A STUDY OF ARSENIC REMOVAL
FROM
AQUEOUS SOLUTION

By
Arthur Ona Martel
A Thesis respectfully submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

Signed: Arthur Ona Martel

Golden, Colorado
Date: May 23, 1967

Approved: M. C. Fuerstenau
M. C. Fuerstenau
Thesis Advisor

A. W. Schlechten
Head of Department
Metallurgical Engineering

Golden, Colorado
Date: May 23, 1967
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT.</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>INTRODUCTION.</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL MATERIALS AND PROCEDURES</td>
<td>5</td>
</tr>
<tr>
<td>Materials</td>
<td>5</td>
</tr>
<tr>
<td>Procedures</td>
<td>6</td>
</tr>
<tr>
<td>Iron Cementation</td>
<td>6</td>
</tr>
<tr>
<td>Metal Ion Precipitation</td>
<td>7</td>
</tr>
<tr>
<td>Ion Exchange.</td>
<td>8</td>
</tr>
<tr>
<td>Molybdenum Blue Method for Arsenic Determination</td>
<td>10</td>
</tr>
<tr>
<td>EXPERIMENTAL RESULTS</td>
<td>11</td>
</tr>
<tr>
<td>DISCUSSION OF RESULTS</td>
<td>26</td>
</tr>
<tr>
<td>SUMMARY AND CONCLUSIONS</td>
<td>37</td>
</tr>
<tr>
<td>BIBLIOGRAPHY.</td>
<td>39</td>
</tr>
</tbody>
</table>

iii
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Relationship Between Arsenic Removal and Degree of Initial Arsenic Oxidation</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Relationship Between Arsenic Removal and Cementation Time with Complete Arsenic Oxidation at pH 3</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Relationship Between Arsenic Removal and pH with Complete Arsenic Oxidation</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Relationship Between Arsenic Removal and Initial Arsenic Concentration at pH 3 with Constant Cementation Time</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>Relationship Between Arsenic Removal and pH at 25°C with 10⁻⁷M Cd⁺⁺ and 5 x 10⁻²M As⁺⁵</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Relationship Between Arsenic Removal and pH at 25°C with 10⁻²M Fe⁺⁺ and 5 x 10⁻²M As⁺⁵</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>Relationship Between Arsenic Removal and pH at 25°C with 10⁻²M Cu⁺⁺ and 5 x 10⁻²M As⁺⁵</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Relationship Between Arsenic Removal and pH at 25°C with 10⁻²M Zn⁺⁺ and 5 x 10⁻²M As⁺⁵</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>Relationship Between Arsenic Removal and pH at 25°C with 10⁻²M Fe⁺⁺⁺ and 5 x 10⁻²M As⁺⁵</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>Relationship Between Arsenic Removal by Ion Exchange and pH at 25°C</td>
<td>25</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.</td>
<td>Arsenic Removal by Copper Cementation</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>as a Function of Time and Percent Oxidation at Constant pH</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Arsenic Removal by Cobalt Cementation</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>as a Function of Time and Percent Oxidation at Constant pH</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Maximum Arsine Pressure for Arsine to be Produced by Iron Cementation</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>from $\text{H}_3\text{AsO}_4$ Solutions</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Maximum Arsine Pressure for Arsine to be Produced by Iron Cementation</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>from $\text{HAsO}_2$ Solutions</td>
<td></td>
</tr>
</tbody>
</table>
ABSTRACT

Three general areas of investigation, cementation, metal ion precipitation, and ion exchange were involved in this study of the removal of arsenic from aqueous solution.

Cementation with finely divided iron powder resulted in the removal of approximately 80 percent of the contained arsenic as arsenic metal at pH 1. The importance of the degree of arsenic oxidation and system pH is shown. Precipitation of arsenic as metal mono-hydrogen or di-hydrogen arsenates showed the insoluble nature of these compounds.

Fifty percent removal of dissolved arsenic was accomplished at pH 2 with an anion exchange resin that had been loaded previously with sodium molybdate.
ACKNOWLEDGMENTS

The author wishes to express his gratitude and appreciation to Dr. Maurice C. Fuerstenau for the guidance and encouragement during the initiation and progress of this investigation.

