ACS ES&T Water

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Perspective

Overlooked Role of Chromium(V) and Chromium(IV) in Chromium Redox Reactions of Environmental Importance

Joshua Bell, Xingmao Ma, Thomas J. McDonald, Ching-Hua Huang,* and Virender K. Sharma*

Cite This: *ACS EST Water* 2022, 2, 932−942

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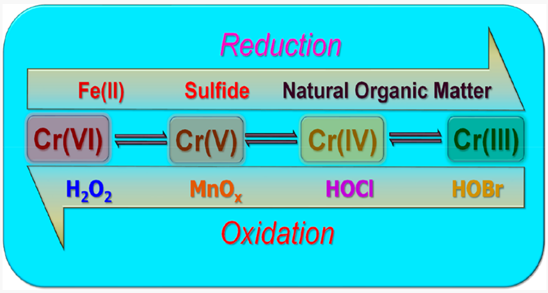
ABSTRACT: Chromium (Cr) is a well-known heavy metal contaminant with toxicity highly dependent on its oxidation state. Hexavalent Cr (Cr(VI)) is a known carcinogen while trivalent chromium (Cr(III)) is significantly less toxic. The reduction of Cr(VI) and oxidation of Cr(III) in different compartments of the environment occur through intermediate species pentavalent Cr (Cr(V)) and tetravalent Cr (Cr(IV)), which are highly reactive. The environmental literature generally lacks information on Cr(V) and Cr(IV) species in various redox processes. This Perspective presents the aquatic chemistry of Cr(V) and Cr(IV), which includes their spectroscopic characterizations and kinetic behaviors under different environmental conditions. Examples are presented to demonstrate the possible existence of the intermediate Cr species in different systems of environmental importance such as the reduction of Cr(VI) by iron(II) (Fe(II)), molecules of natural organic matter (e.g., fulvic acids and carboxylic acids), and oxidation of Cr(III) by hydrogen peroxide, hypochlorite, and manganese oxides (MnO_x). The oxidation of organic pollutants by the Cr(VI)−S(IV) system is also discussed. This Perspective suggests in-depth investigations on the redox reactions of Cr relevant to environmental processes to shed light on the mechanisms of the generation of Cr(V) and Cr(IV) species and their roles in water decontamination.



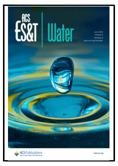
INTRODUCTION

Heavy metals are known to pollute water resources and have both natural and anthropogenic sources. Anthropogenic sources of heavy metals consist of sewage discharge, pesticides, mine tailings, and coal combustion residuals, while natural sources of heavy metals can include soil erosion and weathering.[1,2] Industrial processes to extract metals may illegally discharge waste into the natural environment, creating pollution events that need complete remediation.[3] Anthropogenic disturbances of geochemical processes can cause background levels of heavy metals to elevate and bioaccumulate, posing health risks to humans and the ecosystem because of their persistence in the environment and damage to the nerve system and other organs.[4,5] Among heavy metals, chromium (Cr) is a major pollutant, entering soil from wastes of industrial activities such as coal-fired power generation, chrome pigment production, wood preservation, stainless steel production, galvanization, cement production, electroplating, and leather tanning.[6−9] Chromium has four isotopes in nature: isotopes ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr with respective abundances of 4.35%, 83.79%, 9.50%, and 2.36%.[10]

The oxidation states of chromium range from −2 to +6. Three forms of Cr (Cr(0), Cr(III), and Cr(VI)) are thermodynamically stable and extensively used in various industrial applications. The application of Cr(0) is in its metallic form (e.g., iron-based alloys such as stainless steel). Pollution from incineration of chrome materials results in small Cr(III)- and Cr(VI)-containing particles, which may be inhaled through polluted air exposure and ultimately increase the levels of Cr in surface waters. Considering this and other pollution routes, Cr has been listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) and is regulated in drinking water. The USEPA has set a Cr limit of 100 μg/L in drinking water.[11]

In natural environments, most of Cr is present in Cr(VI) and Cr(III) species and their concentrations depend on the total concentration of Cr, pH, and redox potential ($p\varepsilon$) of water (Figure S1).[12] The oxyanions of Cr(VI) (i.e., $Cr_2O_7^{2-}$ and $HCrO_4^-$) are dominant species between pH 0.0 and 6.0. The other oxyanion of Cr(VI), CrO_4^{2-}, appears at around pH 4.5 with a maximum concentration at pH ≥ 8.0. Comparatively, there are five species of Cr(III) present in water (Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$).[13] The values of $p\varepsilon$ and pH provide information on the equilibrium species of Cr in the water. Insoluble at neutral pH, Cr(III) is the most thermodynamically stable and kinetically inert.[14] The Cr(III) ion exists in a hydration sphere as the hexaaquo ion $[Cr(H_2O)_6]^{3+}$ (pK_a = 4.0) with each water molecule being

Received: October 22, 2021
Revised: May 5, 2022
Accepted: May 6, 2022
Published: May 19, 2022



