THE SEPARATION OF INDIUM, IRON, AND ZINC BY SOLVENT EXTRACTION

by

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This report is on a study of the extraction coefficients iron, zinc, and indium in solutions of chloride, sulfate, or thiocyanate as a function of pH and phase volume ratio with methyl-tri-capryl amine chloride or tri-capryl amine. From work with these pure systems, a method was determined and tested for the separation of indium from a complex hydroxide precipitate of iron, aluminum, arsenic, zinc, and indium. The method involved extracting the zinc as a chloride complex with methyl-tri-capryl amine chloride and separating the indium and iron by extraction from a thiocyanate solution with tri-capryl amine.
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Zinc sulfide concentrates normally contain iron, lead, cadmium, arsenic, indium, and thallium in various quantities. No attempt is made to recover either the iron or arsenic, but lead, cadmium, and thallium are recovered. The indium ends up in a complex precipitate at a concentration of about five percent by weight. Because there is no market for a product of this grade, techniques will have to be devised for up-grading this material. The principal separation will be between that of iron, indium, and zinc from one another, since both cadmium and lead would have already been removed. A convenient way to effect these separations would seem to be with solvent extraction, in that separations of uranium from impurities\(^1\) and, more recently, copper from iron with oximes\(^2\) have already been demonstrated, for example. Uranium, in small concentration, is extracted with amines when the uranium is present in the form of uranyl sulfate complexes. Since indium is also present in relatively small
concentrations in cadmium leach liquors, extraction will likely also be possible only if indium is suitably complexed. In this view, extraction experiments were conducted with amines on zinc, ferrous and ferric iron, and indium in the presence of chloride, thiocyanate, and sulfate as ligands.
The experimental work was divided into two areas: (1) an investigation of pure systems and (2) the extension of the pure systems into a natural system.

**Pure Systems**

All of the work with pure systems involved identical procedures with each series of experiments. These experiments were conducted at pH values of 0.50, 1.00, 1.50, and 2.00 with seven different phase volume ratios of 10, 5, 2, 1, 0.5, 0.2, and 0.1 in some cases and with 0.5 and 1 in others. The phase volume ratio is the volume of organic phase divided by the volume of aqueous phase, $V_{o}/V_{A}$.

The aqueous and organic phases were combined in a 250-ml separatory funnel at a total volume of 75 ml and shaken for two minutes. The mixture, after being allowed to settle for two hours, was sampled for assay.

Since the initial and final metal concentrations in the
aqueous phase were known as well as the phase volume ratio, the metal concentration in the organic phase could be determined. From these values the extraction coefficient was calculated. The extraction coefficient is the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase, $(\text{Me}_o)/(\text{Me})_A$. The following is the calculation of a typical extraction coefficient:

Initial $(\text{Fe}^{III})_{(aq)} = 0.020 \text{ M}$.

Final $(\text{Fe}^{III})_{(aq)} = 0.0020 \text{ M}$.

$V_o/V_A = 5.0$

Then

$$\frac{(\text{Fe}^{III})_{(org)}}{5.0} = \frac{\text{Initial} (\text{Fe}^{III})_{(aq)} - \text{Final} (\text{Fe}^{III})_{(aq)}}{5.0}$$

$$= \frac{0.020 - 0.0020 \text{ M}}{5.0} = 0.0036 \text{ M}$$

Extraction coefficient $= \frac{(\text{Fe}^{III})_{(org)}}{5.0} = \frac{0.0036}{0.0020} = 1.8$.

Sulfate and Chloride as Ligands

Separate solutions, each of approximately 0.020 mole per liter of ZnIII, CdII, FeII, and FeIII were prepared. Adjustments in pH were made with either sulfuric acid or hydrochloric
acid, and pH values of 0.5, 1.0, 1.5, and 2.0 were used.

The organic phase consisting of 92.5 percent kerosene, 5 percent methyl-tri-capryl amine chloride, and 2.5 percent isodecanol by volume was then combined with these aqueous phases.

