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Rates of manganese oxidation in aqueous systems

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Abstract—The rate of crystal growth of Mn_3O_4 (hausmannite) and βMnOOH (feitknechtite) in aerated aqueous manganous perchlorate systems, near 0.01 M in total manganese, was determined at pH levels ranging from 7.00 to 9.00 and at temperatures from 0.5 to 37.4°C. The process is autocatalytic, but becomes psuedo first-order in dissolved Mn^{2+} activity when the amount of precipitate surface is large compared to the amount of unreacted manganese. Reaction rates determined by titrations using an automated pH-stat were fitted to an equation for precipitate growth. The rates are proportional to surface area of oxide and degree of supersaturation with respect to Mn^{2+}. The oxide obtained at the higher temperature was Mn_3O_4, but at 0.5°C only βMnOOH was formed. At intermediate temperatures, mixtures of these solids were formed. The rate of precipitation of hausmannite is strongly influenced by temperature, and that of feitknechtite much less so. The difference in activation energy may be related to differences in crystal structure of the oxides and the geometry of polymeric hydroxy ion precursors.

INTRODUCTION

WHEN SOLUTIONS containing divalent manganese are brought to pH's between 7.0 and 9.0 and are treated with air or oxygen in the laboratory the product is generally a variable mixture of manganese oxyhydroxide species with the manganese valence ranging from about 2.67 to about 3.0. The form of the oxide evidently is dependent on the experimental conditions, but existing literature does not provide a clear indication of the relative importance of such factors or their possible relationship to observed reaction rates. The kinetics of the oxidation process have been studied by several investigators who have in general agreed that the reaction is catalyzed by various mineral surfaces, and especially by pre-existing manganese oxide (MORGAN, 1967; VANDER WIEDGEN, 1975; HEM, 1964). The autocatalytic nature of the oxidation implied by the above effect has also been evaluated (MORGAN, 1967; WILSON, 1980) but the published rate expressions contain terms that are not easily extrapolated to other experimental conditions.

The work described here was done to define more closely some factors that influence the oxidation state and crystal form of laboratory manganese oxide precipitates, and to evaluate the autocatalytic reaction rates in terms that could be more readily applied to natural systems. The effects of temperature, and the crystal form and surface area of the product on kinetics of the reaction also were studied.

EXPERIMENTAL METHODS

The reaction rate measurements were made using an automated titrator operating in a pH-stat mode. This equipment maintained a constant pH (within about ±0.05 pH) in the experimental solutions by adding 0.15 M NaOH solution in small increments. The rate of base addition was recorded continuously. Air that had been passed through a carbon dioxide removal train was bubbled continuously into the solution and solids were kept in suspension by vigorous stirring. The pH sensing elements were saturated calomel and glass electrodes. Reaction temperature was controlled by immersing the container in a constant temperature bath (±0.1°C). The initial solutions were 100 ml aliquots of 0.01 or 0.02 M $Mn(ClO_4)_2$. The $Mn(ClO_4)_2$ stock solution was made by reacting reagent grade manganese metal and perchloric acid. The crystal form of the precipitates was identified by transmission electron microscopy, electron diffraction and X-ray diffraction. Surface areas of selected samples were measured by the BET procedure. Oxidation state of precipitated manganese was determined by dissolving a portion of the oxide in a small known excess of oxalic acid followed by back titration with permanganate. Oxidation numbers obtained by this method have an experimental uncertainty of about ±0.05. Dissolved manganese determinations were made as required using atomic absorption flame spectrophotometry. The automation of the rate titrations facilitated the work by allowing for a series of runs at different temperature and pH, and the pH was closely controlled without the need for a solution buffer which might have affected the reaction mechanism.

A summary of the experimental data for 16 precipitations is given in Table 1. The holding pH's used ranged from 7.00 to 9.00 and temperatures from 37.4 to 0.5°C.

The X-ray diffractograms for the solids containing βMnOOH showed a characteristic strong peak at 4.62 Å and weaker ones at smaller *d* spacings. These results and patterns for Mn_3O_4 correspond to those reported by BRICKER (1965). The thin plates with characteristic hexagonal shapes characteristic of βMnOOH contrasted strongly with the small nearly cubic hausmannite crystals when viewed with the transmission electron microscope. The X-ray identifications were made by R. B. FOURNIER and electron microscopy was done by C. J. LIND, both of the U.S. Geological Survey.

