



Project Summary

Effect of Trace Metals and Sulfite Oxidation on Adipic Acid Degradation in FGD Systems

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The adipic acid degradation rate was measured in a bench-scale flue gas desulfurization (FGD) system designed to simulate many of the important aspects of full-scale FGD systems. Results show that the adipic acid degradation rate depends on the sulfite oxidation rate, the adipic acid concentration, the presence of manganese in solution, and temperature. The degradation rate is also affected by pH, but only when manganese is present. Adipic acid degradation products identified in the liquid phase include valeric, butyric, propionic, succinic, and glutaric acids. When manganese was present, the predominant degradation products were succinic and glutaric acids. Analysis of solids from the bench scale tests shows large concentrations of coprecipitated adipic acid in solids with high sulfite concentrations. By contrast, low quantities of coprecipitated adipic acid were found in solids with low sulfite and high gypsum concentrations.

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 addition of adipic acid to flue gas desulfurization (FGD) wet scrubbers has been shown to benefit both SO₂ removal and limestone utilization. Adipic acid has the effect of buffering scrubber solutions, thereby improving liquid-phase mass transfer. The use of adipic acid was first

proposed by G.T. Rochelle* and has been tested by EPA in pilot systems at its Industrial Environmental Research Laboratory (Research Triangle Park), at TVA's Shawnee test facility, Paducah, KY, and at Springfield City Utilities' Southwest Power Plant, Springfield, MO. Results from these previous test programs show that adipic acid is effective as a scrubber additive at concentrations of 700-2000 ppm. However, overall mass balances on these pilot systems revealed unaccounted-for losses of adipic acid. These losses were presumed to be the result of chemical degradation of adipic acid.

Further testing at Shawnee indicated that adipic acid degradation could be quenched by operating below pH 5.1. Since these unexpected but favorable results could be significant to the future application of adipic acid as a scrubber additive, independent verification was desired. Radian was contracted by EPA to conduct a systematic study of the effect of scrubber operating conditions on adipic acid degradation. This investigation involved two distinct areas of experimentation: (1) a study of the effects of scrubber operating variables on the adipic acid degradation rate (the experiments were performed using a bench-scale FGD unit designed to simulate many of the important characteristics of full-scale FGD systems); and (2) in conjunction with the bench-scale testing, analytical procedures were developed to identify and quantify adipic acid degradation products (these

*Rochelle, G T., Process Synthesis and Innovation in Flue Gas Desulfurization, EPRI FP-463-SR, July 1977.

techniques were used to analyze many samples produced during bench-scale testing). Photomicrographs of the solids produced during bench-scale operation were analyzed to determine the effect of adipic acid on particle size and morphology.

A bench-scale FGD unit was constructed to determine the effects of operating variables on the adipic acid degradation rate. The following variables were investigated: SO₂ absorption/oxidation rate, adipic acid concentration, pH, trace metals (manganese, iron), limestone and limestone plus fly ash (versus reagent grade CaCO₃), boiler (versus synthetic) flue gas, temperature, thiosulfate (as an additive), and sulfite concentration.

A total of 43 bench-scale runs were performed, 21 of which were baseline tests in which the variables were limited to the SO₂ absorption/oxidation rate, the adipic acid concentration, and pH. CaCO₃ was used as the alkaline species for all baseline tests. The ranges for the variables in the baseline tests were:

Variable	Range
SO ₂ absorption rate, g SO ₂ /hr	2.07 - 7.86
Percent solids oxidation (a measure of the total absorbed SO ₂ that is oxidized to sulfate)	9.7 - 100
Adipic acid concentration, ppm	876-10080
pH	4.6 - 5.5

The resulting adipic acid degradation rates were 15.4-600 mg/hr. A computer program was used for a statistical analysis of the baseline test data.

