Oxidation of Cr(III) in tannery sludge to Cr(VI): Field observations and theoretical assessment

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Abstract

Sludge, soil and leachate samples collected from a chromium-contaminated tannery waste dumping site in Kanpur, India, were found to contain considerable amounts of Cr(VI), despite the fresh tannery sludge containing little or no Cr(VI). Literature reports suggested that dry Cr(III) precipitates could be converted to Cr(VI) when heated in the presence of oxygen. Also, Cr(III) in aqueous phase could be oxidized through interaction with manganese dioxide (MnO_2) surface to Cr(VI). Measurement of manganese in the sludge samples collected from the site showed concentrations up to 0.6 mg/g. Based on equilibrium calculations, it was determined that both dry phase Cr(III) oxidation by atmospheric oxygen and aqueous phase Cr(III) oxidation by MnO_2 surface were thermodynamically feasible. It was further suggested that in aqueous phase, manganese may act effectively as an electron transporter between Cr(III) and dissolved oxygen during Cr(III) oxidation, leading to regeneration of MnO_2 solid phase. Further, as dissolved Cr(III) is oxidized, dissolution of $Cr(OH_3)$ will take place to maintain the equilibrium between the dissolved and solid phases of Cr(III). In the pH range of 3–10, and at oxygen partial pressure (P_{O_2}) of 10^{-6} atm or higher, equilibrium conditions stipulate nearly complete conversion of Cr(III) to Cr(VI). At P_{O_2} of 10^{-20} atm or lower, very little Cr(VI) is expected to be present under equilibrium conditions. In the intermediate P_{O_2} regions, incomplete dissolution of the $Cr(OH_3)$ solid phase and only partial conversion of chromium from +3 to the +6 oxidation state is expected, especially at lower pH values.
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1. Introduction

Chromium is used in various industries such as metallurgical, refractory, chemical pigments, electroplating and tanning. The tanning industry is an especially large contributor of chromium pollution in India [1]. Sustenance of tanneries, particularly of the small units, is becoming increasingly difficult due to alarming levels of environmental pollution caused by various tanning operations and practices [2,3]. It is estimated [4] that in India alone, about 2000–3000 tonnes of chromium escape into environment annually from the tanning industries, with chromium concentration ranging between 2000 and 5000 mg/L in the aqueous effluent, compared to the recommended permissible limit of 2 mg/L. Of

late, installation of wastewater treatment plants in tanneries has considerably reduced the chromium content of such effluents [5,6]. However, one of the major emerging environmental problems of the tanning industry is the disposal of chromium-contaminated sludge that is produced as a by-product of wastewater treatment. Since scientific solid waste disposal practices are almost absent in India, large amount of chromium-contaminated sludge is regularly disposed in unlined and ill-maintained solid waste dumping grounds all over the country. Fate of chromium in such disposal sites is a cause of ongoing concern.

2. Field observations

Field studies were carried out in 2002–2003 in one such chromium-contaminated tannery sludge dumping ground in the city of Kanpur, India. The prevailing site conditions at

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this site called 'Rooma Usar' were as follows:

- The whole site was unlined and chromium-contaminated tannery sludge was dumped in heaps on the ground.
- During rainy season, orange/yellow colored leachate from the sludge heaps get collected in the nearby land depressions, and possibly percolates down and mixes with ground water. There is no leachate collection or treatment system at the site.
- Sludge heaps of various colors, viz., black, yellow, brown and gray, could be seen.
- In dry weather, some sludge heaps were found to be burning, with temperature as high as 250 °C inside the heaps. The cause of such burning could not be ascertained.

Based on the field observations, it was decided to collect grab samples of: (i) yellow surface water collected in the depressions, (ii) soil through which the sludge leachate has seeped and (iii) sludge portions with different colors. These samples were collected on July 11, 2002, by a team from IIT Kanpur. Samples were brought to the Environmental Engineering Laboratory of Civil Engineering Department at IIT Kanpur on the same day and analyses started immediately. Hexavalent chromium in the soil and sludge samples was extracted as per USEPA (Method No. 3060A) alkaline digestion procedure and measured colorimetrically by the Diphenyl Carbazide method [7]. Total chromium content in the sludge and soil samples was estimated after acid digestion [8] using atomic absorption spectrophotometer (Varian AA 20 BQ, Australia). Hexavalent and total chromium concentration were also measured in the surface water samples collected. Analysis of various representative sludge, soil and leachate samples collected from the site showed hexavalent chromium concentrations of up to 22.5 mg/g in aged sludge, up to 92 mg/L in leachate, up to 4.30 mg/g in soil and 2.50 mg/g in fresh sludge. Detailed report of the analyses results from the site is given elsewhere [9].

In summary, despite the fresh sludge dumped at the Rooma site having little or no hexavalent chromium, considerable concentrations of hexavalent chromium ware measured in sludge samples resident at the site for some length of time. Also, considerable hexavalent chromium contamination of the surrounding soil and surface water was observed. Hexavalent chromium is a 'Class A' human carcinogen and is considerably more mobile in soil and water systems than the most prevalent trivalent chromium species, i.e., chromium hydroxide precipitate found in natural conditions [10].

