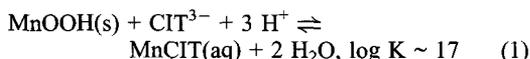


# Rates of dissolution of MnOOH by ligands: pyrophosphate, ethylenediaminetetraacetate, and citrate

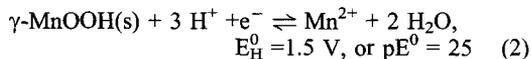
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MnOOH solids are principal products of Mn(II) oxygenation in moderately alkaline waters (Stumm and Giovanoli, 1976). MnOOH is sparingly soluble in the absence of strongly complexing ligands, e.g. the equilibrium concentration of free ion,  $[\text{Mn}^{3+}]$ , would be approximately  $1\text{E}-18\text{ M}$  at pH 6 and  $25^\circ\text{C}$ . However, in the presence of a ligand such as citrate ( $\text{CIT}^{3-}$ ) the solubility of MnOOH is increased (Klewicki and Morgan, 1998); e.g.



At pH 6, with total  $\text{CIT}^{3-} = 50\text{ mM}$ ,  $[\text{MnCIT}]_{\text{eq}} = 2.5\text{ mM}$ . MnOOH(s) is a strong oxidizing agent (Lindsay, 1979), e.g.



At pH 6, with  $[\text{Mn}^{2+}] = 10\text{ }\mu\text{M}$ ,  $E_{\text{H}} = 0.71\text{ V}$ . Thus, MnOOH is an oxidant of considerable strength under near neutral pH conditions, able to oxidize Fe(II) species, reduced sulphur compounds, and a wide variety of organic compounds, e.g. organic acids. Most treatments of manganese cycles in natural waters have devoted rather little attention to Mn(III) chemistry. Recently, Kostka, Luther and Nealson (1995) have argued that Mn(III) and its interaction with naturally-occurring ligands should be an important aspect of manganese cycles. It is of interest to learn something about the time scales for Mn(III) reactions under typical pH conditions in water.

The focus of the research results reported is on rates of dissolution of suspensions of a synthetic  $\beta$ -MnOOH in the presence of three different ligands: pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ), ethylenediaminetetraacetate ( $\text{EDTA}^{4-}$ ), and citrate ( $\text{CIT}^{3-}$ ). These ligands were chosen because of known complexing of Mn(III) and to provide examples of an inorganic, synthetic organic, and naturally-occurring ligand. Dissolution of MnOOH by pyrophosphate takes place without reduction of Mn(II). EDTA and citrate may dissolve MnOOH by coordination or redox mechan-

isms. The variables studied were pH, total ligand concentration, and MnOOH concentration.

## Methods

MnOOH particles were synthesized following a procedure using hydrogen peroxide oxidation of Mn(II) sulphate in ammonia solution. The resulting particles were dried and characterized by X-ray diffraction, total manganese analysis, iodometric titration, and electrophoretic mobility measurements. The product was principally MnOOH (feitknechtite), with a small amount of hausmannite,  $\text{Mn}_3\text{O}_4$ . The average oxidation state of the solid is described by the formula  $\text{MnO}_{1.506 \pm 0.006}$ , and is close to III. The isoelectric pH of the particles was found to be  $6.2 \pm 0.2$ .

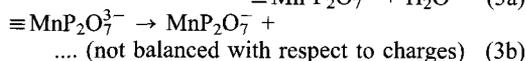
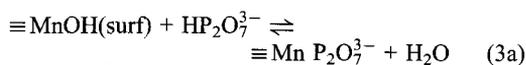
Experiments were carried out at  $20\text{--}22^\circ\text{C}$ , open to the air. The stirred reactor contained 150 ml of distilled water to which was added known amounts of the particular ligand salt, plus acid or base for pH adjustment. The dissolution reaction was initiated by introducing weighed amounts of manganese III, typically in the concentration range  $0.2\text{ to }1.0\text{ g l}^{-1}$ . Samples were taken periodically and filtered through  $0.05\text{ }\mu\text{m}$  pore polycarbonate filters. Filtrate was analysed for total manganese by either ICP-MS or a formaldoxime colorimetric method, and for the concentration of Mn(III)pyrophosphate, Mn(III)EDTA, or Mn(III)CIT complex by light absorbance measurement at the appropriate wavelength (Klewicki and Morgan, 1998). Filtered solids were dried, weighed, and analysed iodometrically (oxidizing equivalents) and colorimetrically (total manganese).