The author also wishes to acknowledge the financial support provided by the St. Joseph Lead Company for this research.
INTRODUCTION

Arsenic elimination from solution is necessary in many hydrometallurgical systems because further processing of the solution often results in the formation of arsine gas. Presently, arsenic is removed from cadmium production solutions by acidifying the system and adding zinc metal powder; these steps result in the liberation of arsine, the handling of which requires elaborate safety precautions. Although this method does remove arsenic it is far from satisfactory. Any technique that will rid the system of this constituent without producing arsine gas will be of considerable value. The purpose of this thesis is to investigate other means to accomplish this removal. Three general methods will be studied, namely cementation with copper, cobalt, and iron powders; metal ion precipitation; and ion exchange.

Previous work on the removal of arsenic from pregnant cadmium solutions has been limited in extent. L. M. Kabanova
and V. D. Ponomarev have studied the precipitation of arsenic from solutions of zinc and cadmium sulfates\(^{(1)}\). The processes of precipitation of arsenic from arsenate-containing solutions were studied in solutions containing: \(\text{H}_3\text{AsO}_4 - \text{ZnSO}_4 - \text{CdSO}_4 - \text{Fe}_2(\text{SO}_4)_3 - \text{CuSO}_4\). Precipitation was effected by addition of \(\text{NH}_4\text{OH}\) with continuous control of the solution pH and composition. Precipitation of arsenic from solutions of \(\text{Zn}, \text{Cd}, \text{Cu},\) and \(\text{Fe(III)}\) sulfates, on neutralization, proceeds because of arsenate formation, with the composition of the latter dependent on the acidity of the solution. At one of the arsenic concentrations in the initial solution (3.0 g/l), arsenic precipitates as the arsenates of \(\text{Fe}, \text{Cu}, \text{Zn},\) and \(\text{Cd}\) in pH intervals 1.1 - 3.0; 1.85 - 5.6; 1.6 - 6.0; and 1.8 - 7.2, respectively. In an alkaline medium, all arsenates re-dissolve, and solution is complete at pH 9 to 10. Precipitation of arsenates begins at pH values lower than those at which the hydroxide precipitates which indicates that the solubility of arsenates is less than that of hydroxides, and consequently, that it is possible to precipitate arsenic before hydroxide precipitation.

R. B. Caples and F. F. Frick indicated that zinc dust addition to neutral cadmium pregnant solutions containing copper was effective in removing arsenic\(^{(2)}\). They discovered that optimum arsenic removal from solution occurred
when the zinc dust addition did not exceed the copper concentration in the solution, and when the solution temperature was greater than 80\(^\circ\)C.

The use of atmospheric oxygen as an oxidant in the purification of cadmium production solutions from impurities was studied by E. S. Pronina and V. G. Neiman\(^{(3)}\). Their method of oxidation of iron with atmospheric oxygen was tested on a large scale and introduced into production at the Leninogorsk Polymetallic Combine. Oxidation of iron and elimination of arsenic and antimony from solution occurs at a pH greater than 5.0 - 5.2, copper content 0.2 - 0.3 g/l, and solution temperature 60\(^\circ\) - 70\(^\circ\)C. Original impurities have a harmful effect on the length of operation and the degree of arsenic removal.

W. Ipatiew, Jr., has studied the hydrogen precipitation of arsenic from aqueous medium\(^{(4)}\). In the presence of HCl, the kinetics of the following reaction were studied:

\[
2 \text{AsCl}_3 + 3 \text{H}_2 \rightarrow \ 2 \text{As} + 6 \text{HCl}
\]

The kinetics, over the range 100 - 225\(^\circ\)C and 15 to 250 atmospheres H\(_2\) gas, were found to be of the form:

\[
-d(\text{AsCl}_3)/dt = k(\text{AsCl}_3) (\text{pH}_2)^3.
\]

Interestingly, Ipatiew found the rate of reduction to increase with increased HCl concentration, which is probably related to the hydrolysis characteristics of arsenic.
Research personnel at the St. Joseph Lead Company, Zinc Smelting Division, have also studied the problem by selective oxidation, controlled acidification of leach plant acid batches, zinc dust additions to acid solutions, and over-feeding of neutral batches (5, 6, 7, 8, 9). These studies did not result in determining a satisfactory method for removing arsenic from aqueous solutions.
EXPERIMENTAL MATERIALS AND PROCEDURES

Materials:

Reagent grade chloride salts of cadmium, cupric, zinc, ferrous, and ferric iron were used in one part of this investigation.

Reagent grade cobalt, copper, and iron powders (325 x 400 mesh) were also used.

Conductivity water was used in all portions of the study. This water, made by passing distilled water through an ion exchange column containing Amberlite MB-3, had an average measured conductivity of one micromho.

Duolite A-30B, an intermediate base resin with an ion exchange capacity of 2.6 meq/ml, was used in the ion exchange portion of the investigation.

