

Kinetics of Chromium(III) Oxidation by Various Manganese Oxides

Jong-Bae Chung*, Robert J. Zasoski¹ and Sun-Uk Lim

Department of Agricultural Chemistry Seoul National University Suwon 441-744, Korea

¹Department of Land, Air, and Water Resources University of California Davis, CA 95616, USA

Abstract : Birnessite, pyrolusite and hausmannite were synthesized and tested for the ability to oxidize Cr(III) to Cr(VI). These oxides differed in zero point of charge, surface area, and crystallinity. The kinetic study showed that Cr(III) oxidation on the Mn-oxide surface is a first-order reaction. The reaction rate was various for different oxide at different conditions. Generally the reaction by hausmannite, containing Mn(III), was faster than the others, and oxidation by pyrolusite was much slower. Solution pH and initial Cr(III) concentration had a significant effect on the reaction. Inhibited oxidation at higher pH and initial Cr(III) concentration could be due to the chance of Cr(III) precipitation or complexing on the oxide surface. Oxidations by birnessite and hausmannite were faster at lower pH, but pyrolusite exhibited increased oxidation capacity at higher pH in the range between 3.0 and 5.0. Reactions were also temperature sensitive. Although calculated activation energies for the oxidation reactions at pH 3.0 were higher than the general activation energy for diffusion, there is no experimental evidence to suggest which reaction is the rate limiting step (Received August 17, 1994; accepted September 14, 1994).

Introduction

Trivalent and hexavalent Cr, the two thermodynamically stable oxidation states, behave very differently. Chromium(VI) is present as an anion, chromate, which can move through the soil and vadose zone. Chromium(VI) is also highly toxic because of the higher oxidation state. On the other hand, Cr(III) is strongly adsorbed on soil constituents and is highly immobile. The mechanisms which control interconversion of Cr between the two oxidation states in the soil have a major influence on the transport and toxicity of Cr in terrestrial systems and transfers 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, the only known oxidants of Cr(III) are Mn-oxides in soil systems below pH 9.0. The presence of Mn-oxides in terrestrial and aquatic environments may have a major influence on the toxicity and bioavailability of Cr in natural systems. Thus it is important to know the rates of, and the energy relationships involved in, Cr(III) oxidation by various Mn-oxides that occur in nature.

The oxides of Mn are widely distributed in soils and sediments as discrete particles and as coatings on other soil/sediment components.¹⁾ Manganese oxides are present in both the colloidal and noncolloidal particle-size fractions. Birnessite (δ -MnO₂) is one of the most common Mn-oxides in terrestrial and aquatic environments.^{2,3)} It occurs in disperse form and is nonstoichiometric.⁴⁾ Pyrolusite (β -MnO₂)

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*Corresponding author : Jong-Bae Chung

and hausmannite (Mn_2O_4) also occur naturally,⁴ although they are less common than birnessite. Pyrolusite is the most stable form of MnO_2 and occurs in mineralized hydrothermal deposits but is not known to occur as a weathering products.⁵ Pyrolusite is expected to be a primary Mn-containing solid in coal fly ashes and smelter wastes that are formed at high temperatures.⁶ Though hausmannite is rare in soil, it is considered as the main initial oxidation product of Mn(II) and is altered to form $\beta\text{-MnOOH}$.⁷

This work was undertaken to investigate the kinetics of Cr(III) oxidation by three different Mn-oxides - birnessite, pyrolusite, and hausmannite - to assess the potential importance of this process in natural systems.

Materials and Methods

Preparation of Mn-oxides

Birnessite was prepared by adding concentrated HCl to an excess of boiling solution of KMnO_4 as described by Buser *et al.*⁸ The oxide was washed with distilled-deionized water, dried at 60°C , and then ground to pass through a 60-mesh sieve. Pyrolusite could be purchased as a reagent grade manganese dioxide. The 0.10~0.15 mm size fraction was washed with a 10% HCl for 30 min and repeatedly rinsed in distilled and deionized water, and dried at 60°C . Hausmannite was prepared by adding 0.5 M NaOH to a stirred 0.05 M MnSO_4 solution which was maintained at 25°C while being flushed with CO_2 -free air.⁹ A radiometer pH-stat controlled the microdrop addition of NaOH at a rate kept the pH at 8.5 ± 0.2 . The fresh suspension of hausmannite was used for the oxidation experiment to avoid further oxidation of hausmannite to manganite ($\gamma\text{-MnOOH}$).