**Thiocyanate as Ligand**

The same procedure, applied in the sulfate and chloride experiments, was used in this series of experiments. Sodium thiocyanate was added so that the total thiocyanate concentration was one mole per liter. Sulfuric acid and sodium hydroxide were employed for pH control.

In addition to the quaternary amine, a tertiary amine, tri-capryl amine, was also used as the organic phase. The same volume mixture as described above was used.

**Natural Indium Concentrate**

This material contained 4.5 percent indium, 5.0 percent iron, 7-10 percent aluminum, 1-2 percent arsenic, 5.9 percent zinc and 1.7 percent cadmium, as oxides and hydroxides. Experimentally, 25 grams of this material was dissolved in concentrated sulfuric acid, and the liquor was diluted to one liter. To this solution sodium chloride was added so that there was 0.5 molar
chloride present. Next, the zinc was extracted in one stage from the chloride solution with methyl-tri-capryl amine chloride at pH 0.5 and a phase volume ratio of 1.0. To the zinc-depleted solution, sodium thiocyanate was added so that the solution was one molar in thiocyanate. After the adjustment of the pH to 1.0, the indium was extracted with tri-capryl amine at a phase volume ratio of 1.0.

**Stripping**

After the organic phase was loaded with metal ions, the organic phase was stripped with a two molar solution of sodium chloride. The phase volume ratio, $V/V_o$, was 0.33, and the pH was 1.0. After the indium was stripped, the pH of the solution was raised with sodium hydroxide to precipitate the indium and other metal ions. The solids were filtered, dried, and assayed. An x-ray spectogram was obtained for product analysis.

**Reagents**

All of the acids and inorganic salts used in this study were of reagent grade.

The amines, isodecanol, and kerosene were the same as those used commercially.

Conductivity water, made by passing distilled water through an ion exchange column, was used.
The first series of experiments involved extraction of ZnII, FeII, FeIII, and InIII as sulfate complexes with methyl-tri-capryl amine chloride. As shown in Figure 1, extraction coefficients of FeIII from a one molar sulfate solution are plotted as a function of pH below pH 2.0. There was no extraction of FeII, ZnII and InIII from a one molar sulfate solution with methyl-tri-capryl amine chloride below pH 2.0.

The next series of experiments involved extraction of ZnII, FeII, FeIII and InIII as chloride complexes with methyl-tri-capryl amine chloride. As shown in Figure 2, extraction coefficients of ZnII from a one molar chloride solution are plotted as a function of pH at two phase volume ratios. It should be noted that coefficients greater than 150 are obtained at a phase volume ratio of 1.0 and pH 0.5. Also, the extraction coefficient at a phase volume ratio of 1.0 at
pH values below 2.0 is at least three times greater than at a phase volume ratio of 0.5.

Extraction coefficients of FeIII from a one molar chloride solution are plotted as a function of pH at two phase volume ratios in Figure 3. It can be noted that coefficients less than one are obtained in all values of pH below 2.0 with the exception of pH 0.5 with a phase volume ratio of 1.0. Also, there is a slight increase in the extraction coefficient with the decrease in pH.

There was no extraction of FeII and InIII from a one molar chloride solution with methyl-tri-capryl amine chloride below pH 2.0.

The third series of experiments involved extraction of FeIII, FeII and InIII as thiocyanate complexes with methyl-tri-capryl amine chloride. As shown in Figure 4, extraction coefficients of FeIII from a one molar thiocyanate solution are plotted as a function of pH at seven phase volume ratios. It can be noted that the extraction coefficient reaches a maximum of about 1000 at pH 1.0 and a phase volume ratio of 1.0.