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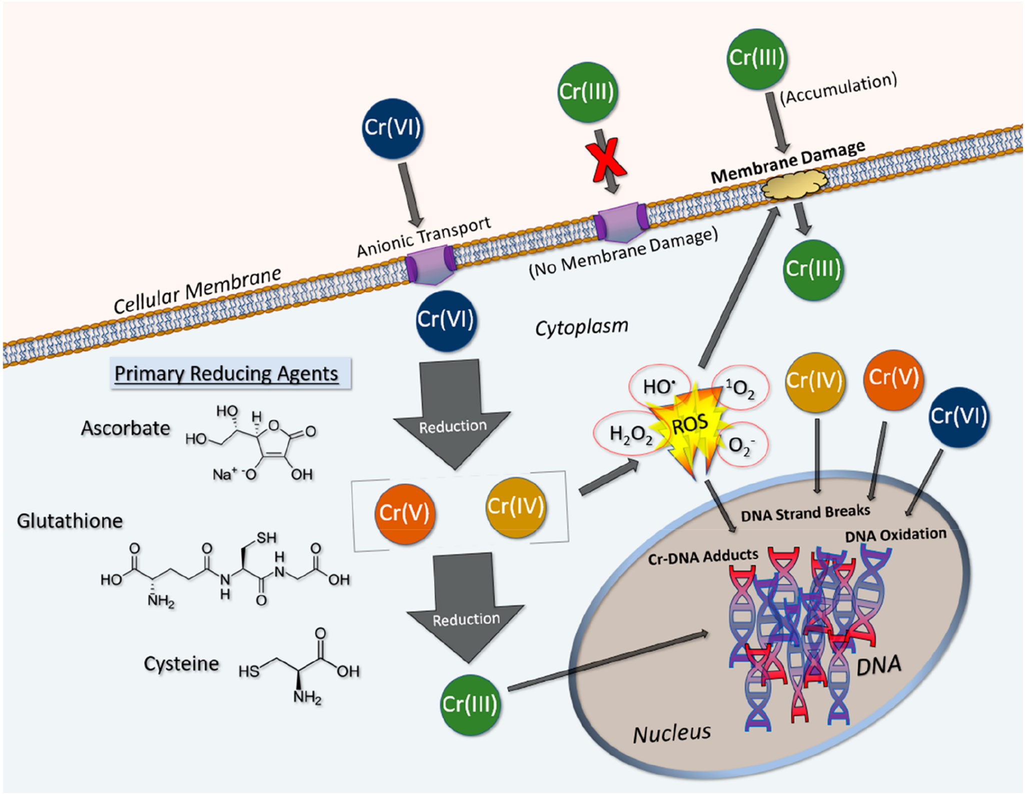

Figure 1. Brief overview of chromium cellular entry and the subsequent intercellular reduction of Cr(VI), which illustrates the role of intermediates Cr(IV) and Cr(V) in causing DNA damage. Reactive oxygen species (ROS) and Cr(III) accumulation may result in membrane damage, allowing Cr(III) cellular entry.

hydrogen-bonded to two other water molecules in a second sphere.[15,16] The speciation of Cr(III) as a function of pH is presented in Figure S2.[13] The dominant Cr species in an acidic medium is Cr^{3+}, whereas $Cr(OH)_3^0$ and $Cr(OH)_4^-$ are the main Cr species in alkaline conditions (Figure S2).[13]

Chromium(III) has also been known as an essential micronutrient for humans; however, the molecular mechanisms are still unclear, bringing into question how essential it is as a supplement.[15] Some studies regard Cr(III) supplementation to be beneficial in weight loss for patients with diabetes, while others postulate that excessive intake could be carcinogenic.[17] Concerns over potential oxidation of Cr(III) supplements to Cr(VI) arise from physiological variations in pH, redox potential, and the occurrence of oxidizing compounds. The Food and Nutrition Board of the National Academics of Sciences, Engineering, and Medicine has set adequate intake values of Cr(III) at 25 and 35 μg/day for women and men, respectively, far less than that provided by chromium supplementation.[17] The World Health Organization has set an upper limit of safe intake of Cr at 250 μg/day; excessive Cr(III) intake is unwarranted at this time because of studies revealing the toxicity of Cr(III) at high concentrations.[18] For example, the popular Cr(III) supplement known as chromium picolinate ($Cr(pic)_3$) has shown clastogenic, cytotoxic, and chromosome damage to Chinese hamster ovary cells with other short-term tests that have revealed deoxyribonucleic acid (DNA) damage.[19,20] Yet, other studies have shown no genotoxic effects in physiological conditions, including a chronic study on rats and mice revealing no toxicity of $Cr(pic)_3$.[20,21] One reason for the apparent discrepancy in toxicity could be due to the low cellular uptake of Cr(III).[21] Significantly, Cr(VI), but not Cr(III), has been reported to potentially cause cancers to humans.[7,22] Therefore, more stringent regulations in the State of California have even set Cr(VI) limits in drinking water to 10 μg/L.[23]

The toxicity of Cr(VI) is potentially related to the production of reactive intermediates Cr(V) and Cr(IV) under biological environments. In earlier research, the presence of Cr(V) and Cr(IV) was largely ignored. However, the detection of Cr(V) with ligands such as thiols, glycols, and phenols and their potential in damaging the DNA have been reported.[15,24,25] The reduction of Cr(VI) to Cr(V) and subsequently to Cr(III) is an intercellular reduction process, possibly carried out by nicotinamide adenine dinucleotide (NADH) and/or nicotinamide adenine dinucleotide phosphate (NADPH).[26] Other intercellular reducing agents include cysteine, lipoic acid, fructose, and ribose as well as redox proteins such as cytochrome P450 and hemoglobin.[15] Under physiological conditions, the reduction of Cr(VI) by ascorbate and glutathione that occurs within cells can also produce reactive oxygen species (ROS) such as singlet oxygen ($^1O_2$), superoxide radical ($O_2^{\bullet -}$), hydroxyl radical ($^\bullet OH$), and hydrogen peroxide (H_2O_2) that can damage DNA.[26,27]

Though ROS have been shown to play a role in Cr(VI)-induced oxidative stress, the direct relationship between DNA−ROS and Cr(VI)-induced DNA damage is still debated.[15] For example, a tetraperoxochromate(V) species has been suggested in the reduction of Cr(VI) by H_2O_2, forming ROS like $^\bullet OH$ that results in DNA damage; yet, another study disproved the generation of $^\bullet OH$ in this system using an electron paramagnetic resonance (EPR) technique.[15]

Additionally, cytotoxicity, genotoxicity, chromosomal aberrations, and DNA lesions, which might lead to carcinogenesis, can occur from the reactions of ROS and Cr(V)/Cr(IV).[27] Also worth mentioning is that Cr(VI) can form complexes with biological thiols, which has been determined by various spectroscopic techniques.[28] The potential cellular mechanisms involving Cr intermediates is illustrated in Figure 1. Cr(III) complexes are not able to pass through cell membranes through anionic transport like Cr(VI) complexes; however, their accumulation may cause morphological alterations to cell surfaces and yield cell membrane lipid injuries, allowing for Cr(III) to pass through and potentially cause DNA damage.[26,27]

