

Arsenic recovery from water containing arsenite and arsenate ions by hydrothermal mineralization

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Abstract

Recovery of arsenic as precipitate of natural mineral from model wastewater containing various initial concentrations and oxidation states of inorganic arsenic oxoanions was investigated by hydrothermal mineralization treatment. The treatment is an earth-mimetic method to produce natural minerals by hydrothermal treatment using $\text{Ca}(\text{OH})_2$ as a mineralizer. The treatment of model wastewater containing arsenate ion or mixed aqueous solution of arsenate and arsenite ions by using $\text{Ca}(\text{OH})_2$ mineralizer and H_2O_2 oxidizer was found to precipitate arsenate apatite which is a natural mineral containing high concentration of arsenic. The feature of this treatment was independent on the initial concentration and the oxidation state of arsenic regardless of mixed ratio of arsenate and arsenite ions. Arsenic concentration in the treated-water at the optimum treatment conditions was 0.02 mg/dm^3 , when treated for the aqueous solution containing $1\text{--}2000 \text{ mg/dm}^3$ of arsenate or arsenite ions. The precipitate obtained by this treatment was a kind of natural mineral (Johnbaumite), which could be easily reused as resources of arsenic compounds. Therefore, the present hydrothermal mineralization treatment with the $\text{Ca}(\text{OH})_2$ mineralizer is an effective technique to recover arsenic from aqueous media.

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Keywords: Arsenite; Arsenate; Wastewater; Detoxification; Recovery; Hydrothermal mineralization

1 Introduction

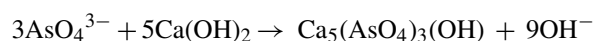
Arsenic is one of the important resources for advanced electronic material production, and wastewaters containing arsenic species are generated from petroleum refining plant or thermal power plant. However, they have extremely high toxicity against human health and the environment. Thus, the national effluent standard of Japan (NESJ) has been set at 0.1 mg/dm^3 , which is the same as WHO guideline (the standard for environmental and drinking water is 0.01 mg/dm^3). An appropriate treatment should be employed for such wastewater to attain the environmental standard. Furthermore, arsenic is a common element found in the earth's crust. It is naturally present in water in different kinds of oxidation states and acid-base species depending on the redox and pH conditions. Therefore, serious environmental problems caused by arsenic pollution of groundwater have emerged in Asian countries such as Bangladesh, India and China [1,2].

Several techniques to remove arsenic from aqueous media have been developed, for example, by adsorption [3–5], electro-coagulation [6], membrane permeation [7,8] and biological methods [9,10]. Especially, the adsorption methods using iron hydroxide or zero-valent irons were actively investigated [3–5,11–14]. These techniques have high ability to remove arsenate ion ($\text{As}^{\text{V}}\text{O}_4^{3-}$) from aqueous media and they are used to treat barely polluted aqueous media by arsenate ion. However, adsorption techniques have problems such as: (1) removal efficiency of trivalent arsenic is low. The cause of this problem is that the arsenite ion ($\text{As}^{\text{III}}\text{O}_3^{3-}$) dissolved in aqueous media under neutral pH does not have negative charge [5,7,14–16]; (2) the applicable concentration range is narrow; (3) arsenic in aqueous media cannot be reused as resources. Additionally, these techniques generate mostly used adsorbents or collected residues polluted by arsenic species, and they must be properly treated again as hazardous wastes. The other treatment methods such as electro-coagulation and membrane methods can be reused as arsenic resource. However, these techniques cannot apply for arsenite ion, because it does not have negative charge. Thus, the treatment methods described above cannot be applied to hardly polluted wastewater or polluted by arsenite. Therefore, it is much

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expected to develop a new technique to recover arsenic species as reusable solid precipitates from aqueous media regardless of its concentration, oxidation number and ionic species in order to avoid cross contamination of arsenic and resource circulation.

