



## Project Summary

# Oxidative Degradation of Organic Acids Conjugated with Sulfite Oxidation in Flue Gas Desulfurization

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**Organic acid degradation conjugated with sulfite oxidation has been studied under flue gas desulfurization (FGD) conditions. The oxidative degradation constant,  $k_{12}$ , is defined as the ratio of organic acid degradation rate and sulfite oxidation rate times the ratio of the concentrations of dissolved S(IV) and organic acid. It is not significantly affected by pH or dissolved oxygen in the absence of Mn or Fe. However,  $k_{12}$  is increased by certain transition metals such as Fe, Co, and Ni and is decreased by Mn and halides. Lower dissolved S(IV) magnifies these effects. A free radical mechanism was proposed to describe the kinetics. Hydroxy and sulfonated carboxylic acids degrade approximately three times slower than saturated dicarboxylic acids; while maleic acid, an unsaturated dicarboxylic acid, degraded an order of magnitude faster. A wide spectrum of degradation products of adipic acid were found including carbon dioxide (the major product), smaller dicarboxylic acids, monocarboxylic acids, other carbonyl compounds, and hydrocarbons.**

*This Project Summary was developed by EPA's Air and Energy Engineering 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

Currently, limestone scrubbing is the dominant commercial technology for flue gas desulfurization (FGD). The performance of limestone scrubbing is chemically limited by two pH extremes: (a) low

pH near the gas/liquid interface, which decreases the solubility and absorption rate of  $\text{SO}_2$ ; and (b) high pH near the liquid/solid interface, which decreases the solubility and dissolution rate of limestone. Organic acids that buffer between pH 3.0 and 5.5 enhance  $\text{SO}_2$  removal efficiency and limestone utilization at concentrations of 5 to 10 mM.

Adipic acid was the first organic acid buffer additive successfully and generally applied to FGD processes up to commercial scale. It has been replaced commercially by waste dibasic acid (DBA), a waste from adipic acid and cyclohexanone production, containing primarily adipic, glutaric, and succinic acids. DBA was found to be as effective as adipic acid. Other potential alternatives include hydrocarboxylic acids and sulfonated carboxylic acids. They are of interest because of reduced volatility and potentially lower degradation rates.

In addition to the expected loss of organic acid additive by entrainment of solution in waste solids, loss by chemical degradation and coprecipitation is also observed. Chemical degradation, which is conjugated with sulfate oxidation, is the most important mechanism of buffer loss under forced oxidation conditions.

Assuming that both oxidation and degradation are free radical reactions proceeded by a common radical, previous investigators proposed a simple kinetic model which can be expressed as:

$$d[A]/dt = k_{12}[A]/[S(IV)]_d d[S(IV)]_d/dt \quad (1)$$

where [A] and [S(IV)] stand for organic acid and sulfite/bisulfite molar concentrations, respectively, and superscripts "d" and "t" denote "dissolved" and

“total,” respectively. The most probable free radical here is  $\text{SO}_4^-$  because of its reactivity toward alcohols which are inhibitors of sulfite oxidation. It has also been cited as the active species in the decarboxylation/oxidation of organic acids by peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ).

Valeric acid, glutaric acid, and hydrocarbons from ethane to butane have been identified as degradation products of adipic acid. Low pH, especially in the presence of Mn, reduced the degradation rate of adipic acid. It was also observed that high dissolved S(IV) reduced the degradation rate.

It is desirable to understand the degradation kinetics, the mechanism, and the additional environmental impact caused by degradation. This work covers the degradation kinetics, mechanism, and products. Since decarboxylation is the major degradation pathway and since it is decarboxylation that significantly affects the buffering capacity,  $\text{CO}_2$  evolution rate instead of the actual degradation rate is of greater interest. The oxidative degradation constant,  $k_{12}$ , will be used for most kinetic studies, since this constant is simply the degradation rate normalized with the oxidation rate and the concentrations of organic acid and dissolved S(IV).

## Experimental Apparatus and Procedure

Since organic acid degradation is conjugated with sulfite oxidation, and experimental design is required that permits measuring the rates of organic acid degradation and sulfite oxidation simultaneously. Two approaches are used for this study: one oxidizes calcium sulfite slurry; and the other, sodium sulfite solution. The slurry system has a large capacity of sulfite to allow significant degradation of organic acid with relatively low  $[\text{S(IV)}]_0$ , typical of actual scrubber conditions. The solution system provides better control of dissolved  $[\text{S(IV)}]$ . Two reactors have been used to study organic acid degradation during sulfite oxidation: one is an open semibatch reactor, while the other is a closed semibatch reactor which enables monitoring the gas-phase degradation products, primarily carbon dioxide. Figure 1 diagrams the experimental apparatus with the closed system reactor.

In a typical slurry experiment, 1.0 M synthesized  $\text{CaSO}_3$  solids were slurred and oxidized in a solution containing 10 mM organic acid and 0.1 M  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

