Kinetics of the Iron(II)- and Manganese(II)-Catalyzed Oxidation of S(IV) in Seawater with Acetic Buffer: A Study of Seawater Desulfurization Process

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Ⓢ Supporting Information

ABSTRACT: Kinetics of iron(II)- and manganese(II)-catalyzed oxidation of S(IV) in seawater were studied here to provide theoretical support for the flue gas desulfurization process (SFGD). Experiments were carried out with artificial seawater and acetic buffer. Results indicated that the reaction order with respect to dissolved oxygen is zero. However, the reaction order with respect to S(IV) is variable: second-order under uncatalyzed condition ($4.0 \leq pH \leq 7.0$); first-order under Fe(II)-catalyzed oxidation ($2.5 \leq pH \leq 3.5$); first-order ($4.0 \leq pH \leq 5.0$) and second-order ($5.5 \leq pH \leq 5.9$) under Mn(II)-catalyzed oxidation. The different S(IV) dependence could be attributed to different metal speciation at different pH values. Also, acetate is found to have significant inhibition effect on Mn(II)-catalyzed oxidation in high ion strength solution. The strong catalytic effect of Fe(II) and Mn(II) ions on S(IV) oxidation could lead to new ideas for the design of SFGD systems.

1. INTRODUCTION

The oxidation of sulfur(IV) oxides is an extremely complicated chemical process. Various oxidants (O_2,[1−5] O_3,[6] H_2O_2,[7] high valence metal ions,[8] free radicals,[7,9,10] etc.), catalysts (Fe,[8,11−16] Mn,[16−19] Cu,[20] Co,[4,21,22] Cr,[23] Cd,[23] V,[23] etc.), and inhibitors (NH_4^+,[20] organic acid,[15,24−30] alcohols,[31] etc.) could be involved in S(IV) oxidation processes under homogeneous or heterogeneous conditions. The oxidation process of S(IV) plays an important role in both atmospheric chemistry[32] and flue gas desulfurization (FGD) process. Since the 1960s, many researchers have focused on the kinetics and mechanism of the S(IV) oxidation process due to the increasingly urgent problem of acidic deposition on the global scale, and many papers have been published in this area. But until now, a general accepted understanding is still missing, and reports from different groups sometimes showed different or even contradictory results.

Under homogeneous conditions, the reported reaction order with respect to S(IV) differs from 0,[19] 1,[1,18,29] 1.5,[5,22] and 2,[2,20]and Grgić et al. found different dependence with the existence of different metal ions.[33] Most of the previous studies found no dissolved oxygen dependence in both uncatalyzed and catalyzed oxidation. But there are exceptions, for example, 0.5 reported by Zhang[2] and 1 reported by Prasad.[34] The pH dependence was also studied by a number of researchers, and the results are also quite different from each other.[1,2,17,19,35] The most complicated issue of the S(IV) oxidation process is the catalytic and redox effects of different transition metals. Among all kinds of transition metals, Fe and Mn are most intensively studied. It is generally believed that trace amounts of these two kinds of metals in aqueous solution have significant catalytic effect on S(IV) oxidation.[18,36,37] It is evident that the

S(IV) oxidation process runs through complicated chain mechanisms.[8,11,18,38] But it might go through a nonradical pathway when free radical scavengers (ethanol, oxalate, etc.) exist.[20] As a result, the oxidation process follows different pathways under different conditions, and more than one pathways might run in parallel.[32]

The understanding of the S(IV) oxidation process is very important for designing flue gas desulfurization systems. The seawater flue gas desulfurization process (SFGD) for power plants along the coast which utilizes seawater to scrub SO_2 in flue gas has been established since the 1970s. A typical SFGD process consists of three steps:[1,39] (1) flue gas contacts with seawater in a scrubber; (2) the effluent seawater from the scrubber (pH = 2−3) is diluted with fresh seawater and then pumped to an aeration basin where the absorbed S(IV) can be oxidized to sulfate; (3) the effluent of aeration basin is further neutralized to pH = 6.8 in a neutralization basin downstream by adding fresh seawater[1] or magnesium hydroxide.[39] Finally, the liquid waste is cooled down and discharged back to the sea. Compared to the wet limestone process, SFGD has two main advantages: (1) because seawater itself is alkaline (pH 7.5−8.3), alkaline absorbent is not necessary in the scrubber, and (2) the effluent seawater treatment process is much simpler, as only a simple aeration basin is needed to oxidize S(IV) to S(VI), a natural component of seawater.[1,40,41] To date, many countries, including Norway,[42,43] Malaysia, Indonesia, Saudi Arabia,[44] and China,[39,45−47] have installed SFGD technology.