These analysis results were surprising, since no obvious source of hexavalent chromium contamination existed at the site. The sludge dumped at the site contained large amounts of trivalent chromium (up to 50 mg/g), but this form of chromium, being relatively insoluble in water under normal conditions, is considered to be quite non-toxic [10]. Also, trivalent chromium is considered to be relatively stable under natural conditions, and no obvious mechanism of con-

version of trivalent chromium to the hexavalent form in large quantities was immediately evident. Literature review was carried out to determine whether any natural chromium oxidation mechanisms existed, which could explain the high hexavalent chromium concentrations observed at the 'Rooma Usar' site. Based on this review, it was determined that dissolved trivalent chromium could be oxidized through interaction with manganese dioxide (MnO_2) surface to hexavalent chromium [11–14]. This reaction occurs at room temperature, in a time frame of days, and over a wide range of pH and Cr(III) concentrations. Measurement of manganese in the sludge samples collected from the site using atomic absorption spectrophotometer (Varian AA 20 BQ, Australia) after acid digestion [8] showed concentrations up to 0.6 mg/g. The source of this manganese could not be ascertained but it was concluded that the detected concentration was low enough to be attributed to natural sources. Additionally, since evidence of sludge burning was available at the 'Rooma Usar' site, it was hypothesized that trivalent chromium precipitate (Cr_2O_3) could also be thermally oxidized to hexavalent chromium (CrO_3) at high temperature prevalent inside the burning sludge piles.
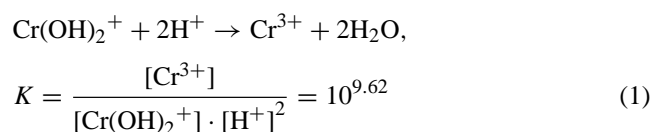
Based on the information gathered through field studies and literature review, it was apparent that a thorough scientific study was needed to assess the extent of chromium oxidation, and the rate of such transformation under various environmental conditions prevalent at the site. Thus, another objective of this study was to derive a theoretical assessment of the extent of chromium oxidation possible under various natural conditions. In addition, experimental evaluation of the rate of chromium oxidation under various environmental conditions prevalent at the site was also carried out, but these data will be discussed in a subsequent paper.
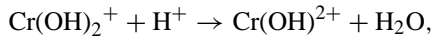
3. Theoretical analysis

Equilibrium calculations described in this section were carried out using the software MINEQL+ [15]. Various speciation equations and values of corresponding equilibrium constants were obtained from the database available with this software.
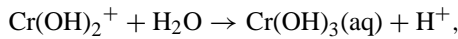
3.1. Chromium speciation

Chromium exists in natural systems primarily in +3 or +6 oxidation states. Major trivalent chromium species are Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3(aq)$, along with a solid phase of $Cr(OH)_3$(amorphous). Speciation of Cr(III) is governed by the equations (Eqs. (1)–(4)) given below:
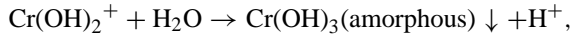
$$Cr(OH)_2^+ + 2H^+ \rightarrow Cr^{3+} + 2H_2O,$$

$$K = \frac{[Cr^{3+}]}{[Cr(OH)_2^+] \cdot [H^+]^2} = 10^{9.62} \tag{1}$$

$$Cr(OH)_2{}^+ + H^+ \rightarrow Cr(OH)^{2+} + H_2O,$$

$$K = \frac{[Cr(OH)^{2+}]}{[Cr(OH)_2{}^+] \cdot [H^+]} = 10^{5.62} \qquad (2)$$

$$Cr(OH)_2{}^+ + H_2O \rightarrow Cr(OH)_3(aq) + H^+,$$

$$K = \frac{[Cr(OH)_3(aq)] \cdot [H^+]}{[Cr(OH)_2{}^+]} = 10^{-7.13} \qquad (3)$$

$$Cr(OH)_2{}^+ + H_2O \rightarrow Cr(OH)_3(amorphous) \downarrow + H^+,$$
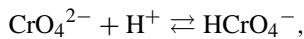
$$K = \frac{[H^+]}{[Cr(OH)_2{}^+]} = 10^{0.75} \qquad (4)$$

Major hexavalent chromium, Cr(VI), species are $CrO_4{}^{2-}$, $HCrO_4{}^-$ and $Cr_2O_7{}^{2-}$. Speciation of Cr(VI) is governed by the equations (Eqs. (5) and (6)) given below:

$$2CrO_4{}^{2-} + 2H^+ \rightleftarrows Cr_2O_7{}^{2-} + H_2O,$$
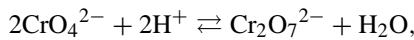
$$K = \frac{[Cr_2O_7{}^{2-}]}{[CrO_4{}^{2-}]^2 \cdot [H^+]^2} = 10^{14.557} \qquad (5)$$

$$CrO_4{}^{2-} + H^+ \rightleftarrows HCrO_4{}^-,$$
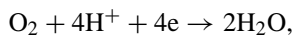
$$K = \frac{[HCrO_4{}^-]}{[CrO_4{}^{2-}] \cdot [H^+]} = 10^{6.509} \qquad (6)$$