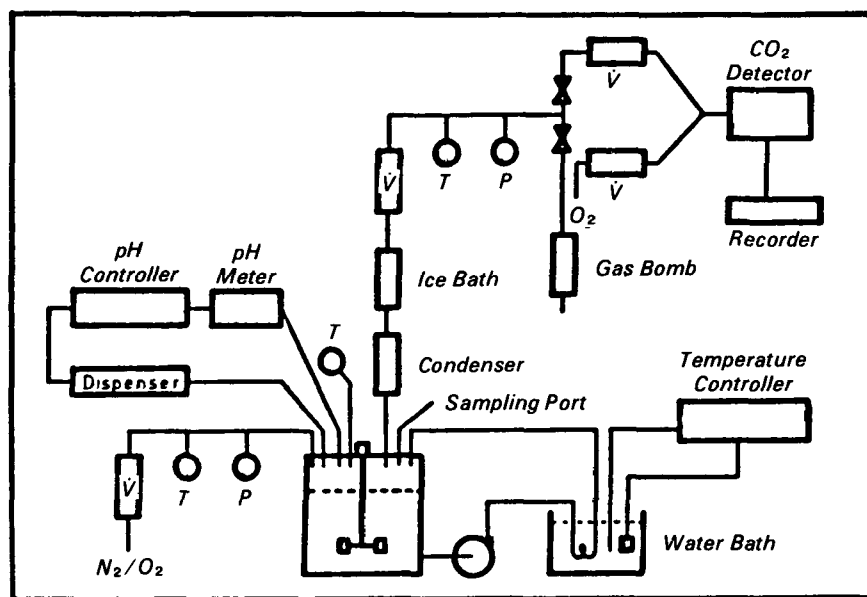


Figure 1. Closed system apparatus.

seed crystals. All experiments were performed at a constant temperature of 55°C. The pH was maintained constant throughout a given experiment. In a typical sodium sulfite solution experiment, ~1 mM dissolved S(IV) was maintained constant by titrating with sodium sulfite solution during the oxidation of S(IV) to S(VI). 0.3 M sodium sulfate was added to prevent dramatic change in the ionic strength. The oxidation rate of S(IV) was reflected by the titration rate of sodium sulfite solution.

Total S(IV) was analyzed by iodimetric titration of the slurry sample. Filtered samples were reheated to 55°C, the experimental temperature, and the pH was adjusted back to the original pH (4.50-5.50 ± 0.01) with sodium sulfite or air oxidation. Then iodimetric titration was used to measure the dissolved S(IV). Carbon dioxide was monitored continuously by an infrared  $\text{CO}_2$  detector. Hydrocarbons, organic acids, and liquid-phase degradation products were analyzed by ion chromatograph exclusion (ICE, Dionex 14), gas chromatograph (GC, Varian 3700), and/or gas chromatograph/mass spectrometer (GC/MS, Finnigan 4023).

## Kinetics

Most of the experiments were performed with adipic or glutaric acid. Adipic

acid is effective, nonvolatile, and has been extensively tested up to commercial scale. Glutaric acid is the major component of waste DBA from adipic acid production. The kinetic results discussed below are applied to adipic and glutaric acids only, unless specified.

## Conjugation with Sulfite Oxidation

No degradation of organic acid is detected when sulfite oxidation is inhibited by adding inhibitors such as sodium thiosulfate and hydroxyl compounds and by depleting oxygen or S(IV) species. When the oxidation rate controlled by the sodium sulfite feedrate increases from 0.0082 to 0.024 M/hr, the oxidative degradation constant,  $k_{12}$ , only changes the  $1.17 \times 10^{-3}$  to  $0.99 \times 10^{-3}$ . In slurry experiments, the sulfite oxidation rate is around 1 M/hr, about 100 times greater than the aforementioned rates. An oxidative degradation constant,  $k_{12}$ , of  $2 \times 10^{-3}$  could be obtained with the introduction of the estimated dissolved S(IV). The higher value of  $k_{12}$  for the slurry system is probably due to the addition of Fe to the system through the dissolution of calcium sulfite and calcium sulfate solids. Therefore, the organic acid degradation rate is directly proportional to the sulfite oxidation rate.

## pH and Dissolved S(IV)

A number of slurry experiments suggest that the degradation rate increases with increasing pH. However, dissolved S(IV) is significantly affected by pH in the slurry system (Table 1). Experiments with the sodium sulfite solution system without Mn or Fe at pH 5.0 suggest that the apparent effect of pH on  $k_{12}$  in the slurry system is due to the variation of dissolved S(IV) as pH changes (Figure 2). In addition to affecting dissolved S(IV) in the slurry system, pH also affects the distribution of sulfite and bisulfite and the degree of protonation or dissociation of organic acid, which might be important in the degradation kinetics. Further studies showed no effect of pH on  $K_{12}$  when the dissolved S(IV) was kept  $\sim 1$  mM for three different catalyst environments (Figure 3). Figure 3 also shows that, in the presence of 0.1 mM Fe,  $k_{12}$  decreases as the pH increases over 5.0.

## Transition Metals

Figure 3 shows that  $k_{12}$  is increased by Fe and decreased by Mn. Sodium sulfite solution experiments show that it is the ratio  $[\text{Fe}]/[\text{S(IV)}]_d$  (Figure 4) or  $[\text{Mn}]/[\text{S(IV)}]_d$  (Figure 5) that controls  $k_{12}$ . In Figure 4, a background level of 0.0007 mM Fe is assumed according to the correlation result which will be discussed later. The decrease of  $k_{12}$  with increasing pH in the presence of 0.1 mM Fe (Figure 3) may be due to decreasing solubility of Fe at higher pH.

The first series of transition metals (except Sc and Zn) were studied in sodium sulfite solution. Among these, Co, Ni, and probably Cu appear to increase the oxidative degradation constant,  $k_{12}$ , while Ti, V, and Cr are inert (Table 2). Ti showed a minor inhibiting effect on the degradation of organic acid in the slurry system. The effect of Ti was not detectable in the sodium sulfite solution system, probably because of interference with the measurement of dissolved S(IV).

