Resource recovery from wastewater containing hazardous oxoanions by hydrothermal mineralization

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Abstract

We developed a new treatment method for wastewater containing various harmful ions such as arsenite, arsenate, boric, fluoride and fluoroboric ions by hydrothermal mineralization using $Ca(OH)_2$ as a mineralizer. As a result, complete recovery of these ions was attained regardless of the initial concentration and oxidation number of these harmful ion species in wastewater. Therefore, the present hydrothermal treatment using $Ca(OH)_2$ mineralizer is recommended as one of the most effective techniques to remove these ions from wastewater and recover them as recyclable resource.

Keywords: hydrothermal mineralization, arsenite, arsenate, recovery.

1 Introduction

Various oxoanions such as arsenite and boric acid have high toxicity against human health and the environment. They are important resource, however, for plating or advanced material manufacturing industries, from which the wastewater containing these oxoanions is generated everyday. Several methods to remove them have been already reported by using adsorption, electro-coagulation, membrane and biological techniques [1–5]. But, these methods have the following problems. (1) Removal yield is low. (2) The applicable concentration range is narrow. In addition, used adsorbent or collected residues are still hazardous wastes, so that they must be treated by proper method, though it is very difficult to convert them to recyclable resource in various industries. These problems are caused by the difficulty to recover these oxoanions as stable

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solid precipitates with low solubility in water. The establishment of recycling system of these hazardous compounds will be one of the world-important issues, especially, in Japan, which is poor in natural mineral.

In the present study, the recovery method of boron, fluorine and arsenic from wastewater containing fluoride, boric, fluoroboric, arsenite and arsenate ions were developed to produce reusable minerals by the hydrothermal treatment, which was analogous to the formation process of minerals in nature [6].

2 Experimental

Model synthetic wastewaters containing 1–3000 ppm of boric, fluoroboric, arsenite and arsenite ions were prepared by dissolving B_2O_3 (Wako Pure Chemical Industries, Ltd.), hydrofluoric acid (48 wt percent, chemical supplier: *ditto*), fluoroboric acid (48 wt percent, *ditto*), As_2O_3 (*ditto*), Na_2HAsO_4 (*ditto*) in distilled and deionized water. These model wastewaters (30 ml) were sealed in a pressure vessel lined with fluorocarbon resin together with reagents. Mineralizer $Ca(OH)_2$ was added into the vessel and in some cases, H_3PO_4 or H_2O_2 was also added in order to increase recovery yield. Hydrothermal treatments were carried out by leaving the vessel in a dry oven for 2 – 36 h at 100 – 200°C. After the hydrothermal treatment, the vessels were cooled down in atmospheric air for 1 h. Precipitates obtained by the hydrothermal treatment were filtered and collected.

The precipitates were identified by X-ray diffraction (XRD: RIGAKU Rint-2500) using CuKα radiation. The microstructural observation and qualitative element analysis of the precipitates were performed by scanning electron microscopy (SEM: JEOL JSM-T20) equipped with energy dispersive X-ray spectrometer (EDS: JED-2140). Thermometric analysis of the precipitates was carried out by thermogravimetry and deferential thermal analysis (TG-DTA: RIGAKU Thermo Plus2 TG8120). Quantitative element analysis of the solvent obtained after hydrothermal treatment was carried out by the inductively couple plasma-atomic emission spectrometry (ICP-AES: Perkin-Elmer Optima3300DV). Concentration of fluoride ion in the treated-water was measured by ion chromatograph (Shimadzu, Shim-pack IC-A3) with conductivity detector (Shimadzu, CDD-10A). Quantitative analysis of the arsenate in water was carried out by molybdenum blue method. Oxidation to determine the total arsenic content in the solvent was carried out by hydrothermal oxidation in concentrated HNO_3 aqueous solution (0.2 dm^3 / 10 dm^3 of treated-water) at 200°C for 12 h.

3 Results and discussion

3.1 Recovery of F from wastewater containing fluoride ion

Figure 1 shows the ion chromatograms of the model wastewater before and after the hydrothermal treatment using 0.5 g of $Ca(OH)_2$ as mineralizer at 200°C for 4h. The peak of fluoride ion was observed in the chromatogram of wastewater before the treatment and its concentration was 18 ppm. On the other hand, the peak disappeared after the treatment. This suggests that the fluoride ion in the wastewater is completely consumed to form precipitates under the hydrothermal conditions using $Ca(OH)_2$ mineralizer. XRD patterns of the precipitates before and after the treatment exhibited that they consisted of CaF_2. However, the concentration of fluoride ion in the treated-water was below enough compared with the concentration that is calculated from the solubility of CaF_2. It is considered that all fluoride ions in the model wastewater would be precipitated as CaF_2 under the hydrothermal condition. Additionally, it is expected that CaF_2 produced under hydrothermal condition may prevent the redissolution in the cooling process.

