Simultaneous Redox Conversion of Chromium(VI) and Arsenic(III) under Acidic Conditions

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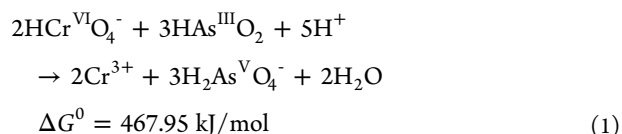
S *Supporting Information*

ABSTRACT: Arsenic and chromium are often abundant constituents of acid mine drainage (AMD) and are most harmful as arsenite (As(III)) and hexavalent (Cr(VI)). To simultaneously change their oxidation state from As(III) to As(V), and Cr(VI) to Cr(III), is a potentially effective and attractive strategy for environmental remediation. The coabundance of As(III) and Cr(VI) in natural environments indicates their negligible direct interaction. The addition of H_2O_2 enables and greatly accelerates the simultaneous oxidation of As(III) and reduction of Cr(VI). These reactions are further enhanced at acidic pH and higher concentrations of Cr(VI). However, the presence of ligands (i.e., oxalate, citrate, pyrophosphate) greatly retards the oxidation of As(III), even though it enhances the reduction of Cr(VI). To explain these results we propose a reaction mechanism where Cr(VI) is primarily reduced to Cr(III) by H_2O_2, via the intermediate tetraperoxochromate Cr(V). Cr(V) is then involved in the formation of •OH radicals. In the presence of ligands, the capacity of Cr(V) to form •OH radicals, which are primarily responsible for As(III) oxidation, is practically inhibited. Our findings demonstrate the feasibility for the coconversion of As(III) and Cr(VI) in AMD and real-world constraints to this strategy for environmental remediation.
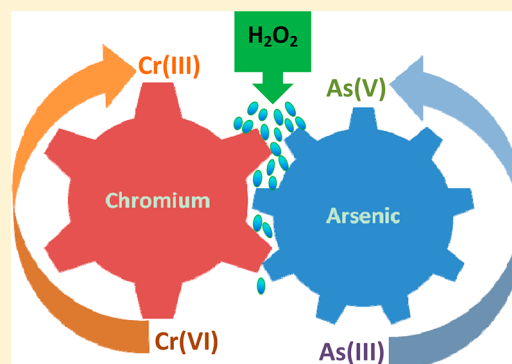
INTRODUCTION

Acidic waste rock from sulfide ore mining is a major environmental problem throughout the world. The oxidation and dissolution of sulfidic waste, particularly those with high contents of pyrite (FeS_2), are responsible for Acid Mine Drainage (AMD) with devastating environmental impacts.[1] Arsenic and chromium are priority pollutants associated with AMD, with arsenic concentrations ranging up to 100−500 mg/L in highly acidic AMD.[2−5] The mobility, toxicity, and environmental fate of arsenic and chromium in AMD are largely dependent on their redox speciation.[6,7] As(III) and Cr(VI) are far more mobile and soluble than As(V) and Cr(III). For example, Le Hécho found that As(III) was the only dissolved arsenic species in AMD, and 70−80% of chromium was present as Cr(VI).[8] To simultaneously oxidize As(III) to As(V) and reduce Cr(VI) to Cr(III) would greatly lower the environmental hazard of these constituents in AMD. The remediation of AMD typically involves neutralization.[9] As pH increases, the less toxic As(V) and Cr(III) can readily coprecipitate or adsorb to the iron oxides such as ferrihydrite and schwertmannite, that commonly occur with AMD.[10]

Until now, the coconversion of As(III) and Cr(VI) was only realized in the ice phase[11] or by *Bacillus Firmus*.[12] The direct abiotic oxidation of As(III) by Cr(VI) in dilute solutions is negligibly slow,[11] although the overall redox reaction between As(III) and Cr(VI) (eq 1) is thermodynamically favorable.[13]

$$2HCr^{VI}O_4^- + 3HAs^{III}O_2 + 5H^+$$
$$\rightarrow 2Cr^{3+} + 3H_2As^VO_4^- + 2H_2O$$
$$\Delta G^0 = 467.95 \text{ kJ/mol} \tag{1}$$

The simultaneous conversion of As(III) and Cr(VI) should be indirectly achievable with the involvement of a third redox-active substance that serves as *oxidant* (for As(III), $E^0(H_2As^VO_4^-/HAs^{III}O_2) = 0.4$ V vs NHE) and *reductant* (for Cr(VI), $E^0(HCr^{VI}O_4^-/Cr^{3+}) = 1.35$ V vs NHE).[14] Hydrogen peroxide (H_2O_2), an industrially available oxidant,[15] is a good candidate that from a thermodynamic perspective can react with both arsenite and chromate ($E^0(H_2O_2/H_2O) = 1.77$ V vs NHE; $E^0(O_2/H_2O_2) = 0.68$ V vs NHE).[16] The Cr(VI)−H_2O_2 reaction has been studied extensively.[17,18] The reduction rates of Cr(VI) by H_2O_2 are dependent on pH, ionic strength, temperature, and Cr(VI):H_2O_2 ratios and are kinetically controlled by the formation of Cr(V) intermediates. Of relevance to AMD, increasing acidity accelerates the reduction of Cr(VI) by H_2O_2.[19] Although thermodynamically feasible, the oxidation of arsenite by H_2O_2 ($H_3As^{III}O_3$−H_2O_2 reaction) is slow under acidic conditions.[20] However, As(III) can be