Agitation of 1700 rpm was used in all of the experiments and was effected with a Precision Scientific overhead stirrer.
Procedures:

The experimental work was divided into a number of general categories, and the procedures employed in these are described separately.

A. Iron Cementation

1. 39.564 mg of arsenic trioxide were dissolved in 10 ml of 6.25 N sodium hydroxide and 355 ml of water and 25 ml of 3 M sulfuric acid were added.

2. A calculated amount of 0.0646 N sodium chlorate solution was added to cause the desired amount of arsenic oxidation.

3. The arsenic solution was allowed to stand for 12 hours.

4. A 25 ml aliquot of the arsenic solution was taken and titrated with 9.72 x 10^{-3} N ceric sulfate. Two drops of 0.01 M osmium tetroxide were added as a catalyst, and one drop of ferroin was added as an indicator. The actual amount of arsenic oxidation was calculated (10).

5. The pH of the solution was adjusted with sodium hydroxide to pH 2.0.

6. A 25 ml aliquot was taken for head sample arsenic analysis.

7. 5 ml of 3.75 x 10^{-7} molar Fe^{2+} solution was added.
8. The volume and temperature of the solution were recorded.

9. Iron powder was added to the solution. The amount of iron powder (325 x 400 mesh) added was equivalent to 100% excess of the theoretical required amount.

10. The pH of the arsenic solution was adjusted to the desired value.

11. The solution was agitated for the desired time, the final volume was measured, and a 25 ml aliquot was removed for arsenic analysis.

12. The final pH of the solution was recorded.

B. Metal Ion Precipitation

The following procedure was used in the metal ion precipitation experiments:

1. 49.500 mg of arsenic trioxide were dissolved in 25 ml of 6.25 N sodium hydroxide and 153 ml of water plus 62 ml of 3 M sulfuric acid were added.

2. 15 ml of 0.646 N sodium chlorate solution were added for 100% arsenic oxidation.

3. The arsenic solution was allowed to stand for 12 hours.

4. A 15 ml aliquot of the arsenic solution was removed and titrated with $9.72 \times 10^{-3}$ N ceric sulfate. Two drops of 0.01 M osmium tetroxide was added as a
catalyst, and one drop of ferroin was added as an indicator. The actual amount of arsenic oxidation was calculated.

5. The pH of the solution was adjusted with sodium hydroxide to the desired value for the experiment.

6. A calculated amount of metal ion solution (zinc, cupric, cadmium, ferrous, or ferric) was added to give a concentration of $10^{-2}$ molar metal in 250 ml of solution volume.

7. The pH of the solution was rechecked, and the solution was agitated for 15 minutes.

8. The suspension was allowed to settle for two hours and filtered through a number 54 filter paper.

9. A 25 ml aliquot was removed from the filtrate for arsenic analysis.

C. Ion Exchange

The following procedure was used in the ion exchange separation of arsenic from solution:

1. 39.564 mg of arsenic trioxide were dissolved in 10 ml of 6.25 N sodium hydroxide, and 355 ml of water and 25 ml of 3 M sulfuric acid were added.
2. A calculated amount of 0.0646 N sodium chlorate solution was added to cause the desired amount of arsenic oxidation.

3. The arsenic solution was allowed to stand for 12 hours.

4. A 25 ml aliquot of the arsenic solution was removed and titrated with $9.72 \times 10^{-3}$ N ceric sulfate. Two drops of 0.01 M osmium tetroxide were added as a catalyst, and one drop of ferroin was added as an indicator. The actual amount of arsenic oxidation was calculated.

5. The pH was adjusted to the desired value with sodium hydroxide solution, and a 25 ml aliquot was removed for head sample arsenic analysis.

6. A 100 ml laboratory burette was converted into an ion exchange column by the insertion of a resin bed support in the bottom of the burette. The bed consisted of a layer of glass wool 1/2 inch deep, above which a layer of three mm diameter glass beads was placed. The glass bead level was coincident with the 100 ml mark on the burette.

7. Conductivity water was added to the column to a depth of several inches.

8. The wet resin, Duolite A-30B, was added to the column.
9. The column was rinsed with conductivity water until the settled resin depth was coincident with the 0 ml mark on the 100 ml burette.

10. One inch of water was left on the top of the bed to prevent resin disturbance during column operation.

11. The stopcock on the burette was opened, and 200 ml of 1.3 N MoO₄⁻ solution was fed through the column. The molybdate effluent was re-circulated through the ion exchange column once.

