

Enhanced Removal of Hexavalent Chromium in the Presence of H₂O₂ in Frozen Aqueous Solutions

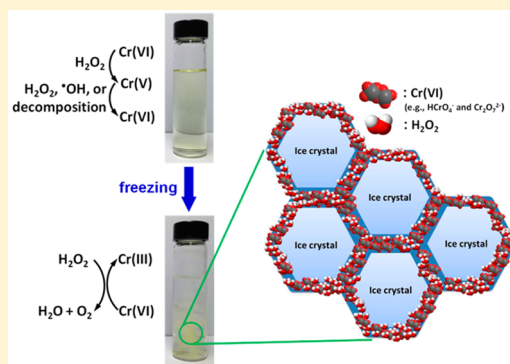
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ABSTRACT: The reductive transformation of Cr(VI) to Cr(III) by H₂O₂ in ice was compared with that in water. The reduction of Cr(VI) was significant at $-20\text{ }^{\circ}\text{C}$ (ice), whereas the reduction efficiency was very low at $25\text{ }^{\circ}\text{C}$ (water). This enhanced reduction of Cr(VI) in ice was observed over a wide range of H₂O₂ concentration (20–1000 μM), pH (3–11), and freezing temperature (-10 to $-30\text{ }^{\circ}\text{C}$). The observed molar ratio of consumed [H₂O₂] to reduced [Cr(VI)] in ice was in close agreement with the theoretical (stoichiometric) molar ratio (1.5) for H₂O₂-mediated Cr(VI) reduction through proton-coupled electron transfer (PCET). The synergistic increase in Cr(VI) reduction in water by increasing the H₂O₂ and proton concentrations confirms that the freeze concentration of both H₂O₂ and protons in the liquid brine is primarily responsible for the enhanced Cr(VI) reduction in ice. In comparison, the one-electron reduction of Cr(VI) to Cr(V) and subsequent reoxidation of Cr(V) to Cr(VI) is the major reaction mechanism in aqueous solution. The reduction efficiency of Cr(VI) by H₂O₂ in the frozen aqueous electroplating wastewater was similar to that in the frozen aqueous deionized water, which verifies the enhanced reduction of Cr(VI) by freezing in real Cr(VI)-contaminated aquatic systems.



INTRODUCTION

Chemical reactions at temperatures above the freezing point (i.e., in aqueous solution) may be different from those at temperatures between the freezing and eutectic points (i.e., in the mixture of ice crystals and liquid brine).^{1–4} Reaction rates in ice crystals are usually lower than those in aqueous solution because of the lower temperature in ice crystals. However, some chemical reactions can be accelerated and enhanced by freezing. The oxidation of nitrite to nitrate in water was markedly accelerated by freezing.^{5–7} In addition, the dissolution of metal oxides, such as iron oxide and manganese oxide, by organic compounds in frozen aqueous solution was accelerated.^{8,9} Recently, it was also reported that the reduction of chromate by organic compounds under acidic conditions is enhanced by freezing.^{10,11} These enhanced chemical reactions are mainly ascribed to the freeze concentration phenomenon, which refers to the increased concentrations of both solutes (e.g., nitrite, metal oxide particles, and organic compounds) and protons in the liquid brine by exclusion from ice crystals during the freezing process.^{1,5–7,12,13} Chemical reactions below the eutectic temperature are generally stopped because the liquid brine is completely solidified. The photochemical degradation mechanism and products of organic compounds in ice can be different from those in water because the coupling/dimerization reactions are enhanced in ice.^{14–17} The different chemical kinetics and mechanisms between ice and water required

various laboratory and field studies of chemical reactions in ice to explain the cycling and fate of contaminants in the cryosphere (e.g., permafrost, polar regions, high latitudes, and midlatitudes during the winter season) and the upper troposphere.^{1,18,19}

Various industries, such as metallurgy, wood preservation, leather tanning, metal electroplating, and pigment manufacturing, use chemical reagents containing high concentrations of chromium,²⁰ which results in a large amount of wastewater containing chromium that needs to be treated. In addition, chromium pollution can naturally occur from weathering and dissolution of chromium-bearing minerals and volcanic eruptions.²¹ Chromium is commonly found as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) in water, and its toxicity, water solubility, and environmental fate are greatly dependent on the oxidation state.²² Between these two chromium species, Cr(III) and Cr(VI), Cr(VI) is more toxic, water-soluble, and difficult to remove using physical treatment processes (e.g., adsorption, ion exchange, and precipitation) than Cr(III).²³ In this regard, the prereduction

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of Cr(VI) to Cr(III) is considered a desirable process in chromium removal.