## Halides

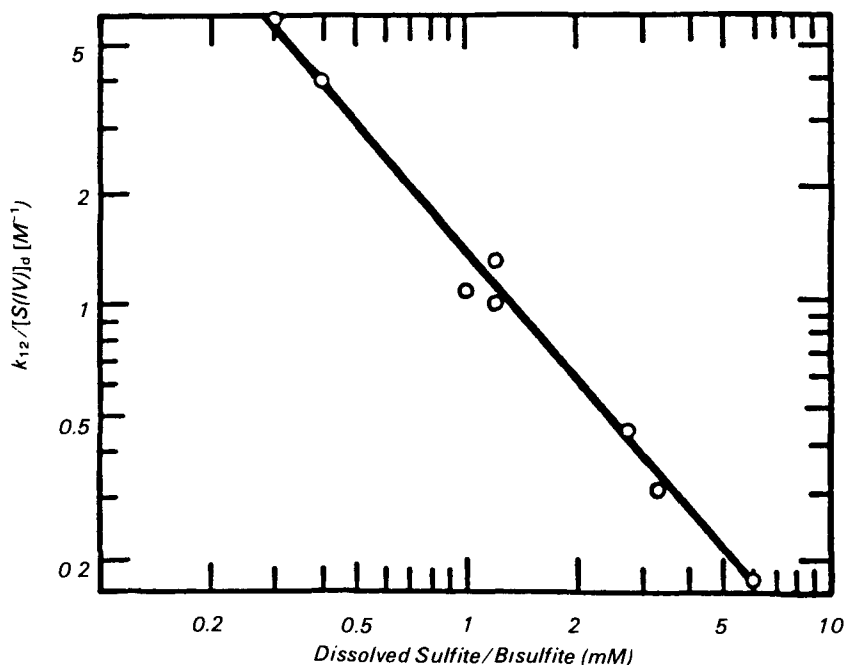
It has been reported that the decomposition of carboxylate salts during sulfite oxidation is suppressed by the presence of 0.5 to 3 M chloride in the aqueous absorbent. Table 3 lists the resulting  $k_{12}$  values of adipic acid with different concentrations of chloride, bromide, and iodide. Manganese effects are included for the convenience of comparison. In sodium sulfite solution,

**Table 1.** Steady State Solution Composition in  $\text{CaSO}_3$  Slurry as a Function of pH, Closed Reactor, 55°C, No Organic Acid

pH	Fe <sup>a</sup> mM	Mn <sup>b</sup> mM	[S(IV)] <sub>d</sub> mM	Sulfite Oxidation Rate, M/hr
4.0	0.15	0.43	34.2	0
4.0	0.13	0.43	27.0	0.5
4.5	0.12	0.45	24.8	0
4.5	0.12	0.46	14.5	0.5
5.0	0.02	0.46	9.3	0
5.0	0.02	0.46	5.9	0.5
5.0	<0.01	0.47	3.9	0
5.0	<0.01	0.46	1.3	0.5

<sup>a</sup>0.1 mM was added

<sup>b</sup>0.5 mM was added



**Figure 2.** Effect of dissolved S(IV) on the degradation of glutaric acid: sodium sulfite solution, closed reactor, 55°C, pH 5

chloride reduces  $k_{12}$  significantly only when its concentration is as high as 100 mM. On the other hand, the iodide effect is so strong that, even in the presence of 0.1 mM Fe, 0.1 mM iodide reduces  $k_{12}$  to  $0.1 \times 10^{-3}$ . The corresponding value for 1 mM Mn in the absence of Fe is approximately  $0.4 \times 10^{-3}$ . The effect of bromide is between that of chloride and iodide. As with Mn and Fe, the effect of halides is magnified by low dissolved S(IV) (Table 3).

## Thiosulfate

Large addition of thiosulfate stops not only sulfite oxidation but also organic

acid degradation. When Mn was applied to suppress the inhibiting effects caused by thiosulfate, it was found that, in the slurry system at pH 5.5, 1 mM thiosulfate caused reduction of  $k_{12}/[\text{S(IV)}]_d$  from 0.6 to  $0.15 \text{ M}^{-1}$ . No significant effects were observed when pH was lower than 5.0. The inhibiting effect of thiosulfate on the degradation of organic acid is probably due to the low dissolved S(IV) at pH 5.5. Being conjugated with sulfite oxidation, the degradation of thiosulfate is faster than that of adipic acid by three orders of magnitude. Reactive free radicals in an environment of low dissolved S(IV) have a significantly higher probability of

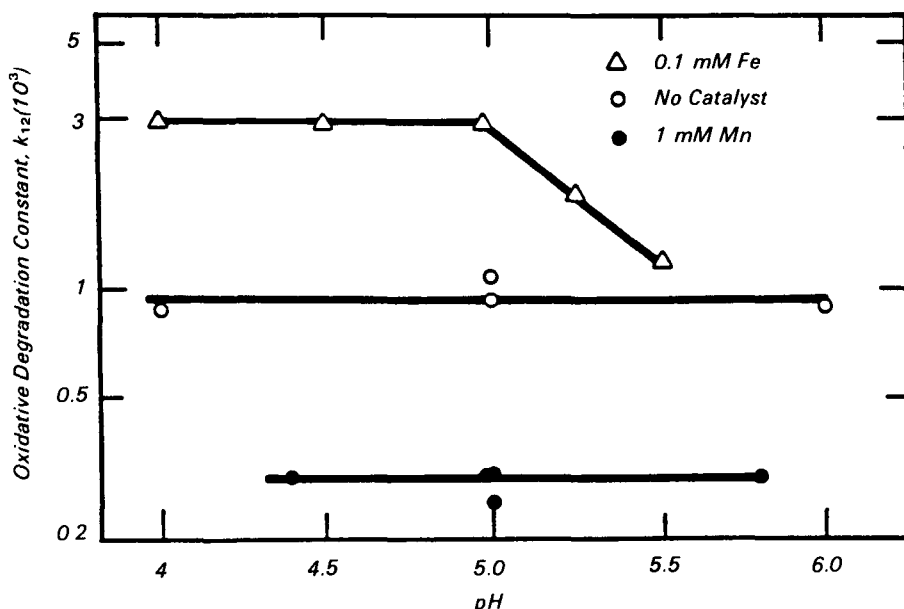


Figure 3. Effect of pH on the degradation of glutaric acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1 mM.