Results and Conclusions

The results showed that the adipic acid degradation rate was a function of the overall SO₂ oxidation rate and the adipic acid concentration. The degradation rate was found not to depend on pH, at least over the range tested, when manganese was not present. The sulfite ion concentration was also included in this analysis; however, it was generally a function of pH and was also found not to influence the adipic acid degradation rate. A weighted least squares analysis was used to correlate the significant variables. For data at 50°C, the resulting correlation, representing the best fit of the experimental data, is:

$$\text{adipic acid degradation rate, mg/g SO}_2 \text{ removed} = 0.00308 \left(\frac{\text{adipic acid concentration, ppm}}{\text{concentration, ppm}} \right)^{0.5542} \left(\text{percent oxidation} \right)^{1.185}$$

Figure 1 plots the above correlation.

A literature search indicated that certain trace elements, notably manganese and iron, catalyzed sulfite oxidation. Since the degradation rate of adipic acid was shown to depend on sulfite oxidation, several bench-scale runs were performed to evaluate the effects of manganese and iron on adipic degradation. The effects of limestone (vs. reagent grade CaCO₃) and fly ash were also evaluated, since these materials are sources of trace metals.

The presence of manganese, at concentrations of 2-21 ppm, significantly reduced the adipic acid degradation rate. Reductions of 42.5 - 85.4 percent below the adipic acid degradation rates predicted from the baseline correlation were observed for forced oxidation runs. Iron was found to be essentially insoluble under wet scrubber operating conditions: no effect on adipic acid degradation was observed.

The results of the forced oxidation runs in which manganese was present are shown in Figure 2, which plots adipic acid degradation rate constant K_d versus pH. Rate constant K_d, used here, is simply the adipic acid degradation rate normalized by the total sulfite oxidation rate and the average adipic acid concentration. K_d is a convenient method of comparing the results of runs at different adipic acid concentrations and levels of oxidation. Values of K_d for the baseline runs without manganese were 1.24 - 1.62 for the range of variables shown in Figure 2. The reduction in degradation due to manganese is evident in Figure 2: the values observed for K_d are 0.2 - 0.93.

Figure 2 also shows a dramatic effect of pH on the adipic acid degradation rate in the presence of manganese. In the baseline runs, in which no manganese was present, no pH effect was observed. At a given pH, the degradation rate also appears to be a function of the manganese concentration. The data supporting this result, however, are somewhat limited.

The concentration of manganese which could be held in solution varied with both pH and the level of oxidation. Generally speaking, more dissolved manganese was observed when operating under forced oxidation conditions than under natural oxidation conditions. At a given level of oxidation, the concentration of dissolved manganese increased with decreasing pH. A survey of the available literature indicates that manganese can remain in solution only in the +2 oxidation state. Further, Mn⁺² is probably not oxidized to the +4 or +7 oxidation states in scrubber solutions. Since less manganese could be

held in solution during natural oxidation tests, the precipitate is most likely MnSO₃. This possibility, however, was not verified by analysis.

One natural oxidation test was performed in which significant concentrations of manganese (≈13 ppm) remained in solution. The resulting adipic acid degradation rate was 59 percent below that predicted by the baseline correlation. This indicates that manganese is also effective in reducing the adipic acid degradation rate under natural oxidation conditions if sufficient quantities of manganese can be held in solution.

Several forced oxidation runs were performed in which Springfield limestone, rather than CaCO₃, was used as the source of alkalinity. The adipic acid degradation rates in the limestone tests were significantly below those in similar baseline tests with CaCO₃. This limestone was analyzed for trace metals, and a significant quantity of manganese was found. Some of this manganese dissolved in the scrubber liquor during the bench-scale tests. The resulting adipic acid degradation rates were about the same as those in runs with CaCO₃ in which manganese was added to the hold tank. In natural oxidation tests with limestone, however, much less of the manganese in the limestone went into solution. In these tests the degradation rates were not significantly different from that predicted from the baseline correlation.

