium can be recovered by the hydrometallurgical means.

Key words: Semiconductor industry, Oxidation/Reduction, Extraction from scrap, Hydrometallurgical means

1. Introduction

The element indium was originated from the brilliant indigo line in its spectrum. The atomic weight of indium is 114.82 and its atomic number is 49. Indium has very interesting characteristics where the melting point is relatively low but the boiling point is very high. Its melting and boiling points are 156.61°C and 2080°C, respectively. It has found application in making low-melting alloys; an alloy of 24% indium -76% gallium (melting point: 29.7°C) is liquid at room temperature, 25°C. Its specific gravity is 7.31.

Indium is most frequently associated in nature with zinc-bearing minerals. It is as abundant as silver. It is a very soft, silvery-white metal with a brilliant luster. It wets glass and also does gallium. It is used in making bearing alloys, germanium transistors, rectifiers, thermistors, and photo-conductors. It can be plated onto metal and evaporated onto glass, forming a mirror as good as that made with silver but with more resistance to atmospheric corrosion.

In this discussion, the way in which indium can be recovered hydrometallurgically from scrap will be presented and discussed.

2. U.S. Production¹⁾

Two companies, one each in New York and Rhode Island were the major producers of indium metal in 2000 by upgrading of lower grade imported indium metal. Thin-film coatings, which are used in applications such as liquid crystal displays (LCD's) and electro-luminescent lamps, continued to be the largest end use. Indium semiconductor compounds were used in infrared detectors, high-speed transistors, and high efficiency photo-voltaic devices.

3. Use of Indium

The use of indium is widely spread: 49% of indium is used in coatings, 33% in solvers and alloys, 14% in electrical components and semiconductors and 4% in research and others.

The estimated value of primary indium metal consumed in 2000, based upon the annual average price, was more than \$10 million. The following table lists amounts of indium imported to the US for the period of 1996-2000 along with internal consumption and prices over the same period.

	1996	1997	1998	1999	2000
Imports for consumption (mtons)	33.2	85.5	75	77	70
Consumption	45	50	50	52	55
Price, \$/kg (99.97%)	370	309	296	303	188

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† E-mail: khan@taz.sdsmt.edu

4. Import Sources (96-99)

As indicated above, indium is primarily imported to the US. Its importation countries include Canada -45%; China -22%; Russia -12%; France -9% and other -12%. Table 1 lists world refinery production of indium and its reserves.

It is apparent in this table that Canada, China and Russia have relatively large reserves of this important element and China, France, Canada and Belgium are the major indium producing countries.

Full understanding of the physico-chemical properties of indium and its associated metals in case of scrap is essential in recovering this metal from various sources.

Table 1. World Refinery Production, Reserves (metric tons)

	Refinery production		Reserves
	1999	2000	
United States	-	-	300
Belgium	35	35	-
Canada	35	35	700
China	40	40	400
France	43	43	-
Japan	25	30	100
Peru	4	4	100
Russia	15	15	200
Other countries	20	20	800
World total	215	220	2,600

5. Oxidation/Reduction

Indium is rather reactive in acid and readily soluble in nitric acid. It obviously requires an oxidant when dissolves in acidic medium. Its oxidation/reduction potential is given in the following table along with other metals for comparison. It should be noted that indium forms three different valences, namely In^+ , In^{+2} and In^{+3} .

As noted in this table, indium is relatively reactive but it gives three different valences, namely In^+ , In^{+2} and In^{+3} whose emf values are quite different. The following figure shows the Eh-pH diagram for the $\text{In}/\text{H}_2\text{O}$ system at 25°C .²⁾ Eh-pH diagrams for other relevant metals which appear closely with indium are

Table 2. Emf values for various metals in solution

Metals	E° Volts (SHE)
Cu/Cu^{++}	0.337
H_2/H^+	0.0
Fe/Fe^{++}	-0.036
Pb/Pb^{++}	-0.126
Sn/Sn^{++}	-0.136
In/In^+	-0.139
Ni/Ni^{++}	-0.250
In/In^{++}	-0.269
Co/Co^{++}	-0.277
$\text{In}/\text{In}^{+++}$	-0.342
Cd/Cd^{++}	-0.403
$\text{Fe}/\text{Fe}^{+++}$	-0.440
Zn/Zn^{++}	-0.763

available in literature.² As can be seen in this diagram, indium is likely to be dissolved in water to produce In^{+3} in normal conditions. It implies that when metals such as copper, iron (ferrous) and lead are present in the solution along with indium metal powder, these metals are likely to cement out from the solution. On the other hand, when zinc metal powder is added into a system containing indium ions, indium will be cemented out. As a matter of fact, indium is often recovered from the solution by cementation with zinc powder.

