

Chromium Speciation in Cr(III) Oxidation by Mn-Oxides: Relation to the Oxidation Mechanism

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Abstract : Various Mn-oxides can oxidize Cr(III) to Cr(VI). Behaviors of chromium species in the oxidation system, especially on the oxide surface, are expected to control the reaction. During Cr(III) oxidation by birnessite and pyrolusite, Cr species in the reaction system were determined to elucidate their effects on the oxidation. Capacities of Cr oxidation of the two Mn-oxides were quite different. Solution pH and initial Cr(III) concentration also had significant effects on the Cr(III) oxidation by Mn-oxides. Chromium oxidation by pyrolusite was less than 5% of the oxidation by birnessite. The high crystallinity of pyrolusite could be one of the reasons and the difficulty of Cr(III) diffusion to the positive pyrolusite surface and Cr(VI) and Cr(III) adsorption seems to be other controlling factors. At pH 3, adsorption or precipitation of Cr species on the surface of birnessite were not found. Small amount of Cr(VI) adsorption was found on the surface of pyrolusite, but any Cr precipitation on the oxide surface was not found. Therefore Cr(III) oxidation at pH 3 seems to be controlled mainly by the characteristics of Mn-oxides. Chromium oxidation by Mn-oxides is thermodynamically more favorable at higher solution pH. However as solution pH increased Cr oxidation by birnessite was significantly inhibited. For Cr oxidation by pyrolusite, as pH increased the oxidation increased, but as Cr(III) addition increased the reaction was inhibited. Under these conditions some unidentified fraction of Cr species was found and this fraction is considered to be Cr(III) precipitation on the oxide surface. Chromium(III) precipitation on the oxide surface seems to play an important role in limiting Cr(III) oxidation by armoring the reaction surface on Mn-oxides as well as lowering Cr(III) concentration available for the oxidation reaction.(Received December 19, 1997; accepted January 19, 1998)

Introduction

Redox reactions at mineral surfaces are prevalent in the environment and often have a dramatic influence on the behavior and hazards of heavy metals. Chromium is one of such metals and trivalent and hexavalent Cr are stable under natural conditions. Chromium can be toxic to plants and humans.^{1,2)} The hexavalent form is the most active in this toxicity regard. Chromium(VI) is an anion which can move through the soil and vadose zone. On the other hand, the cation Cr(III) is strongly adsorbed on soil constituents and is highly immobile. Mechanisms which control interconversions of Cr between the two oxidation states in the soil have a major influence on the toxicity of Cr in terrestrial systems and transport to groundwater or surface water systems.

The mobility and transport of Cr is highly dependent on soil conditions, and oxidation and reduction reactions. Although Cr reduction can occur via many pathways, in soil systems below pH 9, Mn-oxides are the only known naturally occurring oxidant of Cr(III).³⁾ Both the highly crystalline pyrolusite and the disordered birnessite are capable

Key words : birnessite, chromium, chromium oxidation, pyrolusite

of oxidizing Cr(III) to Cr(VI).³⁻⁵⁾

According to the previous studies, in some pH ranges and with higher initial Cr(III) addition levels, Cr oxidation by Mn-oxides is highly inhibited. Eary and Rai³⁾ suggested that, for pyrolusite(β -MnO₂) with a zero point of charge (ZPC) of 7.3, chromate adsorption on the oxide surface was limiting Cr(III) oxidation. Fendorf and Zamoski⁵⁾ found that neither Mn(II) nor Cr(VI) affected the oxidation of Cr(III) by birnessite(δ -MnO₂). They discovered that oxidation was limited by specific combination of pH and Cr(III) levels. As either pH or Cr(III) addition increased, the extent of oxidation decreased. This appears to be due to a surface precipitation of Cr(OH)₃, which armors the oxide surface.⁶⁾ Johnson and Xyla⁷⁾ found that Cr(III) oxidation by manganite(γ -MnOOH) was first order with respect to Cr(III) and manganite, and second order over all, as long as the Cr(III) adsorption on the surface was inhibited and sorption of a Cr-hydroxide phase was believed to be the inhibition factor for the reaction.