The mechanisms involving Cr-induced carcinogenicity depend on multiple factors including cell type, DNA adduct and free radical formation, Cr(VI) concentration, and the reactivity of Cr intermediates.[29] Though Cr(V) and Cr(IV) might be grouped together as reactive Cr intermediates, their function in toxicity differs. For example, both Cr(V) and Cr(IV) were shown to induce DNA double-strand breaks, yet Cr(IV) had more mutation frequencies in the hypoxanthine phosphoribosyltransferase (HPRT) gene compared to Cr(V).[30] More research is needed to identify not only specific mechanisms of Cr-induced carcinogenicity but also the role of intermediates Cr(V) and Cr(IV). Selective detection of Cr(V) has been shown by EPR and UV−visible measurements, electrospray mass spectrometry (ES-MS), and X-ray absorption spectroscopy methods.[25,31−33] Additionally, kinetics data on the interaction of Cr(VI) with reducing agents L-cysteine, glutathione, L-ascorbic acid, and Trolox using stopped-flow UV−visible spectrophotometry have been obtained to gain insights into the information on Cr(V) and Cr(IV) species.[34] Intermediates Cr(V) and Cr(IV) are often responsible for Cr-induced toxicity.

To date, a progress has been made on the Cr(V) and Cr(IV) species due to their biological importance, but their roles in the environmental processes are largely overlooked. Significantly, these reactive species of Cr (i.e., Cr(V) and Cr(IV)) are likely produced from the interaction of Cr(VI) with natural organic ligands (or compounds) and the reaction of Cr(VI) with reducing moieties of natural organic matter (NOM) as well as from the interaction of Cr(III) with oxidants. Thus, the focus of this Perspective is to provide the basic properties and characterization of Cr(V) and Cr(IV) to bring attention to researchers of the need to carry out more mechanistic investigations to shed light on the species involved in the redox reactions of chromium in environmental processes. Examples of studies on chromium of environmental importance are presented below.

■ CHROMIUM(V) AND CHROMIUM(IV) SPECIES

Cr(V) and Cr(IV) species are highly reactive intermediates. This may largely be attributed to the higher standard redox potentials of Cr(V) and Cr(IV) species than Cr(VI) in acidic conditions (Figure 2).[15,35] Cr(VI) is expected under oxidizing conditions, completely soluble across the pH range, and highly mobile overall.[6,14,15] The one-electron redox potential under acidic conditions decreases in the order of Cr(IV) > Cr(V) > Cr(VI). The chemical properties of Cr(V) and Cr(IV) are different from those of Cr(VI) and Cr(III). The redox potentials of Cr(V) and Cr(IV) are not available in alkaline conditions. High-valent Cr species (i.e., Cr(VI), Cr(V), and Cr(IV)) are powerful oxidants. Comparatively, Cr^{II} is a good reductant (see the negative redox potential of Cr^{II}/Cr(0) in Figure 2).[15,35]

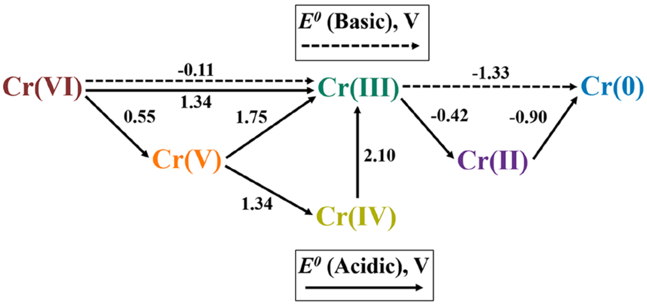

Figure 2. Standard redox potentials (E^0) of various Cr species in basic and acidic conditions (reduction potentials were cited from refs 15 and 35).

Both Cr(V) and Cr(IV) are typically short-lived, making them challenging to quantify. Both Cr species could be stabilized by the complexing agent 2-ethyl-2-hydroxobutanoato (ehba), and UV−visible spectra of the complexes have been obtained (Figure 3).[15] All Cr species have characteristic spectra to distinguish different high-valent Cr species. In the UV range, the Cr(V) complex has reasonable molar absorptivity ($\varepsilon = 10^3$ $M^{-1}cm^{-1}$). The Cr(IV) complex also absorbs over a wide wavelength range with a maximum near 350 nm ($\varepsilon = 1.7 \times 10^3$ $M^{-1}cm^{-1}$). Cr(III) forms a weak complex with ehba (Figure 3).[15] The spectrum of Cr(VI) represents the maximum molar absorptivity of $HCrO_4^-$ at a different wavelength.

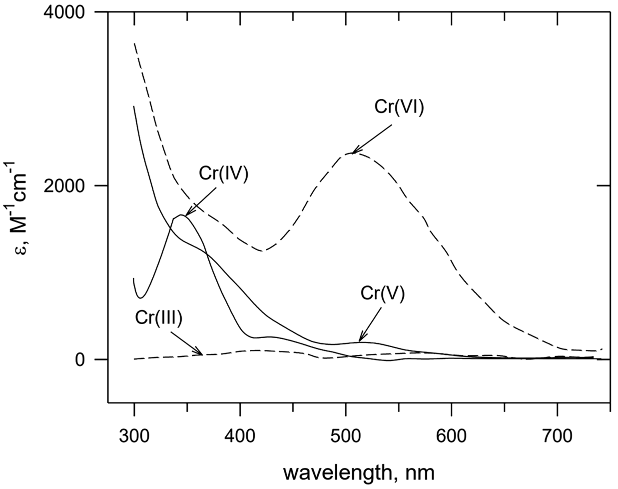

Figure 3. UV−visible spectra of the Cr−ehba buffer complex (ehba = 2-ethyl-2-hydroxobutanoato) at pH 3.5 showing varying Cr oxidation states; the Cr(V) complex was $[CrO(ehba)_2]^-$, and the Cr(IV) complex was $[CrO(ehbaH)_2]^0$ (Adapted from ref 15 with permission from John Wiley & Sons, Inc. Copyright 2012).

