Extent of oxidation of Cr(III) to Cr(VI) under various conditions pertaining to natural environment

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Abstract

Calculations show that oxidation of chromium oxide (Cr_2O_3) by oxygen and oxidation of chromium hydroxide ($Cr(OH)_3$) by manganese dioxide (MnO_2) are thermodynamically feasible in both aerobic and mildly anoxic environments. Experiments were carried out to determine the rate and extent of chromium oxidation under various conditions, i.e., when Cr_2O_3 was heated in the presence of oxygen, when $Cr(OH)_3$ and MnO_2 mixtures were suspended in aerobic or anoxic aqueous media at various pH values, when $Cr(OH)_3$ and MnO_2 mixtures interacted in moist aerobic conditions and when chromium assumed to be $Cr(OH)_3$ and manganese assumed to be MnO_2 interacted in the presence of competing electron donors/acceptors, as is the case in chromium-contaminated sludge. Results indicate that trivalent chromium in Cr_2O_3 could be readily converted to hexavalent chromium at a temperature range of 200–300 °C, with conversion rates of up to 50% in 12 h. In aqueous media, $Cr(OH)_3$ was slowly converted to dissolved Cr(VI) in the presence of MnO_2, both in aerobic and anoxic conditions, with conversion rates of up to 1% in 60 days. In moist aerobic conditions and in the presence of MnO_2, $Cr(OH)_3$ slowly converted to hexavalent chromium, with up to 0.05% conversion observed in 90 days. Chromium oxidation also occurred in sludge samples, especially under aerobic conditions. However, such transformation was found to be transitory, with the Cr(VI) formed being ultimately reduced back to Cr(III) due to the presence of various reducing agents in the sludge. Nevertheless since up to 17% conversion of Cr(III) to Cr(VI) occurred in sludge under aerobic conditions by 30 days, there is real danger under field conditions of spreading Cr(VI) pollution due to possible intervening rainfall, runoff and percolation.
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1. Introduction

Empirical observations suggest that in natural environments and especially at pH > 6, trivalent chromium, Cr(III) is present predominantly as $Cr(OH)_3$ (s). It is also known that in pH range of 3–10 and $P_{O_2} > 10^{-6}$ atm, equilibrium conditions stipulate nearly complete conversion of Cr(III), whether in precipitated or dissolved form, to hexavalent chromium, Cr(VI) [1]. Therefore, presence of Cr(III) in an apparently stable form in natural environments may be attributed to the exceedingly slow rate of conversion of Cr(III) to Cr(VI), even under thermodynamically favorable conditions.

In general, mobility and hence, distribution of chromium in environmental media is controlled by oxidation–reduction, precipitation–dissolution and sorption–de-sorption [2], with Cr(VI) being more mobile than Cr(III). In neutral or basic conditions, chromium predominantly occurs as $Cr(OH)_3$(s) and hence, has limited mobility. According to Rai et al. [3] (Cr, Fe)$(OH)_3$ (s), another common precipitate of Cr(III) in natural soil, has even lower solubility than $Cr(OH)_3$. The Cr(III) solubility and hence, mobility in soil may be enhanced to some extent by complexing of Cr(III) with root exudates, such as organic acids, which react strongly with metal ions in the soil aqueous phases [4].

Under certain conditions, Cr(III) may be oxidized to Cr(VI) in natural environments, a process that can lead to serious environmental consequence [5–9]. Only two constituents

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in the environment are known to oxidize Cr(III) to Cr(VI), oxygen and manganese dioxide [8]. Interaction between dissolved oxygen and Cr(III) revealed very little [10] or no [8] oxidation of Cr(III), even for experiments conducted at pH 12.5 for 24 days. Bartlett and James [6,11] first reported that added Cr(III) oxidized readily to the hexavalent form under conditions prevalent in many field soils. The key to the oxidation appeared to be the presence in the soil of oxidized manganese, which served as the electron acceptor in the reaction. Oxidation of Cr(III) is not possible in highly reducing soils and in soils developed on natural mineral deposits due to the prevalent anaerobic conditions [9]. Palmer and Wittbrodt [12] monitored Cr(VI) concentrations in batch tests using three different geologic media containing both Cr(III) and manganese oxides from a mine site and observed large increases in Cr(VI) concentration.

Eary and Rai [8] reported that the oxidation of Cr(III) by soil manganese oxides is controlled by the surface characteristics of the oxides and by the availability of dissolved Cr(III) to the manganese oxide surface. Drying of the soil alters the manganese oxide surface, decreasing its ability to oxidize Cr(III). The oxidation of Cr(III) to Cr(VI) is also limited by the concentration of dissolved Cr(III), pH, initial available surface area and ionic strength [8,13]. A large portion of chromium in soil will not be oxidized to Cr(VI), even in the presence of manganese oxide and favorable pH conditions, due to unavailability of dissolved Cr(III) [5]. In studies involving addition of dissolved Cr(III) to suspensions containing various concentrations of β-MnO$_2$ maintained at various pH values in both aerobic and anoxic conditions, Eary and Rai [8] concluded that the oxidation of aqueous Cr(III) occurs through direct interaction with the β-MnO$_2$ surface. The reaction stoichiometry was, however, complicated by the parallel rate of intrinsic β-MnO$_2$(s) dissolution under acidic conditions and possible formation of intermediate manganese oxide reaction products, such as MnOOH(s). The rate of Cr(III) oxidation was probably limited by slow de-sorption of anionic Cr(VI) formed due to Cr(III) oxidation from the β-MnO$_2$ surface in acidic solutions and by Cr(OH)$_3$ precipitation in neutral-to-alkaline solutions. Fendorf and Zasoski [13] reported that chromium oxidation by δ-MnO$_2$ occurred over a range of pH values and Cr(III) concentrations. The reaction stoichiometry, i.e., ratio of Mn(II):Cr(VI) formed appeared to be 1.5:1. Rate of formation of Cr(VI) became slower as pH and Cr(III) concentration in the aqueous matrix increased. It appeared that Cr(III) concentration, pH and the amount of initial available δ-MnO$_2$ surface were the parameters controlling the degree of oxidation. Cr(III) adsorption on δ-MnO$_2$ surface also caused the electrophoretic mobility of δ-MnO$_2$ particles to become less negative and induced a surface charge reversal under certain conditions.

