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# Investigation of a Method for Extraction of Indium from Zinc Flue Dust.

Harold L. Tanner

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Tanner, H. L.

INVESTIGATION  
OF A METHOD  
FOR EXTRACTION OF INDIUM FROM ZINC FLUE DUST

by  
Harold I. Tanner

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 3, 1939

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## PART I

In metallurgical practice today some of the relatively rare metal Indium is recovered as a by-product from the ores of other metals. One scheme, advanced by Archibald Duncan\*, for the extraction of indium from zinc flue dusts (Great Falls) was to be investigated to determine whether or not it could be followed by a person other than the original experimenter. The problem was to duplicate Mr. Duncan's experiments using the methods he describes.

The purifying methods used on the leach liquor\*\* were fairly satisfactory and easy to follow. However the final step, the preparation of the electrolytic bath could not be done due to the apparent insolubility of indium hydroxide in acetic acid solutions.

\* Archibald Duncan: M. S. Montana School of Mines, 1938.

\*\* Extraction by leaching in acetic acid was not as efficient as Mr. Duncan observed.

Indium is a soft, silvery-white metal belonging to the third group of the periodic classification. It is situated just above ten in the electrochemical series (very close to hydrogen). Some of its properties are:

Atomic weight <sup>(47)</sup> .....	114.76
Atomic number <sup>(47)</sup> .....	49
Valence <sup>(48)</sup> .....	+1, +2, +3
Valence in stable compounds <sup>(48)</sup> .....	3
Melting point <sup>(47)</sup> .....	155°C
Boiling point <sup>(47)</sup> .....	1450°C
Specific gravity <sup>(47)</sup> .....	7.31
Fused metal <sup>(48)</sup> .....	7.128 @ 20°C
Rolled metal <sup>(48)</sup> .....	7.277 @ 20°C
Hammered metal <sup>(48)</sup> .....	7.422
Thiel : of crystals <sup>(48)</sup> .....	7.12
Specific heat.....joules/gr. atom <sup>(47)</sup> .....	27.3
Electrochemical resistivity <sup>(47)</sup> (ohm/cm. <sup>3</sup> )	
20°C.....	$9 \times 10^{-6}$
155°C.....	$29 \times 10^{-6}$
Thermal expansion <sup>(47)</sup>	
1/L    dl/dt @ 20°C.....	$33 \times 10^{-6}$
Hardness <sup>(47)</sup>	
Brinell.....	1
Tensile strength <sup>(47)</sup>	
99.71% In .....(lb./sq.in.).....	15980

Crystalline structure<sup>(45)</sup>

Unit cell face centered tetragonal:

$$a_0 = 4.583 \text{ \AA}^\circ$$

$$c_0 = 4.936 \text{ \AA}^\circ$$

Four atoms per unit cell with positions

$$000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$$

Ductile<sup>(47)</sup>

Malleable<sup>(47)</sup> - gives very thin foil

Plasticity<sup>(48)</sup>

Plasticity number.....1.28

(Copper = 49.3)

Heat of combustion<sup>(48)</sup>

Cal. per equivalent of In.....37.502

Solution pressure<sup>(48)</sup> (atm).....  $10^2$   $10^3$

(between iron and lead)

Indium is stable at room temperatures but oxidizes readily at its melting point. It is attacked by most acids, with evolution of hydrogen, but not by bases.

