ABSTRACT

The presence of antimony and arsenic in many mineral sulfides leads to a need to understand the way in which both species react in those processes which have been developed for extracting valuable elements from those minerals.

This paper deals in particular with the precipitation reactions of antimonious, antimonic, arsenious and arsenic species in sulfuric acid solution in relation to various hydrometallurgical processes.

The system \( \text{Sb}_2\text{O}_3 (x:3,5) - \text{As}_2\text{O}_5 (y:3,5) - \text{SO}_3\text{-H}_2\text{O} \) has been investigated over a wide range of sulfuric acid concentration. The solubility and stability ranges of \( \text{Sb}_2\text{O}_3, \text{Sb}_2\text{O}_5, \text{As}_2\text{O}_3 \) and compounds formed in the system have been determined at 25°C. Furthermore, the behavior of antimony and arsenic in sulfuric acid solution is discussed.

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ABSTRACT

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This paper deals in particular with the precipitation reactions of antimonious, antimonic, arsenious and arsenic species in sulfuric acid solution in relation to various hydrometallurgical processes.

The system \( \text{Sb}_2\text{O}_x (x:3,5) - \text{As}_2\text{O}_y (y:3,5) - \text{SO}_3 - \text{H}_2\text{O} \) has been investigated over a wide ranges of sulfuric acid concentration. The solubility and stability ranges of \( \text{Sb}_2\text{O}_3, \text{Sb}_2\text{O}_5, \text{As}_2\text{O}_3 \) and compounds formed in the system have been determined at 25°C. Furthermore, the behavior of antimony and arsenic in sulfuric acid solution is discussed.

INTRODUCTION

In copper smelters in Japan, various complex sulfide concentrates are treated. An appreciable quantity of arsenic and antimony is accompanied in the concentrates. Control of both elements is very important for producing high grade copper metal. Many new processes
for their treatment have been developed and installed in some smelters(1),(2), but there are still many problems to be solved.

Onahama Smelter(3) has been producing pure arsenic trioxide by vacuum-cooling the filtrate of liquor (diluted sulfuric acid saturated with \( \text{As}_2\text{O}_3 \)) from a plant for washing converter gas. It is very important for production of pure arsenic trioxide to determine the solubility of arsenic trioxide in concentrated sulfuric acid and to examine the contamination with antimony.

Recently, arsenic and antimony contents tend to increase in a conventional electrolyte for the electrowinning of copper. The elements form often a floating slime which lowers the quality of electrolytic copper(4).

To clarify the behavior of antimony and arsenic in sulfuric acid solution for solving such problems in the hydrometallurgical operations, it is necessary to know the equilibrium for the following systems.

\[(1) \text{The system } \text{Sb}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(2) \text{The system } \text{Sb}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(3) \text{The system } \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(4) \text{The system } \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(5) \text{The system } \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(6) \text{The system } \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(7) \text{The system } \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}\]
\[(8) \text{The system } \text{Sb}_2\text{O}_5 - \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O}\]

In this paper, the equilibrium for these systems is investigated.

THE EQUILIBRIUM FOR THE SYSTEM Sb(III,V) - As(III,V) - SO_3 - H_2O

1. The system \( \text{Sb}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O} \)

The system \( \text{Sb}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O} \) is of great interest in chemical analytical procedures and in the industry of production of various
antimony compounds. There is several information in the literature on the system Sb$_2$O$_3$ - SO$_3$ - H$_2$O. A variety of antimony(III) sulfates are produced by reacting Sb$_2$O$_3$ and H$_2$SO$_4$. The results reported on the chemical composition and solubility of these compounds are inconsistent and contradictory.

The equilibrium for the system Sb$_2$O$_3$ - SO$_3$ - H$_2$O was examined by shaking the mixture of antimony trioxide and sulfuric acid solution (0 - 1820 g/l H$_2$SO$_4$) at 25°C for one month. The results from the chemical analysis of solutions and precipitates are plotted in Figure 1 together with data by Gospodinov et al. (5) at 100°C. Various compounds are formed in the system Sb$_2$O$_3$ - SO$_3$ - H$_2$O at both temperatures.