## Results and discussion

*Pyrophosphate.* In the presence of pyrophosphate at a concentration of  $50\text{ mM}$  in solutions of pH 6.5 to 8.0, MnOOH particles dissolved rapidly, with characteristic times for 50% dissolution of particles initially 2.5

mM in total Mn ranging from 4 hr at pH 6.5 to 20 hr at pH 8.0. The pyrophosphate was present in 20-fold molar excess in suspensions with 220 mg l<sup>-1</sup> MnOOH. Variation of initial MnOOH concentrations between 90 and 900 mg l<sup>-1</sup> produced initial rates which varied approximately 10-fold, i.e. the early stage of the dissolution is quasi zero-order in particle concentration (which we take to reflect proportionality to surface area and reactive sites). Throughout the entire dissolution process total dissolved manganese concentrations, Mn<sub>T</sub>, and [Mn(III)P<sub>2</sub>O<sub>7</sub>] concentrations were equal, within experimental uncertainty. All of the dissolved manganese is in the form of the pyrophosphate complex of Mn(III).

The process may be visualized as:



A predicted rate expression of the form

$$-d[\equiv \text{MnOH}(\text{surf})]/dt = k_d [\equiv \text{MnOH}(\text{surf})] \quad (4)$$

gives the observed kinetic behaviour for long-term, complete dissolution (independence of rate with respect to solid concentration) and for the initial conditions (dependence on solid concentration). The pH dependence is complex, as is generally the case for oxide-ligand adsorption processes. In the circumneutral pH region,  $k_{\text{observed}}$  varies as  $[\text{H}^+]^{0.46}$ .

**EDTA.** Dissolution of MnOOH in 20-fold molar excess of EDTA (50 mM EDTA and 225 mg l<sup>-1</sup> solid) at pH 7.0 proceeds with a 50% dissolution time of ~ 1 hr. At pH 8, with 10-fold ligand excess, the corresponding dissolution time is ~ 3 hr. In contrast to the results observed for pyrophosphate, there is no spectrophotometric evidence for the appearance of the Mn(III)EDTA<sup>-</sup> complex during the dissolution process. The dissolution with EDTA appears as entirely reductive. (Experiments on MnOOH dissolution with EDTA by Stone *et al.* at The Johns Hopkins University (1996) followed the same reaction by observing dissolved products using capillary electrophoresis; no Mn(III)EDTA complex species were detected in solution. Xyla *et al.* (1992) observed the reductive dissolution of  $\gamma$ -MnOOH by oxalate at lower pH (< 6).

**Citrate.** In 20-fold molar excess of citrate at pH 7.8, 50% dissolution of MnOOH occurs in ~ 1 day. At pH 6.3, with 35-fold ligand excess, the corresponding dissolution time was ~ 1/2 hr.

Comparison of Mn<sub>T</sub> in solution with [Mn(III)CIT] throughout the dissolution process reveals that the initial stage of dissolution is non-reductive, producing an Mn(III)CIT(aq) species. As the process advances, increasing amounts of Mn(II) species appear. i.e. Mn<sub>T</sub> > [Mn(III)CIT]. Previous experiments on the decomposition of the Mn(III)CIT complex species in solution (Klewicky and Morgan, 1998) indicated that the reaction Mn(III)CIT(aq) → Mn(II)CIT<sup>-</sup> proceeded via an inner-sphere mechanism. Dissolution by citrate may involve both non-reductive and reductive paths, with a shift in relative importance of each as the process progresses.

### Concluding remarks

The results of this exploratory study of MnOOH dissolution by different Mn(III)-stabilizing ligands in the circum-neutral pH range suggest that the production and loss of MnOOH solids may play a significant role in manganese cycles in natural waters. The results obtained here show that characteristic time scales for MnOOH dissolution in the pH domain ~ 6 to 8 range from ~ 5 × 10<sup>2</sup> to 2 × 10<sup>5</sup> sec. At pH 7, the dissolution times are in the order P<sub>2</sub>O<sub>7</sub> > CIT > EDTA, for comparable ligand excesses.

Of course, in actual systems, there can be a variety of ligands capable of stabilizing the Mn(III) state. The total concentrations of manganese and ligands in nature will be much lower than those employed in the present work, ranging between micromolar and nanomolar levels. However, it might be expected that ligand:manganese ratios could still be high enough, say 10- to 100-fold, to influence dissolution complexation and redox behaviour in water and at particle surfaces.

### References

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