EPR is often applied to detect Cr(V) species. The typical EPR spectra of Cr(V) complex species for hydroxamate complexing agents are given in Figure 4.[36] The hydroxamate groups are likely moieties in humic substances and interact with Cr(VI) to form Cr(V)−hydroxamate species.[37,38] The EPR spectra for the Cr(V) complexes have a center at $g_{iso} \approx 1.98$ with a strong narrow line.[39] Another example is the reduction of Cr(VI) by catecholamines to produce octahedral Cr(V) species, which has been quantified by EPR yielding a

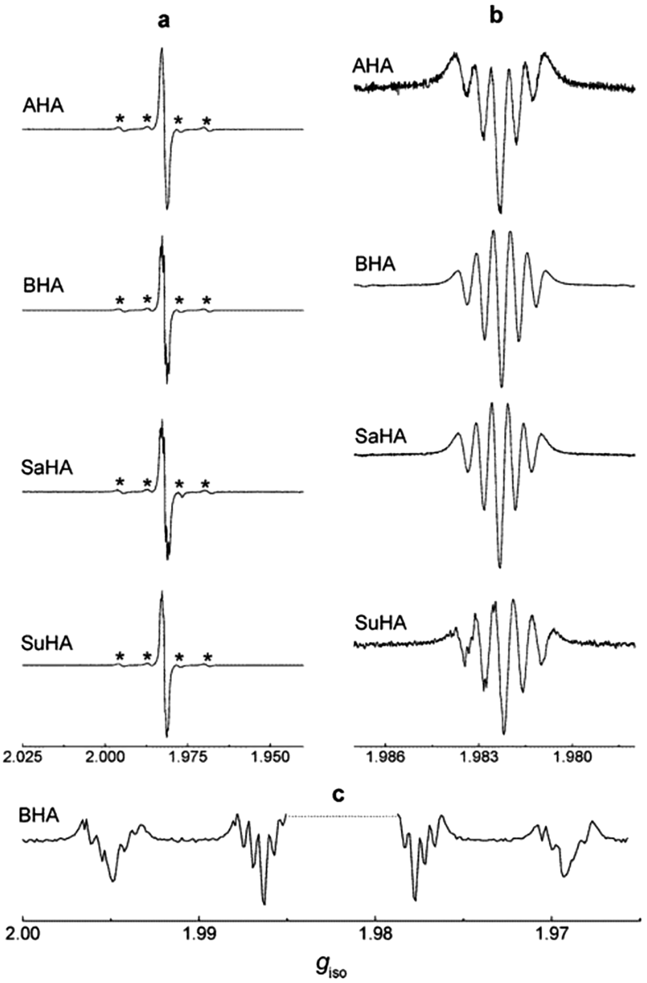

Figure 4. Electron paramagnetic response (EPR) spectra (X-band) of solutions obtained from reaction between 10 mM Cr(VI) and 0.10 M hydroxamic acids (acetohydroxamic acid (AHA), benzohydroxamic acid (BHA), salicylhydroxamic acid (SaHA), and suberohydroxamic acid (SuHA)) in *N*,*N*-dimethylformamide (DMF) for 3.5 h at 22 °C: (a) first derivative spectra with modulation amplitude at 1.0 G and asterisks indicating the satellite signals from ^{53}Cr hyperfine coupling; (b) second derivative spectra showing only central signals with modulation amplitude at 0.40 G; (c) second derivative spectra with modulation amplitude at 1.0 G of satellite signals of the Cr(V)−BHA complex.[36]

signal at $g_{iso} \sim 1.972$ ($A_{iso}(^{53}\mathrm{Cr}) > 23.9 \times 10^{-4}$ cm^{-1}).[31] Many other Cr(V) complexes with EPR signals obtained include Cr(V)−ascorbate, Cr(V)−D-glucose, and Cr(V) with D-ribose-5′-monophosphate.[39] Interestingly, diol ligands might play an important role in stabilizing Cr(V) complexes, which has been noted by the detection of Cr(V) EPR signals after 48 h of reaction.[39] The Cr(V)−glutathione (GSH) complex ([Cr(V)-O(LH$_2$)$_2$]$^{3-}$ (LH$_5$ = GSH)) has been characterized and quantified by electrospray mass spectrometry, X-ray absorption, EPR spectroscopy, and other analytical techniques.[32]

Since Cr(IV) complexes are less stable in aqueous solutions than Cr(V) complexes and the EPR spectroscopy technique cannot be used for Cr(IV) complexes under ambient conditions, less is known about Cr(IV) chemistry.[39] Several studies have investigated Mn(II) as a selective trap for Cr(IV), but that has overall been inconclusive in the determination of the role of Cr(IV) in DNA damage.[39] In other conditions, the fast reaction between Cr(III) and $^{\bullet}$OH/SO$_2^{\bullet-}$ at acidic conditions revealed a Cr(IV) spectrum between 250 and 420 nm with an increasing molar absorption coefficient from 4.3 to 48 M^{-1}cm^{-1}, ultimately producing Cr(VI).[15]

The pulse radiolysis technique was applied to produce Cr(V) from Cr(VI). The reaction of Cr(VI) with $^{\bullet}$CO$_2$ under nitrous oxide saturated solution generates Cr(V) (eq 1).

$$\mathrm{Cr(VI)} + {}^{\bullet}\mathrm{CO_2} \rightarrow \mathrm{Cr(V)}; \quad k \approx 10^8\ \mathrm{M^{-1}s^{-1}} \tag{1}$$

Reaction 1 was performed at different pH values, and the spectra of the obtained Cr(V) and Cr(IV) are presented in Figure 5.[40] In the pH range from 1.85 to 4.75, the spectrum of Cr(V) had no variation.[40] The molar absorptivity of Cr(V) was lower in the acidic pH range compared to that in the alkaline pH range. The spectra of Cr(V) did not change significantly in the pH range from 8.0 to 13.7.[40] The decay of Cr(V) in aqueous solution has been proposed on the basis of the disproportionation of Cr(V) as a function of pH and conductivity measurements, which can be described by reactions 2−6.

