

## KINETICS OF IRON(II) OXIDATION IN SEAWATER OF VARIOUS pH

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### ABSTRACT

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The rate of iron(II) oxidation in North Sea water of pH 5.5–10 in the range 10–25°C has been studied. The oxygenation rate depends linearly on the iron(II) and dissolved oxygen concentrations. The second-order dependence on  $[\text{OH}^-]$ , found by several investigators for synthetic solutions, was confirmed in seawater, but only for  $\text{pOH} > 6.9$ . For  $\text{pOH} < 5.9$  the rate appeared to be independent of the  $\text{pOH}$ . In the intermediate range,  $\text{pOH} 5.9\text{--}6.9$ , corresponding to the natural pH of seawater, a first-order dependence on the  $\text{pOH}$  is obeyed. The important discrepancy in the literature between the second-order rate constant for  $\text{NaCHO}_3$  solutions and for seawater can be attributed predominantly to the incorrect assumption of a second-order  $\text{pOH}$  dependence in natural seawater. The results can be useful, for example, in predicting the effect of dumping acidic iron waste from the titanium-dioxide industry into the ocean.

### INTRODUCTION

The chemistry of aqueous iron is of interest in drinking-water technology, limnology and oceanography, because of its considerable effects on a variety of environmental processes. Iron plays a unique role in many biological systems; its oxidation state changes are a significant factor in geochemical processes such as ore formation, and its tendency to form colloidal and particulate phases provides a mechanism for the removal of dissolved trace constituents by adsorption or coprecipitation. A quantitative knowledge of iron(II) oxidation is essential for an understanding of the many roles of iron in natural waters.

Although the oxygenation kinetics of iron(II) have been studied extensively for dilute aqueous solutions and mineral acids, the reaction rate in seawater has only been preliminarily investigated, by Kester et al. (1975) and Murray and Gill (1978), and their results differ considerably from the data for other media. Moreover, only the natural pH of seawater was considered.

This work reports on the iron(II) oxygenation rate in seawaters of various pH. It was carried out within the framework of a study on the influence on the seawater chemistry of the dumping into the Southern Bight of the North Sea of about 1000 tons per day of acidic iron waste, containing 20% sulfuric acid and 1.5% iron(II) (Van Grieken et al., 1980; Roekens and Van Grieken, 1983). It is only if the iron(II) oxygenation kinetics and the iron(III) solubility are known at every relevant pH that modelling of the acid dilution will

allow prediction of the seawater pH, the resulting turbidity and iron(III) hydroxide accumulation in the seawater, and also the eventual adsorption removal of trace elements and nutrients from the seawater.

In this context it was decided to study the kinetics of iron(II) oxygenation down to pH 4. This was, in practice, the lowest pH-value observed locally — a few seconds after the passage of the barge that discharges 10 tons of acidic iron waste per minute into its wake-water. This strong pH-depression (which was accompanied by locally high turbidity and an iron concentration up to  $13 \text{ mg l}^{-1}$ ) lasted for a very brief period only; more than one minute after the discharge a pH-level below 6 could nowhere be detected (Roekens and Van Grieken, 1983).

#### EXPERIMENTAL PROCEDURE

Seawater of 32‰ salinity was collected in Niskin bottles in the Southern Bight of the North Sea, some 20 km off the Belgian coast, an area where some 1000 tons of waste from the  $\text{TiO}_2$ -industry are dumped daily. The seawater was collected freshly, at most 30 h before all experiments.

Aliquots of 800 ml were transferred to 1 l beakers, which were equipped with a thermostatically controlled water jacket providing temperature adjustment to within  $0.2^\circ\text{C}$ . Air was bubbled through the water, and also  $\text{CO}_2$  for the experiments conducted at low pH. The oxygen saturation was checked with a dissolved-oxygen meter (Electronic Instruments Ltd.). The temperature was measured, and the pH was adjusted with dilute HCl or NaOH and controlled with a glass electrode.