12. 350 ml of a predetermined arsenic solution was then percolated through the ion exchange column, with the stopcock placed in the full flow position.

13. After this volume of solution had been through the column, the effluent was re-circulated once.

14. A 25 ml aliquot of the final effluent was removed for arsenic analysis.

D. Molybdenum Blue Method For Arsenic Determination

All of the liquid aliquots for arsenic analysis taken from the iron cementation, metal ion precipitation, and ion exchange experiments were analyzed by the molybdenum blue method.
EXPERIMENTAL RESULTS

The first general area of investigation involved a study of arsenic removal from solution by cementation with metallic iron. The first series of experiments were conducted to determine the percent arsenic removal as a function of degree of arsenic oxidation. Figure 1 shows data determined with a $10^{-3}$ molar arsenic solution at pH 3 and ambient temperature with 325 x 400 mesh iron powder (approximately 40 microns). It can be noted that significant cementation is effected when arsenic is present in the +5 valence state.

Arsenic removal as a function of cementation time was examined next at pH 3. In this case all of the dissolved arsenic had been oxidized to As$^{+5}$. As shown in Figure 2, about 65 percent of the arsenic is removed after 8 hours under these conditions.

The effect of system pH is shown in Figure 3.
Figure 1. Relationship Between Arsenic Removal and Degree of Initial Arsenic Oxidation. 
10^{-3} M Arsenic; 25^\circ C; pH 3; 4-hour Cementation Time; 325 x 400 mesh Iron Powder.
Figure 2. Relationship Between Arsenic Removal and Cementation Time with Complete Arsenic Oxidation. pH 3; 25°C; 10^{-3}M Arsenic 325 x 400 mesh Iron Powder.
Figure 3. Relationship Between Arsenic Removal and pH with Complete Arsenic Oxidation. 10^{-3}M Arsenic; 25^\circ C; 4-hour Cementation Time; 325 x 400 mesh Iron Powder.
Arsenic removal increases with decreasing pH with a removal of 60 percent being effected at pH 2 and about 80 percent at pH 1. In this system all of the As$^{+3}$ was oxidized to As$^{+5}$ at the start of each experiment and a constant cementation time of 4 hours was used.

The rate of arsenic removal as a function of initial arsenic concentration is presented in Figure 4. When the initial concentration is $5 \times 10^{-3}$ mole/liter As$^{+5}$, $1.02 \times 10^{-3}$ mole/liter is cemented in 4 hours, while $4.30 \times 10^{-4}$ mole/liter is removed when the system contains $5 \times 10^{-4}$ mole/liter As$^{+5}$.

Copper cementation of arsenic was also investigated. Four experiments were conducted in duplicate at constant pH with two cementation times and two degrees of initial oxidation. The data for this series of experiments are listed in Table 1, and it can be seen that about 15 percent removal was obtained even with a cementation time of 4 hours.

Similar experiments were conducted with cobalt metal powder and as shown in Table 2, arsenic removal is low under these conditions.

Arsenic removal by precipitation as metal arsenates was also examined. In this work precipitates of ferrous, ferric, zinc, cupric, and cadmium arsenates were obtained at different values of pH. In each case, arsenic, which had been completely oxidized to As$^{+5}$, was present at $5 \times 10^{-2}$ mole per liter, and the metal ion was present at $1 \times 10^{-2}$
Figure 4. Relationship Between Arsenic Removal and Initial Arsenic Concentration with Complete Arsenic Oxidation. pH 3; 25°C; 4-hour Cementation Time; 325 x 400 mesh Iron Powder.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solution pH</th>
<th>Amount Arsenic Oxidation (%)</th>
<th>Cementation Time (hrs)</th>
<th>Arsenic Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>100</td>
<td>1.5</td>
<td>10.6</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>100</td>
<td>4.0</td>
<td>16.1</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>50</td>
<td>1.5</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>50</td>
<td>4.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

(1) Each experiment run in duplicate.

(2) Average result of samples in each experiment.
TABLE 2 - Arsenic Removal by Cobalt Cementation as a Function of Time and Percent Oxidation at Constant pH. $10^{-3}$ M Arsenic; 25°C; 325 x 400 mesh Cobalt Powder

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solution pH</th>
<th>Amount Oxidation (%)</th>
<th>Cementation Time (hrs)</th>
<th>Arsenic Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>100</td>
<td>1.5</td>
<td>9.2</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>100</td>
<td>4.0</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>50</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>50</td>
<td>4.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>

(1) Each experiment run in duplicate.

