

Chromium and phosphorous recovery from polluted water by hydrothermal mineralization

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Abstract

Detoxification of polluted water containing chromium and phosphorous and its resource recovery were investigated by hydrothermal mineralization using $\text{Ca}(\text{OH})_2$ or CaCl_2 mineralizers. Under the optimum treatment condition for removing chromic acid (at 473 K, for 2 h using CaCl_2 mineralizer in an *in situ* sampling-type autoclave), $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ was recovered as CaCrO_4 and the concentration in the treated-water was 0.3 mg/L, which was lower than that of the standard of discharged water in Japan. The phosphorous concentration in the treated-water, which was obtained by the hydrothermal treatment at the optimum treatment condition (at 473 K, for 12 h with $\text{Ca}(\text{OH})_2$ mineralizer by using the same sampling-type autoclave), was 0.2 mg/L regardless of the ionic states. Phosphorous compounds ($\text{P}^{\text{III}}\text{O}_3^{3-}$, $\text{P}^{\text{I}}\text{O}_2^{3-}$) were recovered as $\text{Ca}(\text{HP}^{\text{III}}\text{O}_3)(\text{H}_2\text{O})$ precipitate. This result indicates that mono-valent phosphinic acid ($\text{P}^{\text{I}}\text{O}_2^{3-}$) was oxidized and simultaneously precipitated by the treatment. Therefore, detoxification of the polluted water and resource recovery was accomplished by the hydrothermal mineralization treatment.

Keywords: detoxification, resource recovery, hydrothermal mineralization, chromium, phosphorous.

1 Introduction

Chromium and phosphorous are widely used as electroplating or metal finishing reagents in modern industries as well as fertilizers, and a large amount of wastewater containing these elements is discharged. The hexa-valent Cr in such



as CrO_4^{2-} is well known as one of the toxic metals affecting human health [1]. On the other hand, phosphorous discharged into surface water causes eutrophication of rivers and lakes. Thus, the national effluent standard of Japan (NESJ) of total chromium concentration has been set at 0.5 mg/dm^3 and phosphorous set at 16 mg/dm^3 . The wastewater containing Cr(VI) is currently treated by various methods, *e.g.*, chemical precipitation, reverse osmosis, ion exchange and adsorption techniques [2-5], but it is necessary to convert Cr(VI) into Cr(III) ions before the treatment. Furthermore, these current processes focus only on the removal of Cr(VI) from wastewater. On the other hand, the recovery techniques for wastewater containing phosphorous species have been reported only for treating $\text{P}^{\text{V}}\text{O}_4^{3-}$ by forming hydroxyapatite. However, phosphorous has different oxidation states such as $\text{P}^{\text{III}}\text{O}_3^{3-}$ and $\text{P}^{\text{I}}\text{O}_2^{3-}$, especially in the wastewater discharged from the Ni-P plating industry [3, 4]. There are no effective treatments of wastewater containing these chemical species. Chromium and phosphorous are exhaustible and precious industrial resources, so that the recovery system of these elements in aqueous media should be established especially in Japan, which has less natural resources. In our previous study, we found that the hydrothermal mineralization using $\text{Ca}(\text{OH})_2$ mineralizer could successfully recover the natural minerals from aqueous media containing oxoanions such as $\text{B}^{\text{III}}(\text{OH})_4^-$, $\text{As}^{\text{V}}\text{O}_4^{3-}$ and $\text{As}^{\text{III}}\text{O}_3^{3-}$ [5, 6]. This technique is referred to as “geo-mimetic precipitation method”, which imitates a natural mechanism for forming minerals from aqueous media under hydrothermal conditions.

In this study, the resource recovery from aqueous media containing chromium and phosphorous oxoanions, such as CrO_4^{2-} , $\text{P}^{\text{III}}\text{O}_3^{3-}$ and $\text{P}^{\text{I}}\text{O}_2^{3-}$ was investigated by hydrothermal mineralization treatment.

