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Kinetics and Mechanisms of Cr(VI) Formation via the Oxidation of Cr(III) Solid Phases by Chlorine in Drinking Water

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S *Supporting Information*

ABSTRACT: Hexavalent chromium Cr(VI), typically existing as the oxyanion form of CrO_4^{2-}, is being considered for more stringent drinking water standards by regulatory agencies. Cr(VI) can be inadvertently produced via the oxidation of trivalent chromium Cr(III) solids. This study investigated the kinetics and mechanisms of Cr(III) solids oxidation by chlorine in drinking water and associated Cr(VI) formation. Batch experiments were carried out with three Cr(III) solids of environmental relevance, i.e., chromium hydroxide $Cr(OH)_{3(s)}$, chromium oxide $Cr_2O_{3(s)}$, and copper chromite $Cu_2Cr_2O_{5(s)}$. Impacts of water chemical parameters including pH (6.0−8.5) and bromide concentration (0−5 mg/L) were examined. Results showed that the rapid oxidation of Cr(III) solid phases by chlorine was accompanied by Cr(VI) formation and an unexpected production of dissolved oxygen. Analysis of reaction stoichiometry indicated the existence of Cr intermediate species that promoted the autocatalytic decay of chlorine. An increase in pH modestly enhanced Cr(VI) formation due to changes of reactive Cr(III) surface hydroxo species. Bromide, a trace chemical constituent in source waters, exhibited a catalytic effect on Cr(VI) formation due to an electron shuttle mechanism between Cr(III) and chlorine and the bypass of Cr intermediate formation. The kinetics data obtained from this study suggest that the oxidation of Cr(III) solids by chlorine in water distribution systems can contribute to Cr(VI) occurrence in tap water, especially in the presence of a trace level of bromide.
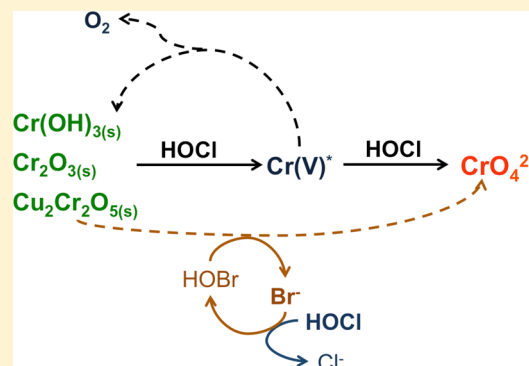
INTRODUCTION

The presence of hexavalent chromium Cr(VI) in drinking water is an increasing concern in recent years because it can cause adverse human health effects, including lung cancer, stomach cancer, and dermatitis.[1−6] Cr(VI) typically exists as an oxyanion (i.e., chromate CrO_4^{2-}) in drinking water and is released from both anthropogenic and natural sources. Anthropogenic sources include industrial waste discharges from tanneries and electroplating, metallurgical smelting of chromite ore, and corrosion of metal alloys.[7−9] Naturally occurring Cr(VI) typically originates from the geological weathering of Cr-containing aquifer minerals.[10−16] As an emerging contaminant, a new drinking water standard of Cr(VI) was set at 10 μg/L in California in 2014,[17] and a new U.S. EPA regulation may also be proposed in the future.[18] On the basis of the most recent sampling data from U.S. EPA's third round Unregulated Contaminant Monitoring Rule (UCMR3), it was determined that 63% of the participating public water systems nationwide detected Cr(VI) at the end point of the drinking treatment plant.[18]

Knowledge of chromium in each oxidation state rather than total chromium is vital for controlling its occurrence. Trivalent chromium Cr(III), which is much less toxic than Cr(VI) and even a micronutrient, mostly exists as a solid with limited solubility at circumneutral pH.[19,20] Typical Cr(III) solids relevant to drinking water systems include chromium hydroxide

$Cr(OH)_{3(s)}$, chromium oxide $Cr_2O_{3(s)}$ and copper chromite $Cu_2Cr_2O_{5(s)}$. Chromium hydroxide $Cr(OH)_{3(s)}$ can form via reductive transformation of Cr(VI) during the coagulation step of water treatment and contribute to Cr(III) residual in drinking water.[21−27] In cases where Fe(II) is used as the reductant during coagulation, $Cr(OH)_{3(s)}$ can coexist with Fe(III) hydroxide.[21,25,28] In addition, chromium has been widely used in plumbing materials (e.g., stainless steel) in water distribution systems.[29−31] As a result, Cr(III) solids are formed in corrosion scales in contact with treated drinking water.[32,33] $Cr_2O_{3(s)}$ is detected in corrosion products from water distribution systems.[34,35] $Cu_2Cr_2O_{5(s)}$ can be potentially found in aquatic environments from anthropogenic sources, given its wide industrial use.[19,33,36] Studies also show that chromium is one of the most abundant inorganic contaminants accumulated in drinking-water distribution systems.[37,38]

The ultimate occurrence of Cr(VI) in tap water is controlled by the complex chromium redox chemistry from the source water to the water distribution system; however, current Cr(VI) control strategies mainly target upstream treatment processes. To develop effective strategies to minimize Cr(VI) in tap water, it is important to understand chromium redox

chemistry in the presence of disinfectants,[39] especially in water distribution systems. Field monitoring data point to the importance of oxidative conversion of Cr(III) to Cr(VI) in drinking water distribution systems. A total of 35% of the monitored water distribution systems in EPA UCMR3 database showed an increase of Cr(VI) concentration from the point of entry to the maximum residence time.[18] This trend was positively correlated to the presence of free chlorine as a residual disinfectant. There are reports that show increases of Cr(VI) and total Cr concentrations in water distribution systems[40,41] and indicate that an inadvertent reoxidation of Cr(III) residual to Cr(VI) by chlorine can potentially occur.

Prior studies have shown that Cr(III) species, especially in soluble forms, can be oxidized by chlorine to generate Cr(VI).[20,42−46] For example, chlorine can oxidize dissolved Cr(III) solutes.[39,42] Residual chlorine can also oxidize Cr from corroded stainless steel pipes.[29] In addition, chlorine at an extremely high concentration (1400 mg Cl_2/L) can oxidize $Cr(OH)_{3(s)}$ via a dissolution-induced pathway at extremely acidic or alkaline pHs.[46] These studies point to the importance of Cr(III) oxidation by chlorine as a source of Cr(VI). There is, however, a very limited understanding of the reactivities of different environmentally relevant Cr(III) solids with chlorine, especially in drinking water chemical conditions.