oxidized rapidly in acidic conditions by reaction with $^{\bullet}OH$ radicals ($k = 8.5 \times 10^9$ M^{-1} s^{-1}),[21] which are usually generated from metal-catalyzed H_2O_2 decomposition (e.g., Fenton reaction).

The recent discovery that $^{\bullet}OH$ radicals are formed via Haber-Weiss-type reactions between Cr(VI) and H_2O_2[22,23] potentially links the simultaneous redox conversions of Cr and As. When Cr(VI) is reduced by hydrogen peroxide under acidic conditions, hydroxyl radicals and other reactive oxygen species are generated which oxidize As(III). The net result is that As(III) can be oxidized while Cr(VI) is being reduced. To the best of our knowledge, these coupled As(III)/H_2O_2/Cr(VI) reactions have not been reported.

Here, we examine the applicability and possible reaction mechanism of simultaneous transformation of As(III) and Cr(VI) under acidic pH conditions. Different inorganic/organic ligands for Cr(V) are used to probe the reaction mechanisms, with consideration of the working assumptions that 1) $^{\bullet}OH$ is the dominant oxidant for As(III); 2) tetraperoxochromate(V) is the major precursor for $^{\bullet}OH$ radical formation; 3) these Cr(V) ligands compete with H_2O_2 and therefore counter the generation of tetraperoxochromate(V).

■ EXPERIMENTAL SECTION

Chemicals. Iron(II) sulfate ($FeSO_4 \cdot 7H_2O$, >99%), diphenylcarbazide (98%), copper(II) sulfate ($CuSO_4$, 98+%), and neocuproine (DMP, 99+%) were obtained from Acros Organics. Sodium arsenite ($NaAsO_2$) and ammonium molybdate tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 99%) were purchased from Sigma-Aldrich. Potassium chromate (K_2CrO_4), sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), tetrasodium pyrophosphate (PPP, $Na_4P_2O_7$), K_2HPO_4, KH_2PO_4, H_2O_2 (30%, unstabilized, Ajax Finechem Pty Ltd.), NaCl, Na_2SO_4, H_2SO_4, HCl, methanol (MeOH), ascorbic acid, oxalic acid (Ox), citric acid (Cit), chromium nitrate ($Cr(NO_3)_3$), methylene blue, and antimony potassium tartrate ($K(SbO)C_4H_4O_6 \cdot 0.5H_2O$) were of reagent grade and used as supplied. Milli-Q UltraPure water (18.3 MΩ cm) was used for all experiments.

Experimental Procedure. Specific aliquots of the stock solutions were added to the reaction vessel to achieve initial reactants concentrations. The addition of chromate was used to initiate an experiment. Unless otherwise noted, the typical reaction conditions were as follows: Cr(VI), 20 μM; As(III), 20 μM; H_2O_2, 2 mM. The pH of reaction solutions were adjusted to the designated value with 1 M HCl standard solution. There was negligible pH shift (<0.03 unit) within the experimental duration at pH_i 3.0 (see Figure S1). All reactions in a 35 mL plastic reactor were carried out in the dark at room temperature (20 ± 2 °C). Samples were taken periodically to measure As(V), Cr(VI), and Fe(II) concentration profiles over time. Prior to As(V) measurement, the withdrawn samples were immediately quenched by 1 mL of methanol. All experiments were performed in duplicate, and error bars in figures represent one standard deviation.

Methods and Analysis. The extent of As(III) oxidation was evaluated by measuring As(V) using the molybdate-based method developed by Dhar et al.[24] Briefly, for each 2 mL quenched aliquot (1 mL of sample + 1 mL of methanol), 0.3 mL of the 2% HCl acidifying solution and 0.3 mL of the coloring reagent were added orderly. The absorbance at 880 nm was determined within 10−15 min on a Varian Cary 50 UV−vis spectrophotometer. The concentration of Cr(VI) remaining in the solution was measured by a diphenylcarbazide

method.[25] The concentrated acids (H_3PO_4:H_2SO_4: H_2O = 1:1:2, v:v:v) should be premixed with diphenylcarbazide reagent to minimize the interference of acidification with Cr(VI) determination, since Cr(VI) can be reduced by As(III) at highly acidic pH (eq 1). The absorbance of sample solutions was detected at 540 nm after full color development (>5 min). H_2O_2 does not interfere with this color reaction. The concentration of H_2O_2 was determined by a Cu(II)/DMP method as previously described by Kosaka et al.[26] Briefly, 1 mL each of DMP, $CuSO_4$, phosphate buffer (pH = 7.0), and 200 μL sample aliquot was added to a 10 mL volumetric flask, which was then filled up to 10 mL with water. After mixing, the sample solution was transferred to 10 mm cell (Starna, Australia). The absorbance was measured at 454 nm. Several blanks and controls were carried out to testify the validity of these methods applied in this study and data shown in the Supporting Information (Tables S1−3). The concentrations of As(V), Cr(VI), and H_2O_2 were calculated by their own calibration curves (R^2 > 0.99), respectively.