Since Cr(III) oxidation is dependent on the oxide characteristics, solution variables, and sorption or desorption of reactants as well as products, complex interactions of such

factors should be examined to resolve the reaction mechanism. In this study, Cr(III) oxidation reaction by birnessite and pyrolusite were characterized and Cr species distribution in the oxidation system after reaction were analyzed to examine the effect of surface sorption and precipitation on Cr(III) oxidation.

Materials and Methods

Preparation and characterization of Mn-oxides

Birnessite was prepared by adding HCl to an excess of KMnO_4 as described by McKenzie.⁹ The resulting oxide was washed with deionized water and 0.5 N HClO_4 alternately until the residual K content was less than 1% and then dried at 40°C, and ground to pass through an 80-mesh sieve.

Pyrolusite could be purchased as a reagent grade manganese dioxide. The 0.106–0.150 mm size fraction was washed repeatedly in deionized water, leached with 10% HCl for 30 min and again repeatedly rinsed in deionized water, and dried at 60°C.

To identify the prepared Mn-oxides, ZPC, O/Mn ratio, and surface area were measured using a salt titration method,⁹ the iodometric method,¹⁰ and the ethylene glycol monoethyl ether method¹¹ respectively. Random powder mounts were used for X-ray diffraction analysis. Copper target and Ni filter were used according to the procedures of Whittig and Allardice.¹² Transmission electron micrographs were also obtained for the oxides.

Cr(III) oxidation and Cr speciation

The ability of Mn-oxides to oxidize Cr(III) was examined using a batch method to obtain steady-state data. Manganese oxides were placed in 50-ml polyethylene tubes to yield an initial solid surface area to solution volume ratio of $\sim 25 \text{ m}^2/\text{L}$; 2.5 mg of birnessite or 95 mg of pyrolusite per 25 ml suspension. The supporting electrolyte was 0.001 M NaNO_3 . Solution pH was adjusted to range between 3.0 and 5.0. Chromium nitrate was used as a Cr(III) source. The Cr (NO_3)₃ stock solution was stored at pH 2 for no longer than 1 week. Prior to the studies at pH 5.0, the solution containing Cr(III) and Mn-oxide was purged of CO_2 with N_2 gas. After oxidation reaction by shaking for 24 hrs at $25 \pm 1^\circ\text{C}$, the suspensions were centrifuged at 8,000 g for 10 min and 10 ml of the supernatant was pipetted for analyses of Cr(III) and Cr(VI) remaining in the solution. The liquid was filtered using 0.45 μm pore membrane filter before analyses. Chromium(VI) was determined by a modified *s*-diphenyl carbazide procedure.¹³ The reagent was made by mixing 120 ml of 85% H_3PO_4 , diluted with 280 ml of water and adding

this solution to 0.2 g of *s*-diphenyl carbazide dissolved in 100 ml of 95% ethanol. One ml of this reagent was added for each 10 ml of Cr(VI) solution to be analyzed. The color was allowed to develop for 20 min and was read at 540 nm on Hitachi U-2000 UV-vis spectrophotometer. Total solution Cr was determined using ICP-optical emission spectrophotometer. To the remaining suspensions of pH 3.0 and 5.0, 1 ml of 0.5 M $(\text{NH}_4)_2\text{SO}_4$ was added and shaken for 5 min to remove Cr(III) and Cr(VI) from the Mn-oxide surface. These suspensions were centrifuged at 8,000 g for 10 min and after filtering using 0.45 μm pore membrane filter the supernatants were analyzed for Cr(III) and Cr(VI) using the same procedure described above. The differences of Cr(III) and Cr(VI) contents between before and after addition of 0.5 M $(\text{NH}_4)_2\text{SO}_4$ were attributed to adsorbed Cr species on the oxide surface.

