Characteristics of Products from the Acid Ammonium Oxalate Treatment of Manganese Minerals

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Abstract: To determine the parameters that control the attack of Mn minerals by acid ammonium oxalate in darkness (AAOD), rhodochrosite, pyrolusite, manganosite, hausmannite, and bixbyite were shaken with AAOD for 2 hr. These treatments were followed systematically by X-ray powder diffraction (XRD) and AAOD-extractable Mn analyses. About 5% of original hausmannite (surface area = 6 m^2/g) remained in the solid residue of the AAOD treatment; however, if the hausmannite surface area was increased to 8 m^2/g, by grinding, it completely dissolved in oxalate. Synthetic hausmannite of high surface area (37 m^2/g) and rhodochrosite were completely dissolved by oxalate. Manganosite (1.5 m^2/g) and especially pyrolusite ($\sim$1 m^2/g) were more resistant to AAOD attack. Ground manganosite (4.2 m^2/g) dissolved completely, but ground pyrolusite (7.2 m^2/g) was only partially attacked by AAOD, inasmuch as about 25% of pyrolusite was found in the residue. An increase of the extraction time to 4 hr did not completely dissolve the ground pyrolusite.

As a result of the AAOD treatment, $MnC_2O_4 \cdot 3H_2O$ and $MnC_2O_4 \cdot 2H_2O$ precipitated from the oxalate solutions with all starting minerals, except pyrolusite ($\sim$1 m^2/g), which only slightly dissolved. The seldom reported $MnC_2O_4 \cdot 3H_2O$ phase was identified in residues of freshly extracted samples by its strong characteristic peak at 6.5. – 6.6 Å, the intensity of which gradually decreased and disappeared over several days when the sample was exposed to ambient conditions (22 ° C and 70% relative humidity). The trihydrate phase also collapsed after heating AAOD-treated rhodochrosite at 50 ° C; α-$MnC_2O_4 \cdot 2H_2O$ was identified as the main crystalline product. Heating the α-$MnC_2O_4 \cdot 2H_2O$ product at 115 ° C overnight transformed most of it to MnC_2O_4. The color of the oxalate-treated samples ranged from pinkish-gray to black (7.5 YR); their surface area ranged from about 20 to 30 m^2/g. The degree of transformation of Mn minerals by oxalate depended on the surface area and structural characteristics of the starting materials.

Key Words: Acid ammonium oxalate • Dissolution • Grinding • Manganese oxides • Surface area • X-ray powder diffraction

Clays and Clay Minerals; June 1991 v. 39; no. 3; p. 264-269; DOI: 10.1346/CCMN.1991.0390306

Clay Minerals Society (www.clays.org)