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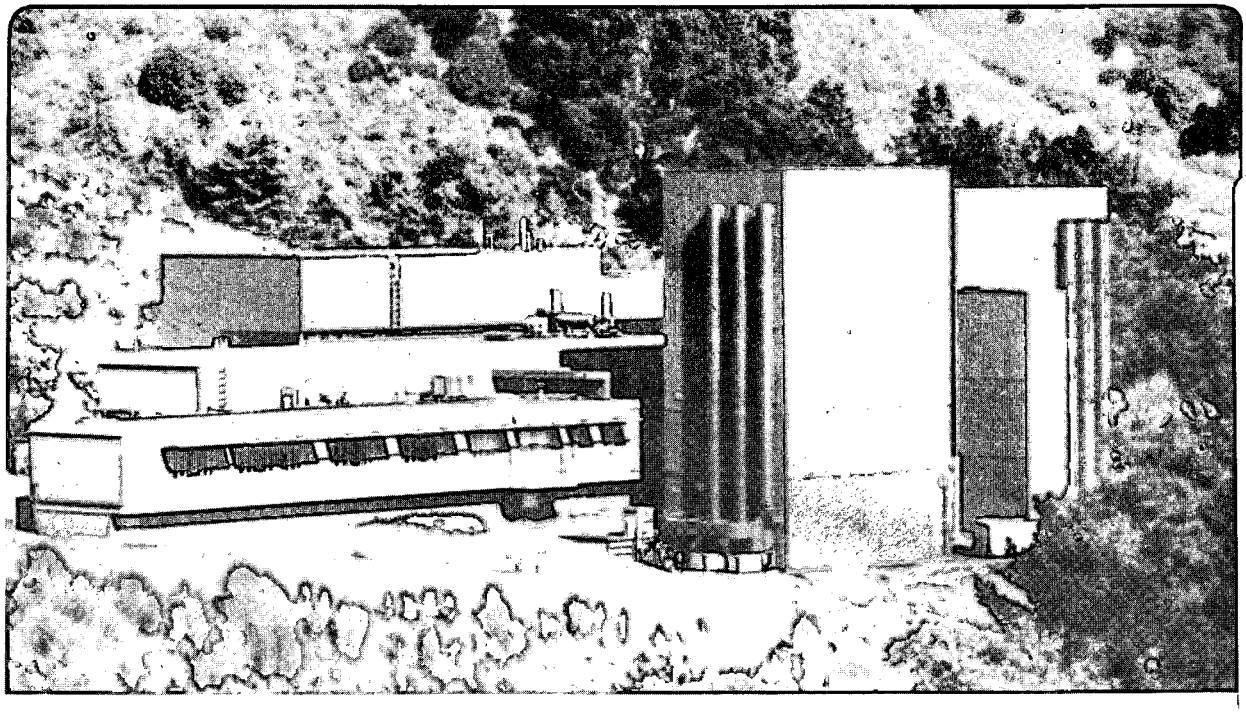

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USE OF TEM FOR CHARACTERIZATION OF REACTIONS OF MnO_2 WITH Cr(III) AND Al(III)

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Metal sorption is an important aspect of surface environmental processes which dramatically affects environmental quality. Sorption phenomena are active in transport and oxidation/reduction reactions, bio-transformation, and in determining the ultimate fate of metals in surficial systems. Although oxide materials often only constitute a small fraction of the solid composition in surficial environments, their high surface area, reactivity, and coating abilities make them extremely influential in sorption. Surface precipitation provides a model for the sorption of hydrolizable metal ions at the solution/solid interface, and was successfully used to explain observed trends in the reaction of various metal ions on oxide surfaces (for example, the sorption of of Co(II) on MnO_2, TiO_2 and Al_2O_3).[1,2]

In this study, transmission electron microscopy (TEM) is used to investigate the hypothesis[3] that surface precipitation explains the limitation in Cr(III) oxidation by δ-MnO_2 at higher pH and Cr(III) concentrations. It is further expected that Al(III) also forms a surface precipitate, thus explaining its inhibition of Cr(III) oxidation.[4] Specimens were prepared for TEM examination by crushing δ-MnO_2 to fine a powder and dispersing the resulting particles on a holey carbon film supported by a copper mesh grid. Reactions with 1mM Cr(III) at pH 4, 400μM Cr(III) at pH 5, and 400μm Al(III) at pH 5 were then carried out at 20°C and 1 atm pressure. All metal solutions were made from their nitrate salts, $Cr(NO_3)_3$ and $Al(NO_3)_3$ respectively.

High-resolution TEM images show that the unreacted MnO_2 is partially crystalline. Interspersed with amorphous material, there are layers of parallel atomic planes exhibiting severe bends and twists, as can be seen in Figure 1. This is similar to structures found to be characteristic of "glassy" (partially graphitized) carbon.[5] Conventional selected area electron diffraction yields patterns (as shown in Figure 2) with well defined but rather broad rings having prominent 2.4Å and 1.4Å spacings (in agreement with x-ray diffraction data), and a spacing of roughly 6.5 Å can also be discerned. In contrast, TEM images of MnO_2 reacted with Cr(III) show that a marked change in crystal structure occurs in this case (see Figure 3). Electron diffraction confirms this, producing patterns containing sharp, well defined rings throughout (Figure 4). The dramatic change in crystal structure is a result of the oxidation of Cr(III) by δ-MnO_2. Images of MnO_2 reacted with Al(III) (Figure 5) are similar to those of the unreacted material. However, upon close inspection these images suggest that an increased amorphous layer is present at the surface, evidence that a precipitation reaction has occurred. The MnO_2+Al(III) diffraction pattern is indistinguishable from that of the unreacted MnO_2. This reaction product is thought to be an aluminum hydroxide, $Al(OH)_x$, since hydroxide reaction products have been identified in other, similar precipitation studies.[1,2,4] In one case, the MnO_2+Cr(III) reaction formed a single-crystal particle on the supporting film in such a way that an apparent 6-fold axis was normal to the film (Figure 6).