We investigated in the previous studies the precipitation recovery of arsenic from the aqueous system containing arsenite ion such as arsenate apatite ($\text{Ca}_5(\text{As}^{\text{V}}\text{O}_4)_3(\text{OH})$) by using hydrothermal mineralization treatment with $\text{Ca}(\text{OH})_2$ mineralizer and H_2O_2 oxidizer [17]. This treatment is derived from the earth-mimetic mineral precipitation phenomena caused by the activity of magma in the presence of water [18,19]. It was found that the reaction between calcium hydroxide and arsenate ion, as shown in the following scheme, occurred only under the hydrothermal conditions, which enabled us to recover arsenic as precipitate from aqueous media.



In order to effectively precipitate arsenic from aqueous solution containing arsenite ion, the addition of oxidizer was necessary to oxidize trivalent arsenite ion to pentavalent arsenate ion, because this enabled the formation of arsenate apatite with extremely low solubility in water. We expected from these considerations that the hydrothermal mineralization treatment for arsenic species would have a possibility to recover arsenic as reusable natural mineral from aqueous media containing any kind of arsenic compounds such as arsenate ion, mixture of arsenate and arsenite ions and organoarsenics. In this study, we investigated the precipitation recovery of arsenic from model wastewater containing various arsenate and/or arsenite ions by using hydrothermal mineralization treatment.

2 Experimental

2.1 Hydrothermal treatment

Model wastewaters with 1–2000 mg/dm^3 of arsenite and arsenate were prepared by dissolving As_2O_3 in 0.5 N NaOH solution and then neutralized by HCl, and by dissolving Na_2HAsO_4 in distilled and deionized water (Wako Pure Chemical Industries, Ltd.), respectively. These model wastewaters (30 ml) were sealed in a pressure vessel lined with fluorocarbon resin together with mineralizer $\text{Ca}(\text{OH})_2$ (Kishida Reagents Chemicals, surface area: 12.6 m^2/g), and in some cases, with H_2O_2 (Wako Pure Chemical Industries, Ltd.) added as oxidizer. In order to examine the dependence of pH, some samples were added with 1–5 ml of 5 M HCl and agitated more than 2 min. The pH of samples was adjusted at 6–12. Hydrothermal treatments were carried out by leaving the vessel in a dry oven for 2–24 h at a given temperature in the range of 100–150 °C. After the hydrothermal treatment, the vessels were cooled down in atmospheric air for 1 h. Precipitates were filtered and collected.

2.2 Analysis

The precipitates were identified by X-ray diffraction (XRD: RIGAKU Rint-2500) using $\text{Cu K}\alpha$ radiation. The microstructural observation and qualitative element analysis of the

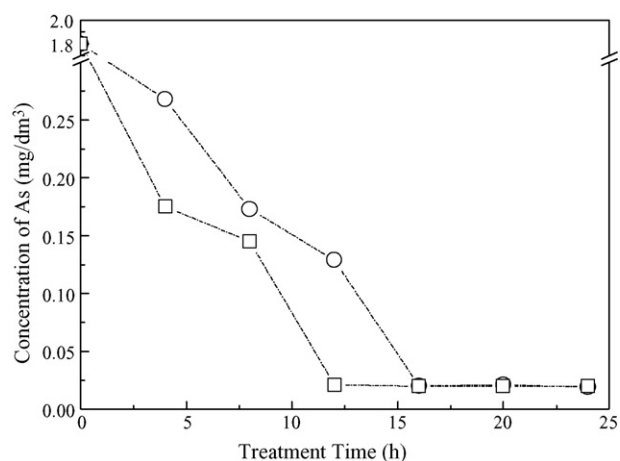


Fig. 1. Dependence of concentration of As in the treated-water on the treatment time. As: 2000 mg/dm^3 , (□) 150 °C, (○) 100 °C.

precipitates were performed by scanning electron microscopy (SEM: JEOL JSM-T20) equipped with energy dispersive X-ray spectrometry (EDS: JED-2140). Quantitative analysis of the arsenate ion in solvent obtained after hydrothermal treatment was carried out by molybdenum blue method [20]. In order to determine the total arsenic content in the solvent, oxidation of arsenite ion by hydrothermal treatment was carried out at 200 °C for 12 h in a solvent with concentrated HNO_3 (0.2–10 ml of treated-water).

