Freezing-enhanced reduction of chromate by nitrite

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HIGHLIGHTS

- Reduction of Cr(VI) by NO_2^- was significantly enhanced during freezing.
- NO_2^- was primarily oxidized to NO_3^- in ice.
- Enhanced Cr(VI) reduction in ice is ascribed to the freeze concentration effect.
- Reduction of Cr(VI) was enhanced by freezing under various conditions.
- Freezing-enhanced reduction of Cr(VI) in the electroplating wastewater was observed.

GRAPHICAL ABSTRACT
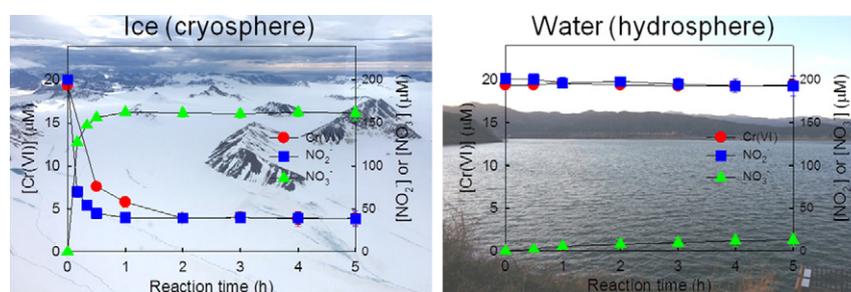
ARTICLE INFO

ABSTRACT

The redox reactions between pollutants and chemicals (e.g., pollutant, oxygen, and water) critically affect the fate and potential risk of pollutants, and their rates significantly depend on the environmental media. Although the kinetics and mechanism of various redox reactions in water have been extensively investigated, those in ice have been hardly explored, despite the large areal extent of the cryosphere, which includes permafrost, polar regions, and mid-latitudes during the winter season on Earth. In this study, we investigated the reduction of chromate (Cr(VI)) by nitrite (NO_2^-) in ice (i.e., at $-20\,°C$) in comparison with its counterpart in water (i.e., at $25\,°C$). The reduction of Cr(VI) by NO_2^- was limited in water, whereas it was significant in ice with the simultaneous oxidation of NO_2^- to nitrate (NO_3^-). This enhanced Cr(VI) reduction by NO_2^- in ice is most likely due to the freeze concentration effect, that concentrates Cr(VI), NO_2^-, and protons (at acidic conditions) in the liquid brine (the liquid region among solid ice crystals). The increased thermodynamic driving force for the redox reaction between Cr(VI) and NO_2^- by the freeze concentration effect (i.e., the increase in concentrations) enhances the reduction of Cr(VI) by NO_2^-. The freezing-enhanced Cr(VI) reduction by NO_2^- was observed under the conditions of NO_2^- concentration = 20 μM–2 mM and pH = 2–4, which are often found in real aquatic systems contaminated by both Cr(VI) and NO_2^-. The reduction kinetics of Cr(VI) in real Cr(VI)-contaminated wastewater (electroplating wastewater) during freezing was significant and comparable to that in the artificial Cr(VI) solution. This result implies that the proposed ice/Cr(VI)/NO_2^- process should be relevant and feasible in real cold environments.

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1. Introduction

Chemical reactions in ice (i.e., at temperatures below the freezing point) are different from those in water (i.e., at temperatures above the freezing point). A liquid region remains among the solid ice crystals

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and on the ice crystal surface at temperatures below the freezing point, although its volume continuously decreases with the growth of ice crystals with time (Bartels-Rausch et al., 2014; Boxe and Saiz-Lopez, 2008; Park et al., 2010). This liquid region in ice is often referred to as liquid brine, liquid-like layer, liquid-like ice grain boundary, unfrozen solution, frozen aqueous solution, or micropocket. It can provide a unique environment for the chemical reactions and induce different reaction pathways from those in water.

The chemical reaction rate generally decreases with decreasing temperature according to the Arrhenius equation. However, some chemical reactions in the liquid region of ice (at relatively lower temperatures) proceed more rapidly than those in water (at relatively higher temperatures). The accelerated chemical reactions in ice can be classified into four categories: (1) reaction between solutes and dissolved gases (e.g., nitrite/oxygen (Takenaka et al., 1996; Takenaka et al., 1992), iodide/oxygen (Kim et al., 2016), and 1,1-diphenylethylene/ozone (Ray et al., 2011)), (2) reaction between solutes and water (e.g., fluorescein diacetate/water (Anzo et al., 2013)), (3) reaction between solutes and solutes (e.g., chromate/arsenite (Kim and Choi, 2011), chromate/hydrogen peroxide (Kim et al., 2015), and mercury/hydrogen peroxide (O'Concubhair et al., 2012)), and (4) dissolution of metal oxides (e.g., iron oxide (Jeong et al., 2012; Kim et al., 2010) and manganese oxide (Kim et al., 2012)). These reaction kinetics in ice are accelerated compared to those in water mostly due to the freeze concentration effect, that concentrates solutes, protons (at acidic conditions), and dissolved gases in the liquid region of ice and increases the thermodynamic driving force for chemical reactions (Finnegan et al., 2001; Takenaka and Bandow, 2007). The fate and behavior of chemical species (i.e., pollutants) in cold regions (e.g., permafrost, polar regions, and mid-latitudes during the winter season) can be notably different from those in warm regions due to the different chemical kinetics and mechanisms between water and ice.

