An Investigation into the Recovery of Indium from Fume Residue

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AN INVESTIGATION INTO THE RECOVERY OF INDIUM FROM FUME RESIDUE

by

Emery J. Turner

A Thesis
Submitted to the Department of Metallurgy in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY 1, 1942
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# TABLE OF CONTENTS

**General**

- Introduction --------------------------------------------------- 1
- Uses of indium -------------------------------------------------- 2
- Properties of indium ------------------------------------------ 4

**Extraction of Indium**

- Introduction --------------------------------------------------- 6
- Flowsheet proposed by J. Ivan Hall -------------------------- 7
- Flowsheet proposed by Archibald Duncan -------------------- 8
- Flowsheet of method attempted ----------------------------- 9
- Analysis of fume residue ------------------------------------ 10
- Discussion of proposed flowsheet --------------------------- 11

**Conclusions** --------------------------------------------------- 18

**Acknowledgements** --------------------------------------------- 19

**Bibliography** --------------------------------------------------- 20
EXTRACTION OF INDIUM FROM GREAT FALLS FUME RESIDUE

Introduction

As recently as 1924, several months were required to produce a single gram of indium. Consequently, the industrial history of the metal is extremely short. In view of the unique properties that indium has demonstrated in this short period, it is probable that indium is still in its early stage of development. However, the commercial applications of the metal are well established and indium is now produced on a commercial scale. It is obtainable as the metal or in solution for electroplating.

The above notwithstanding, Indium is one of the rarest of the elements. J. H. L. Vogt, F. W. Clarke and H. S. Washington estimate that the ten mile crust, the hydrosphere and the lithosphere contain 0.00000000X per cent. Similarly, the content of gold is estimated to be 0.000000X per cent. Indium has been detected in the atmosphere of the sun.

The element was discovered in 1863 by F. Reich and T. Richter during a spectrographic examination of zinc ores from a Freilburg mine. They noticed a new indigo-blue line in the spectrum at 4511.5 Å and hence called the element indium because of this characteristic indigo-blue color. Since then, indium has been found to occur in
zinc blends, siderite, manganese ores, tin ores, smithsonite, calamine and wolframite of Germany, Bohemia, Sardinia and America.

Because of the limited quantities available and the resulting high cost, indium was only a laboratory curiosity until 1924 when Dr. Wm. S. Murray discovered and proved the value of indium in stabilizing non-ferrous metals. The metal has found its chief industrial utility through its ability to confer increased hardness, strength, and corrosion resistance by alloying with other metals. In this form, indium has had wide acceptance in the internal combustion engines in aviation, automotive and diesel fields because of its efficiency in protecting surfaces against corrosion caused by acids in lubricating oils. It has been used for some time in dental alloys. At present, some of the most promising applications of indium appear to lie in the plating field, both for decorative and functional designs. Indium alloy coatings are easily polished and burnished. The relatively soft alloy coating gives a very good surface with high reflectivity and pleasing color. Indium has been used in medicine and this field is expected to expand. Recently it has been discovered that the use of indium in brazing materials gives these materials excellent "wetting" properties. Because of the low melting point of indium, it can be alloyed with
the usual copper base brazing materials and a very wide range in melting points of brazing materials can easily be made.

Indium is being produced in substantial quantities from domestic sources, both in electrolytic and commercial grades, and various salts of the metal are also available. Patented processes for production and uses have been developed.
Properties of Indium

Indium is a white metal, softer than lead, easily malleable, ductile, crystalline and diamagnetic. It is stable at low temperatures but when heated it burns with a blue flame—producing \( \text{In}_2\text{O}_3 \). It unites directly with the halogens and sulphur and dissolves in mineral acids. Chemically, indium resembles zinc in some respects and aluminum and iron in others. In the usual system of qualitative separations, it is classified with iron and aluminum. Indium salts are hydrolized to a very great extent. Indium has a tendency to form basic salts which are sparingly soluble in water. Basic salts of indium are known to exist with the chlorides, nitrates, and sulphates. In its stable compounds it is trivalent and its sulfate forms alums with monovalent metal sulfates. Indium also acts as a bivalent element, and some monovalent compounds have been reported. Indium hydroxide is insoluble in \( \text{NH}_4\text{OH} \) but is soluble in cold \( \text{NaOH} \) and insoluble in hot \( \text{NaOH} \).

