



Project Summary

Buffer Additives for Lime/Limestone Slurry Scrubbing: Sulfite Oxidation with Enhanced Oxygen Absorption Catalyzed by Transition Metals

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Sulfite oxidation was studied by measuring the rate of enhanced oxygen absorption across an unbroken interface into solution containing sulfite (2 - 100 mM) and catalyst (0.01 to 100 mM) at pH 4-6 and 50°C. Fe, Mn, Co, Cu, and Cr ions were potent catalysts under these conditions; Ni was inactive. At 10 mM, these catalysts gave pseudo-first order (in oxygen) rate constants of 8.6, 43, 4.7, 95 and 11 sec, respectively. Dry catalyst added in its upper valence state (ferric, cupric, chromic) produced high initial rates that fell in 1 to 6 hours to steady state, while catalyst added in its lower state (ferrous, manganous, cobaltous) showed no high rates and reached steady state in less than 1 minute. Ferric and ferrous eventually resulted in the same rate. Fe was a much stronger catalyst than Mn or Co, but its rate was limited by Fe solubility of about 0.01 mM at pH 5, resulting in an enhancement factor of 2.4 at all higher concentrations. Thiosulfate (0.05-1mM) had a stronger inhibiting effect and efficiency on Mn than on Fe. EDTA was an effective inhibitor for Fe at equal or greater concentrations. Rates for Fe and Co increased with pH from 4 to 5, while those for Mn were unchanged. Strong positive Mn-Fe synergisms were found to cause absorption rates of up to five times those expected. Dissolved Fe is probably the most important indigenous catalyst in aqueous scrubbing for flue gas desulfurization.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The liquid-phase sulfite oxidation reaction involves adding an oxygen atom supplied by dissolved oxygen to an S(4) species, sulfite or bisulfite, to produce S(6), sulfate or bisulfate. The pH fixes the distribution among protonated and unprotonated species, but the reactants and products are usually referred to as simply "sulfite" and "sulfate." This reaction is a very complex free radical sequence involving a number of highly reactive intermediate species. It is catalyzed by micro-molar or higher amounts of dissolved transition metal ions having more than one valence state and is very sensitive to impurities in general. Recent studies indicate that the reaction does not proceed at all in the absence of a catalyst. The observed kinetics are also sensitive to experimental conditions so that there is no common agreement on rate equation forms, rate constants, or even reaction orders. This widely varying behavior indicates that different elementary reactions become important at different conditions and control the rate, contributing to the complexity of the problem.

The two main engineering uses of sulfite oxidation are to determine mass transfer characteristics in gas/liquid contacting equipment, and to oxidize calcium sulfite waste products in flue gas desulfurization (FGD). Scientific interests focus on the reaction's role in acid precipitation and in free radical reactions in general. Also, the sulfite oxidation reaction has many features in common with the solution-phase free-radical oxidation of hydrocarbons, so there are some opportunities for information cross-over.

The purpose of this project was to study sulfite oxidation under FGD conditions. These conditions differ from those usually used in other studies which tend to be: (1) mass transfer characterization projects at higher S(4) concentrations and pH but lower catalyst levels, or (2) acid precipitation studies at trace amounts of S(4) and catalyst and lower pH. The experiments were performed at pH 4 to 6 and 0.01-0.03 M sulfite to simulate conditions in typical FGD oxidizing units. The reaction occurred under heterogeneous conditions where oxygen was absorbed out of air at 50°C into an agitated, unsparged sulfite/catalyst solution typically containing 0.1 to 100 mM of Mn, Fe, Co, Cu, Cr, or Ni. Under these conditions, reaction kinetics were so fast that all of the incoming oxygen was consumed in a thin reaction zone at the gas/liquid interface, and the bulk solution oxygen concentration was maintained near zero. The absorption rate was measured, using the pH-stat method, which allows solution concentrations to remain constant indefinitely while the absorption rate comes to steady state.

The scope of this project was to determine the important factors in fixing the reaction rate (and therefore the absorption rate) under FGD conditions and to elucidate some aspects of the reaction mechanism when common FGD catalysts are present. The principal solution effects that were considered included catalyst concentration, S(4) concentration, pH, and agitation rate. Catalytic synergism was studied by having two catalysts present simultaneously in the solution. The results of these experiments were correlated to hypothesized reaction steps with equations describing simultaneous reaction and mass transfer under these conditions in order to judge the validity of proposed reaction steps.