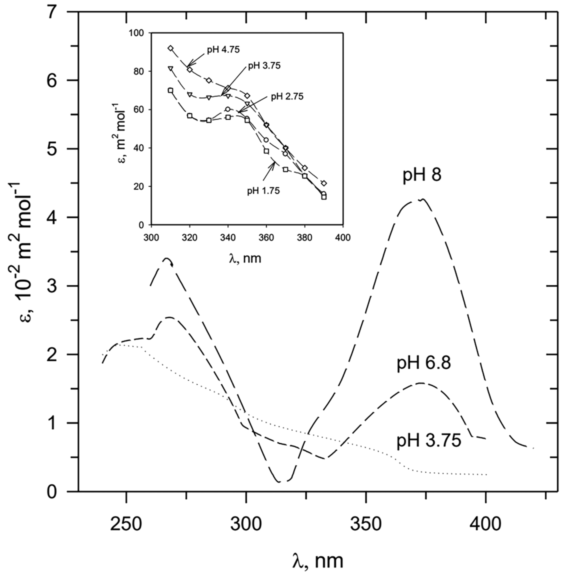

Figure 5. UV−visible spectra of Cr(V) over varying pH obtained by pulse radiolysis from the reaction of Cr(VI) and formate in a N$_2$O saturated solution; the inset illustrates little variance in Cr(V) spectra in acidic conditions from pH 1.75 to 4.75 (Adapted from ref 15 with permission from John Wiley & Sons, Inc. Copyright 2012).

$$\mathrm{HCr^{VI}O_{4(tet)}}^- + \mathrm{CO_2}^{\bullet-} \rightarrow \mathrm{HCr^{V}O_{4(tet)}}^{2-} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{HCr^{V}O_{4(tet)}}^{2-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2Cr^{V}O_4}^- \quad K_3 = 6.0 \times 10^3 \tag{3}$$

$$\mathrm{H_2Cr^{V}O_4}^- + \mathrm{H^+} \rightleftharpoons \mathrm{H_3Cr^{V}O_{4(oct)}} \quad K_4 = 5.6 \times 10^2 \tag{4}$$

$$\mathrm{HCr^{V}O_{4(tet)}}^{2-} + \mathrm{H_3Cr^{V}O_{4(oct)}} \rightarrow \mathrm{HCr^{VI}O_{4(tet)}}^- + \mathrm{H_3Cr^{V}O_{4(oct)}}^- \tag{5}$$

$$\mathrm{HCr^{V}O_{4(tet)}}^{2-} \rightleftharpoons \mathrm{H^+} + \mathrm{Cr^{V}O_4}^{3-} \quad K_6 = 1.0 \times 10^{-7} \tag{6}$$

The constants of protonic equilibria of reactions 3, 4, and 6 suggest that both monoprotonated and deprotonated species of Cr(V) coexist at pH 7.0 (Figure S3).[40]

It has been proposed that octahedral Cr(IV) complexes can slowly react with each other, producing Cr(III) and Cr(V) octahedral coordination, as seen in eq 7.[15] Subsequently, the fast rearrangement of Cr(V) octahedral to tetrahedral complexes allows for a rapid reaction between Cr(V) tetrahedral and Cr(IV) octahedral complexes, which form Cr(VI) and Cr(III) as shown in the following eqs 8 and 9.[15]

$$\mathrm{Cr(IV)_{oct} + Cr(IV)_{oct} \rightarrow Cr(III)_{oct} + Cr(V)_{oct}} \quad \text{slow} \tag{7}$$

$$\mathrm{Cr(V)_{oct} \rightleftharpoons Cr(V)_{tet}} \quad \text{fast} \tag{8}$$

$$\mathrm{Cr(V)_{tet} + Cr(IV)_{oct} \rightarrow Cr(VI)_{tet} + Cr(III)_{oct}} \quad \text{fast} \tag{9}$$

The reactivities of Cr(IV) and Cr(V) have been examined by studying the oxidation of different organic compounds (e.g., carbohydrates, alcohols, thiols, amino acids, and peptides) by Cr(VI). Both Cr(IV) and Cr(V) can oxidize compounds (X) by either a one-electron pathway to form a radical ($X^\bullet$) or a two-electron pathway to form an oxidized product (X(O)) (eqs 10–13).[24,36,41–49] Therefore, different mechanisms may occur, depending on the concentrations of the chromium species and X.

$$\mathrm{Cr(IV) + X \rightarrow Cr(III) + X^\bullet} \tag{10}$$

$$\mathrm{Cr(IV) + X \rightarrow Cr(II) + X(O)} \tag{11}$$

$$\mathrm{Cr(V) + X \rightarrow Cr(IV) + X^\bullet} \tag{12}$$

$$\mathrm{Cr(V) + X \rightarrow Cr(III) + X(O)} \tag{13}$$

Cr(IV) and Cr(V) may form complex species with compounds (e.g., carbohydrates and peptides) to increase their stabilization,[50] similar to high-valent iron species like ferrates.[51,52] These complexes can possibly react with organic compounds as well.[48,50] The role of Cr(IV) and Cr(V) in the degradation of organic pollutants in water is further described below.

INVOLVEMENT OF CR(V)/CR(IV) SPECIES IN CHROMIUM REDOX REACTIONS OF ENVIRONMENTAL IMPORTANCE

Reactions of Cr(III)/Cr(VI) with Hydrogen Peroxide. The chemistry between Cr(III) and H_2O_2 has been extensively studied, and reactive intermediates Cr(V) and Cr(IV) are capable of generating $HO^\bullet$ from H_2O_2 by means of Fenton and Haber-Weiss-type reactions.[53–56] Reactions 14–17 illustrate the production of $HO^\bullet$ as well as the oxidation of Cr(III).[14] The reaction between Cr(III) and H_2O_2 gives Cr(IV) and $HO^\bullet$ species (reaction 14). The Cr(IV) species may react with H_2O_2 to form Cr(V) and $HO^\bullet$ species (reaction 15). The disproportionation of Cr(IV) may also produce Cr(V) species (reaction 16). Further reaction of Cr(V) with H_2O_2 may produce Cr(VI) and $HO^\bullet$ (reaction 17).