When indium is placed in water, there are five different indium bearing species in addition three indium ions can be present in solution. As shown in the indium-hydroxide distribution diagram,^{3,4)} these five indium bearing metal species include, $\text{In}(\text{OH})^{+2}$, $\text{In}(\text{OH})_2^+$, $\text{In}(\text{OH})_3$, $\text{In}(\text{OH})_4^-$ and $\text{In}_3(\text{OH})_4^{+5}$ (Fig. 2). Relevant equilibrium equations are given below:

$$\frac{\{\text{In}(\text{OH})^{+2}\}}{\{\text{In}^{+3}\}\{\text{OH}^-\}} = 10^{10} \quad (1)$$

$$\frac{\{\text{In}(\text{OH})_2^+\}}{\{\text{In}^{+3}\}\{\text{OH}^-\}^2} = 1.58 \times 10^{20} \quad (2)$$

$$\frac{\{\text{In}(\text{OH})_3\}}{\{\text{In}^{+3}\}\{\text{OH}^-\}^3} = 3.98 \times 10^{33} \quad (3)$$

Table 3. Complexing behavior of indium with various complexing anions.^{3,4)}

In-Thiocyanate System	
$\text{In}^{+3} + \text{CNS}^- = \text{In}(\text{CNS})^{+2}$	$K_e = 2.19 \times 10^2$
$\text{In}^{+3} + 2\text{CNS}^- = \text{In}(\text{CNS})_2^+$	$K_e = 3.39 \times 10^3$
$\text{In}^{+3} + 3\text{CNS}^- = \text{In}(\text{CNS})_3$	$K_e = 3.98 \times 10^4$
In-Br-System	
$\text{In}^{+3} + \text{Br}^- = \text{InBr}^{+2}$	$K_e = 1.2 \times 10^2$
$\text{In}^{+3} + 2\text{Br}^- = \text{InBr}_2^+$	$K_e = 2.51 \times 10^3$
$\text{In}^{+3} + 3\text{Br}^- = \text{InBr}_3$	$K_e = 10^4$
$\text{In}^{+3} + 4\text{Br}^- = \text{InBr}_4^-$	$K_e = 6.31 \times 10^4$
In-I-System	
$\text{In}^{+3} + \text{I}^- = \text{InI}^{+2}$	$K_e = 43.7$
$\text{In}^{+3} + 2 \text{I}^- = \text{InI}_2^+$	$K_e = 3.63 \times 10^2$
In- PO_4^{-3} System	
$\text{In}^{+3} + \text{H}_2\text{PO}_4^- = \text{InH}_2\text{PO}_4^{+2}$	$K_e = 26.9$
$\text{InPO}_4 = \text{In}^{+3} + \text{PO}_4^{-3}$	$K_{sp} = 2.34 \times 10^{-22}$
In- S^{-2} System	
$(\text{In}_2\text{S}_3)_s = 2\text{In}^{+3} + 3\text{S}^{=}$	$K_{sp} = 3.98 \times 10^{-70}$

$$\frac{\{\text{In}_3(\text{OH}^-)_4^{+5}\}}{\{\text{In}^{+3}\}^3 \{\text{OH}^-\}^4} = 1.58 \times 10^{50} \quad (4)$$

Fig. 2. was drawn based on these four equations. However, it should be noted that In^{+3} can be precipitated as $\text{In}(\text{OH})_3$ which is determined by Eq. 5.

$$\{\text{In}^{+3}\} \{\text{OH}^-\}^3 = K_{sp} = 1.26 \times 10^{-37} \quad (5)$$

It was found that at pH above 4, most dissolved indium-bearing species will result in precipitation.

At pH less than 3, In^{+3} is obviously the dominant species but at pH greater than 6, $\text{In}(\text{OH})_3$ is dominant. Such behavior can be used in extraction and separation of indium from various sources and dissolved species.

Table 3 summarizes some complexing behavior of indium with various anions.

As can be seen in this table, indium can be extracted in bromine or iodine as an oxidant since it forms stable complexes with these ions. It is also interesting to note that indium can easily be precipitated in solution with hydrogen bi-sulfide or sodium phosphate since the solubility of these indium complexes are shown to be

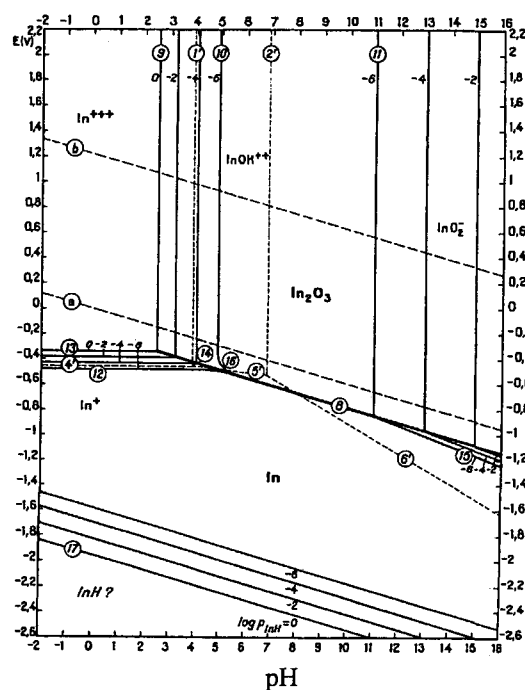


Fig. 1. Eh-pH diagram for the In- H_2O system at 25°C.