Although much relevant research on S(IV) oxidation in homogeneous conditions has been presented, there are few reports concentrating on the S(IV) oxidation in seawater environment. The aim of this project is to study the kinetics of the S(IV) oxidation process in seawater, especially focused on the catalytic effect of Fe(II) and Mn(II). Our previous work[47] indicated that using seawater to scavenge SO_2 in flue gas is a combination of neutralization and oxidation. Some transition metal ions in seawater may play very important roles in the SFGD process.

Many previous studies did not use pH buffer in homogeneous conditions, and some authors found no pH dependence on the initial pH.[19] But it is evident that SO_3^{2-} is more easily oxidized by oxygen than HSO_3^-. Moreover, pH has an important effect on the solvolysis of transition metal ions in aqueous solution.[32,35] In the SFGD process, the initial S(IV) concentration level is relatively high (0.5−2 mM), which could result in dramatic pH decrease during the oxidation process without pH buffer. Dibasic acid is often used to buffer pH in limestone scrubbers, and many dibasic acids can act as strong inhibitors in catalyzed S(IV) oxidation process.[25,30] Different from dibasic acids, acetic acid is a kind of weak inhibitor for S(IV) oxidation, and the inhibition effect of acetic acid has already widely been studied.[19,25] For this reason, the kinetic studies in this project were carried out in artificial seawater and using acetic buffer.

2. MATERIALS AND METHODS

2.1. Experimental Procedure and Materials. The experimental system for kinetic study is shown in Figure 1.
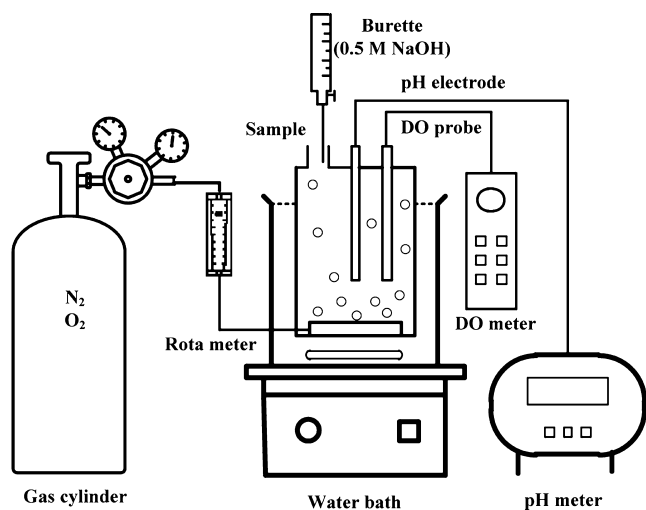
Figure 1. Schematic diagram of the experimental apparatus.

The reactions were conducted in a 2 L glass cylinder reactor, which was placed in a thermostatic water bath. The cylinder contained a gas diffuser at the bottom; a pH electrode and a dissolved oxygen (DO) probe were placed in the top of the reactor; the sampling port was open to the air, and solution was also injected through this port before each experiment.

To eliminate the trace amount of transition metals with catalytic or redox effects in real seawater, we used artificial seawater (salinity = 34 ‰) in our study. The components of artificial seawater are shown in Table 1. To study the catalytic effects, precise amounts of Fe(II) (5−20 μM) or Mn(II) (20−60 μM) were added into the artificial seawater.

Table 1. Artificial Seawater Characteristics

components	concentration (mg/L)
HCO_3^-	130
SO_4^{2-}	4000
Cl^-	18000
Na^+	10800
Ca^{2+}	420
Mg^{2+}	1200
K^+	400

In advance of each experiment, 0.2% saturated sodium acetate solution was added into the artificial seawater as pH buffer. In some cases, pH might still decrease a few tenths of a value during the several 10 minutes of the reaction process. For this reason, pH can be manually adjusted by 0.5 M NaOH to make sure its fluctuation is less than ±0.1.