Hydrogen peroxide (H_2O_2) is ubiquitous in aquatic environments. H_2O_2 can be produced through the photochemical reactions of natural organic matter with dioxygen and by biological processes mediated by algae.^{24,25} In addition, it is well-known that H_2O_2 is present in snow/ice and plays important roles in oxidation reactions in the polar regions as an oxidant and a precursor of hydroxyl radicals ($\cdot\text{OH}$).^{26,27} The interest in redox reactions between H_2O_2 (or $\cdot\text{OH}$) and pollutants in snow/ice has increased because the concentration of H_2O_2 in snow/ice has increased by 50% over the past 200 years.²⁸ In water treatment processes, H_2O_2 has been widely used as an oxidant for the degradation of aquatic pollutants.²⁹ In addition, H_2O_2 can be used as a reducing agent for easily oxidizable metals, such as Fe(III) and Cr(VI), and kinetic and mechanistic investigations of metal reduction by H_2O_2 in water have been extensively performed.^{30–34} However, the reduction of Cr(VI) by H_2O_2 in ice has not been studied despite the high probability of the coexistence of H_2O_2 and Cr(VI). The concentrations of chromium and hydrogen peroxide in the cryosphere vary from a few to 470 ppt and 600 ppb, respectively, depending on region, season, and depth from the surface.^{35–38} The reaction between Cr(VI) (discharged from natural and anthropogenic sources) and H_2O_2 (in situ naturally generated) in frozen aqueous environment might be different from that in aqueous environment, which results in the different fate of Cr(VI) depending on region, altitude, and weather.

In this work, we investigated the reduction of Cr(VI) by H_2O_2 as a reductant in ice and compared it with the corresponding reaction in water. The reduction of Cr(VI) by H_2O_2 in water was limited, whereas it was significant in ice. The reduction process in ice and water was compared as a function of various experimental parameters, such as H_2O_2 concentration, pH, and freezing temperature. Furthermore, the reaction mechanism between H_2O_2 and Cr(VI) in ice was discussed and compared with that in water. The reduction efficiency of Cr(VI) by H_2O_2 , which is the ratio of (initial [Cr(VI)] – final [Cr(VI)])/(initial [Cr(VI)]), in the frozen aqueous electroplating wastewater containing various metals was similar to that in the frozen aqueous deionized water, which verifies the enhanced reduction of Cr(VI) by freezing in real Cr(VI)-contaminated aquatic systems.

EXPERIMENTAL SECTION

Chemicals and Reagents. The chemicals and reagents used in this work include the following: sodium dichromate dihydrate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, Cr(VI), Aldrich), hydrogen peroxide (H_2O_2 , Samchun chemicals), acetone (CH_3COCH_3 , Junsei), sulfuric acid (H_2SO_4 , Aldrich), 1,5-diphenylcarbazide ($\text{C}_6\text{H}_5\text{NHNHCONHNHC}_6\text{H}_5$, DPC, Aldrich), benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, BA, Aldrich), 4-hydroxybenzoic acid ($\text{HOC}_6\text{H}_4\text{CO}_2\text{H}$, 4-HBA, Aldrich), *N,N*-diethyl-1,4-phenylenediamine ($(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{NH}_2$, DPD, Aldrich), peroxidase from horseradish (type VI-A, POD, Aldrich). All chemicals were of analytical grade. The deionized water was ultrapure (18 M Ω -cm) and prepared using a Barnstead purification system. The electroplating wastewater was obtained from a local electroplating plant in Korea.

Experimental Procedure. An aqueous solution containing the desired concentrations of Cr(VI) and H_2O_2 (usually 20 μM and 100 μM , respectively), which was adjusted to the desired

pH value using a HClO_4 or NaOH solution, was put in a conical centrifuge tube (15 mL). For the reaction in ice, the conical centrifuge tube was placed in a stainless steel tube rack in a cryogenic ethanol circulator cooled to the desired temperature (usually $-20\text{ }^\circ\text{C}$) for freezing. The point when the aqueous samples were added to the cryogenic ethanol circulator was defined as time zero ($t = 0$) in the measurements of reaction kinetics. To melt the frozen aqueous samples within 10 min, the conical centrifuge tubes were placed in a beaker containing lukewarm water ($35\text{ }^\circ\text{C}$). The Cr(VI) reduction experiments in aqueous solution were performed at $25\text{ }^\circ\text{C}$ using the same experimental system. Multiple (two or more) experiments were performed for a given condition to confirm data reproducibility. Error bars represent one standard deviation from the mean value.

Chemical Analyses. The concentrations of Cr(VI) and H_2O_2 were measured spectrophotometrically using the DPC³⁹ and DPD⁴⁰ methods, respectively. For the DPC method, 100 μL of the DPC reagent (containing 25 mL of acetone, 250 μL of H_2SO_4 , and 0.05 g of DPC) was added to a vial containing a diluted sample (2.5 mL of deionized water and 0.5 mL of the sample solution). The vial was mixed vigorously and kept in the dark before the analysis. After 30 min, the absorbance measurements at 540 nm ($\epsilon = 6850\text{ M}^{-1}\text{ cm}^{-1}$)³⁹ were performed using a UV–visible spectrophotometer (Biochrom Libra S22). For the DPD method, 0.05 mL of the DPD reagent (containing 0.1 g of DPD and 10 mL of H_2SO_4 (0.1 M)), 0.05 mL of POD solution (containing 0.01 g of POD and 10 mL of deionized water), and 0.4 mL of phosphate buffer (0.5 M, pH 6.0) were added to a diluted sample (2.0 mL of deionized water and 1.0 mL of the sample solution). The solution was mixed vigorously, and its absorbance was measured at 551 nm ($\epsilon = 21000\text{ M}^{-1}\text{ cm}^{-1}$)⁴⁰ after 1 min.