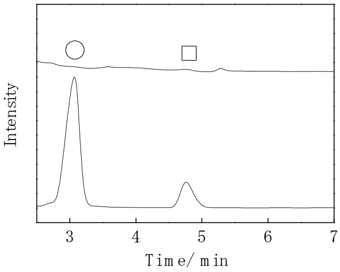

Figure 1: Ion chromatograms of the wastewater before (a) and after (b) the hydrothermal treatment. ○; F^-, □; CO_3^{2-} (F-; 7000 ppm, $Ca(OH)_2$; 0.5g, 200°C, 4 h).

Result of SEM observation of the precipitates obtained before and after the hydrothermal treatment showed that the crystallinity and crystal size of CaF_2 increased dramatically by the hydrothermal treatment. Thus, the recovery of fluorine from wastewater was achieved by decreasing dissolution rate of CaF_2 at room temperature because of decrease in specific surface area. Therefore, the present hydrothermal mineralizing treatment can recover fluorine completely from wastewater using the minimum amount of $Ca(OH)_2$ required to form CaF_2.

3.2 Recovery of B from wastewater containing boric acid

Figure 2 shows the result of hydrothermal mineralization treatment for the model wastewater containing 500 ppm of boron in case of adding $Ca(OH)_2$ and H_3PO_4. It is found that boric acid in the model wastewater decreases considerably in these treatments. However, the concentration was still higher than 100 ppm in case of using only $Ca(OH)_2$. The reason may be caused by redissolution of the precipitate during the cooling process after hydrothermal treatment. On the other hand, the concentration of boron in the treated-water decreased to ca. 5 ppm in case of using both $Ca(OH)_2$ and H_3PO_4. XRD pattern showed that the mineral formed in this process is $Ca_2B_2O_5 \cdot H_2O$ (parasibirskite) and $Ca_5(PO_4)_3(OH)$ (hydroxyl apatite). In order to clarify the crystallization mechanism of calcium phosphate, the variation of diffraction patterns during hydrothermal treatment was examined in detail. Diffraction peaks of $CaHPO_4 \cdot H_2O$ observed before the treatment disappeared gradually with an increase in treatment time. New diffraction peaks of both $CaHPO_4$ and $Ca_{10}(PO_4)_6 \cdot 5H_2O$ appeared after the hydrothermal treatment for 6 h. Then, the diffraction peaks originated from only $Ca_{10}(PO_4)_6 \cdot 5H_2O$ was observed, when treatment time became longer than 12 h. These results indicates that the $CaHPO_4 \cdot H_2O$ contained in the precipitate before the treatment converts into $Ca_{10}(PO_4)_6 \cdot 5H_2O$ via $CaHPO_4$ during longer hydrothermal treatment time. In contrast, the required treatment time to crystallize the $Ca_2B_2O_5 \cdot H_2O$ from the model wastewater in case of using only $Ca(OH)_2$ was 6 h, which was shorter than that for formation of $Ca_{10}(PO_4)_6 \cdot 5H_2O$. Figure 3 shows the SEM photograph obtained by hydrothermal mineralization treatment in using both $Ca(OH)_2$ and H_3PO_4. The fine particles of hydroxyl apatite, which would be separated out and grown on the precipitate of $Ca_2B_2O_5 \cdot H_2O$ and residual $Ca(OH)_2$, can be seen. Therefore, the capsulation with dense intercepting layer of $Ca_{10}(PO_4)_6 \cdot 5H_2O$ is considered to prevent the redissolution of $Ca_2B_2O_5 \cdot H_2O$ into water.

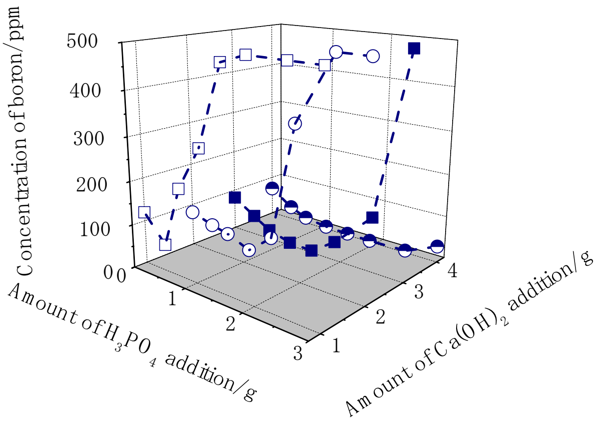

Figure 2: Dependence of the concentration of boron in the treated water after the hydrothermal treatment at 130°C for 14 hours on the added amounts of H_3PO_4 and $Ca(OH)_2$ (B: 500ppm).

