



Project Summary



Buffer Additives for Lime/Limestone Slurry Scrubbing Synthesis, Mass Transfer, and Degradation

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Experimental studies were performed with buffer additives useful for flue gas desulfurization by lime/limestone slurry scrubbing. The rates of reaction of acrylic acid and maleic anhydride with bisulfite at 55°C were sufficiently fast to permit *in situ* synthesis in a slurry scrubber of sulfopropionic and sulfosuccinic acids, respectively. β -Hydroxypropionic acid was synthesized by hydration of acrylic acid at 100 - 140°C with catalysis by H₂SO₄ or cation exchange resin. Enhancement of SO₂ absorption by acetic, adipic, hydroxypropionic, sulfopropionic, and sulfosuccinic acids and by basic aluminum sulfate was measured at 55°C in 0.3 M NaCl and 0.1 M CaCl₂, and was successfully modeled by mass transfer with equilibrium reactions. Oxidation of carboxylic acids conjugated with oxidation of CaSO₃ slurry was studied for seven acids. Oxidative degradation of adipic acid and other aliphatic and sulfocarboxylic acids was least at pH 4.3 with 1.0 mM dissolved Mn and greatest at pH 5.5 without Mn. Hydroxyacetic and hydroxypropionic acids inhibited sulfite oxidation and were less subject to degradation. The most attractive acids for further testing are adipic, mixtures of waste dibasic organic, sulfosuccinic, hydroxypropionic, and hydroxyacetic acids.

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 docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Lime/limestone slurry scrubbing is the dominant commercial technology for flue gas desulfurization. SO₂ is absorbed at 50-55°C and pH 4.5-6.0 in an aqueous slurry of excess limestone and product solids. The calcium sulfite (CaSO₃)/calcium sulfate (CaSO₄) product is disposed of as solid waste. With greater than 500-1000 ppm SO₂ in the flue gas, SO₂ absorption is controlled by liquid/film mass transfer resistance because of the limited solubility of SO₂ gas and alkaline solids. Additives that buffer between pH 3 and 5.5 enhance SO₂ absorption by providing dissolved alkaline species for reaction with SO₂. This is a report of experimental investigations to provide data for the evaluation of buffer additive alternatives. This work was summarized in 1982 and was also included in an extensive review of buffer additives that same year.

An attractive buffer additive should be inexpensive, provide mass transfer enhancement at low concentrations, and be nonvolatile and chemically stable at scrubber conditions. The important classes of inexpensive nonvolatile buffers include polycarboxylic acids (e.g., adipic), hydroxycarboxylic acids (e.g., hydroxypropionic), and sulfocarboxylic acids (e.g., sulfopropionic). Some of these alternatives are not commercially available and must be synthesized from inexpensive raw

materials. The synthesis of hydroxypropionic, sulfopropionic, and sulfosuccinic acids has been demonstrated. This report gives quantitative reaction kinetics for the synthesis of these three alternatives. This work was also published as a master's thesis in 1981.

Mass transfer enhancement depends on the buffering properties and diffusivity of the additive. Effective pK_a values of buffer alternatives at scrubber conditions were measured in 1978. A model of enhancement, based on mass transfer with equilibrium reactions, was developed in 1981, the same year that its effectiveness with acetic and adipic acids was experimentally demonstrated at 25°C. This report gives experimental and model results at 55°C with several buffer alternatives. Details of the work are also given in a master's thesis in 1981.

Organic acids are normally stable to oxidation, but laboratory and pilot plant results have shown that adipic acid oxidizes in conjugation with sulfite oxidation in the scrubber. This report gives oxidative degradation rates of adipic acid as a function of pH and Mn concentration. Results are also presented for glutaric, succinic, sulfopropionic, sulfosuccinic, fumaric, hydroxypropionic, and hydroxyacetic acids. Details of the work are given in master's theses in 1980 and 1981.

Buffer Synthesis

Sulfocarboxylic and hydroxycarboxylic acids are attractive as buffer additives because the additional hydrophilic groups make both the buffer and its degradation products nonvolatile in aqueous solution. Available kinetic data on sulfite addition to maleic or acrylic acid to give sulfosuccinic or β -sulfopropionic acid were evaluated in 1977. The feasibility of hydrating acrylic acid with H_2SO_4 catalysis at 100°C to get β -hydroxypropionic acid was demonstrated in 1978.