Results and Discussion

Characterization of the Mn-oxides

The ZPC, surface area and O/Mn ratio determined for the prepared Mn-oxides corresponded very well with published criteria of each preparation.¹⁴ The characteristic properties of two oxides are summarized in Table 1. The oxides prepared for use in the study are different in their oxidation states, and also different in crystallinity and charge characteristics. The high surface area and nearly amorphous nature of birnessite suggests that it would be highly reactive. The low ZPC for birnessite indicates that at pH values above 2.9 the surface would be negative and capable of adsorbing Cr(III). In contrast, much lower surface area and high crystallinity of pyrolusite suggests it would be much less reactive than birnessite. The higher ZPC of pyrolusite associates with possible strong adsorption of anionic Cr(VI) species at lower pHs. The most intense *d* spacings in X-ray diffraction of the two Mn-oxides are presented in Table 2. Representative transmission electron micrographs of the oxides are

Table 1. Some characteristic properties of the prepared Mn-oxides

Properties	Birnessite	Pyrolusite
ZPC	2.9	7.2
Surface area, m^2/g	263.3	5.6
O/Mn ratio	1.94	2.02

Table 2. X-ray diffraction data for the prepared Mn-oxides

Mn-oxides	The most intense <i>d</i> spacings, nm				
Birnessite	0.752(100)	0.327(50)	0.247(61)		
Pyrolusite	0.312(100)	0.241(43)	0.163(39)	0.211(14)	0.156(14)

* Values in () are relative intensities.

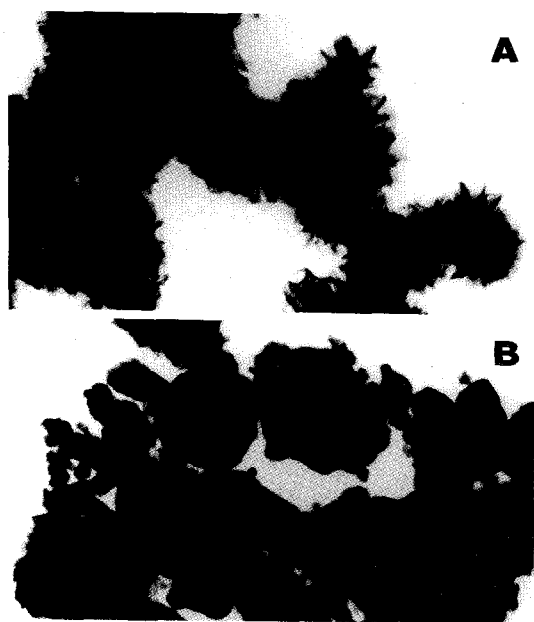


Fig. 1. Transmission electron micrographs of birnessite(A) and pyrolusite(B) prepared for the Cr(III) oxidation experiments.

presented in Fig. 1. The birnessite sample consisted of characteristic clumps or balls of needles and pyrolusite showed much more crystalline form than birnessite.

Cr(III) oxidation

Chromium(III) oxidation by the two different forms of Mn-oxide were characterized over a range of initial Cr(III) concentrations and pH values in a matrix of 0.001 M NaNO₃. The equilibrium isotherms are presented in Fig. 2 and 3. To compare the oxidation capacity (CrO₄²⁻ production) of each Mn-oxides, nearly the same surface area to solution

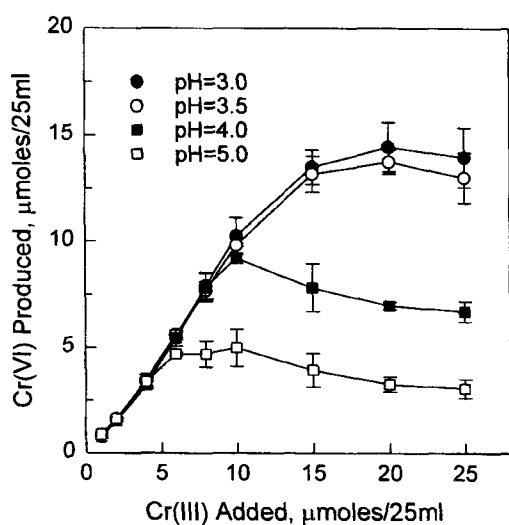


Fig. 2. Cr(III) oxidation by birnessite as a function of added Cr(III) concentration and pH at 25°C. Surface area to solution volume ratio was 25 m²L⁻¹.

