



Monograph

Enhanced reduction of hexavalent chromium by hydrogen sulfide in frozen solution

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ABSTRACT

Significant enrichment of hexavalent chromium [Cr (VI)] has been detrimentally influenced both environment and human's health in the polar regions. We found that reduction of Cr (VI) by hydrogen sulfide (H₂S) was significantly enhanced in ice (−20 °C) but relatively slow in water (25 °C) under the same experimental conditions. This enhancement is ascribed to the freeze concentrations of Cr (VI), H₂S, and proton (H⁺) in ice grain boundaries during freezing. Sulfate (SO₄^{2−}) was produced more appreciably in ice than in water. Cr (VI) reduction in ice was enhanced effectively under various H₂S concentrations (5.0–100 μM), pH_i (2.0–7.7), and increasing the freezing temperature from −30 to −15 °C. Optical and chemical observations with a confocal Raman microscope under frozen state supported the freeze concentration of Cr (VI) in ice grain boundaries. The accumulation of H⁺ (pH decrease) in ice grain boundaries was verified with the UV–visible absorption spectra of cresol red (CR) in ice. Removal of Cr (VI) in electroplating wastewater was significant and comparable to that in distilled water by freezing. Therefore, Cr (VI) reduction by H₂S in ice phase indicates the occurrence of Cr (VI) removal in cold regions.

1. Introduction

Chromium is known to be a ubiquitous source in ground- and surface water and is used mainly in various industrial processes, such as electroplating, metal cleaning, and others, and discharged, finally, into the water bodies without pre-treatment [1–7]. As regards the existence of chromium in the natural environment, it is reported to occur primarily as trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)]. In particular, chromite [FeCr (III)₂O₄] acts as a major geological source of Cr (III)-bearing mineral in ultramafic and serpentinite rocks with relatively low solubility and less immobility at both neutral and alkaline conditions [8]. However, under the presence of natural oxidizing agents, such as manganese oxides (MnO₂ and Mn₂O₃) and hydrogen peroxide (H₂O₂), Cr (III) can be dissolved readily and then oxidized to generate Cr (VI) [9–11]. It has been reported that Cr (VI) is acutely toxic, highly soluble, and easily mobile in soil and water [4,12,13]. Furthermore, significant enrichment of Cr (VI) owing to anthropogenic activities has been reported in Antarctica and/or elsewhere in the Southern Hemisphere [14].

Chemical reactions in ice play a vital role in atmospheric chemistry and have been investigated since the 1980s in the frontiers of food

chemistry and biochemistry [15]. Several redox reactions taking place in ice have been reported to differ significantly from such reactions in water. In addition, several reactions in ice can be markedly accelerated because of the freeze concentration effect [15–21]. All solutes and protons (H⁺)/hydroxides (OH[−]) are excluded from bulk ice crystals and gradually move into the ice grain boundary regions (liquid brine or the contact areas between ice crystals) during freezing. The freeze concentration process leads to an increase in the concentrations of solutes and the decrease in pH (soaring the number of successful collisions between components partaking in reaction and propelling reaction toward the pathway of lower activation energy) [18,22–28]. Accordingly, the freeze concentration effect is considered to facilitate and accelerate the rate of redox reactions in ice. Currently, ice chemistry is attracting more attention from atmospheric scientists because of the global impact of the physical and chemical processes occurring in cold regions (high latitude, mid-latitude in the winter season and polar regions). It is obvious that freezing and melting cycles occur diurnally in the environment every year, and the fate, as well as the behavior of environmental contaminants during these cycles are of global importance. In addition, interest has been sparked by ice grain boundary regions being reservoirs of pollutants, as well as being reactive locations [29].

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Hydrogen sulfide (H_2S) is proposed not only as a robust reducing agent but also as being emitted from oceanic phytoplankton in the Antarctic region [30]. Therefore, the chemical process of Cr (VI) reduction by H_2S in ice should be assessed elaborately in detail with regard to the kinetics aspect, as well as environmental relevance. Although the redox transformation between Cr (VI) and H_2S in aqueous phase has been investigated extensively [31–37], no such investigation in ice has been conducted yet. In this study, Cr (VI) reduction by H_2S in ice phase was investigated systematically compared with that in water. The differing redox behaviors in water and ice are recognized clearly, and the effect of experimental parameters and the environmental implications are discussed comprehensively.

2. Materials and methods

2.1. Material and chemicals

We used chemicals and reagents in this work, including sodium dichromate dihydrate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, Cr (VI), Sigma-Aldrich [USA], $\geq 99.5\%$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich [USA], $\geq 98.0\%$), acetone (CH_3COCH_3 , Junsei [Japan], $\geq 99.5\%$), sulfuric acid (H_2SO_4 , Sigma-Aldrich [USA], $\geq 95.0\%$), 1,5-diphenylcarbazine ($\text{C}_6\text{H}_5\text{NHNHCONHNHC}_6\text{H}_5$, DPC, Sigma-Aldrich [USA]), perchloric acid (HClO_4 , Sigma-Aldrich [USA], 60%), sodium hydroxide (NaOH , Sigma-Aldrich [USA], 0.1 N), and cresol red (Sigma-Aldrich [USA], $\geq 95\%$). All solutions were prepared in ultrapure water (18.2 M Ω .cm) employing a Barnstead (USA) purification system. The Cr (VI)-contaminated wastewater from electroplating company in Korea was used as an alternative source of Cr (VI).