Chromium (Cr) contamination in water occurs from both anthropogenic sources (e.g., discharge of industrial wastewater from corrosion inhibition, metallurgy, electroplating, leather tanning, and dye plants) and natural sources (e.g., weathering and dissolution of Cr-bearing minerals) (Barnhart, 1997; Vaiopoulou and Gikas, 2012). The World Health Organization (WHO) has established a provisional guidance value for Cr in drinking water (1 μM) (WHO, 2011). Cr exists mainly as metallic Cr (Cr^0), trivalent Cr (Cr(III)), and hexavalent Cr (chromate, Cr(VI)) in water. The toxicity of Cr species significantly depends on its oxidation state. Cr(VI) is more toxic than Cr^0 and Cr(III) due to its high transport capacity to the cell (Costa, 2003). Therefore, the European Union (EU) strictly restricts the concentration of Cr(VI) among various Cr species based on the European Restriction of Hazardous Substances Directive (EU, 2011).

Nitrite (NO_2^-) is one of the most abundant nitrogen species in the environment with nitrate (NO_3^-), ammonium (NH_4^+), and dinitrogen (N_2). Among these nitrogen species, NO_2^- is more toxic than the others to humans and animals (Abrol et al., 2007; Chen et al., 2011). Wastewaters from various industries, such as food preservation, corrosion inhibition, pharmaceutical, dye, and fertilizer, contain high concentrations of NO_2^- (Mackerness and Keevil, 1991; Walters, 1991). In addition, NO_2^- is produced from the biological reduction of NO_3^- by microorganisms under anoxic conditions (Cabello et al., 2004; Yan et al., 2016). It indirectly contributes to the eutrophication in surface waters and algal bloom in estuary waters as a source of nitrogen (Anderson et al., 2002). The reaction of NO_2^- with amino compounds in the human body forms N-nitroso compounds, which are highly toxic and carcinogenic (Cammack et al., 1999). NO_2^- can oxidize hemoglobin to methemoglobin, which reduces the oxygen transport ability in the blood and causes blue baby syndrome in infants (Jones et al., 2015). Therefore, the WHO recommends that the concentration of NO_2^- in drinking water should not exceed 4.3 μM (WHO, 2011).

Both Cr(VI) and NO_2^- are ubiquitous in various environments, such as atmospheric water, soil, surface water, groundwater, and wastewater. Therefore, the coexistence of Cr(VI) and NO_2^- in the environment is fairly common. In this work, we compared the reduction of Cr(VI) by NO_2^- in ice (i.e., at −20 °C) with that in water (i.e., at 25 °C). The reduction of Cr(VI) by NO_2^- was significantly enhanced by freezing. The reduction of Cr(VI) to Cr(III) was accompanied by the oxidation of NO_2^- to NO_3^-. The reduction of Cr(VI) in ice was investigated as a function of various experimental parameters, such as NO_2^- concentration, pH, and freezing temperature. The reduction of Cr(VI) in real Cr(VI)-contaminated wastewater was also investigated to verify the environmental relevance of the freezing-enhanced reduction of Cr(VI) by NO_2^-. The mechanism of the enhanced Cr(VI) reduction by NO_2^- in ice and its environmental implications are discussed.

2. Chemicals and methods

2.1. Chemicals

The chemicals were used as received without further purification. They include sodium dichromate dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$, Cr(VI), Sigma-Aldrich, ≥99.5%), sodium nitrite ($NaNO_2$, Sigma-Aldrich, ≥99.0%), sodium nitrate ($NaNO_3$, Sigma-Aldrich, ≥99.0%), acetone (CH_3COCH_3, Junsei, ≥99.5%), sulfuric acid (H_2SO_4, Sigma-Aldrich, ≥95.0%), 1,5-diphenylcarbazide ($C_6H_5NHNHCONHNHC_6H_5$, DPC, Sigma-Aldrich, ≥99.95%), potassium hydrogen phthalate ($C_8H_5KO_4$, Junsei, ≥99.8%), sodium carbonate (Na_2CO_3, Sigma-Aldrich, ≥99.5%), and sodium bicarbonate ($NaHCO_3$, Sigma-Aldrich, ≥99.7%). Ultrapure deionized water (18.3 MΩ·cm) was used and prepared using a water purification system (Barnstead). The Cr(VI)-contaminated wastewater ([Cr(VI)] = 106.2 mM and pH = 0.2) was obtained from a local electroplating plant in Republic of Korea.

2.2. Experimental procedure

An aliquot of NO_2^- and Cr(VI) chemical stock solution was added to the deionized water in a beaker to yield the desired initial concentration (typically [Cr(VI)] = 20 μM and [NO_2^-] = 200 μM). The pH of the solution was adjusted using $HClO_4$ (1 M) or NaOH (1 M) solution (typically pH = 3.0) and measured using a benchtop pH meter (Thermo Orion Star A211). First, 10 mL of this solution was put in a 15 mL conical tube. The conical tube was placed in a stainless steel tube rack in an ethanol bath adjusted to the desired temperature (typically −20 °C) to freeze the aqueous sample. The time point when the conical tube was put into the ethanol bath was defined as reaction time zero in reaction kinetics measurements. The frozen samples were thawed in lukewarm water (35 °C) and immediately analyzed. The experiments in water were identical to those in ice except for the temperature of ethanol bath. The aqueous samples were maintained at 25 °C in the ethanol bath. All experiments were performed at least twice to confirm the data reproducibility.