Combined limestone and fly ash was also tested under forced oxidation conditions. The resulting adipic acid degradation rate did not differ significantly from that of limestone alone. In natural oxidation bench-scale tests at Shawnee and Springfield, in which boiler flue gas with fly ash was utilized, no significant effect of fly ash was observed. A separate run, evaluating the effect of fly ash alone, was not performed.

Manganese ions definitely decrease the adipic acid degradation rate. Manganese probably affects adipic acid degradation through a change in the mechanism of sulfite oxidation, which is thought to proceed through a free radical mechanism. Manganese may catalyze the sulfite oxidation reaction to reduce the concentration of the free radical believed to be involved in adipic acid degradation. Alternatively, manganese may catalyze the sulfite oxidation reaction utilizing a mechanism which does not involve a free radical. The possible existence of at least two competing sulfite oxidation mechanisms, both of which could be functions of pH, may help in interpreting the dependence of the adipic acid degra-

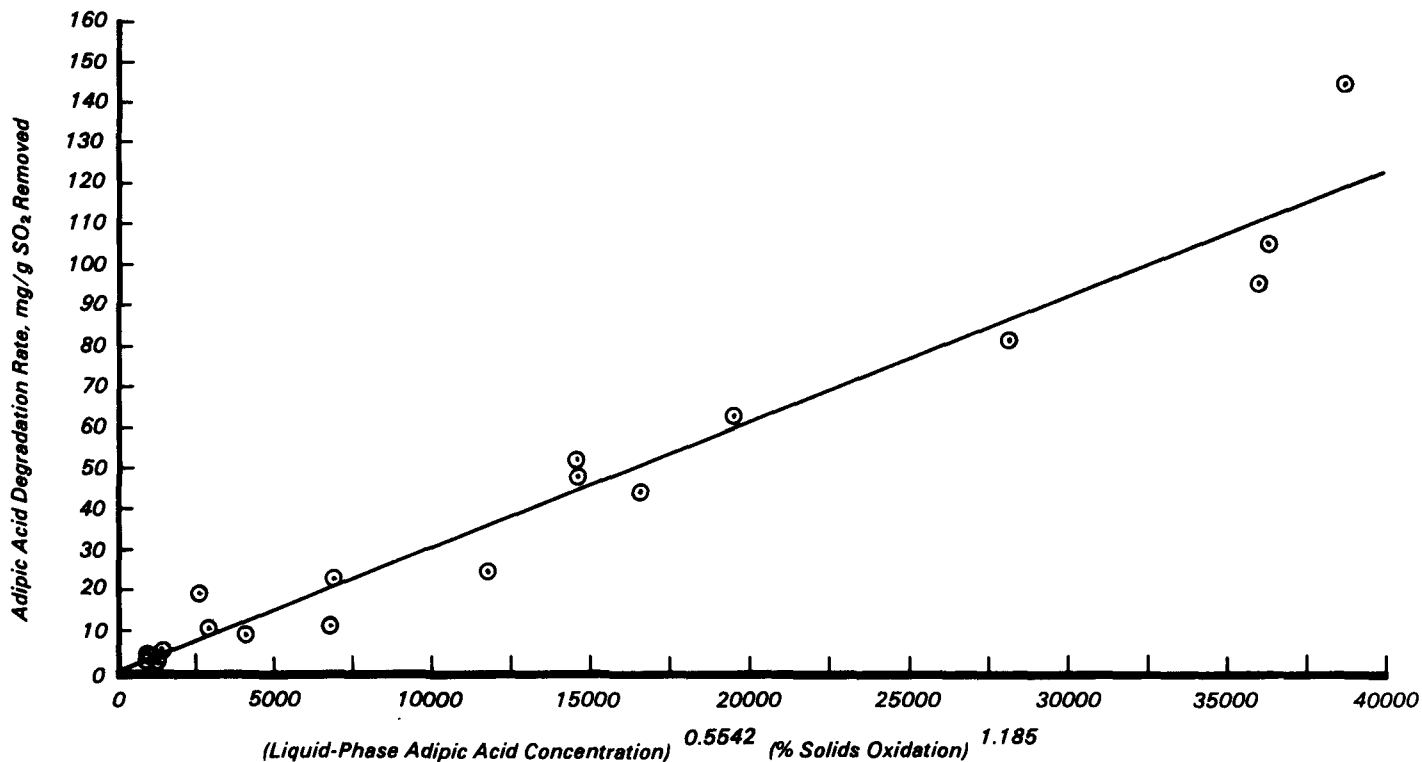


