

LETTER REPORT

TITLE: Review of "The Kinetics of the Oxidation of Ferrous Iron in Synthetic and Natural Waters," by W. Davison and G. Seed, Geochimica et Cosmochimica Acta 47, 67-79 (1983).

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PROJECT TITLE: Technical Assistance in Geochemistry

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SUMMARY

The rate law for the oxidation of Fe(II) to Fe(III) previously established for synthetic groundwater solutions was verified for the first time in a natural water. The anoxic water used in the experiments was taken from one of the most studied lakes in the world, Esthwaite Water, a eutrophic lake in Cumbria, U. K. Sample disturbance was minimal, as only oxygen was introduced to initiate the reaction. Analysis of errors in the measurements demonstrated that measurement of pH was the major source of inaccuracy. The best value of the rate constant determined in natural waters was indistinguishable from that measured in synthetic waters. The rate constant did not appear to be influenced by changes in microbial populations or by changes in particulate or soluble components in the water, including iron and manganese.

The present data, together with a comprehensive survey of the literature, suggest for pH 6.5-7.5 a value for the rate constant of  $2 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  in the rate law

$$-d[\text{Fe II}]/dt = k[\text{Fe II}]p_{\text{O}_2}(\text{OH}^-)^2,$$

where [Fe II] denotes the concentration of Fe(II) in mol/L,  $p_{\text{O}_2}$  the partial pressure of oxygen in atmospheres, and  $(\text{OH}^-)$  the activity of hydroxide ions.

REVIEW OF REPORT

There are many computer programs which model the transport of radionuclides from nuclear waste repositories in geological

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environments. The versatility of these codes has been enhanced in some cases by combining them with geochemical codes capable of estimating the equilibrium chemical composition of groundwater solutions. More sophisticated codes take non-equilibrium situations into account, but basic kinetic data are needed to develop the methodology further.

The article discussed here reports a study of the kinetics of oxidation of ferrous [Fe(II)] to ferric [Fe(III)] iron in natural and synthetic aqueous systems. Because iron is ubiquitous in natural systems, a number of investigations have been reported in the literature on the rate of oxidation of Fe(II). However, most of the published studies were carried out on synthetic solutions, and so the applicability of the rate law to field conditions could be questioned. No rate law had been derived previously for a natural water under controlled conditions. The primary aim of the present work, as stated by the authors, was to measure the rate of oxidation of Fe(II) in natural waters in the laboratory under conditions that were as close as possible to those operating in nature. Verification of the rate law by investigating the effect of pH, partial pressure of oxygen, the influence of natural solid phases, and changing microbial population, was attempted while maintaining natural conditions.

The anoxic water samples were taken from one of the most studied small lakes in the world, Esthwaite Water, a eutrophic lake in Cumbria, U. K. Since the water samples contained ferrous iron, but were devoid of oxygen, the experiments introduced oxygen to initiate the oxidation reaction. Measurements of the concentration of Fe(II) as a function of time were carried out at different values of constant pH in the range 6.5-7.4 and of oxygen partial pressure to verify the rate law most commonly quoted for oxidation of Fe(II) in synthetic solutions, near neutral pH:

$$-d[\text{Fe II}]/dt = k[\text{Fe II}]p\text{O}_2(\text{OH}^-)^2.$$

For convenience, [Fe II] is expressed as concentration in mol/L,  $p\text{O}_2$  as partial pressure of oxygen in atmospheres, and  $(\text{OH}^-)$  as hydroxide ion activity in units of mol/L. The use of  $\text{OH}^-$  activity stems from the measurement of solution pH, which closely approximates  $-\log(\text{H}^+)$ . Activity of  $\text{OH}^-$  may be obtained from the ionic activity product for water,  $K_w$ :

$$K_w = (\text{OH}^-)(\text{H}^+).$$

Experimental procedures are discussed in considerable detail and appear to be quite complete. Another valuable aspect of this paper is the extensive bibliography and discussion of related work.

The data obtained, together with data from other published experiments, were used to obtain a best value of the rate constant of  $2 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  for natural fresh waters in the pH range of 6.5-7.4. In their discussion of errors of measurement, the authors stress

the great sensitivity of this study to the determination of pH. With their calibrations, the authors propose that their precision and that of most other workers was likely to be in the range of  $\pm(0.02 - 0.05)$  pH units; however, if the "true" rate constant has a value  $2 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$ , an uncertainty in the pH of  $\pm 0.05$  pH unit can produce a range of values in the rate constant of  $(1.6 - 2.5) \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$ . Discrepancies of  $\pm 0.2$  pH unit would give rise to a range of values of about a factor of 6.

The indications of the present experiments, and of the best evidence from the literature quoted in the paper, suggest that the oxidation of Fe(II) to Fe(III) is described by the same rate expression in natural systems and in analogous synthetic solutions. The rate constant did not appear to exhibit variations from changes in microbial populations or from changes in particulate or soluble components in the water, including iron and manganese. This behavior may be contrasted with the well-documented influence of bacteria on iron oxidation processes below pH 4.5. Variations in ionic strength in the range of 0.009 - 0.11 M yielded small and contradictory effects on the rate constant in synthetic solutions. However, the rate constant in seawater at pH 8.0 is greatly reduced, presumably because of the very high ionic strength.

This paper is a valuable reference on the kinetics of the oxidation of ferrous iron in natural waters, not only because of the experimental data presented, but also because of the extensive bibliography and critical review of other published work.