Characterization

To identify the prepared Mn-oxides, zero point of charge (ZPC), O/Mn ratio, and surface area were measured using a salt titration method,¹⁰ the iodometric method,¹¹ and the ethylene glycol monoethyl

ether method¹² respectively. Transmission electron micrographs and X-ray diffractograms were obtained for each oxide.

Kinetics of oxidation

Birnessite and hausmannite were suspended in 250 ml 0.001 M NaNO_3 solution in 300 mL Erlenmeyer flasks to yield an initial solid surface area to solution volume ratio of $\sim 25 \text{ m}^2 \cdot \text{L}^{-1}$. Solution pH was adjusted to 3.0 to 5.0 with 0.5 M HNO_3 . Chromium nitrate was used as a Cr(III) source. Prior to the studies at pH 5.0, the solution was purged of CO_2 with N_2 gas. The suspensions were stirred using a magnetic stirring plate at 25 and 6°C , and 5 mL samples were taken during the reaction periods ranged from 0.5 to 50 min. Because of the higher density, pyrolusite was placed in 50 mL polyethylene centrifuge tube to yield the same solid surface area to solution volume ratio ($\sim 25 \text{ m}^2 \cdot \text{L}^{-1}$). The suspensions were shaken on a reciprocal shaker and the reaction period ranged from 1 hr to 7 days. The samples were centrifuged at 8000g for 20 min and filtered using a $0.45 \mu\text{m}$ pore membrane filter. Chromium(VI) was determined by s-diphenyl carbazide procedure¹³ and solution Mn(II) was determined by atomic absorption.

Results and Discussion

The zero point of charge (ZPC), surface area and O/Mn ratio determined for the prepared oxides corresponded very well with published criteria of each preparation as were the X-ray diffraction data. The data are summarized in Table 1 (X-ray diffraction data not shown). Though transmission electron

Table 1. Some characteristics of the prepared Mn-oxides

	Birnessite	Pyrolusite	Hausmannite
ZPC	2.90	7.20	7.30
Surface area, m^2/g	263.30	5.60	30.00
O/Mn ratio	1.94	2.02	1.39

*Zero point of charge

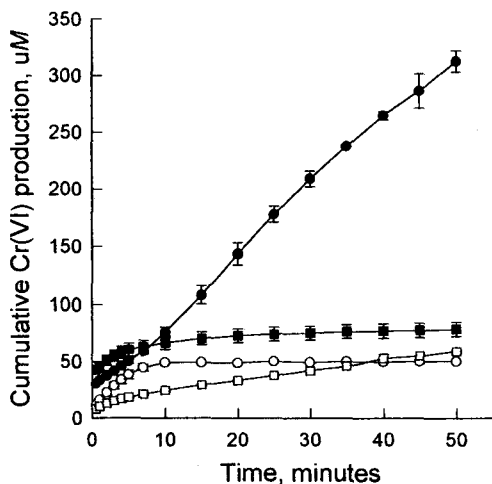


Fig. 1. Cr(III) oxidation by birnessite as a function of time with (●) 800 μM Cr(III) at 25°C and pH 3.0, (○) 100 μM Cr(III) at 25°C and pH 3.0, (□), 800 μM Cr(III) at 6°C and pH 3.0, and (■) 800 μM Cr(III) at 25°C and pH 5.0. Surface area of birnessite to solution volume ratio was equal to 25 $\text{m}^2 \cdot \text{L}^{-1}$.

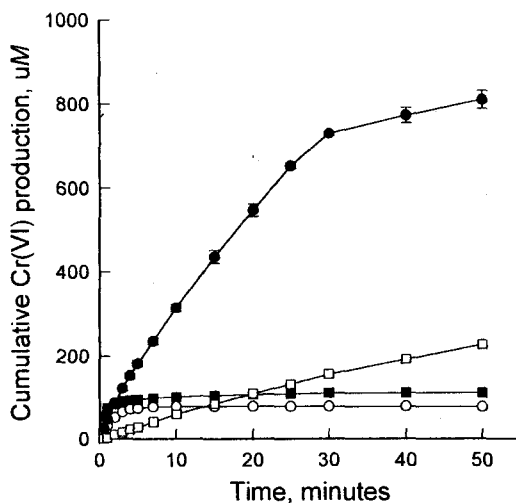


Fig. 3. Cr(III) oxidation by hausmannite as a function of time with (●) 800 μM Cr(III) at 25°C and pH 3.0, (○) 100 μM Cr(III) at 25°C and pH 3.0, (□), 800 μM Cr(III) at 6°C and pH 3.0, and (■) 800 μM Cr(III) at 25°C and pH 5.0. Surface area of hausmannite to solution volume ratio was equal to 25 $\text{m}^2 \cdot \text{L}^{-1}$.