2.2. Experimental procedure

An aliquot of chemical stock solution was added to the distilled water in a volumetric flask (volume = 100 mL) to make the desired initial concentration (usually $[\text{Cr (VI)}]_i = 20 \mu\text{M}$ and $[\text{H}_2\text{S}]_i = 30 \mu\text{M}$). The initial pH (pH_i) of the solution was adjusted by using 60% HClO_4 or/and NaOH 1 M solutions (usually pH_i 4.0). A total of 5 mL sample was transferred into a falcon tube (volume = 15 mL). The falcon tube was placed in a circulating ethanol bath adjusted to the desired temperatures (usually -20°C and 25°C for the reaction in ice and water, respectively). The point when the sample tube was introduced into the circulation ethanol bath (pre-set at -20°C) was defined as time zero ($t = 0$) in the kinetic study. It took 4–6 min to freeze the samples. Finally, the sample tubes were collected from the cryogenic ethanol bath after each time interval tested, and placed in a glass beaker containing warm water (35°C) to thaw frozen samples before analysis. All experiments were performed in triplicate to confirm data reproducibility.

2.3. Chemical analyses

The 1,5-diphenylcarbazine (DPC) method was implemented to identify Cr (VI) concentration. After thawing frozen sample, an aliquot of 500 μL aqueous sample was put into the falcon tube including 2.5 mL distilled water and 100 μL DPC reagent (H_2SO_4 + acetone + DPC). The falcon tube was vortexed and then maintained in the dark within 1 h prior to analysis. The measurement of absorbance values at 540 nm was conducted using UV-visible spectrophotometer (Shimadzu UV-2600, Japan).

Sulfate (SO_4^{2-}) produced from the oxidation of H_2S was quantified by ion chromatograph (IC, Dionex Aquion Thermo Fisher Scientific, USA) connected with a suppressor (AERS 500), 4-mm column (AS 23), and guard column (AG 23). The anion eluent is sodium bicarbonate (NaHCO_3) 0.8 mM and sodium carbonate (Na_2CO_3) 4.5 mM with its flow rate of 1.0 mL/min. The concentration of SO_4^{2-} is proportional to the height of SO_4^{2-} peak obtained. The calibration curve of SO_4^{2-} was

obtained by using 5 known standard solutions of SO_4^{2-} .

The optical images of Cr (VI) distribution in the ice grain boundary regions with the presence of H_2S were observed with a confocal Raman microscope (Renishaw, UK, inVia™ Qontor) equipped with a Linkam (UK) LTS 350 thermal stage (the temperature ranging from -196 to 350°C) and a Linkam (UK) LNP94 liquid nitrogen pump. Several droplets of sample solution ($[\text{Cr (VI)}]_i = 1 \text{ mM}$, $[\text{H}_2\text{S}]_i = 1 \text{ mM}$, and pH_i 3.0) were put onto a cover glass and placed on the stage. The liquid nitrogen pumping system maintained the proper temperature (-40°C) of the airtight stage storing the sample.

The chemical composition of electroplating wastewater was analyzed quantitatively using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific (USA) iCAP 6300 Duo). The concentration of total organic carbon (TOC) in the electroplating wastewater was measured using a total organic carbon analyzer (Shimadzu Corporation, Japan, TOC-L_{CPH}).

2.4. pH estimation in ice grain boundary regions

Cresol-red (CR) was employed as pH probe in the measurement of pH of ice grain boundaries [38,39]. 3 mL of a sample containing Cr (VI) (20 μM), H_2S (30 μM), and CR (6.67 μM) at pH_i 4.0 was added in a rectangular cell and solidified at -20°C in the cryogenic bath for 1 h. Subsequently, the rectangular cell was taken out of the ethanol bath. UV-visible spectrophotometer (Shimadzu Corporation, Japan, UV-2600) was used to record immediately the spectrum of CR. In addition, pure ice made from distilled water was prepared as a reference.