CALCULATION OF OXIDATION RATE

For the precipitation of hausmannite in aerated solutions, the net process can be summarized as

$$3Mn^{2+} + \tfrac{1}{2}O_2(aq) + 3H_2O = Mn_3O_4(c) + 6H^+. \quad (1)$$

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Similarly, for βMnOOH

$$2Mn^{2+} + \tfrac{1}{2}O_2(aq) + 3H_2O = 2MnOOH(c) + 4H^+. \quad (1a)$$

When the pH and oxygen supply are held constant, a rate expression having the form

$$\frac{-d[Mn^{2+}]}{dt} = k_1[Mn^{2+}] + k_2 A_{Mnppt}[Mn^{2+}] \quad (2)$$

can be postulated for either reaction under these conditions. This rate law is analogous to one given by STUMM and MORGAN (1970, p. 535) for autocatalytic oxidation of manganese. The $[Mn^{2+}]$ terms represent thermodynamic activity of dissolved unreacted manganese and A_{Mnppt} represents the availability of reaction sites on the surface of the precipitated manganese oxide. The two rate constants k_1 and k_2 represent, respectively, the relatively slow precipitation reaction of dissolved manganese that is not specifically interacting with any surface, and the autocatalytic influence of an increasing availability of reaction sites as the reaction increases the area of oxide surface.

In the solutions studied, the amount of precipitate present at any given time was calculated from the quantity of hydroxide added up to that point in the titration. The surface area of the precipitate was estimated from BET measurements which were made on some of the preparations of the Mn_3O_4 and βMnOOH at the end of the titrations. It was assumed that the area per unit weight was the same throughout the precipitation process. The area of surface thus derived was used to represent A_{Mnppt}. Activity coefficients for Mn^{2+} were computed from the Debye-Hückel equation and Mn^{2+} solution complexes were assumed to be absent.

Integrated forms of the autocatalytic rate equation, for testing experimental data, were published by MORGAN (1967) and by STUMM and MORGAN (1970). It was shown by the latter authors that a plot of

$$\log \frac{[Mnppt]}{[Mn^{2+}]_0 - [Mnppt]}$$

versus time yields a straight line when the autocatalytic mechanism is predominant and only the last term of eqn (2) needs to be considered. The activity of precipitated manganese was calculated from stoichiometry of the solution and would therefore be in terms of moles per liter. It is the equivalent of A_{Mnppt} in eqn (2). The activity of Mn^{2+} at time t is obviously equal to $[Mn]_0 - [Mnppt]$. The slope of the line could be used to compute an operational rate constant k_2', as described by WILSON (1980).

Also it follows from eqn (2) that when [Mnppt] becomes large and $[Mn^{2+}]$ small the former quantity will remain relatively constant over considerable

Table 1. Results of manganese oxidation rate experiments

Solution number	pH	Temp. °C	Avg Mn oxidn. state	Surface area m^2g^{-1}	Identified solid species	k_2''
K16	7.00	37.0	2.74	-	Hausmannite	$10^{-4.92}$
K15	7.50	37.1	2.63	-	do.	$10^{-3.78}$
K17	8.00	37.4	2.64	-	-	$10^{-3.10}$
K13	8.00	24.6	2.66	-	-	$10^{-4.42}$
K37	8.45	25.0	2.63	-	-	$10^{-3.64}$
K28	8.50	25.4	2.67	-	-	$10^{-3.50}$
K21	8.95	17.0	2.68	-	Hausmannite	$10^{-3.71}$
K24	8.50	17.0	2.67	48	do.	-
K33	8.00	10.0	2.87	-	βMnOOH, some hausmannite	$10^{-5.00}$
K32	8.50	10.0	2.83	-	βMnOOH, some hausmannite	$10^{-4.33}$
K31	8.50	0.5	3.01	-	βMnOOH	$10^{-4.65}$
K44	8.50	0.5	2.97	-	-	$10^{-4.90}$
K27	8.95	0.5	3.03	99	βMnOOH	$10^{-4.18}$
K30	9.00	0.5	3.03	-	do.	$10^{-4.30}$
K29	8.97	0.5	3.07	-	do.	$10^{-4.32}$
K36	9.01	0.5	3.02	83	do.	$10^{-4.39}$

(Units for k_2'' are liter sec.$^{-1}$ meter^{-2}.)