2 Experimental

2.1 Batch-type normal hydrothermal mineralization treatment

Model wastewaters with $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, $\text{P}^{\text{III}}\text{O}_3^{3-}$ or $\text{P}^{\text{I}}\text{O}_2^{3-}$ (2000 mg/dm^3) were prepared by dissolving Na_2CrO_4 , $\text{H}_3\text{P}^{\text{III}}\text{O}_3$ and $\text{H}_3\text{P}^{\text{I}}\text{O}_2$ in distilled and deionized water, respectively. These model wastewaters (30 cm^3) were sealed in a normal pressure vessel lined with fluorocarbon resin with mineralizer $\text{Ca}(\text{OH})_2$ or CaCl_2 . Hydrothermal treatment was carried out by leaving the vessel in a dry oven for 2–24 h at a given temperature in the range of 100–200 °C. After the hydrothermal treatment, the vessel was naturally cooled down for 1 h or cooled down in an ice bath for 15 min. Precipitates were filtered and collected.

2.2 *In situ* sampling-type hydrothermal mineralization treatment

In order to analyze Cr and P concentrations under hydrothermal conditions, the apparatus shown in Fig. 1 was used. In this type of apparatus, the liquid-solid separation under hydrothermal condition was achieved by using a sintered metallic mesh filter. Model wastewaters of 60 cm^3 were sealed in the pressure



vessel as shown in Fig. 1 with mineralizer of 1.0 g CaCl_2 (for chromium treatment) or 1.0 g $\text{Ca}(\text{OH})_2$ (for phosphorous treatment). Temperature adjustment was carried out by using a temperature controller (CHINO Corporation, DZ1000).

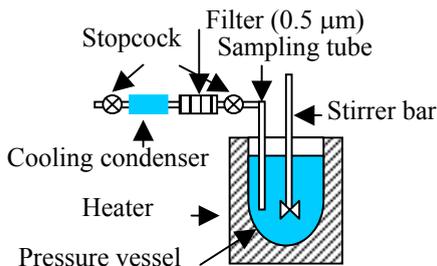


Figure 1: Schematic diagram of *in situ* sampling-type hydrothermal treatment autoclave.

2.3 Analysis

The precipitates were identified by X-ray diffraction (XRD: RIGAKU, Rint-2500) using $\text{CuK}\alpha$ radiation. The residual Cr and Ca concentration in filtrate after hydrothermal treatment was estimated by inductively couple plasma-atomic emission spectrometry (ICP-AES: perkin-Elmer, Optima3300DV). Concentration of phosphorous ions in the solvent obtained after the hydrothermal treatment was measured by ion chromatograph (IC: Shimadzu, CTO-20AC. Mobile phase; 12 mM NaHCO_3 , and 0.6 mM Na_2CO_3 aqueous solution, Column; him-pack IC-SA2) with the conductivity detector (Shimadzu, CDD-10A).

3 Results and discussions

3.1 Treatment for model wastewater containing CrO_4^{2-}

Figure 2 shows the treatment time dependence of Cr concentration in the treated-water by using the batch-type treatment apparatus, where the initial concentration of Cr(VI) is 2000 mg/dm^3 with 0.27 g of CaCl_2 mineralizer, and the treatment temperature is 503 K. Figure 3 shows the XRD pattern of the precipitate obtained by the treatment at 503 K for 12 h. All the diffraction peaks were identified as CaCrO_4 crystal. The Cr concentration in the treated-water obtained by more than 4 h treatment was ca. 400 mg/dm^3 . This result shows that the hydrothermal mineralization treatment is effective to form CaCrO_4 and reduce Cr concentration in aqueous solution. Furthermore, the residual Cr(VI) concentration decreased from 400 to 200 mg/dm^3 by rapid cooling which were carried out by immersing the pressure vessel into an ice bath immediately after the hydrothermal treatment. This result indicates that the solubility of CaCrO_4

into water under hydrothermal conditions is lower than that under the normal pressure and temperature conditions. Re-dissolution of the formed CaCrO_4 would occur during the cooling process due to an increase in its solubility with decreasing temperature of the treated-water. Therefore, suppression of the re-dissolution of CaCrO_4 during cooling process would be achieved effectively to reduce Cr concentration in the treated-water.

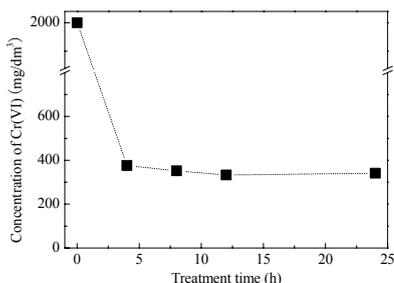


Figure 2: Dependence of concentration of Cr(VI) in the treated-water on treatment time. Sample: 30 cm^3 , Cr(VI): 2000 mg/dm^3 , CaCl_2 : 0.27 g , temperature: 503 K .