The production of hydroxyl radicals ($\cdot\text{OH}$) was indirectly monitored by measuring the concentration of 4-hydroxybenzoic acid (4-HBA), which was generated from the reaction between benzoic acid (BA) and $\cdot\text{OH}$.^{41,42} The concentration of 4-HBA was quantified by comparing the chromatography peak area of the samples with that of the authentic standard at the same retention time using high-performance liquid chromatography (HPLC, Agilent 1100) equipped with a UV–visible detector and a ZORBAX 300SB C-18 column (4.6 mm \times 150 mm). The mobile phase was a binary mixture of a 0.1% phosphoric acid solution and acetonitrile (8:2 by volume) at a flow rate of 1.0 mL/min, and the detection wavelength was 254 nm.

The chemical composition of the electroplating wastewater was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo iCAP 6300 Duo), which was operated under the conditions of RF power 1150 W, pump rate 50 rpm, auxiliary gas flow 0.5 L/min, and nebulizer gas flow 0.7 L/min.

RESULTS AND DISCUSSION

Cr(VI) Reduction by H_2O_2 in Water and Ice. Because the eutectic temperature of H_2O_2 solution is below than $-50\text{ }^\circ\text{C}$,⁴³ the reaction system in this study was not completely solidified. Therefore, the term “ice” in this study refers to the mixture of ice crystals and liquid brine, without indicating a fully frozen state. The reduction of Cr(VI) to Cr(III) by H_2O_2 in ice (more precisely, in the liquid brine) was compared to that in water (Figure 1a). Under the conditions of $[\text{H}_2\text{O}_2] = 100\text{ }\mu\text{M}$, $[\text{Cr(VI)}] = 20\text{ }\mu\text{M}$, and pH 3.0, the reduction of Cr(VI) by

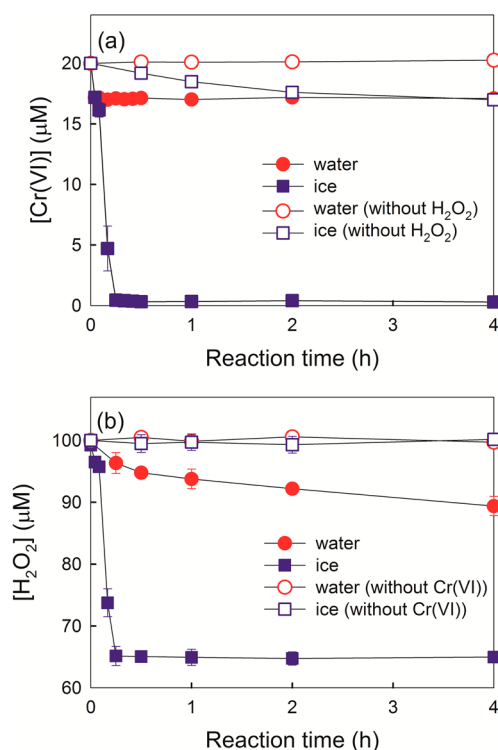
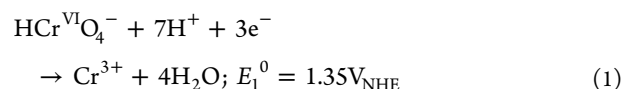


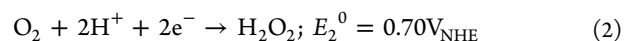
Figure 1. Time profiles of (a) Cr(VI) and (b) H₂O₂ concentrations in water and ice. Experimental conditions were as follows: [Cr(VI)]_i = 20 μM, [H₂O₂]_i = 100 μM, pH_i 3.0, and reaction temperatures = water at 25 °C and ice at −20 °C.

H₂O₂ was stopped in 2.5 and 15 min in water and ice, respectively. The degree of Cr(VI) reduction after 5 min was markedly different between ice and water. The overall reduction of Cr(VI) by H₂O₂ was very small (less than 3 μM) in water, but 100% reduction was achieved in ice. We compared the reduction of Cr(VI) by H₂O₂ in water under both vigorous stirring and nonstirring conditions. However, the results were almost the same in both cases. This result indicates that the limited reduction of Cr(VI) in water cannot be attributed to diffusion limitation. Although the reduction of Cr(VI) in ice continuously proceeded even in the absence of H₂O₂ through a proton-mediated reduction process (i.e., $4\text{HCr}^{\text{VI}}\text{O}_4^- + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{O}_2 + 10\text{H}_2\text{O}$; $E^0 = 0.15 \text{ V}_{\text{NHE}}$),¹¹ its effect was minor in H₂O₂-mediated Cr(VI) reduction (20 μM of Cr(VI) reduction in the presence of H₂O₂ within 15 min vs 1 μM of Cr(VI) reduction in the absence of H₂O₂ for 30 min). In accordance with the higher Cr(VI) reduction in ice, the decrease in the H₂O₂ concentration in ice was higher than that in water (Figure 1b), which indicates that the reaction between H₂O₂ and Cr(VI) is more favored in ice than water. The concentration of H₂O₂ did not decrease in the absence of Cr(VI) in both water and ice.

