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Project Summary

Full-Scale Utility FGD System Adipic Acid Demonstration Program

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This report culminates a series of projects sponsored by the Environmental Protection Agency (EPA), investigating the use of adipic acid as an additive to enhance sulfur dioxide (SO_2) removal in aqueous flue gas desulfurization (FGD) systems using limestone reagent.

A 9-month program at the 194 MW Southwest Power Plant (SWPP) of City Utilities, Springfield, MO, demonstrated the effectiveness of adipic acid and dibasic acids, the latter by-products obtained during production of the former. The test program examined the effect of adipic acid addition to a limestone FGD system under natural and forced oxidation modes of operation.

Major conclusions are: (1) adipic acid addition is a feasible method for improving SO_2 removal in systems that are limited by soluble alkalinity in the scrubber slurry feed; (2) the correlation from TCA prototype testing at Shawnee by TVA adequately predicts full-scale system performance for SO_2 removal as a function of adipic acid concentration and pH; (3) limestone utilization can be improved with adipic acid addition because a lower scrubber feed can be used to achieve a given SO_2 removal; (4) increased limestone utilization from the addition of adipic acid can improve system reliability by reducing the accumulation of precipitating solids, especially in forced oxidation systems; and (5) mixed dibasic acids, an equivalent alternative to adipic acid, were the least expensive alternative examined for the SWPP to meet their SO_2 removal requirement.

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 U.S. Environmental Protection Agency (EPA) has focused a portion of its research activities on developing organic-acid-enhanced aqueous flue gas desulfurization (FGD) technology using limestone reagent for existing and new facilities. In 1981, EPA sponsored a full-scale demonstration at City Utilities of Springfield's Southwest Power Plant (SWPP); Radian Corporation was the test contractor.

Most aqueous FGD systems operated by the electric utility industry employ lime or limestone reagent. Lime/limestone FGD systems are also anticipated to be the most widely used technologies in the future because of lower capital and operating costs compared to other aqueous FGD technologies. Of the two, limestone systems are generally more cost-effective since limestone is less expensive than lime. Although limestone systems are widely used, their performance has been limited by the reactivity of the reagent which produces a lower soluble alkalinity in the scrubber slurry. This limitation results in requirements for relatively higher liquid-to-gas (L/G) ratios and larger reaction tanks than other FGD scrubbing processes.

In response to these limitations, EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) initiated a research and development program to improve the performance of lime/limestone systems. One of the most promising aspects of this effort has been the use of organic acids as buffering agents to increase soluble alkalinity in limestone FGD systems. Adipic acid was identified as a suitable additive because of its physical properties, availability, and cost. EPA has sponsored extensive laboratory-, pilot-, and prototype-scale studies on adipic-acid-enhanced limestone systems. Initial testing indicated that adding adipic acid to limestone FGD systems can provide one or more of the following process improvements: enhanced SO_2 removal, increased limestone utilization, lower capital and operating costs, and greater system flexibility.

The first three improvements are self-explanatory; the fourth requires additional explanation. Limestone systems with adipic acid addition can be used successfully in a wider range of applications than systems using other additives, and will result in a more flexible operating system.

For example, adipic acid enhances performance on both natural and forced oxidation systems, while inorganic buffers are less effective in forced oxidation systems. A forced oxidation limestone system has been projected as a more attractive option compared to a natural oxidation system because of improved sludge disposal operations; however, soluble alkalinity can limit the SO_2 removal performance of limestone systems, and inorganic additives such as magnesium are ineffective in forced oxidized operations because of their low dissolved sulfite concentrations. Alternatively, adipic acid addition is effective in increasing soluble alkalinity in forced oxidation systems.

Another example is the influence coal chloride content has on the effectiveness of additives. Relatively low levels of adipic acid have been effective in high dissolved chloride systems while greater amounts of magnesium are required to counteract the effects of chlorides. Therefore, adipic acid could be quite attractive in a plant where the coal chloride concentration varies significantly.

These are only two examples of how adipic acid addition can be beneficial. Other advantages in flexibility include: (1) ability to respond to changes in coal sulfur content; (2) adaptability to changes in limestone reactivity; and (3) ability to achieve greater than 95 percent removal to aid in achieving 90 percent removal on a rolling 30-day average basis. Reducing the limitations and increasing the flexibility of limestone systems will promote the use of limestone rather than lime which is more reactive but also more expensive.

The improvements resulting from adipic acid addition can be realized in new systems as well as in marginally designed existing systems experiencing performance limitations. Available data indicate that new adipic-acid-enhanced systems can be designed to meet New Source Performance Standards cost-effectively or to attain more stringent removal requirements to comply with local regulations. Existing systems which are not meeting design specifications can be easily adapted to accommodate adipic acid addition to improve SO_2 removal and/or limestone utilization. An excellent potential exists to use adipic acid as a less expensive alternative than other remedial actions.

More recently, a large source of by-product, mixed, organic dibasic acids (DBA) has been identified as a potentially more cost-effective alternative to adipic acid. The DBA selected for testing, a by-product of adipic acid manufacturing, is a mixture of glutaric, adipic, and succinic acids. Other by-product organic-acid-containing streams may also be attractive options.

Program Objectives

Results of previous activities were sufficiently encouraging to warrant the demonstration of the use of organic additives in a full-scale limestone FGD system. Objectives of this program were to demonstrate the effectiveness of adipic acid to improve the performance of limestone systems, and to demonstrate the validity of the previously developed data base as a design tool for full-scale FGD systems. DBA addition was also briefly tested for comparison with the adipic acid data base. In meeting these objectives, SO_2 removal data were collected using monitors that were certified and operated according to EPA procedures.

The test program was influenced by the characteristics of the full-scale system where the demonstration was conducted. City Utilities (C.U.) of Springfield was willing to participate in the demonstration program because it had been actively pursuing methods to improve SO_2 removal in the limestone FGD system at their SWPP. The system had been unable to achieve design SO_2 removals and, consequently, was unable to meet permit requirements of 520 ng/J (1.2 lb SO_2/10^6Btu). This emission limit typically requires 82 - 85 percent SO_2 removal; therefore, the test program focused primarily on the use of adipic acid to improve SO_2 removal.