This report gives measurements of reaction kinetics for sulfonation of maleic, fumaric, and acrylic acids by sulfite addition and for hydration of acrylic acid with catalysis by H_2SO_4 or cation exchange resin. The kinetics were measured by sampling isothermal batch reactors.

Sulfocarboxylic Acids

In sulfonation experiments, the extent of reaction was determined by iodine titration for total sulfite. Solutions initially containing 0.05-0.20 M unsaturated acid

were maintained at approximate pH values by lactate, acetate, or phosphate buffers. NaCl, $CaCl_2$, or $MgCl_2$ was added to change the ionic environment.

The sulfonation reactions follow a second-order mechanism:

$$\text{rate (M/min)} = k_f [\text{acid}]_{\text{Total}} [\text{SO}_3]_{\text{Total}}$$

The measured second-order rate constants, k_f ($M^{-1} \text{min}^{-1}$), for sulfonation at 1.2 N ionic strength in Na^+ solutions at pH 5 are given by:

$$\begin{aligned} \text{acrylic acid: } k_f &= 4.48 \times 10^9 \exp(-14,000/RT) \\ \text{fumaric acid: } k_f &= 372 \exp(-6,100/RT) \\ \text{maleic acid: } k_f &= 2.38 \times 10^{11} \exp(-17,500/RT) \end{aligned}$$

where T is temperature (K) and R is the gas constant (1.987 cal/gmol K). At 55°C with 0.5 N ionic strength, the constants are $0.21 M^{-1} \text{min}^{-1}$ for acrylic, $0.031 M^{-1} \text{min}^{-1}$ for fumaric, and $0.52 M^{-1} \text{min}^{-1}$ for maleic acids.

The rate constants do not vary significantly from pH 3.5 to 7.0, but no reaction occurs at pH 2 or 13. The sulfonation rates increase with ionic strength. With fumaric and maleic acids, there may also be an additional catalytic effect of Mg^{++} or Ca^{++} .

Because dissolved sulfite is present in a typical $CaO/CaCO_3$ scrubber system, it is conceivable that unsaturated acids would sulfonate if added directly to the scrubber system. For the sulfonation reactions, a scrubber system can be characterized as a completely stirred tank reactor with a residence time equal to the ratio of solution inventory and the rate of loss of solution with the waste solids. Assuming 10 mM total dissolved sulfite, 55°C, 0.5 N ionic strength, and 130 hours residence time, the fraction of unsulfonated acid that would leave the system is 6% for acrylic, 29% for fumaric, and 4% for maleic acids. Therefore, *in situ* sulfonation is feasible for acrylic and maleic acids, but it is only partially effective for fumaric acid.

Acrylic acid and maleic anhydride (the commercial form of maleic acid) require some precautions for safe handling. If these precautions are unacceptable to the user, these unsaturated acids can be easily sulfonated offsite by reaction with sodium sulfite. Sodium sulfosuccinate was prepared successfully by adding 3.3 gmol Na_2SO_3 and 3.0 gmol maleic anhydride to 1 liter of water. The temperature increased from 25 to 80°C and the solids dissolved within 1 minute. The solution did not precipitate when cooled to 6°C. Therefore, the sulfonated acids could probably be prepared in a tank car and shipped as concentrated solution directly to the user.

Hydroxypropionic Acid (HP)

In hydration experiments, acrylic acid (AA) was determined by ion exclusion chromatography (ICE) on a Dionex ion chromatograph. HP was evident on the chromatograms, but was not quantified because of the lack of an adequate standard. Hydration was catalyzed at 100 to 140°C by 0.1 to 1.5 M H_2SO_4 or by H^+ -loaded sulfonated polystyrene resin (Dowex 50W-X4) with an exchange capacity of 1.3 meq/cm³ (wet basis) and 67% moisture content.