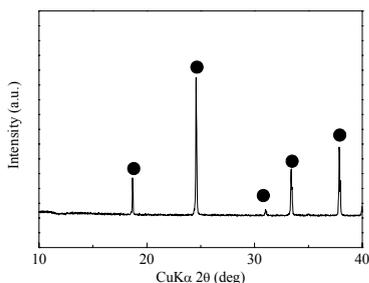


Figure 3: XRD patterns of the precipitates after the treatment at 503 K for 12 h with 0.27 g CaCl_2 . Sample: 30 cm^3 , Cr(VI): 2000 mg/dm^3 , CaCl_2 : 0.27 g , (●) CaCrO_4 .

It is expected from the above results that the solid-liquid separation under hydrothermal condition would be very effective for preventing re-dissolution of the formed mineral. Hydrothermal mineralization treatment was carried out by using the *in-situ* sampling-type autoclave as shown in Fig. 1. Figure 4 shows the Cr concentration in the treated-water obtained by three different cooling methods, *i.e.*, (a) by natural cooling for 1 h , (b) by cooling in ice bath for 15 min , (c) by rapid cooling or separation of the precipitates from water under hydrothermal condition (this means cooling time is mostly 0 min). Cr concentration was found 2.4 mg/dm^3 after the cooling process of (c). Equilibrium pH of these sample water before and after the treatment were 7.8 . This result indicates that the solid-liquid separation under hydrothermal condition can completely prevent the re-dissolution of formed mineral.

The residual Cr concentration in the model wastewater treated at 473 K for 2 h by *in-situ* apparatus is plotted against the added amount of CaCl_2 in Fig. 5. The Cr concentration decreased with an increase in the amount of CaCl_2 addition, and at the added amount of more than 0.68 g CaCl_2 it reduced down to 0.48 mg/dm^3 , which was lower than the NESJ (0.5 mg/dm^3). It is evident, therefore, that the hydrothermal mineralization treatment with solid-liquid separation under hydrothermal condition is effective to detoxify the wastewater containing CrO_4^{2-} and simultaneously recover Cr(VI) as natural solid resource, CaCrO_4 .

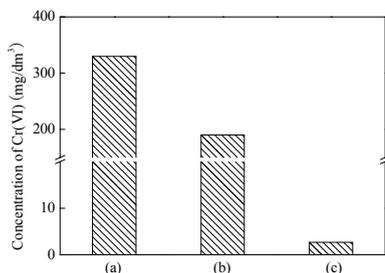


Figure 4: Dependence of concentration of Cr(VI) on different cooling times. (a) 1 h, (b) 15 min for the sample: 30 cm³, Cr(VI): 2000 mg/dm³, CaCl₂: 0.27 g, temperature: 503 K, and (c) 0 min for the sample: 60 cm³, Cr(VI): 200 mg/dm³, CaCl₂: 0.54 g, temperature: 473 K.

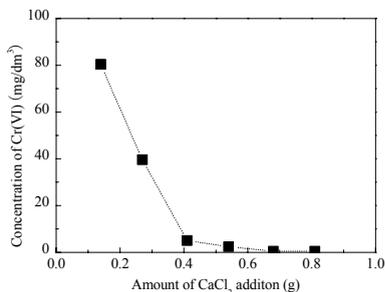


Figure 5: Dependence of Cr(VI) concentration in the treated water after hydrothermal treatment by using the *in-situ* apparatus at 473 K for 2 h on the added amount of CaCl₂. Sample: 60 cm³, Cr(VI): 200 mg/dm³.