Other factors also influenced the test program. The FGD system at SWPP is a natural oxidation system. However, EPA also elected to conduct forced oxidation tests since natural and forced oxidation designs are feasible options for new and retrofit systems, and since adipic acid offers advantages in the forced oxidation system that inorganic enhancement agents (e.g., magnesium and sodium) do not provide. As a result of these considerations the following areas for testing were specified at SWPP:

- forced oxidation tests
  - baseline
  - adipic acid addition for 95 percent removal
- natural oxidation tests
  - baseline
  - adipic acid addition
    - -- 85 percent SO_2 removal
    - -- 95 percent SO_2 removal
  - DBA addition
    - -- 85 percent SO_2 removal
    - -- 95 percent SO_2 removal

The performance of the FGD system at 95 percent removal was investigated to determine the potential of organic acid addition to meet stringent SO_2 removal requirements. Since the SWPP system is a natural oxidation process, 85 percent removal was investigated in natural oxidation tests to assist C.U. in identifying the operating conditions necessary to meet its permit requirements. DBA was also tested at 85 percent removal as a potentially less expensive option for the SWPP.

Tests at SWPP lasted 9 months: first, 4 months was spent investigating adipic acid addition in a forced oxidation system; next, 3-½ months was spent testing adipic acid addition to a naturally oxidized system to achieve 85-95 percent SO_2 removal; and, finally, 1-½ months was spent testing DBA in a naturally oxidized system. Results of these tests are summarized, following a brief process description.

Process Description

C.U.'s Southwest Unit 1 is a 194 MW unit designed to burn coal containing 3.5 - 4.0 percent sulfur. After exiting the boiler, flue gas passes through an air preheater, electrostatic precipitator, and induced draft fans prior to entering the FGD system and subsequently exiting through the stack.

The original FGD system consisted of two parallel turbulent contact absorber (TCA) modules, each sized to handle 60 percent of the design flue gas flow. Three contact levels, each with 100 mm (4 in.) of TCA spheres were provided in each module. The L/G ratio at full load was 6 - 7 l/Nm^3 (40 - 45 gal./1000 acf). The pressure drop across the absorber portion of each module was 25 - 30 cm H_2O (10 - 12 in. H_2O). Prior to the demonstration program, C.U. had experienced reliability problems and excessive maintenance expenses with the TCA modules. During the course of the forced oxidation tests, the TCA spheres were removed from module S-1 and some testing was conducted without the spheres. Then, the spheres were replaced for the remainder of forced oxidation testing. The module was converted to a tray absorber at the conclusion of the forced oxidation tests. Module S-2 was not converted to a tray absorber until the end of the demonstration program so that data were collected for both TCA and tray tower contactors during natural oxidation testing.

Figure 1 is a flow schematic for one module. Flue gas enters the presaturator and is cooled by supernatant liquor (thickener overflow). The gas then passes through three levels where it is contacted by the slurry and SO_2 is removed. Entrained slurry is removed from the flue gas by the mist eliminator and the cleaned flue gas exits through the stack. The lower bank of mist eliminator blades are washed continuously with supernatant liquor to control slurry accumulation and scale formation.

The dewatering system consists of a thickener, a vacuum filter, and a pug mill for mixing ash with FGD sludge. The ash/sludge mixture is landfilled onsite. The thickener overflow is collected in the supernatant tank and returned to the system. The limestone preparation facility consists of a wet ball mill producing a relatively coarse slurry, 50-60 percent passing through 200 mesh. The ground limestone is collected in a sump, diluted, and then pumped to the limestone storage tank. During the demonstration, adipic acid was added to the limestone sump. Since the dewatering and limestone preparation equipment was common to both modules, the adipic acid concentration in each module could not be varied independently.

Two relatively simple modifications were made to the FGD system to accommodate the needs of the demonstration program: 1) an adipic acid feed system was installed and 2) forced oxidation capability was provided temporarily. UOP's Air Correction Division modified the equipment. Both systems were designed for temporary use during the demonstration program and, as a result, suffered from the omission of some design features that would be included in permanent installations. In particular, the forced oxidation modifications were limited to the addition of air compressors and reaction tank spargers. No changes were made to the dewatering system, designed for natural oxidation. The substantial change in sludge properties created some operating problems during forced oxidation tests. Also, the existing reaction tank agitator and gear box were undersized for operation in the forced oxidation mode so that oxidation efficiencies were affected. The types of problems observed, attributable to retrofitting a natural oxidation system to test in a forced oxidation mode, do not indicate problems that would result from the use of adipic acid.