Figure 1. Correlated relationship between the adipic acid degradation rate, the liquid-phase adipic acid concentration, and the percent solids oxidation for the baseline data set.

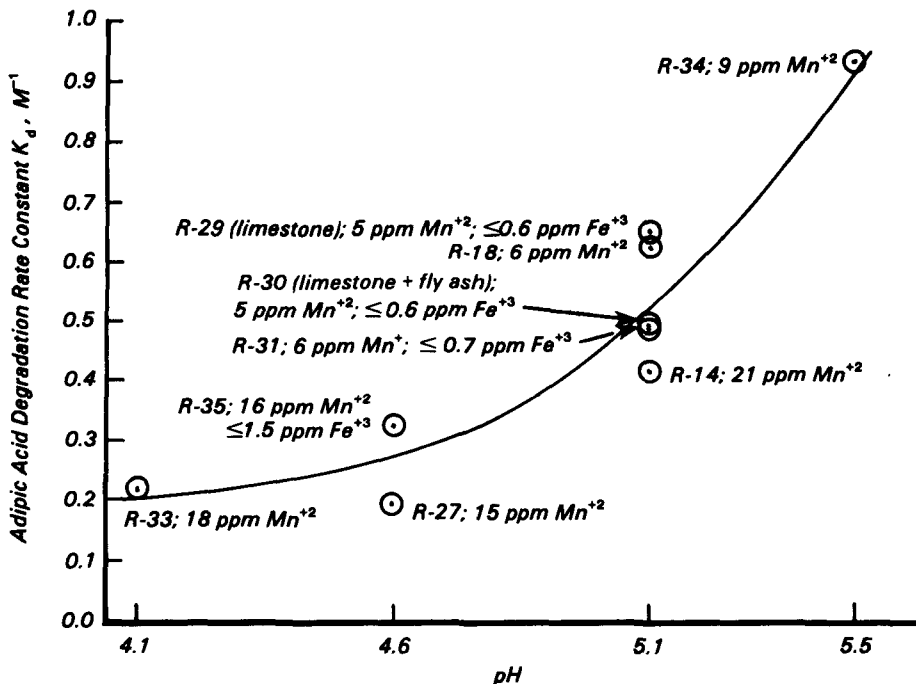


Figure 2. Effect of pH on adipic acid degradation rate constant K_d for forced oxidation runs with manganese, manganese + iron, limestone, and limestone + fly ash. (Adipic acid concentrations for these runs were 1820 - 3310 ppm.)

degradation rate on pH when manganese is present.

Three similar runs were performed in which the temperature of the hold tank increased from 93 to 146°F. Results of these runs showed that the adipic acid degradation rate increased with increasing temperature. The effect of temperature on the rate of a chemical reaction can often be modeled by the following empirical equation:

$$K = A (\exp -E_a/RT)$$

where, K = the chemical rate constant or an equivalent expression for the reaction rate,

A = a pre-exponential constant,

E_a = the Arrhenius activation energy,

R = the ideal gas constant, and

T = the absolute temperature.

From the bench-scale data, the Arrhenius activation energy was determined to be 10.6 Kcals/mole, typical of organic reactions in which the rate is controlled by a chemical reaction rather than a physical process such as diffusion.