Distribution of chromium between the +3 and +6 oxidation states is governed by the equation (Eq. (7)) given below:

$$Cr^{3+} + 4H_2O \rightleftarrows HCrO_4{}^- + 7H^+ + 3e,$$

$$K = \frac{[HCrO_4{}^-] \cdot [H^+]^7 \cdot \{e\}^3}{[Cr^{3+}]} = 10^{-70.487} \qquad (7)$$

Considering oxygen (Eq. (8)) to be the electron acceptor in the chromium oxidation reaction (Eq. (7)), i.e.,

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O,$$

$$K = \frac{1}{P_{O_2} \cdot [H^+]^4 \cdot \{e\}^4} = 10^{83.210} \qquad (8)$$

Eqs. (1)–(6) and the two half-reactions (Eqs. (7) and (8)) were used to construct chromium speciation diagrams as a function of pH and at various P_{O_2} values, where P_{O_2} is the oxygen partial pressure (in atmospheres) of the gaseous phase in equilibrium with the aqueous phase containing chromium. Such speciation diagrams corresponding to total chromium concentration of 0.2 M are shown in Fig. 1. These diagrams depict the scenario to be expected under equilibrium condition, with no consideration given to kinetic limitations in reaching the equilibrium condition. Trivalent chromium is present as the overwhelmingly predominant species over the pH range of 3–10 only in the system with very low P_{O_2} value (10^{-25} atm) shown in Fig. 1D. Here, trivalent chromium is mostly present as the precipitate, $Cr(OH)_3$ at high pH, while
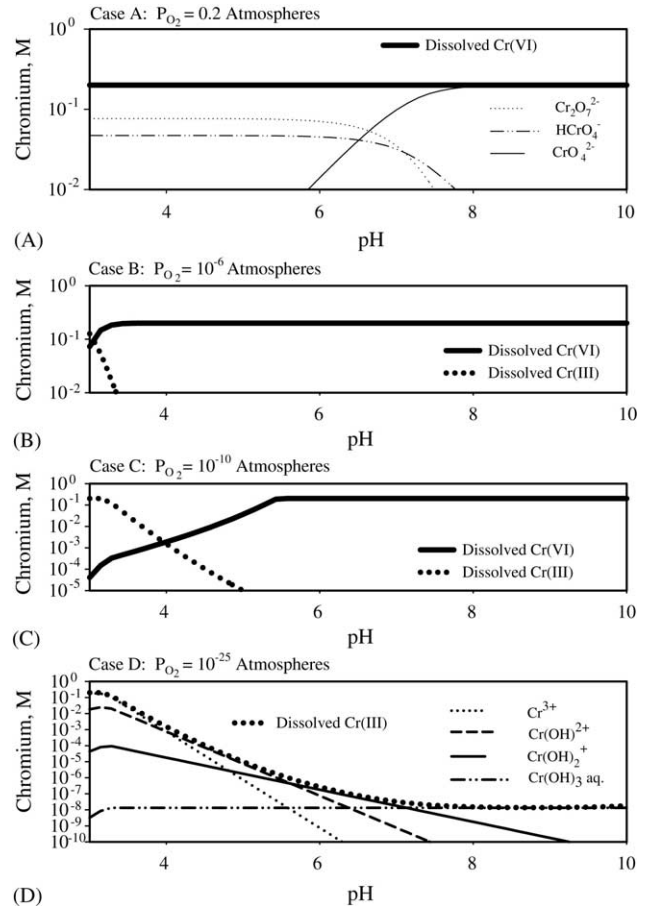

Fig. 1. Equilibrium partitioning of chromium between +3 and +6 oxidation states at various pH–P_{O_2} values in a system containing chromium and dissolved oxygen (total Chromium: 0.2 M). *Note*: P_{O_2} in atmospheres (1 atm = 101.325 kPa).

dissolved trivalent chromium species predominate at lower pH values. At P_{O_2} value of 10^{-10} atm (Fig. 1C), chromium in both +3 and +6 oxidation states are present together under equilibrium conditions, often in equilibrium with a solid phase of $Cr(OH)_3$(amorphous). Here, Cr(III) is the predominant species in the low pH conditions, while Cr(VI) is predominant in high pH conditions. Almost entire amount of chromium is present in the +6 oxidation state in systems with P_{O_2} of 10^{-6} and 0.21 atm (Fig. 1B and A, respectively), with $Cr_2O_7{}^{2-}$ and $HCrO_4{}^-$ being the predominant species at lower pH values and $CrO_4{}^{2-}$ being predominant at higher pH value.