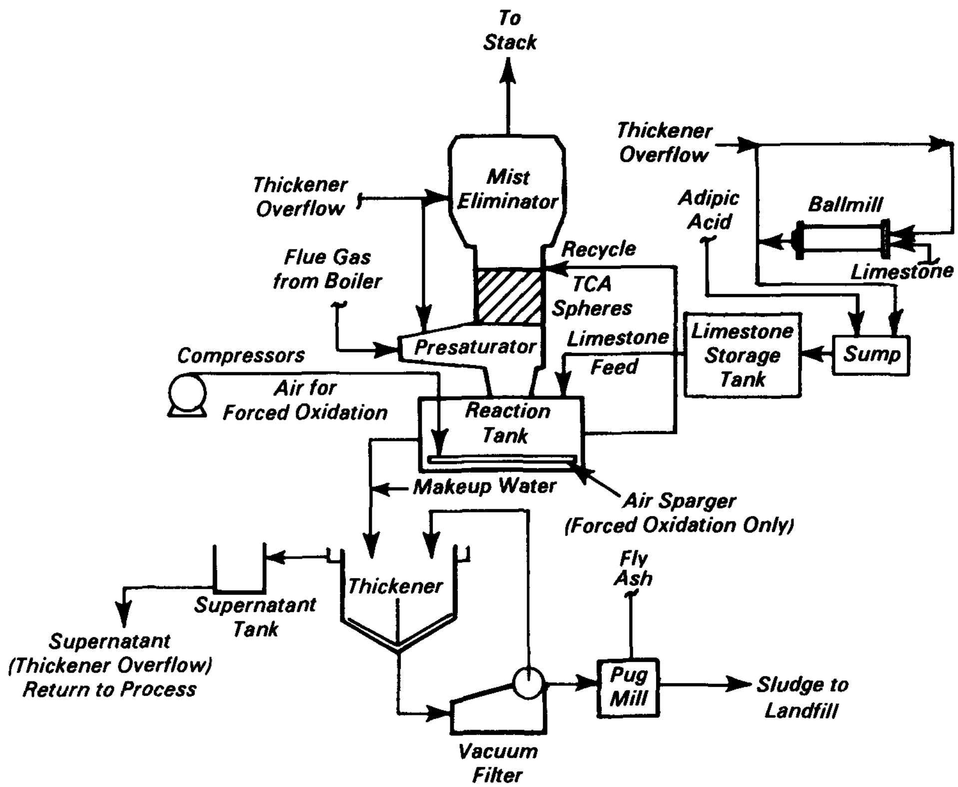

Figure 1. Southwest Unit 1 scrubber module flow diagram.

Forced Oxidation Test Results

Forced oxidation tests were conducted because it is a major design configuration for limestone FGD systems. Furthermore, forced oxidation systems produce waste sludge containing less occluded water than naturally oxidized systems. Test data collected prior to the demonstration program indicated that the small amount of water in the sludge would minimize the loss of adipic acid from the system.

Forced oxidation tests were initially conducted without adipic acid addition to provide baseline performance data. Then, adipic acid was added, and the performance of both modules was monitored. The stringent SO_2 removal goal of 95 percent was established to provide a severe test of the ability of adipic acid to enhance removal performance. Since C.U. was interested in eliminating the TCA spheres from the system because of repeated failures, Module S-1 was operated for a short time with the TCA spheres removed, and the surfaces of the TCA cages provided the only gas/liquid contacting. The rest of the forced oxidation tests were conducted with the TCA spheres restored to S-1. Table 1 summarizes results of the forced oxidation tests.

The results indicate that, in tests without the TCA spheres, adding adipic acid to about 1300 ppm in the slurry with a scrubber feed pH of 5.4 increased the SO_2 removal from less than 50 percent at baseline conditions to about 84 percent. These results represent the performance of a system limited by mass transfer area. In a 1-day test to further increase SO_2 removal without the TCA spheres, the adipic acid level and pH were increased to 2000 ppm and 5.6, respectively. Over 90 percent SO_2 removal was achieved, but the long-term operability of the system under these conditions was not demonstrated.

Table 1. Summary of Forced Oxidation Testing

	Operating Time (days)	Scrubber Feed pH	Adipic Acid (ppm)	Atoms O/ Mole SO_2 Removed	SO_2 Removal (%)	Limestone Utilization (%)	Sulfite Oxidation (%)
Testing Without TCA Spheres (Module S-1)							
Baseline	20	5.4	0	3.1	46	89	95
Adipic Acid Addition	6	5.4	1340	2.8	84	89	90
Testing With TCA Spheres							
Baseline- Module S-2	24	5.4	0	3.0	58	88	91
Adipic Acid Addition -							
Module S-2[a]	49(13)	5.0(5.0)	2410(3323)	3.0(3.2)	91(96)	92(92.5)	94(>99)
Module S-1	40	5.1	2340	1.3[b]	89	91	74[b]

[a]Results are average: results in parentheses represent performance after start-up and shakedown problems had been resolved.
[b]Maintenance problems prevented efficient oxidation for Module S-1 compressors.

In tests with TCA spheres, an average SO_2 removal of 91 percent was achieved in Module S-2 at an adipic acid concentration of 2410 ppm and pH of 5.0. Similarly, an average SO_2 removal of 89 percent was obtained in Module S-1 with 2340 ppm of adipic acid and a pH of 5.1. This compares with a baseline SO_2 removal of only 58 percent at a higher pH (5.4). Note that Module S-1 could not be fully oxidized throughout the program due to continuing compressor maintenance problems. Therefore, the test data from S-1 are more indicative of a natural oxidation system experiencing high oxidation rates than a properly designed forced oxidized system.

Although the 95 percent average SO_2 removal goal was not achieved during the entire forced oxidation test period, it is significant that 90 percent average SO_2 removal and 90 percent limestone utilization were obtained over the 49 day test period. These average results included data collected during start-up and optimization periods when process operating difficulties (e.g., limestone blinding with sulfite, and process water discharge from the dewatering system) were encountered and solved. These difficulties are primarily attributable to retrofitting the FGD system to accommodate forced oxidation as discussed earlier. During 2 weeks in April, near the end of the forced oxidation, the average SO_2 removal in Module S-2 was 96 percent, and 95 percent daily average SO_2 removal was achieved on all but 2 days.

The dramatic increases in SO_2 removal with adipic acid addition in the forced oxidation tests were accomplished without a decrease in limestone utilization. Baseline test results with and without TCA spheres reveal a very good limestone utilization of 88 - 89 percent. Limestone utilization remained high when greater SO_2 removal was attained with adipic acid. In other applications, where an improvement in SO_2 removal is not the primary concern, it is anticipated that limestone utilization could be improved by the addition of adipic acid while maintaining constant SO_2 removal. The improvement in limestone utilization would be due to the ability to operate at a lower pH with adipic acid addition.