3.2 Treatment for model wastewater containing P^{III}O₃³⁻

The hydrothermal mineralization treatment for model wastewater containing 2000 mg/dm³ P^{III}O₃³⁻ with 0.50 g Ca(OH)₂ mineralizer at 150 °C. The pH and Ca concentration in aqueous solutions before and after the treatment at any treatment conditions with Ca(OH)₂ mineralizer were 12 and 200 mg/dm³ because of solubility of residual Ca(OH)₂. Figure 6 shows the treatment time dependence of the phosphorous concentration in treated-water and Figure 7 shows the XRD patterns of the precipitates obtained before and after the treatment. Diffraction peaks of Ca(HP^{III}O₃)(H₂O) was observed as well as those of Ca(OH)₂. The concentration of phosphorous before the hydrothermal treatment was ca. 100 mg/dm³. The decrease in phosphorous concentration only by addition of Ca(OH)₂ is derived from the initial formation of Ca(HP^{III}O₃)(H₂O). However, phosphorous concentration was very high compared with NESJ (16 mg/dm³) because of high solubility of Ca(HP^{III}O₃)(H₂O) under the normal pressure and temperature conditions. On the other hand, phosphorous concentration after the hydrothermal treatment was ca. 5.0 mg/dm³, which was lower than the NESJ. Thus, the detoxification of the aqueous media containing P^{III}O₃³⁻ was easily accomplished by this treatment. The result also indicates that the solubility of the formed precipitate Ca(HP^{III}O₃)(H₂O) under hydrothermal conditions is lower than that under the normal pressure and temperature conditions.

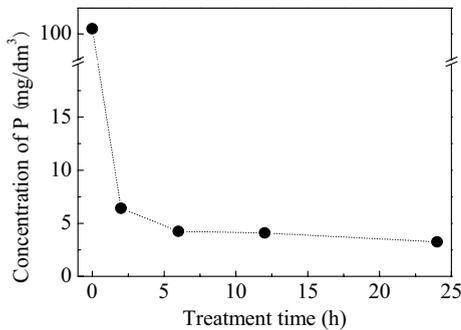


Figure 6: Dependence of concentration of P in the treated-water on treatment time. $P^{III}O_3^{3-}$: 2000 mg/dm³, $Ca(OH)_2$: 0.50 g, 150 °C.

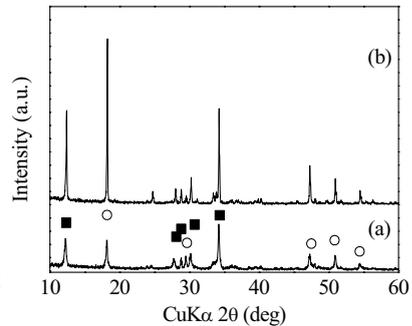


Figure 7: XRD patterns of the precipitates (a) before and (b) after the treatment for 24 h at 150 °C. (○) $Ca(OH)_2$, (■) $Ca(HPO_3)(H_2O)$.

3.3 Treatment for model wastewater containing $P^I O_2^{3-}$

Figure 8 shows the result of hydrothermal mineralization treatment for aqueous solution containing $P^I O_2^{3-}$ (P : 2000 mg/dm³) at 100, 150 and 200 °C with 0.50 g $Ca(OH)_2$ mineralizer. The concentration of phosphorous did not decrease before the hydrothermal treatment, *i.e.*, only by the addition of $Ca(OH)_2$. However, phosphorous concentration in the treated water at 200 °C decreased to 13.3 mg/dm³, which was lower than the NESJ. Therefore, the hydrothermal mineralization treatment is definitely effective for removing $P^I O_2^{3-}$ in the polluted water. Figure 9 shows the XRD patterns of precipitates obtained after the treatment with 0.50 g $Ca(OH)_2$ at various temperatures. The precipitates formed was $Ca(HP^{III}O_3)(H_2O)$, which was the same compound as the precipitate obtained by the treatment for $P^{III}O_3^{3-}$ (see Fig. 7). This result suggested that $P^I O_2^{3-}$ was oxidized from mono-valence to tri-valence by H_2O molecules under the hydrothermal conditions. It was already found in our previous study [7, 8], that H_2O could play the role of oxidant under hydrothermal conditions. At the optimal treatment condition, the present method can reduce the concentration of $P^I O_2^{3-}$ less than the NESJ, and at the same time $P^I O_2^{3-}$ in the aqueous media can be finally recovered as a natural resource, $Ca(HP^{III}O_3)(H_2O)$.