■ RESULTS AND DISCUSSION

Simultaneous Oxidation of As(III) and Reduction of Cr(VI). As(III) and Cr(VI) were simultaneously monitored as a function of reaction time in acidic solutions (Figure 1). The addition of H_2O_2 was the only condition that initiated the simultaneous removal of Cr(VI) and accompanied production of As(V). There was also no evidence of As(III) oxidation in only the presence of H_2O_2, with or without the addition Cr(III) (Figure 1a). Cr(III) is unreactive toward H_2O_2 at pH <4.[23] As
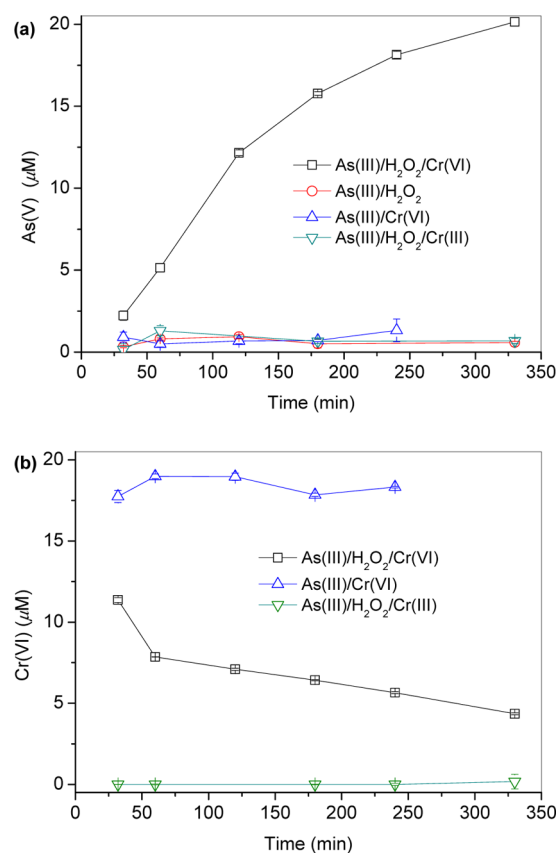
Figure 1. Simultaneous (a) oxidation of As(III) and (b) reduction of Cr(VI) under different conditions. As(III), 20 μM; Cr(VI) (or Cr(III)), 20 μM; H_2O_2, 2 mM; pH_i = 3.0.

such, it is expected Cr(III) does not contribute to formation of $^{\bullet}$OH radicals under the present experimental condition (pH = 3). Importantly, H_2O_2 is required for the reduction of Cr(VI) under acidic conditions, and this is a necessary precursory reaction for the simultaneous oxidation of As(III).

The coconversion of As(III)/Cr(VI) was further investigated at different pH (see Figure S2), reactants concentrations (Figures S3 and S4), and in the presence of 1.6 M CH_3OH as a radical scavenger (Figure S5). Decreasing acidity decelerated the reduction of Cr(VI) by H_2O_2. At all pH examined, the production of As(V) occurred in unison with consumption of Cr(VI) (Figure S2). According to the E^0-pH diagram of the Cr−H_2O system (Figure S6), Cr(VI) speciation at pH < 6.5 is predominantly $HCrO_4^-$. At pH > 6.5, the much weaker oxidant, CrO_4^{2-} is the dominant species (E ($Cr^{VI}O_4^{2-}/Cr_2O_3$) = 0.56 V vs NHE, pH 7.0). Therefore, at near neutral pH (pH > 6.5), the Cr(VI)-induced oxidative decomposition of H_2O_2 is ineffective as compared to its counterpart $HCrO_4^-$ at pH < 6.5 (E ($HCr^{VI}O_4^-/Cr^{3+}$) = 0.94 V vs NHE, pH 3.0). The effect of H_2O_2 and Cr(VI) concentration on As(III) oxidation was examined by varying their initial concentrations. Increasing the concentration of Cr(VI) from 10 μM to 40 μM greatly accelerated the oxidation of As(III) (Figure S3), whereas this was retarded at the higher contents of H_2O_2 (Figure S4). The efficiency of As(III) oxidation dynamically decreased, as accompanied with faster reduction of Cr(VI), when H_2O_2 concentration was increased from 2 mM to 3.5 mM. It is apparent that an excess of H_2O_2 is capable of quenching $^{\bullet}$OH radicals and, thus, slowing As(III) oxidation. In contrast, an excess of Cr(VI) greatly enhanced the oxidation of As(III) to As(V), further supporting the role of Cr(VI) as an activator of H_2O_2. The addition of methanol as a hydroxyl radical scavenger almost completely inhibited the oxidation of As(III) but had no effect on the reduction of Cr(VI) (Figure S5). This is additional evidence that $^{\bullet}$OH radicals are the primary agent responsible for As(III) oxidation.