Milacic and Stupar [14] studied long-term fractionation and oxidation of chromium in tannery waste-amended soils. The initial increase in Cr(VI) during the first 5 months after the tannery waste application was followed by a decrease of water soluble chromium and Cr(VI) concentrations. A part of the soluble chromium was either washed out with rainwater or became bound in the organic and sparingly soluble fractions. At maximum, Cr(VI) concentrations up to 1.1% of chromium from the tannery waste was found in clay, 0.45% in sand and 0.03% in peat soils. Based on this study, it was concluded that larger amounts of tannery waste could be disposed of on peat soil without hazardous effects of toxic chromate on the terrestrial environment, while in clayey and sandy soils rich in manganese(IV) oxides, this application should be carefully controlled. Walsh and O'Halloran [15] reported chromium speciation in a receiving estuary of river 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 sediments from the surrounding areas were found to oxidize Cr(III) present in the tannery effluent. This suggested that oxidation of Cr(III) is likely to be transient in fine grain sediments, due to large anoxic zone and associated organic material, Fe(II) and H$_2$S below the surface capable of rapidly reducing the Cr(VI) produced [10,16]. Chattopadhayay et al. [17] reported the impact of waste chromium of tannery agglomerates in east Calcutta (India) on the surrounding wetland ecosystem. Total chromium concentration in water and sediment samples was in the range 0.025–1.70 mg/L and 0.125–59.86 g/kg, respectively. An astonishing fact was the presence of Cr(VI) in sediment/soil samples of the area in concentrations, which varied form 0.00765–24.319 g/kg, though no Cr(VI) was present in fresh tannery effluent or sludge samples.

Since no solubility-controlling precipitates exist for Cr(VI), it is relatively mobile in natural environments and hence, might cause widespread pollution. Aqueous concentrations of Cr(VI) under acidic to slightly alkaline conditions will primarily be controlled by adsorption/de-sorption reactions. Hexavalent chromium can adsorb on mineral solids that have exposed inorganic hydroxyl groups on their surfaces, including iron and aluminum oxides, kaolinite and to a lesser extent, montmorillonite [18]. On all of these solids, Cr(VI) adsorption increases with decreasing pH [18]. In the environment, iron oxides are the predominant adsorbents of chromate in acidic to neutral oxidized soils and groundwater, with occasional significant contributions from adsorbents carrying Al–OH groups [19].

Based on the literature review presented above, it appears that oxidation of Cr(III) to Cr(VI) in natural environment is quite common and may potentially occur whenever manganese oxides are present along with Cr(III) in aerobic conditions. Considering the relatively greater mobility of Cr(VI), this may lead to widespread Cr(VI) pollution. Field observations by Verma [20] regarding Cr(VI) pollution in Kanpur, India is, however, the main motivation behind the work described in this study. Verma [20] made astonishing observations during field sampling at the "Rooma Usar", a piece of land used for dumping of Cr(III)-contaminated sludge produced from a 36MLD up-flow anaerobic sludge blanket (UASB)-based plant treating a mixture of tannery and

domestic wastewater containing high Cr(III) concentrations. Though the fresh sludge dumped at the site contained little or no Cr(VI), the surface runoff collected in nearby land depressions, as well as aged sludge and soil samples from the surrounding area contained high concentrations of Cr(VI). Sludge dumped at this site was often burnt, with temperatures as high as 250 °C measured inside sludge heaps during such burning. The leachate from burnt sludge-ash also contained high concentrations of Cr(VI). Based on the observations at the above site, it was concluded that oxidation of Cr(III) to Cr(VI) at this and other similar sites may occur in several ways: (1) when Cr_2O_3 is burned in the presence of oxygen; (2) when $Cr(OH)_3$ and MnO_2 are submerged or suspended together in aerobic or anoxic aqueous media at various pH values; (3) when $Cr(OH)_3$ and MnO_2 interact in moist aerobic conditions; (4) when chromium assumed to be $Cr(OH)_3$ and manganese assumed to be MnO_2 interact in the presence of competing electron donors/acceptors, as is the case in chromium-contaminated sludge, also containing manganese dioxide. This study involves evaluation of chromium oxidation in these varied conditions.

2. Experimental procedures and analytical methods

2.1. Experimental procedures

Four types of experiments were carried out during this study: (1) dry Cr_2O_3 was maintained in aerobic environment at high temperature; (2) $Cr(OH)_3$ and β-MnO_2 mixtures were added to de-ionized water and the suspension was maintained under completely mixed conditions either in aerobic or anoxic environments; (3) $Cr(OH)_3$ and β-MnO_2 were mixed together and maintained in moist aerobic environment; (4) sludge samples from effluent treatment plants, containing both chromium and manganese, were maintained in moist aerobic or anoxic environments. In all cases, the extent of conversion of trivalent chromium to the hexavalent form was monitored with time.

2.1.1. Type I experiments

A typical experiment of this type involved taking 250 mg of dried and powdered Cr_2O_3 in a petri-dish and keeping it in an oven (Mahendra Scientific Instrument Company, India) set at a pre-determined temperature of either 200 or 300 °C. Sufficient numbers of identical petri-dishes were used, such that two petri-dishes could be extracted after every 2 h for sample analysis. Normal duration of an experiment of this type was 12–14 h. After the required experimental duration, the perti-dishes were taken out from the oven and cooled in a desiccator. The cooled sample was suspended in 50 mL of de-ionized water and vortex-mixed (SPINIX, India) for 2 min. The sample was then filtered using a 0.45 μm filter and analyzed for Cr(VI). The results were expressed as mg Cr(VI) produced per gram of chromium added initially.

2.1.2. Type II experiments

Experiments of this type were carried out in either aerobic or anoxic environments. Aerobic experiments were carried out in 500 mL bottles with a sample port at the bottom and maintained open to the atmosphere; 500 mL of de-ionized water was placed in the bottle and the pH adjusted to the desired values (see below) with 1 mM HCl solution. Desired amounts (see below) of chromium hydroxide and β-MnO_2 were added to the bottle. The contents were maintained in completely mixed condition through stirring for the experimental duration of 30–80 days. Samples were collected periodically from the sampling port, filtered using a 0.45 μm filter and analyzed for pH, Cr(VI) and dissolved manganese. Six experiments of this type were carried out. Trivalent chromium added in all cases was 0.8 g/L, i.e., 2.15 g chromium hydroxide per bottle. The initial pH in three of these experiments was 5, with β-MnO_2 surface area to reactor volume ratio being 67, 45 and 22 m^2/L, i.e., 6, 4 and 2 g, respectively, of β-MnO_2 was added per bottle. The fourth and fifth experiments were carried out at initial pH values of 3 and 7, respectively, with β-MnO_2 surface area to reactor volume ratio in these cases being 67 m^2/L. The sixth experiment was carried out at initial pH of 5, with a much lower β-MnO_2 surface area to reactor volume ratio of 0.945 m^2/L. Anoxic experiments were carried out in 2 L bottles with a sample port at the bottom and maintained under a nitrogen atmosphere; 1.5 L of de-ionized water was placed in each bottle and de-aerated by bubbling nitrogen. Then, pH of the water was adjusted to the desired value with 1 mM HCl solution, followed by additions of chromium hydroxide and β-MnO_2. The contents were maintained in a completely mixed condition through stirring for the experimental duration of 60 days in a nitrogen atmosphere. Samples were collected periodically from the sampling port, filtered using a 0.45 μm filter and analyzed for hexavalent chromium and dissolved manganese. Three experiments of this type were carried out. Trivalent chromium added in all cases was 0.8 g/L, i.e., 6.45 g chromium hydroxide per bottle. The initial pH in these experiments was 3, 5 and 7, respectively. The β-MnO_2 surface area to reactor volume ratio in all cases was 67 m^2/L, i.e., 18 g β-MnO_2 was added per bottle.