Furthermore, the impacts of water chemical parameters on the reactivities of Cr(III) solids remain largely unexplored. Solution pH can significantly impact the speciation of surface complexes of Cr(III) solids.[39,46] A systematic understanding of pH effects on all relevant Cr(III) solid phases is needed. In addition, bromide is an important drinking water chemical constituent. Its concentration in natural environment ranges from a few μg/L to several mg/L worldwide[47−49] and varies between 24 μg/L and 4.0 mg/L in U.S. source waters.[50,51] Wastewater discharges from energy and oil sectors in United States can increase bromide concentration by as much as 20 times in the future.[52] Although the occurrence of bromide raises concerns on metal release and disinfection by-products formation,[53,54] its impact on Cr release has not been explored.

The objectives of this study were to investigate the kinetics and mechanisms of Cr(VI) formation via the oxidation of three model Cr(III) solids by chlorine in drinking water, with emphasis on the effects of pH and bromide, and to examine the formation of Cr intermediate species during the oxidative process. By the measurement of the rates of chlorine consumption, Cr(VI) formation, and oxygen production in different chemical conditions, it became possible to gain insight into the mechanism of Cr(III) oxidation and the complex nature of elemental reactions involving Cr redox cycles in drinking water systems.

■ MATERIALS AND METHODS

All chemicals used in this study were reagent grade or higher. All solutions were prepared using deionized water (resistivity >18.2 MΩ, Millipore System). A total of three Cr(III) solids were prepared: $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$, and $Cu_2Cr_2O_{5(s)}$. Amorphous $Cr(OH)_{3(s)}$ was synthesized via a precipitation method provided as Text S1. Crystalline $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ were obtained from Fisher Scientific. All three solids were sequentially sieved through no. 50, 170, and 325 mesh sieves. The fractions retained between no. 170 and no. 325 sieves (with nominal particle sizes between 45 and 90 μm) were collected and used in this study.

Oxidation experiments were conducted in a 200-mL glass batch reactor that was continuously stirred at 23 °C. A 300 mg/L stock solution of chlorine (Cl_2) diluted from a NaOCl solution (Sigma-Aldrich) was freshly prepared and kept at a concentration varying between 2 mg Cl_2/L (this chlorine concentration is typical for drinking water) and 20 mg Cl_2/L in different experiments (i.e., between 28 and 280 μM). In some experiments, 20 mg/L of bromine solutions were prepared by adding an excess of bromide (10%) to a chlorine solution at pH 6. The concentration of chlorine was verified by titration with potassium permanganate.[55] The choice of a chlorine concentration higher than 2 mg Cl_2/L in those experiments did not change the redox potential of chlorine compared to that in drinking water conditions (i.e., E^0_{HOCl/Cl^-} = 1.41 V versus standard hydrogen electrode) and provided useful insight into the oxidation kinetics.
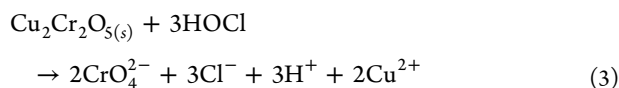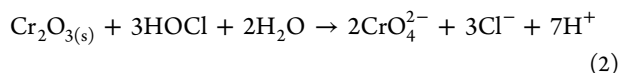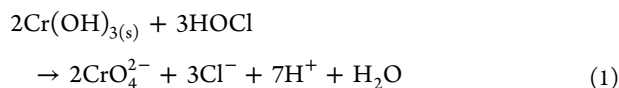
To start an experiment, 200 mL of chlorine solution was quickly mixed with a predetermined amount of a Cr(III) solid. The molar ratio of Cr(III) to chlorine varied between 1:10 and 10:1. The solution pH was maintained at a constant value between 6.0 and 8.5 ($\pm$0.1 pH units from the target) with a Eutech Instrument Alpha pH200 controller. Droplets of 50 mM $HClO_4$ or 50 mM NaOH were automatically titrated to the reactor that was sealed with Parafilm with minimum headspace. In some experiments, bromide ranging between 0.1 and 5 mg/L was added to the reactor. The solution ionic strength was kept at 10 mM by adding a requisite amount of $NaClO_4$.

At predetermined time intervals, samples were taken from the system and filtered through 0.22 μm Millipore filters. For experiments conducted at pH 6.0 and 6.5, the solution pH was raised to 8.0 before sampling to recover any Cr(VI) that could be adsorbed on Cr(III) solids. Less than 20% of Cr(VI) was adsorbed on Cr(III) solids and fully recovered (Figure S1). Chlorine concentration in the filtrate was measured using a modified (DPD) method[55] in which thioacetamide was added to eliminate the potential interference caused by Cr(VI) (Figure S2). The concentration of Cr(VI) was monitored using a modified diphenylcarbazide (DPC) method,[55] with excess $(NH_4)_2SO_4$ added to covert chlorine to chloramine and prevent it from interfering with DPC reagent (Figure S3). Other solution constituents did not cause any interference on the DPC method.

Concentrations of chloride, bromide, and bromate were measured by a Dionex DX-120 ion chromatography connected with an IonPac AS22 column and AG22 guard column. Eluent composed of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was run at a flow rate of 0.6 mL/min using a 250-μL sample loop. The BET surface area of Cr(III) solids was measured using a Micromeritics ASAP 2020 surface area and porosity analyzer. The ζ potential of Cr(III) solids was measured from a 0.2 g/L suspension using a ζ potential analyzer (Brookhaven Instruments).

■ RESULTS AND DISCUSSION

Kinetics of Cr(VI) formation via Cr(III) Solids Oxidation by Chlorine and pH Impact. On the basis of thermodynamics calculation, we determined that the oxidation of Cr(III) solids by chlorine is favorable in typical drinking water conditions (Text S2 and Table S1). This thermodynamics relationship is consistent with prior reports.[20,29,39] The oxidation of Cr(III) solid phases by chlorine proceeds via the following reactions:

$$2Cr(OH)_{3(s)} + 3HOCl$$
$$\rightarrow 2CrO_4^{2-} + 3Cl^- + 7H^+ + H_2O \qquad (1)$$

$$Cr_2O_{3(s)} + 3HOCl + 2H_2O \rightarrow 2CrO_4^{2-} + 3Cl^- + 7H^+ \qquad (2)$$

$$Cu_2Cr_2O_{5(s)} + 3HOCl$$
$$\rightarrow 2CrO_4^{2-} + 3Cl^- + 3H^+ + 2Cu^{2+} \qquad (3)$$