Thus, from purely thermodynamic considerations, i.e., under equilibrium conditions, Cr(VI) is the predominant form of chromium expected in oxidizing of even moderately anoxic environments, while Cr(III) is expected to be the predominant chromium species only in severely reducing environments. However, in natural systems containing chromium, non-equilibrium conditions may prevail due to kinetic limitations on the chromium conversion between the oxidation states. In fact, aqueous phase oxidation of Cr(III) to Cr(VI) by dissolved oxygen is so kinetically unfavorable at ambient

temperatures that Cr(III) is considered to be practically stable [13,16] under conditions where oxygen is the only electron acceptor available for chromium oxidation.

3.2. Manganese speciation

Existence of manganese has been reported in +2 or +4 oxidation state in natural systems. Manganese may also be present in the +7 oxidation state in highly oxidizing environments, generally not encountered in natural systems. Speciation of manganese between the +2 and +4 oxidation states is governed by the equation (Eq. (9)) given below:

$$Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 \downarrow + 4H^+ + 2e,$$

$$K = \frac{[H^+]^4 \cdot \{e\}^2}{[Mn^{2+}]} = 10^{-41.539} \tag{9}$$

Oxidation of manganese from the +2 to the +4 oxidation state requires an electron acceptor, which is molecular oxygen in most natural systems (see Eq. (8)).
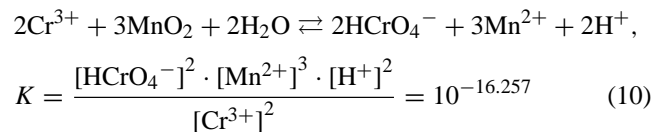
Manganese speciation diagrams constructed by combining the two half-reactions (Eqs. (9) and (8)), i.e., as a function of pH and P_{O_2}, using MINEQL+ are shown in Fig. 2. Under equilibrium conditions, $[Mn^{2+}]$ is present in appreciable concentrations only in systems with low P_{O_2} values, and especially under low pH conditions. At $P_{O_2} = 0.21$ atm, i.e., in aerobic systems which are at equilibrium with atmospheric oxygen, manganese is mainly present as MnO_2 precipitate, i.e., in the +4 oxidation state. If $[Mn^{2+}]$ is present in concentrations higher than stipulated by equilibrium under aerobic conditions, its conversion to MnO_2 through interaction with dissolved oxygen is fast and spontaneous, especially at
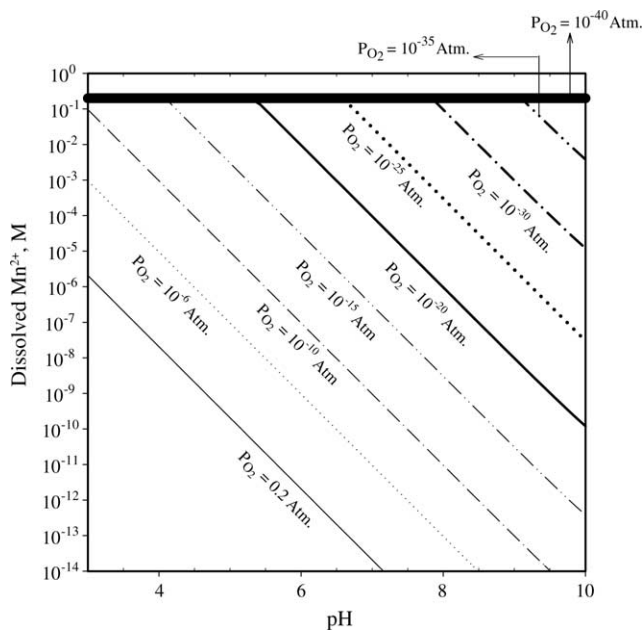

Fig. 2. Equilibrium partitioning of manganese between dissolved (Mn^{2+}) state and solid phase $(MnO_2$ at +4 oxidation state) at various pH–P_{O_2} values (total manganese: 0.2 M). *Note*: P_{O_2} in atmospheres (1 atm = 101.325 kPa).

higher pH values. In highly reducing environments, reductive dissolution of MnO_2 to Mn^{2+} is possible, but the process is kinetically limited in the absence of appropriate reducing agents to effect such transformation. Due to kinetic limitations on the manganese conversion between oxidation states, non-equilibrium conditions may exist under some circumstances. For example, in aerobic systems at low pH, Mn^{2+} concentrations considerably higher than those predicted by equilibrium calculations may be observed due to the slowness Mn^{2+} conversion process to MnO_2 under such conditions. Also, in highly anaerobic, but high pH systems, considerably lesser amount of Mn^{2+} than those predicted by equilibrium calculations may be present because the reductive dissolution of MnO_2 to Mn^{2+} may be kinetically limited under such conditions.