2.1.3. Type III experiments

For experiments of this type, dry chromium hydroxide and manganese dioxide [β-MnO_2] were mixed together in a petri-dish and placed in a closed container under moist aerobic conditions. Duration of an experiment of this type was 90 days. Samples were taken from the petri-dish (in triplicate) after every 30 days for sample analysis. To determine Cr(VI), the sample was suspended in 50 mL of de-ionized water and vortex-mixed (SPHINX, India) for 2 min. The suspension was then filtered through a 0.45 μm filter and hexavalent chromium concentration measured in the filtered sample. The solids retained on the filter were dried for determination of dry weight, based on which the total chromium concentration in the sample could be determined. Cr(VI) concentration was reported as mg Cr(VI)/g total chromium. Four experiments

Table 1
Cr(OH)$_3$ and β-MnO$_2$ proportions used in solid phase experiments

Experiment	Cr(OH)$_3$ (g)	β-MnO$_2$ (g)	Mn:Cr ratio (g/g)
1	6.45	4.500	2.371
2	6.45	3.000	1.581
3	6.45	0.030	0.016
4	6.45	0.015	0.008

of this type were carried out. The chromium hydroxide and β-MnO$_2$ amounts used in these four experiments are given in Table 1.

2.1.4. Type IV experiments

Experiments of this type were carried out using chromium-contaminated sludge obtained from two sources. For aerobic experiments, 2.5 g of dried sludge was moistened with a little water and kept in a petri-dish. Nine petri-dishes were prepared for each type of sludge. These were placed in a closed box containing water to maintain moist conditions. Three petri-dishes of each type were taken out after 30, 60 and 68 days for determination of Cr(VI) concentration after alkaline digestion. For anoxic experiments, 2.5 g of dried sludge was moistened with a little water and kept in sealed bottles with rubber caps. Nine bottles were prepared for each type of sludge. After preparation, two needles were pierced through the bottle cap and the bottles de-aerated by purging the headspace with nitrogen applied through one of the needles. The needle holes on the cap were sealed after purging and removal of the needles. Three bottles of each type were sampled after 30, 60 and 68 days for determination of Cr(VI) concentration after alkaline digestion.

2.2. Analytical methods

pH was measured using a combination pH electrode (Toshniwal CL-51, India) connected to a digital pH meter (Toshniwal CL-54, India). Hexavalent chromium was measured colorimetrically by diphenyl carbazide method (Method No.: 3500-Cr[D] [21]). A spectrophotometer (Spectronic, 20 D$^+$, India) with Borosil glass absorbance cells having 1 cm path length were used for this purpose. Total chromium and manganese was measured using atomic absorption spectrometry (Varian AA 20 BQ, Australia). β-MnO$_2$ specific surface area was measured using the BET method (Instument Make, Coluter SA3100, USA). Carbon and nitrogen content of sludge samples were measured using a CHNOS analyzer (Instrument Make, Leeman Laboratories, CE440, USA). Volatile fraction of sludge was measured as per the relevant method (Method No.: 2540[G] [21]). A muffle furnace (Mahendra Scientific Instruments, India) was used for this purpose. All measurements described above were performed in triplicate and the average values reported. Variation between replicate measurements was within 10% in all cases. Alkaline digestion method (SW-846–3060A [22]) was used for extraction of hexavalent chromium in solid samples.

Table 2
Sludge characteristics

Parameter	Activated sludge-based plant at Unnao	UASB-based plant at Kanpur
Total chromium (mg/g of dry sludge)	29.7	14.1
Total manganese (mg/g of dry sludge)	0.13	0.23
Hexavalent chromium (mg/g of dry sludge)	0.58	0.16
Total carbon (%)	14.9	18.8
Total nitrogen (%)	2.0	2.5
Volatile suspended solids (%)	33.6	37.2

'Aqua-regia' digestion method [23] was used to extract total chromium and manganese in solid samples.

2.3. Experimental materials

The manganese dioxide (MnO$_2$) used in the experiments was predominantly β-MnO$_2$ (80% purity), whose specific surface area was determined to be 5.671 m^2/g. Reagent-grade chromium oxide (Cr$_2$O$_3$) was powdered in mortar and pestle to roughly uniform size and then dried in a desiccator before use.

For preparation of chromium hydroxide precipitate, chromium chloride was dissolved in de-ionized water. The pH of this solution was then raised to 9.0 by adding 0.5 M NaOH to facilitate chromium hydroxide precipitate formation. The precipitate was separated from solution by centrifugation and then dried in desiccators at 25 °C. Dried precipitate was finally powdered and stored in desiccators. Chromium content of the dried precipitate was determined by atomic absorption spectrometry after 'aqua-regia' digestion to be 0.186 g/g of precipitate.

Chromium-contaminated sludge samples were collected from the sludge drying beds of two plants in the Kanpur region treating tannery effluent. One of the effluent treatment plants was up-flow anaerobic sludge blanket (UASB)-based and situated in Jajmau, Kanpur. The other was activated sludge-based and situated in Unnao near Kanpur. Sludge samples collected were powdered, dried in desiccators and stored in airtight containers. Total chromium and total manganese content of sludge samples were determined by atomic absorption spectrometry after 'aqua-regia' digestion. Hexavalent chromium content of sludge samples was also determined after alkaline digestion. Measured chromium concentrations in sludge samples are presented in Table 2.