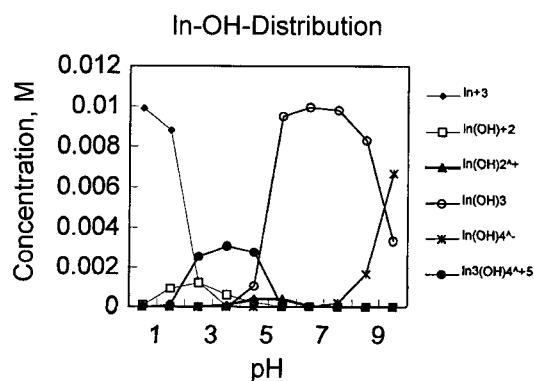


Fig. 2. Distribution of In^{+3} and its compounds as a function of pH at 25°C. The total concentration of dissolved indium is assumed to be 0.01 M.

very stable.

6. Extraction of Indium from Scrap

As seen in the Eh-pH diagram, indium is soluble in acidic solutions and also slightly soluble in alkaline solutions to form InO_2^- . More precisely, in alkaline solutions, indium becomes $\text{In}(\text{OH})_3$ and $\text{In}(\text{OH})_4^-$ as

indicated in Fig. 2. Therefore, the effective recovery of indium metal by hydrometallurgical route is not how to dissolve it but how best it can be separated from surrounding metals. For example, indium is often associated with lead and tin in alloy wire scrap.

When a metal is subject to extraction from such an alloy system, there are in general two approaches taken. One is to try to extract the desired metal selectively leaving undesired elements intact with the substrate. Ammonia leaching of silver from silver-iron system would be a good example. Here silver will be soluble in ammoniacal solutions but iron is not and hence, a selective leaching of silver is possible. However, what is frequently practiced in hydrometallurgical extraction schemes is to extract more than one metal including the desired metal and the desired metal is then recovered from the leach liquor selectively.

There are many different ways to selectively separate a metal from others. These may include selective precipitation, ion exchange, solvent extraction and electro-refining. The final design of the separation strategy is impossible without the full knowledge of the presence of kinds of metal ions present in the system.

In the case of extraction of indium from wire scrap alloys consisting of typically 42% In, 9% Pb and 50% Sn.⁵⁾ This alloy is usually dissolved completely in acidic solutions. Eh-pH diagrams of these three metals clearly show that this would be the case and it has been shown that this is easily done. Usually a mixture of mild HCl and HNO₃ solution is used for this purpose. When complete dissolution occurs, lead is usually removed first by PbCl₂ precipitation at about 10°C. About 70~80% of lead in the solution is removed by this process. It is also noted that lead can be removed by forming lead carbonate since lead carbonate is very insoluble.

Sodium hydroxide is added to make the pH of the solution at about 2 to precipitate SnO₂·xH₂O. By this precipitation process, about 99.5% of Sn is recovered. As noted in the In-OH distribution diagram (Fig. 2), indium is unlikely to be precipitated by OH⁻ as long as pH of the solution is below 3~4.

Fig. 3. shows the distribution of tin-bearing species as a function of pH. In this diagram, Sn⁺², Sn(OH)⁺, Sn₂(OH)₂, and Sn₃(OH)₄⁺² are considered.

It should be noted that the K_{sp} value of tin oxide is

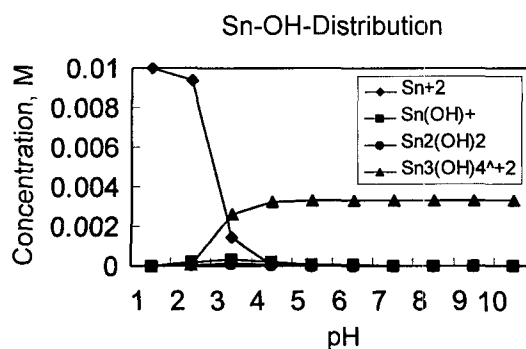


Fig. 3. Distribution of Sn⁺² and its compounds as a function of pH at 25°C. The total concentration of dissolved indium is assumed to be 0.01 M.

6.31×10^{-27} and at pH greater than 2~3, most of tin-bearing species will be precipitated.