PART II

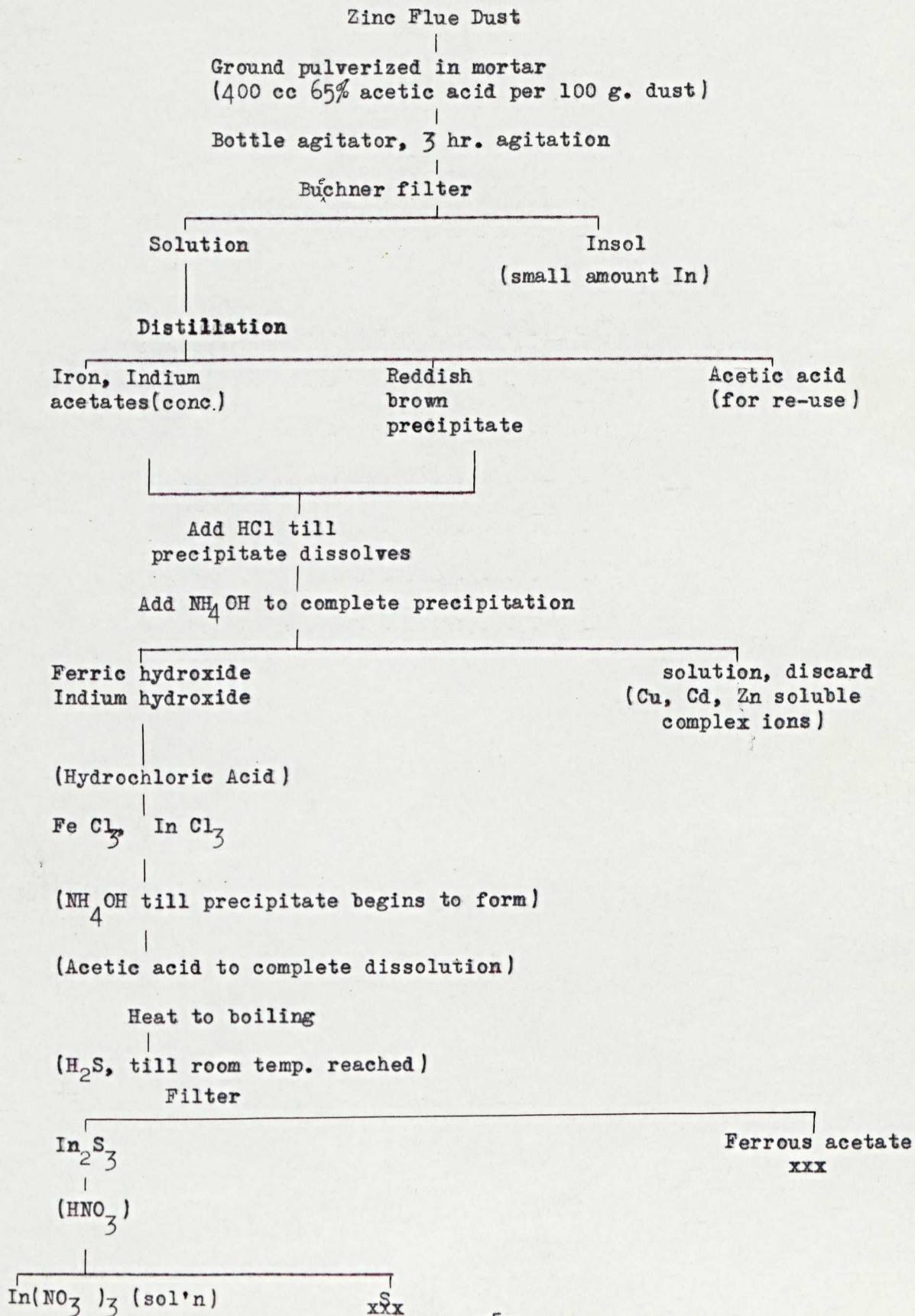
The indium bearing material was the same as that used by Mr. Duncan. It is a flue dust from the Anaconda Copper Mining Company's Zinc Plant at Great Falls. Mr. Duncan gives as the content:

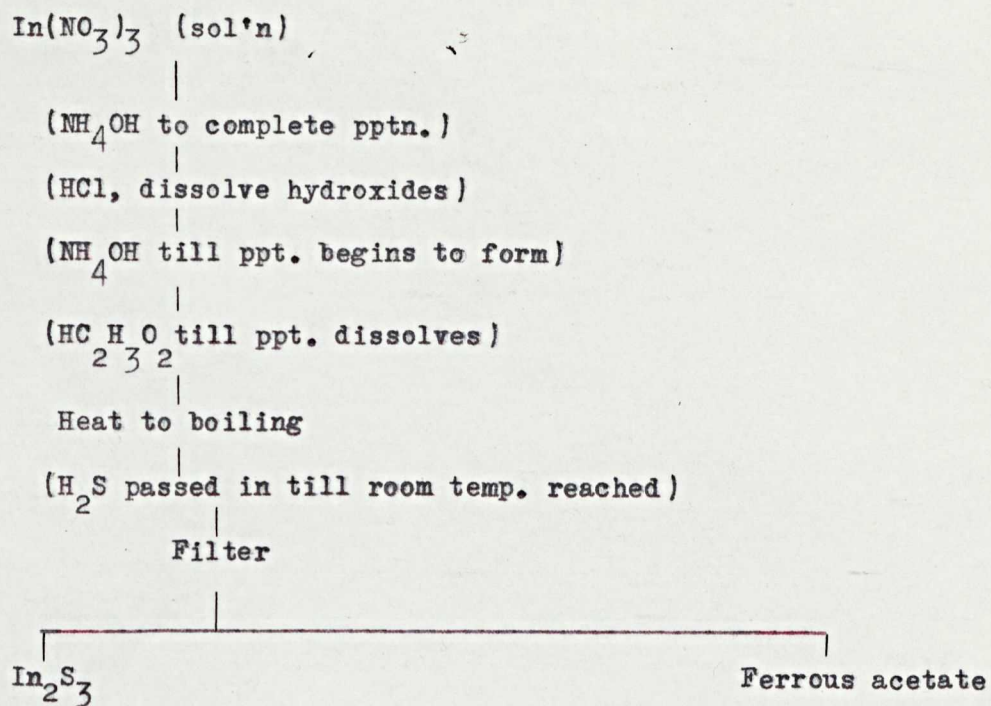
Alumina . . . . .	9.35%
Antimony . . . . .	1.50%
Arsenic . . . . .	10.05%
Copper . . . . .	8.60%
Indium . . . . .	1.00%
Iron . . . . .	16.50%
Lead . . . . .	0.92%
Silica . . . . .	10.15%
Sulphur . . . . .	5.58%
Zinc . . . . .	14.54%

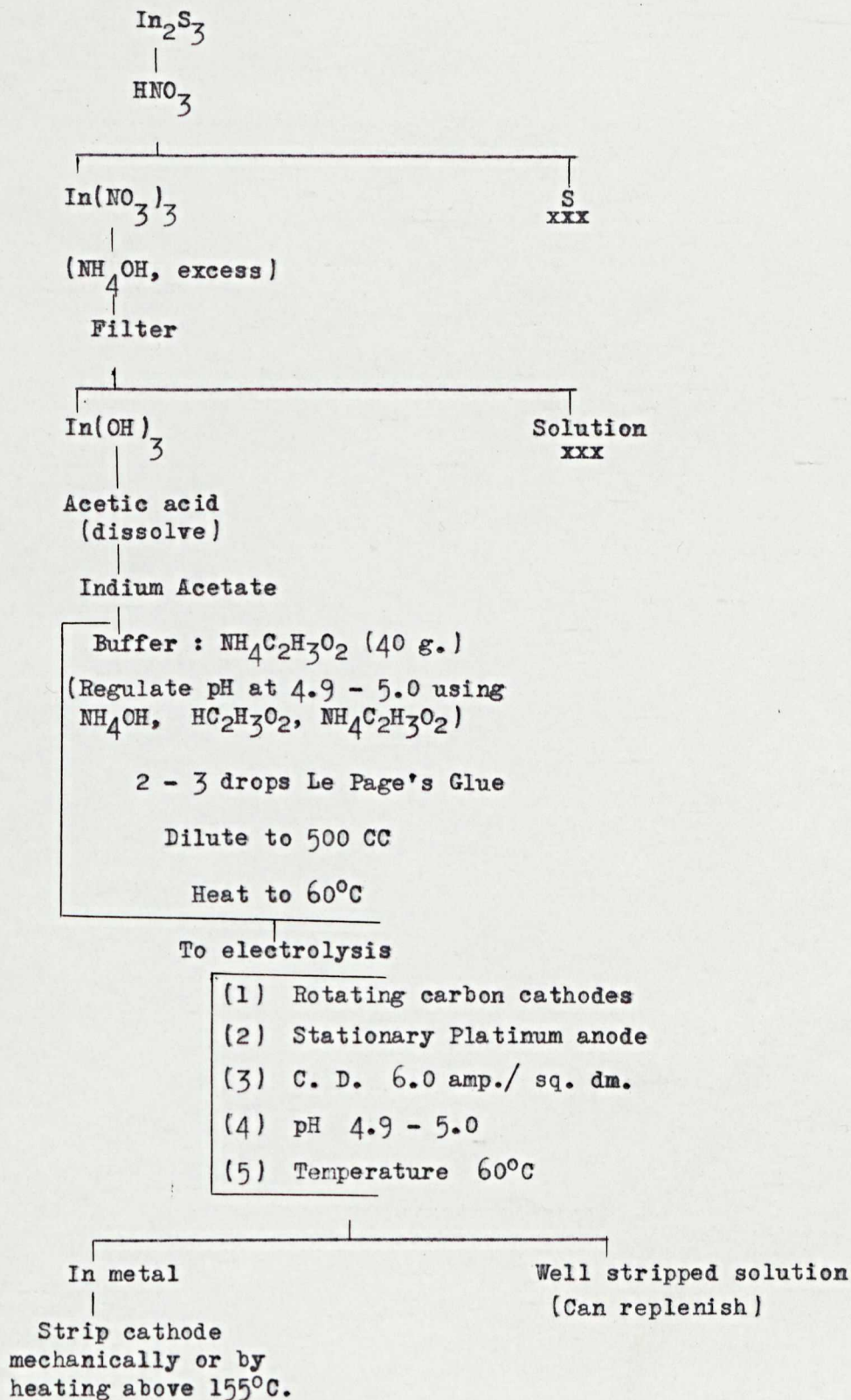
Following is the flowsheet to be tested:



FLWSHEET FOR EXTRACTION OF INDIUM FROM FLUE DUST.







Using the above flowsheet, several samples of flue dust were treated with the acetic acid leach, the solution filtered off and distilled to a small volume to remove excess water and acetic acid. Some brown precipitate is formed during the latter part of the distillation. This was soluble in HCl, but when the distillation was carried to dryness and the residue allowed to bake for a short time, it became highly insoluble, probably due to the presence of basic ferric acetate and ferric oxides in difficultly soluble crystalline forms. If the leach solution was evaporated to about 100 cc. in a suitable distilling flask, the dissolved salts could be kept in solution yet seventy-five percent of the acid recovered with subsequent saving in  $\text{NH}_4\text{OH}$  in the step immediately following.

Acetic acid was chosen to prevent solution arsenic, antimony, and lead\*. It is noted that amorphous indium trioxide is soluble in acids while the crystalline form is highly refractory to acids. (48) Further, in the extraction of indium from its ores much loss is had due to the formation of gelatinous compounds.<sup>x</sup> Some sulphides are present in the ore. If they be indium sulphides, the low extraction would be easily explained on that basis.

No trouble was had in the first  $\text{NH}_4\text{OH}$  precipitation or the HCl dissolution. Strong acids quickly put the whole of the hydroxide precipitate into solution. The  $\text{NH}_4\text{OH}$  was added to the warm solution with stirring. Concentrated HCl was heated and poured over the hydroxides on the filter paper.

On re-neutralizing with  $\text{NH}_4\text{OH}$  for the regulation of acidity for H S precipitation, it was found that if the precipitation were carried

\* Only half the amount of indium, reported by Mr. Duncan was leached out by the author, from an equal charge.

x W. S. Murray, "Production and Deposition of Indium" Ind. and Eng. Chem, News Ed., 11 : 300, 0.20, 1933

to completion, it was impossible to re-dissolve the precipitate in acetic acid. This dissolution was attempted using hot and cold solutions and solutions which were mechanically stirred over periods from a few minutes up to three hours. The volume of solution at this point usually was about 600 cc. Acetic acid was added in amounts varying from just enough to make the liquor acid, to a quantity such that the acetic acid in solution approached the sixty-five percent "ideal solution" proposed by Mr. Duncan. This is the first pertinent evidence that Indium hydroxide becomes sparingly soluble in acetic acid. This conclusion must be modified by adding that considerable amounts of impurity and dissolved salts were present in the solution.