The hydration reaction was found to be first-order in AA and first-order in H^+ . The second-order forward rate constant, k_f ($M^{-1} \text{hr}^{-1}$), for both resin and H_2SO_4 catalysis, was correlated by:

$$k_f = 1.14 \times 10^9 \exp(-17,000/RT)$$

The reaction is reversible at high conversions, where the net reaction is given by: $\text{rate (M/hr)} = k_f [H^+] [AA] - k_r / K [H^+] [HP]$. The equilibrium constant K is defined by:

$$K = [HP] / [AA]$$

In 1942, K was found to be 11.3 at 110.6°C and 6.8 at 134°C.

In at least one experiment (105°C, 4 M AA, 0.5 M H_2SO_4), there was visual evidence of AA polymerization, giving a faster apparent rate constant. Polymerization should be minimized by reduced AA concentrations and increased catalyst concentrations.

Using the 1942 measured rate data and equilibria, the estimated reactor residence times for 85% conversion with 1 M H_2SO_4 at 105°C are 14 hours for a batch or plug flow reactor, 85 hours for a single completely stirred tank reactor (CSTR), and 33 hours for two CSTRs in series. If the reaction was carried out at the scrubber site, no additional purification should be required, but there would be a makeup requirement for sulfuric acid.

Specific results with HP synthesized from AA in 1982 indicate that it inhibits limestone dissolution. Inhibition probably results from polyacrylic acid formed during hydration. In actual operation, the polyacrylic acid may be removed from scrubber solution by precipitation of its calcium salt. If not, removal of polyacrylic acid by other means may be necessary.

Gas/Liquid Mass Transfer Enhancement

In 1981, SO_2 absorption was measured at 25°C in a continuous stirred reactor with an unbroken gas/liquid interface. P_{so_2} , pH, and concentrations of acetic and adipic acids in 0.3 M NaCl were varied. Because SO_2 absorption was quantified by liquid-phase material balance, there

were no experiments with greater than 1 mM total dissolved sulfite.

The apparatus used in the 1981 measurements (above) was modified for this work. Heating tape was added to liquid and gas stream inlets to permit operation at 55°C. Gas-phase analysis and flow measurement were refined, and SO₂ absorption rate was determined by gas-phase material balance, permitting operation with high concentrations of sulfate and total sulfite. Tighter pH control was achieved by continuously adding 1.0 M NaOH directly to the reactor.

The apparatus was characterized at 55°C and 540 rpm by SO₂ absorption into 0.3 M NaOH giving a gas/film mass transfer coefficient ($k_g A$) of 4.93×10^{-3} gmol/bar-sec and into 0.3 M HCl giving a liquid-film mass transfer coefficient ($k_l A$) of 1.5×10^{-3} l/sec, where A is the apparent surface area for mass transfer. Experiments were performed in 0.3 M NaCl or 0.1 M CaCl₂ at pH 5.5 or 4.2 with 0-40 mM of adipic, acetic, sulfopropionic, sulfosuccinic, or hydroxypropionic acid or AlCl₃. The gas-phase SO₂ concentration was adjusted to give about 1000 ppm at the gas/liquid interface. The enhancement of the liquid/film mass transfer coefficient by chemical reaction was calculated from SO₂ absorption rate, SO₂ gas concentration, SO₂ Henry's constant, $k_l A$, and $k_g A$ as in the 1981 measurements.

In 1981, an enhancement factor model was developed, based on approximate surface renewal with multiple equilibrium reactions. The model included equilibria among and diffusion of the solution species: H⁺, SO₂, HSO₃⁻, SO₃²⁻, H₂A, HA⁻, and A²⁻. The pK_a values of the buffer species, H₂A, HA⁻, and A²⁻, could be adjusted to represent any appropriate buffer.

The 1981 model was used in this work with appropriate equilibrium constants and diffusivities to represent operation at 55°C in 0.3 M NaCl or 0.1 M CaCl₂. Empirically, it was found that diffusivities in 0.1 M CaCl₂ were consistently less than in 0.3 M NaCl. To get good correlation of the experimental data, the diffusivities of all monovalent anions were reduced 25% and the diffusivities of all divalent anions were reduced 45% from their values in 0.3 NaCl.