3. Results and discussion

3.1. Type I experiments: thermal oxidation of trivalent chromium in aerobic conditions

Experiments involving the heating of samples of Cr$_2$O$_3$ to 200 and 300 °C under aerobic conditions show that significant
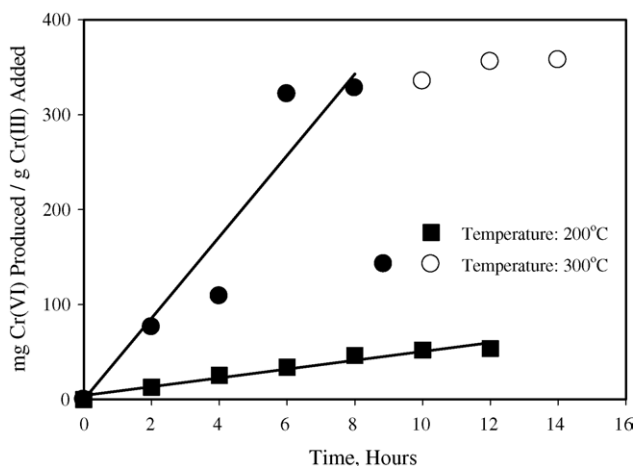
Fig. 1. Chromium oxidation by oxygen in air at elevated temperatures: Cr(VI) produced over 14 h.

amounts of Cr(VI) production at these elevated temperatures occurred (Fig. 1). Also, the initial rates of conversion increased with increase in temperature. However, almost no conversion to Cr(VI) was observed when similar samples were maintained at room temperature. As discussed in Apte et al. [1], aerobic thermal oxidation of chromium involves interaction of the respective anhydrous forms as per the following equation:

$$2Cr_2O_3 + 3O_2 \rightarrow 4CrO_3, \qquad K = \frac{1}{(P_{O_2})^3} = 10^{79.42} \quad (1)$$

Hence, the above reaction will take place spontaneously as written provided the prevalent P_{O_2} is greater than $10^{-26.47}$ atm. However, experimental results indicate that the above reaction is limited by slow kinetics at room temperature. At higher temperatures, the rate of formation of Cr(VI) is dependent on the specific Cr_2O_3 surface area (A_{sp}) available, the prevalent P_{O_2} and the intrinsic kinetic rate of conversion (k) of Cr(III) to Cr(VI),

$$\frac{d\,[Cr(VI)]}{dt} = k(P_{O_2})A_{sp} \quad (2)$$

At constant P_{O_2} and at low rates of conversion, i.e., when $A_{sp} \approx$ constant, the rate of formation of Cr(VI) was pseudo-zero-order. In such cases, a plot of Cr(VI) produced versus time is a straight line with slope "k", the intrinsic rate of conversion as shown in Fig. 1 for experiments conducted at 200 °C. For experiments conducted at 300 °C, the conversion is pseudo-zero-order initially and with a higher "k". However, the conversion rate declined precipitously at higher reaction times, which may be attributed to the decline in A_{sp} due to the formation of a surface coating of Cr(VI) on Cr_2O_3 particles.

Support for such conversions under natural conditions were obtained from field studies carried out in 2002–2003 in a chromium-contaminated tannery sludge-dumping ground in the city of Kanpur, India [1]. Visual inspection of the site showed the presence of sludge heaps of various colors, viz., black, yellow, brown and gray, along with evidence of

Table 3
Hexavalent chromium concentration observed before and after burning of chromium-contaminated tannery sludge samples obtained from a tannery sludge-dumping site

| Sample description	Hexavalent chromium (mg/g dry weight)		Total chromium (mg/g dry weight)
	Oven-dried[a]	Burnt[b]	
Brown sludge	21.4	25.4	35.7
Yellow-green sludge	22.5	24.8	30.3
Black sludge	2.5	5.8	39.7
Soil contaminated with leachate	4.3	5.9	9.8

[a] At 100 °C for 24 h.
[b] At 550 °C for 30 min.

sludge burning. Grab samples of sludge portions of different colors and soil through which sludge leachate had seeped were collected. Total and hexavalent chromium content in these samples were determined after drying and hexavalent chromium content was also measured after burning (Table 3). Results presented in Table 3 indicated that burning of sludge in all cases resulted in the increase in hexavalent chromium content. In summary, despite the fresh tannery sludge having a maximum hexavalent chromium content of 0.5 mg/g dry weight (see Table 2), considerably higher concentrations of hexavalent chromium was present in sludge resident at the dumping site for some length of time. Subsequent burning of these samples in the laboratory resulted in further enhancement in hexavalent chromium concentrations in all cases.

3.2. Type II experiments: aqueous phase interaction between Cr(OH)₃ and β-MnO₂

As proposed by Bartlett and James [6] and subsequently verified by Fendorf and Zasoski [13], interaction between Cr(OH)₃ and MnO₂ occurs in aqueous media due the interaction between dissolved Cr(III) present in the aqueous media in equilibrium with the Cr(OH)₃ solid phase and the MnO₂ surface. The consequent reaction may be described as,

$$2Cr^{3+} + 3MnO_2 + 2H_2O \rightleftarrows 2HCrO_4^- + 3Mn^{2+} + 2H^+ \quad (3)$$
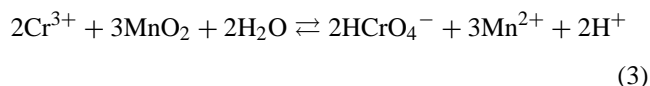
3.2.1. Aerobic conditions

These experiments were carried out to ascertain the effect of initial pH on rate and extent of conversion of Cr(III) to Cr(VI) in aqueous suspensions containing Cr(OH)₃ and β-MnO₂ and maintained under aerobic conditions. Results (see Fig. 2A) indicate that dissolved Cr(VI) concentration in all three reactors, initially at pH values of 3, 5 and 7, respectively, increased from zero at the start of the experiment to 15 mg/L or more after 60 days. The pH in the reactor initially at pH 7 remained nearly constant over the experimental period, while the pH in reactors, initially at pH 3 and 5, increased to approximately 7 fairly rapidly and then became nearly constant (Fig. 2B). Three additional reactors were also operated under similar conditions as above, except that no β-
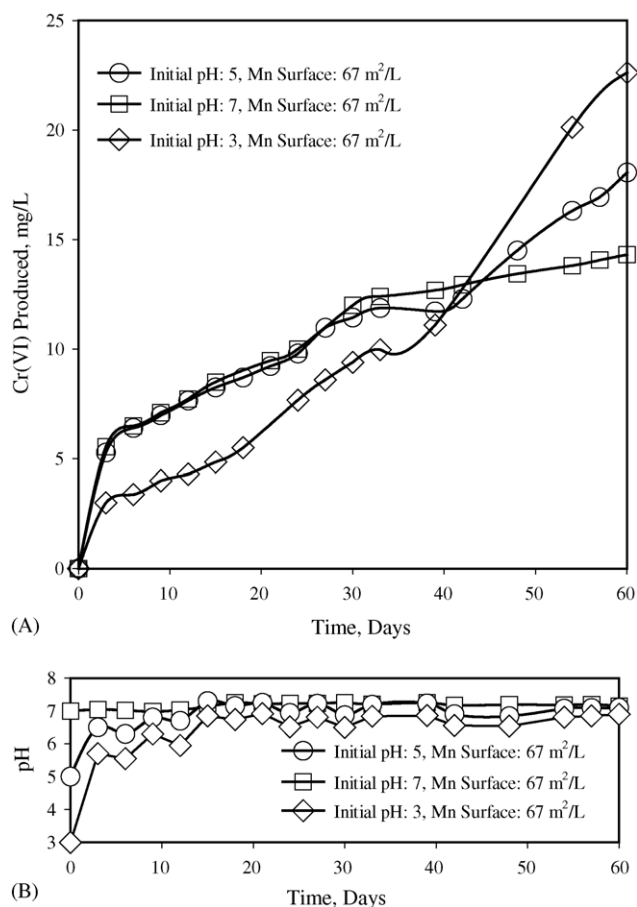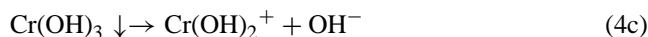
Fig. 2. Aqueous phase chromium oxidation in aerobic conditions. Effect of initial pH on Cr(VI) produced over 60 days (chromium added, 0.80 g/L; reactor volume, 500 mL): (A) hexavalent chromium, Cr(VI) produced and (B) reactor pH changes.

