Oxidation of Chromium(III) to Chromium (VI) by Manganese Oxides : Variability in Mineralogy

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ABSTRACT

Manganese (Mn) oxides in soils and sediments differ in structure and composition. The influence of that diversity on the chromium (Cr) oxidation is the subject of this report. Oxidation of Cr(III) to Cr(VI) by coarse clay size Mn oxides (synthetic pyrolusite and natural lithiophorite, todorokite, and birnessite) was studied. Chromium oxidation by Mn oxides was initially fast and followed by a slow reaction. More Cr was oxidized by the Mn oxides at lower pH and higher initial Cr(III) concentration in solution. Birnessite had the highest chromium oxidation capacity per unit external surface area (COCUESA) and lithiophorite had the lowest COCUESA. The kinetics of Cr oxidation and COCUESA of Mn oixdes were apparently controlled by reactivity of surface Mn, mineralogy, and solution properties (pH and Cr(III) concentration).

1. INTRODUCTION

Although Cr is the tenth metal in abundance in the earth crust, it has been added into the environment by various human activities including mining and smelting of chromite ore, stainless steel (alloy) production, chrome plating, chrome tanning of leather, pigment production, oil well drilling, and petroleum refining. The mobility and toxicity of Cr are depending on its oxidation states. Trivalent Cr is less toxic and mobile than Cr (VI). Manganese oxides, which are the only proven natural oxidants for Cr(III) in the surface environment, are widely distributed as suspended particles in surface waters and as nodules or coatings in soils and sediments. The objective of this study is to examine and compare how the Mn oxide mineral phases affect Cr oxidation.

2. MATERIALS AND METHODS

Natural todorokite, birnessite, and lithiophorite, and Reagent grade pyrolusite (J.T. Baker Chemical Co.) were used for oxidation of Cr(III) to Cr(VI). The Mn oxide samples were ground to coarse clay (2-0.2　m) with an agate mortar. The Mn oxide samples were analyzed by X-ray diffraction (XRD) and infrared (IR). External surface area of the Mn oxide samples was determined by BET measurement using nitrogen gas

(N2) adsorption. The point of zero charge (PZC) of the Mn oxides was determined by a coagulation method (Yopps and Fuerstenau, 1964). To estimate reactivity of surface Mn for Cr oxidation, the solubility of the Mn oxides in hydroquinone [$C_6H_4(OH)_2$] was determined (Stone and Ulrich, 1989). Twenty five ml of pH 4 or pH 7 0.01M KCl and 0.02 g of each Mn oxide sample were placed in a 40 ml polyethylene centrifuge tube. A fresh pH 4 0.1M $CrCl_36H_2O$ stock solution was added to the suspension to yield 200 or 400M initial Cr(III) concentration and then the suspension was shaken for the desired period after filling the head space with N2 gas. For kinetic study, suspension was shaken for 1 to 72 hours after adding Cr(III). For static study (fixed time), the suspensions were shaken for 24 hours after adding Cr(III). The concentrations of Cr(VI) in filtrates were determined with a diphenylcarbazide chromagen method (Bartlett and James, 1979).

3. RESULTS

The lithiphorite, todorokite, and pyrolusite were highly crystalline and birnessite had low crystallinity. The solubility per unit surface area of the Mn oxide samples in the hydroquinone solution showed the following order: pyrolusite > birnessite > todorokite > lithiophorite. The Cr oxidation by the Mn oxides was initially fast and followed by a slow reaction for both 200 and 400M of initial Cr(III) concentrations at pH 4. Chromium oxidation by the lithiophorite reached a steady state after 5 hours while the oxidation continued on the todorokite, pyrolusite, and birnessite for the duration of the experiment (72 hours). The calculated Cr(VI) formation rate per unit external surface area for the initial fast reaction (1 to 7 or 12 hours reaction) using simple linear regression showed the following order: birnessite > pyrolusite > todorokite > lithiophorite. Todorokite, lithiophorite, and birnessite oxidized more Cr in 400 than 200M of initial Cr(III) concentration at pH 4 but the pyrolusite showed lower rate of Cr(VI) formation. For both 200 and 400 M of initial Cr(III) concentration at pH 4 and 7, the Cr oxidation capacity per unit external surface area (COCUESA) of the Mn oxides after 24 hours reaction was the following order: birnessite > pyrolusite > todorokite > lithiophorite. A higher COCUESA was obtained at lower pH (pH 4 over 7) and at higher initial Cr(III) concentration (400M over 200M) except for pyrolusite and birnessite. The pyrolusite had a higher COCUESA value at 200M than at 400M for both pH 4 and pH 7. Chromium oxidation by the pyrolusite and birnessite was limited at pH 7 and 400 M.