The extraction coefficients of FeII from a one molar thiocyanate solution with methyl-tri-capryl amine chloride are presented as a function of pH in Figure 5. It can be noted that the extraction coefficient reaches a maximum at
Figure 1. Extraction coefficient for FeIII as a function of pH from a one molar sulfate solution with methyl-tri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (FeIII) = 0.020 molar.
Figure 2. Extraction coefficient for ZnII as a function of pH from a one molar chloride solution with methyltri-capryl amine chloride. pH adjusted with hydrochloric acid. Initial (ZnII) = 0.020 molar.
Figure 3. Extraction coefficient for FeIII as a function of pH from a one molar chloride solution with methyl-tricapryl amine chloride. pH adjusted with hydrochloric acid. Initial (FeIII) = 0.020 molar.
Figure 4. Extraction coefficient for FeIII as a function of pH from a one molar thiocyanate solution with methyltri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (FeIII) = 0.020 molar.
Figure 5. Extraction coefficient for FeII as a function of pH from a one molar thiocyanate solution with methyl-tri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (FeII) = 0.020 molar.
pH 1.5 and a phase volume ratio of 1.0. In general FeII does not have so high an extraction coefficient as FeIII under similar conditions of pH and phase volume ratio.

Extraction coefficients of InIII from a one molar thiocyanate solution with methyl-tri-capryl amine chloride are plotted as a function of pH at seven phase volume ratios in Figure 6. It can be noted that the extraction coefficient is at a minimum at pH 1.0 and at a maximum of 4.020 at pH 0.5 and 1.5 when the phase volume ratio is 1.0.

Since the extractions at different phase volume ratios give extraction coefficients which depend not only on pH, but on phase volume ratio, too, it is necessary to examine the extraction coefficient as a function of phase volume ratio at constant pH. Figures 7, 8, and 9 represent plots of extraction coefficients of FeIII, FeII and InIII from a one molar thiocyanate solution with methyl-tri-capryl amine chloride as a function of phase volume ratio at four pH's. It can be seen that the extraction coefficient rises steadily to a maximum at a phase volume ratio of 1.0 and drops steeply when the phase volume ratio decreases from 1.0 and 0.1.

The next series of experiments involved extraction of FeIII, FeII and InIII as thiocyanate complexes with tri-capryl amine. The test solutions were either composite FeIII-InIII solutions or FeII-InIII solutions. As shown
Figure 6. Extraction coefficient for InIII as a function of pH from a one molar thiocyanate solution with methyltri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (InIII) = 0.020 molar.
Figure 7. Extraction coefficient for FeIII as a function of phase volume from a one molar thiocyanate solution with methyl-tri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (FeIII) = 0.020 molar.
Figure 8. Extraction coefficient for FeII as a function of phase volume ratio from a one molar thiocyanate solution with methyl-tri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (FeII) = 0.020 molar.
Figure 9. Extraction coefficient for InIII as a function of phase volume ratio from a one molar thiocyanate solution with methyl-tri-capryl amine chloride. pH adjusted with sulfuric acid. Initial (InIII) = 0.020 molar.
in Figure 10, extraction coefficients of FeIII and InIII from a one molar thiocyanate solution are plotted as a function of pH at two phase volume ratios. It should be noted that at all values of pH below 2.0 the extraction coefficient for InIII is greater than FeIII.

A series of experiments was also conducted with a composite of FeII-InIII at pH 1.0 with various phase volume ratios. The extraction coefficients are given in Figure 11, and it can be seen that the ratio of InIII is approximately 120 times greater than that of FeII.