3.3. Interaction between manganese and chromium

Thermodynamic considerations stipulate that in systems open to the atmosphere $(P_{O_2} = 0.21$ atm), Cr(VI) and Mn(IV) species should be overwhelmingly predominant (see Figs. 1 and 2) over the entire pH range of 3–10. However, due to kinetic limitations on conversion of manganese and chromium across their respective oxidation states, non-equilibrium conditions prevail in natural systems containing chromium and manganese. In such systems, solid phases of both chromium and manganese, i.e., $Cr(OH)_3$ and MnO_2, along with dissolved species of Cr(III), Cr(VI) and Mn(II) may all be observed irrespective of the prevalent pH. Further, chromium conversion within its oxidation states, i.e., $HCrO_4^- + 7H^+ + 3e \rightleftharpoons Cr^{3+} + 4H_2O$, and manganese conversion within its oxidation states, i.e., $Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 \downarrow + 4H^+ + 2e$, will be ongoing simultaneously in such systems, until equilibrium conditions are attained.

To determine the thermodynamic feasibility of the chromium conversion and manganese conversion reactions occurring as an oxidation–reduction pair, the respective half-reactions are combined as below:

$$2Cr^{3+} + 3MnO_2 + 2H_2O \rightleftharpoons 2HCrO_4^- + 3Mn^{2+} + 2H^+,$$

$$K = \frac{[HCrO_4^-]^2 \cdot [Mn^{2+}]^3 \cdot [H^+]^2}{[Cr^{3+}]^2} = 10^{-16.257} \tag{10}$$

For the above reaction, the reaction quotient, Q, is defined as the product to reactant ratio of non-equilibrium concentrations. When the $\frac{Q}{K}$ ratio is less than 1, the reaction is spontaneous to the right.

Developing the concept further, based on Eq. (10), at equilibrium:

$$\frac{[HCrO_4^-]}{[Cr^{3+}]} = \left(\frac{10^{-16.257}}{[Mn^{+2}]^3 \cdot [H^+]^2}\right)^{1/2} \tag{11}$$

Thus, equilibrium $\frac{[HCrO_4^-]}{[Cr^{3+}]}$ ratio is a function of pH of the system and the concentration of $[Mn^{2+}]$ in the system. As-

suming that $[Mn^{2+}]$ in such a system is present in equilibrium with a MnO_2 solid phase, as per Eq. (9):

$$[Mn^{2+}] = \frac{[H^+]^4 \cdot \{e\}^2}{10^{-41.539}} \tag{12}$$

where

$$\{e\} = \left(\frac{10^{-83.210}}{P_{O_2} \cdot [H^+]^4} \right)^{1/4} \tag{13}$$

which is calculated from Eq. (8).

Thus, knowing pH and P_{O_2}, and hence, the equilibrium $\lfloor Mn^{2+} \rfloor$ concentration of a system, equilibrium $\frac{[HCrO_4^-]}{[Cr^{3+}]}$ ratio may be calculated. Consequently, equilibrium $\frac{Cr(VI)}{Cr(III)}$ ratio, where Cr(III) and Cr(VI) are the total dissolved trivalent and hexavalent concentrations in the system, can be also be calculated as follows. Based on Eqs. (1)–(3):

$$Cr(III) = [Cr^{3+}] \cdot \left\{ 1 + \frac{10^{5.62}}{[H^+]^2 \times 10^{9.62}} + \frac{1}{[H^+]^2 \times 10^{9.62}} \right.$$
$$\left. + \frac{10^{-7.13}}{[H^+]^3 \times 10^{9.62}} \right\} \tag{14}$$

and, based on Eqs. (5) and (6):

$$Cr(VI) = [HCrO_4^-] + \frac{[HCrO_4^-]}{[H^+] \times 10^{6.509}}$$
$$+ 2 \cdot \frac{10^{14.557} \cdot [HCrO_4^-]^2}{10^{13.18}} \tag{15}$$

therefore, $\dfrac{Cr(VI)}{Cr(III)}$

$$= \frac{[HCrO_4^-] + \frac{[HCrO_4^-]}{[H^+] \times 10^{6.509}} + 2 \cdot \frac{10^{14.577} \cdot [HCrO_4^-]^2}{10^{13.18}}}{[Cr^{3+}] \cdot \left\{ 1 + \frac{10^{5.62}}{[H^+] \times 10^{9.62}} + \frac{1}{[H^+]^2 \times 10^{9.62}} + \frac{10^{-7.13}}{[H^+]^3 \times 10^{9.62}} \right\}} \tag{16}$$

In cases where a chromium solid phase, i.e., $Cr(OH)_3$(amorphous) precipitate is present:

$$[Cr^{3+}] = \frac{[H^+]^3 \times 10^{9.62}}{10^{0.75}} \tag{17}$$

which is calculated from Eq. (4).

In such cases, $\frac{Cr(VI)}{Cr(III)}$ can be calculated explicitly using Eq. (16), when $\frac{[HCrO_4^-]}{[Cr^{3+}]}$ is known. If no chromium solid phase is present, but total dissolved chromium concentration in the system, i.e., Cr(III) + Cr(VI) is known, Eq. (16) may be solved iteratively to calculate the $\frac{Cr(VI)}{Cr(III)}$ ratio.