Figure 1(a) shows that the SO$_3$/Sb$_2$O$_3$ molar ratio in the precipitates is either 0.50, 0.66, 1.0, 2.0 or 3.0, indicating the existence of the five compounds. These compounds are represented without indicating hydration as 2Sb$_2$O$_3$·SO$_3$, 3Sb$_2$O$_3$·2SO$_3$, Sb$_2$O$_3$·SO$_3$, Sb$_2$O$_3$·2SO$_3$ and Sb$_2$O$_3$·3SO$_3$. At 25°C, Sb$_2$O$_3$ is stable as a solid in the range of 0 - 20 g/l H$_2$SO$_4$, 2Sb$_2$O$_3$·SO$_3$ in 30 - 360 g/l H$_2$SO$_4$, 3Sb$_2$O$_3$·2SO$_3$ in 400 - 560 g/l H$_2$SO$_4$, Sb$_2$O$_3$·SO$_3$ in 590 - 880 g/l H$_2$SO$_4$, Sb$_2$O$_3$·2SO$_3$ in 950 - 1280 g/l H$_2$SO$_4$ and Sb$_2$O$_3$·3SO$_3$ in 1370 - 1800 g/l H$_2$SO$_4$. Below 800 g/l H$_2$SO$_4$, the results agree well with those obtained at room temperature by Hintermann et al. (6).

In Figure 1(b), Sb$_2$O$_3$·SO$_3$ and Sb$_2$O$_3$·2SO$_3$ have the highest solubility in 880 g/l and in 1280 g/l H$_2$SO$_4$ at 25°C, respectively. Furthermore, the solubility of these compounds will increase with an increase in temperature.

The data of Figure 1 are also shown in Figure 2 as a ternary diagram of the system Sb$_2$O$_3$ - SO$_3$ - H$_2$O at 25°C. The typical X-ray diffraction patterns of their compounds are shown in Figure 3.
2. The system \( \text{Sb}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \)

There is very little data on the system \( \text{Sb}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \).

The experiment was carried out by shaking the mixture of antimony pentaoxide (amorphous) and sulfuric acid solution (0 - 1540 g/l \( \text{H}_2\text{SO}_4 \)) at 25°C for one month. X-ray diffraction confirmed the nonexistence of antimony(V) sulfate at 25°C. Figure 4 shows that \( \text{Sb}_2\text{O}_5 \) (amorphous) is highly soluble at 1100 g/l \( \text{H}_2\text{SO}_4 \) at 25°C.

3. The system \( \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O} \)

The system \( \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O} \) is of importance in many hydrometallurgical processes for separation and recovery of arsenic as arsenic trioxide from acidic solutions.

The equilibrium for this system was examined by shaking the mixture of arsenic trioxide (cubic) and sulfuric acid solution (0 - 1770 g/l \( \text{H}_2\text{SO}_4 \)) at 25°C for two weeks. X-ray diffraction confirmed the existence of \( \text{As}_2\text{O}_3 \) and \( \text{As}_2\text{O}_3\cdot\text{SO}_3 \) as a solid between 0 to 1550 g/l \( \text{H}_2\text{SO}_4 \) and above 1340 g/l \( \text{H}_2\text{SO}_4 \), respectively. X-ray diffraction pattern of arsenic(III) sulfate, \( \text{As}_2\text{O}_3\cdot\text{SO}_3 \), agreed with that published by JCPDS (Card File No.22-072). The concentration of arsenic (III) in solutions are plotted in Figure 5 together with data by Inomata et al. (7) and Zieren Company (7). The solubility of \( \text{As}_2\text{O}_3 \) decreases significantly with an increase in concentration of sulfuric acid in the range of 100 to 1080 g/l \( \text{H}_2\text{SO}_4 \), but increases slightly in the range of 1080 to 1280 g/l \( \text{H}_2\text{SO}_4 \). Above 1340 g/l \( \text{H}_2\text{SO}_4 \) in which \( \text{As}_2\text{O}_3\cdot\text{SO}_3 \) is stable, the concentration of arsenic (III) is very low.