Theory

Both surface renewal and film theories were used to model the processes

occurring in the system according to the suitability of each to specific applications. Reaction rate constants and reaction orders were correlated with a Danckwerts surface renewal equation that is generalized to include any values of reaction orders:

$$R = R_o \left[1 + \frac{2}{m+1} \frac{D_{ox} k_r [S(4)]^n [cat]^p [O_2]^{m-1}}{k_{ox}^2} \right]^{1/2} \quad (\text{Eq. 1})$$

where: R = the absorption flux, gmols O₂/cm² sec
 R_o = the physical absorption flux = k_{ox}[O₂], 1x10⁻⁹ at 400 rpm agitation
 k_r = the homogeneous reaction rate constant
 m, n, p = homogeneous reaction rate orders
 k_{ox} = the unenhanced liquid-phase mass transfer coefficient, 8.2x10⁻³ cm/sec at 400 rpm

The right-hand term in the brackets dominates the unity at enhancement factors above about three. One basis for comparing catalysts was the first order rate constant with respect to oxygen, k₁ = k_r[S(4)]ⁿ[cat]^p in Eq. 1. Rearranging this equation gives:

$$k_1 = \frac{k_{ox}^2}{D_{ox}} (E^2 - 1) = 1.81 (E^2 - 1) \text{ sec}^{-1} \quad (\text{Eq. 2})$$

where: E = the enhancement factor, R/R_o

Another basis of comparison was established so the absorption rate data from these experiments could be converted to a homogeneous reaction rate for comparison to literature values. The quantity r_{S4} is defined as the average homogeneous rate of S(4) consumption in the interfacial reaction zone in gmols S(4)/liter sec and is equal to twice the rate of oxygen consumption, r_{ox}. r_{ox} is equal to k₁ times the concentration of oxygen in the reaction zone, [O₂]/2:

$$r_{S4} = 2k_1([O_2]/2)(E^2 - 1) = (2.71 \times 10^{-4})(E^2 - 1) \text{ M S(4)/sec} \quad (\text{Eq. 3})$$

Two coupled film theory models were written for the interfacial region: one describes the reaction zone at the interface, the other describes transport between the bulk solution and the reaction zone.

Since the detailed mechanism of sulfite oxidation is not known, a generalized free radical mechanism was derived and used in conjunction with equations relating the oxygen absorption flux (R) to the velocity of the homogeneous reactions (r_{S4}) to model the effects of changing

catalyst and inhibitor concentrations on r_{S4} (and therefore on the observed absorption rate). This generalized mechanism involves some hypothesized initiation and termination reactions (understood to some extent), and uses a generalized form for propagation reactions, which are very numerous and almost never known with any certainty in sulfite oxidation. This model suggests that the observed change in reaction order with respect to Mn catalyst from 1 to 0.5 at 10 mM could be due to a change from first to second order termination kinetics as the free radical population in the reaction zone increases. Including an inhibition step in the model resulted in a rate expression identical to the observed relationship for inhibition by thiosulfate (Eq. 4).

A film theory model was solved on a computer to estimate the differences between bulk and interface (reaction zone) conditions during enhanced oxygen absorption. It was found that, under FGD conditions, significant lowering of pH and S(4) concentration in the reaction zone could occur. The cause of this increased sensitivity at FGD conditions is the low levels of S(4) which act as both a reactant and, at the pH values of interest in this project, a buffer. Reaction at the interface can significantly decrease the interfacial sulfite concentration, which depletes its buffering ability and allows the interface to achieve pH values that are up to two units lower than the bulk pH of 5. At 10 mM, the S(4) mass transfer limited enhancement factor would be about 33. The partial pressure of SO₂ above the solution is predicted to increase because of this lower pH at the surface. A pH 5 and 10 mM sulfite solution would have a SO₂ partial pressure of 20 ppm; but, at an enhancement factor of 15, it could rise almost to levels that would be expected in flue gas from some coal-fired boilers (500 ppm).