Effect of Oxalate. Although the reaction of Cr(VI) and H_2O_2 has been investigated in a number of studies, there is little information on the roles of organic compounds, despite its ubiquity in natural systems and its environmental significance in aquatic redox chemistry. Oxalate (Ox), a diacid commonly present in natural environments, acts both as an electron donor and chelating agent for iron and a broad range of transition metals.[27] Figure 2 shows that addition of Ox diminished the oxidation of As(III) and yet accelerated the reduction of Cr(VI), especially when the concentration of Ox added was up to 25 μM. The control experiment (*data not shown*) indicated Ox alone cannot reduce Cr(VI) under the present experimental conditions. The enhanced reduction of Cr(VI), therefore, can only be considered a combined effect of Ox and H_2O_2.

In the presence of 50 μM Ox, only 10% of As(III) was converted to As(V). To test whether the reduced As(III) conversion is due to the radical scavenging effect of Ox, the same concentration of MeOH (50 μM), instead of Ox, was added under identical conditions. Unexpectedly, 90% of As(III) was oxidized in the presence of 50 μM MeOH. The inhibitory effect of Ox on As(III) oxidation cannot be ascribed to its outcompeting As(III) for $^{\bullet}$OH, since Ox is less reactive toward $^{\bullet}$OH radical ($k_{Ox/\bullet OH}$ = 7.7 × 10^6 M^{-1} s^{-1}) than MeOH ($k_{MeOH/\bullet OH}$ = 9.7 × 10^8 M^{-1} s^{-1}).[28]

Effect of Fe(II), Cu(II), and Other Ligands. In addition to organic matter, divalent metals are often abundant in AMD for sulfidic metals mining waste.[5] Fe(II) readily forms organic
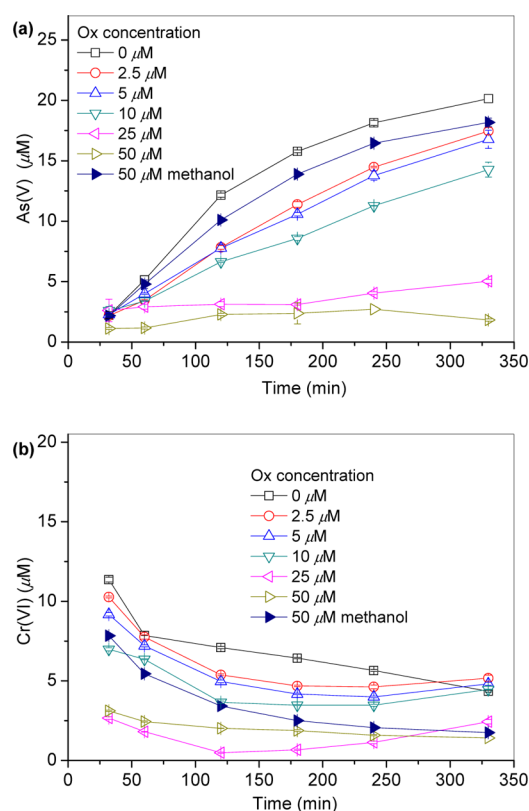

Figure 2. Comparison of oxalate (Ox) and methanol on simultaneous (a) oxidation of As(III) and (b) reduction of Cr(VI). As(III), 20 μM; Cr(VI), 20 μM; H_2O_2, 2 mM; pH_i = 3.0.

complexes. In comparison to inorganic Fe(II), Fe-organic complexes enhance Cr(VI) reduction and As(III) oxidation via the Fenton reaction, as compared with inorganic Fe(II) species. The addition of 20 μM Fe(II) significantly increased the rate of As(III) oxidation in a solution containing As(III)/Fe(II)/H_2O_2/Cr(VI) but did not affect the rate of Cr(VI) reduction (Figure 3). The addition of Fe(II) to As(III)/H_2O_2/Cr(VI)/Ox solution resulted in partial oxidation of As(III), probably due to the enhanced $^{\bullet}$OH formation resulting from reaction of Fe^{II}−Ox with H_2O_2,[29] despite the inhibitory effect of Ox on the As(III) oxidation.