Natural Indium Concentrate

After completing work with the pure systems, a procedure was devised to separate indium from a natural indium concentrate containing 4.5 percent indium. The results from these experiments are listed in Table I. Extraction coefficients were obtained for iron, zinc and indium after each extraction. The first extraction was with methyl-tri-capryl amine chloride for extracting zinc from a 0.5 molar chloride solution at pH 0.5 with a phase volume ratio of 1.0. The indium was extracted from a one molar thio-cyanate solution with tri-capryl amine at pH 1.0 and phase volume ratio of 1.0. Included in Table I are the actual metal concentrations in the aqueous phase after each step.
Figure 10. Extraction coefficients for FeIII and InIII as a function of pH from a one molar thiocyanate solution with tri-capryl amine. pH adjusted with sulfuric acid. Initial (FeIII) = 0.020 molar and (InIII) = 0.010 molar.
Figure 11. Extraction coefficients for FeII and InIII as a function of phase volume ratio from a one molar thiocyanate solution with tri-capryl amine. pH adjusted with sulfuric acid. Initial (FeII) = 0.020 molar and (InIII) = 0.010 molar.
Table I. Assays for iron, zinc, and indium after each stage in tests with the natural indium concentrate.

<table>
<thead>
<tr>
<th>Product</th>
<th>pH</th>
<th>Cl</th>
<th>SCN</th>
<th>Zn</th>
<th>Fe</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Solution</td>
<td>0.5</td>
<td>500</td>
<td>0</td>
<td>27.0</td>
<td>22.6</td>
<td>13.1</td>
</tr>
<tr>
<td>Zinc Extraction</td>
<td>0.5</td>
<td>500</td>
<td>0.013</td>
<td>4.96</td>
<td>21.4</td>
<td>13.0</td>
</tr>
<tr>
<td>Indium Extraction</td>
<td>0.5</td>
<td>500</td>
<td>1000</td>
<td>0.013</td>
<td>3.31</td>
<td>0.97</td>
</tr>
</tbody>
</table>
After completing work with the pure systems, a procedure was devised to separate indium from a natural indium concentrate containing 4.5 percent indium. The concentrate rate also contained 0.97 percent copper, 5.0 percent iron, 1.7 percent cadmium, 0.72 percent lead, and 5.9 percent zinc. After leaching with $H_2SO_4$ for two hours, a solid residue weighing 5.89 was obtained which contained the following: 0.01 percent indium, 0.99 percent copper, 0.96 percent iron, 0.23 percent cadmium, 4.7 percent lead, and 1.6 percent zinc.

Extraction experiments were then performed with the leach solution. The results of these experiments are listed in Table I. The first extraction was with methyl tricapryl amine chloride for extracting zinc from a 0.5 molar chloride solution at pH 0.5 with a phase volume ratio of 1.0. The indium was extracted from a one molar thiocyanate solution with tricapryl amine at pH 1.0 and phase volume ratio of 1.0. Included in Table I are the actual metal concentrations in the aqueous phase after each step.
The results show that 0.77 percent of the indium was removed in the zinc extraction step and that 7.41 percent of the indium initially present in the leach solution was not removed. This value could have been reduced to an acceptable amount with another extraction step or two.

Stripping of the loaded organic was effected in four stages with a one molar sodium chloride solution at pH 1.0. The phase volume ratio of organic to aqueous was 0.33. Following stripping, the pH of the solution was raised with sodium hydroxide, and a product weighing 3.15 grams was obtained containing 30.0 percent indium and 16.0 percent iron. The remainder of the product was the hydroxides of zinc, and aluminum. On this basis, a recovery of 83.7
percent of the indium originally in the concentrate was obtained, and 8.2 percent was still left in the raffinate. Again, additional stages of stripping would have reduced this value to an acceptable level.
Two amines were used in this study. The first was
methyli-tri-capryl amine chloride, \( \left[ (\text{CH}_3\text{(CH}_2)_3\text{NCH}_2\right]_2\text{Cl}^+ \); the second was tri-capryl amine \( (\text{CH}_3\text{(CH}_2)_2\text{N} \).