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periods of time even though $[Mn^{2+}]$ continues to decrease at a constant rate. This implies that the oxidation reaction should become psuedo first order with respect to dissolved manganese, if other factors do not change. This behavior has commonly been observed in laboratory and field systems (WILSON, 1980; LEWIS, 1976).

Natural aqueous systems in which manganese oxide deposition occurs are generally open systems where reactant activities are maintained by convective transport in moving water toward the oxide surface. It can be shown that one liter of ground water or soil moisture can come in contact with as much as $10^4 m^2$ of mineral surface while moving through a porous medium for a net distance of 1 m (HEM, 1977). Water flowing in an open stream channel carries suspended sediment and has a less intimate contact with surfaces in its bed and banks. When these facts are taken into account it is obvious that the role of the surface in mediating or promoting the reaction is vitally important and a kinetic expression in which surface area of precipitate appears directly is desirable. The form in which this factor appears in the STUMM and MORGAN (1970) expression is, in effect, as a concentration of solid surface in a litter of solution in a closed stationary reactor. For some natural systems such information is not conveniently available, nor is the concept of a closed system always realistic.

Reaction rate expressions that are more directly compatible with transport and mass-balance models of open natural aqueous systems can be developed from equations for precipitate accretion or crystal growth rates. Work published by NIELSEN (1964) and by NANCOLLAS (1968) for example, indicated such processes can be represented in general by the relationship

$$R\text{pptn} = k\,A\,S^n \tag{3}$$

when Rpptn is the rate of crystal formation, k is a rate constant, A is a measure of the availability of surface reaction sites and S is the degree of supersaturation in the solution phase. The exponent n represents the order of the reaction with respect to the solute of concern.

In the experimental solutions studied here the reaction

$$Mn^{2+} + 1/2\,O_2(aq) + 6OH^- = Mn_3O_4 + 3H_2O \tag{4}$$

as an equivalent process for the formation of feitknechtite can be evaluated from the recorder chart trace which shows the rate of OH^- addition. This rate should be double the rate of Mn^{2+} oxidation, assuming no feedback of reactants owing to disproportionation of Mn^{3+}. Specific surface area measurements by the BET procedure for precipitated oxide would represent the availability of surface reaction sites. The degree of supersaturation can be formally represented as a reaction affinity or chemical potential, or in a more simple form as the ratio of activity quotient of solutes at time t to the activity quotient at equilibrium. The latter is equal to the thermodynamic equilibrium constant. In this approach

$$S = \frac{Q_t}{K} - 1.$$

The reaction may stop before the activity quotient ratio attains a value of one, owing to an energy barrier that must be surmounted in the crystallization process.

Another approach to the evaluation of S that is appropriate for irreversible experimentally controlled systems is to equate it to the difference between the activity of an uncontrolled solute at time t and its limiting activity at equilibrium. (LIU and NANCOLLAS, 1970). In the experiments discussed here the only solute varying in activity is Mn^{2+}. During the period of the titration $[Mn]_t$ is always substantially greater than $[Mn]$ eq. It is therefore justifiable to postulate that S is directly proportional to $[Mn]_t$ in these experimental solutions.

The rate of precipitation of manganese oxide after an induction period during which a substrate of oxide surface is formed should therefore be predicted by the expression

$$\frac{\Delta\text{Mnppt}}{\Delta t} = k_2'' A_{\text{ppt}} [\text{Mn}]_t^n \tag{6}$$

In a rearranged logarithmic form

$$\log \frac{\Delta\text{Mnppt}}{\Delta t A_{\text{ppt}}} = \log k_2'' + n \log[\text{Mn}]_t. \tag{7}$$

Values for ΔMnppt/Δt were obtained by subdividing the pH-stat recorder trace into 10 min or shorter intervals. Experimental data plotted in this form should give a straight line of slope n and intercept log k_2''.

Data for seven experimental runs at various pH's and temperatures are plotted according to this procedure in Figs 1–3. In Figs 1 and 2, the points lie on or near straight lines of unit slope drawn on the graphs, except for the early part of the reaction. The points in Fig. 3 represent two experimental runs at 0.5°C, where the solid was βMnOOH. In the latter parts of both runs, the reaction order with respect to Mn^{2+} appears to increase to a value between 1.0 and 2.0, but the analytical data have greater uncertainty as concentrations became smaller, and the deviations from first order may be an artifact.

Rate constants are given in Table 1, as k_2'' for data treated in the manner used for preparing Figs 1–3, using a value of 1.0 for n.