MnO$_2$ was added. Detectable concentrations of Cr(VI) was not observed in these reactors in 60 days, though pH increase pattern similar to the corresponding reactors with added β-MnO$_2$ was noticed in all reactors. This proved that oxidation of Cr(III) to Cr(VI) is occurring with the aid of the β-MnO$_2$ surface.

In all reactors containing β-MnO$_2$, Cr(VI) production continued even after 20 days of reaction time, i.e., after pH became nearly constant (at pH 7) in all reactors. In fact, increase in dissolved Cr(VI) beyond 20 days in all reactors are far greater than the expected dissolved Cr(III) concentrations in such systems at equilibrium with chromium solid phase at pH 7. This is only possible, if Cr(III) oxidation and dissolution occur as coupled reactions. Under such circumstances, as dissolved Cr(III) in equilibrium with the Cr(OH)$_3$ solid phase is oxidized to Cr(VI), the resultant decline in dissolved Cr(III) concentration upsets the equilibrium between the Cr(III) solid and dissolved phases and triggers dissolution of the chromium solid phase. Equilibrium calculations presented in Apte et al. [1] suggests that under aerobic conditions and at pH 7, progressive dissolution of chromium and oxidation of dissolved Cr(III) to Cr(VI) will continue until nearly

all Cr(III) is converted to Cr(VI). This will occur irrespective of the amount of β-MnO$_2$ surface area provided, since any Mn^{2+} formed during chromium oxidation (see Eq. (3)) will be converted back to MnO$_2$ at pH 7 and in the presence of dissolved oxygen, i.e., under aerobic conditions.

The increase in pH of reactors initially at pH 3 and 5 to approximately 7 (Fig. 2B) can be explained by considering the partial dissolution of Cr(OH)$_3$ when added to water,

$$Cr(OH)_3 \downarrow \rightarrow Cr^{3+} + 3OH^- \tag{4a}$$

$$Cr(OH)_3 \downarrow \rightarrow Cr(OH)^{2+} + 2OH^- \tag{4b}$$

$$Cr(OH)_3 \downarrow \rightarrow Cr(OH)_2^+ + OH^- \tag{4c}$$

$$Cr(OH)_3 \downarrow \rightarrow Cr(OH)_3 (aq) \tag{4d}$$

Reactions (4a)–(4c) are predominant in reactors initially at pH 3 and 5. Since these reactions release [OH$^-$] ions, pH of the solution increases. In the case of the reactor initially at pH 7, initial dissolution of the chromium solid phase is primarily through reaction (4d), which does not increase the solution pH. Subsequently, a buffering action is established between chromium dissolution (Eqs. (4a)–(4d)) and chromium oxidation reactions (Eq. (3)), through which any release of [H$^+$] ions due to chromium oxidation is neutralized by the release of [OH$^-$] ions due to chromium dissolution. This explains the nearly constant pH in all reactors once the pH has reached approximately 7 even though chromium oxidation was still taking place.

The actual reaction mechanism for chromium oxidation in the above experiments would probably involve adsorption of dissolved Cr(III) ions on the β-MnO$_2$ surface, oxidation of adsorbed Cr(III) to Cr(VI) and subsequent release of dissolved Cr(VI) and Mn(II) ions to the aqueous phase. Based on this supposition, it is probable that surface charge of the MnO$_2$ surface will have a major role to play in determining the rate of the above reaction [13]. The 'point of zero charge' for β-MnO$_2$ surfaces is at pH 7.3 [24]. Therefore, in the pH range of 3–7, β-MnO$_2$ will present a positively charged surface for the initial reaction step (more positively charged at lower pH), i.e., adsorption of positively charged dissolved Cr(III) species on the β-MnO$_2$ surface. Under such circumstances, Cr(III) adsorption on β-MnO$_2$ surface will be less at low pH and will increase with increase in pH. Also, adsorption of Cr(VI) species formed due to chromium oxidation was found to increase greatly as pH was lowered from 8.0 to 2.0 [8]. Thus, any Cr(VI) formed due to Cr(III) oxidation at low pH may not desorb readily, thus, lowering the measured dissolved Cr(VI) concentration at low pH. Considered in totality, the above mechanisms suggest that rate of production of dissolved Cr(VI) species will be lower at low pH values when β-MnO$_2$ surface is used for chromium oxidation. The results presented in Fig. 2A show that initial rate of Cr(VI) production is indeed lower for the reactor in which the initial pH was 3. It is also observed that this pH effect is nullified at higher reactor pH values, as electrostatic barriers to Cr(III) adsorption to and Cr(VI) de-sorption from

the β-MnO$_2$ surface are lowered. Thus, there is no measurable difference between Cr(VI) oxidation rates in reactors with initial pH of 5 and 7 and even for the reactor initially at pH 3, though the initial rate of Cr(VI) formation is observed to be low, as the pH increases, the rate of Cr(VI) formation increases to be comparable with that in the other two reactors. It is also observed that in reactors with initial pH of 3 and 5, there is an increase in the rate of Cr(VI) formation at times beyond 40 days. This increase may be explained by postulating that Cr(VI) which remained adsorbed on the β-MnO$_2$ surface after formation at lower pH values was being desorbed as the β-MnO$_2$ surface becomes less positive with increase in pH.

Though Mn^{2+} is expected to form as a result of chromium oxidation in all the above experiments [8], measurement of dissolved manganese indicated concentrations below detection levels in all cases. This seems to suggest that the manganese, which evolved due to chromium oxidation, was oxidized back to MnO$_2$ under the prevailing aerobic conditions. Equilibrium calculations presented by Apte et al. [1] also suggests that under aerobic conditions and at neutral pH values, manganese is present predominantly in the +4 oxidation state, i.e., as MnO$_2$(s).