The [monoprotonated CR]/[diprotonated CR] was calculated by applying the obtained CR absorbance values with respect to wavelength values ranging from 400 nm to 650 nm to Eq. (1) [38,39]. pH of ice grain boundary regions was determined according to Eq. (2) using ([monoprotonated CR]/[diprotonated CR]) obtained from Eq. (1) and the pK_{a1} value.

$$\sum_{\lambda=400\text{nm}}^{650\text{nm}} (A \cdot x + B \cdot y - C)^2 = \text{minimum value} \quad (1)$$

where C denotes absorbance value of ice grain boundaries, A and B represent absorbance values of only diprotonated CR and monoprotonated CR, respectively. The values of x and y are concentrations of diprotonated CR and monoprotonated CR, respectively.

$$\text{pH} = \text{pK}_{a1} + \log \frac{[\text{monoprotonated CR}]}{[\text{diprotonated CR}]} \quad (2)$$

3. Results and discussion

3.1. Cr (VI) reduction by H_2S in water and ice

The reduction of Cr (VI) was examined both in the absence and presence of H_2S as an electron donor in both water and ice. Fig. 1(a) illustrates the time profile of Cr (VI) reduction with and without H_2S in aqueous and ice phases. In both phases, there was negligible removal of Cr (VI) alone. In particular, 20 μM Cr (VI) solution at pH_i 4.0 remained unchanged until 6 h in aqueous phase and reduced slightly in ice phase. This can be explained by the reaction between Cr (VI) and H^+ containing into ice grain boundary regions to yield Cr (III), oxygen (O_2), and H_2O according to the following chemical equation: $4\text{HCrO}_4^- + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{O}_2 + 10\text{H}_2\text{O}$ $E^0 = 0.15 \text{ V}_{\text{NHE}}$ [18]. However, interestingly, when 30 μM H_2S solution was added to 20 μM Cr (VI) solution, the degree of Cr (VI) change was significantly different between water and ice after 0.5 h, as approximately 10% of Cr (VI) was reduced in water but almost 90% in ice. These results indicated that Cr (VI) is reduced predominantly by H_2S , and the H_2S -mediated reduction process is ascribed to the primary pathway of Cr (VI) reduction in water and ice.

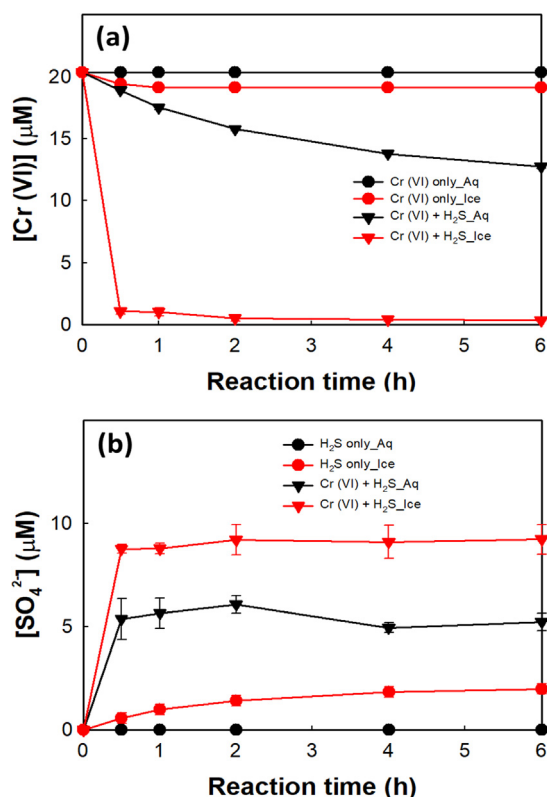
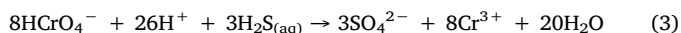


Fig. 1. Time profile of (a) Cr (VI) concentration and (b) the production of SO_4^{2-} with/without Cr (VI) in water and ice. Experimental conditions were as follows: $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{S}]_i = 30 \mu\text{M}$, $\text{pH}_i = 4.0$, and freezing temperature = -20°C .

In the next stage, we investigated the reduction of Cr (VI) accompanied by the oxidation of H_2S to SO_4^{2-} . As shown in Fig. 1(b), a small amount of SO_4^{2-} was generated from the oxidation of H_2S by dissolved oxygen during the freezing of the solution containing only $30 \mu\text{M}$ H_2S according to the following equation: $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$ $E^0 = 0.93 \text{ V}_{\text{NHE}}$ (Supplementary Information). However, this was not achieved in water. The level of SO_4^{2-} generated changed markedly between water and ice by the addition of Cr (VI) $20 \mu\text{M}$. Therefore, we found that the generation of SO_4^{2-} was restricted in water, whereas it was accelerated significantly in ice (Fig. 1(b)). The measure of SO_4^{2-} generated in ice increased relatively compared with that in water ($[\text{SO}_4^{2-}]_{\text{ice}}/[\text{SO}_4^{2-}]_{\text{water}} \approx 1.8$ after 6 h of reaction). These results revealed that SO_4^{2-} can be considered as the major oxidation product of H_2S , with the formation of other sulfur products being negligible. The freezing-induced enhancement of Cr (VI) reduction by H_2S can be attributed by the freeze concentration effect, which provides an improved condition for reducing Cr (VI) by H_2S because of decreasing pH and increasing the concentrations of both Cr (VI) and H_2S . It is documented that the H^+ and all solutes concentrations in ice grain boundary regions increase by 2–4 and 3–6 magnitude orders, respectively, in comparison with these in aquatic environment in acidic solution [40–42]. The alkaline solution has also been reported to become more basic by freezing because of the concentration of OH^- in ice grain boundaries [27].