On the basis of the chemical analysis of solutions and precipitates a ternary diagram of the system \( \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O} \) at 25°C was constructed as shown in Figure 6.

4. The system \( \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \)

There is very little data on the system \( \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \).
Menzies et al.(8) reported that arsenic pentaoxide is stable in water as $\text{As}_2\text{O}_5\cdot4\text{H}_2\text{O}$ below $20^\circ\text{C}$ and as $3\text{As}_2\text{O}_5\cdot5\text{H}_2\text{O}$ above $40^\circ\text{C}$. Arsenic pentaoxide is highly soluble in water (dissolved in water up to 570 g/l As(V) at $25^\circ\text{C}$)(9). It can therefore be presumed that arsenic pentaoxide is highly soluble in sulfuric acid solution.

5. The system $\text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}$

Very little is known about the system $\text{Sb} - \text{As} - \text{SO}_3 - \text{H}_2\text{O}$.

The equilibrium for the system $\text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}$ was examined by shaking the mixture of antimony trioxide(orthorhombic), arsenic trioxide(cubic) (with $\text{Sb}_2\text{O}_3/\text{As}_2\text{O}_3$ molar ratio : 0.10/0.10) and sulfuric acid solution (0 - 1690 g/l $\text{H}_2\text{SO}_4$) at $25^\circ\text{C}$ for one month.

X-ray diffraction confirmed that $\text{Sb}_2\text{O}_3$ or $2\text{Sb}_2\text{O}_3\cdot\text{SO}_3$ and $\text{As}_2\text{O}_3$ (monoclinic) exist as a solid in the range of 0 - 450 g/l $\text{H}_2\text{SO}_4$, while antimony(III) sulfates and $\text{As}_2\text{O}_3$ (cubic) exist in the range of 500 - 1600 g/l $\text{H}_2\text{SO}_4$ at $25^\circ\text{C}$.

The results from the chemical analysis of solutions and precipitates are plotted in Figure 7. The stability range and solubility of antimony(III) sulfates in sulfuric acid solution are invariable in the presence of $\text{As}_2\text{O}_3$ (monoclinic or cubic). The solubility of $\text{As}_2\text{O}_3$ lowers in the range of 0 - 450 g/l $\text{H}_2\text{SO}_4$ in which the crystal form of $\text{As}_2\text{O}_3$ is changed from cubic to monoclinic by the presence of $\text{Sb}_2\text{O}_3$ or $2\text{Sb}_2\text{O}_3\cdot\text{SO}_3$. But the solubility of $\text{As}_2\text{O}_3$ is invariable in the range of 500 - 1600 g/l $\text{H}_2\text{SO}_4$ in which $\text{As}_2\text{O}_3$ (cubic) is stable even in the presence of antimony(III) sulfates.

The results described above suggest that in the presence of large amount of antimony(III) in sulfuric acid solution, arsenic trioxide will be contaminated with antimony (III) because of the very low solubility of antimony(III) sulfates.
6. The system \( \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \)

1) The system \( \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{H}_2\text{O} \)

The equilibrium for the system \( \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{H}_2\text{O} \) was examined by shaking the mixture of antimony trioxide (orthorhombic) and arsenic acid solution (with \( \text{Sb}_2\text{O}_3/\text{As}_2\text{O}_5 \) molar ratio: \( 0.25/0.10 \) - \( 0.10/0.10 \)) at \( 25^\circ\text{C} \) for three months. The results are plotted in Figure 8 as a function of pH.

Figure 8(a) shows the existence of antimony(III) arsenate having \( \text{Sb}_2\text{O}_3/\text{As}_2\text{O}_5 \) molar ratio of 1.0 in the pH range of 1.6 - 2.3. The formula of the compound will be represented as \( \text{SbAsO}_4 \) without hydrate by the chemical analysis and by the thermoanalysis shown in Figure 9. The X-ray diffraction pattern of \( \text{SbAsO}_4 \) shown in Figure 10 is in disagreement with that published by JCPDS (Card File No. 1-728).