$$\mathrm{Cr(III) + H_2O_2 \rightarrow Cr(IV) + HO^\bullet + OH^-} \tag{14}$$

$$\mathrm{Cr(IV) + H_2O_2 \rightarrow Cr(V) + HO^\bullet + OH^-} \tag{15}$$

$$\mathrm{2Cr(IV) \rightarrow Cr(V) + Cr(III)} \tag{16}$$

$$\mathrm{Cr(V) + H_2O_2 \rightarrow Cr(VI) + HO^\bullet + OH^-} \tag{17}$$

Though Fenton reactions have shown oxidation of organic contaminants utilizing transition metals, their use is limited in that the active metal species is consumed as a reagent and lost through precipitation.[14] This means that metal reagents need to be continuously added to activate H_2O_2, resulting in the formation of metal sludge.[14,57] In fact, H_2O_2 can function as an oxidant of Cr(III) ($E^0(H_2O_2/H_2O) = 1.763$ V) and reductant of Cr(VI) ($E^0(O_2/H_2O_2) = 0.695$ V), creating a redox cycle that generates $HO^\bullet$ repeatedly.[14,58] The oxidation of Cr(III) by H_2O_2 can occur at pH > 8.0, and the reduction of Cr(VI) (eq 18[59]) can occur under acidic conditions because the reduction capability of H_2O_2 increases with decreasing pH.[8,14]

$$\mathrm{2CrO_4^{2-} + 3H_2O_2 + 10H^+ \rightarrow 2Cr^{3+} + 3O_2 + 8H_2O} \tag{18}$$

Full reduction of residual Cr(VI) was possible by 1.0 M HCl and 20 mM H_2O_2.[59] Subsequently, the use of H_2O_2 as an advanced oxidation process in chromium-contaminated wastewater to produce $HO^\bullet$ and reduce toxic Cr(VI) can be controlled by adjusting the pH of the solution. This redox chemistry brings forth evidence showing that the utilization of Cr(V)/Cr(IV) species may be feasible in the degradation of pollutants in wastewater.

Oxidation of Cr(III) during Chlorination. Consequently, Cr(III) can generate Cr(VI) by the treatment of chromium-contaminated water using free chlorine. The characterization of the redox chemistry of chromium in water distribution and treatment is vital for the evaluation of the potential of Cr(VI) exposure in drinking water. Chlorine used in the disinfection process has been shown to react with dissolved organic matter and inorganic compounds like bromide (Br^-), forming highly toxic halogenated disinfection byproducts (DBPs).[60] Chlorine in water treatment processes can oxidize Cr(III) to Cr(VI) as well.[61–65] The oxidation of Cr(III) by HOCl is highly problematic, and trace levels of bromide in this system were shown to be a catalyst in Cr(VI) formation.[63–66] Interestingly, Cr(III) species, such as $Cr(OH)_{3(s)}$ and $Cr_2O_{3(s)}$, reveal different reactivities in chlorine consumption on the basis of their surface area and reactive sites.[64] The oxidation of Cr(III) by HOCl typically proceeds through reaction 19.[65]

$$\mathrm{2Cr(III)_{(s)} + 3HOCl + 5H_2O \rightarrow 2CrO_4^{2-} + 13H^+ + 3Cl^-} \tag{19}$$

Corrosion of iron pipes in water distribution systems has been shown to release chromium, forming mixed phases of Cr(III)–Fe(III) hydroxide that can be oxidized by chlorine.[66] This is of concern to public health because roughly 70% of water distribution pipes in the U.S. are composed of iron materials and often have a lifespan of multiple decades, giving ample time for chromium to accumulate to high concentrations.[66] Interestingly, Cr(0), which exists in cast iron corrosion scales, was shown to be more reactive than Cr(III) with HOCl and the dominant factor of the Cr(VI) release in drinking water (reaction 20).[65]

$$\mathrm{Cr(0)_{(s)} + 3HOCl + H_2O \rightarrow CrO_4^{2-} + 5H^+ + 3Cl^-} \tag{20}$$

Additionally, the oxidation of Br^- by HOCl can produce hypobromous acid (HOBr), and this reaction is approximately six times faster than the oxidation of Cr(III) by HOCl.[64] This indicates that even trace levels of Br^- should be addressed with caution in solutions where Cr(III) and HOCl are present. The $Cr(OH)_{3(s)}$ oxidation rate constants at pH 7.0 and 7.5 are 1.2 × 10^{-3} and 1.5 × 10^{-3} M^{-1} min^{-1} for HOBr in reaction 21 and

2.0×10^{-4} and 2.2×10^{-4} M^{-1} min^{-1} for HOCl in reaction 22.[64]

$$2Cr(OH)_{3(s)} + 3HOBr \rightarrow 2CrO_4{}^{2-} + 3Br^- + 7H^+ + H_2O \quad (21)$$

$$2Cr(OH)_{3(s)} + 3HOCl \rightarrow 2CrO_4{}^{2-} + 3Cl^- + 7H^+ + H_2O \quad (22)$$

Oxidation of Cr(III) by Solid Manganese Oxides. Naturally occurring Cr(III) can be oxidized and lead to Cr(VI) groundwater contamination, which has previously caused drinking water concerns.[8] Oxidizing agents of Cr(III) that occur naturally in varying groundwater conditions consist of solid manganese oxides (MnO_x) and other metal oxides (Figure 6).[67] The primary oxidizing agent of Cr(III) in alkaline and aerobic conditions is MnO_x from the birnessite mineral; this is due to its large surface area, high degree of crystallinity, strong electronegativity, and ability to regenerate via the oxidation of Mn(II) by microorganisms and/or dissolved oxygen.[8,67−69] The oxidation of Mn(II) yielding Mn(III)/(IV) oxides at alkaline and oxic conditions was shown to accelerate Cr(VI) production; this was the dominant pathway of Cr(III) oxidation in the long-term analysis (1 year) compared to oxidation by MnO_2 or O_2 (Figure 6).[67,70] The accumulation of MnO_x in groundwater and subsequent oxidation of Cr(III) to Cr(VI) has occurred across the globe, creating drinking water health risks, especially in systems without adequate Cr treatment.[71−73] The following reaction 23 indicates the oxidation of Cr(III) by MnO_x species:[74]