In the analysis of the baseline test results, the sulfite ion concentration was not found to have an effect on the adipic acid degradation rate; however, in these tests, the equilibrium sulfite ion concen-

tration was a strong function of pH. To obtain an independent determination of the effect of the sulfite ion concentration, it was increased from 470 to 2600 ppm by adding sodium ions. In this way, the effect of different sulfite ion concentrations could be evaluated at the same pH. A comparison of the degradation rates from these tests with the values predicted from the baseline correlation indicates that the sulfite ion concentration has little, if any impact on the adipic acid degradation rate.

The effect of thiosulfate, a sulfite oxidation inhibitor, was also evaluated. Even under forced oxidation conditions, the solids oxidation was only 3.4 percent. The resulting degradation rate was extremely low, again emphasizing the important role of sulfite oxidation on adipic acid degradation.

In addition to degradation, adipic acid can be lost from FGD systems by coprecipitation in the scrubber solids. The amount of coprecipitated adipic acid in solids generated in the bench-scale tests is shown in Figure 3 which plots the ratio of the solid- and liquid-phase adipic acid concentrations versus percent oxidation. Note that the solids adipic acid concentration used in Figure 3 refers only to coprecipitated or occluded adipic acid; i.e., adipic acid in the liquid associated with the wet filter cake is not included. These results show that the adipic acid concentration in the solids is high at low oxidation levels and decreases to nearly zero at high oxidation levels.

Photomicrographs of the solids from bench-scale testing showed that adipic acid had an effect on both particle size and morphology under natural oxidation conditions. In general, increasing liquid-phase concentrations of adipic acid caused both a decrease in the calcium sulfite particle size and an increase in aggregate structure.

Adipic acid can be lost from FGD systems by three mechanisms: chemical degradation, coprecipitation in the scrubber solids, and liquid losses with the filter cake solids. The relative magnitude of these losses is shown in Figure 4 in which estimates for each of the three adipic acid losses are plotted versus percent sulfite oxidation. The bases for these estimates are:

- Chemical adipic acid degradation rate constant K_d was assumed to be 0.5 M^{-1} , typical of the degradation expected at pH 5.1 for systems in which manganese is present at concentrations of about 20 ppm.
- The liquid-phase adipic acid concentration was assumed to be 2000 ppm.

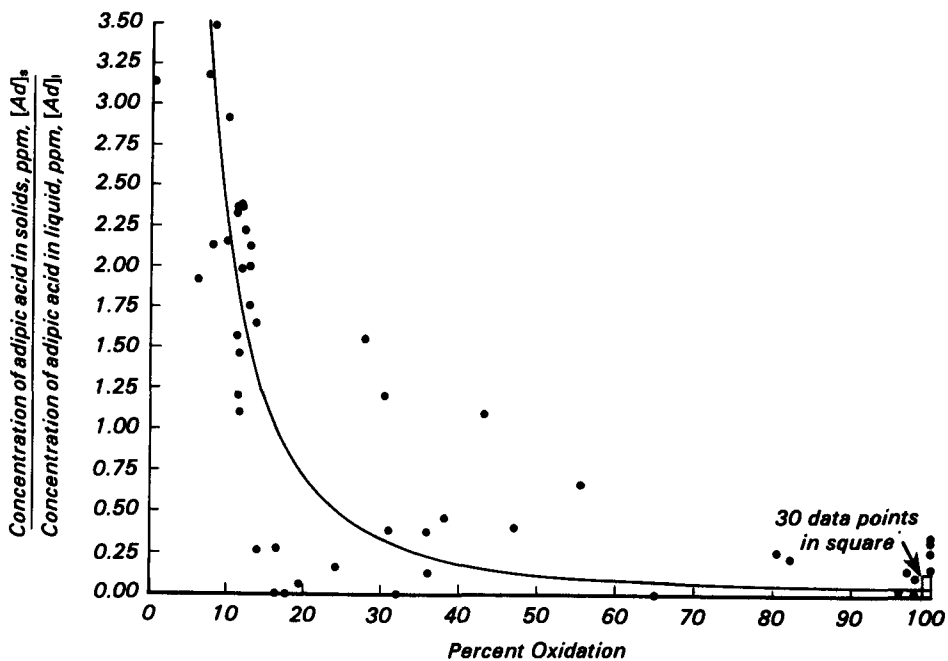


Figure 3. Relationship of adipic acid content of bench-scale solids to percent oxidation.