A total of three Cr(III) solids exhibited different reaction kinetics with chlorine on the basis of experimental observations (Figure 1A). Chlorine was stable in the control without any
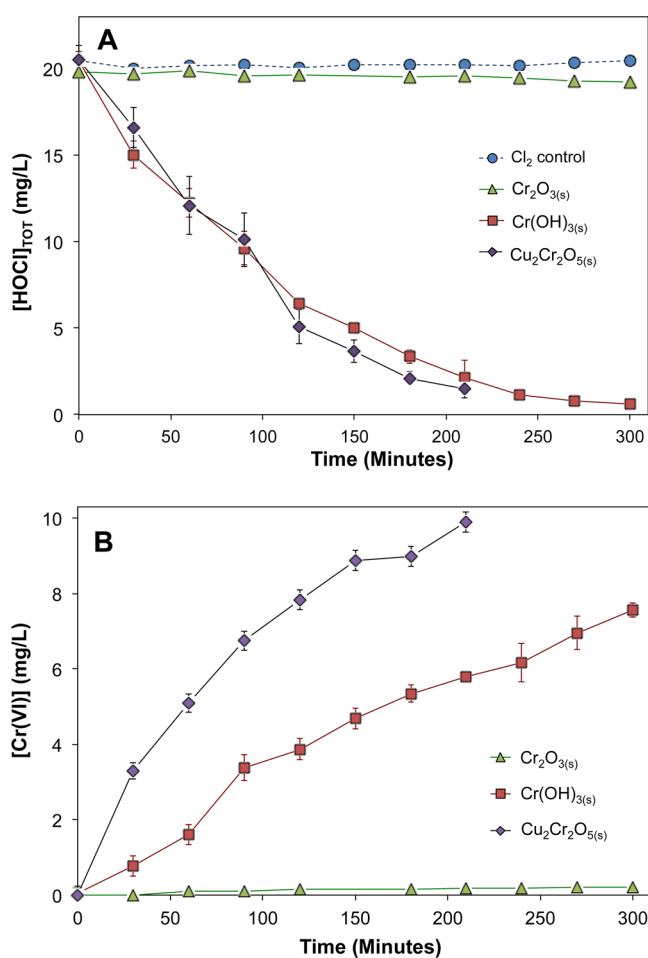
Figure 1. Oxidation of three Cr(III) solids by chlorine. (A) Chlorine consumption profile; (B) hexavalent chromium formation profile. pH = 7.0, initial $[HOCl]_{TOT}$ = 20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2 = 10:1, ionic strength = 10 mM.

Cr(III) solid. Approximately 10% of chlorine was consumed in the presence of $Cr_2O_{3(s)}$ within 300 min. More than 90% of chlorine was consumed in the presence of either $Cr(OH)_{3(s)}$ or

$Cu_2Cr_2O_{5(s)}$ within the same reaction time. Accompanied with chlorine consumption, Cr(VI) was formed (Figure 1B). The difference in reactivity among the three Cr(III) solids was caused by distinct surface areas and reactive sites among the Cr(III) solids. BET surface areas of three Cr(III) solids varied by 2 orders of magnitude (Table 1). The consumption of chlorine and formation of Cr(VI) were consistently observed at varying Cr(III)-to-chlorine molar ratios (Figure S4).

To quantify the reaction kinetics of Cr(III) oxidation by chlorine, we developed a second-order kinetics model to describe the rate of chlorine consumption and Cr(VI) formation:

$$\frac{d[HOCl]_{TOT}}{dt} = -k_{Cl_2}[Cr(III)_{(s)}][HOCl]_{TOT}(S_{Cr(III)_{(s)}}) \qquad (4)$$

$$\frac{d[(Cr(VI)]_{TOT}}{dt} = k_{Cr(VI)}[Cr(III)_{(s)}][HOCl]_{TOT}(S_{Cr(III)_{(s)}}) \qquad (5)$$

where k_{Cl_2} in eq 4 and $k_{Cr(VI)}$ in eq 5 are the surface area normalized rate constants for chlorine consumption and Cr(VI) formation, respectively ($L \cdot m^{-2} \cdot s^{-1}$). $[Cr(III)_{(s)}]$ is the concentration of Cr(III) solids (g/L). $[HOCl]_{TOT}$ is the total concentration of free chlorine including both hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), i.e., $[HOCl]_{TOT} = [HOCl] + [OCl^-]$ (mol/L). $S_{Cr(III)(s)}$ is the BET surface area of a particular Cr(III) solid (m^2/g) (Table 1).

Solution pH had a modest impact on the reaction kinetics (Figures S5–S7). On the basis of data fitting with the kinetics model, we determined that the chlorine consumption rate constant k_{Cl_2} shows a dependence on pH (Figure 2A). For $Cr_2O_{3(s)}$, k_{Cl_2} increased by 200% when the solution pH increased from 6.0 to 8.5. For $Cu_2Cr_2O_{5(s)}$, the rate constant increased by approximately 450% within the same range of pH increase. For $Cr(OH)_{3(s)}$, the rate constant increased with pH and reached the maximum at pH 7.0. The model-fitted rate constant $k_{Cr(VI)}$ was also impacted by pH (Figure 2B). For $Cr_2O_{3(s)}$, the rate of Cr(VI) formation increased by 35% with an increase of pH from 6.0 to 8.5. For $Cu_2Cr_2O_{5(s)}$, the rate increased by 100% with the same change of pH. For $Cr(OH)_{3(s)}$, the rate of Cr(VI) formation increased by approximately 425% when pH changed from 6.0 to 7.0. Comparing all three Cr(III) solids, the rates of Cr(VI) formation at typical drinking water pHs (7.0–8.0) followed the order of $Cu_2Cr_2O_{5(s)} > Cr(OH)_{3(s)} > Cr_2O_{3(s)}$ (Figure 2B). The rate at which $Cu_2Cr_2O_{5(s)}$ was converted to Cr(VI) by chlorine was approximately 1 order of magnitude higher than $Cr_2O_{3(s)}$.