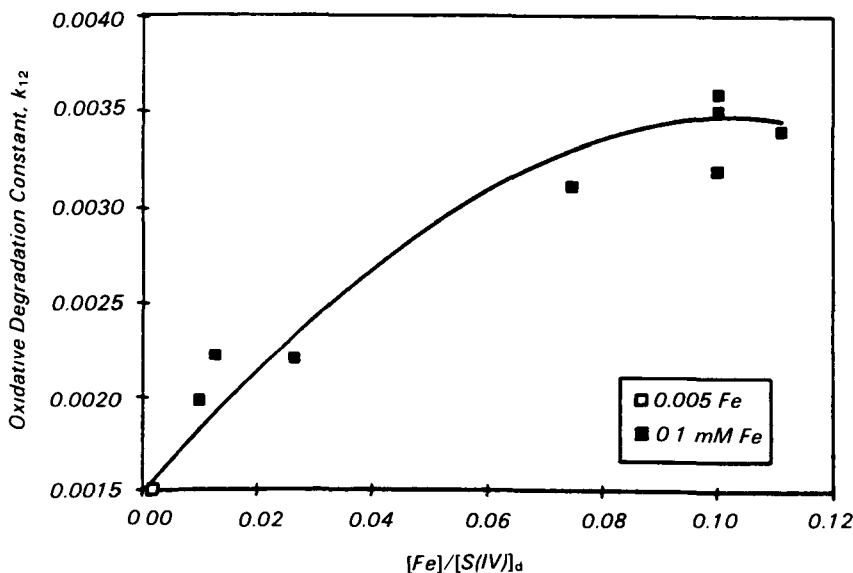


Figure 4. Effect of Fe on the degradation of adipic acid (sodium sulfite solution), closed reactor, 55°C.

reacting with thiosulfate than with organic acid. This effect is not very strong in the presence of high dissolved S(IV) because of the significant reaction of S(IV) with free radicals.

### Oxygen

Figure 6 shows that there is no effect of oxygen partial pressure on  $k_{12}$ , with or without addition of Mn or Fe. There-

fore, the reaction order of oxygen in degradation and oxidation reactions should be equal and cannot be detected in the oxidative degradation experiments.

### Alternatives

Table 4 summarizes the oxidative degradation constants of several potential organic acid buffer additives. Maleic acid degrades about seven times faster than

saturated dicarboxylic acids, probably due to the presence of conjugated double bonds. In reducing the degradation of maleic acid, Mn is not as effective as for saturated dicarboxylic acids. Fe has little effect on maleic acid degradation. On the other hand, hydroxycarboxylic acids degrade about three times slower than dicarboxylic acids. The smaller oxidative degradation constants of hydroxyacids probably are not due to the formation of an intramolecular hydrogen bond because of the indistinguishable degradation behavior between 3- and 2-hydroxybenzoic acids. Sulfosuccinic acid behaves more or less like hydroxycarboxylic acids except that Fe has no significant effect on the degradation of sulfosuccinic acid.

### Degradation Products

The degradation products of adipic acid are widely distributed. They can be classified as dicarboxylic acids, monocarboxylic acids, hydroxycarboxylic acids, keto-acids, furans, hydrocarbons, and carbon dioxide (Table 5). The degradation product distribution is also a strong function of catalyst environment. Carbon dioxide is the primary degradation product for all cases. In the presence of 1 mM Mn, glutaric and valeric acids are major products. In the absence of Mn, glutaric semialdehyde is the major liquid-phase product. Although oxygen would be required to generate a smaller dicarboxylic acid, the dissolved oxygen in the presence of 1 mM Mn should be practically zero because of the mass transfer controlled sulfite oxidation. Therefore, Mn may be an effective carrier of oxygen to the degradation product(s).

### Mechanism

Figure 7 gives a mechanism proposed to rationalize the experimental observations. This mechanism is based on two assumptions: (1) only sulfate radical (Eq. 2) and manganic ion (Eq. 3) react with organic acids to cause significant degradation, primarily decarboxylation; and (2) other reactions of organic radicals, except the degradation of organic acids, are negligible.

$$k_{12} = \frac{Kd_1}{2ki_3} \left( \frac{kp_2'}{kp_2 + kp_2'} + \frac{kp_2'}{kp_2 + kp_2'} \right) \frac{1}{1 + \frac{kp_3}{ki_1} \frac{[S(IV)]}{[Fe]}}$$

$$\left(1 + \frac{kd_2}{kd_1} \frac{ki_4'}{ki_2'} \frac{[Mn]}{[S(IV)]}\right) \left(1 + \frac{ki_4'}{ki_3} \frac{[Mn]}{[S(IV)]} + \frac{ki_4}{ki_3} \frac{[Fe]}{[S(IV)]}\right) \quad (16)$$

Recognizing that sulfate radical (Eq. 2) and manganic ion (Eq. 3) react with organic acids at much slower rates than with S(IV) (Eq. 8, 7) and assuming that intermediates reach steady state concentrations, Eq. (1) and the mechanism proposed above lead to an expression of the oxidative degradation constant,  $k_{12}$ , (Eq. 16) with three variables: dissolved S(IV), Mn, and Fe. Sixty-six data points collected from sodium sulfite solution experiments were used for correlation. These data can be grouped as (1) no Mn/no Fe, (2) no Mn/Fe>0, (3) Mn>0/no Fe, and (4) Mn>0/Fe>0. A background concentration of iron (Fe $\emptyset$ ) is introduced because Fe or a comparable catalyst must be present to initiate the reaction. Therefore, Eq. (16) ends up with seven adjustable parameters determined by nonlinear regression:

$$\begin{aligned} kd_1/(2ki_3) &= 0.0041 \\ kp_2'/(kp_2 + kp_2') &= 0.227 \\ kp_3/ki_1 &= 0.0184 \\ (kd_2/kd_1)(ki_4'/ki_2') &= 0.85 \\ ki_4'/ki_3 &= 11.93 \\ ki_4/ki_3 &= 0.65 \\ [Fe\emptyset] &= 0.0007 \text{ mM} \end{aligned}$$

The experimental and calculated values of  $k_{12}$  are compared in Figure 8.