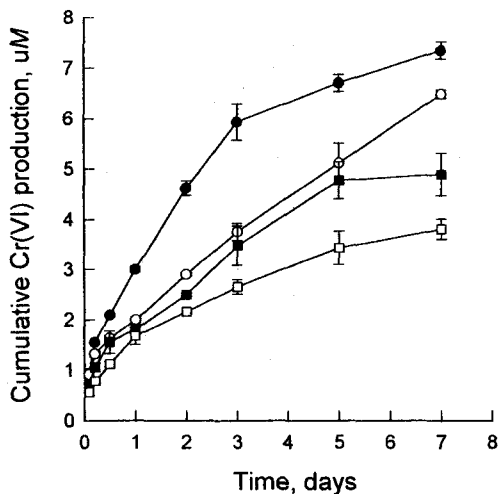


Fig. 2. Cr(III) oxidation by pyrolusite as a function of time with (●) 8 μM Cr(III) at 25°C and pH 5.0, (○) 80 μM Cr(III) at 25°C and pH 5.0, (□), 8 μM Cr(III) at 6°C and pH 5.0, and (■) 8 μM Cr(III) at 25°C and pH 3.0. Surface area of birnessite to solution volume ratio was equal to 25 $\text{m}^2 \cdot \text{L}^{-1}$.

micrographs are not shown, the typical needle like morphology of birnessite was formed when concentrated HCl was added to a boiling solution of

KMnO_4 .⁴⁾ Hausmannite was also poor crystalline of cubic or bipyramid shape. Pyrolusite had a more crystalline form than birnessite or hausmannite.

The oxides prepared for use in this study represent a range of oxidation states and contain varying levels of Mn(II), Mn(III), and Mn(IV). Especially hausmannite contains a significant level of Mn(III) and is represented as $\text{Mn(II)Mn(III)}_2\text{O}_4$. They also vary 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 this preparation indicates that at pH values above 2.9 the surface would be negative and capable of adsorbing Cr(III). In contrast, the ZPC associated with hausmannite and pyrolusite indicates a positive surface and a reduced ability to retain Cr(III) under the experimental conditions examined in this phase of the study. However, at the pH levels used hausmannite and pyrolusite should be able to adsorb and retain negatively charged Cr(VI) species.

Kinetic studies can provide information on the chemical reaction mechanism which complement on

equilibrium techniques. Figs 1, 2 and 3 show the oxidation of Cr(III) as a function of time with various initial Cr(III) concentrations, pH's, and temperatures. The Cr(III) oxidation was much faster and greater by hausmannite and was much slower by pyrolusite. Solution pH, Cr(III) concentration, and temperature have significant effects on the reaction. The reaction pattern was same in birnessite and hausmannite, but quite different in pyrolusite as the pH effect is reversed; faster oxidation at higher pH in the pH range studied.

At pH 3.0, with birnessite and hausmannite, oxidation was gradual and maintained for prolonged periods until the added Cr(III) was depleted. At lower temperature the reaction was much slower, but stayed at the same rate during the study. The rate of reaction at lower pH is linear until the added Cr(III) is nearly diminished. With lower concentration of initial Cr(III) the oxidation was much faster. Very rapid initial rates of oxidation were observed at pH 5.0, but declined rapidly even though there were enough Cr(III) and oxidizing surface. Higher Cr(III) concentration seems to cause such an extensive decrease in the oxidation rate, which indicates that Cr(III) is precipitating and lowering the Cr(III) concentration available for oxidation, and the precipitation can block the oxidizing surface.^{14,15} It should be noted that Cr(III) concentrations are above saturation with respect to Cr(OH)₃ (log K_{sp} = -30) at higher pH value. Increasing temperature increased the reaction rate and the effect was more significant for hausmannite than birnessite.