The physical properties of indium are as follows:

- Atomic weight: 114.76
- Atomic number: 49
- Valence: Commonly 3; also 2 and 1.
- Melting point: 155°C
- Boiling point: 1450°C
- Specific gravity: 7.31
Specific heat \( (1) \) joules/gram atom -- 27.3

Electrical resistivity, ohm-cm \( (1) \)
\[
\begin{align*}
\text{at } 20^\circ C & : -9 \times 10^{-6} \\
\text{at } 155^\circ C & : -29 \times 10^{-6}
\end{align*}
\]

Thermal expansion \( (1) \)
\[
\frac{1}{L} \frac{dL}{dt} \text{ at } 20^\circ C : -33 \times 10^{-6}
\]

Hardness, Brinell \( (1) \) -- 1

Tensile strength \( (4) \) (psi) \( (1) \) -- 15980

Plasticity number \( (2) \) \( (1) \) -- 1.28

Heat of combustion \( (2) \)
Cal. per equivalent of In -- 37,502

Crystalline structure \( (1) \)
Face centered tetragonal
\[
\begin{align*}
a_0 & : 4.583 \text{ \AA} \\
c_0 & : 4.936 \text{ \AA}
\end{align*}
\]

Single electrode potential \( (5) \)
In In --- 0.38 volts
(Between cadmium and thallium in the electromotive series.)
EXTRACTION OF INDIUM

Introduction

Three former students of the Montana School of Mines, J. Ivan Hall, Archibald Duncan, and Harold L. Tanner have worked on the problem of extracting indium from the flue dust of the Great Falls plant of the Anaconda Copper Mining Company. Hall and Duncan succeeded in developing methods of extraction of indium as shown by the flowsheets to follow. Tanner worked on the method developed by Duncan and found it successful up to the point of electrolysis but could not successfully deposit indium electrolytically as proposed by Duncan. Moreover, recovery by this method was relatively low—42.9 per cent when leached at room temperature and 78.6 per cent when the leach was boiled for three hours.

There are several objections to Hall's procedure also. The first objection is the time required and the difficulty to completely precipitate arsenic and antimony with H₂S. Secondly, it is difficult to determine when a slight excess of zinc dust has been added. It is often necessary to repeat the final purification several times to purify the indium compound.

Due to the above objections and also the number of steps necessary in either case as shown by the flowsheets, it was hoped that a separation could be effected by the fact that indium hydroxide is insoluble in NH₄OH, soluble in cold NaOH but insoluble in hot NaOH.
The diagram outlines a process for the extraction of indium, as proposed by J. Ivan Hall. The process begins with flue dust, which is dissolved in 6N HCl (heat for one hour) and then cooled and filtered. Insoluble PbCl₂ and chlorides of As, Sb, Zn, In, Cu, and Pb are separated.

Saturated with H₂S and filtered, the solution contains chlorides of In, Sb, Cu, Fe, Pb. Sulphides of As, Sb, Cu are boil to expell H₂S.

Add zinc dust, and discard Zn, Cu, Sb, Pb, In, Fe. Dissolve in HNO₃, add NH₄OH in excess and boil.

Zn(NH₃)₄(NO₃)₂, Cu(NH₃)₄(NO₃)₂ ppt. of In, Sb, Fe, Pb. Discard. Dissolve in HCl, saturate with H₂S. FeCl₂.

In₂S₃ (yellow) dissolved in HNO₃, add NH₄OH in excess, boil.