The following equations show how the quaternary amine might extract a negative metal complex such as \( \text{ZnCl}_2^- \):

\[
R_2\text{NCl}^{(\text{org})} = R_2\text{NCl}^{(\text{aq})}
\]

\[
R_2\text{NCl}^{(\text{aq})} = R_2\text{N}^+^{(\text{aq})} + \text{Cl}^-^{(\text{aq})}
\]

\[
R_2\text{N}^+^{(\text{aq})} + \text{ZnCl}_2^-^{(\text{aq})} = R_2\text{NZnCl}_3^{(\text{aq})}
\]

\[
R_2\text{NZnCl}_3^{(\text{aq})} = R_2\text{NZnCl}_3^{(\text{org})}
\]

Extraction of metal ions with either a tertiary or quaternary amine is possible only after the metal has been suitably complexed with some negative ligand. Further, extraction probably occurs only if a specific complex is formed between the amine and metal-ligand. The experimental results obtained with indium from sulfate solutions and with
zinc from chloride solutions, together with the following
calculations, show this phenomenon.

Example I

A solution containing 0.02 molar In$^{3+}$ and 1.0 molar sulfate
at pH 2.0. $pK_1 = 1.85$, $pK_2 = 0.75$ and $pK_3 = 0.40^{(3)}$.

Indium balance:

$$[\text{In}^{3+}] + [\text{InSO}_4^+] + [\text{In}^{3+}] + [\text{In}^{3+}] = 0.02 \quad (5)$$

Sulfate balance:

$$[\text{HSO}_4^-] + [\text{SO}_4^{2-}] + [\text{InSO}_4^+] + 2 [\text{In}^{3+}] + 3 [\text{In}^{3+}] = 1.0 \quad (6)$$

from $pK_1$:

$$[\text{InSO}_4^+] = 71 [\text{In}^{3+}] [\text{SO}_4^{2-}] \quad (7)$$

from $pK_2$:

$$[\text{In}^{3+}] [\text{SO}_4^{2-}] = 5.6 [\text{InSO}_4^+] [\text{SO}_4^{2-}] \quad (8)$$

from $pK_3$:

$$[\text{In}^{3+}] [\text{SO}_4^{2-}] = 2.5 [\text{InSO}_4^+] [\text{SO}_4^{2-}] \quad (9)$$

from $H_2\text{SO}_4 pK_1$:

$$[H^+] [\text{SO}_4^{2-}] 1.0 \times 10^{-2} [\text{HSO}_4^-] \quad (10)$$

On the assumption that $[\text{SO}_4^{2-}] = [\text{HSO}_4^-] = 0.50$ at pH 2.0 and on the
solution of equations (5), (7), (8), (9) and (10)

$$[\text{InSO}_4^+] = 2.7 \times 10^{-3} \text{ M}$$

$$[\text{In}^{3+}] = 7.7 \times 10^{-3} \text{ M}$$
\[ \{\text{In(SO}_4\}_3\} = 9.5 \times 10^{-3} \text{ M} \]

\[ \{\text{In}^{3+}\} = 7.7 \times 10^{-5} \text{ M} \]

**Example II**

A solution containing 0.0200 molar Fe\(^{3+}\) and 1.00 molar thiocyanate. \(pK_1 = 1.96\), \(pK_2 = 2.04\), \(pK_3 = -0.41\), \(pK_4 = -0.14\), \(pK_5 = 1.57\) and \(pK_6 = -1.51\).

**Iron balance:**

\[
\{\text{Fe}^{3+}\} + \{\text{FeSCN}^{2+}\} + \{\text{Fe(SCN)}_3^{+}\} + \{\text{Fe(SCN)}_2^{-}\} + \{\text{Fe(SCN)}_3^{-}\} + \{\text{Fe(SCN)}_4^{-}\} = 0.020
\]

(11)

**Thiocyanate balance:**

\[
\{\text{SCN}^{-}\} + \{\text{FeSCN}^{2+}\} + 2\{\text{Fe(SCN)}_3^{+}\} + 3\{\text{Fe(SCN)}_2^{-}\} + 4\{\text{Fe(SCN)}_3^{-}\} + 5\{\text{Fe(SCN)}_4^{-}\} = 1.0
\]