In the precipitation of  $\text{In}_2\text{S}_3$  from a hot\* solution made weakly acid\*\* with acetic acid, the precipitate comes down in quantitative amounts, being brown when hot and canary yellow, if pure, when at room temperature and is readily washed and dissolved on the filter with hot dilute  $\text{HNO}_3$ , forming  $\text{In}(\text{NO}_3)_3$ , with probably some  $\text{H}_2\text{SO}_4$  from the sulphur present, and minute amounts of copper and iron nitrates. The white precipitate gotten by Mr. Duncan when  $\text{H}_2\text{S}$  was passed into the cold solution was probably  $\text{In}(\text{HS})_3$  which precipitates from a neutral solution in the presence of  $(\text{NH}_4)_2\text{S}$ , some of which would be present in the solution.

If much iron is present, as shown by the color of the precipitate formed on precipitation from the nitrate solution by  $\text{NH}_4\text{OH}$ , the  $\text{In}(\text{OH})_3$  must be purified by a second  $\text{H}_2\text{S}$  precipitation.

\* One acetic acid solution gave a reddish brown precipitate, similar to the hydroxides formed before the acetic acid was added, when the solution was boiled.

\*\*  $\text{In}_2\text{S}_3$  will not be precipitated from a strongly acid solution but will precipitate following its dilution.

The hydroxide in any case is filtered off and washed free of dissolved salts as well as copper, zinc, and cadmium as complex ions.

Mr. Duncan's procedure up to this point is satisfactory although long and tedious and the indium recovery is low (42.9% for three hour agitation at room temperature, 78.6% for six hours boiling). However, it is apparently impossible to dissolve  $\text{In}(\text{OH})_3$  in acetic acid of any strength in the presence of electrolytes and minute amounts of  $\text{Fe}(\text{OH})_3$ . The final step, the dissolution of the purified hydroxide in acetic acid proved impossible. Mr. Duncan, however, had no trouble at this point or at least did not mention it if he did. Hope \* found that hot glacial acetic acid poured repeatedly over indium hydroxide on a filter dissolved it but the proportion of solvent to solute was excessively large (1000 : 1).

In the attempt to prepare the acetate bath these methods were tried:

- (1) Cold and concentrated solution
- (2) Cold and dilute
- (3) At  $95^\circ$  (water bath) and concentrated
- (4) Same but dilute
- (5) Glacial acid, warm, repeatedly passed over the hydroxide on the filter paper\*\*.

$\text{In}(\text{OH})_3$  was converted to yellow  $\text{In}_2\text{O}_3$  and this compound placed in acetic acid of various concentrations.  $\text{In}_2\text{O}_3$  failed to dissolve in acetic acid.

In conclusion, the author finds it impossible to dissolve  $\text{In}(\text{OH})_3$  in acetic acid but the solution might be made, as was done in preparing to precipitate indium with  $\text{H}_2\text{S}$ , by dissolving the hydroxide in  $\text{HCl}$ , adding  $\text{NH}_4(\text{OH})$  till precipitation just begins, thus eliminating

free HCl, then reacidifying with enough acetic acid to dissolve the precipitate. This method was not tried experimentally.

\* Hope, Ross, Skelly, Ind. Eng. Chem., Ana. Ed.  
8 : 51-2 1936

\*\* The hydroxide assumed an "oiled" appearance.

Mr. Mayer, a graduate student at the school also tried Duncan's method and found the same difficulty. He used the Westbrook (43) citric-sulphuric acid bath successfully. Not being able to strip his bath's completely of indium, the remainder was turned over to the author to extract the indium. The indium could not be precipitated as  $\text{In}(\text{OH})_3$  due to the formation of soluble complex ions. Three different methods were tried.