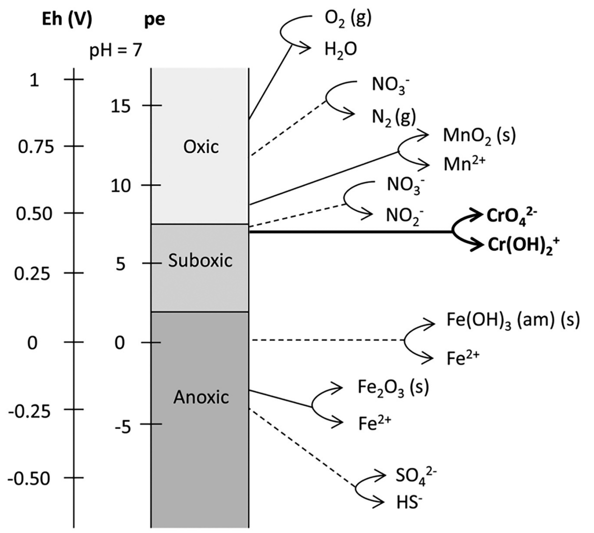

Figure 6. An environmentally relevant redox potential diagram illustrating the primary redox couples that are thermodynamically capable of influencing Cr redox species. Adapted with permission from ref 67. Copyright 2016 Canadian Science Publishing.

$$2Cr(OH)_3 + 3MnO_2 \rightleftharpoons 3Mn^{2+} + 2CrO_4{}^{2-} + 2H_2O + 2OH^- \quad (23)$$

Reduction of Cr(VI) by Natural Reducing Agents. As for the natural reduction of Cr(VI), reducing agents such as organic matter, Fe(II), and sulfides can reduce Cr(VI) to Cr(III) (Figure 6).[8,67,75,76] Not only is Fe(II) an environmentally friendly reducing agent, but its application on adsorbed surfaces has shown the promising removal of Cr(VI) through consecutive one-electron reduction processes (Cr(VI) + Fe(II) → Cr(V); Cr(V) + Fe(II) → Cr(IV); Cr(IV) + Fe(II) → Cr(III)).[77−79] Surface adsorbed Fe(II) is regarded as having higher reducing capabilities than Fe(II) in water, which has been demonstrated in Fe(II)-treated graphene oxide for the adsorption and reduction of Cr(VI).[80] Clay minerals containing Fe(II)/(III) are capable of reducing Cr(VI) with Fe-poor montmorillonite and Fe-rich nontronite clay minerals having second-order rate constants at pH 7.3 of 1.28 and 449 M^{-1} min^{-1}, respectively.[81] Additionally, some organic ligands can enhance Cr(VI) reduction by Fe(II) from the formation of Fe(II)/(III)−ligand and Cr(V)−ligand complexes.[82] Another example is the reduction of Cr(VI) by biological Fe(II) complexes (e.g., hemeproteins), which may result in Cr(V) complexes.[83]

Another effective method in Cr(VI) reduction utilizing Fe(II) has been shown by Fe(II)-doped TiO_2 photocatalysts; in 3.0 h of sunlight irradiation, almost 100% of 102.3 mg/L Cr(VI) from plating wastewater was removed.[84] Methods without Fe(II) adsorbed on surfaces, like the Fe(II)/H_2O_2 Fenton reaction, has also shown the potential to reduce Cr(VI). More recently, the incorporation of the catalyst WS_2 was shown to enhance the oxidation of phenol and the reduction of Cr(VI), achieving 90.9% reduction of 40 mg/L Cr(VI) at pH 3.8.[85] These studies that explored the incorporation of the natural reductant Fe(II) in Cr(VI) reduction yield promising data for its application in Cr-contaminated wastewater. Mechanistic studies involving Cr(V)/Cr(IV) in these systems are lacking.

The reduction of Cr(VI) to Cr(III) can also occur by microorganisms in both aerobic and anaerobic environments.[86] Microorganisms can directly reduce Cr(VI) by intracellular reduction and indirectly reduce Cr(VI) by producing natural reductants.[86] Reductants of Cr(VI) like S(II) and Fe(II) can be produced by bacteria while oxalic acid can be produced by fungi.[8,87] The natural reduction of Cr(VI) has been shown by some fungal species through enzymatic reduction and sorption to mycelia.[75,87] The Cr-resistant fungus *Paecilomyces lilacinus* was shown to reduce 1.24 mg/L of Cr(VI) from tannery effluent to below the detection level in 18 h in both acidic and basic conditions.[88] Additionally, the Cr-tolerant fungus *Penicillium oxalicum* SL2 was shown to reduce 40.6 and 96.1 mg/L of Cr(VI) in 48 and 96 h, respectively, from electroplating wastewater; a remarkable 89.6% of 217.1 mg/L Cr(VI) was also reduced from electroplating wastewater in 96 h.[89] The reduction of Cr(VI) by *Penicillium oxalicum* SL2 was attributed to oxalic acid secreted by *Penicillium oxalicum* SL2 and by biomass uptake through amine, carboxyl, and phosphate functional groups.[87] Interestingly, Mn^{2+} has been shown to promote Cr(VI) reduction by oxalic acid, posing another mechanism for the natural Cr(VI) reduction and application to wastewater remediation.[90]

Remediation of chromium-contaminated systems by bacteria is largely influenced by the bacterial cell surface; Gram-negative bacteria are more efficient at reducing Cr(VI) than Gram-positive bacteria because their outer membranes contain lipopolysaccharides, lipoproteins, and phospholipids.[91] Furthermore, multiple other microorganisms have shown the promising reduction of Cr(VI), making bioremediation of Cr-contaminated environments a viable treatment technology, partly because it can be highly selective to toxic metals.[92] The reduction of Cr(VI) would most likely occur through intermediates Cr(V) and Cr(IV), which warrants in-depth investigations.