3 Results and discussion

3.1 Hydrothermal mineralization treatment for arsenate ion with $\text{Ca}(\text{OH})_2$ mineralizer

Fig. 1 shows the treatment time dependence of the arsenic concentration against the treatment time, when the initial concentration of As^{V} is 2000 mg/dm^3 with the mineralizer of 0.18 g $\text{Ca}(\text{OH})_2$, and the treatment temperatures are 100 and 150 °C. The arsenic concentration reduced down to 1.8 mg/dm^3 only by addition of $\text{Ca}(\text{OH})_2$ to the model wastewater, that is, before the hydrothermal mineralization treatment. Fig. 2 shows the XRD patterns of the precipitates obtained before and after the treatment at 100 °C. Diffraction peaks derived from arsenic compound was not observed before the treatment (Fig. 2(a)). Thus, it is supposed that decrease of arsenic concentration only by addition of $\text{Ca}(\text{OH})_2$ will be caused by the adsorption of the arsenate ion to the hydroxyl group on the surface of $\text{Ca}(\text{OH})_2$. But, the residual arsenic concentration before the hydrothermal mineralization is still higher than the value of NESJ. On the other hand, the arsenic content after hydrothermal mineralization treatment for more than 16 h was 0.02 mg/dm^3 , which is lower than the NESJ value. The diffraction peaks of arsenate apatite were observed after the treatment (Fig. 2(b) or (c)). In our previous study, the precipitation recovery of arsenic from model wastewater containing trivalent arsenite ion was completely achieved by the addition of mineralizer $\text{Ca}(\text{OH})_2$ and oxidizer H_2O_2 in order to progress oxidation of arsenite ion to arsenate ion. Therefore, the formation of arsenate apatite

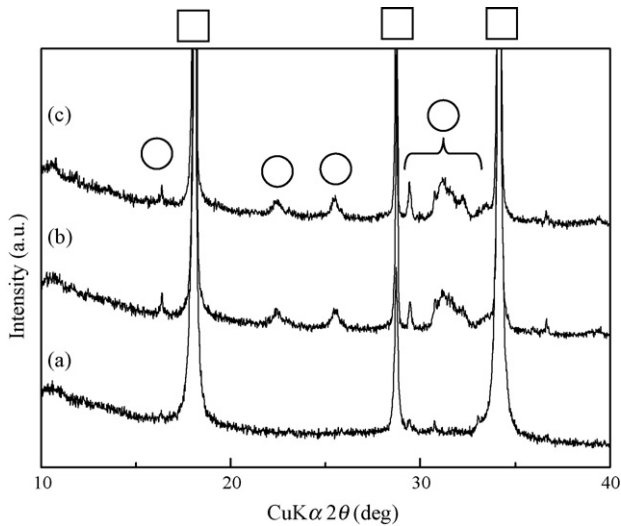


Fig. 2. XRD patterns of the precipitates before (a) and after the treatment for 8 h (b) and 16 h (c) at 100 °C. (□) $\text{Ca}(\text{OH})_2$, (○) $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$.

enables an effective recovery of arsenic because of its very low solubility in water (less than $0.2 \text{ mg As}/100 \text{ dm}^3$) [21,22]. However, the residual arsenic concentration was lower than the above value in equilibrium with water at normal conditions. Thus, the solubility of arsenate apatite under hydrothermal conditions will be lower than that at room temperature and pressure, which promotes the crystal growth of the arsenate apatite. It was considered that the lower arsenic concentration was maintained even during the cooling process because large crystal sizes of arsenate apatite prevented re-dissolution into water.

