

The homogeneous catalytic oxidation of aqueous S(IV) by transition metal ions. The synergistic catalysis

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ABSTRACT

In a series of studies on the effect of transition metal ions on the autooxidation of aqueous S(IV) we have investigated in this study the effect of Cu(II), Fe(III) and Mn(II) ions on the oxidation and concluded that in the absence of oxygen, it is possible for the reaction to be completely inhibited due to complex formation. Furthermore it is possible that no synergism exists for the couples Fe(III) + Cu(II) and Fe(III) + Mn(II) especially at high ratios of these metal ions. We have also investigated the strength of complex formation. The results indicate that in the presence of oxygen, complex S(IV) ions as well as uncomplexed ions are available for oxidation and this is explained in the light of Backstrom's mechanism for autooxidation of aqueous S(IV). We have proposed a reaction sequence for the oxidation of aqueous S(IV) in the presence of oxygen. Our conclusion is that in the presence of oxygen, the most effective catalyst is a mixture of Fe(III) + Mn(II) which produces almost 1 molar sulphuric acid after 7 hours.

INTRODUCTION

Knowledge of reactions of aqueous S(IV) species is very important to the understanding of the process of sulphuric acid formation in the atmosphere (Ibusuki & Barnes 1984) and for flue gas desulphurization (Dickerman 1979). The S(IV) auto-oxidation by dissolved oxygen proceeds very slowly in pure water to produce dithionate or sulphate, but trace amounts of transition metal ions such as Fe(III), Mn(II) and Cu(II) are capable of enhancing the reaction rate. Reda & Plimley (1987) have investigated the effect of ferric ions in the pH range from 1-2.6 and concentrations of Fe(III) between 10^{-2} and 10^{-5} M, and obtained a rate law for oxidation of S(IV) by Fe(III) in deoxygenated solutions, and concluded that

$$\frac{d[\text{S(IV)}]}{dt} = 0.0325(\text{s}^{-1}) \frac{[\text{Fe(III)}][\text{S(IV)}]}{[\text{H}^+]}$$

There are several studies in the literature about the autooxidation of aqueous S(IV) in Fe(III) solution (Karraker 1963; Brimblecome & Spedding 1974), Mn(II) solutions (Hoather & Goodeve 1934) and in Cu(II) solutions (Baron & O'Hern 1966; Mishra & Srivastava 1976). Martin (1984) reviewed the state of the art on the

catalytic effect by transition metal ions and concluded that the studies have given inconsistent results. There have been several reports in the literature on the possibility of a catalytic synergism between Fe and Mn. Martin (1984) studied the synergism between Fe(III) and Mn(II) and concluded that the mixed catalyst system is faster than what one would expect from the sum of the rates determined from each of the two catalysts separately. Martin studied the synergism at S(IV) concentration between 10^{-3} and 10^{-5} molar. The Fe(III) and Mn(II) concentration range was 10^{-4} to 10^{-7} molar. Higher rate of oxidation was obtained at low concentration of Fe(III) and high concentration of Mn(II).

In this study we have investigated the effect of Fe(III), Cu(II) and Mn(II) on the autooxidation of aqueous S(IV) in deoxygenated solution and we have compared the strength of these catalysts for such reaction. We have also investigated the synergistic catalysis of Fe(III) + Cu(II) and Fe(III) + Mn(II) for the autooxidation of aqueous S(IV) both in the presence and in the absence of oxygen. The system pH was 1.5–2.0. Details of the experimental procedures are given in Reda & Plimley (1987). In the experiment, mixtures of SO₂/air or SO₂/N₂ were metered through flow meters 4 and 5 (Fig. 1) and filters 2 and 1. Two runs were tested simultaneously through flow meters 6 and 7 and bottles 8 and 9 containing 500 ml of solution. Bath 3 kept an isothermal condition. Analar reagents were used. Total S(IV) and ferrous

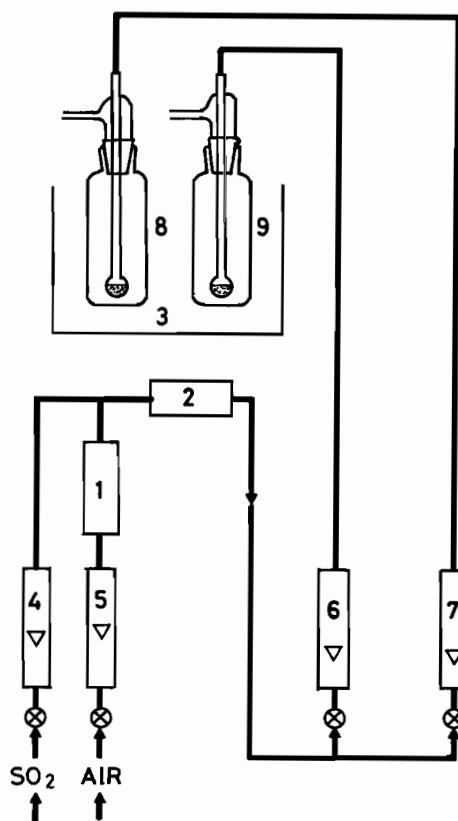


Fig. 1. General layout of apparatus used in the combined absorption and oxidation experiments.

ions were determined iodometrically and colorimetrically (respectively) as described by Vogel (1961). In the experiment, the following were kept constant: temperature at 298 K; total gas flow through each bottle at $3 \times 10^{-5} \text{ m}^3/\text{s}$; SO_2 partial pressure at 2.0 KPa, and scrubbing ratio at $7.75 \times 10^{-2} \text{ m}^3/\text{s}/\text{m}^3$ of solution.