The performance data collected from Modules S-1 and S-2 during the tests with TCA spheres were compared with data from a previous test program collected in a smaller prototype system. The adipic acid prototype testing was sponsored by EPA and conducted at TVA's Shawnee test facility between 1978 and 1980. A correlation relating SO_2 removal with adipic acid concentration and pH was subsequently developed by Bechtel,[1] based on the Shawnee prototype data base:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.0047 \exp(pH + 0.00062\ Ad)\} \quad (1)$$

where pH and Ad represent the pH of the scrubber feed liquor and adipic acid concentration in ppm, respectively.

The full-scale data collected at SWPP were correlated using the form presented in Equation 1 for pH values of 4.8 - 5.5 and adipic acid concentrations of 0 - 4000 ppm. The full-scale correlation is shown as:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.00415 \exp(pH + 0.0065\ Ad)\} \quad (2)$$

Figure 2 compares the predicted SO_2 removal using Equation 2 with observed results. Although the data scatter represents both the operational problems discussed previously and the fluctuations of a full-scale system, 90 percent SO_2 removal was routinely achieved with an adipic acid concentration of 2000 ppm and a scrubber feed pH of 5.0.

The Shawnee (prototype) correlation predicts SO_2 removals which average 2 - 5 percent greater than the actual results observed on the full-scale system at SWPP. Some differences in the Shawnee and SWPP FGD systems which could contribute to the difference in correlation include: 1) a slightly lower TCA sphere charge at SWPP, 2) slightly lower slurry and gas rates on an equivalent cross-sectional area basis at SWPP, and 3) coarser limestone at SWPP. Significant maldistribution of TCA spheres observed at the end of the forced oxidation testing at SWPP would also contribute to the difference. The conclusion that can be drawn from this comparison is that the Shawnee data base can be used as an effective design tool for full-scale systems. Good engineering practice would require consideration of important variables affecting performance that are not included in Equation 1 or the application of some conservatism when predicting system performance.

Natural Oxidation Test Results

After a 1-month scheduled outage following the forced oxidation testing, investigation of FGD system performance in the natural oxidation mode was initiated. During the outage, Module S-1 was converted to a tray tower; however, the resulting tray pressure drop initially was too small. The tray void area was reduced to increase the gas-side pressure drop to specified levels (i.e., 10 - 12 in. across the absorber) after about 6 weeks of natural oxidation testing.

Much of the testing in the natural oxidation mode focused on defining conditions required to meet 85 percent SO_2 removal, since C.U. was interested in gaining experience in operating the FGD system under conditions required to meet its SO_2 emission limitation. Additionally, some testing was conducted to achieve 95 percent SO_2 removal and to determine the operating conditions required to meet more stringent

SO_2 emission limits. Table 2 summarizes the natural oxidation results for both the TCA and tray towers.

After baseline testing was conducted, adipic acid was added to achieve 85 percent SO_2 removal. Initially, screening tests were performed by varying the pH and adipic acid concentration independently and observing the resulting SO_2 removal. The results of these screening tests were then used to select preferred operating conditions for longer term tests at constant pH and adipic acid concentrations. The longer term steady-state tests were conducted at pHs of 5.5 (typically used at SWPP) 5.2 (approached the pH recommended by EPA for reducing adipic acid consumption). Approximate adipic acid addition rates for these pHs were estimated from the screening tests.

Subsequent test results in the tray tower produced an average 90 percent SO_2 removal at a pH of 5.2 and an adipic acid concentration of 760 ppm. An average SO_2 removal of 91 percent was achieved at a pH of 5.5 and an adipic acid concentration of 640 ppm. The data, collected by continuous emission monitors, represent average performance during fluctuating plant loads. The SO_2 removal at full load was about 85 percent at each pH level tested. Test results also show that 95 percent SO_2 removal at full load was achieved with 1700 - 1800 ppm adipic acid at a pH of 5.4.

Results for the TCA module show that system performance deteriorated during the natural oxidation tests. Note that only 78 percent removal was achieved in the TCA, compared to 91 percent in the tray tower during the third set of tests with an 85 percent removal goal. Plugging in the TCA, at least partially responsible for the decline in performance, illustrates the type of problem encountered previously at the SWPP. A more detailed discussion of these problems will be presented later in this section.

Results for limestone utilization shown in Table 2 indicate that an improvement was observed in the adipic acid tests compared to the baseline tests. The primary reason for the improvement is that adipic acid addition allows the desired SO_2 removal to be obtained at a lower pH which, in turn, increases limestone utilization.

Since one module had been converted to a tray tower and the TCA module suffered from operating difficulties which reduced performance efficiency, it is difficult to compare the SWPP full-scale results directly with the Shawnee TCA prototype results for natural oxidation. Most of the correlations reported for prototype natural oxidation testing were derived for higher