(1) Part of the solution was treated with  $\text{HNO}_3$ ,  $\text{HBr}$ , and  $\text{H}_2\text{O}_2$ . The citric acid was decomposed on evaporation and it was found that  $\text{In}(\text{OH})_3$  precipitated satisfactorily on the addition of  $\text{NH}_4\text{OH}$ . Some sublimed salt collected on the watch glass covering the beaker during the evaporation-oxidation. This may have led to a loss of indium. The amount recovered was less than that estimated to be present.

(2) Calcium salts were added to a second portion to precipitate the citrate and sulphate from solution to separate out the indium. The indium was not found in the filtrate so the method was a failure.

(3)  $\text{Na}(\text{HSO}_3)$  precipitated the indium from the neutralized remaining portion as  $\text{In}(\text{HSO}_3)_3$ . This method was satisfactory for recovering indium from the partially stripped Westbrook baths.



PART III

ELECTROLYSIS

Portions of liquor decanted from beakers in which the dissolution of  $\text{In}(\text{OH})_3$  was being attempted and the solution from one sample of  $\text{In}(\text{OH})_3$  which did dissolve readily in cold acetic acid (about 100 mg. in 250 cc. of approximately 50% acetic acid) were heated to  $60^\circ\text{C}$  and electrolyzed at:

C.D. ....	0.06 amps/q.cm.
E.M.F. ....	5.0
pH .....	5.0 down to 4.6
Buffering salt .....	$\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$
Electrode distance .....	2 c.m.

using rotating carbon cathodes and a stationary platinum anode. The compact lustrous deposit first formed became mossy in appearance and some dropped to the bottom as the acidity increased. Evolution of hydrogen and oxygen was rapid, probably due to the high voltage applied. Mr. Duncan does not give the e.m.f. he used.

#### PART IV

- (1) The efficiency of the leach is unsatisfactory yet keeps most of the objectionable dissolved impurities at a minimum.
- (2) Purification, as outlined, above, is satisfactory but might be shortened to advantage.
- (3) The preparation of the acetate electrolytic bath can not be accomplished. Evidence to support the fact that special conditions are necessary for the dissolution of  $\text{In}(\text{OH})_3$  in acetic acid may be cited.
  - A. Indium salts are hydrolyzed\* to a very great extent.
  - B. When a solution of an indium salt is boiled with  $\text{NaC}_2\text{H}_3\text{O}_2$ , basic indium acetate is precipitated.\*
  - C.  $\text{In}(\text{OH})_3$  was reported to have precipitated from its solution in KCN on boiling. This also occurs when solutions made with an indium salt and excess KOH,  $\text{Na}(\text{OH})$ ,  $(\text{HN}_4)_2\text{CO}_3$ , or  $\text{Na}_2\text{CO}_3$  are boiled.\*
  - D.  $\text{KNO}_3$  added to an  $\text{InCl}_3$  solution followed by boiling gives an insoluble mass.\*
  - E. An insoluble oxychloride of indium was prepared by Reich and Richter on evaporation of an  $\text{InCl}_3$  solution.\*
  - F. A solution of  $\text{InF}_3 \cdot 3\text{H}_2\text{O}$  decomposes on boiling to give  $\text{In}(\text{OH})_3$  and  $\text{H}_2\text{F}_2$ . This might also occur with the trihydrated chloride.\*
  - G. Murray found that much trouble is had, when extracting indium from ores, with the formation of gelatinous compounds.
  - H. Indium has a special tendency to form basic salts which are sparingly soluble in water.\*
  - I. Basic salts of indium are known to exist with the chlorides, nitrates, and sulphates as well as with the acetates.

All this material supports the theory that basic salts are formed, preventing the indium hydroxide from going into solution.\*

- (5) The electrolytic deposit of indium was good. Only a very thin coat was obtained on the cathodes.
- (6) Until the problem of the dissolution of indium hydroxide in acetic acid is solved, the method proposed by Mr. Duncan is not practical.
- 

\* Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" 5, Part 1 : 387-405, 1924  
Longmans & Co.

\*\* W. S. Murray, "Production and Deposition of Indium" Ind. and Eng. Chem. News Ed., 11 : 300, 0.20, 1933.

x Downes, A. W. and Kahlenberg, L, "Chemistry of Indium"  
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