RESULTS AND DISCUSSION

1. DEOXYGENATED WATER

Fig. 2 shows the absorption of SO_2 from a SO_2/N_2 mixture in deoxygenated water containing various concentrations of transition metal ion. Cu(II) and Mn(II) appear to increase the solubility of SO_2 in solution, as compared with water. The region of steady and constant concentration of S(IV) in the Cu(II) and Mn(II) curves appears to be due to the formation of stable S(IV) ligands which are not oxidizable. The reaction with ferric ions in solution can be shown by the slow build up of the S(IV) concentration, indicating that the Fe(III) ions act as an effective catalyst. However, when copper ions are added to the solution containing ferric ions, the S(IV) concentration increased rapidly indicating no oxidation. Similar results are obtained if Mn(II) ions are added to the solution containing ferric ions. However, in this case the strength of stable S(IV) ligands formation bond is not as strong as that for Cu(II). This is indicated by the initial slow build up of the couple Mn(II) + Fe(III) as compared to the couple Cu(II) + Fe(III). Further evidence for complex formation

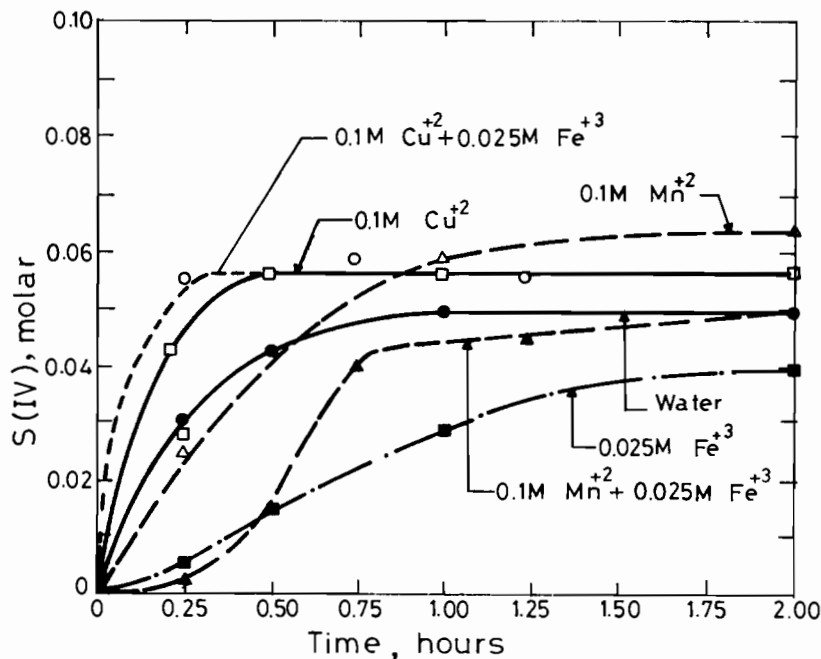


Fig. 2. Aqueous S(IV) concentration in combined absorption and oxidation of SO_2 in deoxygenated solution containing various transition metal ion.

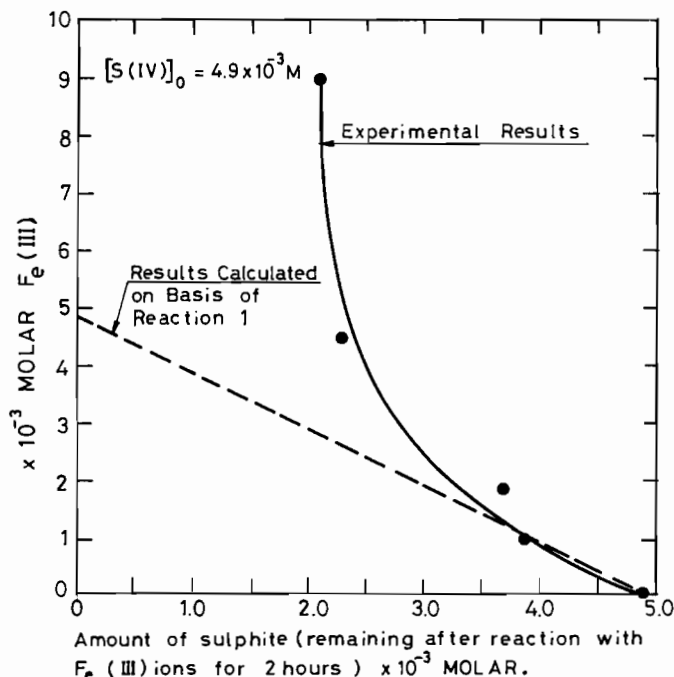
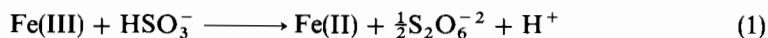