For the study of DO dependence, feed-gas cylinders containing different ratios of O_2/N_2 gas mixture were connected to the gas diffuser in the reactor. The flow rate was controlled by a rotor meter to obtain suitable aeration intensity; thus, no stirrer was needed. The thermostatic water bath was used to maintain a desired temperature level (15−50 ± 0.1 °C).

When the artificial seawater with sodium acetate buffer was injected into the reactor, the gas valve was opened for several minutes stabilization, and then 2 mL of 20 M S(IV) solution was added into the reactor, the reaction was initiated immediately. In this study, the induction period[12,14,18] of catalyzed S(IV) oxidation should be avoided, so the samples were taken 2 min after the S(IV) was added. Therefore, it is not possible to maintain the same initial S(IV) concentration for every single experiment, so the measured initiate S(IV) concentration ranged from 0.5 to 2.0 mM for all experiments in this study.

Manganese(II) chloride (Aladdin, 99.99% metals basis) and ammonium iron(II) sulfate hexahydrate (Aladdin, GR grade) was used to prepare 20 mM Mn(II) and Fe(II) storage solution in deionized water; all the other chemicals used were reagent grade, and their solutions were prepared in deionized water. Because EDTA can strongly chelate with some transition metal ions, in the study of uncatalyzed oxidation, 1 μM EDTA was added in the artificial seawater as chelating agent in order to minimize the influence of some undesirable trace metal ions.

Gas pressure was measured by pressure gauge with a range of 0−0.5 MPa. pH value was measured by a pH meter (Shanghai Precision & Scientific Instrument Co., LTD, China) with the range of 0−14 and accuracy of ±0.01. DO was measured by HQ30d portable meter with LDO101 dissolved oxygen probe (HACH, USA). For aqueous S(IV) analysis, samples were diluted 25 times, pH was adjusted below 2.0 using 1 M HCl, and then the samples were analyzed by a Dionex ICS-1100 ion chromatography (Dionex AS14 column, conductivity detector), in which the quantitative detection limitation is 0.1 mg/L.

2.2. Kinetic Methods. The reaction rate can be described by the equation

$$r = -\frac{d[S(IV)]}{dt} = k[O_2]^\alpha [S(IV)]^\beta [M]^\gamma \tag{1}$$

where α, β, and γ are the partial reaction orders with respect to dissolved oxygen, total S(IV) concentration, and transition metal concentration (Fe(II), or Mn(II) in this study),

respectively, and k is the kinetic constant, which could be a function of temperature and proton concentration.[1,2]

In the experiments with constant DO concentration and without Fe(II) or Mn(II) added, the oxidation rate could be expressed in the following way:

$$r = -\frac{d[S(IV)]}{dt} = k'[S(IV)]^{\beta} \tag{2}$$

The reaction order with respect to S(IV) can be determined by this method. For the study of oxygen dependence, the k' values under different DO concentrations were determined. The α value can be determined by the $\ln k' - \ln[DO]$ plot under certain pH value.

3. RESULT AND DISCUSSION

3.1. Dissolved Oxygen Dependence. Figure 2 illustrates the typical [DO] variation during Fe(II)-catalyzed oxidation.
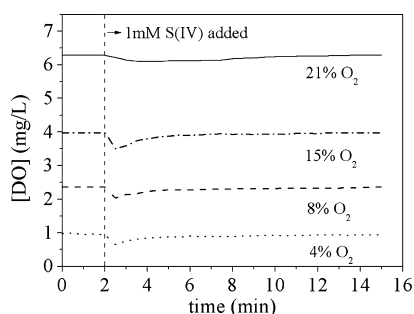

Figure 2. DO variation at different O_2 concentration in feeding gas with 5 μM Fe(II) added in artificial seawater, T = 35 °C.
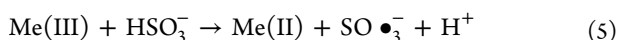
When S(IV) was added, DO concentration dropped immediately and then gradually recovered in approximately 2 min. The initial [DO] drop is attributed to the induction period which is reported by many researchers.[12,14,18] The reactive intermediates, such as Fe(III)−sulfito complexes, are rapidly generated during the induction period.[8] Except for the induction period, the DO fluctuations were less than 5%. In uncatalyzed circumstances, [DO] drop was also observed but not significant; see details in the Supporting Information.

