Removal Mechanism in Anionic Co-precipitation with Hydroxides in Acid Mine Drainage Treatment

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Abstract
Acid mine drainage from approximately 80 abandoned or closed Japanese mines has been treated by neutralization over the last forty years. A more efficient and cost-effective treatment process is required, as the national government spends billions of yen each year to protect the environment from acid mine drainage discharge.

Surface complexation at the interface between hydroxides such as ferrihydrite or aluminum hydroxide and wastewater is the most important mechanism for the removal of dilute toxic ions. We have categorized the immobilization mechanism of inorganic toxic elements at the hydroxide solid/liquid interface into surface complexation and surface precipitation. We have introduced this concept using experimental methods to understand their mechanism, for example arsenate co-precipitation with ferrihydrite, fluorine co-precipitation with aluminum hydroxide, and boron co-precipitation with magnesium hydroxide. From detailed investigations using isotherm formation, X-ray diffractometry, and Fourier-transform infrared spectroscopy analysis, we found that co-precipitation achieved a more efficient removal of toxic anions than simple adsorption, because of surface precipitation or surface complexation of multiple complexes.

Key words: Co-precipitation, Surface complexation, Surface precipitation, Acid mine drainage

1. Introduction

Acid mine drainage (AMD) is a major source of mining pollution in Japan and globally. In Japan, AMD occurs in approximately 450 mines and wastewater treatment facilities are in operation at approximately 80 mines. General treatment processes for AMD consist of neutralization and solid/liquid separation. This process requires large amounts of neutralizer, such as slaked lime, and flocculating agent, as well as substantial amounts of energy over many years. It also generates voluminous waste sludge that contains heavy metals in the form of hydroxides. To reduce this costly chemical input and waste generation, a more adequate process design for AMD treatment is desired, because AMD treatment will be necessary for many years to come.

AMD contains different components in a wide range of concentrations and is always acidic because of the high concentration of sulfate. It also contains several toxic elements such as zinc, lead, cadmium, arsenic, fluorine, and/or boron with ferric (Fe(III)), aluminum (Al(III)), and/or magnesium (Mg(II)) ions, which play a significant role in toxic element removal.

We have investigated the removal mechanisms in anion co-precipitation with several hydroxides, especially for arsenate (As(V))$^{6–14}$, fluorine (F)$^{15}$, and boron (B)$^{16}$, which sometimes contaminate AMD, to establish an effective method for their removal from AMD. In these investigations, synthetic wastewater that contains As(V), F, or B and ferric, aluminum, or magnesium ions was prepared in acidic solution, and the pH was then increased rapidly to the target pH. Because co-precipitation is influenced by solution conditions such as pH and ionic strength, these factors were controlled precisely in these studies. Simple adsorption experiments in which anions were adsorbed on hydroxides were also conduct-
ed and compared with co-precipitation experiments because the comparison between co-precipitation and simple adsorption is useful for elucidating the anion–hydroxide co-precipitation removal mechanism.

We have reviewed the sorption mechanism of As(V) co-precipitation with ferrihydrite, F co-precipitation with aluminum hydroxide, and B co-precipitation with magnesium hydroxide. As(V), F, and B can be removed successfully by ferrihydrite, aluminum hydroxide, and magnesium hydroxide co-precipitation, respectively. However, the co-precipitation mechanism is unclear, and the amount of addition agent such as Fe(III), Al(III), or Mg(II) salts is controlled empirically. Sorption isotherm shapes were compared to discuss their sorption mechanisms. Residues were evaluated using X-ray diffractometry (XRD) and/or Fourier-transform infrared spectroscopy (FTIR) to investigate the mineralogical form of the precipitates and the form of anion sorption in the precipitates. After a detailed explanation of the As(V), F, or B removal mechanism by hydroxides, we discuss how and why their mechanism is different from chemical equilibrium calculations including the surface complexation model (SCM).

2. Overview of sorption mechanism in hydroxide co-precipitation

Sorption is a physical and/or chemical phenomenon in which one substance is attached or incorporated into another by absorption, adsorption, or ion exchange. Surface complexation, which is a type of chemical sorption, and precipitation are the main processes involved in co-precipitation between toxic ions and hydroxide in AMD treatment. Surface precipitation can occur when special conditions are met. The sorption mechanism in co-precipitation between toxic ions and hydroxides can be categorized mainly into surface complexation and surface precipitation.

Surface complexation is a type of chemical adsorption in which many ions in solution are bonded chemically to the surface elements at the interface between the hydroxide and the solution. For example, no charged hydroxyl group, $\equiv$FeOH$^0$, exists on the ferrihydrite surface and every ion, including $H^+$ and $OH^-$ in solution, can complex with its surface, according to their chemical and physical affinity to ferrihydrite, as follows:

$$\begin{align*}
\equiv$FeOH$^0 + H^+ &\leftrightarrow \equiv$FeOH$_2^+$, \quad (1) \\
\equiv$FeOH$^0 &\leftrightarrow \equiv$FeO$^- + H^+, \quad (2)
\end{align*}$$

where, “$\equiv$” indicates that these reactions are limited only to the interface.