Fig. 3. Amount of S(IV) oxidized in oxygen-free solution containing excess amount of ferric ions. Comparison between experimental results and results based on Equation 1.

may be found in Fig. 3 which shows that using a solution of 4.9×10^{-3} M S(IV), about $2 \times 10^{-3} - 2.5 \times 10^{-3}$ M solution remains after addition of excess amounts of ferric ions. The reaction



appears not to proceed to 100% completion. This shows that sulphite ions complexed with Fe(II) ions are not oxidizable. This is in agreement with the result of Higginson & Marshall (1957) who observed that, when starting with equal concentrations of Fe(III) and Fe(II) ions the rates of Fe(III) reduction and S(IV) oxidation are very slow. This effect is more pronounced when Cu(II) ions are added to the reacting solution, forming even stronger sulphite ligands. From Table 1 we can see that with a Cu(II) : Fe(III) ratio of 0.4 : 1, and a S(IV) concentration of 0.79 molar, all the ferric ions present are reduced. At the higher ratio of 4 : 1 and a more dilute solution, the reaction can be completely inhibited. These results agree with the result of Higginson & Marshall (1957) who observed that the rates of Fe(III) reduction and S(IV) oxidation are dependent upon the ratio of Fe(III)/Cu(II). However, no conclusion can be obtained from their result since in their experiments an initial Fe(II) concentration of 2×10^{-3} M was included. Manganese (II) ions also have the same effect but do not completely inhibit the reaction. This is also in agreement with the observation of Basset & Parker (1951) that complex formation can interfere with the S(IV) oxidation by Mn(II). At high concentrations of Fe(II) and Cu(II) ions, the limited amounts of S(IV) ions, even in the presence of a continuous supply of

Table 1. Synergistic catalysis of aqueous SO₂ by various ratios of transition metal ions in deoxygenated solutions

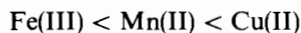
Fe(III) × 10 ³	Other metal ions (M(II))	M(II), molar	S(IV), molar × 10 ³	Dithionate, molar × 10 ⁴	Sulphate, molar × 10 ⁵	F(III)/ M(II)	Dithionate expected, molar × 10 ⁴	% Fe(III) reduced
25	Cu ²⁺	10 ⁻²	790	117	2000	1.0/0.4	125	100.0
25	Cu ²⁺	10 ⁻²	34	34	2400	1.0/0.4	30	24.0
25	Cu ²⁺	10 ⁻¹	50*	6	16	1.0/4.0	0	0.0
25	Mn ²⁺	10 ⁻²	790	67	1000	1.0/0.4	115	92.0
25	Mn ²⁺	10 ⁻²	34	83	8400	1.0/0.4	50	40.0
25	Mn ²⁺	10 ⁻¹	50*	82	530	1.0/4.0	60	53.0

* Values kept constant during the experiment.

SO₂/N₂ (Table 1), may be completely complexed, forming stable S(IV) legands according to



Thus, the proposed strengths of possible S(IV) complex formation are

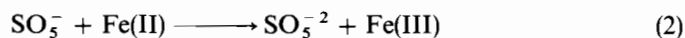


Snoeyink & Jenkins (1980) reviewed the subject of complex formation by metal ions and concluded that it is difficult to formulate a scale of strengths for complex stability because so many exceptions to the rules exist. The literature contains no data for the stability constants of metal ions with S(IV) ions. Although direct comparison for HSO₄⁻ and OH⁻ ions indicate that Fe(III) has the highest stability constant, the result of the present work is in excellent agreement with the result of Lunak *et al.* (1978) and is in direct opposition to the results of other investigators, (e.g. Mishra & Srivastava (1976) and Baron & O'Hern (1966)). The results of this work indicate that in the absence of oxygen no synergism exists for the couples Fe(III) + Cu(II) and Fe(III) + Mn(II) especially at high ratios of the metal ions and dilute S(IV) solutions.