3.2 Treatment for model wastewater containing arsenate and arsenite ions with $\text{Ca}(\text{OH})_2$

The result of hydrothermal mineralization treatment against model wastewater is shown in Fig. 3, where a mixed aqueous solution of arsenate ($1000 \text{ mg}/\text{dm}^3$) and arsenite ion ($1000 \text{ mg}/\text{dm}^3$) is treated at 100 °C with $\text{Ca}(\text{OH})_2$. The arsenic

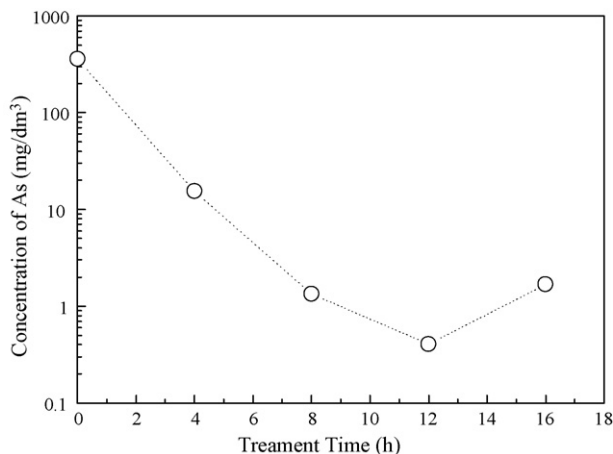


Fig. 3. Dependence of concentration of As in the treated-water on the treatment time. As(III): $1000 \text{ mg}/\text{dm}^3$, As(V): $1000 \text{ mg}/\text{dm}^3$, $\text{Ca}(\text{OH})_2$: 0.36 g , 100 °C.

content decreased before the treatment (only by addition of $\text{Ca}(\text{OH})_2$), though it was higher than that of model wastewater containing arsenate ion only. Additionally, majority of arsenic species in the model wastewater before the hydrothermal treatment was found arsenate ion by detailed analysis. The formation of $\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$ occurred only by addition of $\text{Ca}(\text{OH})_2$, as described in our previous study. Thus, adsorption site of arsenate ion would be decreased due to the formation of $\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$ and the consumption of $\text{Ca}(\text{OH})_2$. In contrast, the arsenic species in the model wastewater after the treatment were arsenite ion. By performing the hydrothermal treatment, arsenic concentration draws a concave curve against the treatment time and the minimum value of arsenic was $0.3 \text{ mg}/\text{dm}^3$ when treated for 12 h. The tendency of the variation of arsenic concentration in treated-water is same as the treatment for the model wastewater containing arsenite ion only, as shown in our previous study [17]. XRD patterns of the precipitates after the treatment showed diffraction peaks derived from arsenic compounds of arsenate apatite and $\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$. Thus, arsenate ions were precipitated as arsenate apatite by hydrothermal mineralization treatment as shown above. But, partial arsenite ions were still in the water because of the nature of precipitate ($\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$) formed by this treatment. The solubilities of $\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$ and $\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})$ in water, were 13.79 and $29.10 \text{ mg As}/100 \text{ dm}^3$, respectively, according to a simple solubility test. These values are higher than that of arsenate apatite. As we already reported, the crystal water of ($\text{Ca}_5(\text{As}^{\text{III}}\text{O}_3)_3(\text{OH})4\text{H}_2\text{O}$) was eliminated by a prolonged hydrothermal treatment. Therefore, the increase in residual As at more than 12 h in Fig 3 would be caused by the removal of crystal water from $\text{Ca}_5(\text{AsO}_3)_3(\text{OH})4\text{H}_2\text{O}$ and the formation of $\text{Ca}_5(\text{AsO}_3)_3(\text{OH})$ which has higher solubility in water than $\text{Ca}_5(\text{AsO}_3)_3(\text{OH})4\text{H}_2\text{O}$. Therefore, it is expected that oxidation treatment of arsenite ion enables effective recovery of arsenic species finally to form $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$.