Along with the treatment for CrO_4^{2-} , it is expected that the re-dissolution of the formed $Ca(HP^{III}O_3)(H_2O)$ would occur during the cooling process, because its solubility under the normal pressure and temperature conditions is higher than that under hydrothermal condition. Thus, the solid-liquid separation under hydrothermal condition would be effective for reducing phosphorous concentration in the treated-water. Figure 10 shows the results of hydrothermal mineralization treatment using a normal batch type autoclave and an *in-situ*

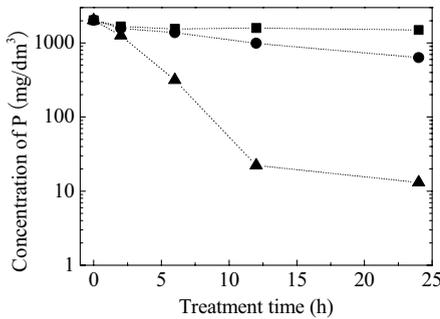


Figure 8: Dependence of concentration of P in the treated-water on the treatment time. $P^I O_2^{3-}$: 2000 mg/dm³, $Ca(OH)_2$: 0.50 g, (■) 100 °C, (●) 150 °C, (▲) 200 °C.

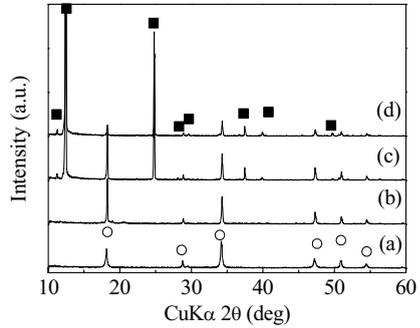


Figure 9: XRD patterns of the precipitates (a) before and after the treatment for 24 h, (b) at 100 °C, (c) at 150 °C, (d) at 200 °C; (○) $Ca(OH)_2$, (■) $Ca(H_2PO_3)_3(H_2O)$.

sampling-type autoclave (see Fig. 1). As a result, phosphorous concentration after the treatment for 12 h was 0.20 mg/ dm³, which indicated that the separation of precipitates from the treated-water under hydrothermal conditions improved the phosphorous recovery yield. This treatment can completely prevent the re-dissolution of the formed minerals during cooling process. Therefore, the hydrothermal treatment using the *in-situ* sampling-type autoclave is effective to detoxify the wastewater and recover phosphorous in wastewater as natural resources.

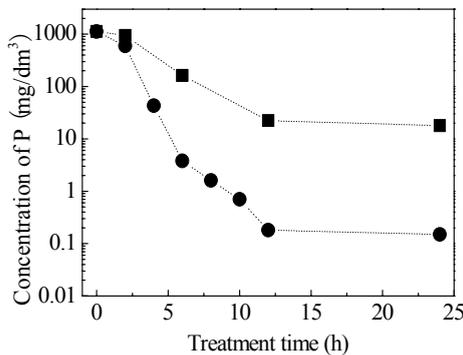


Figure 10: Dependence of concentration of P in the treated-water on the treatment time 200 °C. $P^{III} O_3^{3-}$: 1000 mg/dm³, $P^I O_3^{3-}$: 1000 mg/dm³, $Ca(OH)_2$: 1.0 g, (■) normal batch, (●) *in-situ*.

4 Conclusions

Precipitation recovery of CrO_4^{2-} , $\text{P}^{\text{III}}\text{O}_3^{3-}$ or $\text{P}^{\text{I}}\text{O}_2^{3-}$ from wastewater was investigated. As a result, detoxification of aqueous media and resource recovery was accomplished by using hydrothermal mineralization method. It was found that hydrothermal mineralization with CaCl_2 mineralizer could recover CrO_4^{2-} as a natural resource of CaCrO_4 . Furthermore, solid-liquid separation under hydrothermal condition was very effective to improve the recovery yield of Cr, because the solubility of formed CaCrO_4 is very low under hydrothermal condition. Cr concentration in the treated-water at optimum treatment condition was 0.48 mg/dm^3 , which was less than NESJ. $\text{P}^{\text{III}}\text{O}_3^{3-}$ was easily recovered as $\text{Ca}(\text{HP}^{\text{III}}\text{O}_3)(\text{H}_2\text{O})$. $\text{P}^{\text{I}}\text{O}_2^{3-}$ was also recovered as $\text{Ca}(\text{HP}^{\text{III}}\text{O}_3)(\text{H}_2\text{O})$ by the hydrothermal mineralization and hydrothermal oxidation. Solid-liquid separation under hydrothermal conditions was also effective for treating phosphoric species in wastewater. Thus, it is considered that the present hydrothermal mineralization method is very promising technique as one of the practical wastewater treatment techniques.

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