2.3. Chemical analyses

The concentration of Cr(VI) was measured spectrophotometrically using the 1,5-diphenylcarbazide (DPC) method (Eaton et al., 1995). First, 100 μL of DPC reagent solution prepared with 0.05 g of DPC, 25 mL of acetone, and 250 μL of sulfuric acid was added to an amber vial containing 3 mL of aqueous sample. The aqueous solution was mixed vigorously and kept in the dark for 1 h. Then, its absorbance was measured at 540 nm using a UV–visible spectrophotometer (Shimadzu UV-2600).

The concentrations of NO_2^- and NO_3^- generated from the oxidation of NO_2^- were measured using an ion chromatograph (IC, Dionex ICS-1100) equipped with a Dionex IonPac AG14 guard column (4 mm × 50 mm), a Dionex IonPac AS14 column (4 mm × 250 mm), and a conductivity detector. The eluent consisted of a binary mixture

of sodium carbonate (3.5 mM) and sodium bicarbonate (1 mM). Its flow rate was 1.0 mL/min.

Concentrations of Cr(VI), NO_2^-, and NO_3^- were determined based on the calibration curves, which were obtained using standard solutions (chromate standard (Sigma-Aldrich) for Cr(VI) and Dionex combined seven anion standard (Thermo) for NO_2^- and NO_3^-) with every measurement. The correlation coefficients (r^2) of calibration curves were higher than 0.99.

The types of elements in Cr(VI)-contaminated wastewater and their concentrations were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo iCAP 6300 Duo). The concentration of total organic carbon (TOC) in Cr(VI)-contaminated wastewater was measured using a TOC analyzer (Shimadzu TOC-V_{CSH}). The concentration of TOC was obtained by subtracting the concentration of inorganic carbon (IC) from the concentration of total carbon (TC).

PlasmaCAL multi-element standard (SCP science), potassium hydrogen phthalate, and sodium carbonate/sodium bicarbonate were used to make calibration solutions for ICP-OES, TC, and IC analyses, respectively. The correlation coefficients (r^2) of calibration curves were better than 0.99

3. Results and discussion

3.1. Reduction of Cr(VI) by NO_2^- in water and ice

At temperatures below the freezing point, chemicals are excluded from ice crystals (frozen compartment) and subsequently concentrated in the liquid region (unfrozen compartment) (Finnegan et al., 2001; Takenaka and Bandow, 2007). Therefore, chemical reactions occur in the liquid region, but not in ice crystals. In this study, the term "ice" refers to the liquid region of ice (not the ice crystals of ice), and the term "liquid brine" is used to denote the liquid region of ice among various descriptions for the liquid region of ice.

The reduction of Cr(VI) by NO_2^- (i.e., the simultaneous reduction of Cr(VI) to Cr(III) and oxidation of NO_2^- to NO_3^-) in water (i.e., at 25 °C) was compared with that in ice (i.e., at −20 °C) (Fig. 1). The reduction of Cr(VI) was negligible in water at [Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, and pH = 3.0. However, it proceeded rapidly in ice under the identical experimental conditions (Fig. 1a). The concentration of Cr(VI) in the ice sample gradually decreased with the reaction time, and only 3.9 μM of Cr(VI) remained after 2 h of reaction. The reduction of Cr(VI) in ice proceeded even in the absence of NO_2^-. This behavior is ascribed to the concentrations of protons and Cr(VI) in the liquid brine during freezing that increases the driving force for the proton-mediated reduction process ($4HCrO_4^- + 16H^+ \rightarrow 4Cr^{3+} + 3O_2 + 10H_2O$) (Kim and Choi, 2011; Kim et al., 2015). However, the degree of Cr(VI) reduction in the absence of NO_2^- was much lower than that in the presence of NO_2^-, which indicates that the reduction of Cr(VI) in the presence of NO_2^- primarily occurred by NO_2^-.