3.3 Treatment for model wastewater containing arsenate and arsenite ions with $\text{Ca}(\text{OH})_2$ mineralizer and H_2O_2 oxidizer

Fig. 4 shows the result of the hydrothermal treatment with $\text{Ca}(\text{OH})_2$ and 3% H_2O_2 against the model wastewater containing $2000 \text{ mg}/\text{dm}^3$ of arsenate ion. Arsenic concentration before the treatment was much higher than that without H_2O_2 . XRD analysis of the precipitate before the treatment showed diffraction peaks derive from CaO_2 only (figure is not shown). This result indicates that the oxidation of $\text{Ca}(\text{OH})_2$ occurred by addition of H_2O_2 . The cause of decrease the arsenic concentration before the treatment is adsorption of As to the hydroxyl group of $\text{Ca}(\text{OH})_2$. Thus, the formation of CaO_2 from $\text{Ca}(\text{OH})_2$ would bring about the desorption of arsenate ion that adsorbed on the surface of $\text{Ca}(\text{OH})_2$. On the other hand, arsenic concentration in the treated-water treated for more than 12 h was very low ($0.02 \text{ mg}/\text{dm}^3$) which was the same value of the treatment without H_2O_2 . Therefore, the addition of H_2O_2 is not an interfering factor to form arsenate apatite from aqueous media containing arsenate

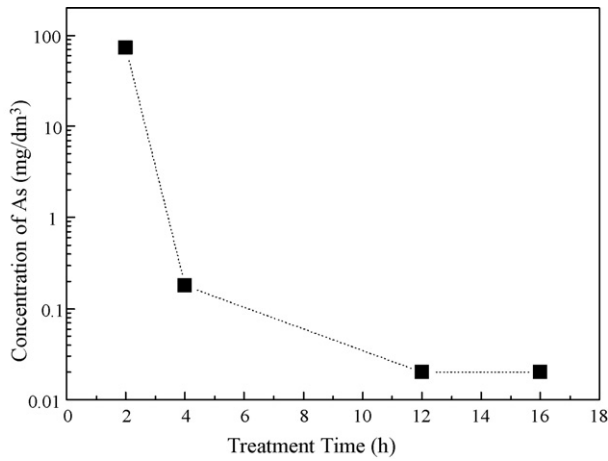


Fig. 4. Dependence of concentration of As in the treated-water on the treatment time. As(V): 2000 mg/dm³, Ca(OH)₂: 0.36 g, H₂O₂: 3%, 100 °C.

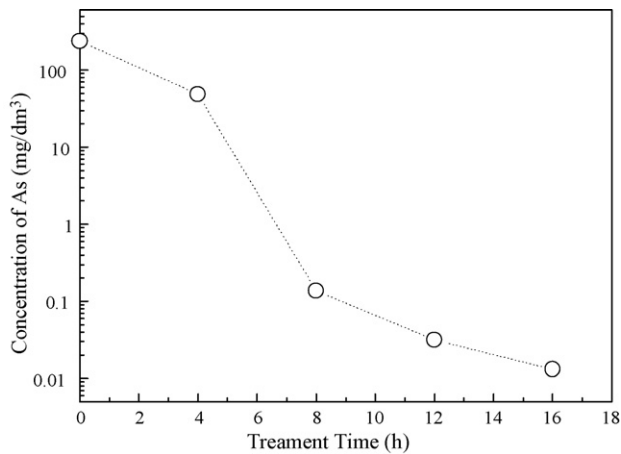


Fig. 5. Dependence of concentration of As in the treated-water on the treatment time. As(III): 1000 mg/dm³, As(V): 1000 mg/dm³, Ca(OH)₂: 0.36 g, H₂O₂: 3%, 100 °C.

ion. The treatment time dependence of arsenic treated for the mixed aqueous solution of arsenite (1000 mg/dm³) and arsenate (1000 mg/dm³) ions on the treatment time with Ca(OH)₂ and 3% H₂O₂ is shown in Fig. 5. Arsenic concentration decreased