The formation of surface complexation and chemical equilibrium calculations are covered in SCMs. We have reported previously that the removal properties of many toxic ions in co-precipitation with ferrihydrite can be represented quantitatively by the diffuse layer model, which is a type of SCM, except for several special cases.

Surface precipitation occurs only at the interface between hydroxide and solution, when the solubility product of precipitation is saturated partially at the interface, despite it being unsaturated in bulk solution. At the solid/liquid hydroxide interface, partial saturation of the solubility product for precipitation can occur because counterions are attracted by electrostatic action. Farley et al. proposed that zinc (Zn(II)) can form surface precipitates with ferrihydrite and they attempted the construction of a quantitative surface precipitation model. Jia et al. also revealed experimentally the existence of surface precipitation between As(V) and ferrihydrite. We also confirmed conditions for surface precipitation between As(V) and ferrihydrite in co-precipitation and proposed a surface precipitation model in which their surface precipitation could be represented quantitatively.

In our research, we reduce the sorption mechanism of As(V) co-precipitation with ferrihydrite, F co-precipitation with aluminum hydroxide, and B co-precipitation with magnesium hydroxide to surface complexation and surface precipitation.

3. As(V) co-precipitation with ferrihydrite

Sorption isotherms from the As(V) co-precipitation and adsorption experiments for ferrihydrite at pH 5 are shown in Fig. 1. The initial
As(V) concentration was fixed at 10, 20, or 30 mg dm$^{-3}$ (0.13, 0.27, or 0.40 mmol dm$^{-3}$) and the Fe(III) concentration was changed to provide initial target As/Fe molar ratios. The initial As(V) concentration of 0.13 mmol dm$^{-3}$ (10 mg dm$^{-3}$ As) is approximately the same as the concentration of As(V) in AMD from the abandoned Horobetsu sulfur mine, which is one of the main As(V)-containing AMD sites in Japan.

The isotherms in Fig. 1 are Langmuir-like with a saturated sorption density of ~0.2. This value of saturated sorption density corresponds to approximately 0.205 of the exchange capacity proposed by Dzombak and Morel for hydrous ferric oxide, which suggests that As(V) has a high affinity to ferrihydrite and almost all sites for surface complexation could be adsorbed by As(V) in this experiment. This Langmuir-like isotherm observed in the adsorption experiments indicates that the mechanism of adsorption of As(V) onto ferrihydrite is a simple two-dimensional adsorption of surface complexation.

In the co-precipitation process, the isotherm was not Langmuir-like, but a Brunauer–Emmett–Teller (BET)-like isotherm, for all initial concentrations of As(V). A considerably larger sorption density was obtained in co-precipitation than in adsorption. The BET-like isotherms and large sorption density indicate that the mechanism of co-precipitation of As(V) and ferrihydrite is not only simple two-dimensional adsorption on the ferrihydrite surface, but also involves some three-dimensional processes, such as surface precipitation, or the formation of several adsorbate layers.

XRD patterns of As(V) adsorbed and co-precipitated with ferrihydrite as a function of As/Fe molar ratio are shown in Fig. 2. The XRD patterns of poorly crystalline ferric arsenate and ferrihydrite are also shown as reference materials. From Fig. 2(a), we confirm that the XRD patterns of As(V)-adsorbed ferrihydrite in the adsorption experiments show similar patterns of ferrihydrite in any initial As/Fe molar ratio.

In the As(V) co-precipitates in Fig. 2(b), the XRD patterns are similar to ferrihydrite when the
initial As/Fe molar ratio is below 0.25. When the co-precipitated products are generated using more than 0.5 of the initial As/Fe molar ratio, the XRD patterns are almost identical to those of poorly crystalline ferric arsenate. The As(V) sorption mechanism in co-precipitation was therefore predominantly the formation of poorly crystalline ferric arsenate when the initial As/Fe molar ratio was greater than 0.5. It is important to note that the As(V) and Fe(III) concentrations are unable to reach the thermodynamic solubility products of ferric arsenate in bulk solution. In general equilibrium calculations using the solubility product in bulk solution, we have confirmed that the bulk precipitation of ferric arsenate never occurs under these conditions. Thus, the poorly crystalline ferric arsenate formed was a surface rather than a bulk precipitate that was generated on the ferrihydrite surface.