Most published S(IV) oxidation mechanisms are based on the early work reported by Backström.[48,49] In the study of homogeneous transition metal catalytic effects, Berglund et al.[18] concluded that only metal ions with at least two oxidation states have significant catalytic effect. Brandt et al.[8] proposed a redox cycling mechanism for the transition metal-catalyzed oxidation of S(IV); some of the simplified reactions are given below (Me represents metal ions with two valence states).
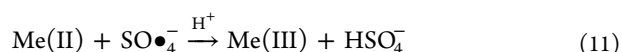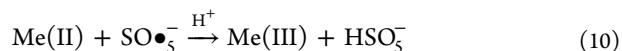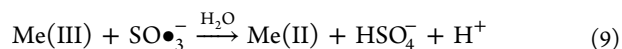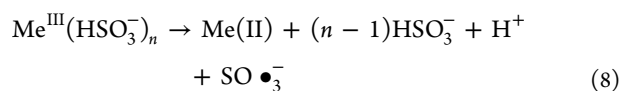
Initiation:

$$Me(II) + O_2 \rightarrow Me(III) + O_2^- \tag{3}$$

$$Me(II)(HSO_3^-)_n + O_2 \rightarrow Me(III)(HSO_3^-)_n + O_2^- \tag{4}$$
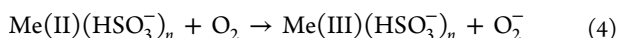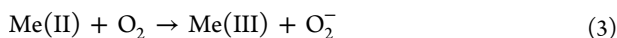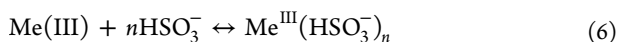
Berglund et al.[18] argued that because reactions 3 and 4 are energy unfavorable, the oxidation actually initiates by trace impurities in water, such as Fe(III):

$$Me(III) + HSO_3^- \rightarrow Me(II) + SO\bullet_3^- + H^+ \tag{5}$$

The redox cycling of transition metal:

$$Me(III) + nHSO_3^- \leftrightarrow Me^{III}(HSO_3^-)_n \tag{6}$$

$$SO\bullet_3^- + O_2 \rightarrow SO\bullet_5^- \tag{7}$$

$$Me^{III}(HSO_3^-)_n \rightarrow Me(II) + (n-1)HSO_3^- + H^+ \\ + SO\bullet_3^- \tag{8}$$

$$Me(III) + SO\bullet_3^- \xrightarrow{H_2O} Me(II) + HSO_4^- + H^+ \tag{9}$$

$$Me(II) + SO\bullet_5^- \xrightarrow{H^+} Me(III) + HSO_5^- \tag{10}$$

$$Me(II) + SO\bullet_4^- \xrightarrow{H^+} Me(III) + HSO_4^- \tag{11}$$

In our case, all Fe(III) and Mn(III) came from the "redox cycling" of Fe(II) and Mn(II). Because oxygen is continuously supplied, pseudosteady state of Me(III)−sulfito complexes could established after the induction period. In that case, catalyzed S(IV) oxidation rate should be determined by the formation and decomposition of Me(III)−sulfito complexes.

Most published mechanisms presented that the oxygen consumption step is reaction 7. This reaction is very fast (k = $1.1-1.5 \times 10^9$ s^{-1}). Chen and Barron[22] suggested that this reaction is not the rate-determining step in the S(IV) oxidation mechanism . Brandt et al.[8] proved that the rate of reaction 7 is determined by the formation of $SO\bullet_3^-$, rather than O_2 concentration. The plot of $-\ln k'$ versus $\ln[DO]$ in this study is illustrated in Figure 3 (uncatalyzed), Figure 4 (10 μM
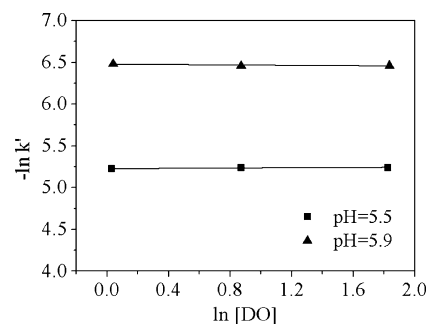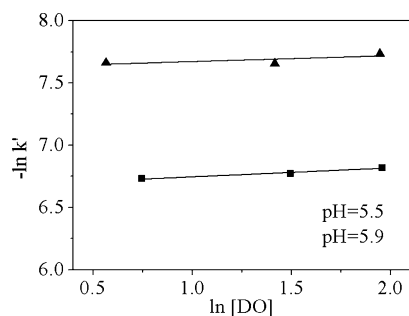