(2) Average result of samples in each experiment.
mole per liter. See Figures 5, 6, 7, 8 and 9. Arsenic removal was increased with increased values of pH. In the case of precipitation with Zn\(^{++}\), (Figure 8), about 35 percent of the arsenic was removed at pH 2, while about 75 percent was obtained at pH 7. Zinc and ferric iron appeared to be the most effective of those metal ions examined, while cadmium was the least effective.

Ion exchange was also studied as a means of removing arsenic from aqueous solution. As shown in Figure 10, extraction of arsenic increased with decreasing pH and also with degree of initial oxidation.
Figure 5. Relationship Between Arsenic Removal and pH at 25°C with $10^{-2}$M Cd$^{++}$ and $5.0 \times 10^{-3}$M As$^{3+}$. 

Figure 6. Relationship Between Arsenic Removal and pH at 25°C with $10^{-2}$ M Fe$^{++}$ and $5.0 \times 10^{-2}$ M As$^{+5}$. 
Figure 7. Relationship Between Arsenic Removal and pH at 25°C with $10^{-2}$ M Cu$^{++}$ and $5.0 \times 10^{-2}$ M As$^{+5}$. 
Figure 8. Relationship Between Arsenic Removal and pH at 25°C with $10^{-2}$ M Zn$^{++}$ and $5.0 \times 10^{-2}$ M As$^{+5}$. 
Figure 9. Relationship Between Arsenic Removal and pH at 25°C with $10^{-2}$ M Fe$^{+++}$ and $5.0 \times 10^{-2}$ M As$^{5+}$. 
Figure 10: Relationship Between Arsenic Removal by Ion Exchange and pH at 25°C. 10^{-3} M Arsenic Solution.
DISCUSSION OF RESULTS

Arsenic like most other Group V-A elements does not exist as a simple cation in solution; rather, it combines with oxygen to form various complex anions. The form of anion depends both on pH and state of oxidation of arsenic. This fact may be seen from the following reduction equilibria (12):

\[
\text{HAsO}_2 + 3\text{H}^+ + 3e^- \rightleftharpoons \text{As} + 2\text{HOH}; \quad E^o = +0.248 \text{ volt} \quad \text{(Eq. 1)}
\]

\[
2\text{H}_3\text{AsO}_4 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{As}_2\text{O}_3 + 5\text{HOH}; \quad E^o = +0.581 \text{ volt} \quad \text{(Eq. 2)}
\]

\[
\text{H}_3\text{AsO}_4 + 5\text{H}^+ + 5e^- \rightleftharpoons \text{As} + 4\text{HOH}; \quad E^o = +0.370 \text{ volt} \quad \text{(Eq. 3)}
\]

\[
\text{H}_3\text{AsO}_4 + 8\text{H}^+ + 4\text{Fe}^{++} \rightleftharpoons \text{AsH}_3 + 4\text{Fe}^{++} + 4\text{HOH};
\]

\[
\Delta F^o = -82.2 \text{ kcal/mole As} \quad \text{(Eq. 4)}
\]
Of importance also are the arsenic acid equilibria:

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \quad K = 2.5 \times 10^{-4} \quad \text{(Eq. 5)}$$

$$H_2AsO_4^- \rightleftharpoons H^+ + HASO_4^- \quad K = 5.6 \times 10^{-8} \quad \text{(Eq. 6)}$$

$$HASO_4^- \rightleftharpoons H^+ + AsO_4^{3-} \quad K = 3.0 \times 10^{-13} \quad \text{(Eq. 7)}$$

Cementation studies were conducted with iron, cobalt, and copper at various values of pH. Calculations can be made utilizing the above equilibria to determine which arsenic species was formed during cementation. As a sample calculation, the iron-arsenic system will be used at pH 2.

From Eq. 1,

$$\text{HAsO}_2 + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{As} + 2\text{HOH} \quad E^0 = +0.248 \text{ volt}$$

and

$$\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^- \quad E^0 = +0.440 \text{ volt}.$$

Eq. 8 results from adding half cells.

$$\frac{\text{HAsO}_2 + 3\text{Fe} + 3\text{H}^+ \rightleftharpoons \text{As} + 3\text{Fe}^{2+} + 2\text{HOH}}{2} \quad \text{(Eq. 8)}$$

$$\Delta F^0 = -47.6 \text{ kcal/mole As}$$
Since \( \Delta F = \Delta F^0 + RT \ln Q \), assuming the following conditions:

\[ \text{Fe}^{++} = 1.0 \times 10^{-6} \text{ M}, \text{pH} = 2, \text{and HAsO}_2 = 1.0 \times 10^{-3} \text{ M}, \]

\( \Delta F = -47.6 \text{ kcal}. \)

The value for the \( \text{Fe}^{++} \) concentration is simply a nominal low value; \( 1 \times 10^{-4} \) or \( 1 \times 10^{-7} \) mole/liter could have been used equally as well. This calculation shows thermodynamically that \( \text{As}^{+3} \) should be reduced to arsenic metal with metallic iron at pH 2.