A 0.01 to 0.1 M solution of Mohr's salt ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) was then injected to bring the initial Fe(II) concentration to  $0.5\text{--}10 \text{ mg l}^{-1}$ . In a few cases, partially neutralized acidic iron waste was added instead of Mohr's salt, to simulate better the conditions of waste disposal at sea. Some 30 series of experiments were carried out, in which the remaining Fe(II) concentration was measured as a function of time, in some 5 to 10 intervals after the Fe(II) addition. In each of about 200 experiments a 10 ml aliquot was taken from the sample and the oxidation reaction was immediately quenched by adding 10 ml of ammonium acetate buffer to reduce the pH to about 4. In all these aliquots Fe(II) was determined after filtration by spectrometry at 533 nm after addition of bathophenanthroline as a highly specific reagent (American Public Health Association et al., 1971; Koenings, 1976).

#### RESULTS AND DISCUSSION

It has long been recognized that the oxidation of Fe(II) to Fe(III) at neutral pH in  $\text{NaHCO}_3$  and other dilute solutions proceeds according to the following kinetic law (Just, 1908, Stumm and Lee, 1960; Schenck and Weber, 1968; Morgan and Birkner, 1968; Singer and Stumm, 1970; Ghosh, 1974; Tamura et al., 1976):

$$-\frac{d[\text{Fe(II)}]}{dt} = k_2 [\text{Fe(II)}] p_{\text{O}_2} [\text{OH}^-]^2 \quad (1)$$

where  $[\text{Fe(II)}]$  denotes the concentration of total ferrous iron,  $p_{\text{O}_2}$  is the partial pressure of oxygen in solution and  $[\text{OH}^-]$  denotes the hydroxyl ion concentration. The literature values of the rate constant  $k_2$  are discussed below. The first-order dependence on  $p_{\text{O}_2}$  and  $[\text{Fe(II)}]$  in  $\text{NaHCO}_3$  solutions appears to be a characteristic feature of the reaction, but not in a highly acidic medium ( $\text{pH} < 2$ ) where the rate is second order with respect to  $[\text{Fe}^{2+}]$  (George, 1954). The second-order dependence on  $[\text{OH}^-]$  has been reported to persist down to  $\text{pH}$  4–5, but the rate seems to be rather independent of the acidity below  $\text{pH}$  3–4 (Stumm and Lee, 1961; Singer and Stumm, 1970). Several complex reaction mechanisms have been proposed to explain all these characteristics (Weiss, 1935; Abel, 1955; Goto et al., 1970; Kester et al., 1975). None of these features has been confirmed for seawater, and, in particular, the  $\text{pH}$  dependence of the reaction rate has never been studied.

Some illustrations of our experimental results at  $15^\circ\text{C}$  are represented in Fig. 1. Since eq. 1 can be rewritten as

$$R = -\frac{d \ln [\text{Fe(II)}]}{dt} = k_2 \cdot p_{\text{O}_2} \cdot [\text{OH}^-]^2 \quad (2)$$

the values of  $\ln[\text{Fe(II)}_t]/[\text{Fe(II)}_{t=0}]$  should vary linearly with the time  $t$ , if a first-order dependence on  $[\text{Fe(II)}]$  is obeyed. This appears to be the case.

A set of curves such as in Fig. 1 can be used to derive the value of  $k_2$  and to check the second-order dependence of the oxygenation rate on  $[\text{OH}^-]$ . Indeed, eq. 1 or 2 can also be written as

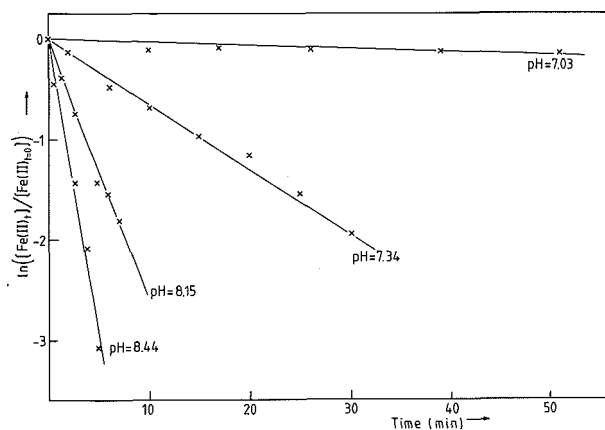


Fig. 1. Decay ratio of  $\text{Fe(II)}$  by oxygenation; a few examples of experimental results at different  $\text{pH}$ , at oxygen saturation

$$\log(R/p_{O_2}) = \log k_2 - 2pOH \quad (3)$$

and plotting the left side of eq. 3 versus the corresponding pOH leads to both  $k_2$  and the order of  $[OH^-]$ -dependence.