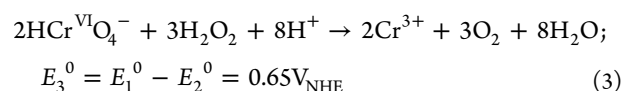
Cr(VI) can be reduced to Cr(III) by H₂O₂ through proton-coupled electron transfer (PCET, reaction 3), which is obtained from the half-reduction reactions of Cr(VI) (reaction 1) and dioxygen (reaction 2).⁴⁴ According to reaction 3, the reduction of Cr(VI) by H₂O₂ should be favored at high concentrations of H₂O₂ and protons.



$$E_1 = E_1^0 - 0.14\text{pH} - 0.02\log\left(\frac{[\text{Cr}^{3+}]}{[\text{HCr}^{\text{VI}}\text{O}_4^-]}\right)$$



$$E_2 = E_2^0 - 0.06\text{pH} - 0.03\log\left(\frac{[\text{H}_2\text{O}_2]}{[\text{O}_2]}\right)$$

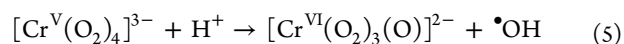
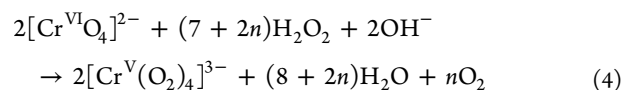


$$E_3 = E_1 - E_2 = 0.65 - 0.08\text{pH} + 0.02\log\left(\frac{[\text{HCr}^{\text{VI}}\text{O}_4^-]}{[\text{Cr}^{3+}]}\right) + 0.03\log\left(\frac{[\text{H}_2\text{O}_2]}{[\text{O}_2]}\right)$$

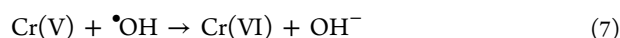
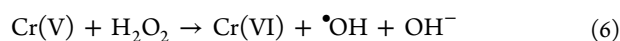
The solutes and protons are excluded from the ice crystals into the liquid brine during freezing.^{1,5-7,12,13} As a result, the concentrations of the solutes and protons in the liquid brine increase by freezing. This freeze concentration phenomenon (i.e., the increased concentrations of H₂O₂ and protons in the liquid brine by freezing) can enhance the reduction of Cr(VI) to Cr(III) by providing better conditions for PCET reaction (reaction 3).

In ice, the concentration of H₂O₂ rapidly decreased in the initial period but did not decrease further after 15 min (Figure 1b). This behavior is consistent with the complete removal of Cr(VI) (behaving as an electron acceptor) within 15 min (Figure 1a). Thus, 35 μM of H₂O₂ (added [H₂O₂] – residual [H₂O₂]) reduced 20 μM of Cr(VI) in ice neglecting reduced [Cr(VI)] in the absence of H₂O₂, which amounts to a molar ratio value of H₂O₂ to Cr(VI) (consumed [H₂O₂]/reduced [Cr(VI)]) equal to 1.75. This value is close to the theoretical (stoichiometric) molar ratio of 1.5 according to reaction 3. Therefore, reaction 3 accounts for the major consumption of H₂O₂ and all other side reactions are very minor in ice. In contrast, the reduction of Cr(VI) in aqueous solution was stopped after 2.5 min, although high concentrations of both Cr(VI) and H₂O₂ still remained in aqueous solution (Figure 1a and b). In addition, the concentration of H₂O₂ continuously decreased without the reduction of Cr(VI) (Figure 1a and b). These results imply the existence of other pathways for the reaction between H₂O₂ and Cr(VI) in water.

The reaction mechanism between Cr(VI) and H₂O₂ is critically dependent on the solution pH. Under acidic conditions, the complete reduction of Cr(VI) to Cr(III) by H₂O₂ is favored through PCET reaction (reaction 3).³¹ On the other hand, under neutral and basic conditions, the tetraperoxo chromate(V) anion ([Cr^V(O₂)₄]³⁻) is preferentially formed by the simultaneous single-electron transfer from H₂O₂ to Cr(VI) and sequential substitution of oxo ligands by peroxy groups (reaction 4).³⁰ However, [Cr^V(O₂)₄]³⁻ is easily decomposed into [Cr^{VI}(O₂)₃(O)]²⁻ with the generation of •OH (reaction 5),^{45,46} which creates a null cycle combining with reaction 4 (Cr(VI) → Cr(V) → Cr(VI)).



In addition, the intermediate Cr(V) species generated from reaction 4 can react with residual H₂O₂ to regenerate Cr(VI) with producing \bullet OH (reaction 6),^{32,47} and \bullet OH generated from reactions 5 and 6 can reoxidize Cr(V) back to Cr(VI) (reaction 7).



These coupled redox reactions (reaction 4 + reaction 5, 6, or 7) consume H₂O₂ without the reduction of Cr(VI) to Cr(III). Because the concentration of the protons in water at pH 3.0 should not be sufficient to drive reaction 3, the reduction of Cr(VI) to Cr(III) was very small. Alternatively, Cr(V) should be primarily formed by the single-electron transfer from H₂O₂ to Cr(VI) (reaction 4) and then reoxidized back to Cr(VI) (reactions 5–7). These null reactions that occur in water limit the reduction of Cr(VI) to Cr(III) with continuously consuming H₂O₂.