2. IN THE PRESENCE OF OXYGEN

Before discussing the effect of synergistic catalysis of Fe(III) with other metal ions, the effect of Fe(III) ions on catalytic oxidation will be discussed. In Fig. 4 the oxidation state of iron is shown during the experiments. It shows evidence of two competing mechanisms of reactions. The following sequence may occur in solution:

- (a) At the start of the experiment the SO₂ : O₂ concentration in solution is high. In the absence of oxygen, a reaction of the type described in Reda & Plimley (1987) may occur producing dithionic acid and Fe(II) sulphite complexes (reaction 1). However, as oxygen is absorbed into solution, a small concentration of SO₅⁻ or HSO₃ radical ions (Backstrom 1930) may be produced by oxidation of S(IV) ions. These may reoxidize the Fe(II) ions according to the following reaction proposed by Brimblecombe & Spedding (1974) and Barrie & Georgii (1976)



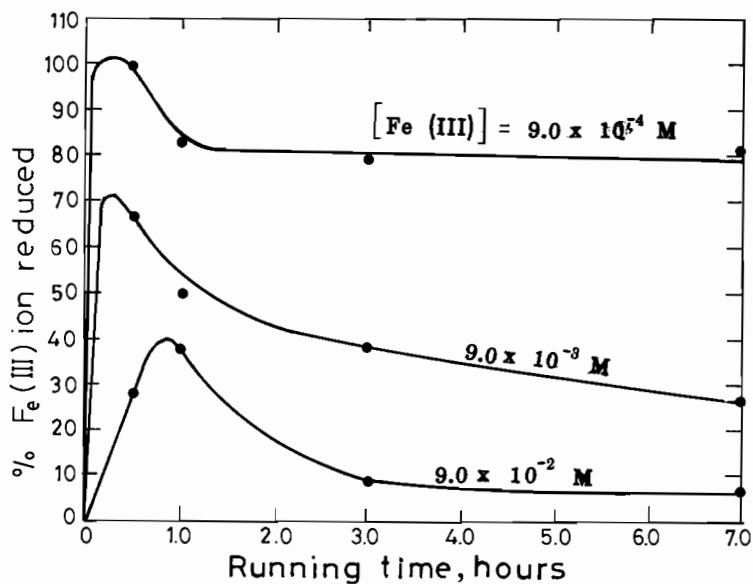


Fig. 4. % Fe(III) reduced in combined absorption and oxidation of SO_2 in ferric solution containing oxygen, for various ion concentrations.

Table 2. Results of the combined absorption and oxidation of SO_2 in ferric solutions containing oxygen, for various ferric ion concentrations

Fe(III) molar, $\times 10^5$	Time, hours	Total acid*	S(IV), molar $\times 10^3$	Dithionate, molar $\times 10^4$	Nett sulphate, molar $\times 10^4$	Fe(II), molar $\times 10^5$	% Fe(III) reduced
0	1-00	1-55	49	—	8	—	—
0	3-00	1-20	43	—	20	—	—
0	7-00	2-30	45	36	90	—	—
9	0-50	—	—	—	—	7	77-0
9	1-00	1-25	37	—	250	5	55-0
9	3-00	1-70	40	—	500	6	66-0
9	7-00	2-05	29	31	680	6	66-0
90	0-50	—	—	—	—	9	100-0
90	1-00	1-75	40	—	620	75	83-0
90	3-00	2-20	29	—	970	72	80-0
90	7-00	3-25	33	28	1970	45	83-0
900	0-05	—	—	—	—	600	67-0
900	1-00	4-10	90	—	540	450	50-0
900	3-00	3-55	27	33	1360	350	39-0
900	7-00	4-75	20	29	2300	250	28-0
9000	0-50	—	—	—	—	2550	28-0
9000	1-00	8-25	82	—	1570	3400	38-0
9000	3-00	10-20	25	95	3030	875	9-7
9000	7-00	13-35	18	99	5300	700	7-8

* milliliters of 0-1 molar sodium hydroxide solution needed to titrate the solution.

— = not detected.

This reaction may dominate, thus reducing the number of SO_5^- or HSO_3 available for reaction with S(IV).

- (b) A steady state will be attained which will depend upon the concentration of iron ions and mass transfer of SO_2 and O_2 into solution. It is clear from Table 2 that Fe(III) ions act as an effective catalyst which produce up to 1300 times the amount of oxidation products expected from this reaction without the ferric ions.

When a solution of 0.05 M ferrous sulphate was used, the ferrous ions were oxidized forming ferric ions and the S(IV) oxidation produced sulphate and no dithionate. The amount of sulphate reached 0.016 M after 3 h—an order of magnitude smaller than expected. This may indicate that a larger number of the SO_5^- or HSO_3 radical ions produced, is consumed in reaction with Fe(II) ions, thus reducing the number available for reaction with S(IV). In order to reduce the number of experiments required to test the various possibilities of synergistic catalysis among metal ions, only 1 : 1 ratio of ions was used and the effect of two concentrations was examined.