**Figure 3.** $\ln k'$ versus $\ln[DO]$ for the uncatalyzed S(IV) oxidation at T = 35 °C.
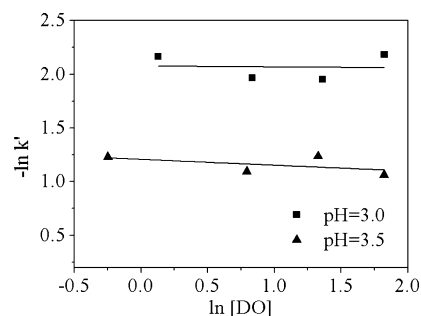
Figure 4. $\ln k'$ versus $\ln[DO]$ for the Fe(II)-catalyzed S(IV) oxidation with 10 μM Fe(II) added at T = 35 °C.

Fe(II) added), and Figure 5 (60 μM Mn(II) added). The results turn out that the DO concentration is independent of the determined kinetic constant. The reaction order with respect to dissolved oxygen is zero, which coincides with most previous studies. Although the result show no dependence of [DO] on the kinetics, maintaining sufficient O_2 will still be required in the aeration basin.

Figure 5. ln k' versus ln[DO] for the Mn(II)-catalyzed S(IV) oxidation with 60 μM Mn(II) added at $T = 25$ °C.

3.2. Uncatalyzed Oxidation.

The reaction order with respect to S(IV) in artificial seawater under uncatalyzed condition without Fe(II) and Mn(II) is discussed in this section. Figure 6 is the plot of reciprocal of S(IV) concentration
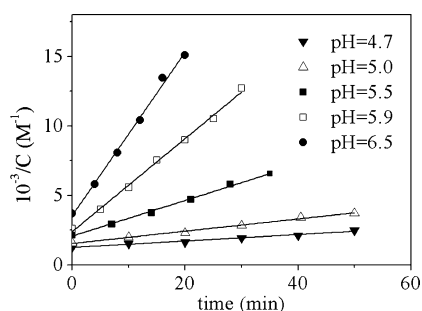
Figure 6. Second-order fitting for the uncatalyzed oxidation at $T = 25$ °C.

versus time at different pH values. It is clearly indicates that the reaction order with respect to S(IV) is second, and the oxidation rate increases dramatically with the increase of alkaline in the solution. Experiment data at pH < 4.7 were not included in this study because the oxidation rate is too slow to be measured. Figure 7 is the log(k) versus pH plot at different temperatures. Maximum oxidation rate can be found at the pH around 6.5, which is in accordance with Zhang's report.[2]
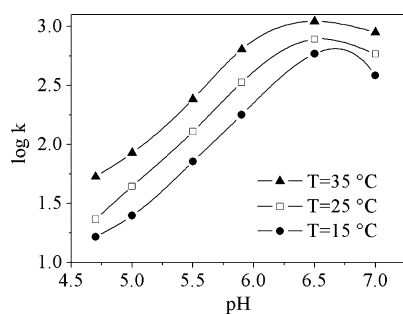

Figure 7. Log(k) vs pH at different temperatures in uncatalyzed conditions.