To provide convincing evidence of different reaction mechanisms between Cr(VI) and H₂O₂ in water and ice (i.e., reactions 4–7 in water vs reaction 3 in ice), the production of \bullet OH was monitored by measuring the production of 4-hydroxybenzoic acid (4-HBA) that was generated from the reaction between \bullet OH and benzoic acid (BA) (Figure 2). If the

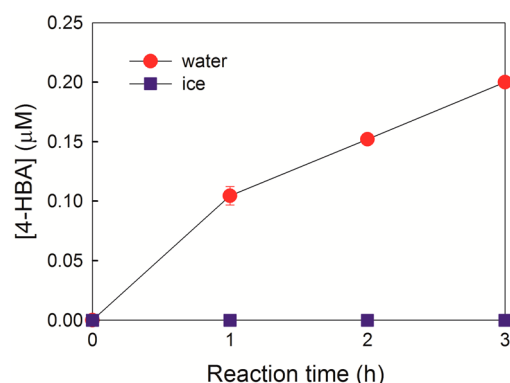


Figure 2. Time profiles of \bullet OH production in water and ice. Experimental conditions were as follows: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{O}_2]_i = 100 \mu\text{M}$, $[\text{BA}]_i = 1 \text{ mM}$, pH 3.0, and reaction temperatures = water at 25 °C and ice at –20 °C.

reaction between Cr(VI) and H₂O₂ is initiated through the single-electron transfer (reaction 4), \bullet OH should be generated through the decomposition of Cr(V) (reaction 5) or the reaction between Cr(V) and H₂O₂ (reaction 6). In contrast, \bullet OH is not produced in the course of Cr(VI) reduction by H₂O₂ through PCET reaction (reaction 3).

As shown in Figure 2, the production of 4-HBA, which is directly proportional to the production of \bullet OH, gradually increased in the aqueous Cr(VI)/H₂O₂ system. This result indicates that the single-electron transfer from H₂O₂ to Cr(VI) (i.e., the formation of Cr(V), reaction 4) and subsequent reoxidation of Cr(V) to Cr(VI) (reactions 5–7) is favored in water. However, the formation of 4-HBA was negligible in the frozen aqueous Cr(VI)/H₂O₂ system. Therefore, the formation of Cr(V) by single-electron transfer from H₂O₂ to Cr(VI) (reaction 4) can be ruled out in ice, with the PCET reaction (reaction 3) proposed as the major reaction pathway between H₂O₂ and Cr(VI).

Cr(VI) Reduction by H₂O₂ in Various Conditions. The effect of the H₂O₂ concentration on Cr(VI) reduction was investigated in both water and ice (Figure 3a). The reduction of Cr(VI) increased with increasing H₂O₂ concentration in water. However, approximately 40% of Cr(VI) (8 μM) still remained even at $[\text{H}_2\text{O}_2] = 1 \text{ mM}$, which should be attributed to the fact that the complete reduction through PCET reaction (reaction 3) is less favorable than the coupled redox reactions (reaction 4 + reaction 5, 6, or 7) in water. In contrast, the reduction of Cr(VI) (20 μM) was completed at $[\text{H}_2\text{O}_2] \geq 50 \mu\text{M}$ in ice. At $[\text{H}_2\text{O}_2] = 20 \mu\text{M}$ and $[\text{Cr(VI)}] = 20 \mu\text{M}$, 14 μM of Cr(VI) was reduced and 20 μM of H₂O₂ was completely consumed after 2 h. Because 2 μM of Cr(VI) was reduced for 2 h in the absence of H₂O₂ (Figure 1a), the observed molar ratio of H₂O₂ to Cr(VI) (consumed $[\text{H}_2\text{O}_2]$ /(reduced $[\text{Cr(VI)}] - 2 \mu\text{M}$)) was 1.67, which was similar to the theoretical (stoichiometric) value of 1.5 (reaction 3). This result also corroborates the proposed PCET reaction between H₂O₂ and Cr(VI) in ice.

The effect of the pH on Cr(VI) reduction by H₂O₂ was also investigated (Figure 3b). The reduction of Cr(VI) gradually decreased from pH 3 to pH 11 in both ice and water. This behavior is expected because the reduction of Cr(VI) to Cr(III) through PCET reaction is favored under acidic conditions. However, it should be noted that approximately 45% of Cr(VI) (9 μM) was reduced in the presence of 100 μM of H₂O₂ at neutral pH in ice, whereas the reduction in water was very small under the same conditions. This result implies that the enhanced reduction of Cr(VI) by H₂O₂ in ice is not particularly restricted to acidic conditions only. A significant portion of Cr(VI) in natural waters (e.g., river water, lake water, and groundwater), where the pH is generally neutral, can be reduced to Cr(III) in the presence of H₂O₂ by freezing. The reduction of Cr(VI) in ice at neutral pH was negligible in the absence of H₂O₂, which implies that the reduction of Cr(VI) is initiated only by H₂O₂ at neutral pH in contrast to acidic pH.