The unique effects of pH on the oxidation rate of Cr(III) solids can be attributed to three factors. First, pH affects chlorine speciation. Chlorine exists as HOCl or OCl^- with a pK_a of 7.6. HOCl is more oxidative and more electrophilic than OCl^-.[56,57] Second, pH affects speciation of Cr(III) surface

Table 1. Summary of the Chemical Properties and Environmental Relevance of Three Cr(III) Solids Investigated in This Study

| Cr(III) solids	pH_{pzc}	BET surface area (m^2/g)	relevance to drinking water	references
chromium hydroxide $Cr(OH)_{3(s)}$	7.9	159.3	precipitate during Fe(II)-assisted coagulation step in drinking water treatment	21–27, 33, 34
chromium oxide $Cr_2O_{3(s)}$	3.5	1.9	corrosion product in water distribution systems	33–35, 37
copper chromite $Cu_2Cr_2O_{5(s)}$	7.4	39.9	potential wastewater contaminant and corrosion product in copper piping	36
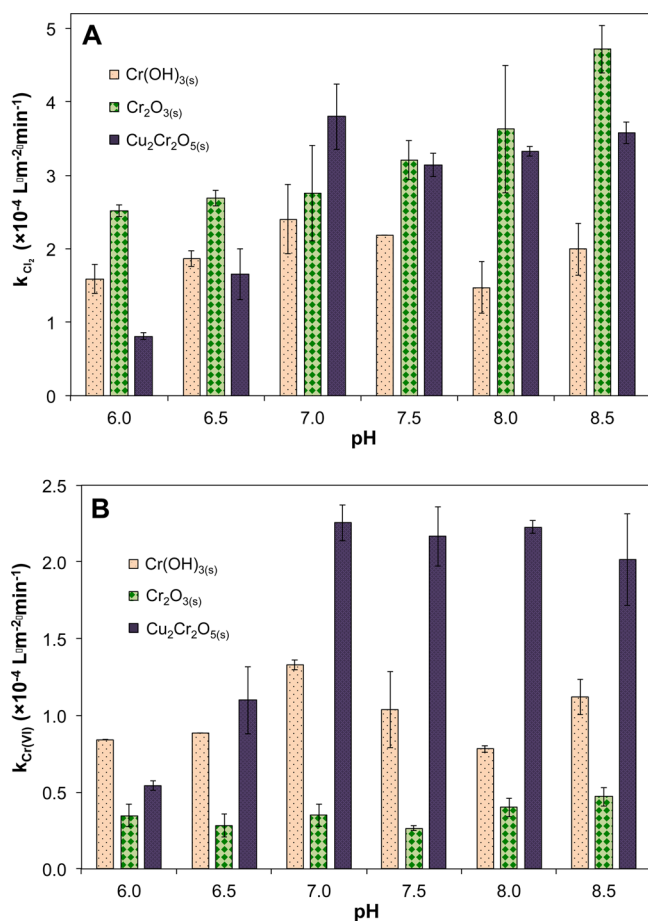
Figure 2. Effect of pH on the surface area normalized second-order rate constants of Cr(III) oxidation by chlorine. (A) Chlorine consumption rate; (B) Cr(VI) formation rate. Initial $[Cr(III)]$ = 2.8 mM, initial $[HOCl]_{TOT}$ = 20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2 = 10:1, ionic strength =10 mM.

hydroxo species. Similar to other transition metals,[58−61] the predominance of Cr(III) surface hydroxo complexes with different coordination numbers of −OH groups varies with pH.[7,62,63] Because each surface hydroxo species possesses distinct reactivity with chlorine, the resultant reactivities of Cr(III) solids changes with pH.

Third, each Cr(III) solid has distinct Cr(III) surface species, as shown by the changes of ζ potential with pH (Figure S8). At neutral pH, the surface of $Cr_2O_{3(s)}$ was negatively charged, whereas the other two Cr(III) solids were positively charged. Change of ζ potential that exceeded 40 mV between pH 6.0 and 8.5 suggests that protonation-active Cr(III) hydroxo species exist on the surface of all three Cr(III) solids. The negative shift of ζ potential with pH suggests the formation of negatively charged Cr(III) hydroxo surface species whose existence has been postulated.[64] These negatively charged Cr(III) hydroxo species are stronger nucleophiles and more likely to be oxidized by HOCl. The differences among the three Cr(III) solids are evidently due to a higher prominence of protonation-active surface sites on the surface of $Cr(OH)_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ and a very different structural organization among these Cr(III) solids.

Reaction Stoichiometry and Chlorine Autocatalytic Decay by Cr(III). On the basis of the theoretical stoichiometry of chlorine oxidation (reactions 1−3), we determined that the

ratio of cumulative Cr(VI) formation to cumulative chlorine consumption at any reaction time (denoted as $\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$) is expected to be 0.67. However, experimental data showed that this ratio was much less than the theoretical value (Figure 3 and Figures S9−S10). Therefore, the yield of Cr(VI) did not account for all the chlorine consumed during chlorine oxidation of Cr(III) solids.
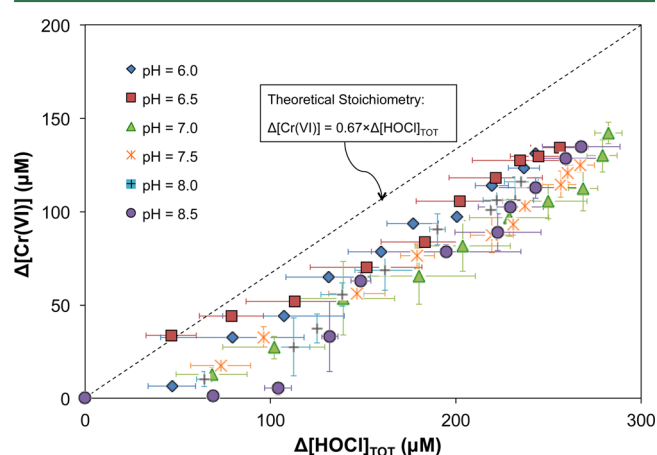

Figure 3. Experimentally observed stoichiometry of cumulative Cr(VI) formation with respect to cumulative chlorine consumption. The theoretical stoichiometry is 0.67, but the experimentally observed values were below 0.67. Initial $[HOCl]_{TOT}$ = 20 mg Cl_2/L, $[Cr(OH)_{3(s)}]$ = 2.8 mM, Cr(III)/HOCl = 10:1. Bromide was not present.
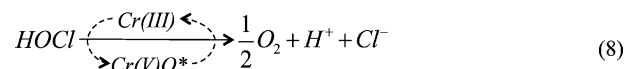
The observed stoichiometry suggests that the oxidation of Cr(III) by chlorine is simultaneously accompanied by an autocatalytic decay of chlorine, and it proceeds with the formation of chromium intermediates as part of a multistep oxidation process. The oxidation of Cr(III) solids by chlorine can generate Cr(V) intermediate species in the form of Cr(V) oxide (denoted as Cr(V)O*) as the first step (Reaction 6):

$$Cr(III)_{(s)} + HOCl \rightarrow Cr(V)O^* + Cl^- + H^+ \tag{6}$$
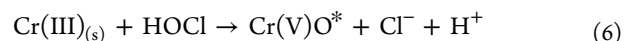
Unstable Cr(V)O* intermediates can quickly decompose to Cr(III) and generate dissolved oxygen (Reaction 7):

$$Cr(V)O^* \rightarrow Cr(III)_{(S)} + \frac{1}{2}O_2 \tag{7}$$
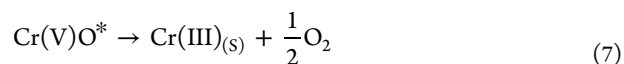
The overall reaction becomes

$$HOCl \xrightarrow[\quad \rightarrow Cr(V)O^* \quad]{\quad Cr(III) \quad} \frac{1}{2}O_2 + H^+ + Cl^- \tag{8}$$