Results and Discussion

The measured oxygen absorption rates for single catalysts (Figure 1) were correlated with Eq. 2 and 3 to obtain the kinetic information in Table 1. The slopes of the lines in Figure 1 equal half the catalyst reaction order, so Mn shifts from first-to half-order at 10 mM, possibly due to a change in termination reactions at the higher reaction rates; Co tends toward first order, and Ni shows too little enhancement to determine a slope. Under the same conditions, Fe catalyst showed apparent zero order kinetics at E=2.4 at pH 5, making it the most potent catalyst below 1 mM. The homogeneous

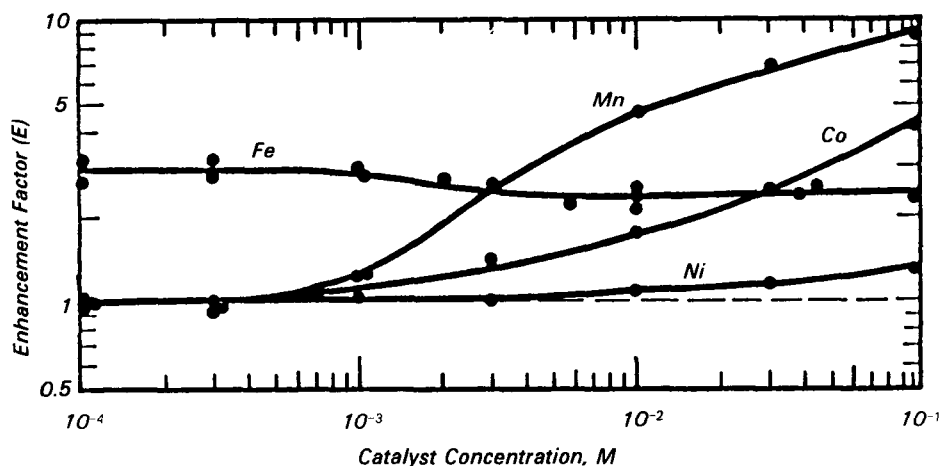


Figure 1. Effect of Mn, Co, Fe, and Ni catalyst concentration on the enhancement factor at 10 mM S(4) and pH 5.

oxidation rates in the reaction zone were on the order of 1 mM S(4)/liter sec.

Table 1. Comparison of Catalytic Activities During Enhanced Oxygen Absorption into 10 mM S(4) and 300 mM S(6) at pH 5, 50°C, and 400 RPM Agitation

mM catalyst		E^a	k_1^b	r_{S4}^c
5	Mn	2.5	9.5	0.0011
10	Mn	5.0	43	0.0050
50	Mn	7.5	99	0.0120
0.1	Fe	3.1	16	0.0019
0.5	Fe	3.1	16	0.0019
5	Fe	2.6	10	0.0012
10	Fe	2.4	8.6	0.0010
50	Fe	2.4	8.6	0.0010
5	Co	1.5	2.3	0.0003
10	Co	1.9	4.7	0.0005
50	Co	3.2	17	0.0020
10	Ni	1.1		
50	Ni	1.2		
10	Cr	2.7	11	0.0013
10	Cu	7.3	94	0.0110

^a E = enhancement factor.

^b k_1 = first order (in O_2) rate constant, sec^{-1}

^c r_{S4} = average homogeneous oxidation rate in the reaction zone, gmols S(4)/liter sec.

Comparisons were made between r_{S4} values in Table 1 and homogeneous reaction rates from published rate expressions extrapolated to the conditions of this project. The expressions were evaluated at 5 mM Mn or Co and 0.1 mM Fe (the lower level for iron was used since experiments indicate that the catalyst is solubility-limited above this point) and were found to give rate values higher than those reported here for Mn and Co but seemed to be of the right order of magnitude for Fe. Most of these expressions came from experiments performed at pH values comparable to those in this project, but they were mostly at lower

sulfite and catalyst concentrations in order to obtain rates low enough to use homogeneous reactors. The agreement for Fe catalyst may be the result of the published rate expressions' being extrapolated less for this case.

The distribution of catalyst valence states is at steady state since the catalyst ion (reduced during initiation) reoxidized by dissolved oxygen in the reaction zone or by other oxidizing species in solution. Experiments, involving adding catalysts to the solution in different valence states, and literature data support the idea that the upper valence state of the metal ion is the catalytic agent, acting by removing an electron from an S(4) ion to create a free radical chain reaction in the reaction zone.