Equilibrium $\frac{Cr(VI)}{Cr(III)}$ ratio calculations based on the above protocol are presented in Fig. 3A and B for systems containing 0.2 and 0.001 M total manganese, respectively. The total chromium concentration in both systems was 0.2 M. These
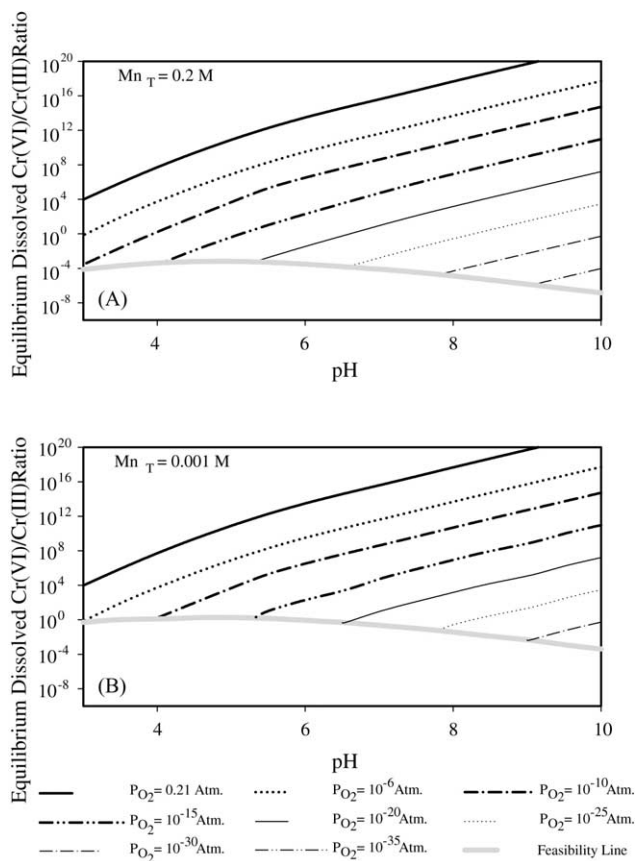

Fig. 3. Equilibrium partitioning of chromium between the +3 and +6 oxidation states through interaction with manganese at various pH–P_{O_2} values: equilibrium dissolved Cr(VI)/Cr(III) ratios (total chromium: 0.2 M). *Note*: P_{O_2} in atmospheres (1 atm = 101.325 kPa).

calculations assume that any dissolved $\lfloor Mn^{2+} \rfloor$ present is at an approximate equilibrium with MnO_2 solid phase, i.e., rate of $\lfloor Mn^{2+} \rfloor$ formation due to chromium oxidation as per Eq. (10) is much slower than the rate of re-conversion of $\lfloor Mn^{2+} \rfloor$ formed to MnO_2 solid phase through oxidation by dissolved oxygen (see Eq. (9)). Oxidation of chromium through interaction with manganese is only feasible when MnO_2 solid phase is present in the system, i.e., above the feasibility lines for existence of MnO_2 solid phase as shown in Fig. 3A and B. Results presented in Fig. 3A and B further suggest that for a system not at equilibrium with respect to chromium, i.e., if the dissolved $\frac{Cr(VI)}{Cr(III)}$ ratio in the system at a particular pH and P_{O_2} value is less than the equilibrium value shown in Fig. 3A and B, Eq. (10) will proceed to the right and dissolved Cr(III) will continue to be converted to Cr(VI) until equilibrium is attained. As Cr(III) is consumed, dissolution of $Cr(OH)_3$ solid phase, if present, will take place to maintain the equilibrium between the dissolved and solid phases of trivalent chromium. Within the feasibility region, total manganese concentration in the system will not be a factor in such conversion, since any $[Mn^{2+}]$ formed due to chromium oxidation will be re-converted to MnO_2 solid phase through oxidation by dissolved oxygen.

Comparison between Fig. 3A and B shows that the feasibility line is shifted upwards when total system manganese concentration is lower because the pH–P_{O_2} region where MnO_2 solid phase can exist becomes less extensive at lower manganese concentrations. However, as mentioned earlier, inside the region of feasibility, manganese concentration in the system will have no impact on the equilibrium $\frac{Cr(VI)}{Cr(III)}$ ratio, since the concentration of dissolved $\lfloor Mn^{2+} \rfloor$ in the system is assumed to be effectively constant at a particular pH–P_{O_2} condition, irrespective of amount of MnO_2 solid phase present in the system. Below the feasibility line, chromium oxidation–reduction is no longer controlled through interaction with manganese, but by other species, e.g., S^{2-}/SO_4^{2-}, which may be present in natural environments. Thus, if MnO_2 and Cr(III) is present under non-feasible pH–P_{O_2} conditions, i.e., where re-conversion of $\lfloor Mn^{2+} \rfloor$ to MnO_2 is not possible through interaction with dissolved oxygen, a one time conversion of MnO_2 to $\lfloor Mn^{2+} \rfloor$ and corresponding formation of a stoichiometric amount of Cr(VI) may occur, as per Eq. (10). After reduction of all MnO_2, the system may subsequently approach equilibrium with another species. Under such circumstances, Cr(VI) concentration in the system may increase initially, as Cr(III) is oxidized through interaction with MnO_2. However, a decline of Cr(VI) concentration may be noticed subsequently, as chromium is reduced when it approaches equilibrium with another species.