The redox conversion of As(III) and Cr(VI) in the presence of Fe(II), Cu(II), and other inorganic/organic ligands are compared in Figure 4. Fe(II) apparently enhanced the oxidation kinetics of As(III) (Figure 3a) but did not affect the extent of As(III) oxidation and Cr(VI) reduction (Figure 4). Cu(II) inhibited the oxidation of As(III) and to a lesser degree the reduction of Cr(VI), probably due to an inhibitory effect produced by Cu(II) on the catalytic activity of Cr(VI) toward H_2O_2 decomposition.[30] Pyrophosphate (PPP), Ox, and Cit share a common capacity to form stable organic complexes with Cr(V).[31] Specifically it is the alpha-hydroxycarboxylate and 1,2-diol moieties in organic materials that can form stable Cr(V) complexes.[27,32] Sugden and Wetterhahn have described how a model Cr(V) complex undergoes ligand exchange bind in a bidentate chelate with PPP.[31] In the presence of these ligands, As(III) oxidation was largely inhibited. MeOH had no significant effect, due to its poor binding capacity for Cr(V), even though it is a good $^{\bullet}$OH radical scavenger.[28] Therefore, it is most likely that prevention of $^{\bullet}$OH radicals formation, rather
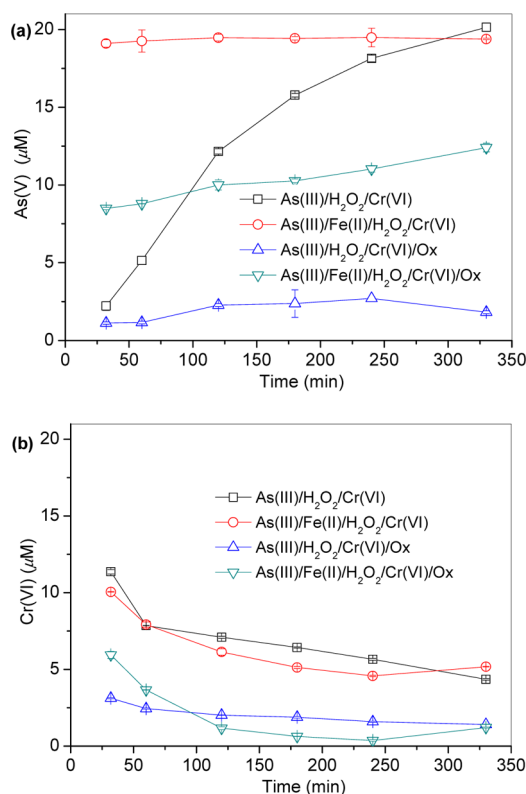
Figure 3. Effects of Fe(II) on simultaneous (a) oxidation of As(III) and (b) reduction of Cr(VI) under acidic conditions in the presence and absence of the organic ligand oxalate. As(III), 20 μM; Cr(VI), 20 μM; H$_2$O$_2$, 2 mM; Fe(II), 20 μM; Ox, 50 μM; pH$_i$ = 3.0.
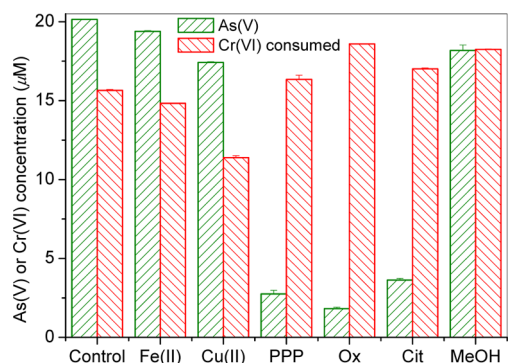
Figure 4. Effects of coexisting transition metal ions and organic/inorganic ligands on simultaneous oxidation of As(III) and reduction of Cr(VI) in Cr(VI)/H$_2$O$_2$/As(III) systems. As(III), 20 μM; Cr(VI), 20 μM; H$_2$O$_2$, 2 mM; Fe(II) or Cu(II), 20 μM; oxalate (Ox), citrate (Cit), methanol (MeOH), or pyrophosphate (PPP), 50 μM; pH$_i$ = 3.0; reaction time, 330 min.

than oxidative competition with As(III), is the main effect of ligands on As(III) oxidation.