Table I lists the results of all 30 series of measurements on the  $[Fe(II)]$ -decay with time, for various temperatures and pH-values. Except when indicated otherwise, the experiments were carried out in solutions saturated with oxygen by air bubbling and involved the addition of Fe(II) as Mohr's salt. In Fig. 2, the values of  $\log[R/p_{O_2}]$  are plotted versus pOH for all these experiments. The pOH-values were calculated from the measured pH's using the  $pK_w$  values of 14.53, 14.35, 14.17, 14.00 at 10, 15, 20 and 25°C, respectively.

Although the dependence on  $p_{O_2}$  has not been studied in detail since marine surface waters are usually saturated with  $O_2$ , the few experimental points in Fig. 2 that correspond to a lower  $p_{O_2}$  do not seem to deviate systematically; the first-order dependence on  $p_{O_2}$  is thus respected. Also, there is no difference between the results of experiments where Fe(II) was

TABLE I

Results of experiments on the oxygenation rate of Fe(II) at varying temperature and pH, with  $R = -d\ln[Fe(II)]/dt$  (see text). The solutions were saturated with  $O_2$  ( $p_{O_2} = 0.19-0.22$ ) except when indicated otherwise. Fe(II) was added as Mohr's salt, except when indicated otherwise

pH	Measured $R/p_{O_2}$	pH	Measured $R/p_{O_2}$
$T = 15^\circ C$		$T = 10^\circ C$	
5.96	0.00067	7.36 <sup>a</sup>	0.153
6.74	0.0028	7.65	0.216
7.03	0.011	7.81 <sup>a</sup>	0.372
7.20	0.020		
7.32	0.097	$T = 20^\circ C$	
7.34	0.267	7.22 <sup>a</sup>	0.246
7.37	0.425	7.49 <sup>a</sup>	0.365
7.48 <sup>a</sup>	0.186		
7.65 <sup>b</sup>	0.238	$T = 25^\circ C$	
7.70	0.652	5.45	0.00020
7.80	0.708	6.86	0.216
7.96 <sup>c</sup>	1.139	6.87 <sup>a</sup>	0.204
8.15	1.225	7.14	0.432
8.44	2.460	7.29 <sup>a</sup>	0.469
8.50	3.191	7.50	0.843
9.36	2.171	7.72	1.090
		9.04	4.88
		9.85	2.69

<sup>a</sup>Fe(II) added in the form of acidic iron waste.

<sup>b</sup> $p_{O_2} = 0.17$ . <sup>c</sup> $p_{O_2} = 0.10$ .