Reaction 8 predicts an autocatalytic decay of chlorine in the presence of Cr(III) solids. This process involves unstable Cr intermediates that facilitate the decomposition of chlorine to Cl⁻ and dissolved O_2. On the basis of the experimental data, we determined that the fraction of chlorine that underwent autocatalytic pathway accounted for 5%, 30%, and 70% of total chlorine consumption during the oxidation of $Cu_2Cr_2O_{5(s)}$, $Cr(OH)_{3(s)}$, and $Cr_2O_{3(s)}$, respectively. This follows exactly the descending order of Cr(VI) formation rates among the three solids (Figure 2B). As more chlorine undergoes the autocatalytic pathway (reaction 8), less chlorine is readily available to converts Cr(III) to Cr(VI) (reactions 1−3), which results in the overall stoichiometry of

$\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$ to be less than the theoretical value of 0.67. Previous studies reported Cr intermediates including pentavalent Cr(V) and tetravalent Cr(IV) during the redox cycling between Cr(III) and Cr(VI).[65−68] These intermediates are also formed when Cr(VI) is reduced by cytoplasmic fluids in human cells.[69−72] Autocatalytic decay of chlorine by other transition metals such as Cu(II) in drinking water was also reported.[73,74]

To further assess the autocatalytic decay of chlorine by Cr(III) solids, we conducted additional oxidation experiments in the absence of oxygen with a suspension of $Cr(OH)_{3(s)}$, $Cr_2O_{3(s)}$, and $Cu_2Cr_2O_{5(s)}$, respectively, and dissolved O_2 concentrations were measured. Results showed that dissolved O_2 was produced when $Cr(OH)_{3(s)}$ was mixed together with chlorine in 300 min (Figure 4A). This was accompanied by the
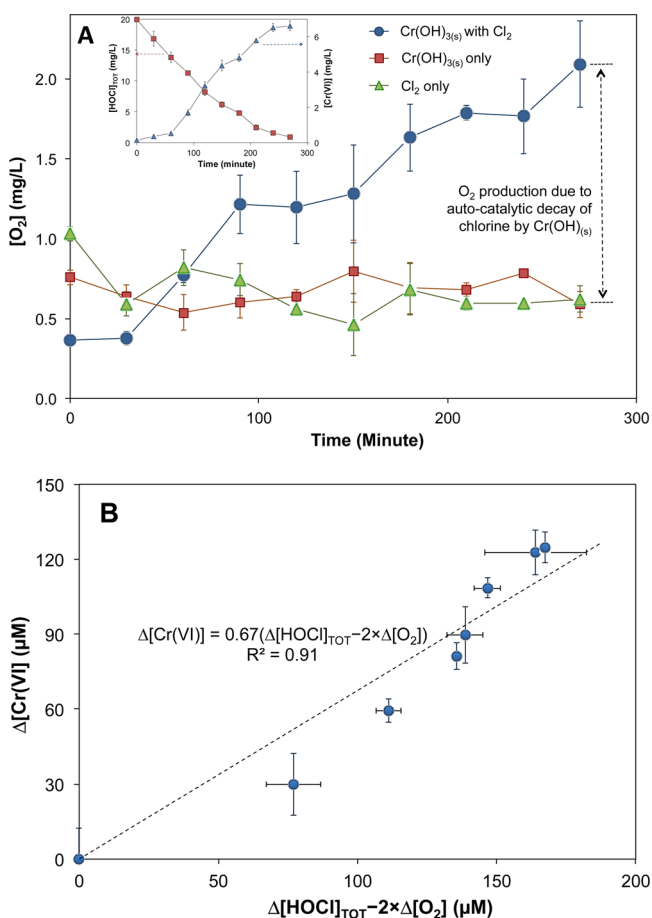
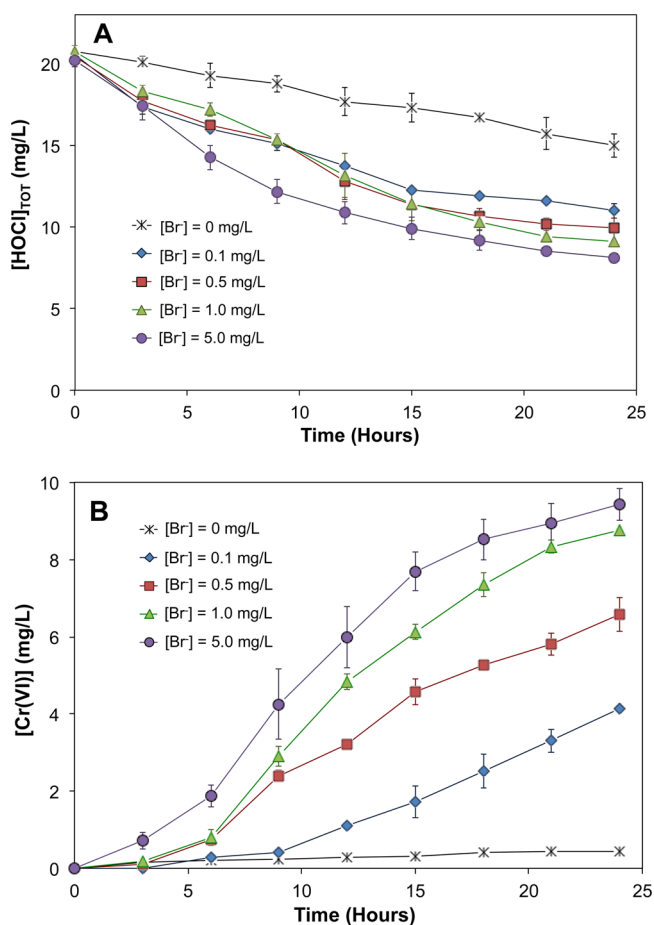**Figure 4.** Oxidation of $Cr(OH)_{3(s)}$ by chlorine. (A) Production of dissolved O_2; (B) revised stoichiometry of Cr(VI) formation considering the autocatalytic decay of chlorine. Initial $[HOCl]_{TOT}$ = 20 mg Cl_2/L, molar ratio of Cr(III)/Cl_2 = 10:1, pH = 7.0, ionic strength =10 mM.