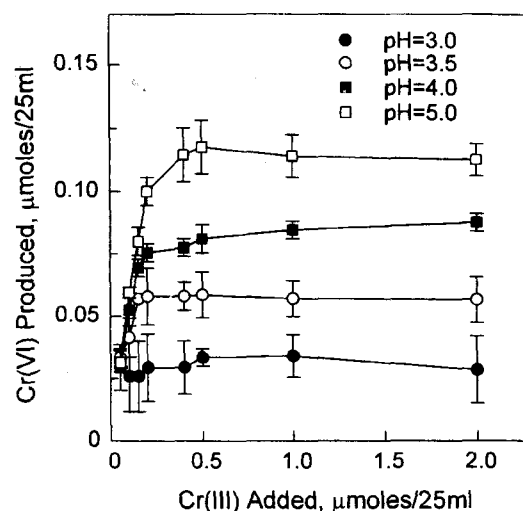


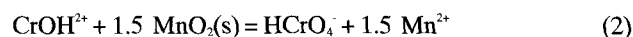
Fig. 3. Cr(III) oxidation by pyrolusite as a function of added Cr(III) concentration and pH at 25°C. Surface area to solution volume ratio was 25 m²L⁻¹.

volume ratio were used in all of the equilibrium studies. Birnessite oxidized much greater amounts of Cr(III) than pyrolusite. The lower amounts of oxidation by pyrolusite related well to a lower surface area and a higher crystallinity of the oxide. Solution pH and initial Cr(III) concentration had significant effects on Cr(III) oxidation by Mn-oxides.

Fig. 2 illustrates the Cr(III) oxidation by birnessite with varying initial Cr(III) concentrations over the pH range of 3~5. At pH values less than 3.5, Cr(VI) production approached near the maximum potential oxidizing capacity of birnessite; however, as solution pH increased, oxidation capacity gradually decreased. The following reaction has been suggested for the oxidation of Cr(III) by birnessite⁹ and it is written in a pH dependent manner:



Eary and Rai³ suggested the following reaction for the oxidation of Cr(III) by pyrolusite in the pH range of 3.0 to 4.7:



The birnessite used in this study contained 50% Mn by weight and based on a 1.5:1 Mn:Cr stoichiometry can be applied to the oxidation reaction, therefore 2.5 mg birnessite should be capable of oxidizing approximately 19 μmoles of Cr(III). However, in Fig. 2, the reaction of Cr(III) and birnessite was clearly not completed as pH and Cr(III) concentrations increased.

The Gibbs energies (ΔG°) of reaction (1) and (2) are 21.4 and 43.1 kJ mol⁻¹, and this indicates that the reactions will not proceed under standard condition. But Fendorf and Za-

soski⁵⁾ calculated ΔG_{rxn} for eq. (1) using a form of the Lewis equation ($\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q$), and they concluded that from a thermodynamic standpoint the reaction should proceed to a greater extent at higher pH values and at higher reactant concentrations. However, this was not observed in the oxidation process under experimental conditions of this study. Therefore if we assume the reaction stoichiometry of eq. 1 is correct, the limited Cr(III) oxidation found in this study must not be thermodynamically related. Using the reaction stoichiometry in eq. (2), Fendorf and Zasoski⁹⁾ found that the thermodynamic calculations at pH 5 still predict a favorable ΔG_{rxn} for Cr(III) oxidation by birnessite after a steady state is reached.