3.2.2. Effect of β-MnO$_2$ surface area

Two additional experiments, where 6.45 g of Cr(OH)$_3$ (amorphous) and 4 and 2 g, respectively, of β-MnO$_2$ were added to 500 mL of un-buffered de-ionized water maintained at pH 5, were conducted to determine the effect of β-MnO$_2$ surface area on Cr(III) oxidation. The β-MnO$_2$ surface area provided was 45 and 22 m^2/L, respectively, in these two cases. Other experimental conditions remained the same as in previous cases. Evolution of Cr(VI) during these two experiments were monitored for a period of 30 days. These results are presented in Fig. 3. For the purpose of comparison, data (presented earlier in Fig. 2A) obtained under similar conditions, but corresponding to β-MnO$_2$ surface area of 67 m^2/L is also presented in the same figure. The results indicate no decline in Cr(VI) formation rate with decrease in β-MnO$_2$ surface area under the experimental conditions investigated. These results are surprising, since according to Eary and Rai [8], in a reactor maintained at pH 4 and containing 5 mg/L initial dissolved Cr(III) concentration, increasing of β-MnO$_2$ surface area by an order of magnitude, i.e., from 7.1 to 71.3 m^2/L resulted in an increase in Cr(VI) concentration, as measured after 300 h of reaction time, from 0.1 to 1 mg/L. These apparently anomalous results may be reconciled by noting that the dissolved Cr(III) concentration interacting with the β-MnO$_2$ surface in our case is controlled by the Cr(III) solubility in the pH range of 5–7, which is an order of magnitude or more lower than the Cr(III) solubility at pH 4. This low dissolved Cr(III) concentration in our case ensured that the β-MnO$_2$ surface provided is in excess and hence, the effect of surface area on Cr(VI) formation is not apparent. To further elucidate this point, another experiment, similar to others in all respects, but with very low β-MnO$_2$ surface area (0.945 m^2/L), was
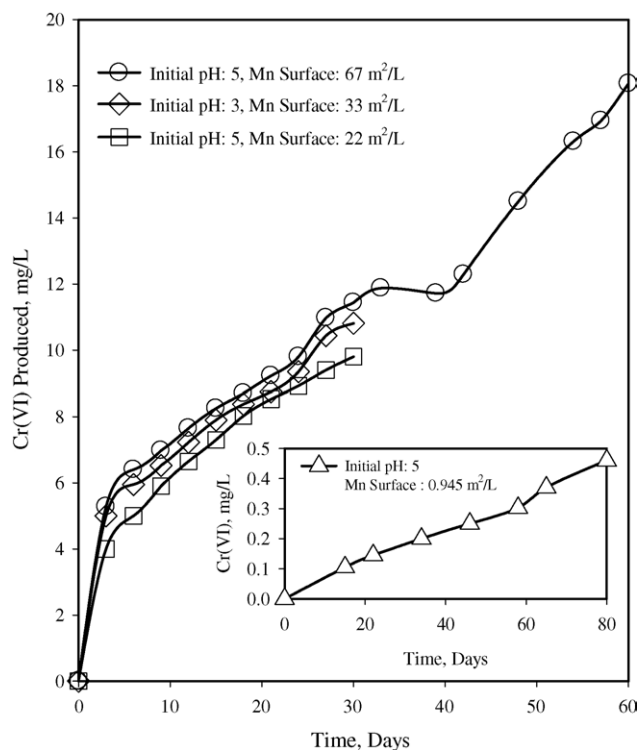

Fig. 3. Aqueous phase chromium oxidation in aerobic conditions. Effect of β-MnO$_2$ surface area on Cr(VI) produced over 30 days. *Inset:* effect of very low β-MnO$_2$ surface area on Cr(VI) produced over 80 days (chromium added, 0.80 g/L; reactor volume, 500 mL).

carried out. Cr(VI) formation during this experiment was monitored for 80 days and the data are presented in Fig. 3 (inset). These results indicate that provision of very much less β-MnO$_2$ causes the surface area to become a rate limiting factor in Cr(VI) formation, leading to drastic decline in Cr(VI) formation rate.

3.2.3. Anoxic conditions

Three experiments were carried out under anoxic conditions. The conditions for these experiments were the same for experiments described in Fig. 2 carried out under aerobic conditions, except that air in the headspace of these reactors was replaced by nitrogen to maintain anoxic conditions. Cr(VI) formation during these experiments are shown in Fig. 4A. For comparison, data (presented earlier in Fig. 2A) obtained under aerobic condition corresponding to β-MnO$_2$ surface area of 67 m^2/L and initial pH 7 is also presented in the same figure.

Based on results presented in Fig. 4A, it appears that there is no difference between chromium oxidation rates at pH 5 and 7 under anoxic conditions. This is similar to observations about chromium oxidation under aerobic conditions, obtained based on results presented in Fig. 2A. However, rate of chromium oxidation at initial pH 5 and 7 is less under anoxic conditions as compared to aerobic conditions. It appears that enhanced manganese dissolution when β-MnO$_2$ is added to water under anoxic conditions may be responsi-
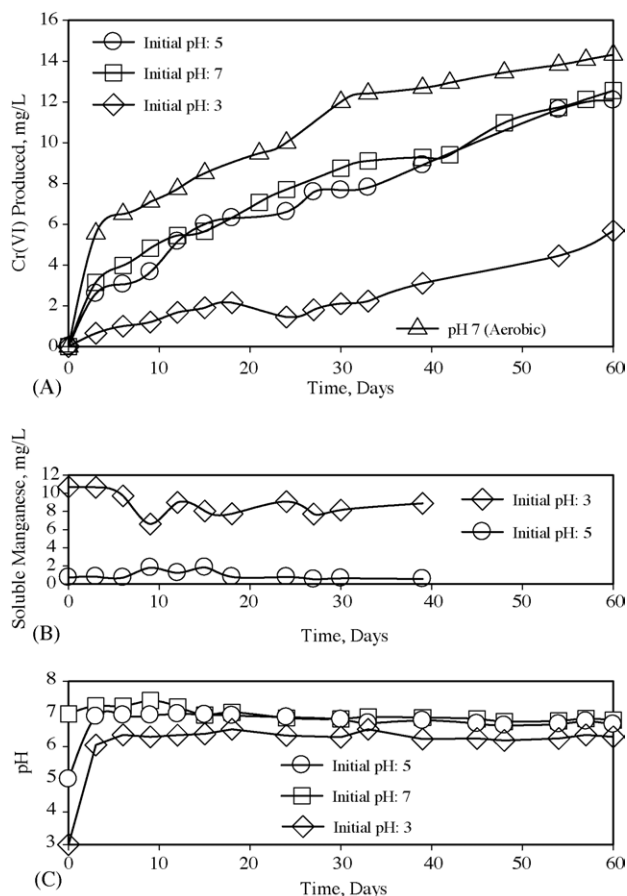
Fig. 4. Aqueous phase chromium oxidation in anoxic conditions. Effect of initial pH on Cr(VI) produced over 60 days (chromium added, 0.80 g/L; reactor volume, 1500 mL): (A) hexavalent chromium, Cr(VI) produced; (B) soluble manganese concentration changes; (C) reactor pH changes.