The diagram illustrates the flow and separation of elements throughout the extraction process.
FLOW SHEET FOR THE RECOVERY OF INDIUM FROM ZINC FLUE DUST
PROPOSED BY ARCHIBALD DUNCAN

Flue dust
leached with 65% HCO\textsubscript{2}H\textsubscript{3}O\textsubscript{2}

Insol. containing small % indium (discarded)
Sol'n containing In, Zn, Cu, Fe as acetates
Excess NH\textsubscript{4}OH added and sol'n heated

Ppt. contains Fe(OH)\textsubscript{3}, In(OH)\textsubscript{3}
Sol'n contains Cu(NH\textsubscript{3})\textsubscript{4}(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}

HCl added forming FeCl\textsubscript{3} and InCl\textsubscript{3}

NH\textsubscript{4}OH added until ppt just forms then made acid with
HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} forming iron and
indium acetates

H\textsubscript{2}S passed in

ppt. contains In\textsubscript{2}S\textsubscript{3}
Sol'n contains Fe(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}

HNO\textsubscript{3} added

sulphur (discarded)

ppt. contains In(OH)\textsubscript{3} and any Fe(OH)\textsubscript{3}

HCl to dissolve

NH\textsubscript{4}OH until neutral

HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} until ppt. dissolves

H\textsubscript{2}S passed in

ppt. of In\textsubscript{2}S\textsubscript{3} (pure)
Sol'n contains any Fe(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}

sulphur discarded

NH\textsubscript{4}OH

ppt. of pure In(OH)\textsubscript{3}
Sol'n discarded

ppt. dissolved in HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2}
to electrolysis
FLOWSHEET OF METHOD ATTEMPTED TO RECOVER INDIUM

Fume residue
  ↓
Dissolve in 6N HCl (boil)
  ↓
Cool and filter
  ↓
Chlorides of Zn, Cu, As, Sb, Pb, Fe, In
  ↓
NH₄OH
  ↓
Ammonical sol’n contains Zn, Cu, As, Sb
  ↓
Ppt. contains Fe, In, As, Sb
  ↓
HCl
  ↓
NaOH
  ↓
Solution of sodium indiumate (boil)
  ↓
Sol’n NaOH
  ↓
Ppt In(OH)₃
  ↓
Repeat to purify
  ↓
to electrolysis
This work was based on the assumption that the material used was approximately the same composition as that used by Dr. Peretti. As no quantitative work was done, the approximate ratios of indium to the various impurities was thought to be sufficient.

The analysis of the material used by Dr. Peretti is as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>9.35%</td>
</tr>
<tr>
<td>Antimony</td>
<td>1.50%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>10.05%</td>
</tr>
<tr>
<td>Copper</td>
<td>8.60%</td>
</tr>
<tr>
<td>Indium</td>
<td>1.00%</td>
</tr>
<tr>
<td>Iron</td>
<td>16.50%</td>
</tr>
<tr>
<td>Lead</td>
<td>0.92%</td>
</tr>
<tr>
<td>Silica</td>
<td>10.15%</td>
</tr>
<tr>
<td>Sulphur</td>
<td>5.58%</td>
</tr>
<tr>
<td>Zinc</td>
<td>14.54%</td>
</tr>
</tbody>
</table>
Discussion of proposed flowsheet

As previously stated the scheme for the removal of impurities from the fume residue depended on the fact that indium hydroxide is insoluble in ammonium hydroxide, soluble in cold sodium hydroxide but insoluble in hot sodium hydroxide. This scheme produced indium as expected but the product was relatively impure and had to be purified by sulphide precipitation because it contained arsenic, copper, zinc and lead in appreciable quantities. The recovery was not good and very inconsistent.

One of the main objections to the method is that it depends primarily on the purification by hydroxide precipitation. This caused the separations to be imperfect because heavy hydroxide precipitates tend to drag out elements in solution and hence clean separations could not be made nor could a relatively complete recovery be realized. The difficulty of filtering hydroxides is also a major problem because of the time element.

The plan worked on was as follows: The fume residue was first digested in 6N HCl -- approximately 100 grams of dust to 500 cc. of acid -- by boiling for a half an hour and then allowed to cool so as to precipitate most of the lead as a chloride. The solution was filtered and the residue discarded. One solution was allowed to stand unfiltered two days. A spectrographic analysis was made of this particular residue and found to contain more indium than the original dust which was possibly due to the tend-
ency of indium to form slightly soluble basic salts. Because the material was a fume, the particles were fine and this filtering was very slow. A precipitate formed on standing after filtering probably containing a basic salt of indium, the oxochlorides of arsenic and antimony, and lead chloride because of incomplete precipitation. One test was made and the above mixture was filtered hot but the large amount of PbCl₂ formed made it difficult to determine when complete solution was obtained on a following step and consequently an excess of acid was necessary.