4. DISCUSSION

Pyrolusite and lithiophorite (PZC: pH 7.2 and pH 6.9) have positively charged surfaces but todorokite and birnessite (PZC: pH 3.2 and pH 2.8) have negatively charged surfaces at the experimental condition for the kinetic study, pH 4. Therefore, the pyrolusite and lithiophorite prefer to adsorb anionic Cr(VI)-complex (HCrO4-) rather than Mn(II) cation but the todorokite and birnessite prefer to adsorb Mn(II) cation at pH 4. Adsorption of Mn(II) and Cr(VI) on the surface reduces the accessibility of Cr(III) to the reactive surface Mn(IV). Both oxidation and polymerization of Cr(III) simultaneously occur during the oxidation reaction (Silvester et al., 1995). The Cr(III)-polymer is less reactive than the monomer in the oxidation (Fendorf et al., 1992) and is too big to diffuse into the tunnel, structural vacant sites, or interlayer of Mn oxides (Manceau and Charlet, 1992). Therefore, polymerization of Cr(III) reduced the reaction rate by reducing the activity of the more reactive Cr(III)-monomer and the accessibility of Cr(III) to internal reactive sites such as tunnels, structural vacant sites, and interlayer of Mn oxides.

Aluminum in the structure of lithiophorite may be released into the solution during the Cr oxidation and the released Al competes with Cr(III) for the adsorption sites (Fendorf et al., 1993). Adsorption of the released Al on the surface of lithiophorite would reduce the reactivity of surface Mn and retard the oxidation reaction.

Difference in the duration of Cr oxidation reaction by different species of Mn oxide was apparently due to different reactivity of surface Mn, crystal structures, and chemical compositions. Chromium oxidation by lithiophorite with low reactivity of surface Mn, no structural tunnels or vacant sites, and Al in the crystal structure reached a steady state in short period (24 hours). Whereas, Cr oxidation by the pyrolusite, todorokite, and birnessite with high reactivity of surface Mn, interlayer, tunnel, or structural vacant sites continued for longer time (72 hours). Both the larger number of reactive sites on the surface indicated by high reactivity of surface Mn and slow migration of Cr(III) into the structural may cause a longer Cr oxidation by pyrolusite, todorokite, and birnessite (Manceau and Charlet, 1992; McKenzie, 1970). The COCUESA of the Mn oxides was apparently controlled by combination of reactivity of surface Mn, crystal structure, and chemical composition of Mn oxides, and the solution properties such as pH and initial Cr(III) concentration. Birnessite with high reactivity of surface Mn, interlayer, structural vacant sites, and low crystallinity had the highest COCUESA. While, lithiophorite with low reactivity of surface Mn, no interlayer, tunnel, or vacant sites, and Al in the crystal structure had the lowest COCUESA. The high COCUESA of pyrolusite may be due to clean surface giving high reactivity of surface Mn and to Cr retention in the tunnels.

The increased solubility of the Mn oxides and activity of Cr(III) in solution at lower pH (pH 4 over 7) may increased the COCUESA. While, the precipitation of relatively stable chromium hydroxide [Cr(OH)3] on the surface at pH 7 reduced the COCUESA by blocking reactive surface Mn and reducing Cr(III) activity in solution (Fendorf et al., 1992). The lower COCUESA of pyrolusite at 400M than at 200 M of initial Cr(III) may be due to higher polymerization rate of Cr(III) at 400M and small tunnel (2.9 Å) (Mancheau and Charlet, 1992). On the other hand, birnessite had higher COCUESA at 400M than at 200M for pH 4 even though it had similar size of structural vacant site with tunnel of pyrolusite. This indicates that the negative effect of polymerization of Cr(III) is not significant on the whole oxidation capacity of birnessite at pH 4 and 400M: The high density of reactive surface Mn and interlayer controls the COCUESA of birnessite rather than Cr retention in structural vacant sites. The COCUESA of todorokite with relatively larger tunnels (6.5 Å) apparently was not influenced by the Cr polymerization at 400M. The lower COCUESA of pyrolusite and birnessite for 400M than for 200mM at pH 7 was probably due to the precipitation of Cr(OH)3 on the surface forming a barrier.

5. CONCLUSIONS

Chromium oxidation reaction by Mn oxides was initially fast and followed by a slow reaction. The kinetics of the reaction and the Cr oxidation capacity of Mn oxides were depending on structure, reactivity of surface Mn, and chemical composition of Mn oxides.

6. REFERENCES

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