3.3 Recovery of B and F from wastewater containing fluoroboric acid

Figure 4 shows the treatment time dependence of the B and F concentrations in the wastewater treated at 150°C. The significant enhancement of recovery yield of fluorine was observed at 2 h and it was completed by 4 h. However, the recovery yield of boron was only 30% at 2 h, and then gradually increased. XRD patterns of precipitates before the hydrothermal treatment showed only the diffraction peaks of $Ca(OH)_2$. On the other hand, the diffraction peaks of CaF_2 and $Ca_2B_2O_5 \cdot H_2O$ were observed after the treatment and the intensities of diffraction peaks of $Ca_2B_2O_5 \cdot H_2O$ increased up to 24 h. Thus, it is expected that the decomposition of fluoroboric acid takes place during the treatment, and the recovery of F and B is achieved by forming CaF_2 and $Ca_2B_2O_5 \cdot H_2O$, respectively, in the same manner as the case of wastewater containing fluoride or boric ion only. Therefore, the thermal decomposition of BF_4^- would occur at the initial stage of treatment (within 4 h), and then the mineralization reaction between Ca^{2+}, and F^- / $B(OH)_4^-$ would be followed.

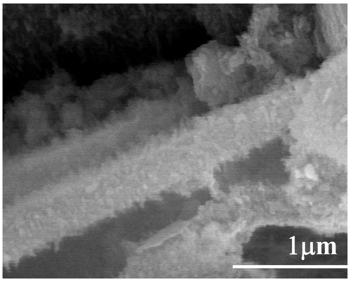

Figure 3: SEM photograph of precipitate obtained by the hydrothermal treatment at 130°C for 14 hours ($Ca(OH)_2$: 3.0g, H_3PO_4:1.5g, B: 500ppm).

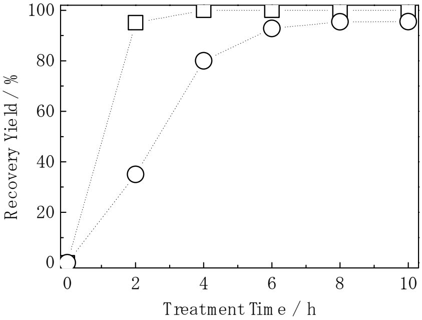

Figure 4: Dependence of recovery yield of B and F in the treated-water on treatment time at 150°C (BF_4^-: 8000 ppm, $Ca(OH)_2$: 1.0g). ○: B, □: F.

The optimal conditions to recover both F and B from model wastewater containing 8000 ppm fluoroboric ion were at 200°C for 36 h, when the concentrations of F and B were 0.3 ppm and 20 ppm, respectively. As described in the previous section, we observed that $Ca_2B_2O_5 \cdot H_2O$ redissolved in aqueous solution during the cooling process in the case of the treatment for boric acid and the boron concentration in the treated-water was ca. 100 ppm on account of its solubility. However, the boron concentration in the case of fluoroboric acid solution was reduced down to ca. 20 ppm even in the absence of the inhibition reagent against redissolution, phosphoric acid. Therefore, it is considered that the coexistence of CaF_2 would affect the increase in recovery yield of boron.

SEM photographs of a bulky precipitate obtained by the hydrothermal treatment were shown in Figure 5. Three layers were observed in the overview photograph (Figure 5-a). From the results of EDS and XRD analyses, the first surface layer (Figure 5-b) was CaF_2, the second layer (Figure 5-c) was the mixture of CaF_2 and $Ca_2B_2O_5{\cdot}H_2O$, and the third layer (Figure 5-d) was the mixture of $Ca_2B_2O_5{\cdot}H_2O$ and residual $Ca(OH)_2$. As a result of detailed analysis, the formation of $Ca_2B_2O_5{\cdot}H_2O$ layer in this study would have started in an earlier time range of 2 – 4 h and completed for 8 – 10 h by heterogeneous nucleation on the surface of $Ca(OH)_2$, after which the suspended CaF_2 wrapped over $Ca_2B_2O_5{\cdot}H_2O$ because of the slow sedimentation rate of CaF_2 fine particles. Possibly this dense sediment layer would play a role to inhibit the redissolution of $Ca_2B_2O_5{\cdot}H_2O$ into aqueous media.