Fig. 5. Chromium oxidation in moist aerobic conditions. Effect of diminishing Mn:Cr ratios on Cr(VI) produced over 30, 60 and 90 days.

ble for this phenomenon. Ross and Bartlett [25] observed that adsorption of added Mn^{2+} on soil manganese oxides blocked chromium oxidation, until the adsorbed Mn^{2+} is re-converted to MnO_2. Thus, it is probable that the β-MnO_2 surface under anoxic conditions will be partially covered with adsorbed Mn^{2+} ions, thus, reducing the number of sites available for Cr(III) adsorption and subsequent Cr(VI) formation.

Chromium oxidation rate in the reactor at initial pH 3 (see Fig. 4A) was markedly slower compared to reactors maintained at initial pH 5 and 7. This is surprising because the pH in all three reactors reached the steady state pH value of approximately 7 quite quickly (see Fig. 4C). However, measurement of dissolved manganese concentration in the three reactors (Fig. 4B) showed that while dissolved manganese was undetectable in the reactor initially at pH 7, dissolved manganese concentration of approximately 1 mg/L was consistently measured in the reactor initially at pH 5 and 6–10 mg/L in the reactor initially at pH 3. It appears that manganese dissolution on addition of β-MnO_2 to anoxic water was more in reactors initially at acidic pH. This dissolved manganese competes with dissolved Cr(III) for adsorption on the β-MnO_2 surface, with increased competition occur-
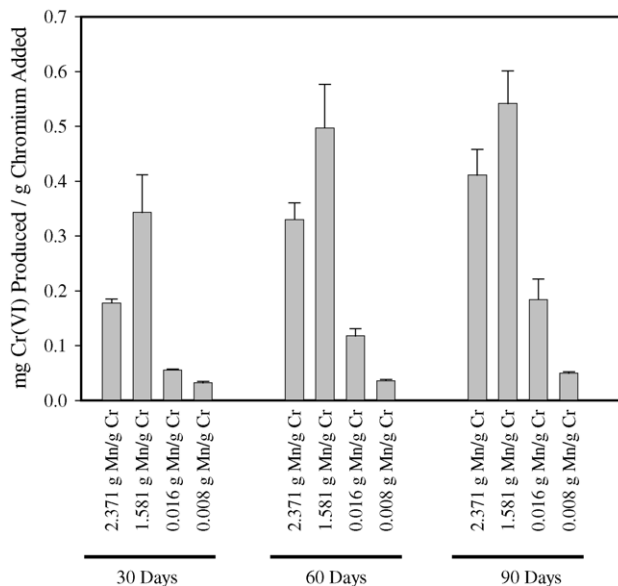
ring at lower pH values. This results in a lower rate of Cr(VI) formation in the reactor initially at pH 3. Even when the pH of this reactor increases to pH 7, dissolved Mn^{2+} concentration in the reactor does not decrease appreciably because of the slowness of MnO_2 re-formation under anoxic conditions. Thus, the competition between dissolved Cr(III) and Mn^{2+} for adsorption on the β-MnO_2 surface persists even at higher pH values. This explains the lower rate of Cr(VI) formation in the reactor initially at pH 3, even when the pH increases to become comparable with reactors initially at pH 5 and 7.

3.3. Type II experiments: Cr(OH)$_3$–β-MnO$_2$ interaction in moist aerobic conditions

These experiments involved mixing various amounts of dry $Cr(OH)_3$ and β-MnO_2 (see Table 1) and maintenance of the mixtures in moist aerobic conditions. The objective was to determine whether such mixtures could absorb moisture from the atmosphere and the chromium oxidation could occur in such moist conditions. A mixture of $Cr(OH)_3$ and β-MnO_2 was kept under dry conditions in a desiccator as a control. $Cr(OH)_3$ with no β-MnO_2 added was also kept in moist conditions as a control. No Cr(VI) formation was detected in either control sample.

Results of these experiments presented in Fig. 5 indicate that formation of Cr(VI) was possible under these conditions. As in aqueous systems described earlier, the rate of Cr(VI) formation generally decreased with decrease of β-MnO_2 content in the mixture, i.e., decrease in Mn:Cr ratio, except for one anomalous result (corresponding to Mn:Cr ratio of 2.371), which could be attributed to the inability to obtain a homogeneous sample of the mixture. However, the rates of conversion seen in this case were much lower than that for aqueous samples described in the previous experi-

ment. For example, in the reactor having β-MnO$_2$ specific surface area of 0.945 m^2/L (see Fig. 3 (inset)), with corresponding Mn:Cr ratio of 0.131, conversion of approximately 0.062% of added chromium to Cr(VI) was noticed in 80 days. In comparison, the solid phase experiment corresponding to a much higher Mn:Cr ratio of 1.581 showed comparable, i.e., 0.055% conversion (see Fig. 5) of added chromium to Cr(VI) in 90 days. This difference in rates is probably due to non-saturated conditions prevailing and diffusion-limited transport of dissolved Cr(III) ions to the β-MnO$_2$ surface in case of the solid phase experiments due to the absence of mixing.

3.4. Type IV experiments: chromium oxidation in tannery sludge samples

In addition to chromium–manganese interactions leading to chromium oxidation, several pathways for reduction of oxidized chromium may also be present in chromium-contaminated tannery sludge samples. For example, in anaerobic sludge samples, organic matter, ferrous ion and sulfide ions are some of the species that may reduce chromium. Even in stabilized sludge samples or compost, organic matter or humic substances can act as a reducing agent effecting chromium reduction. Under such conditions, chromium oxidation is defined by an inter-play between competing oxidative and reductive pathways.

3.4.1. Sludge characteristics

Chromium-contaminated tannery sludge from two effluent treatment plants treating tannery effluents was obtained. Results of analysis of the sludge samples are provided in Table 2. Both sludge samples were found to contain considerable amounts of Cr(III), probably, as Cr(OH)$_3$ and relatively small amounts of Cr(VI). Both sludge samples also contained manganese, probably as MnO$_2$. Organic content of both sludge samples was around 35%, and approximately 50% of this organic content was organic carbon.