The peroxochromate(V) complex, formed as an intermediate of Cr(VI) reduction, is potentially the most significant controlling factor for $^\bullet$OH.[17,18,33] UV−vis absorption spectra of the chromate solutions were used to investigate the possible roles of these ligands in the formation of peroxochromate(V) complex.[22] Figure 5 illustrates the changes in the absorption spectra of chromate containing different ligands before and after the addition of H$_2$O$_2$. The maximum absorption peak at 352 nm corresponds to the oxygen-to-chromium charge-
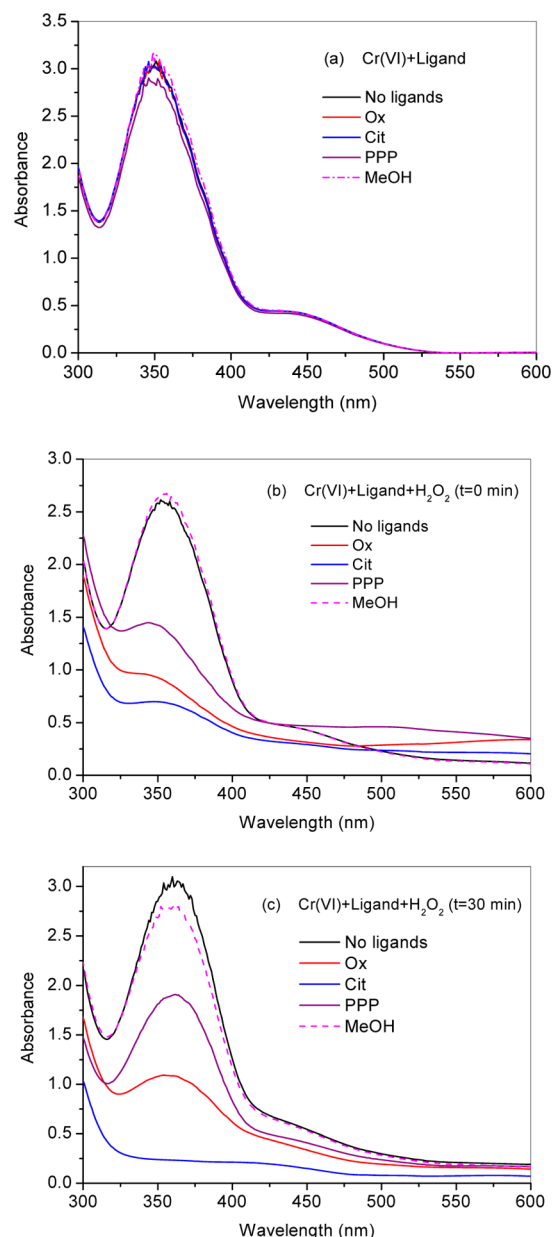
Figure 5. UV−visible absorption spectra of chromate/ligand solutions at pH$_i$ = 3.0 before (a) and after the addition of H$_2$O$_2$ at 0 min (immediately measured after H$_2$O$_2$ addition) (b) and 30 min (c). Cr(VI), 2 mM; H$_2$O$_2$, 20 mM; oxalate (Ox), citrate (Cit), methanol (MeOH), or pyrophosphate (PPP), 1 mM.

transfer band in $[Cr^{VI}O_4]^{2-}$.[17] Addition of the four ligands (see Figure 5a), did not alter the absorption spectra, indicating that under these experimental conditions the ligands formed neither strong complexes with Cr(VI) nor reduced Cr(VI) to Cr(III). Once H$_2$O$_2$ was added in the solution, the 352 nm peak declined and absorbance >500 nm increased (Figure 5b), with copious gas evolution. At pH 3.0, Cr(III) occurs in its aqueous ion form rather than solid oxides (Figure S7). Therefore, the absorption spectrum above 500 nm did not result from the interference of small solid particles. Based on this evidence and the published literature, the resulting spectrum (>500 nm) can be assigned to tetraperoxochromate-(V) anion complex (ε = 200 M^{-1} cm^{-1}).[18,22]

The spectrum of chromate solution containing MeOH essentially corresponds to that of the control experimental

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conditions. As for the other three ligands, the spectra differs in pattern and intensity, implying a diversity of peroxochromate-(V) has formed. The ligands used in our experiments can react to form peroxochromate(V) with mixed-ligands complex structures, such as peroxo−Cr(V)−ligand complex, analogous to the Cr(V)/glutathione/peroxo complex[34] and Cr(V)/ascorbate/peroxo complex.[35] For example, Zhang and Lay[35] tentatively assigned an ESR signal at g_{iso} = 1.9818 to a highly reactive Cr(V)/ascorbate/peroxo complex. This complex is known to decay very quickly, which is consistent with the time frame of our observations (Figure 5c).

The absorbance in the >500 nm spectrum for the chromate solution containing Ox, Cit, and PPP became less than both the control and Cr(VI)-MeOH solutions after 30 min. An increase in the absorbance at 352 nm for solutions of Cr(VI) alone and Cr(VI)/MeOH was observed, indicating a de novo formation of Cr(VI). This provides a plausible explanation for why Cr(VI) reduction slowed after 30 min in the reaction between Cr(VI) and H_2O_2, despite the consistent oxidation of As(III) (see Figure 1). The ligand-dependent formation and decay of peroxochromate(V) is consistent with the ligand-dependent oxidation of As(III), providing evidence that tetraperoxochromate(V) species is a predominant precursor of •OH, instead of mixed-ligand peroxochromate(V) complexes.