In summary, the formation of a surface metal precipitate prior to bulk solution precipitation has important implications for environmental quality, since the precipitate will mask the properties of the original sorbent and only the surface properties of the metal hydroxide will be exhibited by the resulting conglomerated colloid. We have found that high resolution TEM has proven very useful in the characterization of the type of oxidation reactions described here, as it allows direct viewing of the surface structure after a reaction has been carried out. This technique indicates that surface precipitation does indeed occur during the reaction of δ-MnO_2 with Al(III). Work is now underway to identify the phase which results from the Cr(III)/MnO_2 reaction.[6]

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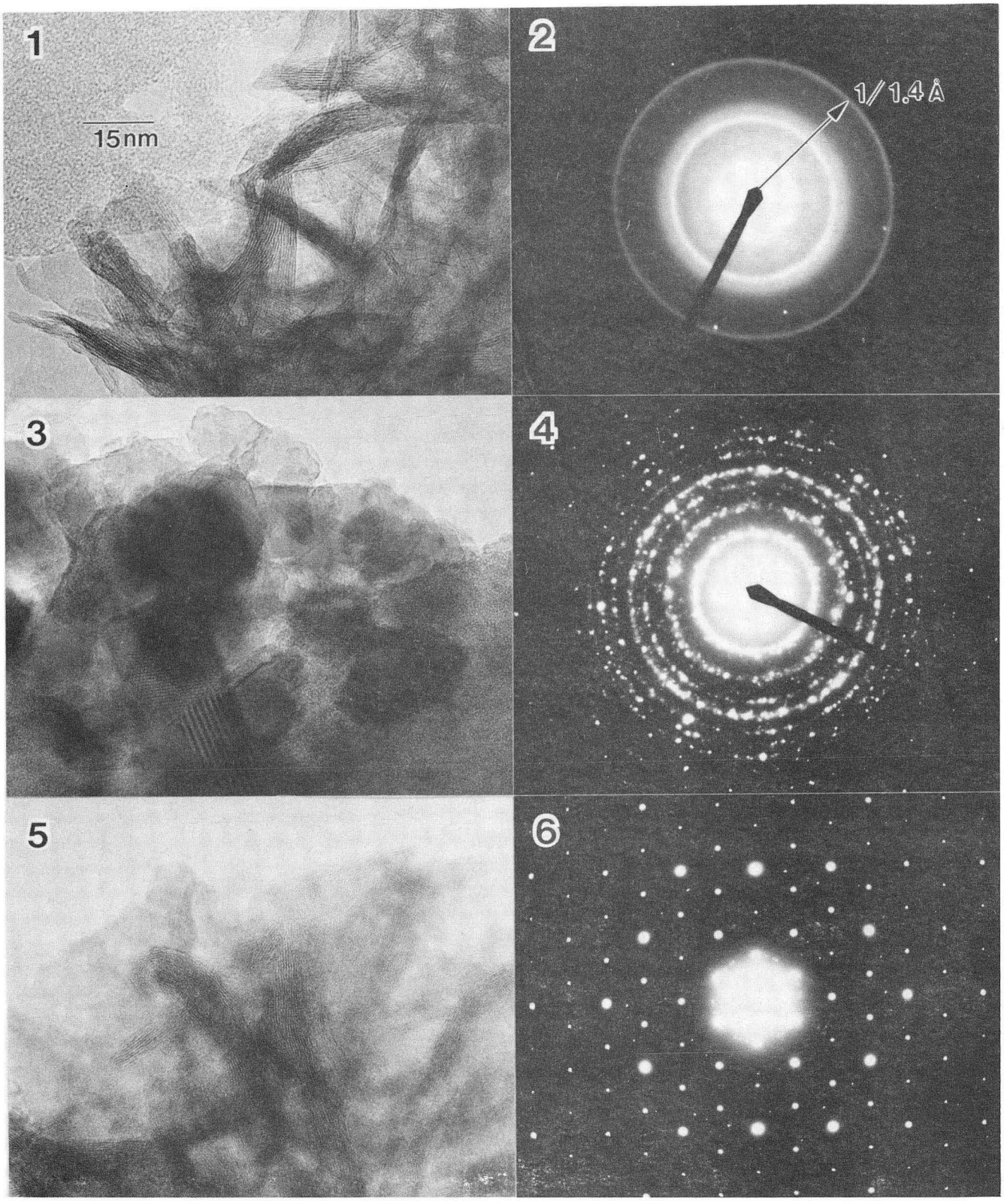

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FIG. 1. -- High resolution TEM image of unreacted MnO_2.
FIG. 2. -- Diffraction pattern from unreacted MnO_2.
FIG. 3. -- High resolution TEM image of MnO_2 reacted with Cr(III).
FIG. 4. -- Diffraction pattern from from MnO_2 reacted with Cr(III).
FIG. 5. -- High resolution TEM image of MnO_2 reacted with Al(III).
FIG. 6. -- Selected area diffraction pattern from single crystal MnO_2/Cr(III) reaction product.

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