The coupled redox reaction of Cr (VI) and H_2S (Reaction (3)) was obtained from the half-reduction reactions of Cr (VI)/Cr (III), $\text{SO}_4^{2-}/\text{H}_2\text{S}$ (Supplementary Information), which is expressed as follows:



$$E_3 = 1.05 - 0.07\text{pH} + 0.02 \log \frac{[\text{HCrO}_4^-]}{[\text{Cr}^{3+}]} - 0.007 \log \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{S}]_{\text{aq}}}$$

The equation of E_3 points out that the decrease in pH and/or increase in Cr (VI) and/or H_2S concentrations assist in the enhancement of the Cr (VI) removal rate by H_2S by increasing the driving force for Reaction (3) (i.e., E_3 value).

The theoretical molar ratio of Cr (VI) to H_2S ($[\text{Cr (VI)}]_{\text{reduced}}/[\text{H}_2\text{S}]_{\text{oxidized}}$) is approximately 2.67 according to Reaction (3). In actual fact, approximate $8.63 \mu\text{M}$ SO_4^{2-} was formed from the consumption of roughly $20 \mu\text{M}$ Cr (VI) in ice phase for 6 h, resulting in an actual molar ratio of Cr (VI) to H_2S ($[\text{Cr (VI)}]_{\text{reduced}}/[\text{H}_2\text{S}]_{\text{oxidized}}$) of approximate 2.31. This value is relatively close to the stoichiometry of Reaction (3), and Reaction (3) is concluded to be the main pathway of the reaction between Cr (VI) and H_2S in ice. Although the concentration of SO_4^{2-} generated must equal or closely equal the initial concentration of H_2S (approximately $8.63 \mu\text{M}$) according to the stoichiometry of Reaction (3), the actual concentration of H_2S for the full reduction of $20 \mu\text{M}$ Cr (VI) required approximately $30 \mu\text{M}$ at $\text{pH}_i = 4.0$ in ice phase. This could be appropriate because of the loss of H_2S by the reaction with dissolved oxygen, and possibly by evaporation as H_2S . This experiment was set up at $\text{pH}_i = 4.0$ in aquatic media and, thereby, H_2S is claimed to become the main form of sulfide at this condition. During freezing, pH of ice grain boundary regions even decreased further than that in aqueous phase and some of the H_2S molecules were expelled from the ice grain boundary regions.

The pH change during freezing in this system is crucial. CR as acid-base indicator was employed to measure the pH in ice grain boundaries with UV–visible absorption spectrum of the ice grain boundary regions consisting of both Cr (VI), H_2S , H^+ , and CR (Fig. 2). The result obtained showed only one peak appearing at 434 nm in aqueous phase at $\text{pH}_i = 4.0$ whereas the intensity peak at 434 nm decreased, and the peak at 518 nm was formed when the sample solution containing both Cr (VI), H_2S , CR at $\text{pH}_i = 4.0$ was frozen. These results support the finding that approximately 99% CR species exists as monoprotonated CR ($\lambda_{\text{max}} = 434 \text{ nm}$) at $\text{pH}_i = 4.0$. In contrast, several monoprotonated CR ions were transformed into diprotonated CR molecules ($\lambda_{\text{max}} = 518 \text{ nm}$) by solidification. The ratio of [monoprotonated CR] to [diprotonated CR] in the ice grain boundary regions was identified by applying the data shown in Fig. 2 to Eq. (1), with an estimated value of 2.96 obtained. Therefore, the calculated pH value of ice grain boundary regions was approximately 1.57 in the experimental conditions of $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{S}]_i = 30 \mu\text{M}$, $\text{pH}_i = 4.0$ in aqueous phase and freezing temperature at -20°C . The above calculated pH value was obtained by inserting the ratio of [monoprotonated CR] to [diprotonated CR] value (2.96) and pK_{a1} value of CR (1.10) [43] into Eq. (2).