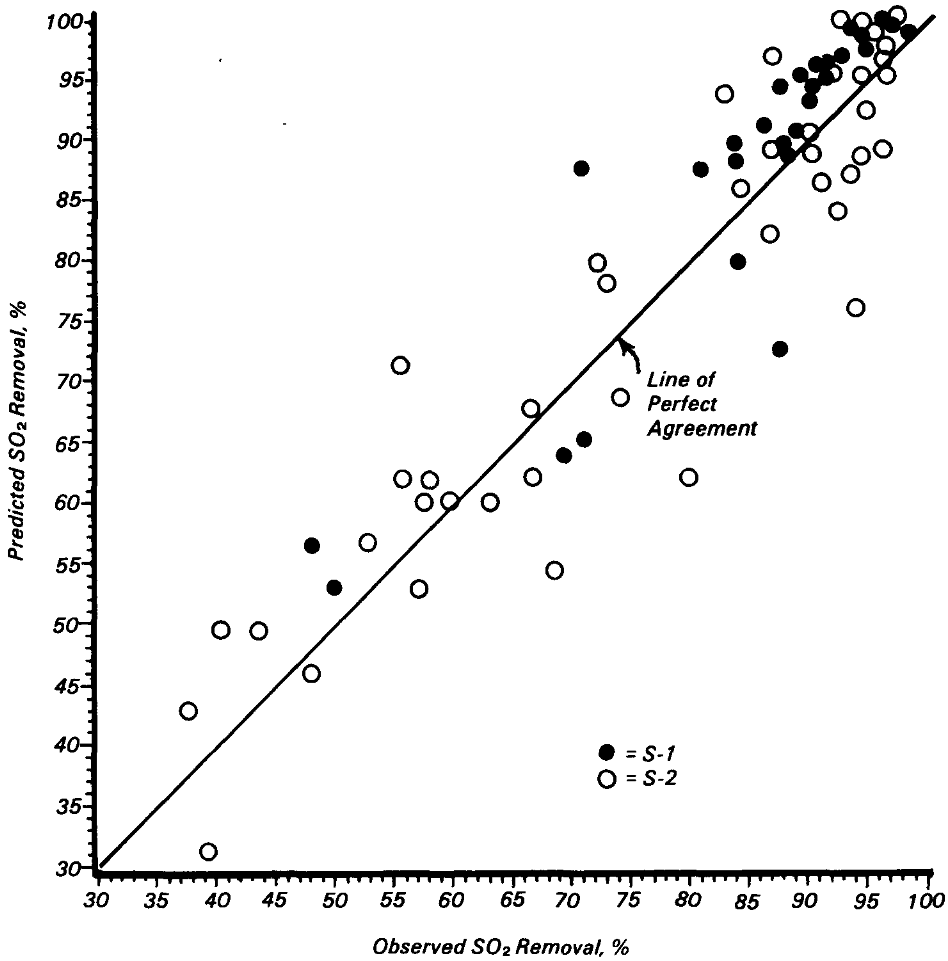

Figure 2. Fit of Springfield data to revised Bechtel model: Fractional SO_2 removal = $1 - \exp\{-0.00415 \exp(pH + 0.00065\ Ad)\}$.

Table 2. Summary of Natural Oxidation Testing

	Operating Time (days)	pH	Adipic Acid Conc. (ppm)	SO_2 Removal (%)	Limestone Utilization (%)
Tray Tower (S-1)					
Baseline[a]	24	5.6	0	68	79
Goal - 85% Removal[a] (Screening)	17	5.4	1000	87	81
Goal - 85% Removal (5.2 pH)	12	5.2	760	90	86
Goal - 85% Removal (5.5 pH)	10	5.5	640	91	-[c]
Goal - 95% Removal	17	5.4	1750	96	78
TCA Tower (S-2)					
Baseline	24	5.6	0	72	69
Goal - 85% Removal (Screening)	17	5.3	890	91	92
Goal - 85% Removal (5.2 pH)	12	5.2	700	88	82
Goal - 85% Removal[b] (5.5 pH)	10	5.4	550	78	75
Goal - 95% Removal[b]	13	5.2	1690	94	86

[a]The void area in the tray tower was about 10 percent higher during these tests than in the later tests.
[b]These goals were obtained in the tray module but not in the TCA module. The goals for the TCA module were not attained due to deteriorating conditions in the TCA module and a common adipic acid addition system which prevented independent control of adipic acid levels.
[c]No data collected.

pH levels than at SWPP. However, spot checks of full-scale data obtained at higher pH levels before the TCA module performance deteriorated indicate that the Shawnee correlations predict full-scale performance results reasonably well. As in the forced oxidation test series, the prototype correlations for natural oxidation tests predict slightly higher SO_2 removals than achieved in the full-scale system.

The data collected in the demonstration program from the full-scale tray tower were fit to the following equation:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.00131\,Ad - 0.00216\exp(pH) - 0.00996\,L/G\} \quad (3)$$

The L/G ratio is expressed in gallons per 1000 cubic feet of gas. Note that the effects of liquid and gas rates resulting from load changes could be observed and correlated to SO_2 removal during the natural oxidation testing. The wider range of SO_2 removals observed during the natural oxidation tests compared to the narrow range resulting from the forced oxidation removal goal of 95 percent permitted the effect of L/G to be observed.

The agreement between actual SO_2 removal and the removal predicted by Equation 3 is shown in Figure 3. This equation was developed to describe the trends noted during the program. Be careful when using the equation for design purposes, especially for extrapolation beyond the conditions tested at the full-scale system.