### Organic Acid Reactions

Peroxydisulfates have been extensively studied for oxidizing organic compounds, especially organic acids. The sulfate radical anion is a well established intermediate in the thermal and photolytical decomposition of peroxydisulfates and is believed to be responsible for the degradation of organic compounds (Eq. 2). Oxidative degradation of organic acids by Mn<sup>3+</sup> has also been studied (Eq. 3).

Additional evidence demonstrates that sulfate radical reacts with organic acid under FGD conditions:

1. Sulfate radical can be easily derived from peroxymonosulfate, SO<sub>5</sub><sup>-2</sup>, an expected intermediate, by analogy to peroxydisulfate, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

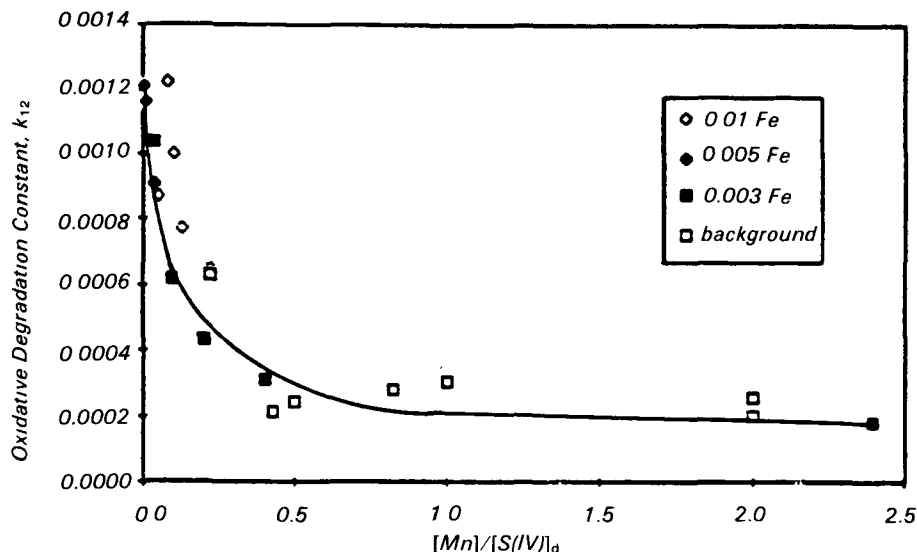


Figure 5. Effect of Mn on the degradation of adipic acid (sodium sulfite solution): closed reactor, 55°C, pH 5.

Table 2. Effects of Transition Metals on  $k_{12}$  in Sodium Sulfite Solution by CO<sub>2</sub> Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Conc. mM	Oxidative Degradation Constant, $k_{12} \times 10^3$					
	Co	Ni	Cu	Ti	V	Cr
0	0.81	0.89	0.87	0.86	1.10	0.99
0.03	0.84	--	0.89	--	--	--
0.1	0.76	1.18	0.93	--	1.23	1.03
0.3	0.82	--	1.00	0.90	1.43	1.02
1.0	0.99	2.48	1.31	0.86	1.46	1.02
3.0	1.60	--	1.33	0.84	1.54	--
100	3.30	--	--	--	--	--
Oxidation State	2,3	2,3	1,2	3,4	2,3,4,5	2,3,6

Table 3. Effects of Halides on  $k_{12}$  in Sodium Sulfite Solution by CO<sub>2</sub> Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Conc., mM	Oxidative Degradation Rate Constant, $k_{12} \times 10^3$			
	KCl	KBr <sup>a</sup>	KI <sup>a</sup>	MnSO <sub>4</sub>
0	2.0	2.7	3.1	1.0
0.1	--	2.3	0.1	0.7
0.3	--	2.0	--	0.3
1	--	1.5	--	0.3
10	--	0.2	--	--
30	0.8	--	--	--
100	0.6	--	--	--
300	0.3	--	--	--

<sup>a</sup>with 1.0 mM Fe

2. The ratio of sulfate radical reacting with organic acid to that reacting with S(IV) is consistent between experimental results and literature predictions.
3. Previous work on oxidative degradation of organic acids by sulfate

radical indicates that decarboxylation is the major pathway, which is consistent with experimental observations (Table 5).

The hydroxyl radical is probably not responsible for organic acid degradation at FGD conditions. It is known to react

with organic acids and can be generated from sulfate radical by reacting with water or hydroxyl ion. However, reaction of hydroxyl radical with organic acids does not result in simple decarboxylation, and at pH less than 8.5 the reactions making hydroxyl radicals are negligible.

### Sulfur Compounds Reaction

**Sulfite radical.** The reaction of sulfite radical with  $O_2$  (Eq. 11) provides a way to "activate" oxygen for the oxidation of S(IV). The sulfite radical is not very reactive toward organic compounds but reacts at a much higher rate with oxygen and at an even greater rate with itself. The latter reaction is probably the major termination reaction when the reaction rate is controlled by mass transfer of oxygen and has also been proposed as a termination reaction. The stable termination products were reported to be sulfur trioxide and dithionate which will be hydrolyzed to sulfate and sulfite.