Interaction of Cr(VI) with Natural Organic Matter. Natural organic matter (NOM) contains different components like polysaccharides, proteins, polyphenols, and humic substances (HSs). HSs are produced from microbial and abiotic degradation of different plants and animal wastes. HSs are commonly found in river and surface waters, soil, groundwater, and sediments. The typical levels of HSs are in the ranges of sub mg/L to mg/L.[93−97] NOM contains many organic compounds with different functional groups such as thiols, carbohydrates, carbonyls, and carboxylic acid.[98−102] Researchers have subclassified HSs into fulvic acids (FAs), humic acids (HAs), and humin. FAs are considered soluble components over a broad pH range and have low molecular weight constituents while HAs are insoluble at low pH and encompass high molecular weight constituents.[103]

Many studies have been carried out on the interactions of Cr(VI) with NOM.[104−107] In an earlier work, it was shown that the reduction rate of Cr(VI) with soil FA decreased with the increase in pH.[106,107] The empirical rates from the experimental data indicated that different functional groups of FA reduced Cr(VI). Another study using EPR measurements showed the formation of Cr(V) from the reduction of Cr(VI) by FA (see Figure S4).[108] Model compounds of FA like 1,2-dihydroxybenzene also reduced Cr(VI) to Cr(V) species. The reduction of Cr(VI) is highly dependent on the ionic strength, coexisting ions, and source of NOM.[104,109] The investigations of carboxylic acids (e.g., formic, malic, and malonic acids) as model compounds of HA have examined their capacity to reduce Cr(VI). The formation of reactive Cr(V) and Cr(IV) complexes in the Cr(VI)−carboxylic acid interaction has been explored.[110] The literature has clearly suggested the formation of Cr(V) and Cr(IV) complex species with functional groups of NOM like carbohydrates, carboxylates, hydroxamate, peptides, and proteins. Importantly, the formation of the reactive Cr(V) and Cr(IV) in the Cr(VI)−NOM system may react with organic contaminants coexisting in the aquatic environment to cause their degradation.

Oxidation of Organic Pollutants by the Cr(VI)−S(IV) System. In the past few years, the oxidation of emerging organic contaminants by the Cr(VI)−S(IV) system has been investigated.[35,111] The reduction of Cr(VI) by S(IV) ($HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$, $pK_a = 7.2$[111]) gives Cr(V) and Cr(IV) species and sulfite radical (eqs 24−26).

$$\mathrm{Cr(VI)} + HSO_3^- \rightarrow \mathrm{Cr(V)} + SO_3^{\bullet-} + H^+ \tag{24}$$

$$\mathrm{Cr(V)} + HSO_3^- \rightarrow \mathrm{Cr(IV)} + SO_3^{\bullet-} + H^+ \tag{25}$$

$$\mathrm{Cr(IV)} + HSO_3^- \rightarrow \mathrm{Cr(III)} + SO_3^{\bullet-} + H^+ \tag{26}$$

The generated $SO_3^{\bullet-}$ is converted to reactive sulfate radical ($SO_4^{\bullet-}$) through a series of reactions.[111] The degradation kinetics of a wide range of organic contaminants are presented in Figure S5a.[35] The properties of functional groups in the organic molecules determine their degradation kinetics. The formation of Cr(V)/Cr(IV) and $SO_4^{\bullet-}$ was particularly studied. The methyl phenyl sulfoxide (PMSO), which reacts selectively with Cr(V)/Cr(IV), could indirectly determine the formation of high-valent Cr intermediates in the Cr(VI)−S(IV) system. EPR measurements using ehba as a stabilizer of Cr(V)/Cr(IV) provided signals of Cr(V)/Cr(IV). The kinetic modeling of the reactions involved in the degradation of organic contaminants by the Cr(VI)−S(IV) system allowed the evaluation of the individual contribution of Cr(V) and $SO_4^{\bullet-}$ for the degradation of a wide range of contaminants (Figure S5b). The relative contributions of each reactive species varied with the properties of the target organic contaminants.

■ CONCLUSIONS

The environmental ubiquity of chromium, its industrial applications, and its varying toxicity based on the oxidation state give reasons for the continued interest in this widespread element. Toxicity studies under biological environments clearly suggest the role of high-valent Cr(V) and Cr(IV) species. Comparatively, the roles of such intermediate Cr species in environmental processes and the exploration of their potential uses in redox reactions of Cr are greatly lacking. This Perspective provides current fundamental knowledge for Cr(V) and Cr(IV) in aquatic environments to guide researchers to characterize them using spectroscopic methods like UV−visible and EPR techniques and subsequently perform the mechanistic evaluation of the redox system. Additionally, examples presented on various redox reactions of Cr will assist in the design of the experiments to evaluate the potential of Cr(V) and/or Cr(IV) species in the environmental systems of interest. Moreover, the formation of Cr(V) and Cr(IV) during the interaction of Cr(VI)/Cr(III) with functionalities of NOM needs further in-depth investigations to learn their roles in various natural and engineered processes, including the decontamination of organic contaminants. Lastly, a Cr(VI)-reductant system may effectively degrade many organic contaminants in water, which warrants greater attention in future studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00409.

> Chromium Pourbaix diagram, fractions of Cr(III) and Cr(V) species as a function of pH, and electron paramagnetic resonance (EPR) spectra of Cr(V) in aqueous solution (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Virender K. Sharma − *Program for the Environment and Sustainability, Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, College Station, Texas 77843, United States*; Email: vsharma@tamu.edu

Ching-Hua Huang − *School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*; Email: ching-hua.huang@ce.gatech.edu

Authors

Joshua Bell − *Department of Water Management and Hydrological Science, Texas A&M University, College Station, Texas 77843, United States; Program for the Environment and Sustainability, Department of Environmental and Occupational Health, School of Public*

Health, Texas A&M University, College Station, Texas 77843, United States

Xingmao Ma − *Department of Civil and Environmental Engineering, Texas A&M University, College Station, Texas 77843, United States;* orcid.org/0000-0003-4650-2455

Thomas J. McDonald − *Program for the Environment and Sustainability, Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, College Station, Texas 77843, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsestwater.1c00409

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

V.K.S. and C.-H.H. are thankful for the support by the National Science Foundation Grants CHE 2107967 and CHE 2108701. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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