(12)

from \(pK_1\):

\[
\{\text{FeSCN}^{2+}\} = 97.5 \{\text{Fe}^{3+}\} \{\text{SCN}^{-}\}
\]

(13)

from \(pK_2\):

\[
\{\text{Fe(SCN)}_3^{+}\} = 104 \{\text{FeSCN}^{2+}\} \{\text{SCN}^{-}\}
\]

(14)

from \(pK_3\):

\[
\{\text{Fe(SCN)}_2^{-}\} = 0.391 \{\text{Fe(SCN)}_3^{+}\} \{\text{SCN}^{-}\}
\]

(15)

from \(pK_4\):

\[
\{\text{Fe(SCN)}_3^{-}\} = 0.735 \{\text{Fe(SCN)}_2^{-}\} \{\text{SCN}^{-}\}
\]

(16)
from $pK_r$:

\[
\{\text{Fe(SCN)}^\mu\} = 0.0261 \ {\text{Fe(SCN)}^\mu}^3 \ \{\text{SCN}^-\} \tag{17}
\]

from $pK_c$:

\[
\{\text{Fe(SCN)}^\Xi\} = 0.0311 \ \{\text{Fe(SCN)}^\Xi\}^2 \ \{\text{SCN}^-\} \tag{18}
\]

On the assumption that $\text{SCN}^- = 1.0$ and on the solution of equations (11), (13), (14), (15), (16), (17) and (18)

\[
\{\text{Fe}^{+3}\} = 1.18 \times 10^{-6} \text{ M} \\
\{\text{FeSCN}^\mu\} = 1.15 \times 10^{-4} \text{ M} \\
\{\text{Fe(SCN)}^\mu\} = 4.61 \times 10^{-3} \text{ M} \\
\{\text{Fe(SCN)}^\Sigma\} = 3.39 \times 10^{-3} \text{ M} \\
\{\text{Fe(SCN)}^\Xi\} = 8.85 \times 10^{-5} \text{ M} \\
\{\text{Fe(SCN)}^\Xi\} = 2.75 \times 10^{-6} \text{ M}
\]

From Example I and under the conditions used in the experimental work, the indium was present primarily as $\text{In(SO}_4)^{\Sigma}$ and $\text{In(SO}_4)^{\Xi}$; whereas from Example II less than one fourth of the iron was present as $\text{Fe(SCN)}^\Sigma$, $\text{Fe(SCN)}^\Xi$ and $\text{Fe(SCN)}^\Xi$.

**Pure Systems**

FeII, ZnII and InIII were not extracted from one molar sulfate solutions with methyl-tri-capryl amine chloride.
FeIII was extracted to a small extent as shown in Figure 1; as the pH was decreased from 2.0 to 0.5, the extraction coefficient decreased from a maximum of 0.50 to zero.

As shown in Example I, it was thought that indium might be extracted from sulfate solutions, but in all tests there was virtually no extraction.

FeII and InIII were not extracted from one molar chloride solutions with methyl-tri-capryl amine chloride. Zinc was extracted readily from chloride solution as shown in Figure 2. The extraction coefficient for Zn increased to a maximum of 157 as the pH decreased from 2.0 to 0.5.

In Figure 3, the extraction coefficients for FeIII from a one molar chloride solution are plotted as a function of pH. The extraction coefficient for FeIII decreases from a maximum of 1.3 at pH 0.5 and phase volume ratio of 1.0 to
a minimum of 0.43 at pH 2.0 and phase volume ratio of 0.5. Since InIII is not extracted from a chloride solution with methy-tri-capryl amine chloride, while zinc is extracted, indium and zinc can readily be separated.