It is possible that excess ligands can also scavenge the •OH radicals themselves, inhibiting the As(III) oxidation. Also, absorbance spectra in Figure 5 shows that the ligand-stabilized Cr(V) complex decays within 30 min. However, the Cr(VI) absorption peak at 352 nm becomes much more prominent after the decay. This means that the ligand−Cr(V) complex is probably dissociated with regeneration of Cr(VI). In such a circumstance, the generation of •OH radical is still possible but gets scavenged by excess ligand before it can participate in further reactions. In this case, As(III) oxidation is not necessarily inhibited by loss of •OH radical generation but rather by competitive scavenging. The competitive scavenging effect of the selected ligands does warrant consideration, nevertheless, based on our experimental data this process should be negligible because 1) As(III) oxidation was greatly inhibited in the presence of 50 μM oxalate, while no obvious inhibitory effect was observed with 50 μM methanol (Figure 2a), although methanol is more reactive toward •OH radical ($k_{MeOH/•OH}$ = 9.7 × 10⁸ M⁻¹ s⁻¹) than oxalate ($k_{Ox/•OH}$ = 7.7 × 10⁶ M⁻¹ s⁻¹).[28] 2) Pyrophosphate does not react with •OH radical (no radical scavenging ability) but still impedes the oxidation of As(III) (Figure 4). Therefore, our proposed mechanism is convincingly supported by experimental results.

To test whether the presence of Cr(V) ligands decreases the •OH yield, •OH concentrations in the absence and presence of ligands were quantified by a simple methylene blue method.[36] As shown in Figure S8, Ox, Cit, and PPP significantly inhibited the decoloration of dye, indicating their abilities to block the generation of •OH radical by activation of H_2O_2 with chromate. This experiment provides additional solid evidence for our proposed mechanism, by demonstrating that Cr(V) ligands minimize the generation of •OH radicals in the Cr(VI)/H_2O_2 system and thereby inhibit the arsenite oxidation.
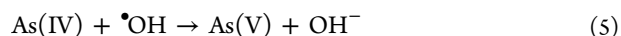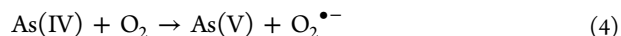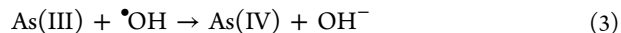
Mechanistic Discussion. The reaction between Cr(VI) and H_2O_2 and its mechanism is not well understood, even though it has been extensively studied.[17−19,33] Mechanistic investigations using ESR and spectrophotometric studies have confirmed that superoxide ($O_2^{•-}$), singlet oxygen ($^1O_2$), and

•OH should be generated from tetraperoxochromate(V) decomposition during the chromate reduction by H_2O_2.[37−40] The simultaneous removal of Cr(VI) and As(III) in acidic solution is achieved by addition of H_2O_2. This kind of coconversion should be initiated by a key reaction between Cr(VI) and H_2O_2, but its conversion effectiveness appears to be significantly affected by the Cr(V) ligands. Therefore, the resolution of the overall reaction pathways in As(III)/H_2O_2/Cr(VI) systems first requires a thorough consideration of interactions among Cr(VI)/H_2O_2/ligands. Here we contribute for discussion two reaction pathways in the absence and presence of organic ligands, taking Ox as an example.

No Ligands. The reaction between Cr(VI) and H_2O_2 generates tetraperoxochromate(V) (*a*) complexes (eq 2) via complicated rearrangement reactions and ligand substitution pathways.[19] Accumulation of the Cr(VI,V) intermediates at the early stage of reaction in the Cr(VI)/H_2O_2/As(III) system can be reflected by the increasing ΔAs(V)/-ΔCr(VI) with time (Figure S9). The tetraperoxochromate(V) (*a*) is metastable and ultimately produce •OH or quickly undergoes decomposition to Cr(III).[38,39]

$$2[Cr^{VI}O_4]^{2-} + 9H_2O_2$$
$$\rightarrow \rightarrow 2[Cr^V(O_2)_4]^{3-}(\boldsymbol{a}) + 2H^+ + 8H_2O + O_2 \qquad (2)$$
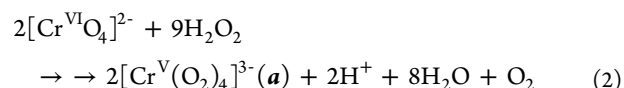
In this scenario, the •OH radical can be responsible for As(III) oxidation.[41] As(III) is oxidized by donating an electron to the •OH radical (eq 3). The resulting As(IV) is highly unstable and readily undergoes further oxidation with either dissolved oxygen (eq 4) or another •OH radical (eq 5), to generate relatively stable and less mobile As(V).

$$As(III) + {}^{•}OH \rightarrow As(IV) + OH^- \qquad (3)$$

$$As(IV) + O_2 \rightarrow As(V) + O_2^{•-} \qquad (4)$$

$$As(IV) + {}^{•}OH \rightarrow As(V) + OH^- \qquad (5)$$

Presence of Cr(V) Ligands. Ox is capable of binding to Cr(V) intermediate during photoreduction of Cr(VI).[27] Therefore, similar to glutathione and ascorbate, Ox is very likely to complex with monoperoxochromate(V) to then form intermediate *b* (eq 6). This assumption is reasonable because 1) UV−vis spectrum of Cr(VI)/H_2O_2/Ox is different from that of Cr(VI)/H_2O_2 (Figure 5b), verifying the involvement of Ox in *b*; and 2) no new absorption peak is observed in Cr(VI)/Ox alone (Figure 5a), indicating the contribution of H_2O_2 in *b*. The quantification of this intermediate is an interesting area for future investigations.