**Sulfate radical.** The sulfate radical is a very reactive on-electron transfer oxidizing agent. Some correlated and literature reaction rate constants are compared in Table 6. The reaction of sulfate radical with  $HSO_3^-$  is believed to be at least 2.5 times faster with  $SO_3^{2-}$ . Therefore, the sulfate radical will react with S(IV) faster at lower pH. In contrast, the sulfate radical reacts with organic acid slower at lower pH. Therefore, a smaller oxidative degradation constant,  $k_{12}$ , is expected at lower pH, although experimental data do not confirm this projection.

**Peroxymonosulfate.** The peroxymonosulfate radical ( $SO_5^-$ ) is logically derived from the reaction of sulfite radical with oxygen (Eq. 11). The  $SO_5^-$  thus formed reacts with S(IV) to produce sulfate radical, sulfite radical, and peroxymonosulfate ( $HSO_5^-$ ) in parallel reactions (Eq. 12, 13). The coexistence of these two reactions suggests a minimum  $k_{12}$  corresponding to the fraction of  $SO_5^-$  that reacts with S(IV) to form sulfate radical.

It is suggested (Eq. 16) that the direct production of  $SO_4^-$  from  $SO_5^-$  (Eq. 13) is not affected by Fe, while the indirect production of  $SO_4^-$  from  $SO_5^-$  (Eq. 5) through the formation of  $SO_5^{2-}$  intermediate (Eq. 12) is catalyzed by Fe. Therefore,  $SO_5^-$  is the precursor of  $SO_4^-$ , which is the major species responsible for the degradation of organic acid. Since the formation of  $SO_5^-$  is inevitable, the degradation of organic acid in conjugation with S(IV) oxidation is also inevitable.

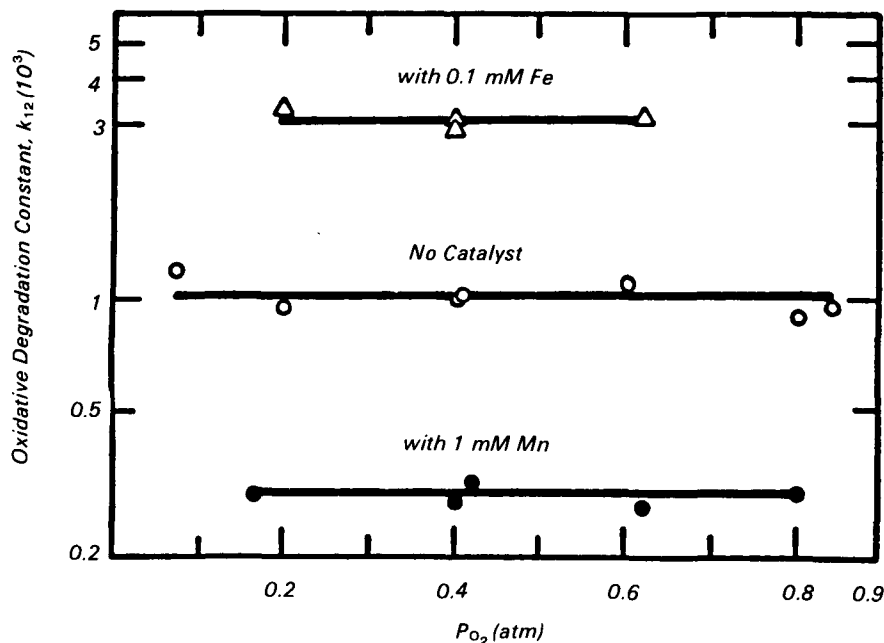


Figure 6. Effect of oxygen on the degradation of glutaric acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1 mM.

Table 4. Comparison of Organic Acids Buffer Additives in Terms of  $k_{12}$  at pH 5.0, 55°C, in Sodium Sulfite Solution by  $CO_2$  Evolution

Organic Acid	[S(IV)] <sub>0</sub> mM	Oxidative Degradation Rate Constant, $k_{12} \times 10^3$		
		1 mM Mn	No Catalyst	0.1 mM Fe
Adipic	1.0	0.3	1.0	3.0
Glutaric	1.0	0.3	1.0	3.0
4-Hydroxybutyric	1.0	0.1	--	1.4
Hydroxyacetic	1.0	0.2	--	1.0
Malic	6.0	--	--	1.4
3-Hydroxybenzoic	2.0	0.3	--	--
2-Hydroxybenzoic	3.0	0.4	--	--
Benzoic	1.5	0.8	--	--
Sulfosuccinic	1.5	0.1	0.3	0.3
Maleic	5.0	3.6	6.7	7.0

### Iron Reactions

In the proposed mechanism, free radicals are primarily generated by the reaction between ferrous ion and peroxymonosulfate (Eq. 5). It is well known that ferrous ion reacts with peroxides to form ferric and a free radical formed by splitting the peroxide bond. Also, the free radical is thought to be sulfate radical instead of hydroxyl radical.

Ferrous ion also reacts with sulfate radical (Eq. 9) at a significant rate. Therefore, Fe generates sulfate radical by reaction with peroxymonosulfate (Eq. 5) but also depletes sulfate radical by direct reaction (Eq. 8). As a result, Fe can

inhibit or enhance organic acid degradation depending on solution conditions.