Experimentally, it was found that the rate of cementation was greater when the arsenic had been oxidized to \( \text{As}^{+5} \). With reference to Eq. 2 and 3, it can be noted that \( \text{As}^{+5} \) can be reduced to either \( \text{As}_2\text{O}_3 \) or to arsenic metal. Whether the oxide or metal will be produced will be determined by the reaction which results in the greater decrease in free energy. Calculations, similar to those involving Eq. 1 and the iron-ferrous couple at pH 2 with \( 1 \times 10^{-3} \) molar arsenic and \( 1 \times 10^{-6} \) molar \( \text{Fe}^{++} \) present initially, revealed the following results:

\[ \text{H}_3\text{AsO}_4 + \text{Fe} + 2\text{H}^+ \rightarrow \frac{1}{2} \text{As}_2\text{O}_3 + \text{Fe}^{++} + 5 \text{HOH}; \Delta F = -45.7 \frac{2}{2} \text{ kcal} \]

and

\[ \frac{1}{2} \text{H}_3\text{AsO}_4 + 5 \text{Fe} + 5\text{H}^+ \rightarrow \frac{1}{2} \text{As} + 5 \text{Fe}^{++} + 4 \text{HOH}; \Delta F = -96.4 \text{ kcal} \]
Arsenic acid should be reduced to arsenic metal rather than arsenious oxide under these conditions.

Eq. 4 shows the reduction of arsenic acid to arsine gas with metallic iron. The formation of this gas is, of course, undesirable in cementation, and the following thermodynamic calculations show that it should form in preference to arsenic metal only with extremely small partial pressures of arsine gas. That is,

\[
H_3AsO_4 + 4 \text{Fe} + 8H^+ \rightarrow AsH_3 + 4 \text{Fe}^{++} + 4 \text{HOH};
\]

\[\Delta F^0 = -82.2 \text{ kcal/mole As}\]

For this reaction to occur, \(\Delta F\) will have to be greater than -96.4 kcal, and in the system under study, i.e. pH 2, \(10^{-3}\) molar \(H_3AsO_4\), and \(10^{-6}\) molar \(\text{Fe}^{++}\);

\[
\Delta F = \Delta F^0 + 1.364 \log (\text{Fe}^{++})^4 (p\text{AsH}_3)/(H^+)^8 (H_3AsO_4)
\]

\[-96.4 = -82.2 + 1.364 (-5) + 1.364 \log p\text{AsH}_3\]

The partial pressure of \(\text{AsH}_3\) will have to be less than \(4 \times 10^{-6}\) atmosphere for this reaction to occur in preference to cementation to metallic arsenic. Additional values, calculated in a similar manner for other values of pH and initial \(\text{Fe}^{++}\) concentration, are listed in Table 3.
TABLE 3 - Maximum Partial Pressure of Arsine for Arsine Production (Eq. 4) to take Precedence over Arsenic Metal Cementation (Eq. 3) with $10^{-3}$ molar $H_3AsO_4$ at Various Values of pH and Two Different Initial Fe$^{++}$ Concentrations

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe$^{++}$ (M)</th>
<th>$H_3AsO_4$ (M)</th>
<th>pAsH$_3$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$10^{-6}$</td>
<td>$10^{-3}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>1</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
<td>$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$10^{-6}$</td>
<td>$10^{-3}$</td>
<td>$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
<td>$4 \times 10^{-9}$</td>
</tr>
<tr>
<td>3</td>
<td>$10^{-6}$</td>
<td>$10^{-3}$</td>
<td>$8 \times 10^{-10}$</td>
</tr>
<tr>
<td>3</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
<td>$6 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Similar calculations are presented in Table 4 for arsenic in the +3 oxidation state.
TABLE 4 - Maximum Partial Pressure of Arsine for Arsine Production to take Precedence over Arsenic Metal Cementation with \(10^{-3}\) molar HAsO\(_2\) at Various Values of pH and Two Different Initial Fe\(^{++}\) Concentrations