consumption of chlorine and formation of Cr(VI) (inserted graph in Figure 4A). In the control experiments with only $Cr(OH)_{3(s)}$ or chlorine, no O_2 was produced (Figure 4A). By the subtraction of the amount of chlorine consumed by autocatalytic decay based on O_2 production (i.e., $2 \times \Delta[O_2]$, based on Reaction 8) from total chlorine consumption, the amount of chlorine that directly oxidized $Cr(OH)_{3(s)}$ (i.e., $\Delta[HOCl]_{TOT} - 2 \times \Delta[O_2]$) showed the expected stoichiometry of 0.67 with respect to Cr(VI) formation (Figure

4B). Similar trends of dissolved O_2 production and stoichiometry were observed for $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, respectively (Figures S11−S12). This correlation strongly supports the existence of autocatalytic decay of chlorine and the involvement of Cr intermediate species, e.g., Cr(V).

Impact of Bromide on Cr(III) Solids Oxidation by Chlorine. The presence of bromide significantly accelerated the oxidation of Cr(III) solids by chlorine (Figure 5). For


Figure 5. Impact of bromide concentration on the oxidation of $Cr_2O_{3(s)}$ by chlorine. (A) Chlorine consumption profile; (B) Cr(VI) formation profile. Initial $[HOCl]_{TOT}$ = 20 mg Cl_2/L, $[Cr_2O_{3(s)}]$ = 2.8 mM, Cr(III)/Cl_2 = 10:1, pH = 7.5, ionic strength = 10 mM.

example, after 24 h of oxidation of $Cr_2O_{3(s)}$, chlorine consumption increased by 50% when bromide concentration increased from 0 to 0.1 mg/L and further increased by 50% when 5 mg/L of bromide was present after reaction (Figure 5A). Meanwhile, Cr(VI) formation increased by 1 order of magnitude when bromide concentration increased from 0 to 0.1 mg/L and further increased by 100% when 5 mg/L of bromide was present (Figure 5B). The enhancement in reaction rate was particularly significant at bromide levels less than 1 mg/L. In systems with $Cr(OH)_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$, similar catalytic effects in the presence of bromide were observed (Figures S13−S14).

The effects of bromide on chlorine consumption and Cr(VI) formation result from a catalytic reaction mechanism. Bromide readily reacts with HOCl to generate bromine, specifically, hypobromous acid (HOBr) in the pHs examined in this study:[75]
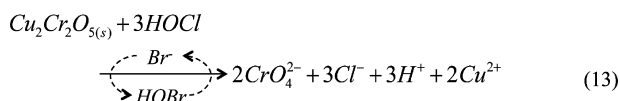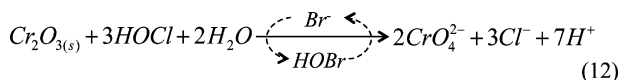
$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad k_5 = 1.55 \times 10^3 \ M^{-1}s^{-1}$$
$$(9)$$
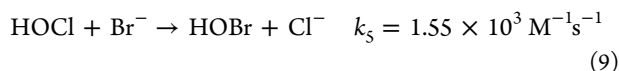
Under the conditions studied here (i.e., $[Br^-]$ = 0.1–5.0 mg/ L; $[Cr(III)_{(s)}]$ = 2.8 mM), reaction 9 is much faster than any of reactions 1−3 and essentially accounts for all the chlorine consumption. As reaction 9 proceeds, HOBr can oxidize $Cr(III)_{(s)}$ to generate Cr(VI) and reproduce bromide. In the case of $Cr(OH)_{3(s)}$:

$$2Cr(OH)_{3(s)} + 3HOBr$$
$$\rightarrow 2CrO_4^{2-} + 3Br^- + 7H^+ + H_2O \quad (10)$$
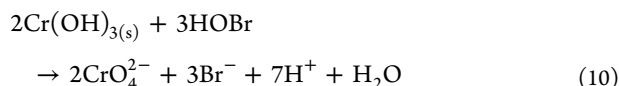
The surface area normalized rate constants of reaction 10 at pH 7.0 and 7.5 are 1.2×10^{-3} and 1.5×10^{-3} (L·m^{-2}·min^{-1}), respectively, calculated from the oxidation of $Cr(OH)_{3(s)}$ by HOBr (Figure S15). Meanwhile, the rates of $Cr(OH)_{3(s)}$ oxidation by HOCl (reaction 1) are 2×10^{-4} and 2.2×10^{-4} (L·m^{-2}·min^{-1}) at these two pHs (Figure 2A). Bromine oxidation rates are approximately 6 times of the chlorine oxidation rates with respect to $Cr(OH)_{3(s)}$ (reaction 10 versus reaction 1). Prior studies demonstrated that HOBr is more electrophilic than HOCl and, therefore, more reactive toward electron-rich compounds including Mn(II),[53] ammonia,[76] phenols,[77,78] steroid estrogens,[79] and dissolved organic matter with amines and phenolic moieties.[80,81] In the redox system of this study, the reactive surface sites of Cr(III) solids serve as electron-rich centers to react with HOBr. Combining reactions 9−10, the overall bromide-catalyzed oxidation of $Cr(OH)_{3(s)}$ by chlorine becomes (reaction 11):

$$2Cr(OH)_{3(s)} + 3HOCl \xleftrightarrow[\ \to HOBr\ ]{\ \cdots Br \leftarrow\ } 2CrO_4^{2-} + 3Cl^- + 7H^+ + H_2O$$
$$(11)$$
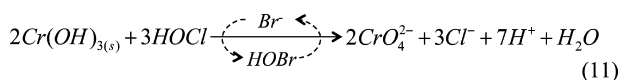
Similarly, bromide-catalyzed oxidation of $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ by chlorine can proceed, respectively (reactions 12−13):

$$Cr_2O_{3(s)} + 3HOCl + 2H_2O \xleftrightarrow[\ \to HOBr\ ]{\ \cdots Br \leftarrow\ } 2CrO_4^{2-} + 3Cl^- + 7H^+$$
$$(12)$$

$$Cu_2Cr_2O_{5(s)} + 3HOCl$$
$$\xleftrightarrow[\ \to HOBr\ ]{\ \cdots Br \leftarrow\ } 2CrO_4^{2-} + 3Cl^- + 3H^+ + 2Cu^{2+}$$
$$(13)$$

Bromide essentially acts as an electron shuttle that catalytically promotes the oxidation of $Cr(III)_{(s)}$ by chlorine. Based on the kinetics model (eqs 4−5), surface area normalized rate constants of reactions 11−13 were obtained with different bromide concentrations (Figure 6). In general, the presence of bromide ranging between 0.1 and 1.0 mg/L increased both k_{Cl_2} and $k_{Cl(VI)}$ by 3 to 20 times. The catalytic effect was less prominent when bromide concentration was higher than 1 mg/L, indicating that the oxidation rate was limited by the availability of reactive Cr(III) surface sites at higher bromide concentrations.