The solubility of \( \text{SbAsO}_4 \) can be characterized by the reaction

\[
\text{SbAsO}_4(s) + 2\text{H}_2\text{O} = \text{HSbO}_2 + \text{H}_3\text{AsO}_4
\]

The solubility product for \( \text{SbAsO}_4 \) is given by

\[
K_{sp} = [\text{HSbO}_2][\text{H}_3\text{AsO}_4]
\]

By calculating from data of Figure 8(b), the value of \( K_{sp} \) is \( 10^{-6.67} \) and the value of the standard free energy for formation of \( \text{SbAsO}_4 \) is - 176.2 kcal/mol.

By using this free energy data, the equilibrium log \( [\text{As}(\text{V})] - \text{pH} \) diagram was calculated and illustrated in Figure 11. An increase in concentration of total antimony(III) in acidic solution leads to further stabilization of \( \text{SbAsO}_4 \).

2) The system \( \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \)

The equilibrium for the system \( \text{Sb}_2\text{O}_3 - \text{As}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O} \) was examined by shaking the mixture of antimony trioxide (orthorhombic), arsenic acid solution (with \( \text{Sb}_2\text{O}_3/\text{As}_2\text{O}_5 \) molar ratio: \( 0.10/0.10 \)) and sulfuric acid solution (0 - 1410 g/l \( \text{H}_2\text{SO}_4 \)) at \( 25^\circ\text{C} \) for one
The results are plotted in Figure 12.

Figure 12(a) shows the existence of three compounds having the Sb$_2$O$_3$/As$_2$O$_5$ molar ratio of 1.0, 1.5 or 2.0. From the results of the chemical analysis, the formula of these compounds will be represented as SbAsO$_4$ formed in the range of 0 - 930 g/l H$_2$SO$_4$, 3Sb$_2$O$_3$·2As$_2$O$_5$·4SO$_3$ in 1020 - 1100 g/l H$_2$SO$_4$ and 2Sb$_2$O$_3$·As$_2$O$_5$·4SO$_3$ in 1150 - 1370 g/l H$_2$SO$_4$. X-ray diffraction patterns of these two antimony(III) arsenate sulfates are shown in Figure 13.

Figure 12(b) shows that the level of antimony(III) in sulfuric acid solution was reduced by the precipitation of SbAsO$_4$. Furthermore, the solubility behavior of SbAsO$_4$ in sulfuric acid solution (200 g/l H$_2$SO$_4$) is studied at 25°C. The results are shown in Figure 14. X-ray diffraction confirmed that only SbAsO$_4$ is formed at initial Sb$_2$O$_3$ / As$_2$O$_5$ molar ratio in the mixture below 1.0, while 2Sb$_2$O$_3$·SO$_3$ is formed together with SbAsO$_4$ at initial Sb$_2$O$_3$ / As$_2$O$_5$ molar ratio above 1.5.

Figure 14(b) shows that antimony(III) concentration equilibrated with the mixture of SbAsO$_4$ and 2Sb$_2$O$_3$·SO$_3$ become equal to the solubility of 2Sb$_2$O$_3$·SO$_3$. Corresponding to this antimony(III) concentration, arsenic(V) concentration trends toward a minimum value which is controlled by the solubility product of SbAsO$_4$.

Therefore, SbAsO$_4$ will be one of the constitutive compounds in the floating slime formed during the electrorefining of copper.

7. The systems Sb$_2$O$_5$ - As$_2$O$_3$ - SO$_3$ - H$_2$O and

Sb$_2$O$_5$ - As$_2$O$_5$ - SO$_3$ - H$_2$O

The experiments were carried out by varying the Sb$_2$O$_5$/As$_2$O$_3$ or As$_2$O$_5$ molar ratio in the mixture of Sb$_2$O$_5$·2H$_2$O and arsenious or arsenic acid solution and sulfuric acid solution (200 g/l H$_2$SO$_4$) at 25°C. The results proved the nonexistence of compounds of Sb$_2$O$_5$ with As$_2$O$_3$ or As$_2$O$_5$ in sulfuric acid solution.
CONCLUSION