The calculated values of the liquid/film enhancement factor are within 10% of the measured values for adipic, acetic, sulfosuccinic, and hydroxypropionic acids. To fit the measured data, the diffusivity of sulfopropionic acid was reduced by an additional 50% from the value estimated in 1981.

Experiments with up to 20 mM AlCl₃ in 0.1 M CaCl₂ at pH 3.8 gave no measurable enhancement of SO₂ absorption, even though basic AlCl₃ is an excellent buffer at pH 3.8. The lack of effectiveness of the aluminum buffer may result from the formation of large, slow-moving polynuclear aluminum complexes, or it may reflect a slow reaction rate between aluminum complexes and H⁺.

Figure 1 shows the calculated liquid/film enhancement factor for five buffers as a function of buffer concentration in 0.1 M CaCl₂ at pH 5.5 with 1000 ppm SO₂ at the gas/liquid interface. On a molarity basis, adipic acid is most attractive, and sulfopropionic acid is least attractive. With no buffer, the enhancement factor is 7.3 because of the hydrolysis of SO₂ and because of enhancement by SO₃²⁻. At 10 mM total adipic acid, the enhancement factor is 20, or about 3 times greater than in the absence of buffer.

Figure 2 illustrates the effect of adipic acid on the overall enhancement of SO₂ absorption. It gives the ratio of the overall mass transfer coefficient, K_g , to the gas/film coefficient, k_g , as a function of the dimensionless liquid-phase driving force, $(HP_{SO_2} + [HA^-] + 2[A^{2-}])/HP_{SO_2}$, where H is the Henry's constant, P_{SO_2} is the bulk gas SO₂ partial pressure, and HA⁻ and A²⁻ represent H adipate and adipate species. The overall coefficient includes an effect of $k_l A$ and the liquid/film enhancement factor which increases with adipic acid concentration. The ratio, K_g/k_g , representing the fraction resistance of the gas film, cannot exceed 1.0.

Greater values of K_g/k_g represent proportionately better scrubber performance. This specific figure is valid for scrubbers with the ratio of mass transfer coefficients without enhancement given by $H k_l A/k_g$ equal to 0.2.

As shown in Figure 2, adipic acid has a greater effect with higher SO₂ gas concentration because, at lower concentration, SO₂ absorption is already controlled mostly by gas/film resistance. With less total dissolved sulfite, liquid/film resistance is reduced by SO₂ hydrolysis to H⁺ and HSO₃⁻, even in the absence of buffer.

In all cases, the curves asymptote to gas-phase control with an abscissa value of 10 - 40. 10 mM adipic acid and 10 mM sulfite at pH 5 with 2500 ppm SO₂ gives K_g/k_g of 0.91. This corresponds to an improvement of 1.8 because of adipic acid addition.

Table 1 gives the calculated concentrations of 12 buffers required to get an enhancement factor of 20 in 0.1 M CaCl₂ with 10 mM total sulfite at pH 5.0 with

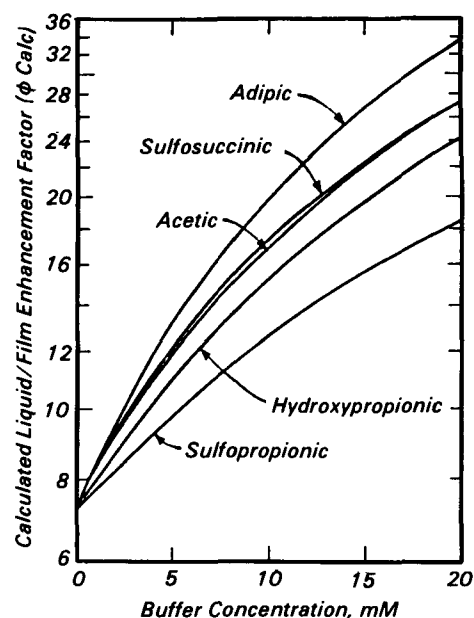


Figure 1. Calculated effect of buffer alternatives on the liquid/film enhancement factor, 0.1 M CaCl₂, 55°C, pH 5.5, 3 mM total sulfite, 1000 ppm SO₂.

1000 ppm SO₂ at the gas/liquid interface. Relative costs are calculated assuming that makeup rates are proportional to concentration.