DISCUSSION OF THE RESULTS

Values of k_2'' are in unconventional units and relate to the specific system from which they were derived. However, because volume of solution and total

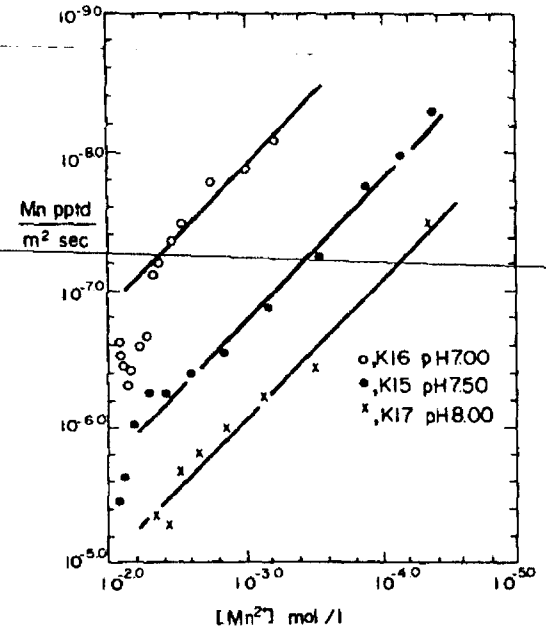

Fig. 1. Effect of dissolved Mn^{2+} activity and pH on manganese oxide precipitation rate at temperatures near 37°C.

amount of manganese were nearly the same in all these experiments, the constants should be comparable among themselves for indicating reaction order with respect to H^+ activity and to indicate effects of temperature on reaction rate.

Manganese precipitates formed at 37°C (Fig. 1) did not have average oxidation states above $Mn^{2.67+}$. The derived rate constants increase by about a factor of 100 between pH 7.0 and 8.0, which indicates an apparent second-order dependence on hydroxide ion activity in agreement with earlier work (HEM, 1964; MORGAN, 1967). Precipitates that were formed at 0.5°C (Fig. 3) had an Mn oxidation state near 3.00.

The effect of temperature on the manganese precipitation reaction is particularly interesting. In systems held at 25 and 37°C, the oxidation state of the precipitated manganese is near the the theoretical value for hausmannite in most instances, as indicated by data in Table 1. In a few of the precipitations made at these temperatures, feitknechtite could be detected by X-ray diffraction, but it always was present in only minor amounts, compared to the predominant hausmannite species.

When the reaction was carried on near 0°C, the oxidation state of the manganese precipitated was always nearly 3.0 and only βMnOOH could be detected by X-ray diffraction. At intermediate temperatures, especially between 10 and 20°C, the product was a rather unpredictable mixture, but βMnOOH was about half or a little more than half of the oxide precipitated at 10°C. Precipitations made at 17°C had a rather wide range of oxidation states and some exhibited rather poorly defined kinetic behavior.

KESSICK and MORGAN (1975) reported the synthesis of a manganese 3+ oxide at 25°C which was identified chemically as manganite. No determination of crystal structure was reported. Their experimental conditions were significantly different from those described here and the results cannot be directly compared.

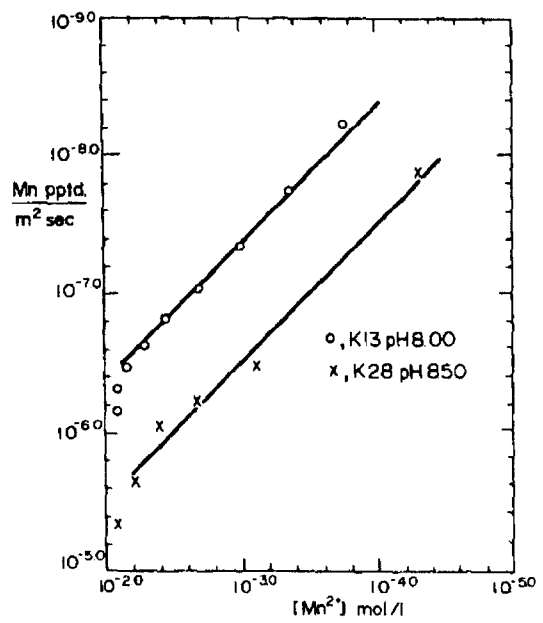

Fig. 2. Effect of dissolved Mn^{2+} activity and pH on manganese oxide precipitation rates at temperatures near 25°C.