In order to clarify the behavior of antimony and arsenic in sulfuric acid solution, the system $\text{Sb}_2\text{O}_x(\ x:3,5\ )-\ \text{As}_2\text{O}_y(\ y:3,5\ )-\ \text{SO}_3-\ \text{H}_2\text{O}$ at 25°C was investigated by mixing method. Six antimony sulfates in the system $\text{Sb}_2\text{O}_3-\ \text{SO}_3-\ \text{H}_2\text{O}$, one arsenic sulfate in the system $\text{As}_2\text{O}_3-\ \text{SO}_3-\ \text{H}_2\text{O}$ and one antimony arsenate and two antimony arsenate sulfates in the system $\text{Sb}_2\text{O}_3-\ \text{As}_2\text{O}_5-\ \text{SO}_3-\ \text{H}_2\text{O}$ were identified. The solubility and stability ranges of those compounds, $\text{Sb}_2\text{O}_3$, $\text{Sb}_2\text{O}_5$ and $\text{As}_2\text{O}_3$ were determined.

In production of arsenic trioxide from sulfuric acid solution containing a large amount of antimony(III) by crystallization, the produced arsenic trioxide will be contaminated with antimony(III) because of very low solubility of antimony(III) sulfates formed.

Only antimony(III) arsenates are formed as antimony arsenic compound in sulfuric acid solution. Therefore, $\text{SbAsO}_4$ which is stable below 900 g/1 $\text{H}_2\text{SO}_4$, is one of the constitutive compounds in the floating slime during the electrorefining of copper. To further know distinctly the mechanism of formation of the floating slime, more detailed studies will also be necessary in the presence of bismuth and copper at higher temperature.

REFERENCES

Fig. 1 (a) The $\text{SO}_3$/Sb$_2$O$_3$ molar ratio in precipitates
(b) The antimony(III) concentration in solution after equilibrating various mixtures of antimony trioxide and sulfuric acid solution at 25 and 100°C.

Fig. 2 The system Sb$_2$O$_3$ – SO$_3$ – H$_2$O at 25°C.
Fig. 3 X-ray diffraction patterns of compounds in the system Sb$_2$O$_3$ - SO$_3$ - H$_2$O.
Fig. 4 The solubility of Sb$_2$O$_5$ (amorphous) in sulfuric acid solution at 25°C.

Fig. 5 The arsenic(III) concentration in solution after equilibrating various mixtures of arsenic trioxide and sulfuric acid solution at 25°C.
Fig. 6 The system $\text{As}_2\text{O}_3 - \text{SO}_3 - \text{H}_2\text{O}$ at 25°C.

Fig. 7 (a) The $\text{Sb}_2\text{O}_3/\text{As}_2\text{O}_3$ molar ratio in the precipitates
(b) The antimony(III) and arsenic(III) concentrations in solution after equilibrating mixture of antimony trioxide and arsenic trioxide at various sulfuric acid concentrations at 25°C.
Fig. 8 Relationship between pH and (a) the $\text{Sb}_2\text{O}_3/\text{As}_2\text{O}_5$ molar ratio in the precipitates and (b) the antimony(III) and arsenic(V) concentrations in solution after equilibrating various mixtures of antimony trioxide and arsenic acid solution at $25^\circ\text{C}$.

Fig. 9 X-ray diffraction pattern of $\text{SbAsO}_4$.

Fig. 10 Thermoanalytical curves of $\text{SbAsO}_4$. 
Fig. 11 Equilibrium log [As(V)] - pH diagram for the system Sb(III) - As(V) - H2O at 25°C.

Fig. 12 (a) The Sb2O3/As2O5 molar ratio in precipitates
(b) The antimony(III) and arsenic(V) concentrations in solution after equilibrating mixture of antimony trioxide and arsenic acid solution at various sulfuric acid concentrations at 25°C.
Fig. 13 X-ray diffraction patterns of antimony arsenate sulfates.

Fig. 14 (a) The Sb$_2$O$_3$/As$_2$O$_5$ molar ratio in precipitates
(b) The antimony(III) and arsenic(V) concentrations in solution after equilibrating various mixtures of antimony trioxide and arsenic acid solution in sulfuric acid solution, 200 g/l H$_2$SO$_4$, at 25°C.