The filtrate was then neutralized with an excess of NH₄OH with the hope of eliminating all of the impurities except iron and the arsenic and antimony taken out of solution by ferric hydroxide. The solution should contain Zn(NH₃)₄Cl₂; Cu(NH₃)₄Cl₂; (NH₄)₃AsO₄; and (NH₄)₃SbO₄. The residue should be indium and ferric hydroxides and the arsenic and antimony taken down with the ferric hydroxide. The precipitate should be washed as free from NH₄OH as possible and no odor of ammonia should be evident. Because of the large amount of zinc, it was difficult to keep the solution ammonical—that is to let it stand until equilibrium is reached. Indium hydroxide is soluble to some extent in NH₄OH and so, because of the small quantity of indium, it did not seem advisable to allow the precipitate to stand for any length of time in a strongly ammonical solution. Accordingly, when an excess of NH₄OH was obtained, the mixture was allowed to stand only a few minutes and filtered.
In spite of the fact that the solution was ammonical, due to the slow filtering enough Zn(OH)$_2$ was dissolved while on the filter to neutralize the excess NH$_4$OH so that Zn(OH)$_2$ would precipitate when a small amount of water was added to the filtrate. The above fact would indicate that there is considerable zinc in the precipitate. But because Zn(OH)$_2$ is soluble in hot NaOH, this was thought not to be a problem. Considerable zinc was shown to be present in a later dissolution of the residue by neutralizing the hot solution containing sodium zincate with acid. If the amount of zinc as sodium zincate is too large, zinc hydroxide will precipitate on boiling.

The next step is to dissolve the iron and indium hydroxides in a minimum of HCl. The possibility that indium hydroxide might be dissolved directly from the precipitate was investigated but this did not work at all. After the hydroxides were dissolved, they were re-precipitated with cold NaOH. The scheme depends on the fact that In(OH)$_3$ is soluble in cold NaOH but insoluble in hot NaOH. Consequently, even though the bath was water cooled and air agitated, the heat of reaction was great and this probably resulted in the formation of some In(OH)$_3$ instead of the sodium indiumate as desired. As stated above, the NaOH does not seem to dissolve In(OH)$_3$ when precipitated with iron, possibly because of common ion effect of (OH)$^-$. which tends to make the reaction go in the direction of the precipitate. It was also hoped
that the solution would be purified from the arsenic previously precipitated with the ferric hydroxide by this iron hydroxide precipitation. However, arsenic was shown to still be in the solution by the characteristic arsenic odor noted on boiling and arsenic was found in the final product. This precipitate, Fe(OH)₃, was extremely fine and difficult to filter, possibly due to the fact that NaOH is a dispersant. Not only was it difficult to filter but colloidal Fe(OH)₃ would come through the filter paper and be precipitated with the indium hydroxide. It was thought that some flocculator such as lime could be used to counteract this objection. Because of the low recovery, consideration was given to the fact that indium might be removed by iron hydroxide similar to the removal of germanium in zinc electrolyte purification but this possibility was discounted because indium is recovered from spent zinc electrolyte.(8)

The low recovery seems to be due to the fact that indium hydroxide is soluble in a large excess of sodium hydroxide even when hot and consequently would be lost in that operation. There seems to be a critical concentration of sodium hydroxide upon which the scheme depends. This fact was further evidenced by the relatively poor and very inconsistent results obtained. One time a large precipitate was obtained but would grade down to nothing on other occasions. For this reason, I repeated
the process and, by hit and miss, hoped to determine the right concentration of sodium hydroxide. This critical concentration could probably be easily determined if there were a quantity of indium hydroxide of known purity to work with but this was not obtainable. Were further work to be done with this method, it should begin here. Indium hydroxide should be obtained by a proven method and an attempt be made to learn this critical concentration and if the scheme depends upon it. Two methods of obtaining indium are included in this paper. The above reason, the slight solubility of indium hydroxide in ammonium hydroxide, and the mechanical difficulty of obtaining clean separations by hydroxide precipitation seems to account for the low recovery and impure product.