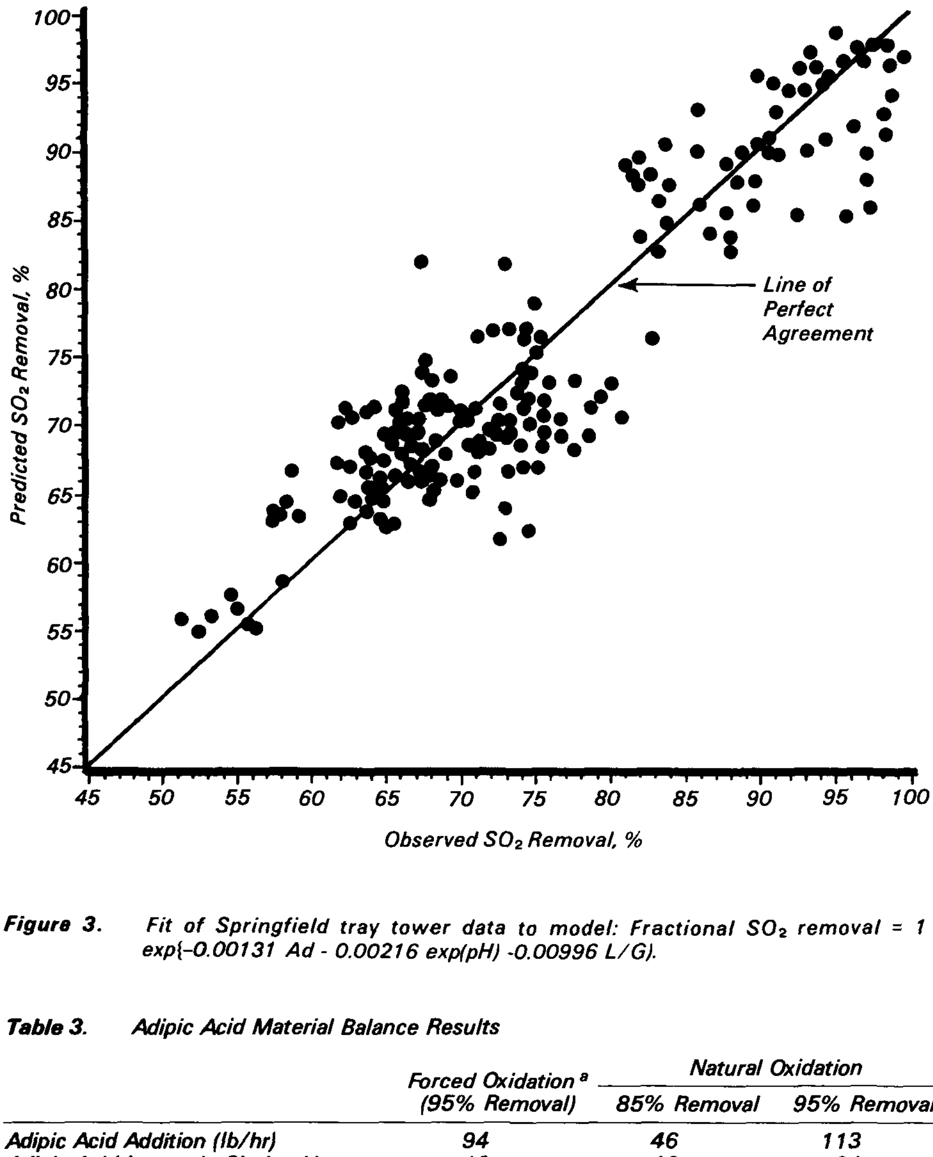

Figure 3. *Fit of Springfield tray tower data to model: Fractional SO_2 removal = 1 - exp{-0.00131 Ad - 0.00216 exp(pH) -0.00996 L/G}.*

Adipic Acid Consumption

Adipic acid which is added to a limestone FGD system can leave the system several ways: 1) soluble adipic acid is lost in the water occluded with the solids of the scrubber sludge, 2) adipic acid is coprecipitated with the solids in the sludge, 3) adipic acid is degraded in the system (e.g., oxidation), 4) adipic acid is contained in fugitive liquid or slurry losses, and 5) adipic acid exits with the flue gas. An actual-to-theoretical ratio used to describe adipic acid consumption has been defined in previous studies to be the actual amount of adipic acid fed to the system divided by the amount of adipic acid exiting in the sludge liquor.

Adipic acid consumption data for both natural and forced oxidation operating modes is summarized in Table 3. The actual-to-theoretical ratios of approximately 9 for forced oxidation and 5 for natural oxidation are somewhat greater than those observed in the Shawnee prototype testing,[2] but are roughly equivalent to values obtained in bench scale testing under similar conditions.[3] In spite of lower losses of adipic acid in the sludge liquor, higher chemical degradation in the forced oxidation configuration was responsible for the higher actual-to-theoretical ratio observed.

Table 3. *Adipic Acid Material Balance Results*

	Forced Oxidation [a] (95% Removal)	*Natural Oxidation 85% Removal*	*Natural Oxidation 95% Removal*
Adipic Acid Addition (lb/hr)	94	46	113
Adipic Acid Losses in Sludge Liquor (lb/hr)	10	10	21
Actual/Theoretical Ratio [b]	9.4	4.6	5.4
Adipic Acid Consumption (lb/ton SO_2 removed)	18	11	29
Cost (¢/kWh) [c]	0.029	0.017	0.047

[a] During forced oxidation numerous losses of adipic resulted from water discharges in dewatering plant operations. These numbers have been adjusted to reflect more normal operation.
[b] Actual/theoretical ratio = actual adipic acid added/adipic acid lost in sludge liquor.
[c] Cost of adipic acid assuming 60¢/lb.

The adipic acid consumption in pounds per ton SO_2 removed is a useful ratio in estimating consumption for proposed systems. During forced oxidation (95 percent SO_2 removal), 9 g/kg SO_2 (18 lb/ton SO_2) was consumed. The adipic acid consumption for the combined TCA and tray tower modules nearly tripled during natural oxidation testing when the SO_2 removal was increased from 85 (6 g/kg SO_2 [11 lb/ton SO_2]) to 95 percent (15 g/kg SO_2 [29 lb/ton SO_2]). The consumption rate in forced oxidation tests was less than during natural oxidation testing at 95 percent SO_2 removal as well. This comparison illustrates that the losses in the scrubber liquid were sufficiently reduced by improving dewatering efficiency during forced oxidation to overcome the higher degradation rates.

Operating Characteristics

In addition to the significant increase in SO_2 removal capability and the ability to operate at reduced scrubber feed pH to improve limestone utilization, improvements in operating reliability were observed during the demonstration program. FGD system reliability prior to and during the demonstration program is shown in Table 4. After the demonstration start-up and shakedown in January and February, 1981, both scrubber modules exceeded an average reliability of 85 percent from March through August. The significant improvement in reliability, compared to the 2 previous years, can be attributed to several factors. First, a number of mechanical improvements were implemented by C.U. As a result of the demonstration program, some process operating procedures were revised, and additional process engineering input was available. The use of adipic acid also helped improve system reliability by modifying process chemistry so that less scale accumulated on equipment surfaces. While the influence of adipic acid addition on reliability cannot be quantified, some of the operating characteristics attributable to adipic acid are discussed below.

Table 4. Scrubber Reliability[a] During Adipic Acid Demonstration Program

	Module S-1	Module S-2
Average for 1979	34	42
Average for 1980	59	31
1981 Demonstration Program		
Forced Oxidation Tests		
January 10-31	66	85
February	54	35
March	88	81
April	67	97
May	87	66
Natural Oxidation Tests		
June	78	74
July	94	94
August	90	80
Average January 10 - August 31	79	86
Average March 10 - August 31[b]	86	87

[a]Defined as $\frac{\text{hours operated}}{\text{hours required}} \times 100$.