3.4.2. Chromium oxidation–reduction

Moistened sludge samples were maintained in both aerobic and anaerobic conditions and analyzed for Cr(VI) over a period of 68 days. The results of this analysis are presented in Fig. 6. In case of the sludge from the activated sludge plant maintained in aerobic conditions, the Cr(VI) concentration increased from an initial value of 0.58–5.15 mg/g of dry sludge in 30 days, after which the chromium concentration decreased to below 1 mg/g of dry sludge over the next 38 days. The same sludge, when maintained under anoxic conditions, also showed the same trend in results, though the Cr(VI) concentration was only 1 mg/g dry sludge after 30 days. The sludge from the UASB plant, when maintained in aerobic conditions, showed only marginal increase in Cr(VI) content, i.e., from the initial value of 0.155 mg/g dry sludge to 0.195 mg/g in 30 days. As in previous cases, the Cr(VI) content in the sludge declined after 30 days. The
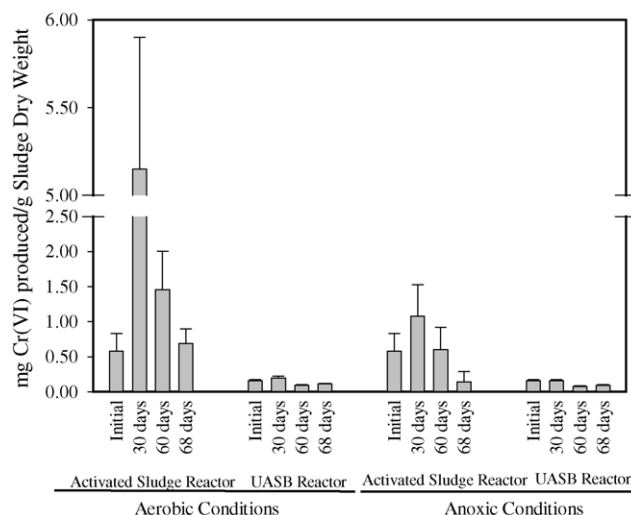

Fig. 6. Chromium oxidation in activated sludge and UASB reactor sludge samples under aerobic and anoxic conditions: Cr(VI) produced over 30, 60 and 68 days.

same sludge, when maintained in anoxic conditions, did not show significant increase in Cr(VI) concentration over 30 days and the Cr(VI) concentration in the sludge declined after 30 days. These results indicate that in the sludge samples studied, parallel mechanisms are at work, simultaneously oxidizing Cr(III) to Cr(VI) and reducing Cr(VI) to Cr(III). In the sludge samples containing lesser concentrations of reducing agents capable of reducing chromium, i.e., the sludge sample from activated sludge process, the initial chromium oxidation process is more rapid than the parallel chromium reducing process. This results in a build up of Cr(VI), which is then reduced back to Cr(III) as chromium reduction reactions gain precedence. This happened irrespective of whether the sludge was maintained in aerobic or anoxic conditions, but intermediate formation Cr(VI) was more in the aerobic case. Again, irrespective of aerobic or anoxic conditions, in the sludge sample containing higher concentrations of reducing agents (e.g., sulfide) capable of reducing chromium (i.e., sludge sample from the USAB process), the reduction reactions are more predominant and hence, high Cr(VI) concentrations are never encountered. The pattern of chromium oxidation reported here is very similar to that reported in a study involving flooded soils [5]. In that study, it was found that a thin redox interface of electron acceptors, e.g., manganese oxides, developed on soil surface, sandwiched between the anaerobic soil below and the oxygenated water above. As a result, the addition of Cr(III) resulted in its rapid oxidation followed by a decrease in Cr(VI) concentration over time. This decrease was thought to be due to the Cr(VI) produced diffusing across the redox interface, where it was reduced in the underlying anaerobic region.

It may be concluded that oxidation of Cr(III) is likely to be transient in un-stabilized sludge samples, where initial rapid oxidation of chromium is followed by reduction back to the trivalent state due to the presence of reducing agents

like organic material, Fe(II) and sulfide in sludge samples, capable of rapidly reducing the Cr(VI) produced [10,16].

4. Conclusions

Investigations carried out at a chromium-contaminated tannery sludge-dumping site in Kanpur, India revealed evidence of widespread hexavalent chromium pollution, though the fresh tannery sludge dumped at the site contained little or no hexavalent chromium. Based on a subsequent literature review, it was determined that trivalent chromium oxide could be oxidized by atmospheric oxygen at high temperature. Trivalent chromium could also be oxidized to hexavalent form through interaction with manganese dioxide surface. Experiments were carried out to determine the rate and extent of hexavalent chromium formation under conditions expected in the natural environment. The results of these experiments may be summarized as follows:

- Dry trivalent chromium oxide, i.e., Cr_2O_3 could be readily converted to hexavalent chromium when heated in the presence of oxygen at temperatures of 200–300 °C. The conversion rate was up to 50% at 300 °C in 12 h (Fig. 1).
- Burning of chromium-contaminated tannery sludge samples obtained from a tannery sludge-dumping site in the vicinity of the city of Kanpur, India also showed evidence of enhancement of hexavalent chromium concentration (Table 3).
- When $Cr(OH)_3$ and β-MnO_2 were suspended in water, $Cr(OH)_3$ was slowly converted to dissolved Cr(VI). This happened both in aerobic and anoxic conditions, with conversion rates of up to 1% in 60 days. Conversion was higher under aerobic conditions. Irrespective of the initial pH of the system, final pH in all experiments stabilized to 7 fairly rapidly. However, initial conversion rate to hexavalent chromium was more rapid in systems, where the initial pH of the system was higher (Figs. 2 and 3).
- When a mixture of $Cr(OH)_3$ and β-MnO_2 was maintained in moist aerobic conditions, $Cr(OH)_3$ slowly converted to hexavalent chromium, with up to 0.05% conversion observed in 90 days. The rate of conversion increased with increase in β-MnO_2 surface area (Fig. 4). The rate of conversion was slower in this case compared to similar interactions in aqueous media, probably, due to non-saturated conditions prevailing and diffusion-limited transport of dissolved Cr(III) ions to the β-MnO_2 surface.
- Chromium oxidation was observed in chromium-contaminated sludge tannery samples obtained from an activated sludge plant. However, such transformation was found to be transitory, with the Cr(VI) formed being ultimately reduced back to Cr(III) due to the presence of various reducing agents in the sludge. The maximum transitory hexavalent chromium concentration was found to be higher in samples maintained under aerobic conditions. Chromium-contaminated tannery sludge samples obtained

from an UASB plant did not exhibit similar transitory chromium oxidation when maintained under either aerobic or anoxic conditions (Fig. 5). It is postulated that strong reducing agents like sulfides present in this sludge prevented chromium oxidation.

It is likely that burning of the chromium-contaminated tannery sludge samples investigated in this study will produce ash rich in hexavalent chromium. Also, though Cr(VI) formation through interaction with manganese oxide at normal temperature was determined to be transitory in sludge samples from the activated sludge plant, it is still undesirable. Cr(VI) is mobile and hence, may not be confined to the location of its initial production. It can potentially spread relatively rapidly through environmental media via surface runoff and percolation, thus, polluting a larger area.

Acknowledgement

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