Fig. 3 illustrates the data for Cr(III) oxidation by pyrolusite as a function of pH and initial Cr(III) concentrations. At low levels of added Cr(III) oxidation increased with increasing pH, but the oxidation was relatively insensitive to concentrations above 0.5 μmoles of Cr(III). Chromium(III) oxidation by pyrolusite has been examined by Eary and Rai⁹⁾ in the pH range between 3.0 and 4.7, and they reported that the oxidation rate increased at lower pH. However, in this study, oxidation capacity increased as pH increased from 3 to 5. Since O/Mn ratio of the pyrolusite is 2.0, 95 mg of solid (1092 μmoles) should be capable of oxidizing 730 μmoles of Cr(III) based on the assumed stoichiometry of 1:1.5 Cr:Mn. The ΔG_{rxn} at steady state conditions were estimated to be -24 (at pH 3) and -32 (at pH 5) kJ mol^{-1} for the reaction (1), and -45 (at pH 3) and -60 (at pH 5) kJ mol^{-1} for the reaction (2). Therefore the reactions are favorable under conditions employed in this study and should proceed more at higher pH.

Effects of Cr species on Cr(III) oxidation

Since the thermodynamically favorable reactions do not go to completion, the limited oxidation can be attributed to the alterations of reaction surface. Adsorption or precipitation of Cr species on the surface of Mn-oxides are possible. Adsorption of cationic Cr(III) on net negative birnessite surface and adsorption of anionic Cr(VI) on net positive pyrolusite surface is expected. Cr(III) precipitation can be another reason for the limited oxidation by both oxides.

Chromium species in solution and on the oxide surface were quantitatively determined after the oxidation reactions at pH 3.0 and 5.0 (Figs. 4 and 5). At pH 3.0, very little or no Cr(III) and Cr(VI) was adsorbed on the birnessite surface. Anionic Cr(VI) species should be weakly, if at all, adsorbed on the negatively charged birnessite surface, and detection of Cr(III) adsorption is also unlikely since Cr(III) oxidation on the birnessite surface is rapid and extensive at

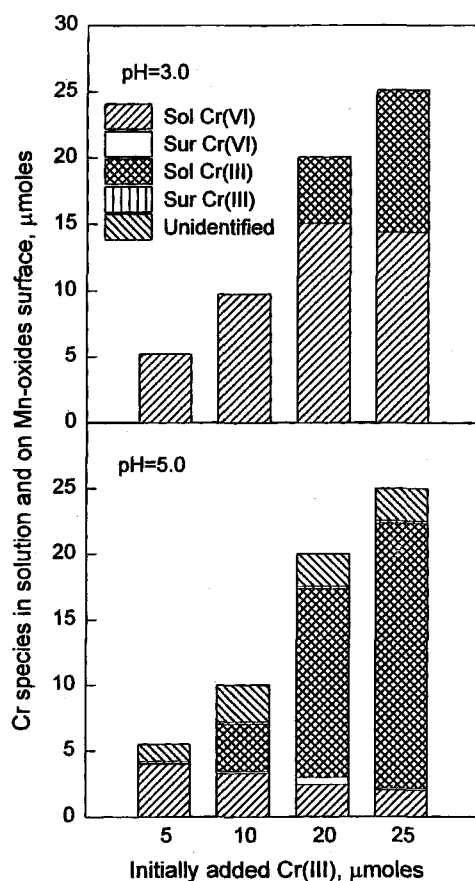


Fig. 4. Speciation of Cr in solution and on birnessite surface after oxidation with various initial Cr(III) additions and pHs at 25°C.

pH 3.0, and also the surface can be less negative at this pH of near to ZPC. When the initial addition of Cr(III) was higher than 20 μmoles at pH 3, Cr oxidation were not completed. In this case any alteration of the oxide surface was not found. So the reason for this reduced oxidation seems to be due to the significant consumption of birnessite and then lack of oxidation surface. Chromium(III) oxidation at pH 5.0 was much reduced in comparison to the oxidation at pH 3.0 with all initial Cr(III) additions. Most of the added Cr(III) remained in the solution with initial Cr(III) concentrations of 20 and 25 μmoles . Less than 5 μmoles of Cr(VI) was measured in solution and very small amounts of Cr(VI) and Cr(III) was detected on the birnessite surface. There was an unidentified fraction of Cr which is believed to be associated with the oxide surface. Including this unidentified fraction, 1 to 3 μmole of Cr(III) might be adsorbed or precipitated on the oxide surface. It should be noted that at higher pH value the higher initial Cr(III) concentrations were above saturation with respect to $\text{Cr}(\text{OH})_3$ ($\text{Log}K_{\text{sp}} = -30$). Higher Cr(III) precipitation and/or adsorption on the oxide surface at pH 5.0 might block the reaction surface. Inhibition of further Cr(III) oxidation at the higher