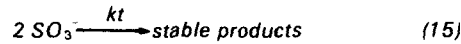
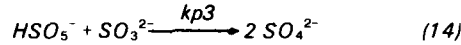
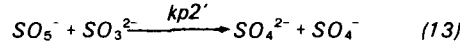
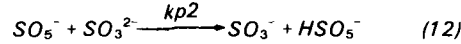
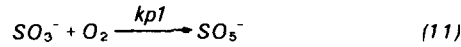
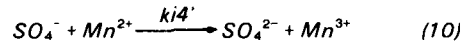
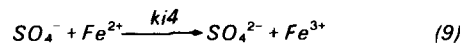
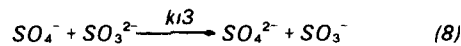
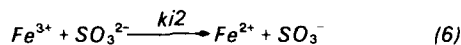
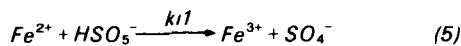
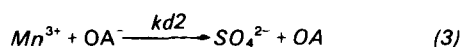
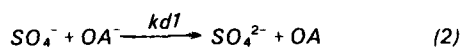
### Manganese Reactions

By analogy to the reaction between ferrous ion and sulfate radical (Eq. 9), manganous reacts with sulfate radical (Eq. 10). The latter reaction is necessary for the mechanism to match the observation that manganese decreases  $k_{12}$ . The reaction rate constant is estimated to be  $1.8 \times 10^{10}$ . To provide a route for manganous regeneration, manganic ion should also react with S(IV) (Eq. 7) by analogy to the reaction between ferric ion and S(IV) (Eq. 6). The ratio of the

**Table 5.** Degradation Products from 80% Degradation of 10 mM Adipic Acid in Calcium Sulfite Slurry with 0.1 mM Mn at pH 5.0, 55°C in Terms of the Percentage of the Initial Concentration (mM C)

Dicarboxylic	Monocarboxylic	Hydroxycarboxylic	Hydrocarbons	Others
C6 Adipic (20)				Tetrahydro 2,5 furan Dicarboxylic <sup>a</sup>
C5 Glutaric (1.5)	Valeric (0.7)	5-Hydroxyvaleric (2.5)		Glutaric Semialdehyde (6.7) 4-Oxo- pentanoic (0.3)
C4 Succinic (0.1)	Butyric (0.4)	4-Hydroxybutyric (2.5)	Butane (1.0)	Succinic Semialdehyde <sup>a</sup>  Furane (0.6)
C3 Malonic (2.3)	--		Propane <sup>a</sup>	
C2	--		Ethane <sup>a</sup>	
C1	Formic (2.0)		Methane <sup>a</sup>	Formaldehyde <sup>a</sup> CO <sub>2</sub> (49)

<sup>a</sup>less than 0.1%



**Figure 7.** A mechanism for the oxidative degradation of organic acid conjugated with the oxidation of S(IV) to S(VI).

reaction rates of  $\text{Mn}^{3+}$  with organic acid and  $\text{Mn}^{3+}$  with S(IV),  $kd2/ki2'$ , was found to be 0.0006, which is an order of magnitude smaller than the sulfate radical counterpart,  $kd1/ki3$  (0.0082).

### Halide Reactions

By analogy to Mn, halides inhibit organic acid degradation by reacting with sulfate radical. The experimental and calculated values of  $k_{12}$  with bromide present are compared in Figure 8.

The correlated value of  $ki4(\text{Br})/ki3$  (1.26) leads to a prediction of  $1.7 \times 10^9$  as the reaction rate constant between  $\text{SO}_4^-$  and  $\text{Br}^-$ . This constant has been measured as  $(3.5 \pm 0.4) \times 10^9$ .

Not enough iodide data are available for the prediction of the reaction rate constant between iodide and sulfate radical. However, halides tend to react with organic compounds in decreasing order ( $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ ), while halides tend to react with  $\text{SO}_4^-$  in increasing order ( $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ). Therefore, iodide would inhibit organic acid degradation most efficiently, while chloride would be the least efficient inhibitor. These trends are expected because of their relative strength in standard electrode potentials.

### Conclusions

1. The degradation of organic acid is conjugated with sulfite oxidation and can be expressed kinetically in terms of the "oxidative degradation constant,"  $k_{12}$ , which is defined as:

$$k_{12} = \frac{\text{organic acid degradation rate}}{\text{sulfite oxidation rate}} \times \frac{\text{dissolved S(IV) concentration}}{\text{organic acid concentration}}$$

The oxidative degradation constant,  $k_{12}$ , is independent of oxygen mass transfer conditions, organic acid concentration, and pH.

2. The proposed free radical mechanism correlates the experimental  $k_{12}$  from 0.0001 to 0.0036 within 30% for 0.3-10 mM S(IV), 0-0.1 mM Fe, 0-1.2 mM Mn, and 0-10 mM Br.
3. Sulfate is the primary free radical responsible for the oxidative degradation of organic acids.
4. Iron competes with dissolved S(IV) for peroxymonosulfate to produce sulfate radical and hence increases  $k_{12}$  from 0.001 to 0.0036 when Fe concentration increases from background level (0.0007 mM) to 0.1 mM. No  $k_{12}$  over 0.004 has been observed.
5. Manganese competes with dissolved S(IV) for depleting sulfate radical and hence decreases  $k_{12}$  from 0.001 to 0.0002 when Mn concentration increases from zero to 1.0 mM. In addition to sulfate radical, manganic ion also causes the degradation of organic acids. Therefore, the effect of Mn is bounded, and no  $k_{12}$  less than 0.0001 has ever been observed.
6. Halides resemble Mn in reducing  $k_{12}$ . With 1 mM dissolved S(IV), 0.1 mM Mn gives effects comparable to <0.1 mM iodide, 1 mM bromide, or 100 mM chloride.
7. Lower dissolved S(IV) magnifies the catalytic and inhibiting effects of Fe, Mn, and halides.
8. Thiosulfate inhibits sulfite oxidation and therefore stops organic