The next step after the solution of indium as sodium indiumate has been obtained is to boil and filter. According to the scheme, the sodium indiumate should dissociate and precipitate indium hydroxide and regenerate the sodium hydroxide which could be used again. This residue was tested by two methods for indium. First a flame test was made for indium through a cobalt glass and the blue flame of indium was obtained thus making the test positive. The residue was then ignited and during ignition, an indigo flame was noticed in the crucible. After ignition, a yellow amorphous powder was obtained and according to Mellor, \( \text{In}_2\text{O}_3 \) fits this description. This yellow powder was examined on the spectroscope and a very
strong line was obtained at 4511.5 Å. This is a principal line of indium. The other principal line is at 4101.95 Å but is close to the violet potassium line and is observed only when large amounts of indium are present. The lines of the impurities were not determined.

After the impure indium hydroxide was obtained, purification by two methods was attempted. Direct dissolution with ammonium hydroxide was tried but as expected, the indium hydroxide did not dissolve. However, zinc hydroxide, when boiled, is insoluble in ammonium hydroxide. Another test was made by dissolving the impure product in hydrochloric acid and then precipitating with ammonium hydroxide—thereby eliminating any residual zinc, copper, arsenic or antimony that might be left. A precipitate did form but went back into solution when a large excess of ammonium hydroxide was added. To re-precipitate the product, the solution was carefully neutralized with hydrochloric acid but the precipitate did not form, probably due to the large amount of ammonium chloride formed. This has nothing to do with the scheme but indicates that in the first precipitation with ammonium hydroxide, the large amount of ammonium chloride formed by neutralization would cause some of the indium to go into solution and be discarded. The other method of attempted purification was the repetition of the last step. The impure indium hydroxide was dissolved in hydrochloric acid and then cold sodium hydroxide
was added to form sodium indiumate. When this solution was boiled, no indium hydroxide was precipitated. As this residue had just previously been precipitated in such a manner, this indicates that indium hydroxide is soluble in a large excess of hot sodium hydroxide.

From the analysis on page 10, it will be seen that indium is very small in amount as compared with iron and zinc. Because indium resembles zinc in some properties and iron in others, it was thought that if the large ratios of these impurities could be reduced, subsequent operations would be more successful. Iron and zinc hydroxides began precipitation in a strongly acid solution. If a further investigation were to be made, it might be advisable to determine the pH at which indium hydroxide precipitates, thus effecting a partial separation of the iron and zinc.

A method proposed by Dyer\(^{(2)}\) is somewhat similar to the proposed method. It involves precipitation of indium hydroxide from waste liquors of zinc leaching with ammonium hydroxide. Any iron present would be removed by precipitation of indium with zinc dust. This method was tried and the characteristic 'oily' indium hydroxide resulted but the product still contained considerable amounts of iron, zinc, arsenic and antimony. This proposal was for the recovery of indium from spent zinc electrolyte in which the iron content was small and the zinc had been removed by electrolysis and the arsenic and antimony had been removed in the purification of the electrolyte.
CONCLUSIONS

1. In its present form, this proposed method for the extraction of indium seems unworkable but the increasing utility of the metal and its compounds seem to justify further investigation. Other methods are known but if this one could be made workable, a number of steps could be eliminated in the other methods.

2. This scheme depends on the insolubility of indium hydroxide in ammonium hydroxide, its solubility in cold sodium hydroxide but insolubility in hot sodium hydroxide.

3. Observed objections include:
   A. Results are inconsistent.
   B. The product obtained is impure.

4. Probable causes of the above objections.
   A. The formation of ammonium chloride by the initial neutralization results in a probable loss because indium hydroxide appears to be soluble in a strong solution of this salt.
   B. Indium hydroxide is slightly soluble in ammonium hydroxide.
   C. Indium hydroxide is soluble in a large excess of sodium hydroxide, even when hot.
   D. Indium forms slightly soluble basic salts.
   E. Difficulty of obtaining clean separations by hydroxide precipitation.
   F. Difficulty of filtering hydroxide precipitates.
   G. Apparent critical concentration of the hydroxyl ion in both precipitations.
Acknowledgements

I wish to express my gratitude and appreciation for the opportunity offered for pursuing this study at the Montana School of Mines, and for the cooperation and encouragement of the faculty and graduate students.

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