The apparent zero-order kinetics of Fe catalyst were due to solubility limitations on a catalytically active ferric species. Hydrated Fe does not have a sufficient oxidizing potential (0.77 V) to remove an electron from sulfite (0.89 V) but FeOOH might (0.908 V). Fe scans at 0.001 to 0.1 mM (Figure 2) showed a change of reaction order from one to zero at some pH-dependent Fe concentration. These breakpoints were due to the catalytically active species' reaching a solubility limit at 0.01 mM total Fe at pH 5. The solubility of FeOOH is much lower (about 10^{-9} mM) and, if it is in fact the active species, its concentration reaches this point at 0.01 mM total Fe. These breakpoints shifted to higher concentrations at lower pH due to the increased solubility of the ferric species. The reaction rate with Fe catalyst was higher at higher pH because the catalyst regeneration reaction (ferrous oxidation to ferric) is base-catalyzed. Red-brown Fe precipitates were visible at total Fe concentrations above 0.5 mM at pH 5. The amounts of these solids were observed to increase with time and pH, and were found to be catalytically inactive.

FGD systems operating under the conditions of this project with Fe catalysis would be expected to show enhancement factors that are independent of pH. A decrease in pH retards the Fe-catalyzed oxidation reaction (Figure 2), but the increase in total dissolved S(4) concentration, together with the observed half-order dependency on S(4), results in equal offsetting effects.

Thiosulfate was found to inhibit the Mn and Fe catalyzed rate by acting as a free

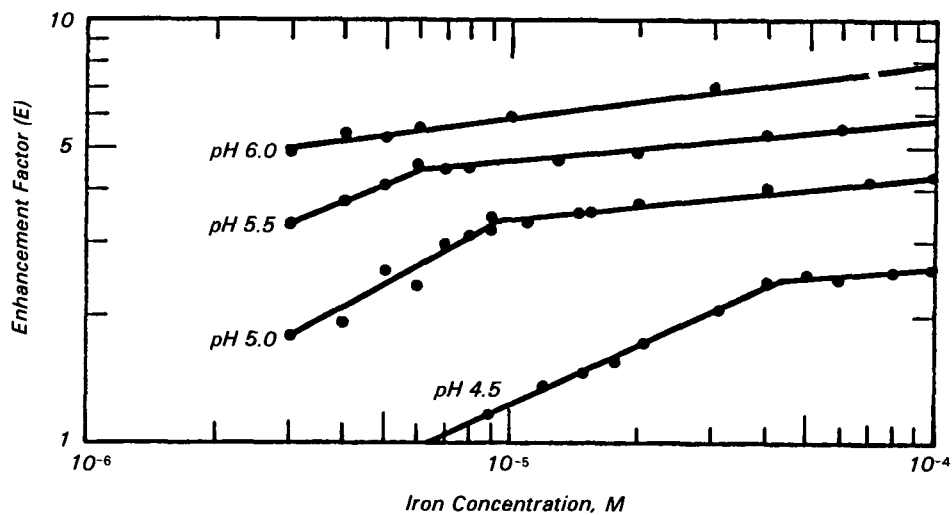


Figure 2. Effect of low Fe concentration on the enhancement factor at 30 mM S(4) and various pH values.

radical scavenger. It was degraded only in the presence of sulfite oxidation in a few hours, and was consumed at a rate proportional to the remaining thiosulfate concentration raised to the three-halves power. Thiosulfate additions of 0.05 to 0.15 mM to Mn systems completely recovered to the uninhibited rate in 1 to 3 hours. No significant induction time followed the addition of thiosulfate, and the absorption rate recovered linearly from the lowered value. The absorption rate was inversely proportional to the square-root of the thiosulfate concentration (Figure 3), and this rate form was also successfully modelled by the generalized radical mechanism. At 30 mM Mn, 10 mM S(4), and pH 5:

$$E = \frac{6.17}{(1 + 46.8 [S_2O_3^{2-}, \text{mM}])^{1/2}} \quad (\text{Eq. 4})$$

Thiosulfate required between one and two orders of magnitude more concentration to have the same percentage of retardation on Fe catalyzed systems than on those with Mn. Also, each thiosulfate ion prevented the oxidation of about 40 sulfite ions with Mn, but prevented only about 3 with Fe. Therefore, the radicals that react with thiosulfate must be generated more rapidly by Fe catalyst than by Mn.

EDTA (ethylenediamine-tetraacetic acid) retarded the reaction by chelating metal ions, thereby sterically hindering their catalytic action. The Fe/EDTA complex seemed to be totally inactive. With 5 mM Fe giving obvious formation of a precipitate, an equivalent amount of EDTA was required. Therefore, EDTA would not be an effective inhibitor in systems with an excess of iron salt solids.