Fe(III) + Cu(II):

Unlike the reaction carried out in the absence of oxygen, Cu(II) ions appear not to inhibit the catalytic effects of ferric ions and there exists a synergism for the couple Fe(III) + Cu(II). Fig. 5 shows the oxidation state of ions during the experiment and exhibits different types of reaction behaviour depending on the mixture concentration. At low Fe(III) + Cu(II) ion concentration (9.5×10^{-4} molar total mixture

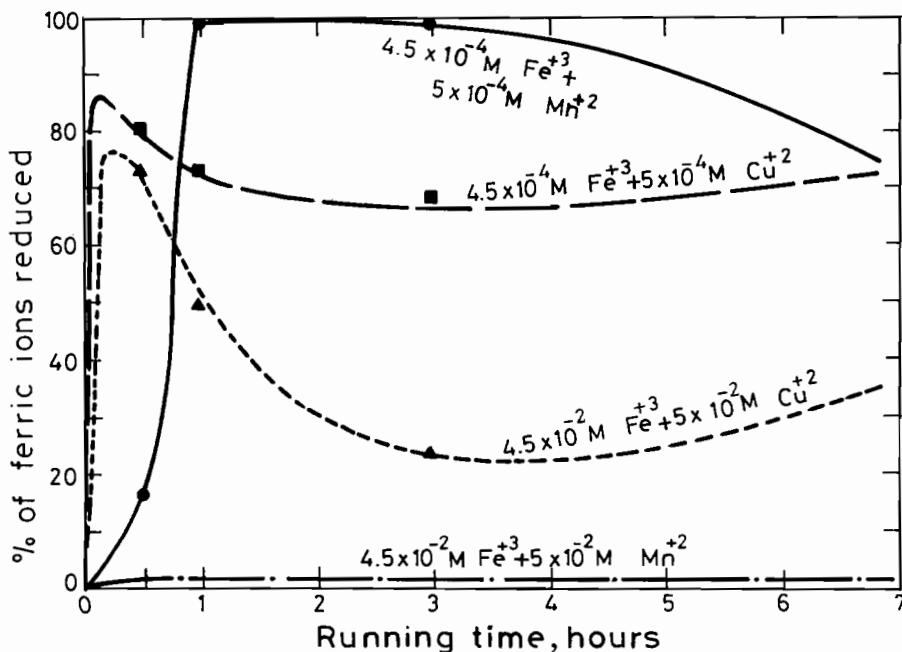


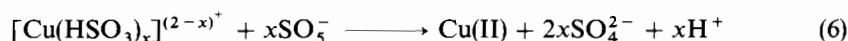
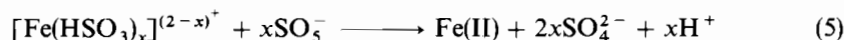
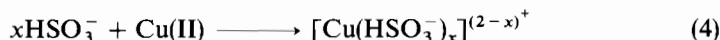
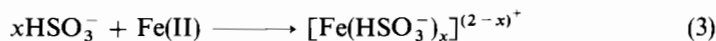
Fig. 5. % Ferric ion reduced in combined absorption and oxidation of SO_2 in ferric solution containing oxygen, for various combinations of transition metal ions.

Table 3. Synergistic catalysis of aqueous SO₂ by 1 : 1 ratio of Fe(III) and Cu(II) ions in oxygenated solutions

Fe(III), molar × 10 ⁵	Cu(II), molar × 10 ⁴	Time, hour	Total acid*	Sulphite, molar × 10 ³	Dithionate, molar × 10 ⁴	Sulphate, molar × 10 ⁴	Fe(II), molar × 10 ⁵	%Fe(III) reduced
0	0	1.0	1.55	44	—	8	—	—
0	0	3.0	1.20	43	—	20	—	—
0	0	7.0	1.30	45	36	90	—	—
45	5	0.5	—	—	—	—	36	80.0
45	5	1.0	1.20	28	—	330	33	73.0
45	5	3.0	1.45	20	—	620	37	69.1
45	5	7.0	2.25	31	25	780	32	71.0
4500	500	0.5	—	—	—	—	3300	73.0
4500	500	1.0	4.55	14	—	1440	2250	50.0
4500	500	3.0	8.10	20	—	2700	1075	24.0
4500	500	7.0	10.25	18	9	4000	1650	37.0

* milliliters of 0.1 molar sodium hydroxide solution needed to titrate the solution.
— = not detected.

concentration) it shows a similar type of reaction to that seen in the absence of Cu(II), i.e. low Fe(III) concentration in Fig. 4. But at high Fe(III) + Cu(II) ion concentration the behaviour is similar to that of a pure ferric ion solution at medium concentration of ferric ions (9×10^{-3} molar given in Fig. 4). The ratio of sulphate/dithionate produced from the reaction was investigated in order to seek a possible mechanism. In case of high Fe(III) + Cu(II) ion concentration the amount of dithionate is less than that of sulphate, since at a total mixture concentration of 9.5×10^{-2} M the sulphate/dithionate ratio is 444 (Table 3), indicating suppression of the oxygen-free reaction. Reda & Plimley (1987) have indicated that in the absence of oxygen, dithionate is the main product. Fig. 6 shows that the effect of the synergistic catalysis of Fe(III) + Cu(II) on sulphate production is about the same as that expected using Fe(III) alone, if we allow for the reduced SO₂ level in solution which was observed in the pure Fe(III) solution shown in Fig. 2. Now in the presence of oxygen, SO₅⁻ or HSO₃⁻ radical ions may be produced (Backstrom 1930), leading to the oxidation of S(IV) ions complexed with ferrous and copper ions according to:



Therefore in the presence of SO₅⁻ ions, complexed S(IV) ions are available for oxidation, as well as uncomplexed ions.