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe(^{++})(M)</th>
<th>HAsO(_2)(M)</th>
<th>pAsH(_3)(atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(10^{-6})</td>
<td>(10^{-3})</td>
<td>(6.3 \times 10^{-3})</td>
</tr>
<tr>
<td>1</td>
<td>(10^{-4})</td>
<td>(10^{-3})</td>
<td>(7.9 \times 10^{-8})</td>
</tr>
<tr>
<td>2</td>
<td>(10^{-6})</td>
<td>(10^{-3})</td>
<td>(6.3 \times 10^{-6})</td>
</tr>
<tr>
<td>2</td>
<td>(10^{-4})</td>
<td>(10^{-3})</td>
<td>(6.3 \times 10^{-12})</td>
</tr>
<tr>
<td>3</td>
<td>(10^{-6})</td>
<td>(10^{-3})</td>
<td>(6.3 \times 10^{-9})</td>
</tr>
<tr>
<td>3</td>
<td>(10^{-4})</td>
<td>(10^{-3})</td>
<td>(5.0 \times 10^{-16})</td>
</tr>
</tbody>
</table>

Thermodynamically, arsenic metal should be produced readily by iron cementation when arsenic is in the +3 state. Experimentally, however, almost no cementation occurs, which indicates that the kinetics are not favorable under these conditions and also that arsenious oxide is probably not one of the intermediate reduction steps when As\(^{+5}\) is reduced by Fe.
The data contained in Figure 3 show that the rate of cementation increases as the pH is reduced. This result is anticipated with any of the cementation reactions, in that increased hydrogen ion concentration will tend to drive the reactions to the right.

Copper was less effective in reducing arsenic acid than was iron, and this is expected thermodynamically. From Eq. 2 and the copper-cupric couple,

\[ \frac{H_3AsO_4 + 5Cu + 5H^+}{2} \rightarrow \frac{As + 5Cu^{++} + 4 HOH}{2} \]

\[ \Delta F = -6.9 \text{ kcal/mole As} \]

This free energy calculation also involved pH 2, $10^{-3}$ molar arsenic, and $10^{-6}$ molar Cu$^{++}$ ion initially.

Precipitation of arsenic as metal arsenates was also examined, and because of the various forms of arsenic acid that may exist, depending on system pH, precipitation was studied at pH 2, 4.7, and 7. With reference to Eq. 5, 6, and 7, it can be seen that at pH 2, the predominant species of arsenic acid is $H_3AsO_4^-$, and at pH 4.7, di-hydrogen arsenate, $H_2AsO_4^-$. At pH 7, the mono- and di-hydrogen arsenates are present at about the same concentration. Arsenate ion, $AsO_4^{3-}$, will be present predominantly only at high values of pH.
Precipitation was not attempted beyond pH 7 due to the insolubility of the various metal hydroxides. A list of the dissociation equilibria of these hydroxides is given below (13, 14, 15, 16, 17):

\[
\begin{align*}
\text{Fe(OH)}_3 (s) & \rightleftharpoons \text{Fe}^{+++} + 3\text{OH}^- \\
\text{Cu(OH)}_2 (s) & \rightleftharpoons \text{Cu}^{++} + 2\text{OH}^- \\
\text{Zn(OH)}_2 (s) & \rightleftharpoons \text{Zn}^{++} + 2\text{OH}^- \\
\text{Fe(OH)}_2 (s) & \rightleftharpoons \text{Fe}^{++} + 2\text{OH}^- \\
\text{Cd(OH)}_2 (s) & \rightleftharpoons \text{Cd}^{++} + 2\text{OH}^-
\end{align*}
\]

\[
\begin{align*}
K &= 6.0 \times 10^{-38} \\
K &= 1.6 \times 10^{-19} \\
K &= 4.5 \times 10^{-17} \\
K &= 1.8 \times 10^{-15} \\
K &= 2.0 \times 10^{-14}
\end{align*}
\]

The precipitates obtained at pH 2 are probably those of the metal - di-hydrogen arsenates. No precipitation of the metal hydroxides will have occurred under these conditions, and between 20 percent of the arsenic was removed with $10^{-2}$ molar Cd$^{++}$ and 40 percent with $10^{-2}$ molar Fe$^{+++}$. Assuming that the metal - di-hydrogen arsenates are quite insoluble, and that two moles of di-hydrogen arsenate are consumed with one mole of Cd$^{++}$, this arsenic removal represents a recovery of about 50 percent of the amount that could be removed with these additions.
In the case of Fe$^{+++}$ iron (Figure 9), assuming the precipitate to be Fe(H$_2$AsO$_4$)$_3$, the 40 percent removal represents a removal of about 67 percent of the amount that could be removed.