Equilibrium dissolved total chromium and Cr(VI) concentrations corresponding to Fig. 3A are presented in Fig. 4A and B, respectively. In the pH range of 3–10, if the prevalent P_{O_2} is 10^{-6} atm or higher, equilibrium conditions stipulate nearly complete conversion of Cr(III), whether initially in dissolved or precipitated state, to soluble Cr(VI). If P_{O_2} is 10^{-20} atm or lower, very little Cr(VI) is expected to be present under equilibrium conditions, irrespective of the system pH. In the intermediate P_{O_2} regions, incomplete dissolution of the Cr(OH)$_3$ solid phase and only partial conversion of chromium from +3 to the +6 oxidation state is expected, resulting in Cr(III) and Cr(VI) dissolved phases and Cr(OH)$_3$ solid phase co-existing under equilibrium conditions at low pH, while nearly complete oxidation of chromium to the hexavalent form is expected at higher pH values.

3.4. Thermal oxidation of chromium in the presence of oxygen

In solid state and under anhydrous condition, trivalent chromium exists as Cr_2O_3, while the corresponding hydrous form is $Cr(OH)_3$:

$$Cr_2O_3 + 3H_2O \rightarrow 2Cr(OH)_3 \qquad (18)$$
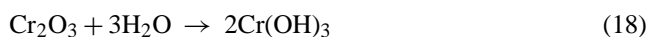
In solid state and under anhydrous condition, hexavalent chromium exists as CrO_3, while the corresponding hydrous form is H_2CrO_4:

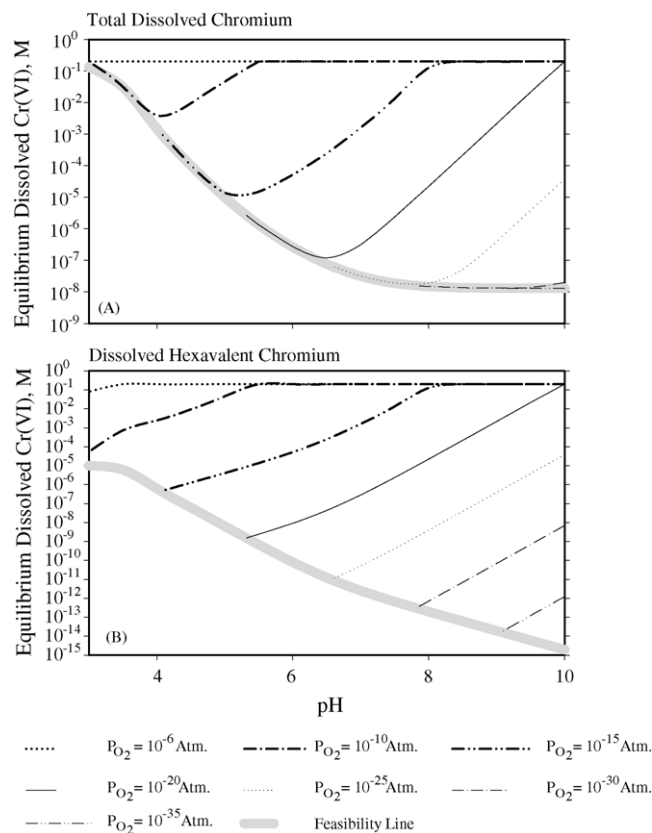$$CrO_3 + H_2O \rightarrow H_2CrO_4 \qquad (19)$$

Fig. 4. Equilibrium partitioning of chromium between the +3 and +6 oxidation states through interaction with manganese at various pH–P_{O_2} values: equilibrium dissolved Cr(VI) and Cr(III) values (total chromium: 0.2 M, total manganese: 0.2 M). *Note*: P_{O_2} in atmospheres (1 atm = 101.325 kPa).

Aerobic thermal oxidation of chromium involves interaction of the anhydrous forms as per the following equation:

$$2Cr_2O_3 + 3O_2 \rightarrow 4CrO_3, \qquad K = \frac{1}{(P_{O_2})^3} = 10^{79.42} \quad (20)$$
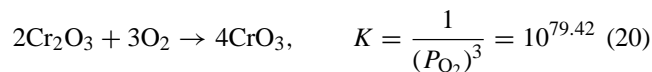
where P_{O_2} is the oxygen partial pressure in the gaseous phase in contact with the chromium solid phase. Hence, thermodynamic calculations stipulate that the above reaction will take place spontaneously as written provided the prevalent P_{O_2} is greater than $10^{-26.47}$ atm. However, such reaction is limited by slow kinetics at room temperature, where almost no conversion of Cr_2O_3 to CrO_3 is observed.