4. F co-precipitation with aluminum hydroxide

Sorption isotherms for the F co-precipitation and adsorption experiments for aluminum hydroxide at pH 7 are shown in Fig. 3. The initial F concentration was fixed at 30 to 90 mg dm$^{-3}$ (1.58 to 4.74 mmol dm$^{-3}$) and the Al(III) concentration was changed to provide the initial target F/Al molar ratios.

Fig. 3 shows that the isotherms were a BET type for co-precipitation and adsorption, although the sorption density in co-precipitation was slightly higher than in the adsorption process. These BET-like isotherms observed in the co-precipitation and adsorption experiments indicate that the mechanism of adsorption/co-precipitation of F and aluminum hydroxide is not only a simple two-dimensional adsorption on the aluminum hydroxide surface, but also involves some three-dimensional processes. Surface precipitation was not observed from the XRD patterns of F-adsorbed/co-precipitated aluminum hydroxide, because all XRD patterns were identical to aluminum hydroxide.

The FTIR patterns of F-adsorbed/co-precipitated aluminum hydroxide are shown in Fig. 4. In the co-precipitation and adsorption processes, a slight shift of Al-O bonding attributed to F adsorption was observed when the initial F/Al molar ratio was below three. However, a shift of Al-O bonding was observed when the initial F/Al molar ratio was above three. A shift of this magnitude would be generated by surface complexation of multiple complexes, such as AlF$_3^-$ or AlF$_4^{2-}$. Therefore, a high sorption density and BET-type isotherm of F

![Fig. 3](image)

**Fig. 3** Sorption isotherm of F-adsorbed and co-precipitated aluminum hydroxide. The number in parentheses shows initial F concentration (mg dm$^{-3}$).

![Fig. 4](image left)  ![Fig. 4](image right)

**Fig. 4** FTIR patterns of F-adsorbed aluminum hydroxide (left) and F-co-precipitated aluminum hydroxide (right).
co-precipitation with aluminum hydroxide would result from the surface complexation of multiple complexes of AlF$_3^0$ or AlF$_4^-$.

5. B co-precipitation with magnesium hydroxide

Sorption isotherms for the B co-precipitation and adsorption experiments for magnesium hydroxide at pH 10.5 are shown in Fig. 5. The initial B concentration was fixed at 50 to 100 mg dm$^{-3}$ (4.6 to 9.3 mmol dm$^{-3}$) and the Mg(II) concentration was changed to provide initial target B/Mg molar ratios. A Langmuir-type isotherm was obtained in the adsorption process. This result suggests that the main mechanism is surface complexation of B to magnesium hydroxide in adsorption. A BET-type isotherm observed in co-precipitation indicates that the mechanism of co-precipitation of B and magnesium hydroxide is not only simple two-dimensional adsorption on the magnesium hydroxide surface, but also involves some three-dimensional processes such as surface precipitation.

XRD patterns of B adsorbed and co-precipitated with magnesium hydroxide as a function of B/Mg molar ratio are shown in Fig. 6. From Fig. 6(a), we confirm that the XRD patterns of B-adsorbed magnesium hydroxide in the adsorption experiments showed similar patterns of magnesium hydroxide in any initial B/Mg molar ratios. For the B co-precipitates in Fig. 2(b), the peak around 19° 2θ of magnesium hydroxide was split into two peaks of 16° 2θ and 22° 2θ, which were identical to basic magnesium carbonate. However, in these co-precipitation experiments, all experiments were conducted in a glove box through which N$_2$ gas flowed and from which CO$_2$ gas in the air was removed. Therefore, in B co-precipitation with magnesium hydroxide, surface precipitates structured like basic magnesium carbonate would form when the initial B/Mg molar ratio was increased.

6. Probability of surface precipitation during co-precipitation

As mentioned previously, experimental evidence of surface precipitation was confirmed in As(V) co-precipitation with ferrihydrite and B co-precipitation with magnesium hydroxide. Some researchers have proposed$^{23,24}$ that surface precipitation consists of four steps. For example,

![Fig. 5](image1.png)

**Fig. 5** Sorption isotherm of B-adsorbed and co-precipitated magnesium hydroxide. The number in parentheses shows initial B concentration (mg dm$^{-3}$).