The reduction of Cr(VI) was accompanied by the oxidation of NO_2^- to NO_3^-. The oxidation of NO_2^- to NO_3^- was limited in water, whereas it was significant in ice (Fig. 1b). The total nitrogen-mass balance was satisfied throughout the reaction time in both water and ice. This result indicates that NO_2^- was primarily oxidized to NO_3^-, and the generation of other nitrogen products was minor. In contrast to the case of Cr(VI), a significant oxidation of NO_2^- to NO_3^- was observed in ice even in the absence of Cr(VI). This result is consistent with previous studies, where the concentrations of NO_2^- and O_2 in the liquid brine during freezing accelerate the oxidation of NO_2^- to NO_3^- ($2HNO_2 + O_2 \rightarrow 2NO_3^- + 2H^+$) (Takenaka et al., 1996; Takenaka et al., 1992). However, the presence of Cr(VI) (20 μM) enhanced the oxidation of NO_2^- to NO_3^- in ice, which indicates that the oxidation of NO_2^- by Cr(VI) is favored compared to that by O_2.
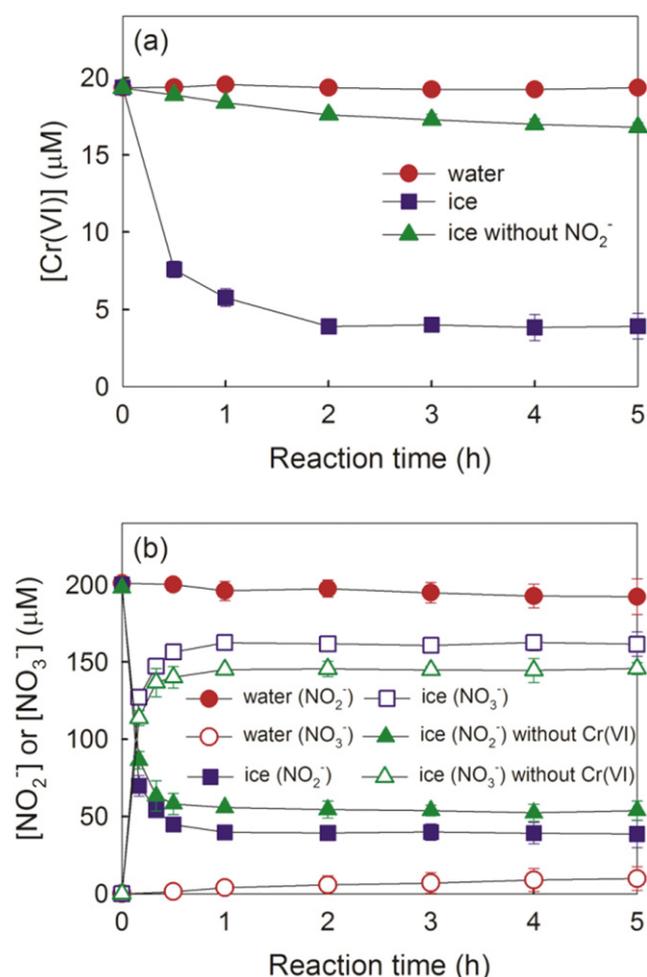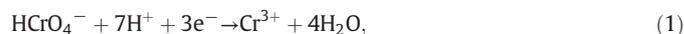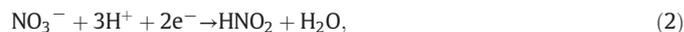

Fig. 1. Time profiles of (a) Cr(VI), (b) NO_2^-, and NO_3^- (generated from NO_2^- oxidation) concentrations in water and ice ([Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, pH = 3.0, and reaction temperature = 25 °C in water and −20 °C in ice).

The reduction potentials (i.e., the driving force, E) of Cr(VI)/Cr(III) (reaction (1)) and NO_3^-/NO_2^- (reaction (2)) are E_1 and E_2, respectively.

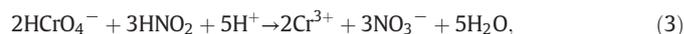$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O, \tag{1}$$
$$E_1 = E_1^0 - 0.14pH + 0.02 \log\left(\left[HCrO_4^-\right]/\left[Cr^{3+}\right]\right) V_{NHE}$$

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O, \tag{2}$$
$$E_2 = E_2^0 - 0.09pH + 0.03 \log([NO_3^-]/[HNO_2]) V_{NHE}$$

where E_1^0 and E_2^0 are 1.35 V_{NHE} and 0.93 V_{NHE}, respectively (Lide, 1996).

The reduction potential of the net reaction (reaction (3), reduction of Cr(VI) by NO_2^-) obtained from reactions (1) and (2) is E_3. The equation of E_3 indicates that the decrease in pH and increase in Cr(VI) and NO_2^- concentrations enhance the reduction of Cr(VI) by NO_2^- by increasing the driving force for reaction (3) (i.e., E_3 value).

$$2HCrO_4^- + 3HNO_2 + 5H^+ \rightarrow 2Cr^{3+} + 3NO_3^- + 5H_2O, \tag{3}$$
$$E_3 = E_1 - E_2$$
$$= 0.42 - 0.05pH + 0.02 \log\left(\left[HCrO_4^-\right]/\left[Cr^{3+}\right]\right) + 0.03 \log([HNO_2]/[NO_3^-]) V_{NHE}$$

The enhanced reduction of Cr(VI) in the presence of NO_2^- in ice is most likely due to the freeze concentration effect during freezing, that

creates a better environment for the Cr(VI) reduction by NO_2^- by increasing the Cr(VI) and NO_2^- concentrations and decreasing the pH. It has been reported that the concentrations of solutes and protons (at acidic conditions) in ice increase by 3–6 and 2–4 orders of magnitude, respectively, compared with those in water (Heger et al., 2005; Heger et al., 2006). It should be pointed out that the alkaline solution becomes more basic by freezing due to the concentration of hydroxides in the liquid brine (Heger et al., 2006). The theoretical molar ratio of NO_2^- to Cr(VI) ([NO_2^-] oxidized/[Cr(VI)] reduced) is 1.5 according to reaction (3). In fact, 13.7 μM of Cr(VI) was reduced by NO_2^- ([Cr(VI)] reduced in the presence of NO_2^- – [Cr(VI)] reduced in the absence of NO_2^-), and 17.2 μM of NO_2^- was oxidized by Cr(VI) ([NO_2^-] oxidized in the presence of Cr(VI) – [NO_2^-] oxidized in the absence of Cr(VI)) for 2 h. Therefore, the experimental molar ratio of NO_2^- to Cr(VI) is 1.3. The similar molar ratio of NO_2^- to Cr(VI) between theoretical and experimental values indicates that reaction (3) is the main reaction pathway between Cr(VI) and NO_2^- in ice.