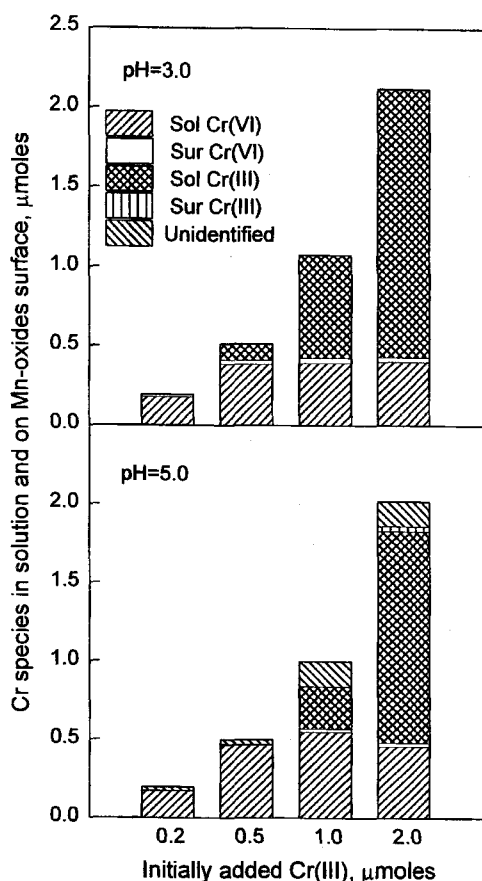


Fig. 5. Speciation of Cr in solution and on pyrolusite surface after oxidation with various initial Cr(III) additions and pHs at 25°C.

solution pH seems to be due to lack of oxidizing surface and reduced reactant concentration.

In Cr(III) oxidation by pyrolusite, since the oxidation was slow and not so extensive, large amount of the added Cr remained in solution as Cr(III) when the initially added Cr(III) was high. Small amount of Cr(VI) adsorption on the oxide surface was found at pH 3 and 5. In agreement with the adsorption study (author's unpublished data), more Cr(VI) was present on the surface at pH 3 than at pH 5. Although the difference was small, this higher adsorption of reaction product Cr(VI) on the pyrolusite surface could be one of the reasons for the lower oxidation at lower solution pH which was found in this study. Chromium(III) adsorption or Cr(III)-hydroxides precipitation on pyrolusite surface was not found at pH 3.0. At this pH since the surface of pyrolusite is highly positive, approach of cationic Cr(III) to the oxide surface would be limited. And this could be another reason for the lower Cr(III) oxidation at lower solution pH. Although the surface has net positive charges, a small amount of Cr(III) adsorption was found at pH 5.0. Since oxidation by pyrolusite is slow, such Cr(III) adsorption can be detected. At this pH, there was also a fraction of Cr which

could not be detected. This unidentified fraction is again believed to be associated with pyrolusite surface. As mentioned above, higher Cr(III) concentrations are above saturation with respect to Cr(OH)₃ at pH 5.0. The lower Cr(III) oxidation with higher initial Cr(III) addition at pH 5.0 could be explained also by the precipitation or adsorption of Cr(III) on the oxide surface.

Fendorf and Zamoski⁹ found that higher Cr(III) concentration in 10 to 1000 µM of initial Cr(III) addition caused a substantial decrease in the rate of Cr(III) oxidation by birnessite. Fendorf *et al.*⁶ found the formation of Cr(OH)₃ precipitation on birnessite surface with initial concentration of 400 µM Cr(III) at pH 5 and with 1 mM Cr(III) at pH 4.0. However since pyrolusite has a positive net surface charge in the pH range of this study, the possibility of surface nucleation of Cr(III) is reduced, but the oxidation at pH 5.0 seems to be further inhibited in the later period of the reaction by slow Cr(III) precipitation in addition to the Cr(VI) adsorption on the oxide surface-especially with higher initial Cr(III) additions. Charlet and Manceau¹⁵ found Cr-clusters on the surface of goethite at solution pH levels below its ZPC.