![Fig. 6](image2.png)

**Fig. 6** XRD patterns of B-adsorbed magnesium hydroxide (left) and B-co-precipitated magnesium hydroxide (right).
in As(V) co-precipitation with ferrihydrite, the first step is As(V) surface complexation with ferrihydrite at the solid/liquid interface as follows:

\[
\equiv \text{FeOH}^0 + \text{AsO}_4^{3-} + H^+ \rightleftharpoons \equiv \text{FeAsO}_4^{2-} + H_2O.
\]  

(3)

The second step is Fe\(^{3+}\) surface complexation with \(\equiv \text{FeAsO}_4^{2-}\), which is the precursor of surface precipitation, \(\text{FeAsO}_4(s)\).

\[
\equiv \text{FeAsO}_4^{2-} + \text{Fe}^{3+} \rightleftharpoons \equiv \text{FeAsO}_4(s)\text{Fe}^+.
\]  

(4)

In the third step, part of the ferrihydrite is dissolved to compensate for \(\text{Fe}^{3+}\) in solution and this step would be the rate-determining step for surface precipitation.

\[
\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-.
\]  

(5)

The final step is As(V) surface complexation with surface precipitation, as follows:

\[
\equiv \text{FeAsO}_4(s)\text{Fe}^+ + \text{AsO}_4^{3-} \rightleftharpoons \equiv \text{FeAsO}_4(s) + \equiv \text{FeAsO}_4^{2-}.
\]  

(6)

Therefore, the existence of a solid/liquid interface and the formation of surface complexes as precursors are preconditions for surface precipitation. The tendency of surface complexation as precursor could therefore be one of the indices for surface precipitation.

The tendency for surface complexation of several ions with ferrihydrite has been studied extensively, and Dzombak and Morel assembled values of surface complexation equilibrium constants for many ions with ferrihydrite. According to their database, \(\equiv \text{FeH}_2\text{AsO}_6^0\) and \(\equiv \text{FeOH}_2^+\) are major surface complexes at pH 5 and 10 mg dm\(^{-3}\) initial As(V) concentration, and \(\equiv \text{FeAsO}_4^0\) is dominant rather than \(\equiv \text{FeOH}_2^+\) when the initial As/Fe molar ratio is larger than 0.5, unless no ferrihydrite precipitates. These results suggest that surface precipitation of \(\text{FeAsO}_4(s)\) tends to occur when solution complexes between ferric and arsenate are dominant because the probability of surface precipitation of solution species could be estimated from major species in solution.

For the B co-precipitation with magnesium hydroxide, \(\text{Mg}^{2+}\) and \(\text{H}_2\text{BO}_3^-\) are major species and \(\text{MgH}_2\text{BO}_3^+\) and \(\text{MgOH}^+\) are the second major species in solution at pH 10.5 and 50 mg dm\(^{-3}\) initial B concentration. These results imply that less surface precipitation occurs between magnesium and boron than between ferric and arsenate. This tendency could be observed from the experimental results in Figs. 1 and 5. Here, the difference between co-precipitation and adsorption and sorption density were smaller in B uptake with magnesium hydroxide than in As(V) uptake with ferrihydrite. The activity of \(\text{MgH}_2\text{BO}_3^+\) becomes larger than that of \(\text{MgOH}^+\) when the initial B/Mg molar ratio is larger than 0.13. This suggests that more surface precipitation tends to occur when the initial B/Mg molar ratio is greater than 0.13.

For F co-precipitation with aluminum hydroxide, no evidence for surface precipitation was observed from experiments. According to chemical equilibrium calculations, \(\text{AlF}_3^0\) and \(\text{Al(OH)}_4^-\) are dominant species in solution at pH 7 and 30 mg dm\(^{-3}\) initial F concentration, and \(\text{Al(OH)}_4^-\) is more dominant than \(\text{AlF}_3^0\) for two of the initial F/Al molar ratios. This implies that surface precipitation could result when the initial F/Al molar ratio is larger than two. However, it is difficult to achieve these conditions because the stable precipitation of aluminum hydroxide is difficult to achieve when the initial F/Al molar ratio is large.

7. Conclusions

The mechanisms of As(V) co-precipitation with ferrihydrite, F co-precipitation with aluminum hydroxide, and B co-precipitation with magnesium hydroxide were discussed from experimental isotherms and XRD analysis, by comparison with simple adsorption processes. In all processes, sur-
face complexation was the main and important mechanism for anion uptake by hydroxides. However, for As(V) co-precipitation with ferricydrate and B co-precipitation with magnesium hydroxide, evidence for surface precipitation was observed in the isotherm and XRD patterns. A greater difference in removal properties between co-precipitation and adsorption was observed in As(V) than B co-precipitation, which suggests that more surface precipitates could form in As(V) co-precipitation. Experimental evidence for no surface precipitation but surface complexation of multi complexes was observed in F co-precipitation with aluminum hydroxide. The probability of surface precipitation was discussed from the main species in solution and the main surface complex species.

For more efficient AMD treatment, the active formation of surface complexation and multi-surface complexes is desirable because they result in sludge reduction after AMD treatment. To accomplish this, the continuous addition of small amounts of Fe(III), Al(III), or Mg(II) ions, is necessary to obtain a high As/Fe, F/Al, or B/Mg molar ratio in AMD treatment.

Acknowledgement

This study was supported partially by Japan Oil, Gas, Metals National Corporation.

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