In addition, calculation based on steady-state assumption of HOBr and Br^- shows that HOBr concentration was approximately 8 times higher than that of Br^- at a given reaction time (Text S3). The formation of bromate (BrO_3^-) was negligible from the reaction, although other studies reported the formation of BrO_3^- via HOBr decay during the chlorination of transition metals such as Cu(II).[54] Furthermore, the observed stoichiometry of $\Delta[Cr(VI)]/\Delta[HOCl]_{TOT}$ during the chlorine oxidation of
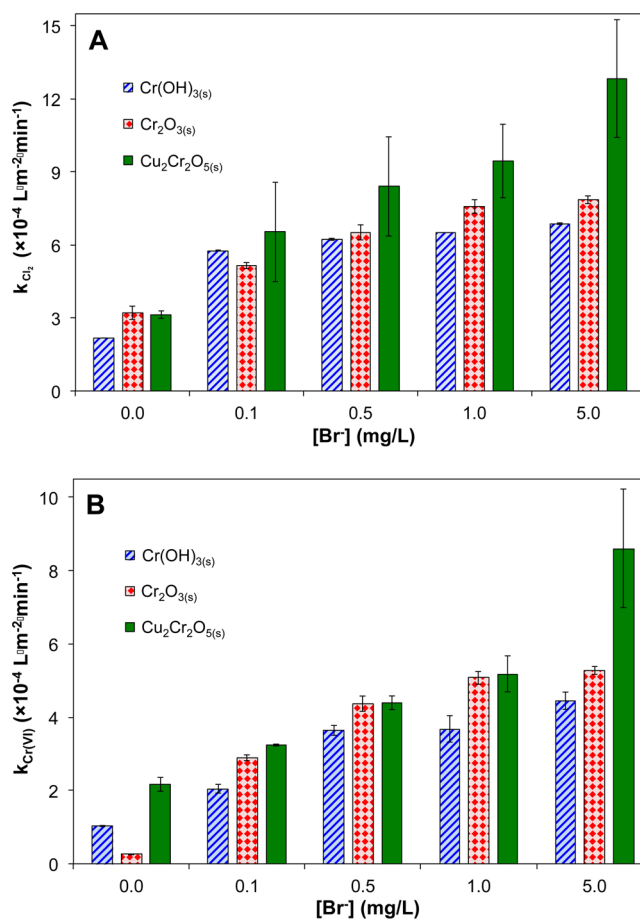

Figure 6. Effect of bromide on the effect of pH on the surface-area normalized second-order rate constants of Cr(III) oxidation by chlorine. (A) Chlorine consumption rate; (B) Cr(VI) formation rate. Initial [Cr(III)] = 2.8 mM, $[HOCl]_{TOT}$ = 20 mg Cl$_2$/L, Cr(III)/Cl$_2$ = 10:1, ionic strength =10 mM, pH = 7.5.

$Cr(III)_{(s)}$ increased significantly and approached 0.67 in the presence of bromide (Figure S16), which was consistent with the expected stoichiometry (reactions 11−13). Because HOBr is the actual oxidant that drives the oxidation of Cr(III) in bromide-catalyzed oxidation, the data suggest that HOBr oxidizes Cr(III) solid phases with a stoichiometric conversion to Cr(VI), possibly without the autocatalytic decay of HOBr or the formation of Cr intermediate species.

To further examine the unique pathway of $Cr(III)_{(s)}$ oxidation involving bromide, we conducted additional oxidation experiments between each Cr(III) solid and HOBr. Results show that the pathway of $Cr(III)_{(s)}$ oxidation by HOBr is very different from oxidation by HOCl. Oxidation of $Cr_2O_{3(s)}$ by HOBr at pH 7.0 exhibited a negligible production of dissolved O$_2$ (Figure 7A), although rapid HOBr consumption and Cr(VI) formation occurred (inserted plot in Figure 7A). In contrast to the chlorine system, the stoichiometry of $[Cr(VI)]/\Delta[HOBr]_{TOT}$ followed the expected value of 0.67 (Figure 7B). The other two Cr(III) solids also exhibited stoichiometry similar to 0.67 during HOBr oxidation (Figure S17).
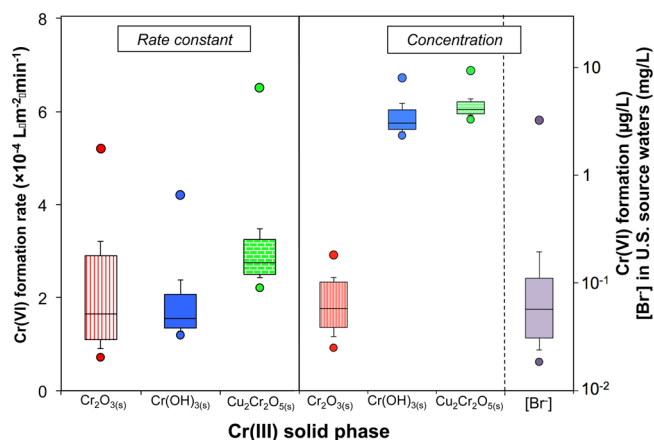
The stoichiometry analysis indicate that bromine oxidation of Cr(III) solids does not generate significant Cr intermediates that can subsequently dissociate to produce O$_2$. Bromine does not undergo autocatalytic decay in the presence of Cr(III)
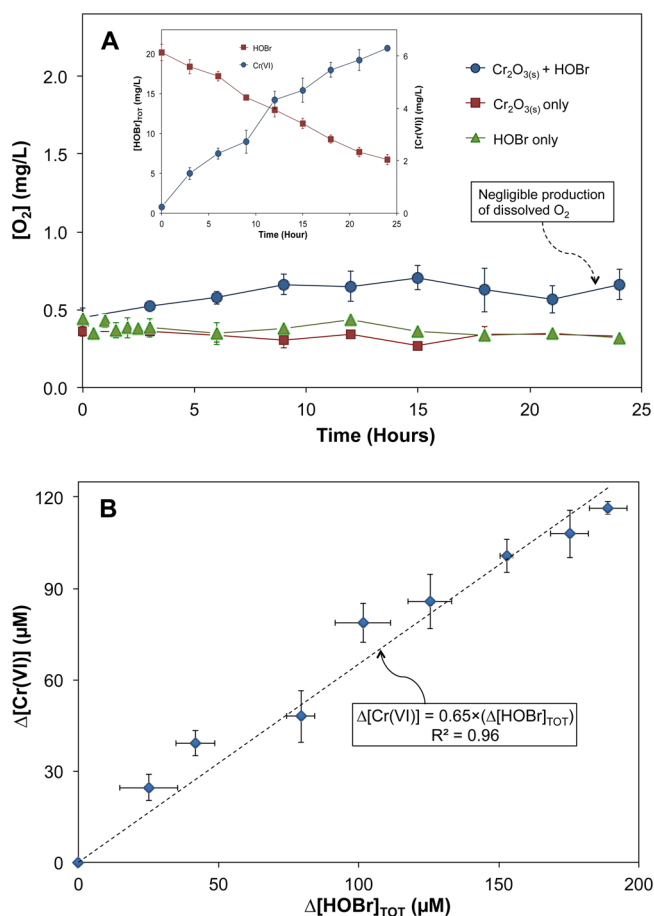
Figure 7. Oxidation of $Cr(OH)_{3(s)}$ by HOBr. (A) Measurements of dissolved O_2; (B) stoichiometry of Cr(VI) formation with HOBr consumption. Initial $[HOBr]_{TOT} = 280\ \mu M$, molar ratio of $Cr(III)/Br_2 = 10:1$, pH = 7.0, ionic strength = 10 mM.