It has been estimated that the concentration of protons in the liquid brine increases by 2–3 orders of magnitude compared to that in aqueous solution.^{48,49} If so, the pH in water can be changed from 7.0 up to 4.0 by freezing. However, the reduction of Cr(VI) at pH 7.0 in ice was more significant than that at pH 4.0 in water, which indicates that the pH decrease by freezing is not the only reason for the enhanced Cr(VI) reduction in ice. In addition to protons, H₂O₂ can be concentrated in the liquid brine during freezing. This behavior should result in a synergistic enhancement of the Cr(VI) reduction through PCET reaction, because reaction 3 is also favored at high concentrations of H₂O₂. The alkaline aqueous solution may become more basic by freezing due to the accumulation of OH[–] in the liquid brine, which constitutes an unfavorable condition for PCET reaction (reaction 3). Therefore, the observed positive effect of freezing on Cr(VI) reduction at basic conditions should be ascribed to only the increased concentration of H₂O₂ in the liquid brine.

Figure 3c shows the temperature-dependent kinetic profiles of Cr(VI) reduction at the same $[\text{H}_2\text{O}_2]$. The apparent Cr(VI) reduction rate, which is the ratio of (initial $[\text{Cr(VI)}] - \text{final } [\text{Cr(VI)}])$ /(reaction stop time), in the ice samples increased with decreasing freezing temperature (0.52 μM/min at –10 °C, 0.93 μM/min at –20 °C, and 1.21 μM/min at –30 °C). The freezing temperature should have an effect on the volume of the liquid brine by affecting the freezing speed. The size of the ice crystals should be larger at higher freezing speed (i.e., at lower freezing temperature). Therefore, the volume of the liquid

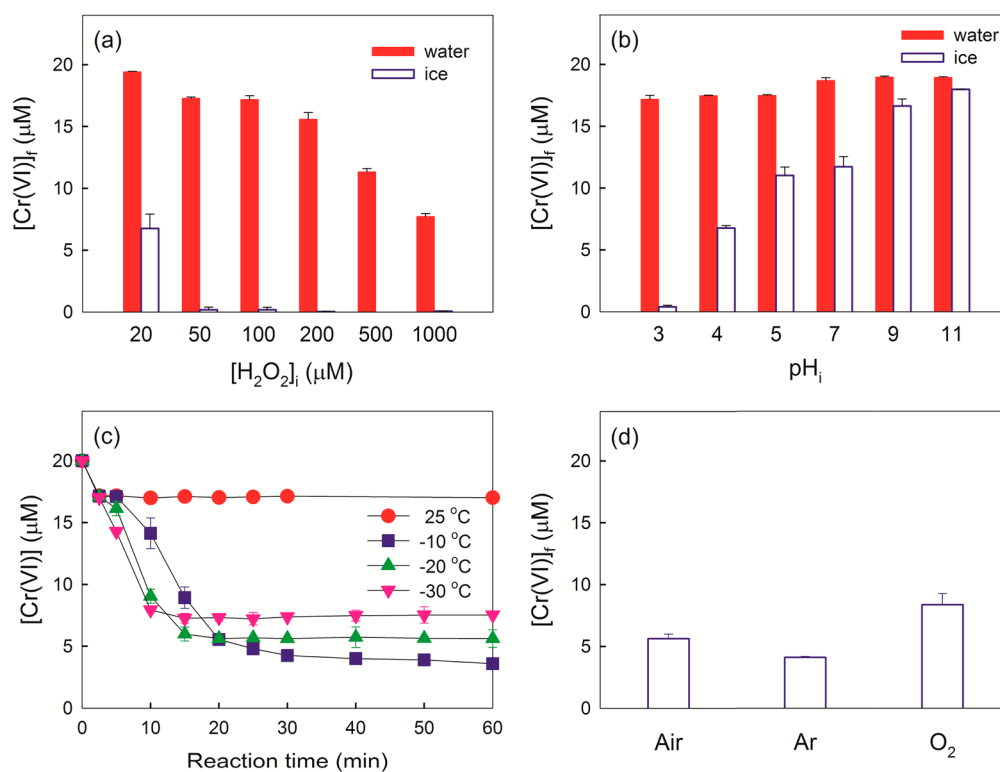


Figure 3. Effect of (a) H_2O_2 concentration, (b) pH, (c) temperature, and (d) dioxygen concentration on Cr(VI) reduction in water and ice. Experimental conditions were as follows: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{O}_2]_i = 100 \mu\text{M}$ (for b, c, and d), $\text{pH}_i = 3.0$ (for a), $\text{pH}_i = 4.0$ (for c and d), reaction temperatures = water at 25°C and ice at -20°C (for a, b, and d), and reaction time = 2 h (for a, b, and d). A conical centrifuge tube containing Cr(VI) and H_2O_2 was sealed with a rubber septum. Then, Ar or O_2 (99.999%) was purged for 30 min prior to freezing (for d).

brine, which is inversely proportional to the size of the ice crystals, should be smaller at lower freezing temperatures. The smaller volume of the liquid brine (i.e., more highly concentrated H_2O_2 and protons) at lower freezing temperature increases the apparent reduction rate of Cr(VI).