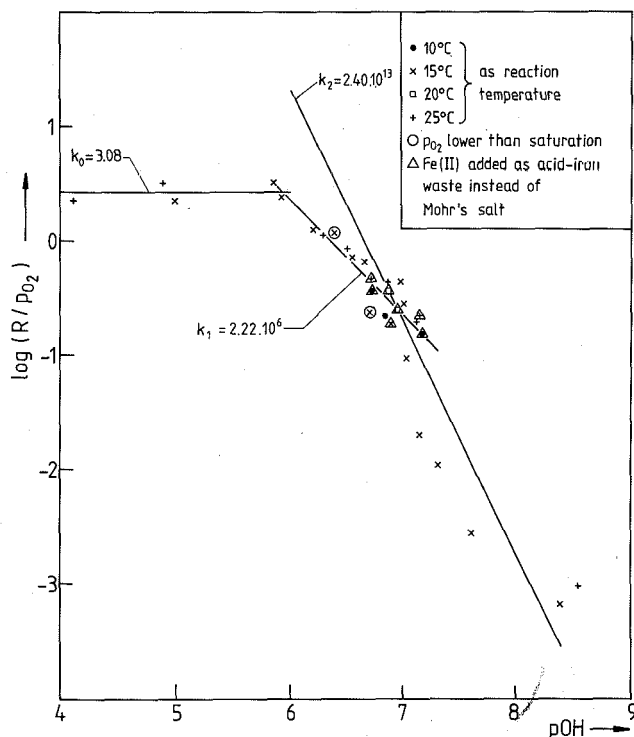


Fig. 2. Results of oxygenation rate experiments as a function of pOH.

added as analytical grade Mohr's salt and those involving typical acidic iron waste addition. Hence, the waste does not contain components that increase or lower the oxygenation rate significantly. Also, in the data in Fig. 2 no temperature influence can be observed. The strong effect of the water temperature (a 15°C temperature increase has been reported to increase the reaction rate for a given pH by a factor of about ten (Stumm and Lee, 1961; Sung and Morgan, 1980)) can fully be accounted for by the variation of  $[\text{OH}^-]$  with temperature for a given pH, owing to the temperature variation in  $K_w$ .

The most important result is that not only at low pH does the reaction rate deviate strongly from the second-order dependence on  $[\text{OH}^-]$ , but also at high pH. The rate appears to become independent of the pH for  $\text{pOH} < 5.9$ , corresponding to  $\text{pH} > 8.4$  for seawater at 15°C, and can be expressed as

$$-\frac{d[\text{Fe(II)}]}{dt} = (3.1 \pm 0.5) [\text{Fe(II)}] p_{\text{O}_2} \quad (4)$$

In the interval  $\text{pOH} 5.9\text{--}6.9$  or  $\text{pH} 7.4\text{--}8.4$ , i.e. in natural seawater, the rate can probably best be described by

$$-\frac{d[\text{Fe(II)}]}{dt} = (2.2 \pm 0.2) \times 10^6 [\text{Fe(II)}] p_{\text{O}_2} [\text{OH}^-] \quad (5)$$

From this, the half-life,  $\tau_{1/2}$ , the interval during which the Fe(II) concentration decreases by a factor of 2, in North Sea water of  $p_{\text{O}_2} = 0.21$ , is given by

$$\log \tau_{1/2} = \text{p}K_w - \text{pH} - 5.82 \quad (6)$$

At pH 8.3,  $\tau_{1/2}$  is thus around 1.1 min and 2.6 min at 20°C and 10°C, respectively, and for pH 7.9,  $\tau_{1/2}$  is 2.8 min and 6.5 min at 20°C and 10°C, respectively. The relative standard deviation is around 10% in all cases. These values are in good agreement with those of Kester et al. (1975), who found a  $\tau_{1/2}$  of 5.5 min and 3.3 min for water from the Narragansett Bay and Sargasso Sea, and those of Murray and Gill (1978) who reported  $\tau_{1/2} = 3.9$  min for Puget Sound seawater. In North Sea water of pH 8.0 at 25°C we find a  $\tau_{1/2}$  of 1.5 min while Sung and Morgan (1980) reported a  $\tau_{1/2}$  in the order of 1 min for 0.50 M NaCl or 0.165 M Na<sub>2</sub>SO<sub>4</sub>.

Only for  $\text{pOH} > 6.9$  does eq. 1 seem to be followed strictly, and truly second-order dependence on  $[\text{OH}^-]$  persists. We find

$$k_2 = (2.4 \pm 0.4) \times 10^{13} \text{ min}^{-1} \text{ atm}^{-1} \text{ mol}^{-1} \text{ l}^2$$