The redox reaction between Cr(VI) and NO_2^- in ice completely stopped within 2 h, although 3.9 μM of Cr(VI) and 39.4 μM of NO_2^- remained in ice (Fig. 1). It has been reported that chemical reactions in ice are stopped by complete solidification when the temperature of ice falls below the eutectic point (Takenaka et al., 2006; Takenaka et al., 1996). To verify the incomplete redox reaction between Cr(VI) and NO_2^- by complete freezing, the ice sample was thawed and refrozen after the redox reaction between Cr(VI) and NO_2^- was stopped (i.e., after 2 h of reaction). The reduction of Cr(VI) and oxidation of NO_2^- proceeded again by refreezing (Fig. 2), which indicates that the redox

reaction between Cr(VI) and NO_2^- is stopped by complete freezing and it can be enhanced by the freeze/thaw cycling process through day/night and seasonal temperature variation.

3.2. Reduction of Cr(VI) by NO_2^- in water and ice under various conditions

The effects of NO_2^- concentration, pH, and freezing temperature on the reduction of Cr(VI) in ice were investigated and compared with those in water (Fig. 3). The final concentrations of Cr(VI) remained in the samples ([Cr(VI)]$_f$) were measured after 2 h of reaction. The reduction of Cr(VI) in ice was more significant than that in water at all NO_2^- concentrations tested (20 μM ≤ [NO_2^-] ≤ 2 mM) under the conditions of [Cr(VI)] = 20 μM and pH = 3.0 (Fig. 3a). This result indicates that the freezing-enhanced reduction of Cr(VI) by NO_2^- is valid in various NO_2^--contaminated aquatic systems, where the concentration of NO_2^- varies from a few μM to mM (e.g., a few μM in surface water (Rawat et al., 2012), hundreds of μM in surface water near the solid waste landfill site (Pandey and Tiwari, 2016), and a few mM in wastewater (Li et al., 2010)).

The reduction of Cr(VI) to NO_2^- concentration (i.e., [Cr(VI)] reduced/[NO_2^-] added) was higher at lower NO_2^- concentrations. This behavior is because the freeze concentration effect in dilute solution is more significant than that in concentrated solution (i.e., the concentration factor is higher at lower solute concentrations (Grannas et al., 2007)). The reduction of Cr(VI) (i.e., only [Cr(VI)] reduced) gradually increased with increasing [NO_2^-] in ice. However, the reduction of Cr(VI) in water remained negligible despite the increase in [NO_2^-] by 10 times from 20 μM to 200 μM, and it was observed from [NO_2^-] = 400 μM. This result indicates that the reduction of Cr(VI) by NO_2^- is initiated above a critical concentration of NO_2^-, which provides the sufficient driving force for reaction (3).

Fig. 3b shows the pH-dependent Cr(VI) reduction by NO_2^- in water and ice. The reduction of Cr(VI) in water was negligible in the pH range of 2–6 at [Cr(VI)] = 20 μM and [NO_2^-] = 200 μM. However, a significant reduction of Cr(VI) was observed in the pH range of 2–4 in ice and its degree gradually increased with decreasing pH. This result is ascribed to the fact that the reduction of Cr(VI) by NO_2^- is primarily initiated by a proton-coupled redox mechanism (reaction (3)). A decrease in pH increases the driving force for reaction (3) (i.e., E_3 value) by increasing the concentration of protons, which eventually enhances the reduction of Cr(VI) by NO_2^-.

In addition, this behavior may be related to the speciation of NO_2^- ($pK_{a1} = 1.7$ and $pK_{a2} = 2.8$) (Anastasio and Chu, 2009) depending on the pH (Fig. 3c). The pH of aqueous solution decreases from 4.0 to below 2.0, where nitrous acidium ion (H_2ONO^+) can exist, by freezing (Heger et al., 2006). The molar fraction of H_2ONO^+ increases with decreasing pH. The reaction between cationic H_2ONO^+ and anionic Cr(VI) ($HCrO_4^-$ or $Cr_2O_7^{2-}$) should be favored compared to the reaction between neutral nitrous acid (HONO) (or anionic NO_2^-) and anionic Cr(VI) due to the electrostatic attraction. Therefore, the increase of cationic H_2ONO^+ species at lower pH can synergistically enhance the reduction of Cr(VI) in ice.

Although NO_2^--contaminated water is generally neutral (Li et al., 2010; Pandey and Tiwari, 2016; Rawat et al., 2012), the pH of Cr(VI)-contaminated water is extremely low (Bokare and Choi, 2010; Chen et al., 2007; Sheoran and Sheoran, 2006). When NO_2^--contaminated water is mixed with Cr(VI)-contaminated water, the pH of the mixture should be low, which is a good condition for the redox reaction between NO_2^- and Cr(VI) in ice.