[b]Excludes demonstration start-up and shakedown in January and February.

During forced oxidation, almost 36 days of continuous operation were logged for both modules. At the end of the testing, only a small amount of solids had accumulated in the TCA cages and mist eliminators. During natural oxidation testing, reliable operation continued although a greater buildup of solids was observed, particularly in the TCA cages. Increased solid accumulation was also observed in the mist eliminators during natural oxidation, but the major cause of the accumulation was probably plugged mist eliminator wash nozzles.

The excellent performance observed during forced oxidation tests is due in part to the relatively high limestone utilization which results in less calcium carbonate dissolution in the absorber. In addition, forced oxidation provided beneficial effects; e.g., more gypsum seed crystals available as precipitation sites.

The lower pH and forced oxidation resulted in higher limestone utilization than was observed during the natural oxidation tests. The increase in calcium carbonate and sulfite dissolution during natural oxidation can increase the tendency to scale or plug. While an increase in solids accumulation in the TCA module during natural oxidation was observed, the tray module had only a small amount of solids accumulated on the trays, and the solids could be removed with a minimum of effort.

It can be concluded that adipic acid addition, while not the sole contributor to improved reliability at SWPP, can allow an FGD system to operate at lower pH correspondingly higher limestone utilization which should reduce accumulation of solids in the system and improve reliability. Reduced solids accumulation was particularly evident in the forced oxidation testing at SWPP.

Although overall system performance was excellent during most of the program, the air compressor, dewatering equipment, and adipic acid feed system caused operating problems which had to be overcome. Most of these problems, directly attributable to the temporary retrofit of the system to accommodate the demonstration program, do not reflect the general use of adipic acid in FGD systems.

A phenomenon that occurred during natural oxidation tests should be considered in systems requiring high SO_2 removals. Limestone blinding (calcium sulfite precipitation on limestone particles) apparently occurred during natural oxidation tests, particularly during testing to achieve 95 percent SO_2 removal. As a result, pH control response was slow. During tests at a pH of 5.5, the limestone feed could be turned off or on for 2 hours without a noticeable change in pH. Operation under these conditions can reduce limestone utilization. However, procedures were implemented to reduce the effect of blinding. Limestone blinding was also observed during forced oxidation tests, but it was caused by air compressor maintenance problems which reduced oxidation efficiency. Sulfite precipitation on the surface of limestone particles can reduce the limestone dissolution rate or reactivity, contributing to reduced limestone utilization.

Dibasic Acid Testing

Approximately 1-½ months of testing was conducted to evaluate the performance of dibasic acid (DBA). DBA is a less expensive buffering agent than adipic acid, and the feed system for the DBA solution is simpler than the solids handling system required for adipic acid. DBA was tested at 85 percent removal to assess its feasibility at SWPP and at 95 percent removal to evaluate its performance under more stringent SO_2 removal requirements. DBA results are summarized in Table 5.

The 85 percent removal goal was exceeded in the tray tower at a slightly lower buffer concentration (500 ppm equivalent adipic acid) than required in adipic acid testing (640 ppm adipic acid). However, the average unit load was lower during the DBA tests, so the L/G was greater. Lower SO_2 removal was observed in the TCA module, reflecting deterioration due to solids accumulation as observed near the end of the adipic acid natural oxidation tests.

A brief test was conducted with DBA to achieve 95 percent SO_2 removal. This goal was achieved in the tray tower at 1300 ppm DBA as adipic acid at a pH of 5.4 compared to 1750 ppm during adipic acid testing. In the TCA module, 94 percent SO_2 removal was achieved at only 1020 ppm DBA as adipic acid, but the gas flow through the TCA module was less than that passing through the tray module.

The concentration of DBA necessary to achieve a given SO_2 removal appeared to be less than for adipic acid on an equivalent basis, but the amount of DBA consumed on a weight basis was greater. A feed rate of about 27 kg DBA/hr (60 lb/hr) was required to achieve 85 percent SO_2 removal at a 75 percent load, compared to 20 kg/hr (45 lb/hr) of adipic acid. This translates to about 8g DBA/kg SO_2 (15 lb/ton) compared to 6 g/kg SO_2 (11 lb/ton) with adipic acid.

The reliability of both modules remained relatively high during the DBA test period. The tray tower operated 98 percent of the time it was required. The TCA module operated with 89 percent reliability. These figures compare favorably with the adipic acid reliability figures.

Table 5. *DBA Test Results*

Test Period	*Average Scrubber Feed pH*	*Average DBA Conc. (ppm as adipic acid)*	*Average SO_2 Removal (%)*
85% SO_2 Removal			
Module S-1 (tray)	*5.4*	*480*	*90*
Module S-2 (TCA)	*5.4*	*420*	*78*
95% SO_2 Removal			
Module S-1 (tray)	*5.4*	*1310*	*96*
Module S-2 (TCA)	*5.4*	*1020*	*94*

Solid Waste Testing

Solid wastes generated during the demonstration program were evaluated for: 1) H_2S generation by fermentation, 2) bioassay results including cytotoxicity, mutagenicity, and acute toxicity, and 3) leachate composition in RCRA and ASTM extraction tests. Four samples were tested to represent the following operating modes: natural oxidation without organic acid addition (baseline), forced and natural oxidation with adipic acid addition, and natural oxidation with DBA addition. The sludge samples were mixed with fly ash collected at SWPP to examine the effects of trace elements in the fly ash. Small quantities of river bank soil (less than 1 percent) were added to the samples to provide a source of bacteria for the fermentation tests.