The rate of oxygen absorption into sulfite/catalyst solutions under FGD conditions was measured as a function of the agitation rate (Figure 4), to estimate the liquid-phase mass transfer coefficient and the interfacial contact area, using a method that has the advantage of not requiring detailed prior knowledge of the reaction kinetics. The bottom curve is the physical absorption line since 0.1 mM Mn is enough to deplete the bulk-phase oxygen, but not enough to cause enhancement (Figure 1). The upper absorption rate curves were made with enough catalyst to cause enhancement at low agitation rates, but E falls to unity when a catalyst's line converges with the physical absorption line. The calculated values of k_{ox} and A were found to be much too large and small, respectively, at high agitation intensities, perhaps due to a slowing down of the local reaction rate. This effect has been observed by other investigators

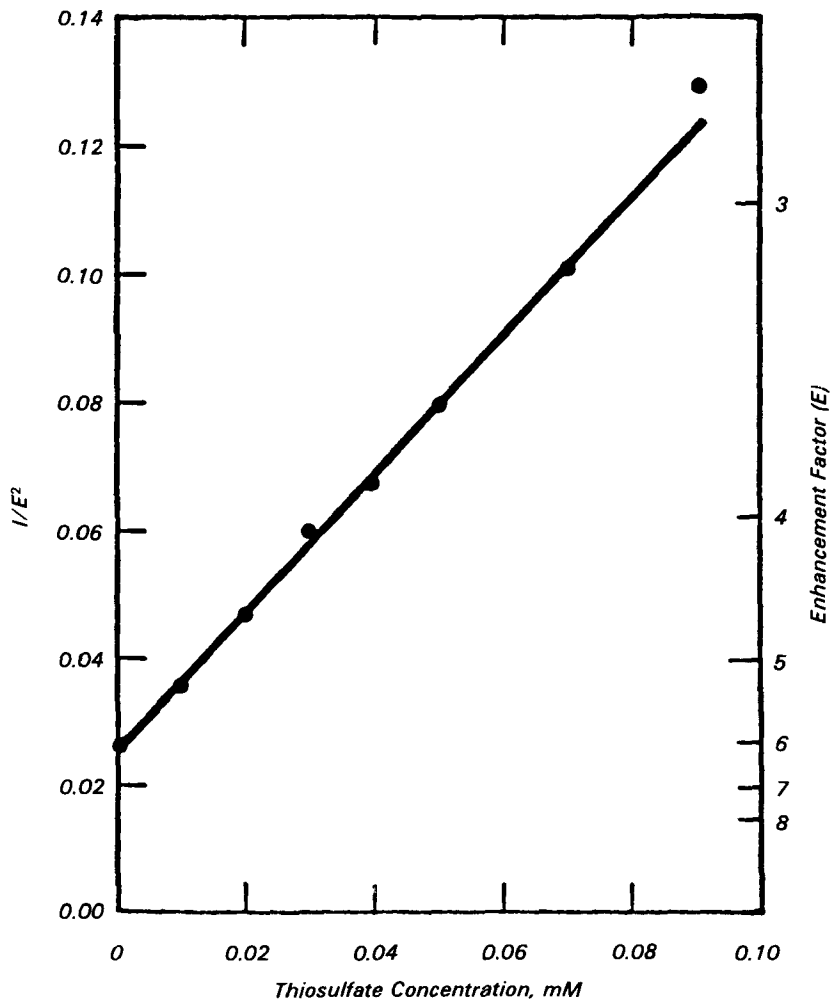


Figure 3. Decrease of enhancement due to adding thiosulfate at 30 mM Mn, 10 mM S(4), and pH 5.

and is hypothesized to occur because the average length of time that fluid elements spend at the surface is shorter than the induction time of the free radical reaction in the elements: the average rate is less than that which would be observed at steady state.

The phenomenon of catalytic synergism was studied by measuring the rate with two catalysts in the solution simultaneously. Strong positive interactions were found for the Mn-Fe couple, and strong negative interactions for the Mn-Cu pair. Some combinations of Mn and Fe were strong enough to cause the rate to reach the S(4) mass transfer limit at E=33, so no kinetic information could be developed on faster rates. A dimensionless "synergism coefficient" was defined as the ratio of the absorption rate observed with both catalysts present to the absorption rate which would be expected from surface renewal theory if the catalysts did not

interact. The separate rates cannot be added linearly (as can homogeneous rates) because of the effects of mass transfer considerations, so a more involved approach is necessary. This synergism coefficient was found to be as high as 5 for Mn-Fe, and as low as 0.1 for Mn-Cu.