Formic and acetic acids are most attractive, but would probably be volatile under scrubber conditions. Succinic and lactic acids would not be cost-effective if purchased at market price. Fumaric acid is more subject to oxidative degradation. Phthalic and benzoic acids may give undesirable aromatic degradation products. Therefore, the most useful buffers appear to be hydroxypropionic, sulfosuccinic, sulfopropionic, adipic, and hydroxyacetic acids.

Waste or byproduct organic acids could be cost-effective alternatives. Adipic acid production by nitric acid/oxidation of cyclohexanol/cyclohexanone generates a byproduct consisting of glutaric, succinic, and adipic acids which should perform like adipic acid. Air-oxidation of cyclohexane, to produce cyclohexanone as an intermediate for caprolactam, generates a byproduct solution of adipic, hydroxyvaleric, glutaric, and other acids. The performance of this product should be comparable to a mixture of adipic and hydroxypropionic acids.

Oxidative Degradation

Adipic acid and other carboxylic acids are usually stable to oxidation in aqueous

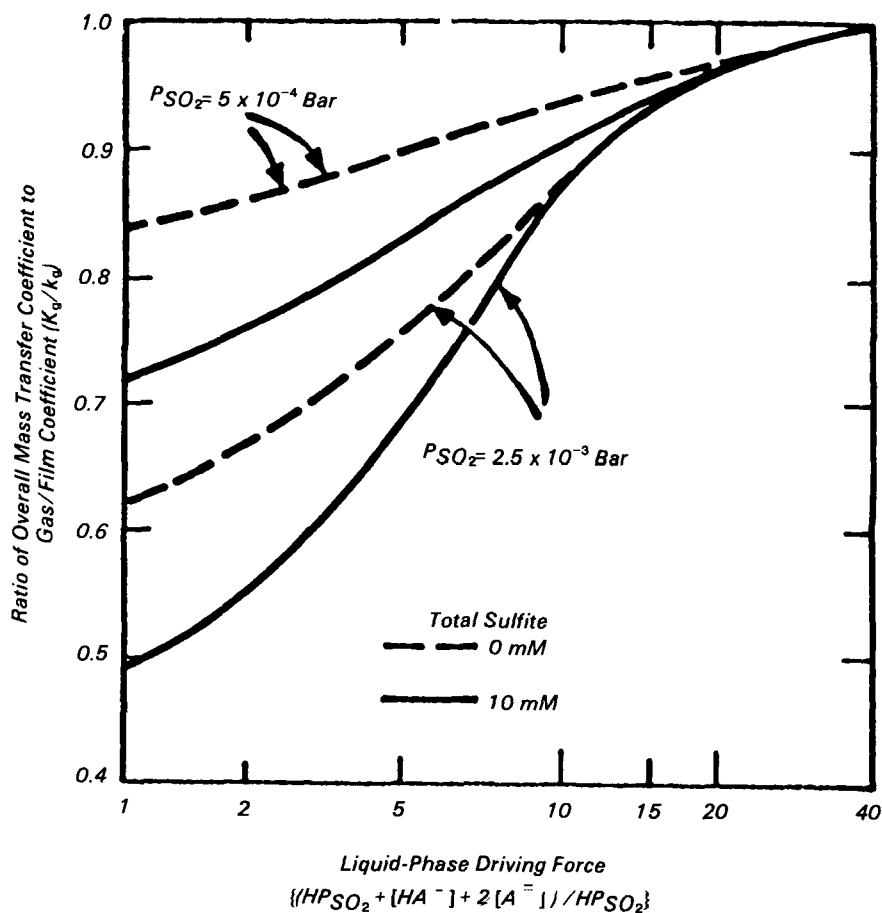


Figure 2. Overall mass transfer enhancement by adipic acid, 55°C, 0.1 M CaCl₂, pH 5.

solution. However, free radicals generated in the oxidation of hydrocarbons or alcohols will attack carboxylic acids that are present, producing CO₂ and mono- or dicarboxylic acids of shorter chain length than the original acid.