Fermentation test results indicate that anaerobic decomposition of the solid waste was minimal, both with and without the addition of organic acids. Bioassay results indicate no detectable toxicity or mutagenicity from any of the samples except on the fresh water invertebrate test. In the fresh water invertebrate test, high TDS levels from the solids extracts may be responsible for the toxic effect seen for all of the samples, including the baseline sample without organic acid addition. None of the leachates from any of the sludges exceeded RCRA limits. Likewise, no high values for elements were observed from the ASTM extraction other than those normally associated with FGD systems (calcium, magnesium, sodium, chloride, and sulfate). Therefore, testing of solid wastes from a full-scale organic-acid-enhanced FGD system did not reveal any significant difference from an unenhanced system.

For a savings to be realized from the use of organic additives in limestone FGD systems, the cost of the organic acid and the associated feed system must be offset by reductions in other operating and equipment costs. Improved SO_2 removal capability and more efficient limestone utilization will allow reductions in L/G and limestone stoichiometry. Associated cost for power, limestone, pumps, headers, reagent preparation and solid waste disposal can result.

Based on studies conducted by TVA[4], annual costs can be reduced by about 8 percent by using an adipic-acid-enhanced limestone FGD system in a new 500 MW plant firing high sulfur coal. The savings are influenced by site specific factors such as sulfur and chlorine content of the coal and permit requirements for SO_2 removal. While the incremental cost savings may not be a large percentage, the cost reduction can have a substantial impact on a plant's operating budget.

For existing facilities, the cost reduction that can be realized by using organic acids depends on the specific requirements at that facility and the cost of other alternatives. The types of problems at existing facilities that can be effectively addressed by the use of organic acids include increasing SO_2 removal to meet permit requirements and fuel switching to accommodate higher sulfur coals.

For C.U.'s SWPP, incremental cost estimates for three alternatives to achieve 85 percent SO_2 removal were considered: 1) increasing the L/G in the tray tower, 2) adding adipic acid, and 3) adding DBA. The option to increase L/G is a more capital intensive solution because new pumps and headers are required. The adipic acid and DBA options require lower incremental capital costs but higher operating costs.

A present worth analysis of the alternatives was performed using escalation factors consistent with C.U.'s long range planning. The escalation of adipic acid cost ($0.60/lb in 1981 dollars [$0.32/kg]) and DBA cost ($0.30/lb in 1981 dollars [$0.66/kg]) closely approximated C.U.'s assumed escalation rate of fuel oil. The escalation cost of electricity (production only) closely approximated C.U.'s assumed escalation rate. The discount factor for the analysis was assumed to be equal to the general inflation rate.

Results of the analysis are shown in Figure 4. The adipic acid cost option is projected to be less expensive than increasing the L/G during the first 9 years. Beyond that time, L/G modifications are projected to be less expensive. While the adipic acid cost estimates are based on test data at SWPP, the L/G cost estimates are based on experience with similar systems, and greater uncertainty exists in the resulting L/G analysis.

The DBA option is estimated to be less expensive than either of the first two alternatives for the 15 years used in the analysis. The estimated DBA cost is based on the limited data base provided during the demonstration program. Other options for reducing the cost of DBA that have not been fully investigated might result in a further reduction in cost.

Conclusions

The major conclusions concerning the operation of an adipic-acid-enhanced limestone FGD system based on the results of the demonstration program at SWPP are:

- Adipic acid addition is a feasible method for improving SO_2 removal in systems that are limited by soluble alkalinity in the scrubber slurry feed.
- Correlations from TCA prototype testing at Shawnee adequately predict full-scale system performance for SO_2 removal as a function of adipic acid concentration and pH.
- Limestone utilization can be improved with adipic acid addition because

lower scrubber feed pH is required to achieve a given SO_2 removal.

- Increased limestone utilization from the addition of adipic acid can improve system reliability by reducing the accumulation of precipitating solids, especially in forced oxidized systems.
- The performance of DBA is sufficient to provide an alternative to the use of adipic acid. DBA addition is the least expensive alternative examined for the SWPP to meet requirements for SO_2 removal.

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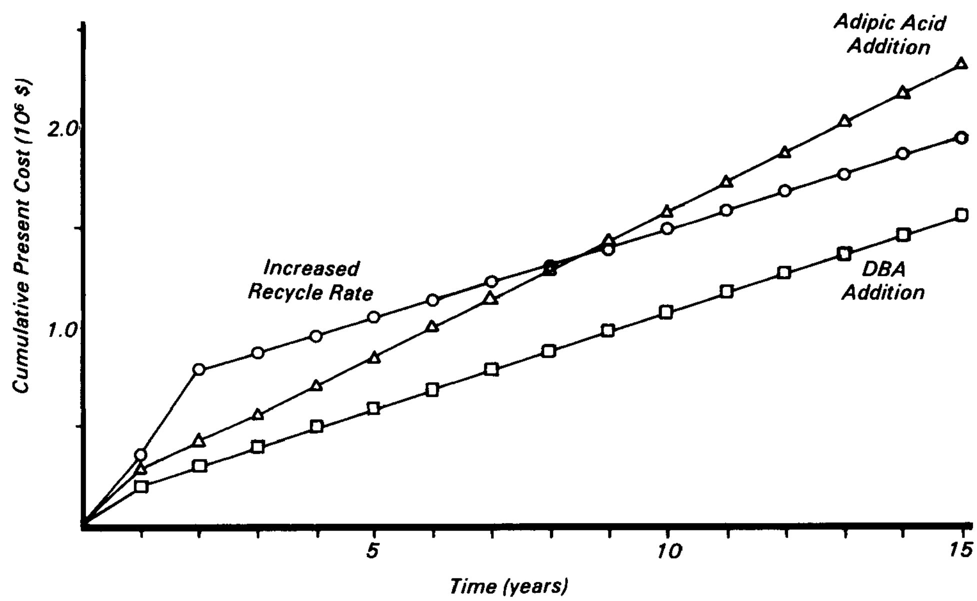

Figure 4. *Comparison of alternatives for meeting 85% removal at Springfield.*

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