$$[(O_2)Cr^VO(OH_2)]^+ + L \rightarrow [L-Cr^V(O_2)O(OH_2)]^-(\boldsymbol{b})$$
$$(L = Ox, Cit, and PPP) \qquad (6)$$
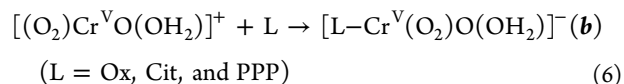
Considering the affinity of Ox to Cr(V), H_2O_2 may not replace a coordinated ligand in the intermediate *b*. Consequently, the precursor of •OH radical-tetraperoxochromate(V) was negligible. However, product *b* may quickly decompose to Cr(III), but not •OH radical (eq 7), as the absorbance above 500 nm disappeared rapidly as compared to *a* in Figure 5c.

$$6[L-Cr^V(O_2)O(OH_2)]^-(\boldsymbol{b}) + 8H^+$$
$$\rightarrow \rightarrow 6L^{2-} + 6Cr^{III} + 10H_2O + 7O_2 \qquad (7)$$
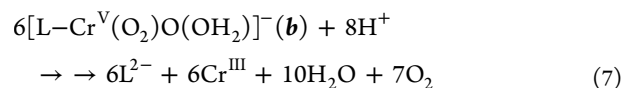
In this case, Cr(III) generation was very rapid, while As(III) oxidation was largely inhibited and H_2O_2 consumption should be minimal, which was in good agreement with experimental data. Figure S10 illustrates that the presence of oxalate ligand favors the rapid generation of Cr(III), whereas the total consumption of H_2O_2 after 330 min decreased with the concentration of Ox (Figure S11). In addition, the presence of PPP and Cit also reduced the consumption of H_2O_2 (Figure S12). However, in the case of MeOH, the decomposition of H_2O_2 was close to that in the control system, because it cannot form a mixed-ligand Cr(V) complex and thus did not change the reaction pathways between Cr(VI) and H_2O_2. In the presence of Fe(II), the $^\bullet OH$ radical may be produced from the well-known Fenton reaction at the expense of H_2O_2. Hence, as shown in Figure S12, the amounts of H_2O_2 decomposed nearly doubled that of the control system. Therefore, As(III) via these reaction steps can be partially oxidized even in the presence of Ox.

Implications. The most important recommendation from our study involves the sequencing of oxidation and neutralization intervention as part of the remediation of AMD.[9] Plumlee et al. reported arsenic ranging to 340 mg/L in 180 AMD samples from the U.S,[3] with an exceptional 850 mg/L in a localized acid seep at Iron Mountain, California.[4] In a similarly broad spatial study of 62 AMD water samples from 25 mines of the Iberian Pyrite Belt, Sánchez-España et al. found chromium on average was 118 μg/L (see details in the Supporting Information).[1] Chromium and arsenic species can be also found in many industrial wastewaters and wood preservative-contaminated soils.[11] Since acidic pH is favorable for efficient conversion of both Cr(VI) and As(III), the addition of H_2O_2 before a neutralization stage in AMD remediation/treatment processes is highly recommended. Our results demonstrate that H_2O_2 can be effective in enabling the redox conversion of As(III) and Cr(VI) in acidic solution. We have demonstrated the process viability by using real AMD water from an abandoned gold/silver mine in northeastern Australia (28°54′35.48″S, 152°22′31.69″E) (Figure S13).

To simultaneously reduce the environmental hazard of As and Cr in AMD is the desired outcome for environmental scientists and engineers. Although potentially feasible, the broad applicability of simultaneously removing these constituents will be confounded by a number of site specific attributes of AMD, such as Fe(II), Cu(II), organic matter, and pH.[5] The presence of Fe(II) may be beneficial for As(III) oxidation via Fenton-based reactions.[41] However, organic matter, particularly those involving Cr(V) ligands, can equally inhibit the formation of $^\bullet OH$ radicals via tetraperoxochromate(V) decomposition and therefore inhibit the oxidation of As(III). The reduction of Cr(VI) is less sensitive to these variables, and, therefore, its removal would appear more easily achievable under the broader spectrum of AMD conditions.

Our study has briefly considered the inhibitory effect of Cr(V) ligands. Further detailed investigations of Cr(V) ligands promise to greatly expand the current mechanistic understanding of Cr(VI)/H_2O_2 reactions, with direct implications for aquatic redox chemistry of chromium and biological toxicity of chromate.[27,42]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental evidence. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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