Fe(III) + Mn(II):

This mixture produced the most effective catalyst studied (Fig. 6) producing almost 1 molar sulphuric acid after 7 h (Table 4). From Fig. 6 it can be seen that the total catalytic effect produced appears to be equal to the sum of the individual effects.

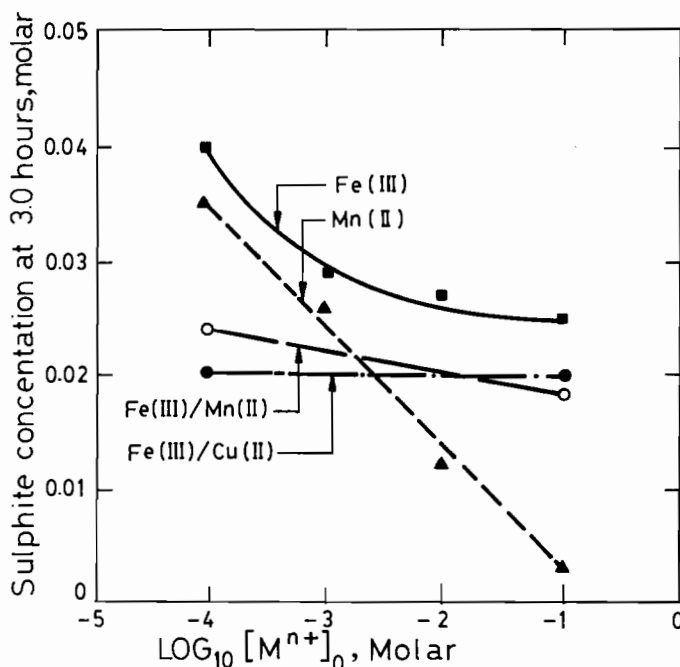


Fig. 6. Aqueous S(IV) produced in combined absorption and oxidation of SO₂ in oxygenated solution by the synergistic catalysis of metal ions. [M] is the total mixed concentration.

The line (Fig. 7) for the calculated effect is computed on the basis of the reactions 2–5 above, and a similar type of reaction was assumed for Mn⁺². This would indicate that the two reactions (the synergistic effect) are completely separate and proceed by different mechanisms. However, mass transfer effects may complicate this simple view. This is similar to the work of Barrie & Georgii (1976) who reported that an apparent synergism exists between Fe(III) and Mn(II) in the catalytic autooxidation of S(IV). However, they noted that the addition of either Fe(III) or Fe(II) to equimolar solutions of Mn(II) in the presence of S(IV) and oxygen resulted in a nonlinear increase in the absorption of SO₂. Barrie & Georgii (1976) concluded that the mixed catalyst system exhibited an overall oxidation rate that was greater than the sum of the individual transition metal ion-catalyzed rate. The actual mechanism of the synergistic effect was investigated by some authors (Edward *et al.* 1968; Bunnet 1974). Martin (1984) studied the synergism between Fe(III) and Mn(II) for S(IV) concentrations from 10⁻³ to 10⁻⁵ molar and the system at pH = 2 containing 10⁻⁴ molar Fe(III) and 2.5 × 10⁻⁶ molar Mn(II). He concluded that the rate is 10 times faster than that without synergism. Martin (1984) indicated that the individual reactions proceeded by a different mechanism. This means that the overall oxidation rate is greater than the sum of the individual reaction rates.

From Fig. 6 the Mn(II) catalyst appears to proceed by a faster reaction rate than that of the Fe(III) catalyst as indicated by the low concentration of S(IV) present in solution. However, the S(IV) concentrations obtained for the synergistic couple Fe(III) + Mn(II) appear to remain constant over a 100 times range in the mixed metal ion concentration (0.024–0.01 moles/l). Therefore ferric ions may increase the