Natural seawater may contain many trace elements which could change the oxidation kinetics; therefore, studies using natural seawater from different regions with different quality could cause significant conflict results among researchers.[50,51] Some researchers argued that the "uncatalyzed oxidation" might not happen at all in pure water without any trace amount of transition metal ions,[3,16] but in this theory it is difficult to

explain why the reaction rate is very sensitive to pH in most of the uncatalyzed studies. In this study, it is evident that the trace transition metal ions in natural seawater play a very important role in S(IV) oxidation, because the reaction rate of uncatalyzed oxidation determined in this study is much slower than that in Vidal and Zhang's reports, which was determined in natural seawater.[1,2] The determined k values are available in Table S1, Supporting Information.
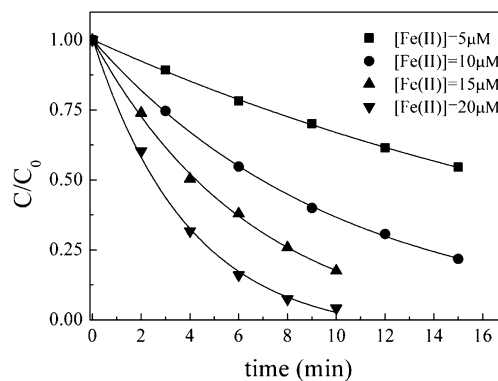
3.3. Fe(II)-Catalyzed Oxidation.

Fe(II)-catalyzed S(IV) oxidation was studied with the initial Fe(II) concentration ranging from 5 to 20 μM. Figure 8a illustrates the linear
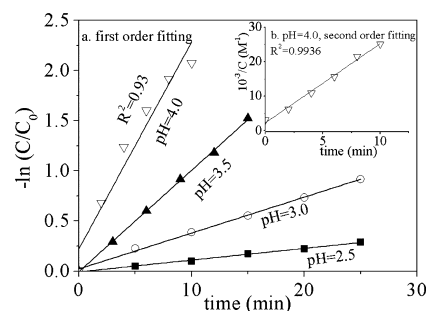
Figure 8. Reaction order with respect to S(IV) of Fe(II)-catalyzed oxidation at $T = 25$ °C and [Fe(II)] = 10 μM.

dependence between ln(C/C_0) and time. At the pH ranging from 2.5 to 3.5, first-order dependence is observed. But at a higher pH of 4.0, second-order fitting has a better agreement to the experimental data (compare with Figure 8b). The variation of reaction order may be attributed to the change of distributions of Fe(II), Fe(III) species, and Fe(III)−sulfito complexes at different pH values. This phenomenon is more obvious in Mn(II)-catalyzed oxidation (see section 3.4 below) because the solubility of Fe(III) is very sensitive to pH. Under our experimental conditions, precipitation would take place when the experiments were carried out under pH ≥ 4.0 condition. For this reason, our experiments were carried out under pH ranging from 2.5 to 3.5

The catalytic effect of different initial concentration of Fe(II) is illustrated in Figure 9. Because the complexity of the metal speciation at different pH values and the reaction order are not constant, the analysis of the reaction order with respect to metal ions is not included in this paper, and further investigation is required. The rate constant values of Fe(II)-

Figure 9. Effect of Fe(II) concentration on S(IV) oxidation at $T = 25$ °C and pH = 3.5.
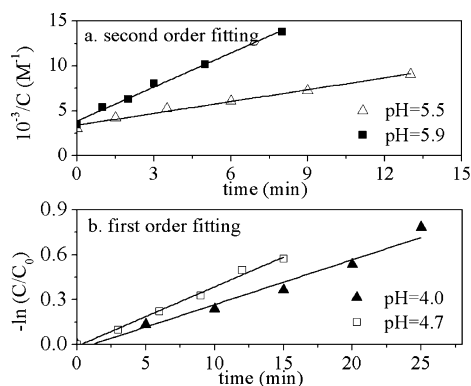
catalyzed oxidation at different pH and temperature values are available in Table S2.

3.4. Mn(II)-Catalyzed Oxidation. This study implied that the catalytic effect of Mn(II) is weaker compared to Fe(II) in artificial seawater with acetic acid buffer. Under the conditions of pH < 4.7, initial Mn(II) concentration <20 μM, and T = 25 °C, the initial oxidation rate is close to the uncatalyzed oxidation rate. This result has great discrepancy with some previously published reports.[14,17] The reason could be that the high concentration of acetic buffer used in the artificial seawater strongly inhibited the catalytic effect of Mn(II) more than expected.