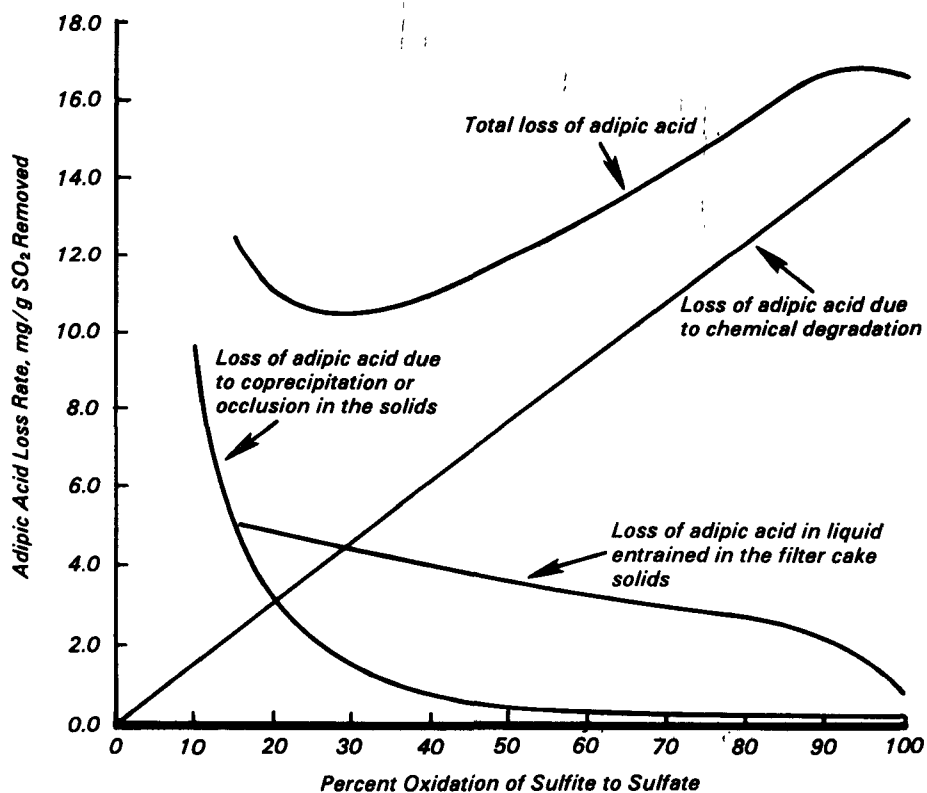


Figure 4. Estimated total adipic acid losses due to chemical degradation, coprecipitation or occlusion in the solids, and liquid entrained in the filter cake versus percent oxidation.

- The weight percent solids in the filter cake, from which the adipic acid loss in liquid associated with the filter cake is calculated, was assumed to be that determined during full-scale adipic acid testing at Springfield. Ten percent of the total solids were assumed to be inerts, either from the fly ash or the limestone.
 - The loss of adipic acid coprecipitated or occluded in the waste solids was estimated from the bench-scale relationship shown in Figure 3.
 - Closed-loop operation was assumed; i.e., blow-down or miscellaneous slurry losses were not considered.
- Adipic acid losses from actual full-scale systems may differ somewhat from that shown in Figure 4 for at least three reasons:
- 1) Manganese concentrations higher than those evaluated in this program may be seen in full-scale systems.
 - 2) Manganese is more soluble under forced oxidation conditions.
 - 3) Operation under forced oxidation conditions may result in higher concentrations of liquid-phase degradation products.

These three factors tend to reduce the forced oxidation adipic acid losses relative to natural oxidation losses.