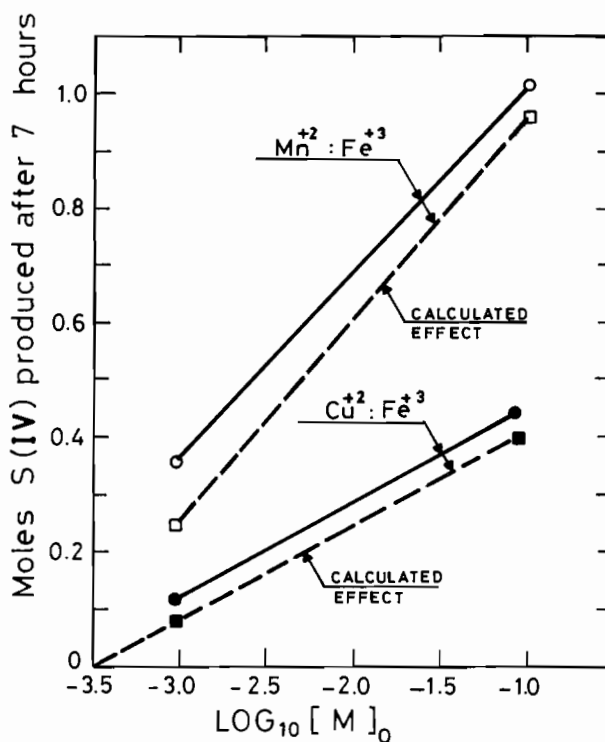


Fig. 7. Total S(IV) concentration at 3 hours running time for various catalysts. [M] is the total concentration, moles/l.

Table 4. Synergistic catalysis of aqueous SO₂ by 1:1 ratio of Fe(III) and Mn(II) ions in oxygenated solutions

Fe(III), molar × 10 ⁵	Mn(II), molar × 10 ⁴	Time, hour	Total acid*	Sulphite, molar × 10 ³	Dithionate, molar × 10 ⁵	Sulphate, molar × 10 ⁴	Fe(II), molar × 10 ⁵	% Fe(III) reduced
0	0	1.0	1.55	49	—	8	—	—
0	0	3.0	1.20	43	—	20	—	—
0	0	7.0	1.30	45	36	50	—	—
45	5	0.5	—	—	—	—	8	17.0
45	5	1.0	1.60	20	—	670	46	100.0
45	5	3.0	3.35	24	—	1770	45	100.0
45	5	7.0	5.50	53	5	2460	34	75.0
4500	500	0.5	—	—	—	—	50	1.1
4500	500	1.0	4.65	15	—	1690	50	1.1
4500	500	3.0	10.40	18	—	4950	50	1.0

* milliliters of 0.1 molar sodium hydroxide solution needed to titrate the solution.

— = not detected,

Table 5. Synergistic catalysis of aqueous SO₂ by 1 : 1 ratio of Cu(II) and Mn(II) ions in oxygenated solutions

Cu(II), molar × 10 ⁴	Mn(II), molar × 10 ⁴	Time, hour	Total acid*	Sulphate, molar × 10 ³	Dithionate, molar × 10 ⁴
500	500	1.0	2.70	28	—
500	500	3.0	3.25	46	—
500	500	7.0	3.50	73	12
5	5	1.0	1.45	4	—
5	5	3.0	1.35	5	—
5	5	7.0	1.75	5	13

* milliliters of 0.1 molar sodium hydroxide solution needed to titrate the solution.

— = not detected.

rate of oxidation in Mn(II) solution by increasing the rate of SO₂ mass transfer, S(IV) ions being removed from a Fe(III) complex to form a stronger Mn(II) complex. However, any SO₃⁻ or HSO₃⁻ radical ions produced by the Fe(III) ions would still be able to oxidize Mn(II)-S(IV) ligands. Evidence for these two competing reactions can be seen from Fig. 5. The figure shows that at high concentrations of Fe(III) + Mn(II) (0.095 molar) the % Fe(III) ion reduced is very low. This could be due to the competition between the two metal ions for S(IV) ions and may indicate that most of the available S(IV) ions are being consumed by the Mn(II)-catalyzed reactions, hence producing a very high sulphate/dithionate ratio (Table 4).

At a low mixed metal ion concentration (9.5×10^{-4} mixed concentration) and excess S(IV), there may be competition for a limited amount of molecular oxygen in solution and this may account for the very high % of ferrous ions between 1 and 3 h running time (Fig. 5). As more SO₂ is absorbed and acid concentration builds up, more SO₂·H₂O will be produced at the expense of HSO₃⁻ ions due to the shift in the SO₂/HSO₃⁻ equilibrium condition. This will in turn slow down the Mn(II) catalyst reaction, making more oxygen available for the oxidation of Fe(II) ions according to:



This could also account for the absence of the steady-state condition observed at lower Mn(II)/Fe(III) ions ratio.

CONCLUSIONS

1. Fe(II), Cu(II) and Mn(II) appear to increase the solubility of SO₂ in deoxygenated water. However, the concentration of S(IV) in these solutions remains constant due to complex formation of the form



and the proposed strength of complex formation is Fe(III) < Mn(II) < Cu(II). In the absence of oxygen the reaction can be completely inhibited for the couples Fe(III) + Cu(II) and Fe(III) + Mn(II), especially at high ratios of the metal ions and dilute S(IV) solutions.