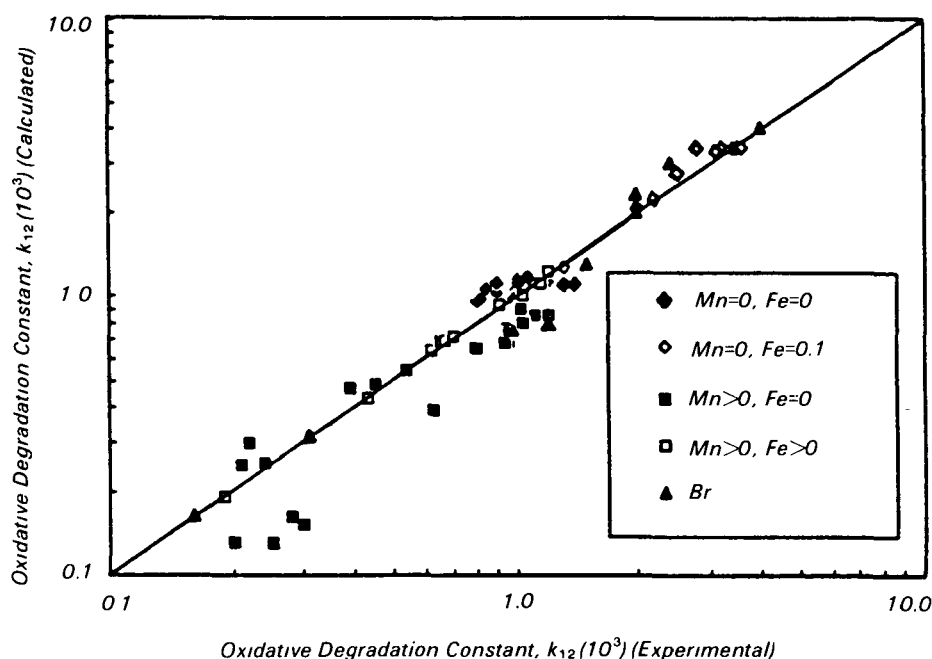


Figure 8. Comparison of calculated and experimental value of  $k_{12}$

- acid degradation. In the presence of Mn, thiosulfate decreases  $k_{12}$  at low levels of dissolved S(IV).
- Among other transition metals, Co and Ni increase  $k_{12}$  an order of magnitude less efficiently than Fe, while Tl appears to reduce  $k_{12}$ , and Ti, V, Cr, and Cu have no significant effects.
  - Decarboxylation is the major degradation pathway. In the presence of 0.03 mM Mn, 1.3 mole carbon dioxide is generated from every mole of glutaric acid degradation up to 30% conversion. At high conversion (80%), as much as 49% of the carbon of adipic acid is degraded to carbon dioxide.
  - With 0.1 mM Mn at 80% conversion, the other degradation products of adipic acid are smaller dicarboxylic acids (4%), monocarboxylic acids (3%), hydroxycarboxylic acids (5%), hydrocarbons (1%), glutaric semialdehyde (7%), and other carbonyl compounds (1%).
  - In the presence of high Mn (1.0 mM), the retained degradation products of adipic acid are primarily valeric and glutaric acids.

- Hydroxyacids and sulfonated acids degrade slower than simple dicarboxylic acids by a factor of three, while maleic acid, an unsaturated dicarboxylic acid, degrades an order of magnitude faster. Therefore, hydroxyacids and aldehydeacids, which are sulfonated under FGD conditions, accumulate as ultimate liquid-phase degradation products.

### Recommendations

- The oxidation of S(IV) under FGD conditions should be studied further with emphasis on the individual and combined effects of Mn, Fe, halides, and free radical scavengers to better understand the mechanism. Dissolved S(IV) and oxygen should be monitored during the experiments to confirm the effects of these two variables.
- Organic acids and their deliberate derivatives should be studied for oxidative degradation to differentiate electron transfer mechanism and hydrogen abstraction. Decarboxylation and general degradation can then be discriminated and compared as a function of functional group composition and catalyst environment.

Table 6. Rates of Sulfate Radical Reactions in Aqueous Solution

Reactant	Estimated $k(M^{-1}S^{-1})$	Literature $k(M^{-1}S^{-1})$
$SO_3^{2-}$	--	$\geq 5.3 \times 10^3$
$HSO_3^-$	--	$> 2.5 \times 5.3 \times 10^3$
Succinate	--	$7.1 \times 10^6$
Fumarate	--	$1.6 \times 10^7$
Adipate	$1.0 \times 10^7$	--
$Fe^{2+}$	$8.6 \times 10^3$	$9.9 \times 10^3$
$Mn^{2+}$	$1.8 \times 10^{10}$	--
$Br^-$	$1.7 \times 10^9$	$(3.5 \pm 0.4) \times 10^9$
$Cl^-$	--	$1.3 \times 10^3$
$OH^-$	--	$4.6 \times 10^7$
$H_2O$	--	$10^3 - 10^4$
$HSO_5^-$	--	$< 10^5$

- The degradation product distribution should be studied as a function of reaction time or conversion to understand better the oxidative degradation of organic acids.
- The oxidative degradation experiments should be conducted over a broad pH range, 3 to 7, to observe the effect of pH on the degradation of organic acids.
- Thiosulfate and halides, especially iodide and bromide, should be tested in combination with organic acids in FGD scrubbing systems on a pilot plant scale to investigate possible beneficial effects. If oxidation is inhibited, then unsaturated acids such as maleic acid would have makeup rates comparable to DBA or adipic acid.
- If high level of sulfite oxidation is expected, formic and maleic acids are inferior to other alternatives such as DBA and adipic acid.



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*The complete report, entitled "Oxidative Degradation of Organic Acids Conjugated with Sulfite Oxidation in Flue Gas Desulfurization," (Order No. PB 88-180 674/AS; Cost: \$19.95, subject to change) will be available only from:*

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