The Cr(VI) reduction efficiency, which is the ratio of (initial $[\text{Cr(VI)}] - \text{final } [\text{Cr(VI)}]) / (\text{initial } [\text{Cr(VI)}])$, seems to be independent of the freezing temperature because all experiments were performed above the eutectic temperature (i.e., the reduction of Cr(VI) was not stopped by complete solidification). However, more Cr(VI) was reduced at higher freezing temperatures ($16.5 \mu\text{M}$ at -10°C , $14.5 \mu\text{M}$ at -20°C , and $12.5 \mu\text{M}$ at -30°C). This result is consistent with the previous report that the freeze concentration phenomenon is more significant at higher freezing temperatures.¹¹ Highly concentrated dioxygen may completely inhibit the reduction of Cr(VI) to Cr(III) through PCET reaction (reaction 3) with Cr(III) generated from Cr(VI) reduction by reducing the driving force (i.e., E_3 value). The concentration of dioxygen should be higher at lower freezing temperatures because dioxygen can also be more confined in the smaller liquid brine.^{6,7} This can help explain why the efficiency of Cr(VI) reduction by H_2O_2 decreased with decreasing freezing temperature. In order to confirm the dioxygen concentration-dependent Cr(VI) reduction efficiency in ice, the Cr(VI) reduction efficiency at -20°C of the sample purged with Ar or O_2 prior to freezing was measured and compared with that of the sample under air-equilibrium conditions (Figure 3d). The reduction efficiency of Cr(VI) increased by Ar purge (i.e., in relatively O_2 -poor condition), but decreased after O_2 purge (i.e., in relatively O_2 -rich condition). This result supports that

the faster increase of dioxygen concentration at lower freezing temperature stops the Cr(VI) reduction process earlier and then subsequently decreases the reduction efficiency of Cr(VI).

Verification of Freeze Concentration Phenomenon.

The enhanced reduction of Cr(VI) in ice should be due to the freeze concentration of H_2O_2 and protons in the liquid brine. To verify the freeze concentration phenomenon as the reason for the enhanced Cr(VI) reduction in ice, we investigated the reduction of Cr(VI) in water at high H_2O_2 (1 mM) and/or proton concentrations ($\text{pH} = 2.0$) and compared their results to those of the reference experiment ($[\text{H}_2\text{O}_2] = 100 \mu\text{M}$ and $\text{pH} = 3.0$) (Figure 4). The reduction of Cr(VI) by H_2O_2 was enhanced when the concentration of either H_2O_2 or protons increased by 10 times. In addition, the reduction of Cr(VI) in water was more significant and comparable to that in ice when both the concentration of H_2O_2 and protons increased by 10 times. Therefore, the enhanced reduction of Cr(VI) in ice should be attributed to the freeze concentration of both protons and H_2O_2 (not protons or H_2O_2 alone) in the liquid brine.

H_2O_2 -Mediated Reduction of Cr(VI) in Electroplating Wastewater in Water and Ice. To verify the enhanced H_2O_2 -mediated Cr(VI) reduction by freezing in real Cr(VI)-contaminated aquatic systems, the reduction of Cr(VI) in the diluted electroplating wastewater was investigated in both water and ice (Figure 5). The electroplating wastewater was obtained from a local electroplating plant in Korea and its chemical composition is listed in Table 1. The concentration of Cr(VI) in the electroplating wastewater was $\sim 0.6 \text{ M}$ and the pH was ~ 0.4 . The raw electroplating wastewater was diluted $\sim 30,000$ times with deionized water. After the addition of H_2O_2 (100

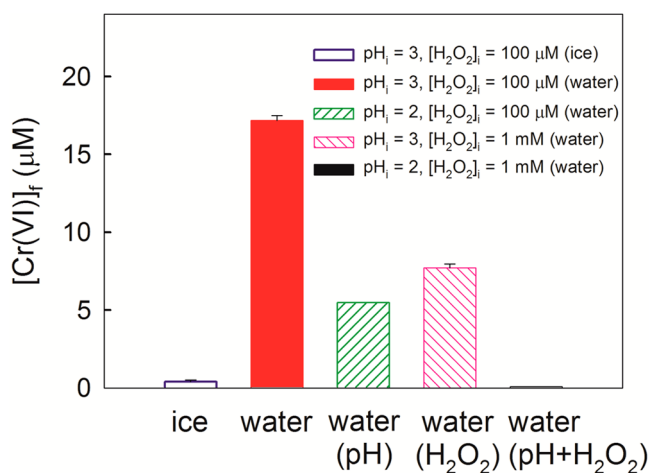


Figure 4. Effect of H₂O₂ concentration and pH on Cr(VI) reduction in water and ice. Experimental conditions were as follows: [Cr(VI)]_i = 20 μM, reaction temperatures = water at 25 °C and ice at −20 °C, and reaction time = 2 h.