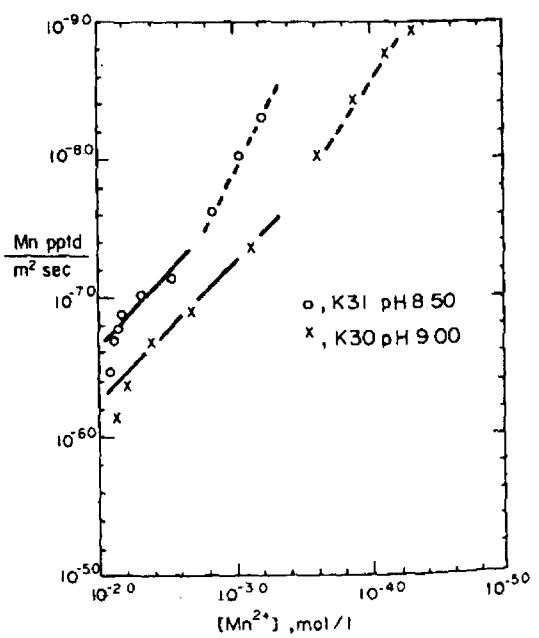

Fig. 3. Effect of dissolved Mn^{2+} activity and pH on manganese oxide precipitation rate at 0.5 C.

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Data in Table 1 show that the rate of precipitation of hausmannite is strongly influenced by temperature. The value of k_2'' for K17 at 37.4 C is about 20 times as great as the correspvonding value for K13 at 24.6 C. Both solutions were reacted at pH 8.0. An exactly matching pair for temperatures of 25 and 17 C is not available, but if the pH dependence of the rate at 25°C is second order, the calculated value for k_2'' at pH 9.0 would be near $10^{-2.5}$ and about 16 times as great as the k_2'' value given in Table 1 for K21 which represents 17.0°C and pH 8.95.

Direct comparisons for the kinetics of feitknechtite precipitation at different temperatures are less clear-cut because the material obtained at 10°C contained substantial amounts of hausmannite. However the two solutions, K32 and K31, show only an approximate doubling of the values for k_2'' between 0.5 and 10°C at pH 8.50. Between K32 and K44, there is nearly a 4-fold difference in the values for k_2''. The temperature effect for feitknechtite precipitation is therefore substantially less than that for hausmannite.

The precision of the determined k_2'' values is not sufficiently good to permit a meaningful calculation of activation energies and a part of the observed temperature effect stems from a decrease of OH^- activity with temperature at the selected pH values. However, it seems evident that a higher energy barrier is present in the hausmannite precipitation mechanism than exists for feitknechtite precipitation. A possible explanation for the predominance of the latter oxyhydroxide at 0.5°C may be derived from crystal structures of the oxide species and reaction paths that lead to them.

The first step in the precipitation process can be postulated as the deprotonation of aquo-Mn^{2+} ions which then polymerize to form macro ions having a sheet-like hexagonal structure, a precursor of pyrochroite and approaching the composition $Mn(OH)_2$. The very similar structure of βMnOOH would be reached with minimal disruption during the subsequent oxidation because all that is required is a loss of protons to maintain charge balance. The structure of hausmannite, however, is different and requires a greater degree of disruption (higher energy barrier) owing to a need for ejection of surplus water molecules. Thus one would predict that the rate of formation of Mn_3O_4 would be more strongly temperature dependent than that of βMnOOH, and the latter turns out to be kinetically favored below about 10°C.

In systems where a substantial area of mediating surface is present at the start of the reaction, A_{ppt} will remain nearly constant and a psuedo first-order mechanism may be dominant throughout. LEWIS (1976) observed first-order kinetics of Mn^{2+} precipitation with respect to dissolved Mn in the Susquehanna River in Pennsylvania. First-order kinetics were observed by HEM (1964) in laboratory systems containing feldspathic sand. Fig. 4 is a plot of log $[Mn^{2+}]$ vs time for experiments K29 and K44 (Table 1) showing straight-line relationships for the latter parts of the titrations. The slope indicates a half time of about 64 min and a psuedo first-order rate constant of $10^{-3.74}$ sec^{-1} for K44, and half time of 7.5 min and k of $10^{-2.81}$ for K29. These constants, it should be emphasized, are not equivalent to k_1 in eqn (2).