Such conjugated oxidation of sulfite and adipic acid results in degradation of

adipic acid to CO₂ and shorter chain acids (e.g., glutaric and valeric acids). The rate of degradation is directly proportional to the rate of sulfite oxidation and the total organic acid concentration ([A]):

$$\frac{d[A]}{dt} = k_d[A] \frac{d[SO_3^{2-}]_T}{dt}$$

Table 1. Relative Costs of Organic Acids ($\phi = 20$, 55°C, pH 5.0, 0.1 M CaCl₂, 10 mM Total Sulfite, 1000 ppm SO₂)

Organic Acid	Concentration	Price (\$/lb mol)	Relative Cost
Formic	21.1	12.28	0.28
Acetic	15.6	21.62	0.37
Hydroxypropionic	19.7	34.59	0.75
Sulfosuccinic	16.3	43.15	0.77
Sulfopropionic	25.6	34.59	0.97
Adipic	11.8	77.45	1.00
Phthalic	18.1	55.58	1.10
Benzoic	17.9	57.46	1.13
Fumaric	19.1	66.16	1.38
Hydroxyacetic	32.0	39.66	1.39
Succinic	12.3	134.11	1.80
Lactic	34.4	78.82	2.97

Pilot, prototype, and demonstration plant tests of adipic acid have shown significant levels of degradation. The degradation losses are generally reduced at pH less than 5.0 and increased by forced oxidation.

The objective of this work was to quantify the rates and products of the degradation of adipic acid and alternative carboxylic acids. Parallel work by Radian Corporation has measured rates and products of adipic acid degradation.

In this work, degradation of 5 - 20 mM carboxylic acid was measured during batch oxidation of 1 - 2 M CaSO₃ slurry at 55°C with pure oxygen sparged into an agitated reactor. Slurry was analyzed for total sulfite by iodine titration. Filtered solution was analyzed for specific carboxylic acids by ion (or ion exclusion) chromatography. Additional solution analyses were performed by gas chromatography with extraction into chloroform before and after aqueous methylation.

Figure 3 gives typical results on the rate of sulfite oxidation. At pH 4.3 or 4.5 or with 1 mM Mn, the sulfite oxidation rate was maximum, limited by either mass transfer or the supply of O₂ to the reactor. Without Mn, the sulfite oxidation rate decreased with increasing pH and essentially stopped at pH 6.0.

Both hydroxycarboxylic acids and thio-sulfate inhibited sulfite oxidation. At pH 5.0, 0.3 mM Mn was sufficient to compensate for inhibition by 10 mM hydroxyacetic acid. With 1 mM Mn, sulfite oxidation was completely inhibited by 2 mM thiosulfate at pH 5.5, and by 3 mM thiosulfate at pH 5.0. 10 mM thiosulfate was insufficient to inhibit sulfite oxidation at pH 5.0 in the presence of 1 mM Mn and 0.3 M MgSO₄.

Figure 4 gives the degradation rate constant (k_d) of adipic acid as a function of pH with and without Mn. In the absence of Mn, k_d is only a weak function of pH. With 1 mM Mn, k_d is significantly reduced and is a strong function of pH. At pH 4.5, the degradation of succinic acid was almost completely inhibited by 0.3 mM Mn, but hardly affected by 0.2 mM Mn.

These data are generally consistent with degradation rates measured at both the Shawnee 10 MW test facility and the Radian bench-scale scrubber in 1982.

No adipic acid degradation was observed in experiments with no sulfite oxidation, resulting from high pH or the presence of hydroxyacids or thiosulfate. At pH 5.5 with 1 mM Mn, the presence of 1 mM thiosulfate reduced k_d from 0.6 to 0.25 M⁻¹, while hardly affecting the rate of sulfite oxidation.