The reduction of Cr(VI) by NO_2^- in ice was also measured as a function of the freezing temperature (−5, −10, −15, and −20 °C) and compared with that in water (25 °C) (Fig. 3d). The reduction of Cr(VI) was significantly enhanced by freezing at all freezing temperatures tested. The concentration rate is higher at lower freezing temperatures. Therefore, the reduction rate of Cr(VI) in ice increased with decreasing freezing temperature. Although the effect of the freezing temperature
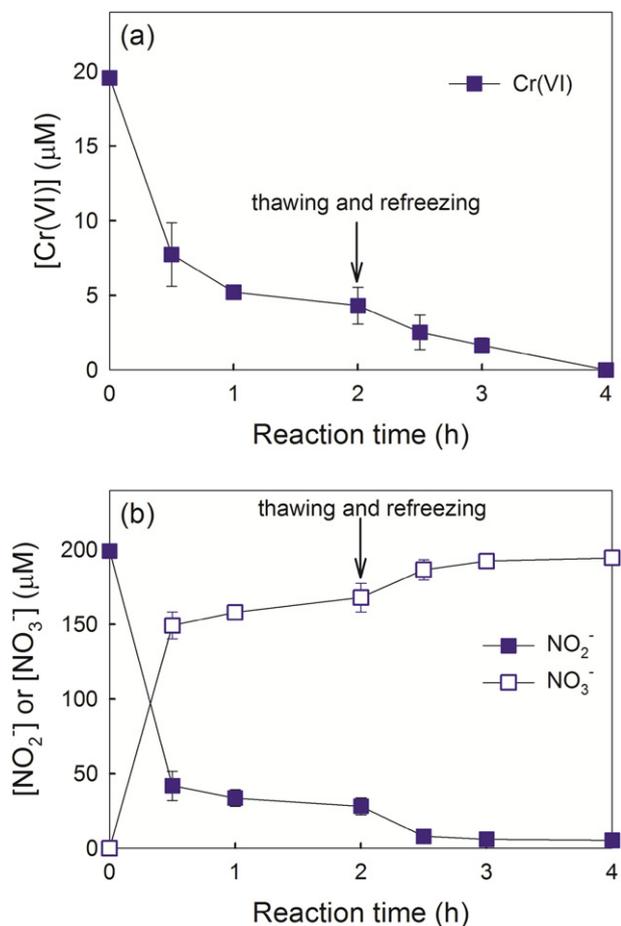

Fig. 2. Time profiles of (a) Cr(VI), (b) NO_2^-, and NO_3^- (generated from NO_2^- oxidation) concentrations during the freeze/thaw cycling process. After 2 h of reaction (as indicated by arrows), the frozen samples were thawed in lukewarm water (at 35 °C) and refrozen in the ethanol bath (at −20 °C) ([Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, pH = 3.0, and reaction temperature = −20 °C).
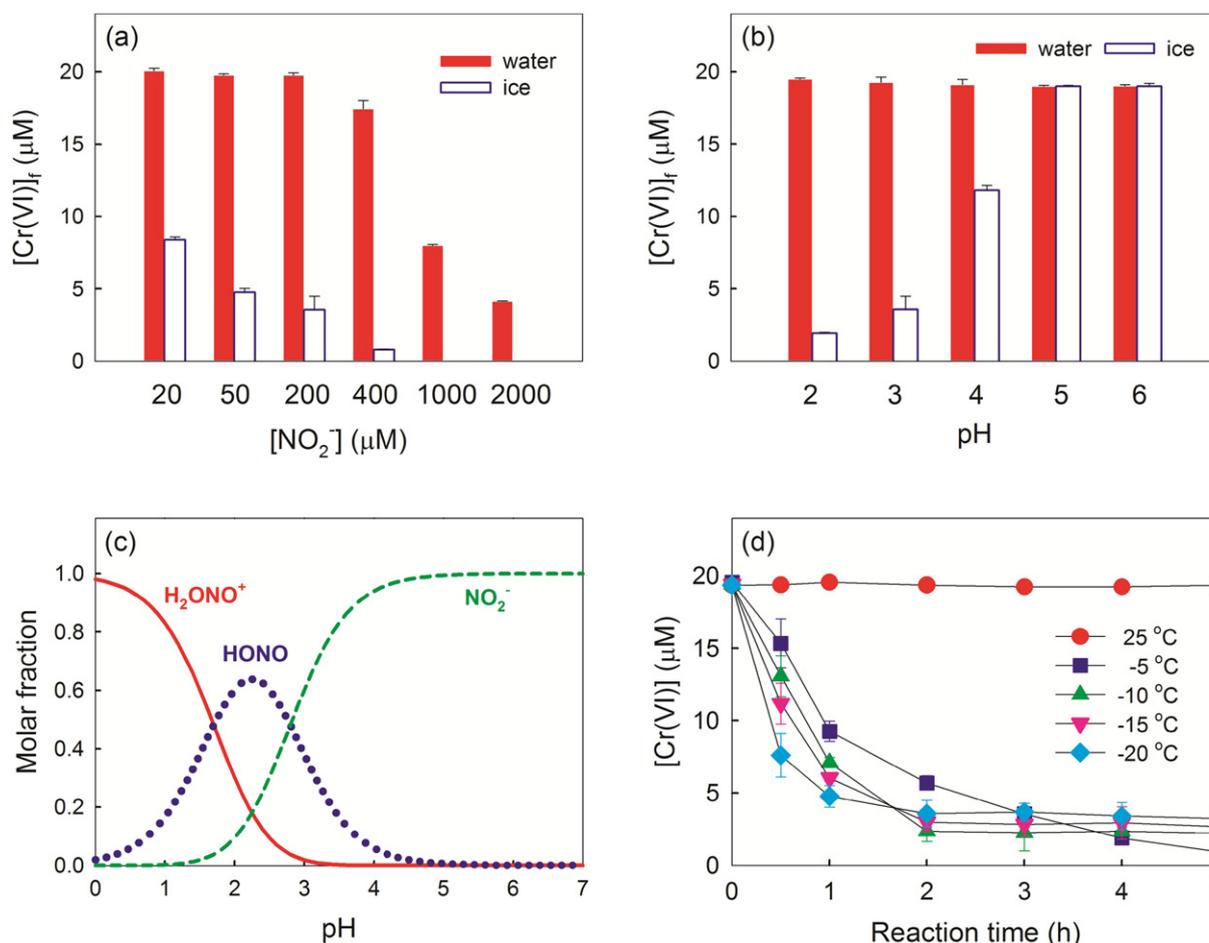
Fig. 3. Effect of (a) NO_2^- concentration and (b) pH on the reduction of Cr(VI) in water and ice. (c) Molar fraction of nitrogen species (NO_2^-, HONO, and H_2ONO^+) as a function of pH. (d) Reduction of Cr(VI) depending on the temperature in water and ice ([Cr(VI)] = 20 μM for parts a, b, and d, [NO_2^-] = 200 μM for parts b and d, pH = 3.0 for parts a and d, reaction temperature = 25 °C in water and −20 °C in ice for parts a and b, and reaction time = 2 h for parts a and b).