The next series of experiments involved extraction of FeIII, FeII and InIII from one molar thiocyanate solutions. Previous work\(^5\) has shown FeIII to be readily extracted as thiocyanate complexes with amines. As shown in Figure 4, the extraction coefficient for FeIII reached a maximum of 1020 at pH 1.0 and phase volume ratio of 1.0, and the extraction coefficient decreases with either increasing or decreasing the pH from 1.0. The extraction coefficients for FeII, as shown in Figure 5, reach a maximum of only 365. With most conditions of pH and phase volume ratio, the extraction coefficient of FeIII is greater than that for FeII. In Figure 6, the extraction coefficient for InIII is
at a maximum of 4020 at pH values of 0.5 and 1.0 with a phase volume ratio of 1.0. The extraction coefficient is a minimum for all phase volume ratios at pH 1.0. In a comparison of Figures 4, 5, and 6, it is evident that indium extracts considerably better than either FeIII or FeII under almost all conditions.

The extraction coefficient is a function not only of pH but also of phase volume ratio. Figures 7, 8, and 9 represent plots of extraction coefficients of FeIII, FeII and InIII, respectively, as a function of phase volume ratio at four values of pH. In Figures 7, 8, and 9, the extraction coefficients reach a maximum at a phase volume ratio of 1.0. With decreasing phase volume ratio, the extraction coefficient rises steadily to a maximum at a phase volume ratio of 1.0 and decreases sharply as the
phase volume ratio drops below 1.0. The organic phase is beginning to saturate at a phase volume ratio of 1.0. The saturated organic phase contains about 0.045 to 0.05 molar FeIII, FeII or InIII.

Figure 10 represents results of initial experimentation with tri-capryl amine. Extractions were made from a solution containing 0.02 molar FeIII, 0.01 molar InIII and one molar thiocyanate. The tertiary amine proved to be more selective than the quaternary amine. In Figure 10, the greatest difference between the extraction coefficients of iron and indium was at pH 1.0. So two series of experiments were conducted with a composite solution of 0.020 molar FeII, 0.010 molar InIII and one molar thiocyanate. Tri-capryl amine was used to extract the thiocyanate complexes from a solution at pH 1.0. As shown in Figure 11, extraction coefficients for FeII and InIII are plotted as a function of phase volume ratio at pH 1.0. The extraction coefficient
for InIII ranges from five to one hundred times greater than the extraction coefficient for FeII. The greatest difference was at a phase volume ratio of 1.0, where the coefficient for InIII was 184 and that for FeII was about 1.8. With this much of a difference between InIII and FeII, it should be relatively easy to separate indium from ferrous iron.

Natural Indium Concentrate

From the work with pure systems, a procedure for producing a relatively pure indium yield was devised. From Table I, it can be seen that 81.6 percent of zinc was extracted in the first stage without appreciable extraction of indium. After the zinc extraction, approximately 92 percent indium and 85 percent of the iron was extracted from the thio-cyanate solution with a tertiary amine. The extraction coefficient of indium is much greater than that of ferrous iron but not that
of ferric iron (Figures 10 and 11). Much of the iron contained in the natural concentrate must have oxidized to ferric, since the concentrate was produced in a strongly reducing environment.

Finally, the reasons are not known as to why complexes such as zinc chloride extract with an amine, while zinc sulfate complexes do not. It is likely, though, that this phenomenon is probably related to the electronic configuration of these complex ions. Additional study is obviously required. When these reaction mechanisms are learned, solvent extraction technology will be advanced significantly.
CONCLUSIONS

Using a procedure developed from work with pure systems, an indium concentrate containing 30 percent indium was obtained from a roast-leach product containing 4.5 percent indium.

The final method developed involved dissolution of the solid with sulfuric acid and adjustment of the pH to 0.50. Sodium chloride was added so that the chloride was 0.5 molar. Next, the zinc from the chloride solution was extracted in one stage with methyl-tri-capryl amine chloride. Following this step, sodium thiocyanate was added to the aqueous phase, and the pH was increased to 1.0. The indium was then extracted with tri-capryl amine. After extraction, the organic phase was stripped in four stages with a one molar sodium chloride at pH 1.00. A hydroxide precipitate was obtained upon the addition of sodium hydroxide.