Although the unidentified fraction of Cr in the oxidation system was not identified in this study, it is believed as Cr(III) precipitation on the oxide surface.^{6,15} Chromium(III) precipitation seems to play an important role in limiting Cr(III) oxidation by lowering the Cr(III) concentration available for the oxidation reaction as well as armoring the reaction surface on Mn-oxides. Ionic species of Cr on the oxide surface or in solution do not have any significant influence on the Cr(III) oxidation.

Although reduced Cr has been considered to be the stable form in soils, added Cr(III) can be readily oxidized to Cr(VI) under conditions prevalent in many field soils. For disposal in the environment, higher levels of Cr(III) at elevated pH values would be preferable since they would inhibit oxidation and enhance the formation of a surface precipitation.

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망간 산화물에 의한 3가 크롬의 산화반응에 미치는 크롬 화학종들의 영향
정종배(대구대학교 자연자원대학 농화학과)

초 록 : 크롬의 산화는 자연계에 존재하는 여러 가지의 Mn-oxide에 의해 일어나며 산화과정에 존재하는 크롬 화학종들은 반응계 내에서 흡착, 침전 현상을 유발할 수 있고 결과적으로 산화반응을 조절할 수 있을 것이다. 본 연구에서는 birnessite와 pyrolusite에 의한 크롬의 산화에서 크롬 화학종이 반응에 미치는 영향을 조사하였다. Mn-oxide는 그 종류에 따라 크롬 산화력에서 큰 차이를 보였으며 용액의 pH와 초기 3가 크롬 첨가량도 산화반응에 큰 영향을 미쳤다. 동일 표면적당의 산화력을 비교하면 pyrolusite의 산화력은 birnessite의 5% 정도에 불과하였다. 이는 pyrolusite의 결정도에 크게 기인하며 또한 양으로 하전된 표면 특성 때문에 반응물인 3가 크롬의 접근이 어렵고 반응산물인 6가 크롬의 흡착 등에 기인하는 것으로 보인다. Birnessite에 의한 산화반응에서 pH 3에서는 oxide의 표면에서의 크롬 화학종들의 흡착이나 침전 현상은 발견되지 않았으며 pyrolusite의 경우 일부 6가 크롬의 흡착이 나타났으나 침전현상은 발견되지 않았다. 따라서 pH 3의 경우 산화반응은 Mn-oxide의 특성에 따라 결정된다. Mn-oxide에 의한 크롬의 산화는 열역학적으로 용액의 pH가 높아질수록 더 진행되어야 한다. Birnessite의 경우 pH 5에서 오히려 산화반응이 현저히 저해되었는데 이는 birnessite의 표면에 형성되는 3가 크롬의 침전이 반응표면을 감소시킴으로써 나타나는 현상으로 판단된다. Pyrolusite의 경우 pH 3보다 pH 5에서 크롬의 산화는 더 일어나나 초기 3가 크롬의 첨가량이 많아지면서 반응이 억제된다. 일부 3가와 6가 크롬의 흡착이 일어나나 이 경우도 역시 pyrolusite의 표면에 형성되는 3가 크롬의 침전이 반응을 조절하는 주 요인으로 생각된다. Mn-oxide의 표면에 형성되는 3가 크롬의 침전은 산화가 일어날 수 있는 반응표면을 감소시키고 또한 반응물의 농도를 낮춤으로써 용액의 pH가 높고 3가 크롬의 첨가량이 많아질 때 크롬의 산화반응을 억제하는 주 요인이 되는 것으로 판단된다.

찾는말 : Birnessite, Chromium, Chromium oxidation, Pyrolusite