The very strong oxidation of Cr(III) by hausmannite is not easily explained. As lower oxide hausmannite contains Mn(III) instead of Mn(VI), the electron transfer from Mn(III) to Cr(III) could be different from birnessite and/or pyrolusite which contain Mn(IV). Rophael and Boulis¹⁶ suggested that the rate of Cr(III) oxidation in solution is dependent on the availability of free Mn³⁺ ions in the solution. However Manceau and Charlet¹⁷ suggested that the oxidation rate strongly depends on the structure of the oxides and, especially, on the

density of octahedral vacancies. Oxidation process on Mn(III) oxides (Mn₂O₃ and MnOOH) was similar to that depicted from birnessite.¹⁷

Chromium(III) oxidation by pyrolusite was much faster at pH 5.0 than at 3.0. The slower rate at pH 3.0 can be explained by the adsorption of negatively charged Cr(VI) species on pyrolusite surface. Since pyrolusite has a ZPC at pH 7.2, the oxide could have more positively charged surface at lower pH in the range of pH studied. At pH 5.0, the oxidation was faster at lower Cr(III) concentration (8 μM) and the reaction slowed down as Cr(III) in solution declined. The reaction was slower at higher Cr(III) concentration (80 μM) but continued with the same reaction rate until the end of study. Although hausmannite has the same surface charge characteristics, positive surface at pH range studied, as pyrolusite, the pH effect on the Cr(III) oxidation by hausmannite was different-oxidation was faster at lower pH. But this phenomenon is not explained well.

The added Cr(III) can either be oxidized to Cr(VI) by Mn-oxide or adsorbed on Mn-oxide. Adsorption of Cr(III) may be limited since it could be oxidized easily on the surface of the Mn-oxides. A first-order rate equation for this depletion of Cr(III) can be written

$$\frac{-d[\text{Cr(III)}]}{dt} = k[\text{Cr(III)}]$$

The integrated expression is

$$\ln[\text{Cr(III)}] = -kt + C$$

where [Cr(III)] is the concentration of Cr(III) remaining in solution at time t, k is the rate constant, and c is a constant. The reaction is therefore first-order if a plot of ln [Cr(III)] vs. t gives a straight line. The rate constants can be determined from linear least squares analysis. Although at higher initial Cr(III) addition at higher solution pH there might be some precipitation of Cr(OH)₃ on the oxide surface. If we could neglect this precipitation, the rate of Cr(III) depletion could be equal to the rate of Cr(III) oxidation by Mn-oxides.

Table 2. Rate constants for Cr(III) depletion by Mn-oxides

Mn-oxides	Treatments	Rate constants, $\times 10^3$
Birnessite	pH=3.0, 25°C, 100 μ M	104.16 min ⁻¹
	pH=3.0, 25°C, 800 μ M	9.40
	pH=3.0, 6°C, 800 μ M	1.28
	pH=5.0, 25°C, 800 μ M	0.74
Hausmannite	pH=3.0, 25°C, 100 μ M	266.56 min ⁻¹
	pH=3.0, 25°C, 800 μ M	65.55
	pH=3.0, 6°C, 800 μ M	6.85
	pH=5.0, 25°C, 800 μ M	1.09
Pyrolusite	pH=5.0, 25°C, 8 μ M	352.88 day ⁻¹
	pH=5.0, 25°C, 80 μ M	10.94
	pH=3.0, 6°C, 8 μ M	89.17
	pH=3.0, 25°C, 8 μ M	137.50

Although Johnson and Xyla¹⁸⁾ found that Cr(III) oxidation by manganite was a second-order reaction, the linear relationship in all cases examined in this study indicates that the depletion of Cr(III) by all three Mn-oxides is a first-order reaction except the very early reaction period (first-order plot not shown). In a first few minutes (for birnessite and hausmannite) or in the first several hours (for pyrolusite), the oxidation was rapid, especially at higher solution pH.

Rate constants for the depletion of Cr(III) by the Mn-oxides are presented in Table 2. The rate constant for a first-order reaction is numerically equal to the logarithm of the amount of Cr(III) that is depleted per unit time. Therefore the rate constant k is a measure of the relative rate of Cr(III) depletion.