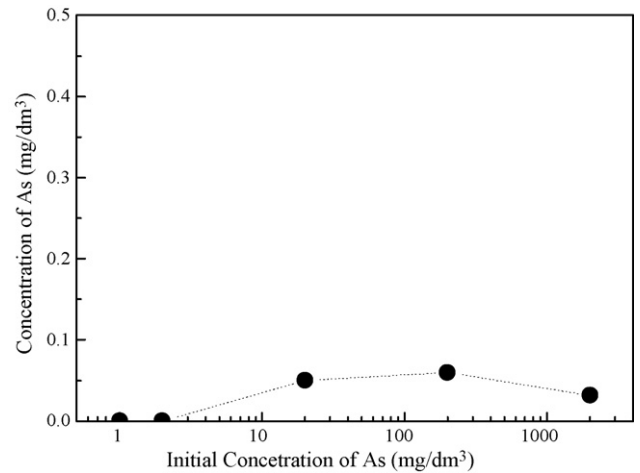


Fig. 7. Dependence of concentration of As in the treated-water on the initial concentration of As. As(III):As(V) = 1:1, H₂O₂ 3%, 100 °C for 12 h.

with an increase of treatment time and it was 0.02 mg/dm³ at optimum treatment time (12–16 h). Thus, it was found that the hydrothermal mineralization treatment with Ca(OH)₂ and H₂O₂ enabled effective recovery of arsenic regardless of the model wastewater containing both arsenite and arsenate ions. Fig. 6 shows the XPS spectra of As 3d orbital and XRD patterns of the precipitates before and after the treatment. The data indicate that the valence state change of arsenic species from three to five occurs at 4–12 h and the precipitate of the treatment after 12 h is a single-phase of arsenate apatite. Thus, the treatment with oxidizer H₂O₂ immediately oxidizes arsenite ion to arsenate ion and forms arsenate apatite. The low solubility of arsenate apatite was found to cause effective recovery of arsenic species from model wastewater.

Fig. 7 shows the initial arsenic concentration dependence on the final arsenic concentration after the treatment time of 12 h with added Ca(OH)₂ and H₂O₂. This result indicates that the arsenic concentration below NESJ value is attained regardless of the initial concentration of arsenic species, because the final concentration is responsible for only the solubility of formed minerals.

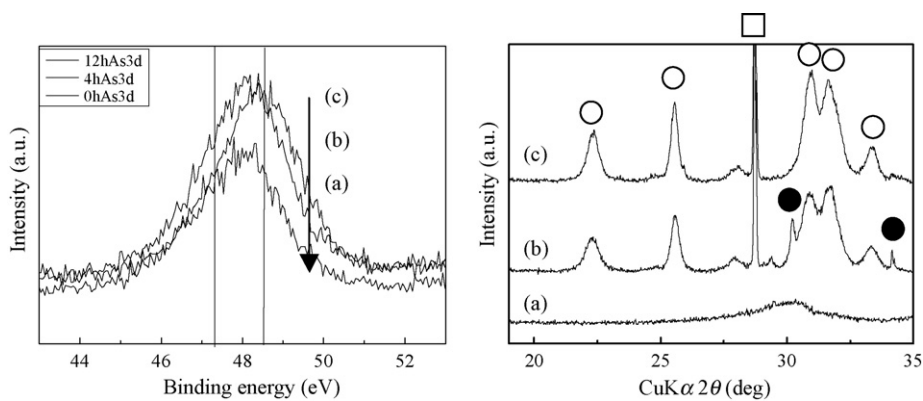


Fig. 6. XPS spectra (left figure, vertical lines of left side and right side mean the binding energies of As(III) and As(V), respectively) and XRD patterns (right figure) of the precipitates before (a) and after the treatment for 4 h (b) and 12 h (c) As(III): 1000 mg/dm³, As(V): 1000 mg/dm³, Ca(OH)₂: 0.36 g, H₂O₂: 3%, 100 °C. (□) Ca(OH)₂, (○) Ca₅(AsO₄)₃(OH), (●) Ca₅(AsO₃)₃(OH)·4H₂O.