Implications for Full-Scale Application

The bench-scale results suggest that the following variables have the greatest impact on adipic acid degradation:

- Sulfite oxidation rate (percent solids oxidation).
- Adipic acid concentration.
- pH (only if manganese is present).
- The manganese concentration in solution.

- Temperature (hold tank temperature in forced oxidation systems and scrubber temperature in natural oxidation systems).

At a given type of operation (i.e., natural or forced oxidation) the minimum total loss of adipic acid must be determined by optimizing pH and the adipic acid concentration. Naturally, the optimization procedure must be performed within the constraints of the desired SO₂ removal efficiency. A result of the optimization procedure would be the equilibrium concentration of manganese. The use of additional manganese, however, is probably not a realistic option in a full-scale FGD system.

An additional means of reducing adipic acid losses is the use of two-tank forced oxidation, in which sulfite oxidation and limestone addition take place in separate tanks; scrubber effluent is routed to the oxidation tank where sulfite oxidation occurs; and oxidation tank slurry is sent to the hold tank where limestone is added and gypsum precipitates. The advantage of this system over conventional single-tank forced oxidation is that sulfite oxidation, and the resulting adipic acid degradation, take place at pH values below that of the hold tank. The resulting decrease in the total adipic acid consumption rate can be illustrated by comparing the estimated adipic acid consumption of a two-tank forced oxidation system with that of single-tank natural and forced oxidation systems. Data for the total loss rates of adipic acid from single-tank forced and natural oxidation were given in Figure 4. The total adipic acid loss for the two-tank system can be estimated by assuming that the oxidation tank operates at 0.5 pH units below that of the hold tank. This would

decrease the effective adipic acid degradation rate constant from roughly 0.5 to 0.2 M⁻¹ at 20 ppm manganese (see Figure 2). Estimates comparing the total adipic acid consumption rate of a two-tank system with both natural and forced oxidation single-tank systems are given in Table 1.

Table 1 shows that the total adipic acid consumption rate can be minimized using the two-tank forced oxidation design.

Two-tank forced oxidation may offer several other advantages:

- Low pH in the oxidizer tank can promote sulfite oxidation, while high pH in the hold tank promotes SO₂ removal.
- The extra residence time provided by two tanks allows for more complete precipitation of calcium sulfate as well as improved limestone dissolution.
- The limestone blinding problem, which is common in adipic acid enhanced forced oxidation systems, can be minimized by oxidizing sulfite prior to limestone addition.
- Gypsum solids from forced oxidation systems are easier to dispose of than solids from natural oxidation systems.

A disadvantage of the two-tank forced oxidation design is the necessity of two tanks. Economic factors will center on a trade-off between higher capital costs for the two tanks and lower operating costs due to a decrease in adipic acid consumption. The two-tank forced oxidation design has been tested at TVA's Shawnee test facility; no serious operating problems were encountered.

Table 1. Comparison of Total Adipic Acid Consumption for a Two-Tank Forced Oxidation Design with Conventional Single-Tank Natural and Forced Oxidation Systems

	Natural Oxidation System ^a (Single-Tank)	Forced Oxidation ^b (Single-Tank)	Forced Oxidation ^b (Two-Tank)
Loss of adipic acid through chemical degradation, mg/g SO ₂ removed	6.25	15.6	6.25
Loss of adipic acid through coprecipitation or occlusion in the scrubber solid, mg/g SO ₂ removed	0.78	0.27	0.27
Loss of adipic acid in liquid associated with the filtered solids, mg/g SO ₂ removed	4.02	0.75	0.75
Total adipic acid consumption, mg/g SO₂ removed	11.05	16.62	7.27

^a40% solids oxidation.

^b99+ % solids oxidation.

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The complete report, entitled "Effect of Trace Metals and Sulfite Oxidation on
Adipic Acid Degradation in FGD Systems," (Order No. PB 83-148 379; Cost:
\$17.50, subject to change) will be available only from:
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