In natural systems where the available reactive surface area is in large excess, the pseudo first-order interpretation of our data suggests that the precipitation half-time could be as short as a few days for systems at neutral pH and a temperature of 10 to 15°C. Rate constants determined by LEWIS (1976) from his Susquehanna River data give half-times of about 1 day at 20°C and about 7 days at 5°C, at pH's near or a little below 7.0.

The potential growth rate of a manganese oxide deposit can be estimated from values for k_2'' and eqn (6) or (7). For example, a layer 0.1 mm thick of oxide

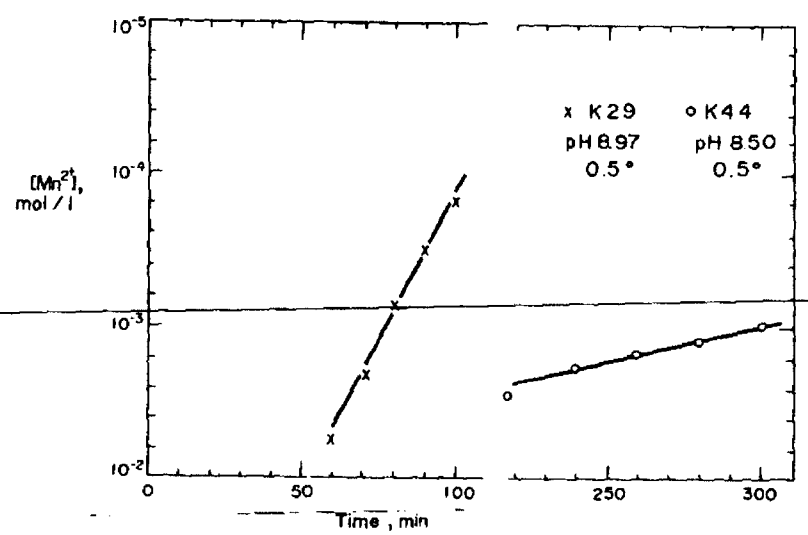

Fig. 4. Psuedo first-order kinetic behavior of manganese in two test solutions at 0.5°C.

on a square meter of pre-existing surface, assuming a density of 5.0 g/cc for the oxide, amounts to 500 g or 5.69 moles of MnOOH. The rate of precipitation per square meter per second at a dissolved Mn^{2+} activity of $10^{-8.0}$ M, at 0.5°C can be computed from data in Table 1. At a pH of 8.5, this rate will be $10^{-12.65}$ moles m^{-2} sec^{-1} assuming a first-order dependence on $[Mn^{2+}]$. The time required for this amount of growth is a little over 800,000 yr if it is assumed that the effective area of substrate is a constant 1 m^2 throughout the precipitation process.

Another factor in the growth rate is the rate at which reactants can be moved to the surface. In this system, it would be necessary to have a sufficient rate of movement of solution toward the surface to maintain the dissolved Mn^{2+} activity near $10^{-8.0}$. The thermodynamic stability of βMnOOH is probably similar to that of hausmannite and is certainly sufficient to give a substantial supersaturation at this Mn^{2+} activity, at pH 8.5, in water with a dissolved oxygen activity of $10^{-3.5}$ M, approximately the level attained in water in contact with the atmosphere. If the dissolved manganese activity in water leaving the reaction site is decreased to $10^{-8.50}$ M by oxide precipitation, the precipitation rate computed above can be sustained by water moving at the rate of about 3 mm per day. This flux should be relatively easy to attain, even in systems where circulation is sluggish. However, if the effective area of reacting surface per unit cross section of flow increases, the limiting flux will be greater. The rate of influx of reactants can easily become the major limiting factor on the precipitate growth rate.

In systems where water movement is rapid and the kinetics of precipitation are pseudo first-order, the flux rate may support accumulation of precipitate over an extensive surface area and, the zone of reaction in the system may be elongated in the main direction of water flow. In a surface stream, for example, there may be manganese oxide coatings on bed material for long distances downstream from points where Mn^{2+} is introduced.

The disproportionation of MnOOH to produce MnO_2, the final form of the oxide, must keep pace with the precipitation rate, and the feedback of Mn^{2+} that results probably will exert a catalytic effect that is not included in k_2'' (HEM, 1977).

Some of the foregoing computations require rather broad assumptions but they demonstrate that the rates of precipitation that were determined in our experiments are useful for evaluating some extremely slow reaction rates that may occur in natural environments. The influence of the disproportionation step in the reaction mechanism and probable catalysis effects related to coprecipitation of other transition-metal ions will be evaluated in continuing research.

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