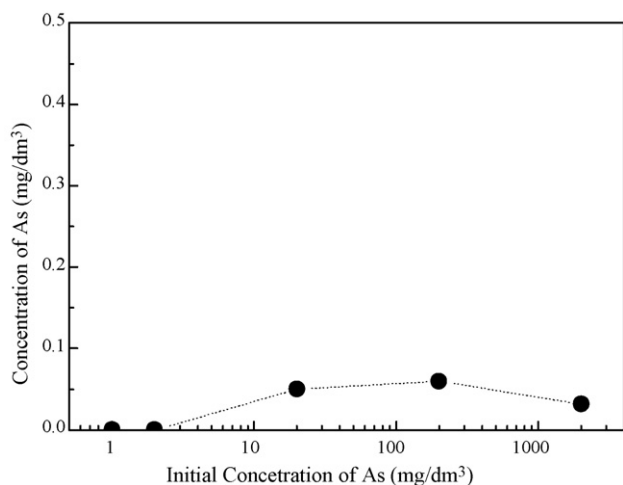


Fig. 8. Dependence of the concentration of As in the treated-water on the amount of added $\text{Ca}(\text{OH})_2$. As(III): 1000 mg/dm^3 , As(V): 1000 mg/dm^3 , H_2O_2 3%, 100°C for 12 h.

3.4 Effects of pH and added amount of $\text{Ca}(\text{OH})_2$

The pH of the treated-water was 13 at any treatment condition, because it is saturated with $\text{Ca}(\text{OH})_2$. The dependence of pH was investigated in the range of 6–12, controlled by addition of HCl to the model wastewater containing 2000 mg/dm^3 of arsenate ion. Arsenic concentration in the treated-water increased with a decrease of pH. Especially, in the treatment at pH 6, arsenic content in treated-water was 2000 mg/dm^3 , which was the same value before the treatment. This result suggests that the existence of precipitated $\text{Ca}(\text{OH})_2$ is essential in order to mineralize arsenic species under hydrothermal conditions. Fig. 8 shows the As concentration dependence on the amount of $\text{Ca}(\text{OH})_2$ added for 30 ml of model wastewater containing 1000 mg/dm^3 of arsenite and 1000 mg/dm^3 of arsenate ions along with 3% H_2O_2 . More than 0.36 g addition is required in order to meet the NESJ value. This amount of $\text{Ca}(\text{OH})_2$ added is higher than the stoichiometric amount to form $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$. Moreover, the concentration of Ca^{2+} in the solution and pH does not change at any amount of $\text{Ca}(\text{OH})_2$ in Fig. 8, because the solubility of $\text{Ca}(\text{OH})_2$ is low ($0.056 \text{ g/30 dm}^3 \text{ H}_2\text{O}$ at 0°C , 0.023 g/30 dm^3 at 100°C). These results suggest that the formation of arsenate apatite occurs by heterogeneous nucleation on the surface of $\text{Ca}(\text{OH})_2$ under the hydrothermal conditions. Therefore, the increase of the amount of added $\text{Ca}(\text{OH})_2$ means the increase of surface area of $\text{Ca}(\text{OH})_2$ precipitates, that is, the accommodation sites for deposition of $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ microcrystals.

4 Conclusions

We have demonstrated the precipitation and recovery technique of arsenate and arsenite ions by hydrothermal mineralization, which imitates the natural mechanism to form insoluble minerals in the crust. The hydrothermal mineralization treatment with $\text{Ca}(\text{OH})_2$ precipitates arsenate ions effectively as reusable arsenate apatite mineral ($\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$). The arsenic con-

centration of the treated-water was approximately 0.02 mg/dm^3 regardless of its initial concentration, but it depended on only the solubility of $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$. In order to precipitate arsenic from mixed solution of arsenate and arsenite ions, simultaneous treatment with mineralization and oxidation by using H_2O_2 oxidizer was found effective. Formation of arsenate apatite was carried out by heterogeneous nucleation. Therefore, the precipitation of $\text{Ca}(\text{OH})_2$ was essential to recover arsenic compounds from aqueous media by hydrothermal mineralization treatment.

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