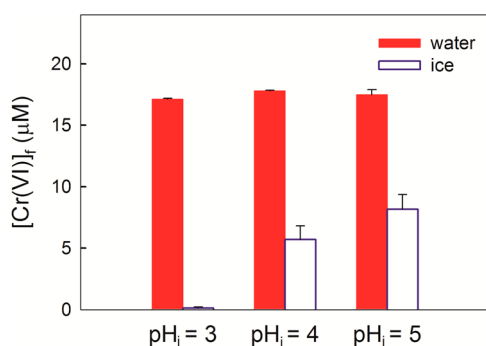


Figure 5. Reduction of Cr(VI) in the electroplating wastewater by H₂O₂ at various pH in water and ice. The electroplating wastewater was diluted to the desired concentration, H₂O₂ was added, and then the pH was adjusted with a HClO₄ solution. Experimental conditions were as follows: [Cr(VI)]_i = 20 μM, [H₂O₂]_i = 100 μM, reaction temperatures = water at 25 °C and ice at −20 °C, and reaction time = 2 h.

mM, 100 μL) to the diluted electroplating wastewater ([Cr(VI)] ≈ 20 μM, 99.9 mL), the pH of the diluted electroplating wastewater containing H₂O₂ ([Cr(VI)] = 20 μM, [H₂O₂] = 100 μM, and pH 5.1) was adjusted to the desired pH (i.e., pH 3.0, 4.0, or 5.0) with a HClO₄ solution. The reduction of Cr(VI) in the electroplating wastewater by H₂O₂ was also markedly enhanced by freezing at all pH ranges tested (pH 3–5). In addition, the reduction efficiency of Cr(VI) in the electroplating wastewater was similar to that in the deionized water despite the presence of other metals, which implies that H₂O₂ can selectively reduce Cr(VI) among the various metals.

Environmental Implications. Both Cr(VI) and H₂O₂ are ubiquitous in atmospheric water, natural waters, and soil,^{50,51} and chemical reactions in ice can occur in various geographical regions, such as permafrost, polar regions, high latitudes, and

midlatitudes during the winter season, and the upper troposphere. Therefore, the reaction in ice between Cr(VI) and H₂O₂ can significantly influence the concentrations of both Cr(VI) and H₂O₂ in the global environment. In particular, the pH of atmospheric water, such as rain and clouds, is in the range of 2–6,⁵² which is a good condition for the proposed ice/Cr(VI)/H₂O₂ process. Therefore, the freezing of atmospheric water containing both Cr(VI) and H₂O₂ in the cryosphere and the upper troposphere can significantly reduce its toxicity and potential risk through the reduction of Cr(VI) to Cr(III).

Cr(VI) is one of the most notorious pollutants generated from various industries due to its high production volume and toxicity, and the pH of Cr(VI)-contaminated wastewaters is very low.⁵³ In addition, the pH of acid mine drainage (AMD), which contains high concentrations of chromium (up to 15 mM), is usually lower than 5.0.^{54,55} The results of this study imply that a respectable amount of Cr(VI) in Cr(VI)-contaminated wastewater and AMD can be removed by reacting with naturally generated H₂O₂ in cold environments.

We investigated the reduction of Cr(VI) by H₂O₂ in frozen aqueous solutions compared with the corresponding reaction in aqueous solutions. In water, the reaction between Cr(VI) and H₂O₂ is very slow and the intermediate Cr(V) species, which is generated from the one-electron reduction of Cr(VI) by H₂O₂, is immediately reoxidized back to Cr(VI). Therefore, the reduction of Cr(VI) to Cr(III) by H₂O₂ was limited in water. In contrast, the reduction of Cr(VI) by H₂O₂ proceeded rapidly at pH 3.0 in ice until either Cr(VI) or H₂O₂ was completely consumed. The reaction between Cr(VI) and H₂O₂ in ice was primarily initiated by a proton-coupled electron transfer (PCET) mechanism and the observed H₂O₂ to Cr(VI) molar ratio value ~1.5 satisfied the theoretical (stoichiometric) requirements. The enhanced reduction of Cr(VI) in ice should be attributed to the freeze concentration of both H₂O₂ and protons in the liquid brine, which provide a better reaction medium for the reduction of Cr(VI) to Cr(III) through PCET reaction. The observed synergistic effect of higher H₂O₂ concentration and lower pH on Cr(VI) reduction in water corroborates the freeze concentration phenomenon as the reason for the enhanced Cr(VI) reduction in ice. The reduction efficiency of Cr(VI) by H₂O₂ in ice varied depending on the H₂O₂ concentration, pH, and freezing temperature. However, the reduction of Cr(VI) in ice was more significant than that in water under all experimental conditions. This study provides useful information for understanding the fate and cycling of Cr(VI) in the cryosphere and the upper troposphere. However, the exact concentrations of H₂O₂ and proton in the liquid brine are unknown at this stage. Based on precise modeling and/or in situ measurement of H₂O₂ and proton concentrations in the liquid brine during freezing, more detailed quantitative investigations of the Cr(VI) reduction kinetics in ice need to be performed.

Table 1. Chemical Composition of the Electroplating Wastewater

element ^a	Al	As	B	Ca	Cr	Cs	Cu	Fe	Mg	Mo	Na	Pb	Tl
concentration (ppm) ^a	56	100	62	306	39524	9104	281	1348	69	50	125	75	37

^aConcentrations of other elements (Ag, Ba, Be, Cd, Co, Mn, Ni, Sb, Se, Si, Ti, V, and Zn) were negligible.

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Notes

The authors declare no competing financial interest.

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