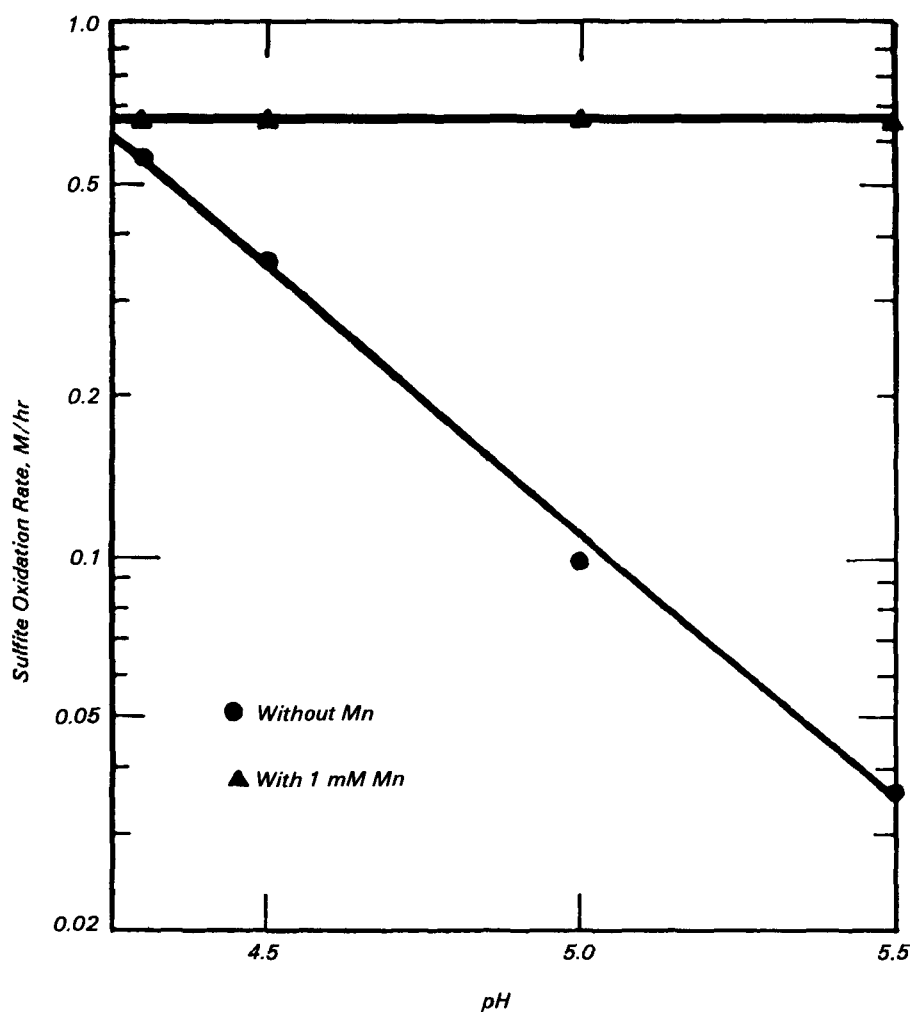


Figure 3. Effect of pH on sulfite oxidation—1340 rpm, 200 ml O₂/min.

Table 2 compares degradation rate constants measured for eight organic acids. The aliphatic acids (succinic, glutaric) and sulfoacids (sulfopropionic, sulfosuccinic) behaved much like adipic acid. Dibasic waste acid (mostly glutaric) also degraded like adipic acid. Fumaric acid degraded much faster than adipic acid because of its carbon-carbon double bond. The hydroxyacids both degraded much more slowly, probably because of the alcohol function. In one experiment with a mixture of hydroxyacetic and adipic acids, the adipic acid degraded as usual, but the hydroxyacetic acid degraded much more slowly than adipic acid.

Table 3 gives the typical degradation products of adipic acid at pH 5.0 with and without Mn. With Mn, there are nominal concentrations of the expected products, malonic and glutaric acids. Without Mn, there is also an appreciable accumulation of the aldehyde-acid, 4-carboxybutanal.

In both cases most of the adipic acid that degrades is probably lost as CO₂.

Conclusions

1. Adipic acid was attractive buffer properties, and is cost-effective, non-toxic, and commercially available in large quantities. It coprecipitates with CaSO₃ and is subject to oxidative degradation, but these problems should be minimized by using forced oxidation at low pH with high concentrations of dissolved Mn.

2. Byproduct dibasic acid (DBA), containing primarily glutaric acid, is a cost-effective alternative equivalent to adipic acid.