The rate constant k , increases with increasing temperature (Table 2). At a given temperature, the constants for the depletion of Cr(III) by hausmannite are significantly greater than the rate constants for the depletion by birnessite even though the specific surface area of birnessite is greater than that of hausmannite. The rate constants for the depletion of Cr(III) at a given temperature by pyrolusite are much less than they are for the depletion by birnessite and hausmannite. This is attributed to the relatively low specific surface area (Table

Table 3. Activation energies for the depletion of Cr(III) by Mn-oxides at pH=3.0 and with the initial Cr(III) concentrations of 800 μ M for birnessite and hausmannite, and 8 μ M for pyrolusite

Mn-oxide	Activation energy, kJ/mol
Birnessite	72.55
Pyrolusite	49.50
Hausmannite	82.18

1) and the highly ordered nature of pyrolusite. Therefore, there is relatively little Mn on the surface of the oxide accessible to Cr(III) and this would result in a relatively small rate constant.

From the rate constants, the energies of activation for the depletion of Cr(III) by the Mn-oxides were determined. The dependence of k on temperature takes the form

$$k = A \exp(-E_a/RT)$$

The logarithmic expression is

$$\ln k = \ln A - E_a/RT$$

where k is the rate constant, E_a the activation energy, R the molar gas constant, T the absolute temperature, and A is a pre-exponential factor. The activation energy was determined from the slope of a plot of $\ln k$ vs. $1/T$ using linear least-squares analysis (Table 3). Although the rate constants for the depletion of Cr(III) by the two Mn-oxides are significantly different, there is no significant difference in the activation energy between birnessite and hausmannite. This means that the same process could be controlling the depletion rate in the two systems. Activation energy for Cr(III) oxidation by pyrolusite was smaller than that of birnessite or hausmannite.

There may be several steps in order for the oxidation to occur—diffusion of Cr(III) to the Mn-oxides particle, sorption to a reaction site on the particle, transfer of electron, desorption of Cr(VI) from the particle, and diffusion of the desorbed Cr(VI) into the solution. The activation energies found here are higher than the general activation energy for

diffusion (21 kJ/mol).¹⁹ Therefore the rate-limiting step for Cr(III) oxidation by Mn-oxides could be the step which need a higher activation energy than diffusion. Oscarson *et al.*²⁰ suggested the rate limiting step for As(III) oxidation by Mn-oxides is diffusion of As(III) through the solution to a Mn-oxide particle. In Cr(III) oxidation by manganite, Johnson and Xyla¹⁸ suggested rather electron transfer is the rate limiting step. Manceau and Charlet¹⁷ also suggested that electron transfer reaction is indeed the rate limiting step rather than the reductant adsorption in Cr(III) oxidation by various Mn-oxides. The detail mechanism of Cr(III) oxidation on the Mn oxide surface is not clear and need to be further investigated.

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망간 산화물에 의한 3가 크롬의 산화

정종배 · R.J. Zasoski¹ · 임선옥(서울대학교, ¹Univ. of California, Davis)

초록 : 망간 산화물 birnessite, pyrolusite, hausmannite의 표면에서 일어나는 3가 크롬의 산화현상을 조사하였다. 이들은 zero point of charge, 표면적, 그리고 결정도 등에서 차이가 많은데, 크롬 산화현상은 모두 1차 반응이었으며 반응용액의 pH 및 최초 3가 크롬농도가 반응에 큰 영향을 미쳤다. 일반적으로 hausmannite에 의한 산화가 가장 빨랐으며 pyrolusite에 의한 산화는 상대적으로 매우 느렸다. 용액 pH와 최초 3가 크롬농도의 상호 작용이 전체 반응속도를 조절하는 것 같으며 pH가 높고 3가 크롬농도가 높을 경우 망간산화물 표면에 3가 크롬 침전되거나 complex를 형성할 수 있을 것이다. Birnessite와 hausmannite에서는 pH 3.0~5.0 범위에서 pH가 낮을수록 산화력이 높았으나 pyrolusite의 경우에는 pH가 높을수록 산화력이 증가하였다. 반응속도는 온도에 또한 민감했다. pH 3.0에서의 산화반응의 activation energies는 일반적으로 diffusion에 필요한 activation energy보다 크게 나타났으나 반응속도를 결정하는 단계가 무엇인지는 확실하지 않다.

찾는말 : 산화, 크롬, birnessite, hausmannite, kinetics, Mn-oxides, pyrolusite