The solution containing all of indium, remaining lead and 0.5% tin is then subject to cementation with indium powder. Sponge lead is produced which is then subject to electrolysis to obtain pure lead. The solution concentrated with indium is then subject to cementation with zinc powder to produce sponge indium which is subject to electrolysis to produce pure indium ingot. Phosphoric acid and sodium hydroxide are added into the remaining solution to precipitate pure InPO₄. As shown in Table 3, InPO₄ is very insoluble. The precipitate is then subject to conversion to In(OH)₃ with concentrated NaOH, which is then decomposed to In₂O₃ by thermal decomposition. This oxide is then subject to reduction to obtain metallic indium.

This process is summarized in the following chart shown in Fig. 4.

Chelyabinsk Electrolytic Zinc Plant in Russia recovers indium (III) from a sulfuric acid solution (200 g/l) by cementation with aluminum.⁶⁾ Such produced spongy indium is then subjected to melting in caustic soda bath where nearly 25% of indium is lost. Maslii *et al.*,⁶⁾ have shown that indium (III) from sulfuric acid leach liquor can be recovered by electro-deposition at 2.7~3.5 Volts with 62~250 A m⁻² current density with 61~94% current efficiency.⁶⁾

Indium is also recovered from solution by solvent extraction. Solvent extraction of In (III) by LIX 973N was made from sulfate system.⁷⁾ Another study is concerned with solvent extraction of In(III) by

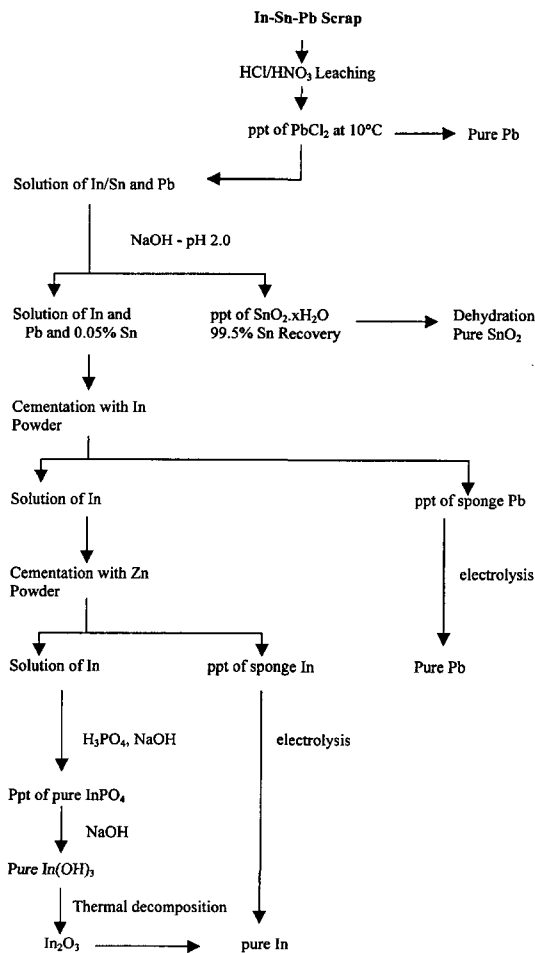


Fig. 4. Flowchart depicting the process of In-scrap to produce various metals.

organophosphorus compounds.⁸⁾ In this study, indium dissolved in sulfuric, hydrochloric and nitric acid was treated with D2EHPA (diethylhexyl-phosphoric acid and EHEHPA (2-ethylhexyl 2-ethylhexyl-phosphonic acid) and it was found that D2EHPA was more effective in pulling indium than EHEHPA. The efficiency of extraction of indium was also found in order of $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$. In yet another study, indium was separated from gallium by D2EHPA.⁹⁾

7. Concluding Remarks

Indium is becoming an important metal and its recovery from secondary sources is very relevant in

countries like Korea since its primary source is practically non existence. The literature information reveals that indium is easily soluble in acids such as hydrochloric and nitric acids. It also shows that it forms stable complexes with hydroxide, bromide, iodide and thiocyanate indicating its dissolution in these media being worth investigating.

The key to the effective recovery of indium from scrap is not how best to dissolve it hydrometallurgically but how best to separate from the leach liquor after dissolution. In order to achieve this objective, it is most critical to understand the physico-chemical properties of the system as a whole including those of associated metals already dissolved in solution.

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Kenneth N. Han

- 1961년 서울대학교 학사
- 1963년 서울대학교 석사
- 1967년 Univ. of Illinois, Urbana (Surface chemistry of clay minerals) 석사
- 1971년 Univ. of California, Berkeley (hydrometallurgy & surface chem) 박사
- 1971~80년 Lecturer, Monash Univ., Melbourne, Australia
- 1981~현재 South Dakota School of Mines and Technology, Professor