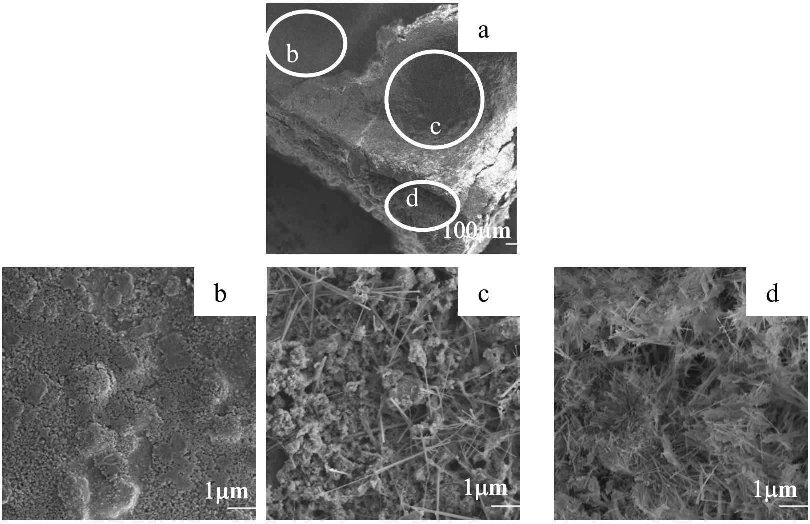

Figure 5: SEM photographs of the precipitates obtained by the hydrothermal treatment. a; over view of precipitate, b; first layer, c; second layer, d; third layer (BF_4^-: 8000 ppm, $Ca(OH)_2$: 1.0g, 150°C, 24 hours).

3.4 Recovery of As from wastewater containing arsenite and arsenate ions

Treatment time dependence of As concentration in the model wastewater containing 2000 ppm of arsenite (AsO_3^{3-}) treated at 100 - 150°C with or without 5% of H_2O_2 is shown in Figure 6. Precipitate containing As was observed by adding $Ca(OH)_2$ to the model wastewater, when the concentration of As was reduced to 4 ppm. However, this does not meet the standard of discharged water in Japan (0.1 ppm). When the hydrothermal mineralization was performed in using this model wastewater added by $Ca(OH)_2$ only, As concentration showed concave curve against treatment time. The optimum treatment condition showed the minimum As concentration of ca. 0.4 ppm, which was one tenth of that before the hydrothermal treatment. However, this concentration is still higher than the standard of discharged water. On the other hand, the addition of H_2O_2 was found effective to reduce the As concentration down to 0.02 ppm under optimal hydrothermal condition, which is lower than the standard of discharged water. This result verifies that the hydrothermal mineralization is an effective method to recover arsenite (AsO_3^{3-}) from aqueous media as precipitate, even when the model wastewater contains large amount of arsenite. It is suggested, therefore, that the As recovery mechanism in this treatment is considerably different from that of the conventional lime precipitation method.

Various analyses on the obtained precipitates were carried out in order to clarify the mechanism of the As recovery by the hydrothermal mineralization. From XRD, SEM-EDS and TG-DTA analyses, the precipitate obtained only by addition of $Ca(OH)_2$ was identified as $Ca_3(AsO_3)_3(OH)\cdot 4H_2O$. The same analysis of the precipitate after the hydrothermal treatment using $Ca(OH)_2$ showed that the crystal water was eliminated. The solubilities of $Ca_3(AsO_3)_3(OH)\cdot 4H_2O$ and $Ca_3(AsO_3)_3(OH)$ to water were estimated 13.79 mg As / 100 dm^3 and 29.10 mg As / 100 dm^3, respectively by a simple solubility test. Therefore, the concave tendency in Figure 1 would be caused by the elimination of crystal water from $Ca_3(AsO_3)_3(OH)\cdot 4H_2O$ with an increase in the treatment time. On the other hand, XRD patterns of the precipitates obtained by hydrothermal treatment with $Ca(OH)_2$ and H_2O_2 exhibited $Ca_5(AsO_4)_3(OH)$ as final product. Thus, the coexistence of H_2O_2 with $Ca(OH)_2$ immediately would give rise to the oxidation of arsenite ion and produce simultaneously arsenate apatite which is known as one of the insoluble natural mineral. Therefore, it is concluded that the hydrothermal mineralization with $Ca(OH)_2$ and H_2O_2 is effective to reduce the concentration of As in the wastewater with arsenite ion (AsO_3^{3-}), which is usually difficult to remove from wastewater.