Conclusions

Results of the study led to several conclusions:

(1) Fe, Mn, Co, Cr, and Cu are potent catalysts under FGD conditions, but their relative activities depend on the specific conditions. Significant enhancement factors could be possible in actual scrubbers at Mn and Fe concentrations typically observed. Fe alone could give enhancements of 2 to 5 depending on pH and S(4) concentration, while Fe-Mn synergisms could result in enhancements as high as 30. FGD units operating under

these conditions with Fe catalysis would exhibit enhancement factors that are independent of pH.

(2) The upper state of multivalent transition metal ions initiates the free radical reaction chain by removing an electron from a sulfite or bisulfite ion. The catalytic mechanisms of Fe and Mn are quite different. Fe generates free radicals at a faster rate. Therefore it comes as no surprise that organic acid degradation is less severe in the presence of Mn.

(3) Some catalytically active ferric ion is solubility-limited, resulting in apparent zero order kinetics above 0.01 mM total Fe at pH 5. Precipitated Fe solids are inactive.

(4) 0.05 to 0.15 mM thiosulfate effectively inhibits the reaction catalyzed by Mn, but has less effect on Fe systems. Oxidation in FGD systems can be effectively inhibited by thiosulfate, although it degrades rapidly, especially with Fe catalysis.

(5) EDTA inhibits Fe catalysis at equal or higher concentrations by chelating the ferrous and ferric ions into an inactive complex. EDTA would not be an effective catalyst in FGD systems, since enough EDTA would have to be added to complex all of the dissolved and precipitated iron.

(6) Significant reductions in pH and $[S(4)]$ can occur in the interfacial reaction zone under FGD conditions due to the combination of high absorption fluxes and low bulk $S(4)$ levels.

(7) Oxygen absorption from air into sulfite/catalyst solutions under FGD conditions as a method of mass transfer characterization can lead to overestimation of the liquid-phase coefficient and underestimation of contact area, perhaps due to reduced reaction rates at higher agitation intensities. The enhancement factors measured in this project may not be directly applicable to a real scrubber because of changes in k_{ox} and variation of the heterogeneous reaction kinetics with agitation.

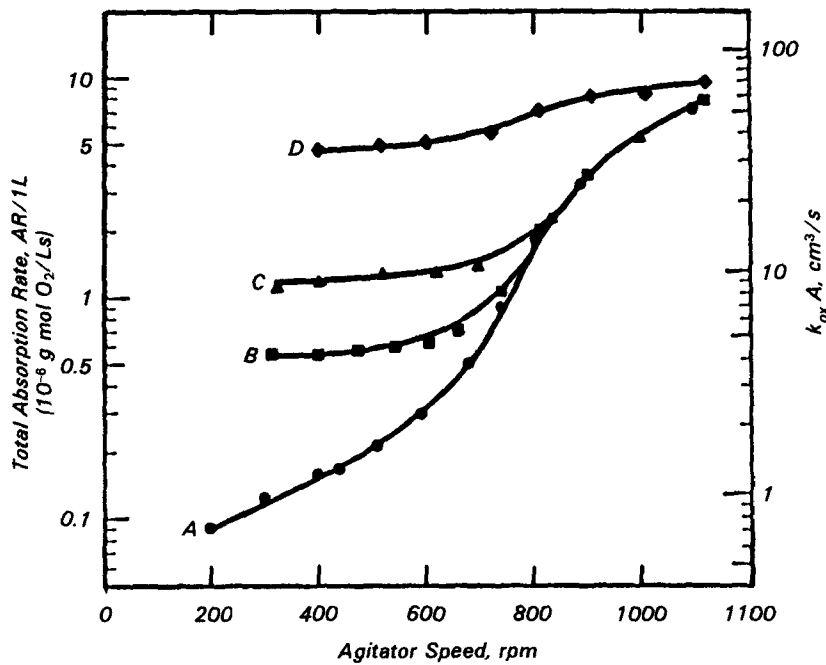


Figure 4. Effect of agitator speed on the total oxygen absorption rate, Mn and Mn-Fe synergistic catalysts at pH 5.

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The complete report, entitled "Buffer Additives for Lime/Limestone Slurry Scrubbing: Sulfite Oxidation with Enhanced Oxygen Absorption Catalyzed by Transition Metals," (Order No. PB 84-189 950; Cost: \$17.50, subject to change) will be available only from:

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