on the degree of Cr(VI) reduction is not significant, a general trend is clearly observed. More Cr(VI) was reduced at higher freezing temperatures. The chemical reaction proceeds during freezing and stops when the aqueous solution is completely frozen (i.e., when there is no liquid brine at temperatures below the eutectic point) (Takenaka et al., 2006; Takenaka et al., 1996). Therefore, the reduction of Cr(VI) by NO_2^- in the liquid brine can last a longer time at higher freezing

temperatures, which helps explain the increase in the degree of Cr(VI) reduction by NO_2^- with increasing freezing temperature. The reduction of Cr(VI) by NO_2^- in ice stopped at a specific time at lower freezing temperatures than −10 °C, whereas it continuously proceeded at −5 °C. Therefore, the eutectic temperature of solution at [Cr(VI)] = 20 μM,
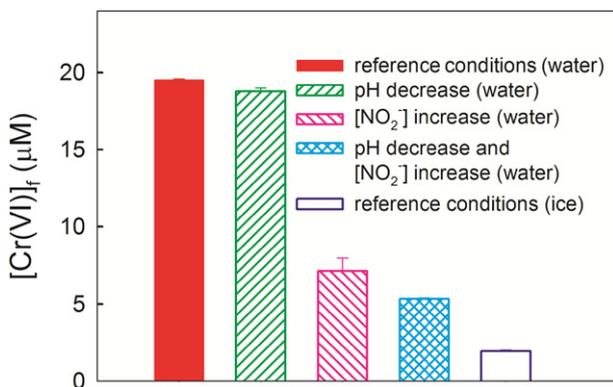

Fig. 4. Effect of increase in NO_2^- concentration and/or decrease in pH on the reduction of Cr(VI) in water (reference conditions: [Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, and pH = 2.0; pH decrease: [Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, and pH = 1.0; [NO_2^-] increase: [Cr(VI)] = 20 μM, [NO_2^-] = 2 mM, and pH = 2.0; pH decrease and [NO_2^-] increase: [Cr(VI)] = 20 μM, [NO_2^-] = 2 mM, and pH = 1.0; and reaction time = 2 h).
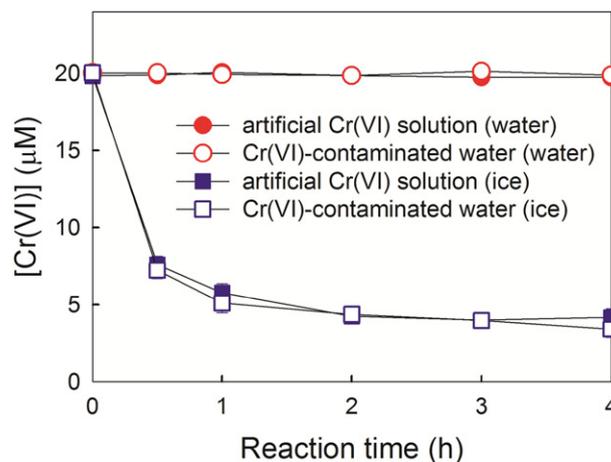

Fig. 5. Reduction of Cr(VI) in Cr(VI)-contaminated wastewater and artificial Cr(VI) solution in water and ice ([Cr(VI)] = 20 μM, [NO_2^-] = 200 μM, pH = 3.3, and reaction temperature = 25 °C in water and −20 °C in ice).

Table 1
Types of elements in electroplating wastewater and their concentrations.

Type	Al	As	B	Ca	Cr	Cs	Cu	Fe	Mg	Mo	Na	Pb	Tl
Concentration (mM)	4.1	1.3	7.7	8.6	122.1	75.5	22.4	42.1	2.8	0.7	5.4	0.7	0.5

$[NO_2^-] = 200\ \mu M$, and pH = 3.0 is estimated to be between $-5\ °C$ and $-10\ °C$.