It is proved that acetate has minor effect on iron-catalyzed S(IV) oxidation at low pH. Martin et al.[29] reported that the inhibition of acetate and formate did not occur at a pH below 4.0. Grgić et al.[25] reported that the effect of acetate on Fe(III)-catalyzed S(IV) is insignificant at the concentration ratio of $C_{(acetate)}:C_{(Fe(III))}$ = 500.

Wilkosz and Mainka[19] reported that the oxidation rate decreased no more than 50% at the maximum ratio of $C_{(acetate)}:C_{(Mn(II))}$ = 100, and the inhibition effect at pH = 5.0 was very weak compared to that at pH = 4.0 and 3.5. It should not be the situation in high ion strength solution such as seawater.

The Mn(II)-catalyzed experiment results indicated first-order dependence at pH ranging from 4.0 to 5.0, and second-order dependence at pH = 5.5−5.9 (Figure 10). As mentioned in the

Figure 10. Reaction order with respect to S(IV) of Mn(II)-catalyzed oxidation at T = 25 °C and [Mn(II)] = 40 μM.

above section, it is interesting that the S(IV) oxidation presents different reaction orders at different pH ranges. It may be interpreted by different metal speciation that leads to formation of different Mn(III)−sulfito complexes. Generally, the chain reaction in the presence of $SO\bullet_3^-$ and $SO\bullet_5^-$ is very fast, and the oxidation rate is determined by the formation and decomposition of Me(III)−sulfito complexes (reaction 8). As a result, the apparent reaction order might change as the change of $Me(III)(HSO_3^-)_n$ species at different pH values.

The catalytic effect of different initial concentration of Mn(II) is shown in Figure 11. Because the solubility of Mn(II) and Mn(III) is much higher than Fe(III), no precipitation was observed in all Mn(II)-catalyzed experiments. The rate constant values of Mn(II)-catalyzed oxidation at different pH and temperature values are summaries in Table S3.
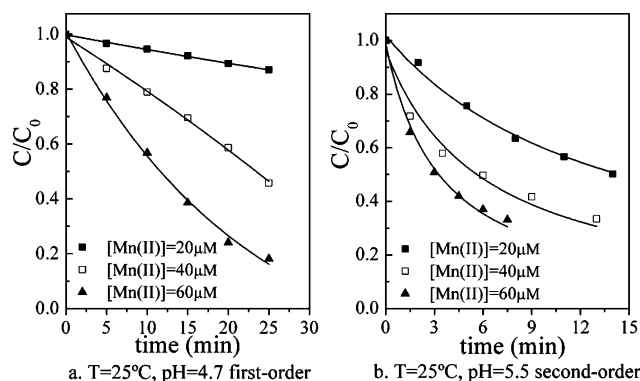
Figure 11. Effect of Mn(II) concentration on S(IV) oxidation.

4. CONCLUSION

(1) The reaction order with respect to dissolved oxygen is zero in both uncatalyzed and catalyzed S(IV) oxidation processes.

(2) S(IV) oxidation process in natural seawater could be strongly affected by the catalytic effects of trace amount of transition metal ions.

(3) The reaction order with respect to S(IV) under uncatalyzed conditions is second. But under catalyzed conditions, the reaction order is variable: first-order at Fe(II)-catalyzed oxidation (pH ranges from 2.5 to 3.5); first-order (pH ranges from 4.0 to 5.0) and second-order (pH range from 5.5 to 5.9) at Mn(II)-catalyzed oxidation. A possible explanation is that the reaction order may be affected by the metal speciation at different pH values.

(4) Acetic can cause strong inhibition on Mn(II) catalytic S(IV) oxidation in high ion strength solution, but the inhibition on Fe(II) catalytic S(IV) oxidation is weaker.

(5) According to this kinetic study, the oxidation rate can be greatly accelerated by transition metal catalytic effects. This result may inspire some useful ideas for the design of SFGD and other wet FGD processes.

■ ASSOCIATED CONTENT

⑤ Supporting Information
DO variation at different feed gas O_2 concentrations in uncatalyzed conditions (Figure S1); determined rate constants for uncatalyzed S(IV) oxidation (Table S1); determined rate constants for Fe(II)-catalyzed oxidation (Table S2); determined rate constants for Mn(II)-catalyzed oxidation (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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