Figure 8. Box-plot of predicted Cr(VI) formation rate constants and the enhanced Cr(VI) formation in drinking-water distribution systems. The solid line in each box is the median value; the lower and upper box edges are the 25th and 75th percentiles, respectively. Whisker bars represent the 5th and 95th percentiles. Solid dots are the minimum and maximum values. The percentile distributions are predicted on the basis of statistical distributions of bromide concentration in U.S. source waters (refs 49−51). The kinetics model simulation on enhanced Cr(VI) formation is based on a water distribution system with 0.3 mg/L chlorine residual, 100 μg/L residual Cr(III) solids, and a residence time of 2 days.

solids. This mechanism explains the observed higher rate constants of Cr(VI) formation during bromine oxidation. Because the oxidation of Cr(III) solids by chlorine in the presence of bromide is essentially driven by bromine (reaction 9), a reaction pathway that bypasses the formation of Cr intermediates can significantly increase the yield of Cr(VI), which is consistent with the observed catalytic effect of bromide on Cr(VI) formation.

Environmental Implications. Findings from this study demonstrated possible Cr(VI) reoccurrence in drinking-water distribution systems due to the oxidation of Cr(III) solids by chlorine, especially in the presence of trace levels of bromide. On the basis of the rate constants obtained from this study and the statistical distribution of bromide concentrations in U.S. source waters, we determined that the kinetics model predicts Cr(VI) can be generated in drinking-water distribution systems from cumulated Cr(III) solids (Text S4). For example, considering a typical residence time of 2 days in a drinking-water distribution system that contains 100 μg/L of $Cr(OH)_{3(s)}$ and a chlorine residual of 0.3 mg/L, Cr(VI) concentration in tap water can increase by 2.5, 3.0, and 4.6 μg/L by the catalytic effect of bromide (determined based on the 5th, 50th, and 95th percentile distribution of bromide concentrations, respectively (Figure 8). The existence of $Cr_2O_{3(s)}$ and $Cu_2Cr_2O_{3(s)}$ as Cr(III) solids in water distribution system can increase Cr(VI) level by 0.3 to 5 μg/L. In addition, Cr(VI) formation in the tap

can be further enhanced with an increase of residence time in water distribution systems (Figure S18).

Because adaptive strategies including water reuse are widely employed to augment water supplies, an accumulation of salts, including bromide, over time can take place. In addition, an increase of salinity can come from sources including effluent from gas drilling operations, agricultural runoff, and seawater intrusion. Strategies to reduce bromide levels in source waters can be effective for water utilities to minimize the occurrence of Cr(VI) in chlorinated water distribution systems. Additionally, the mitigation of Cr(VI) occurrence in drinking water could be achieved by the use of a residual disinfectant less oxidative than chlorine.

Examination on the reaction stoichiometry suggests the importance of Cr intermediates including Cr(V) to the yield of Cr(VI) during Cr(III) oxidation. Formation of Cr intermediates can promote the catalytic decay of chlorine without producing Cr(VI). Beyond the three Cr(III) solids investigated in this study, Cr(III) can exist as a co-precipitate with Fe(III) oxyhydroxides in water distribution systems. The reactivities of Fe(III)−Cr(III) oxides also need to be further ascertained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05739.

Additional text detailing synthesis of chromium hydroxide $Cr(OH)_{3(s)}$, standard redox potential calculation for Cr(III) solids, calculation on bromide catalytic effects, and kinetics model prediction on Cr(VI) formation in drinking water. Table showing a summary of redox potential of different redox couples at pH 7. Figures that show experiments on the adsorption and desorption of Cr(VI) on $Cr(OH)_{3(s)}$, measurements of free chlorine by the DPD method, measurements of Cr(VI) by the DPC method, effect of initial Cr(III)-to-chlorine molar ratio

on the Cr(III) oxidation by chlorine, impact of pH on the oxidation of $Cr_2O_{3(s)}$ and $Cr(OH)_{3(s)}$ by chlorine, change in ζ potential with pH for all three Cr(III) solids, cumulative Cr(VI) formation versus Cl_2 consumption at varying pHs for $Cr_2O_{3(s)}$ oxidation by chlorine, cumulative Cr(VI) formation versus Cl_2 consumption at varying pHs for $Cu_2Cr_2O_{5(S)}$, impact of bromide concentration on the oxidation of $Cr(OH)_{3(s)}$ and $Cu_2Cr_2O_{5(s)}$ by chlorine, correlation between cumulative Cr(VI) formation and cumulative chlorine consumption $\Delta[Cl_2]$ in the presence of bromide during the oxidation of $Cr(OH)_{3(s)}$ by chlorine, stoichiometry of Cr(VI) formation with HOBr consumption during the oxidation of Cr(III)(s) by HOBr, and kinetics model prediction of enhanced Cr(VI) formation via Cr(III) solid-phase oxidation by chlorine due to the catalytic effect of bromide in U.S. source waters. (PDF)

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Notes
The authors declare no competing financial interest.

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