2. In the presence of oxygen, complexed and uncomplexed S(IV) ions are available for oxidation. This was explained to be due to the presence of SO_5^- or HSO_3 radical ions which are also able to reoxidize Fe(II).
3. The synergistic catalysis between Cu(II), Fe(III) and Mn(II), Fe(III) appears to proceed by a rate which is equal to the linear sum of the rate determined from each of the two catalysts independently.
4. The most effective catalyst is a mixture of Fe(III) + Mn(II) producing almost 1 molar sulphuric acid after 7 hours.

REFERENCES

- Backstrom, H.** 1934. Der Kettensmechanisms bei der Autoxydation von Natriumsulfitlösungen. *Zeitschrift für Physikalische Chemie* **25B**: 122–38.
- Baron, C.H. & O'Hern, H.A.** 1966. Reaction kinetics of sulfur oxidation by the rapid mixing method. *Chemical Engineering Science* **21**: 397–404.
- Barrie, L.A. & Georgii, H.W.** 1976. An experimental investigation of the absorption of sulfur dioxide by water drops containing heavy metal ions. *Atmospheric Environment* **10**: 743–49.
- Basset, H. & Parker, W.J.** 1951. The oxidation of S(IV). *Journal of the Chemical Society*: 1540–60.
- Brimblecombe, P. & Spedding, D.J.** 1974. The catalytic oxidation of micromolar aqueous sulfur dioxide. *Atmospheric Environment* **8**: 937–45.
- Bunnet, J.F.** 1974. Investigation of rates and mechanisms of reactions, part I. Wiley Interscience, New York.
- Dickerman, J.C.** 1979. Flue gas desulfurization. *Environmental Protection Agency-600*, **17**: 79–178.
- Edward, J.O., Green, E.F. & Ross, J.J.** 1968. From stoichiometry and rate law to mechanism. *Journal of Chemical Education* **45**: 381–85.
- Higginson, W.C.E. & Marshall, J.W.** 1957. Some aspects of the oxidation of sulphurous acid. *Journal of the Chemical Society*: 447–58.
- Hoather, R.C. & Goodeve, C.F.** 1934. The oxidation of sulfurous acid III. *Transactions of the Faraday Society* **30**: 1149–56.
- Ibusuki, T. & Barnes, H.M.** 1984. Sulfur dioxide oxidation in aqueous solution at environmental concentrations. *Atmospheric Environment* **18(1)**: 145–51.
- Karraker, D.G.** 1963. The kinetics of the reaction between sulfurous acid and ferric ion. *Journal of Physical Chemistry* **67**: 871–74.
- Lunak, S.A., El-Wakil, A. & Yepresk-Siska, J.** 1978. Autooxidation of S(IV) catalyzed by 3rd transition metal. *Colloquia of Czechoslovakia Chemical Communication* **43**: 3306–16.
- Martin, L.R.** 1984. SO_2 , NO and NO_2 oxidation mechanisms. Acid precipitation series, Vol. 3. Ann Arbor Science Book Co., London.
- Mishra, G.C. & Srivastava, R.D.** 1976. Homogenous kinetics of potassium sulfate oxidation. *Chemical Engineering Science* **31**: 969–71.
- Reda, M.R. & Plimley, R.** 1987. The homogenous catalytic oxidation of S(IV) by transition metal ions. International Symposium on Environmental Management, Istanbul, Turkey, Vol. I, pp. 125–40.
- Snoeyink, V.L. & Jenkins, D.** 1980. Water chemistry. John Wiley and Sons, New York, 197 pp.
- Vogel, A.I.** 1961. A text-book of quantitative inorganic analysis. Longman, London, 343 pp.

(Received 15 May 1987, revised 30 November 1988)

الأكسدة المحفزة المتجانسة للمحلول المائي للكبريت بوساطة الايونات الفلزية الانتقالية - المحفزات المعاونة

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خلاصة

ضمن سلسلة دراسات عن تأثير الأيونات الفلزية الانتقالية على عملية الأكسدة الذاتية لمحلول الكبريت ، لقد بحثنا في هذه الدراسة تأثير أيونات كل من النحاس والحديد والمنجنيز على عملية الأكسدة ، ولقد استنتجنا أنه بغياب الاوكسجين من الممكن أن يتوقف التفاعل تماما وذلك بسبب تكوين المتراكبات ، كما أنه من الممكن أن تحدث أكسدة محفزة لكل من الزوجين : النحاس + الحديد ، والمنجنيز + الحديد .

لقد بحثنا قوة تكوين المتراكب ، وقد دلت النتائج على أنه بوجود الاوكسجين فان متراكبات أيون الكبريت المائية وكذلك أيونات الكبريت غير المترابطة مستعدة لعملية الأكسدة . وقد تم شرح ذلك على ضوء ميكانيكية باكستروم لعملية الأكسدة لمحلول الكبريت المائي . لقد استنتجنا أنه في وجود الاوكسجين تكون المادة المحفزة الأكثر فعالية هي مزيج من النحاس والحديد ، والتي تنتج ١ مولار من حمض الكبريتيك في سبع ساعات .