3.3. Effect of freeze concentration on the Cr(VI) reduction by NO_2^-

Fig. 3 shows that the reduction of Cr(VI) by NO_2^- increased with increasing NO_2^- and proton concentrations and freezing temperature. This result indirectly supports that the freeze concentration of NO_2^- and protons in the liquid brine enhances the Cr(VI) reduction in ice. To provide convincing evidence of this mechanism, the reduction of Cr(VI) for 2 h in water was investigated at a high concentration of NO_2^- (2 mM) and/or low pH (1.0) and compared with the result at the reference conditions ($[NO_2^-] = 200\ \mu M$ and pH = 2.0) (Fig. 4). The decrease in pH by 1 order of magnitude (i.e., a 10 times increase in proton concentration) slightly increased the reduction of Cr(VI). The increase in NO_2^- concentration by 10 times also increased the reduction of Cr(VI). When both NO_2^- and proton concentrations increased by 10 times (i.e., at $[NO_2^-]$ = 2 mM and pH = 1.0), the reduction of Cr(VI) in water was more significant than that when either NO_2^- (i.e., at $[NO_2^-]$ = 2 mM and pH = 2.0) or proton concentration (i.e., at $[NO_2^-] = 200\ \mu M$ and pH = 1.0) increased. This result indicates that the enhanced Cr(VI) reduction in ice is most likely due to the freeze concentration effect, and the concentrations of both NO_2^- and protons in the liquid brine synergistically enhance the reduction of Cr(VI).

3.4. Reduction of Cr(VI) in real Cr(VI)-contaminated wastewater by NO_2^-

We investigated the reduction of Cr(VI) in Cr(VI)-contaminated wastewater by NO_2^- in water and ice to verify the environmental relevance of the proposed freezing-enhanced Cr(VI) reduction by NO_2^- (Fig. 5). Cr(VI)-contaminated wastewater obtained from an electroplating plant was mixed with the NO_2^- solution. The initial concentrations of Cr(VI) and NO_2^- in the aqueous mixture were 20 μM and 200 μM, respectively and the pH was 3.3. The reduction of Cr(VI) in Cr(VI)-contaminated wastewater by NO_2^- was negligible in water, whereas it was significant in ice. Importantly, the reduction kinetics of Cr(VI) in the Cr(VI)-contaminated wastewater during freezing was similar to that in the artificial Cr(VI) solution ($[Cr(VI)]$ = 20 μM, $[NO_2^-]$ = 200 μM, and pH = 3.3). In the elemental analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES), various elements (i.e., Al, As, B, Ca, Cs, Cu, Fe, Mg, Mo, Na, Pb, and Tl) were found in the Cr(VI)-contaminated wastewater in addition to Cr. Their concentrations were 0.5–75.5 mM (Table 1). The Cr(VI)-contaminated wastewater also contained 23,200 ppm of organic compounds based on total organic carbon (TOC). These results indicate that other matters hardly affect the reduction of Cr(VI) by NO_2^- in ice. Therefore, the proposed ice/Cr(VI)/NO_2^- process should be relevant and feasible in the real cold environment. The concentration of Cr has gradually increased in the Arctic regions by sea salt contribution and atmospheric deposition. Even a trace amount of Cr(VI) can affect the Arctic ecosystem (Garbarino et al., 2002; Nriagu and Nieboer, 1998). However, the enhanced conversion of Cr(VI) to Cr(III) in ice in the presence of NO_2^- can reduce the toxicity and potential risk of Cr(VI) in the Arctic regions.

4. Conclusions

Chemical reactions in ice are different from those in water in terms of kinetics, mechanism, and environmental implication. Although the chemical reaction rates in ice are usually lower than those in water,

the reverse is observed in this case. In this study, we investigated the reduction of Cr(VI) by NO_2^- in ice (i.e., at $-20\ °C$) compared with that in water (i.e., at 25 °C). The reduction of Cr(VI) by NO_2^- was limited in water, whereas it was significant in ice. NO_2^- was simultaneously oxidized to the less toxic NO_3^- with the reduction of Cr(VI) to the less toxic Cr(III). Therefore, the enhanced redox reaction between Cr(VI) and NO_2^- in ice can be called the natural detoxification process in cold regions (e.g., permafrost, polar regions, and mid-latitudes during the winter season). The freezing-enhanced reduction of Cr(VI) was observed over a wide range of NO_2^- concentration (20 μM – 2 mM) and pH (2–4). These conditions are often found in real aquatic systems contaminated by both Cr(VI) and NO_2^-. The reduction efficiencies of Cr(VI) ($[Cr(VI)]$ = 20 μM and pH = 3) in ice were 58% and 100% at $[NO_2^-]$ = 20 μM and $[NO_2^-]$ ≥ 1 mM, respectively. 41% and 90% Cr(VI) ($[Cr(VI)]$ = 20 μM and $[NO_2^-]$ = 100 μM) reduction were achieved at pH = 4 and pH = 2, respectively. In addition, the NO_2^--mediated reduction of Cr(VI) in real Cr(VI)-contaminated wastewater during freezing was significant and comparable to that in the artificial Cr(VI) solution. This result verifies the environmental relevance of the proposed freezing-enhanced Cr(VI) reduction by NO_2^-. This study provides a new pathway to simultaneously convert NO_2^- and Cr(VI), which are abundant species in aquatic systems, to NO_3^- and Cr(III).

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