3. The hydroxycarboxylic acids are uniquely inert to oxidative degradation and inhibit sulfite oxidation in the absence of Mn. Hydroxypropionic acid is economically attractive; however, its synthesis from acrylic acid gives polyacrylic

acid impurities that would probably have to be separated. Glycolic acid is commercially available, but economically somewhat less attractive.

4. Sulfosuccinic acid is economically attractive when synthesized *in situ* or offsite from maleic anhydride. It is subject to oxidation, but should give nonvolatile degradation products.

5. Basic aluminum salts are ineffective for mass transfer enhancement.

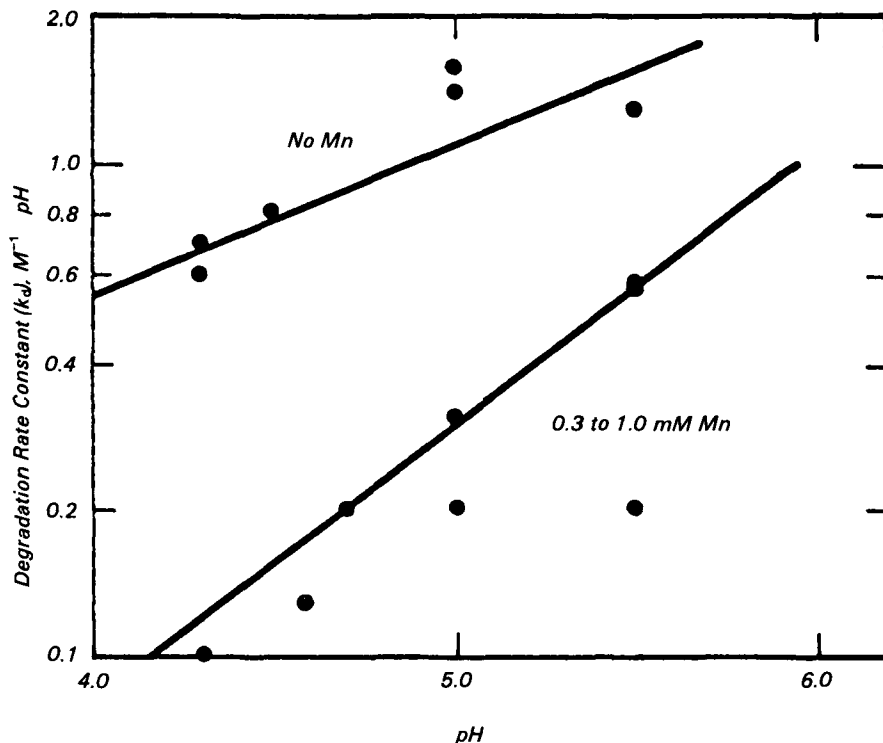


Figure 4. Adipic acid degradation.

Table 2. Measured Degradation Rate Constants of Buffer Alternatives

Organic Acid	pH	Mn, mM	k_d , M^{-1}
Adipic	4.5	0.0	0.8
		1.0	0.15
	5.5	0.0	1.6
		1.0	0.6
Glutaric	5.5	0.1	1.6
Succinic	4.5	0.0	0.5
Sulfopropionic	5.0+	0.0	1.0
Sulfosuccinic	5.0+	0.0	1.0
Fumaric	5.5	1.0	2.4
Hydroxyacetic	5.0	0.3	0.1
Hydroxypropionic	4.5	0.0	0.2

Table 3. Organic Acids in a Solution of 10 mM Adipic Acid Degraded at pH 5.0

Product	Concentrations, mM	
	Mn, 0.1 mM	Mn, 3.0 mM
Adipic	1.40	5.20
Glutaric	0.55	0.45
Unknown 117 (C5)	0.50	-
4-Carboxy-butanal	2.50	0.04
Succinic	0.20	0.04
Malonic	0.50	-
Valeric	0.09	0.50
Unknown 422 (C4)	0.40	0.03
Butyric	0.06	0.03
Carbon lost (CO ₂)	29.3	23.5

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The complete report, entitled "Buffer Additives for Lime/Limestone Slurry Scrubbing Synthesis, Mass Transfer, and Degradation," (Order No. PB 84-184 233; Cost: \$23.50, subject to change) will be available only from:

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