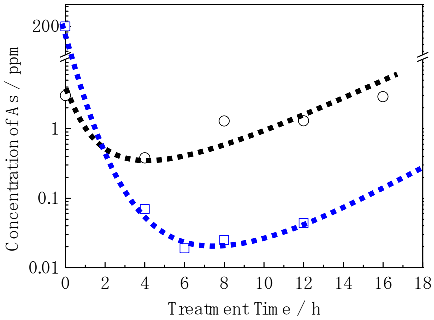

Figure 6: Dependence of the concentration of As in the treated water on treatment time. $Ca(OH)_2$; 0.36g. ○; 150°C, without H_2O_2, □; 150°C, with 5% H_2O_2.

Figure 7 shows the initial arsenite (AsO_3^{3-}) concentration dependence of arsenite in the treated-water using $Ca(OH)_2$ and 3% of H_2O_2 at 100°C for 12h. The residual As concentration was reduced at less than 0.1 ppm except for the case of the wastewater containing 2000 ppm of As. Moreover, it was mostly independent on the initial concentration. This result suggests that the As concentration after the treatment may be determined by only the solubility of the precipitate produced during the hydrothermal mineralization, if the amount of H_2O_2 is enough to convert the arsenite ions (AsO_3^{3-}) into the arsenate ions (AsO_4^{3-}). Whereas, this hydrothermal conditions for model wastewater containing 2000 ppm of arsenite (AsO_3^{3-}) could not sufficiently decrease the residual As concentration. However, the addition of 5% of H_2O_2 achieved the As concentration reduction less than 0.1 ppm, even when As concentration was 2000 ppm. This result shows that the lowest limit of added H_2O_2 amount may be fixed by the initial concentration of arsenite dissolved in water. Figure 8 shows the As recovery from model wastewater containing arsenate (AsO_4^{3-}) or mixture of arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) by the treatment with $Ca(OH)_2$ and 3% of H_2O_2. The As in the model wastewater was completely reduced for 12 h by the treatment. In addition, the treatment for model wastewater containing the mixture of arsenate and arsenite decrease As concentration significantly with 3% of H_2O_2 addition. These results support the speculation for addition of H_2O_2 because the maximum concentration of arsenite in this mixed solution was 1000 ppm. The concentration of As in the treated-water depends only on the solubility of arsenate apatite when enough amounts of H_2O_2 and $Ca(OH)_2$ were added. Therefore, it was elucidated that the hydrothermal mineralization treatment could recover As regardless of the initial concentration and oxidation number of As.

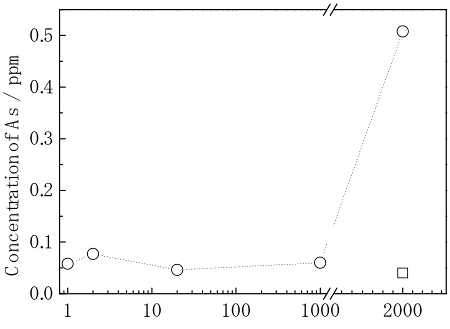

Figure 7: Dependence of the concentration of As in the treated-water on initial concentration of arsenite . $Ca(OH)_2$; 0.36g, 100°C, ○;3% H_2O_2, □; 5% H_2O_2

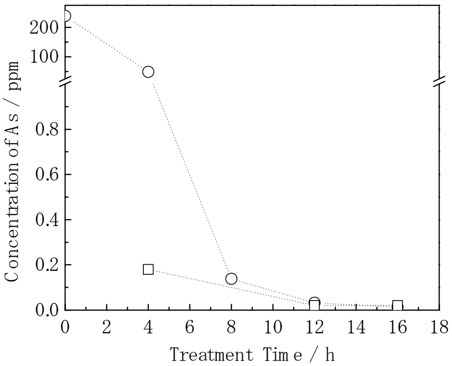

Figure 8: Dependence of the concentration of As in the treated-water on treatment time. $Ca(OH)_2$; 0.36g, 3% H_2O_2, 100°C, ○; AsO_3^{3-} 1000ppm, AsO_4^{3-} 1000ppm, □; AsO_4^{3-} 2000ppm,

4 Conclusions

The hydrothermal mineralization treatment can recover boron, fluorine and As from model wastewater containing fluoride, fluoroboric, arsenite and arsenate ions. All concentrations of these harmful elements in the synthetic model wastewater were reduced down below the standard of discharged water in Japan. The minerals formed in this treatment had the same composition as natural ones. Thus, they can be reused easily in the production processes of pure raw materials from natural minerals. Furthermore, this treatment is independent on the initial concentration and oxidation number of ions. Therefore, the present hydrothermal mineralization treatment can be used for various kinds of wastewaters.

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