To provide further evidence of the concentration effect of Cr (VI), H_2S , and H^+ in the ice grain boundary regions, the optical images of

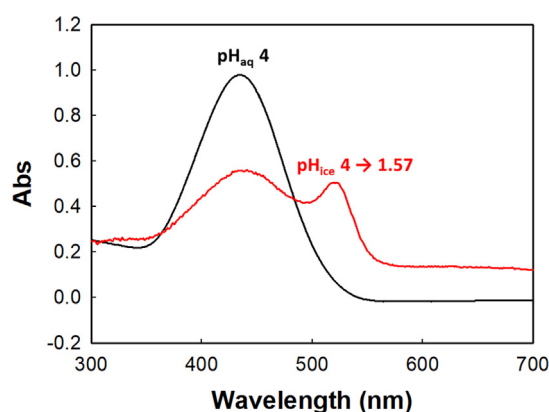


Fig. 2. UV–visible absorption spectra of CR in aqueous and ice phases containing Cr (VI), H_2S , and CR. Experimental conditions were as follows: $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{S}]_i = 30 \mu\text{M}$, $[\text{CR}]_i = 6.67 \mu\text{M}$, $\text{pH}_i = 4.0$, aqueous solution temperature = 25°C , and freezing temperature = -20°C .

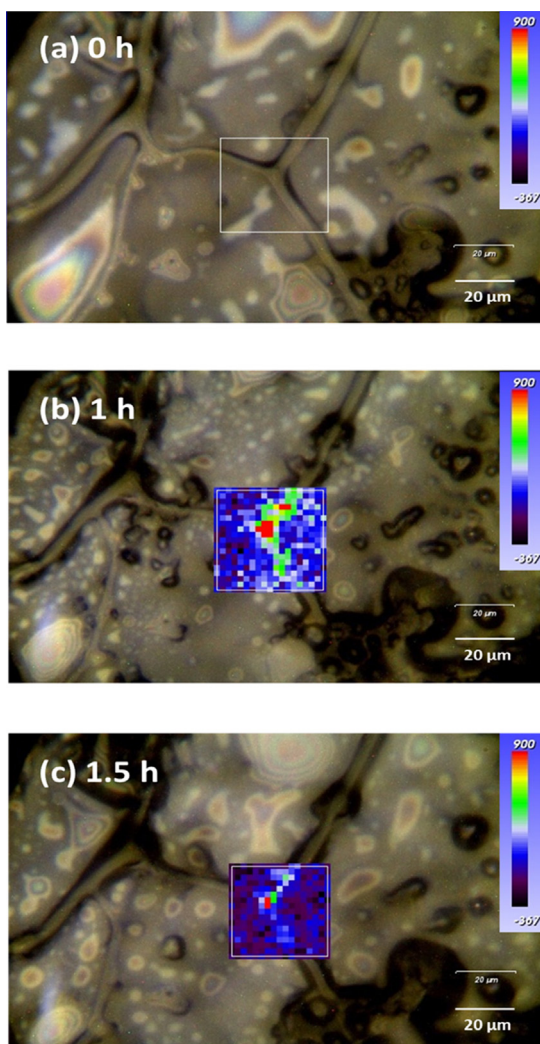


Fig. 3. Optical images of Cr (VI) distribution in the ice grain boundary regions after (a) 0 h, (b) 1 h and (c) 1.5 h, respectively. Experimental conditions were as follows: $[\text{Cr (VI)}]_i = 1 \text{ mM}$, $[\text{H}_2\text{S}]_i = 1 \text{ mM}$, $\text{pH}_i 3.0$, and freezing temperature = -40°C .

these accumulated species were observed in the frozen sample (i.e., without melting) (Fig. 3). Based on Fig. 3(a), the liquid region between two ice crystals was visualized, with a size estimation of approximately 5–10 μm . Further, the degree of Cr (VI) was shown through a rainbow spectrum (red: high $\rightarrow$ violet: slight) (Fig. 3(b) and (c)). The highly concentrated Cr (VI) (red) in the ice grain boundaries at the edge of ice crystals was observed clearly (Fig. 3(b)). It was observed that the intensity of the red color area after 1.5 h was lower than that after 1 h (Fig. 3(c)), implying that the concentration of Cr (VI) had undergone a downward trend over the period of reaction time in the presence of H_2S through the transformation to Cr (III).

3.2. Cr (VI) reduction by H_2S under various conditions

The effect of varying H_2S concentrations, pH_i , and freezing temperatures on Cr (VI) reduction by H_2S was studied both in water and ice to explore the optimal conditions for this process. Firstly, with different H_2S concentrations ranging from 5.0 to 100 μM applied, along with a fixed Cr (VI) concentration of 20 μM , the conversion of Cr (VI) to Cr (III) increased slightly within 0.5 h of reaction. Subsequently, the conversion increased gradually during the rest of the reaction time interval tested by increasing the H_2S concentration in aqueous phase (Fig. 4(a)). This result implied that the redox reaction of Cr (VI) by H_2S