This implies that, for pH 7, the  $\tau_{1/2}$  is 158 min, 68 min, 30 min and 13.7 min, for  $T = 10, 15, 20$  and 25°C respectively, and that it increases by one order of magnitude for an increase in pH of 0.5 unit. As seen in Table II, this  $k_2$ -value is comparable to literature data for dilute sodium bicarbonate and acetate media. A quantitative agreement is not expected because the rate is influenced by: (1) the oxidants used: the reaction is five times faster with air than with oxygen (Shigematsu et al., 1975); (2) the ionic strength, the alkalinity and the presence of anions such as  $\text{ClO}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  which retard the reaction (Stumm and Lee, 1961; Tamura et al., 1970; Liang and Kester, 1977; Sung and Morgan, 1980); (3) trace metal cations such as  $\text{Cu}^{2+}$  which catalyse the reaction (Stumm and Lee, 1961) and (4) the presence of organic material (Theis and Singer, 1974). The  $k_2$ -values reported for seawater by Kester et al. (1975) and Murray and Gill (1978) are thirty times lower than our value, but these authors have erroneously assumed eq. 1 to be valid at the pH of natural seawater. Their  $k_2$ -results are therefore not quite meaningful. If in our results, a second-order curve, which is valid only for  $\text{pOH} > 6.9$ , would also be used in the  $\text{pOH}$ -range of natural seawater, a  $k_2$ -value of  $8 \times 10^{11}$  to  $90 \times 10^{11}$  would be calculated, for  $T = 25^\circ\text{C}$  and pH 8.3 to  $T = 10^\circ\text{C}$  and pH 7.9. The difference, by a factor of 1 to 10, with the data of Kester et al. (1975) and Murray and Gill (1978) could well be attributed to a difference in the organic matter type and content in the water samples (Theis and Singer, 1974).

TABLE II

Literature values for the reaction constant  $k_2$  in eq. 1

Temperature (°C)	$k_2$ ( $\text{min}^{-1} \text{atm}^{-1} \text{mol}^{-1} \text{l}^2$ )	Examined pH range	Medium	Oxidant	Reference
10-25	$2.4 (\pm 0.4) \times 10^{13}$	Applicable for 6.1-7.6	North Sea water; 32‰ salinity	air	This work
20	$6 \times 10^{11}$	7.9-8.3	Narragansett seawater; 31.2‰ salinity	n.g.	Kester et al., 1975
20	$10 \times 10^{11}$	8.2	Sargasso seawater; 36‰ salinity	n.g.	Kester et al., 1975
n.g. <sup>a</sup>	$8.9 \times 10^{11}$	8.0	Puget Sound seawater	air	Murray and Gill, 1978
25	$5 (\pm 0.4) \times 10^{13}$	5.5-7.2	$\text{NaHCO}_3$ ; $2.8$ to $4.1 \times 10^{-2} \text{ eq l}^{-1}$	oxygen	Ghosh, 1974
25	$2.1 (\pm 0.5) \times 10^{13}$	6.6-7.1	$\text{NaHCO}_3$ ; $3$ to $5 \times 10^{-2} \text{ eq l}^{-1}$	oxygen	Schenk and Weber, 1968
20	$8 (\pm 2.5) \times 10^{13}$	6-7.5	$\text{NaHCO}_3$ ; $2.9$ to $3.9 \times 10^{-2} \text{ eq l}^{-1}$	oxygen	Stumm and Lee, 1961
25	$14 (\pm 5) \times 10^{13}$	6-7.5	$\text{NaHCO}_3$ ; $2.9$ to $3.9 \times 10^{-2} \text{ eq l}^{-1}$	oxygen	Stumm and Lee, 1961
5-30	$10^{(13.76-2.06\sqrt{t})}$	6.5-7.2	$\text{NaHCO}_3$ ; $9 \times 10^{-3} \text{ eq l}^{-1}$	air	Sung and Morgan, 1980
25	$2.7 \times 10^{13}$	5.4-6.5	$\text{CH}_3\text{COONa}$ ; $4 \times 10^{-2} \text{ eq l}^{-1}$	oxygen	Shigematsu et al., 1975
25	$12.2 \times 10^{13}$	5.8-6.5	$\text{CH}_3\text{COONa}$ ; $4 \times 10^{-2} \text{ eq l}^{-1}$	air	Shigematsu et al., 1975

n.g. = not given.

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