When the pH is increased to 4.7, the concentration of H$_2$AsO$_4^-$ is increased, and the amount of arsenic removed from solution is increased.

At pH 7, however, removals of about 60, 65, and 75 percent were obtained with Fe$^{+++}$, Cu$^{++}$, and Zn$^{++}$ ion additions, respectively. This represents about the maximum amount of arsenic that could be removed with this addition of Fe$^{+++}$ iron (assuming again, Fe(H$_2$AsO$_4$)$_3$), but it should be mentioned that the precipitate was brown, indicating precipitation of some ferric hydroxide. In addition, at this pH, the iron arsenate precipitated would surely be a basic iron arsenate, so that the amount of arsenic removed is actually more than would be expected. These facts suggest then that some of the arsenic was removed by occlusion of some form of arsenate in the precipitate, or perhaps some arsenic is adsorbing on the precipitate. These phenomena are even more apparent with the additions of copper and zinc, where far more removal was obtained than could be obtained by precipitation under these conditions. Zinc and copper hydroxides may have been present at pH 7; in water, for example, both hydroxides would have precipitated under these conditions.
With cadmium and ferrous, though, the precipitates obtained even at pH 7 would have to be the metal mono- or di-hydrogen arsenates. In view of the fact that more arsenic was removed than should have been removed theoretically, some of the arsenic was either occluded or adsorbed on the precipitate.

Arsenic was found to extract on an anionic exchange resin in acid media after pre-treating the resin with sodium molybdate. Since extraction increased with lower pH, exchange is probably related to the polymerization of molybdate in acid media, which may be seen from the following equilibria:\(^{18}\):

\[
\begin{align*}
\text{MoO}_4^{2-} + H^+ \rightleftharpoons & \text{HMO}_4^- & K = 2.0 \times 10^4 \\
7\text{MoO}_4^{2-} + 8H^+ \rightleftharpoons & \text{Mo}_7\text{O}_{24}^{6-} + 4 \text{HOH} & K = 5.0 \times 10^{5.7} \\
\text{Mo}_7\text{O}_{24}^{6-} + H^+ \rightleftharpoons & \text{HMO}_7\text{O}_{24}^{-5} & K = 2.1 \times 10^4 \\
\text{HMO}_7\text{O}_{24}^{-5} + H^+ \rightleftharpoons & \text{H}_2\text{Mo}_7\text{O}_{24}^{-4} & K = 5.0 \times 10^3
\end{align*}
\]

Molybdenum occurs as MoO\(_4^{2-}\) predominantly in solution above say pH 5; below this pH polymers are formed. Since arsenic, fully oxidized, will be present as undissociated H\(_3\)AsO\(_4\)\(^{12}\) at pH 2, where about 50 percent extraction is obtained, it is probable that simple anion exchange is not occurring.
It has been observed in other systems, however, that polymers more complex than those listed above can be formed under certain conditions. In the presence of Na\(^+\) at pH 1, for example, the polymolybdate, Na\(_3\)H\(_7\)Mo\(_2\)\(_4\)\(\cdot\)12 H\(_2\)O, has been reported\(^{(19)}\). It would seem that arsenic might be functioning in a similar manner, but since arsenic will be present as a complex anion, should this phenomenon be occurring, the exchange mechanism must be very complex.
SUMMARY AND CONCLUSIONS

The results of this investigation can be summarized with the following conclusions:

1. Dissolved arsenic can be cemented from solution by iron powder, according to the following reaction:

   \[ 2H_2AsO_4^- + 5Fe + 10H^+ \rightarrow 2As + 5Fe^{++} + 8 \text{HOH} \]

2. The higher the state of arsenic oxidation, the greater the rate of cementation.

3. Cementation is increased with decreasing pH.

4. Arsine gas is not produced under these conditions.

5. Copper and cobalt are less effective than iron in removing dissolved arsenic by cementation.

6. Removal of arsenic from solution by precipitation can be effected with any of a number of metal ions. The precipitate is probably a metal-hydrogen arsenate.

7. Some extraction of arsenic is effected in acid media with ion exchange by loading the anion exchanger with molybdate prior to feeding the arsenic solution.
The extraction of arsenic was not great even in the pure system, so that this technique does not look too promising. As a matter of fact, separation of arsenic from solution by ion exchange techniques does not look promising under any conditions. At higher values of pH, dissociated species of arsenic acid will be present, but in a normal leach liquor concentrations of anions will be very high with respect to arsenic and preferential exchange of arsenic will be most unlikely.
BIBLIOGRAPHY