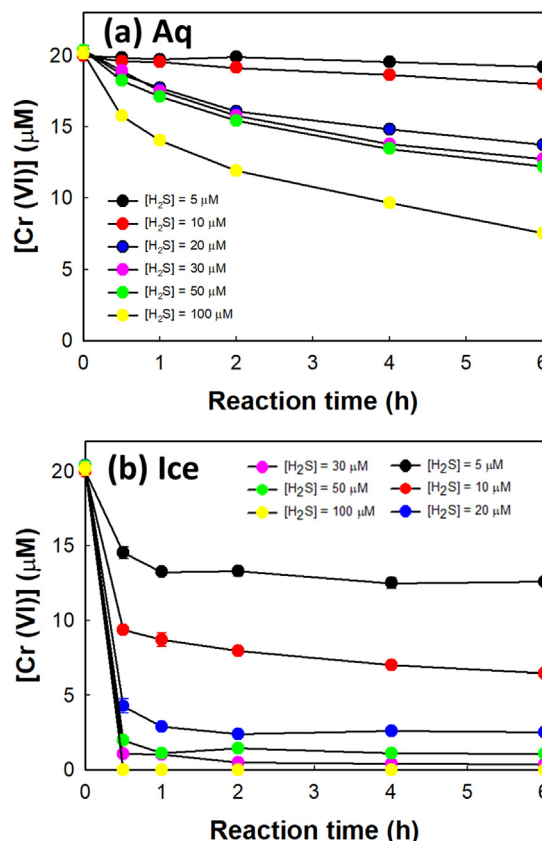


Fig. 4. Effect of H_2S concentration on the reduction of Cr (VI) in water (a) and in ice (b). Experimental conditions were as follows: $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $\text{pH}_i 4.0$, freezing temperature = -20°C .

is favored more at a higher concentration of H_2S (Reaction (3)). On the other hand, the complete degradation of 20 μM Cr (VI) was achieved when $[\text{H}_2\text{S}]_i \geq 30 \mu\text{M}$ in ice after 0.5 h of reaction time (Fig. 4(b)). This is ascribed to the number of H_2S components entering the ice grain boundary regions increasing when the H_2S concentration increased, which is considered a determining factor to induce this reaction to occur more kinetically and thermodynamically. This finding supports the above proposed reaction (Reaction (3)). Through the above results, the optimal concentrations of $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{S}]_i = 30 \mu\text{M}$ were selected to investigate the pH impact on the redox reaction of Cr (VI) by H_2S in the subsequent experiment.

Secondly, the pH-dependent Cr (VI) reduction by H_2S was tested in water and ice (Fig. 5). It has been mentioned that the pH value of ice

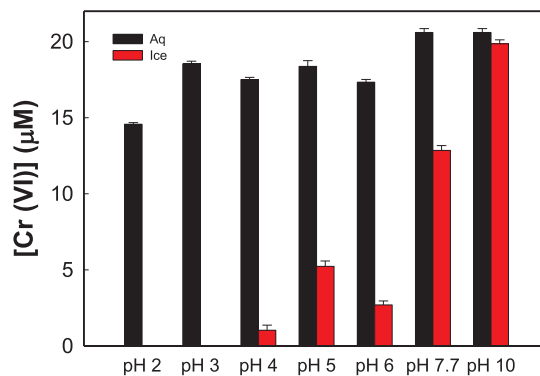


Fig. 5. Effect of pH_i on the redox conversion of Cr (VI) by H_2S in water and ice. Experimental conditions were as follows: $[\text{Cr (VI)}]_i = 20 \mu\text{M}$, $[\text{H}_2\text{S}/\text{HS}^-/\text{S}^{2-}]_i = 30 \mu\text{M}$, freezing temperature = -20°C , and reaction time = 2 h.

grain boundary regions can be affected not only by the freeze concentration effect of H^+ or OH^- but also by the freezing potential effect that is likely to be created by the non-uniform distribution of cations and anions during freezing [44]. To illustrate, the addition of sodium chloride (NaCl) has been reported to increase pH of ice grain boundaries [45]. To specify, chloride ions (Cl^-) have a desirable attraction force with bulk ice crystals, which induces sodium ions (Na^+) to migrate from the ice surface to ice grain boundaries. Consequently, more OH^- ions are accumulated in ice grain boundaries to neutralize the positive freezing potential, and a more basic environment is achieved. Accordingly, when studying the impact of pH, the composition or concentration of electrolytes has to be considered, as it probably indicates a sophisticated pH effect reliant on solution identity, as well as behavior. Generally, the reduction of Cr (VI) decreased from pH_i 2.0 to pH_i 10 in both phases. It should be noted that the degradation of Cr (VI) in water at pH_i 7.7 was negligible, whereas significant consumption of Cr (VI) was observed in ice, which increased dramatically at lower pH. This behavior is expected, as H_2S is known as the major form of sulfide, with pH_i range from 2.0 to 4.0 (pK_{a1} of $H_2S = 7.0$) [46], while both H_2S and singly protonated sulfide anion (HS^-) coexist at pH_i 7.7 ($[H_2S]_{aq}/[HS^-] \approx 5$ at pH_i 7.7) and both HS^- and deprotonated sulfide (S^{2-}) are capable of existing simultaneously at pH_i 10 (pK_{a2} of $H_2S = 12.9$) [46]. Notably, their reactivity decreases in the order of H_2S , HS^- , and S^{2-} . Further, the reduction of Cr (VI) to Cr (III) is more favored under acidic media. Accordingly, in view of the evidence, the rate of the reaction accelerating at low pH is understandable. In addition, the pH value of ice grain boundaries can decline by 2 or 4 units of magnitude by freezing because of the freeze concentration effect [17] (pH value decreased from 4.0 to 1.57 by freezing $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$ at $-20^\circ C$ in this study). By increasing the concentration of H^+ and eventually enhancing the reduction of Cr (VI) by H_2S , this result indicated the synergistic effect of all three components (i.e., H_2S , Cr (VI), and H^+) on the accelerated redox reaction rate.