4. Discussion

Conclusions derived from the thermodynamic calculations presented above are in qualitative agreement with several experimental studies [11–13,17,18] which report chromium oxidation in certain natural conditions. Studies on the interaction between dissolved oxygen and Cr(III) revealed very little [13] or no [16] oxidation of Cr(III) even for experiments conducted at pH as great as 12.5 for 24 days. Therefore, the transformation of Cr(III) by dissolved oxygen

is not likely to be important mechanism for the oxidation of Cr(III). Manganese oxides, present in reactive forms almost universally in fresh, moist, non-acid field soil samples, may, however, serve as the electron link between the added Cr(III) and dissolved oxygen [11], and lead to Cr(III) oxidation. The oxidation of Cr(III) by soil manganese oxides is controlled by the surface characteristics of the oxides and by the availability of the Cr(III) to the surface [13]. The drying of the soil alters the manganese surface, decreasing its ability to oxidize Cr(III). The oxidation of Cr(III) to Cr(VI) is also limited by the concentration of water-soluble chromium, pH, initial available surface area and ionic strength [14]. A large portion of Cr(III) in soil will not be oxidized to Cr(VI), even in the presence of manganese oxide and favorable pH conditions, due to unavailability of mobile Cr(III) [12].

A study on fractionation and oxidation of chromium in tannery waste amended soils [19] indicated that the initial increase in Cr(VI) during the first five months after the tannery waste application was followed by a decrease of water-soluble chromium and Cr(VI) concentrations. The theoretical basis for such observations, which involve competitive oxidation–reduction of chromium, has also been presented in this paper. In a study [20] concerning the impact of waste chromium of tannery agglomerates in east Kolkata, India, on the surrounding wetland ecosystem, observed Cr(VI) concentration in sludge/sediment/soil samples varied form 0.00765 to 24.319 g/kg, though fresh tannery effluent and sludge disposed at the site contained almost no Cr(VI). Another study [21] reported chromium speciation in receiving estuary of Colligan, Ireland, as a result of discharge of tannery effluent. Hexavalent chromium was undetected in the estuary during field sampling. However, in laboratory studies, some sediment from the surrounding areas were found to oxidize Cr(III) present in the tannery effluent.

5. Conclusions

Field observations by Verma [9] regarding Cr(VI) pollution at a tannery sludge dumping site in Kanpur, India, is the main motivation behind this study. The theoretical assessment of chromium oxidation potential presented in this study is also in general agreement with the experimental observations and field studies by other researchers, which report chromium oxidation in the natural environment under certain conditions. Specifically, this study has led to the following conclusions:

- Sludge and soil samples collected from a chromium-contaminated tannery sludge dumping site in Kanpur, India, contained considerable amounts of Cr(VI). Also, surface runoff collected in land depressions near this site was reported to contain high concentrations of Cr(VI). It was observed that the sludge dumped at this site was often burned, and the leachate from burnt sludge also contained high concentrations of Cr(VI).

- Thermodynamic calculations suggest that chromium oxidation is possible through interaction of dissolved Cr(III) species with MnO_2 solid phase.
- It is also suggested that manganese may act effectively as an electron transporter between Cr(III) and dissolved oxygen during Cr(III) oxidation. In the process, MnO_2 solid phase is reduced to $[Mn^{2+}]$ during chromium oxidation. However, this $[Mn^{2+}]$ may subsequently be re-converted through interaction with oxygen to MnO_2 solid phase, and participate in further chromium oxidation. Thus, the total manganese concentration in such systems may not have substantial effect on the extent of Cr(III) oxidation.
- Also, presence of Cr(III) as precipitate may not hamper its eventual oxidation, since as dissolved Cr(III) is oxidized, dissolution of $Cr(OH)_3$ solid phase, if present, will take place to maintain the equilibrium between the dissolved and solid phases of trivalent chromium. This dissolution process will continue until equilibrium conditions are attained.
- In the pH range of 3–10, if the prevalent P_{O_2} is 10^{-6} atm or higher, equilibrium conditions stipulate nearly complete conversion of Cr(III), whether initially in dissolved or precipitated state, to soluble Cr(VI).
- If P_{O_2} is 10^{-20} atm or lower, very little Cr(VI) is expected to be present under equilibrium conditions, irrespective of the system pH.
- In the intermediate P_{O_2} regions, incomplete dissolution of the $Cr(OH)_3$ solid phase and only partial conversion of chromium from +3 to the +6 oxidation state is expected, resulting in Cr(III) and Cr(VI) dissolved phases and $Cr(OH)_3$ solid phase co-existing under equilibrium conditions, especially at low pH.
- Conversion of Cr_2O_3 to CrO_3 under aerobic conditions was shown to be thermodynamically feasible under natural conditions, though kinetic limitations on such conversion will probably limit substantial conversion at room temperature.

It is again emphasized that the conclusions above pertain to the expected system state under equilibrium conditions, with no consideration given to rate at which such equilibrium is attained. Thus, in natural systems, complete oxidation of Cr(III) to Cr(VI) may never be observed in environmentally significant time frames.

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