The reduction rate of Cr (VI) by H_2S at concentrations of $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$, and pH_i 4.0 was also measured as a function of various freezing temperatures (-15 , -25 , and $-35^\circ C$) and subsequently compared with temperatures in water (25 and $0^\circ C$) (Fig. 6). The removal of Cr (VI) at $0^\circ C$ was much slower compared with that at $25^\circ C$. The reason is that the solution samples were not frozen at these temperatures, leading to the decrease in the reaction rate when decreasing the temperature as well. The reduction of Cr (VI) was enhanced dramatically by freezing at all freezing temperatures tested, but the rate decreased at lower freezing temperatures. This can be ascribed to the influence of the growing speed of ice crystals when the freezing temperature decreases. More specifically, the lower freezing temperature is a primary cause of ice crystals growing more rapidly, which

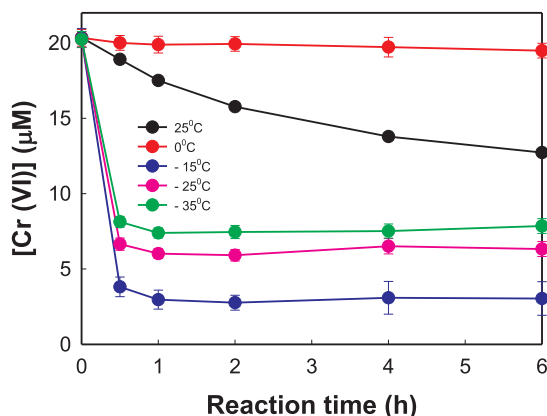


Fig. 6. Effect of freezing temperature on the redox reaction of Cr (VI) by H_2S compared with that in water. Experimental conditions were as follows: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$, and $pH_i = 4.0$.

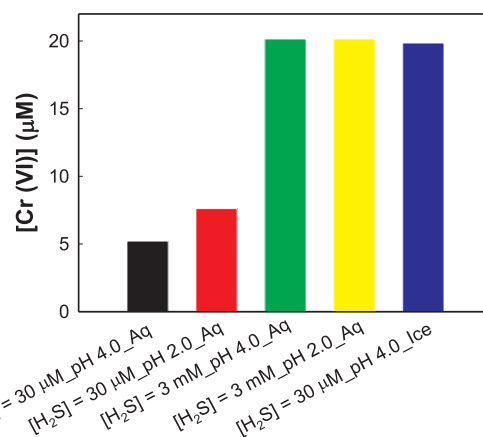


Fig. 7. Effect of increase in H_2S concentration and/or decrease in pH_i on the reduction of Cr (VI) by H_2S in water. Experimental conditions were as follows: pH_i decrease: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$, and pH_i 2.0. $[H_2S]$ increase: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 3 mM$, and pH_i 4.0. $[H_2S]$ increase and pH_i decrease: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 3 mM$, and pH_i 2.0. Reference conditions: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$, and pH_i 4.0 in both water and ice. Reaction time = 2 h.

implies narrowing the volume of ice grain boundary regions, and less Cr (VI), H_2S , and H^+ concentrating in the ice grain boundary regions. Consequently, the rate of reaction decreases. Despite the insignificant impact of the freezing temperature on the degree of Cr (VI) reduced, a general trend was observed clearly.

3.3. Verification of freeze concentration phenomenon on redox conversion of Cr (VI) by H_2S

We conducted a series of experiments with high concentrations of H_2S (3 mM) and/or H^+ (pH_i 2.0) to confirm whether the reduction of Cr (VI) by H_2S could be accelerated appreciably in ice because of the freeze concentration effect. We compared the results obtained with the results of the reference conditions ($[H_2S]_i = 30 \mu M$ and pH_i 4.0 in ice) (Fig. 7). As shown in Fig. 7, the depletion of Cr (VI) by H_2S was accelerated and became more significant and comparable to that in ice when increasing the concentration of either H_2S or H^+ a hundred fold. Accordingly, the effectively enhanced reduction efficiency of Cr (VI) in ice can be attributed mainly to the freeze concentration effect in ice grain boundary regions.

3.4. H_2S -mediated removal of Cr (VI) in electroplating wastewater in ice

We investigated the practical application of the enhanced reduction of Cr (VI) by H_2S in an actual Cr (VI)-polluted aqueous system (electroplating wastewater containing Cr (VI)) in ice (Fig. 8). The electroplating wastewater was collected from a local electroplating company in Korea. The primitive concentration of Cr (VI) in the electroplating wastewater was approximately 0.76 M with pH_i 0.35. The wastewater was diluted with distilled water before adding H_2S solution to reach 20 μM Cr (VI) concentration. The pH_i of the diluted wastewater containing H_2S was adjusted to 4.0 with 60% $HClO_4$ solution. In both instances, the degradation of Cr (VI) in ice was improved remarkably by freezing at the conditions examined. We found that the reduction efficiency of Cr (VI) in the electroplating wastewater by freezing did not differ much from that in the distilled water despite the presence of various other metals in the electroplating wastewater (Table S1). This finding shows the selective reductive capability of Cr (VI) by H_2S among various other metals.

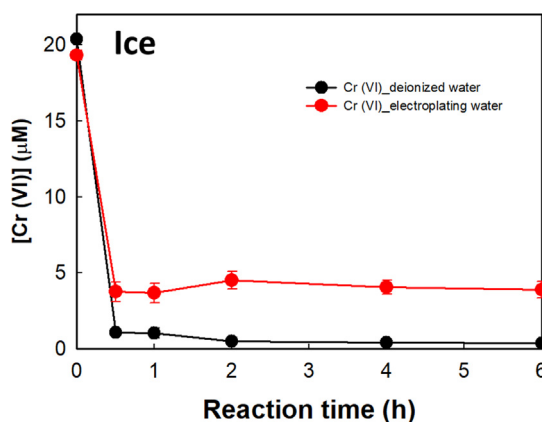


Fig. 8. Cr (VI) reduction in Cr (VI)-contaminated in electroplating wastewater and artificial Cr (VI) solution in ice. Experimental conditions were as follows: $[Cr(VI)]_i = 20 \mu M$, $[H_2S]_i = 30 \mu M$, $pH_i = 4.0$, and freezing temperature = $-20^\circ C$.

4. Conclusions

It is acknowledged that both Cr (VI) and H_2S are ubiquitous in natural water and soil [47–50]. Therefore, the redox reaction between Cr (VI) and H_2S in ice can occur in widely varying of geographical areas, such as permafrost, upper atmosphere, polar regions, and mid-latitudes during the winter season. Accordingly, the reaction between Cr (VI) and H_2S can influence significantly the contents of both Cr (VI) and H_2S in the global environment in general and cold areas in particular. The pH of atmospheric water, such as rain and clouds, has been recorded to range from 2.0 to 6.0 [17,51], and the pH of snowpack has been reported to range from 4.5 to 5.5 [52,53]. These are the appropriate conditions for the redox process of Cr (VI) by H_2S in ice. Accordingly, the freezing of atmospheric water, as well as snowpack consisting of Cr (VI) and H_2S in the cryosphere and upper troposphere can induce the rapid reduction of Cr (VI) to Cr (III) through the reaction between Cr (VI) and H_2S .

In this work, we investigated the reduction of Cr (VI) by H_2S in ice compared with that in water. We found that the redox reaction between Cr (VI) and H_2S in water was slow compared with the significantly accelerated reaction in ice at $pH_i = 4.0$ until either Cr (VI) or H_2S was removed completely. The reaction between Cr (VI) and H_2S in ice complies mainly with the mechanism of proton-coupled electron transfer. The concentration effect of Cr (VI), H_2S , and H^+ can be considered the main factor in providing enhanced media to reduce effectively Cr (VI) to Cr (III). The chemically optical observation and the calculated pH in ice grain boundaries support the freeze concentrations of Cr (VI) and H^+ in ice grain boundaries. The synergy of a higher concentration of H_2S and lower pH on the reduction of Cr (VI) in water was in good agreement with the freeze concentration effect as the appropriate explanation for the markedly enhanced Cr (VI) reduction in ice. Depending on H_2S concentration, freezing temperature, and pH values, the reaction efficiency of Cr (VI) by H_2S in ice varied. Nevertheless, there was a substantial enhancement of the reaction rate in ice compared with that in water under all the tested experimental conditions.

Our conclusion is that this study provides improved understanding of the chemical fate and cycling of Cr (VI) in the cryosphere and upper troposphere. Further, freezing-assisted Cr (VI) removal is one of the applicable pathways in the treatment of wastewater. Future studies will focus on effect of addition of inorganic anions on the removal of Cr (VI), and total chromium $[Cr(VI) + Cr(III)]$ by H_2S in ice toward the treatment of Cr(VI)-contaminated soil.

CRediT authorship contribution statement

Quoc Anh Nguyen: Investigation, Writing - original draft, Writing - review & editing. **Bomi Kim:** Formal analysis. **Hyun Young Chung:** Resources. **Jungwon Kim:** Writing - review & editing. **Kitae Kim:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2020.117377>.

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