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RECENT ADVANCES IN COMMERCIAL ORGANIC-ACID-ENHANCED FGD SYSTEMS

Prepared by:

J. David Mobley
U. S. Environmental Protection Agency
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

and

James C. Dickerman
Radian Corporation
Post Office Box 13000
Research Triangle Park, North Carolina 27709

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J. DAVID MOBLEY, Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

JAMES C. DICKERMAN, Radian Corporation, Post Office Box 13000, Research Triangle Park, North Carolina 27709

ABSTRACT

The application of organic-acid buffer enhancement to flue gas desulfurization (FGD) systems is a recent development that has resulted in lowered costs and improved performance for those systems that have adopted its use. A process which uses organic acids as an additive has several advantages over conventional limestone scrubbing systems. These advantages include improved SO_2 removal, decreased limestone consumption, increased system flexibility (e.g., ability to respond to unplanned fluctuations in coal sulfur content), and improved process reliability. This paper summarizes the results of several cost analyses which were performed to evaluate the potential economic benefits of converting operating FGD systems to organic-acid-enhanced limestone scrubbing systems. In addition, a summary of the first 2 years of operation for the first full-scale system to convert to organic-acid-enhanced operations—City Utilities' Southwest Power Plant (SWPP)--is also included.

BACKGROUND

The ability of a limestone FGD system to remove SO_2 is limited by the absorptive capacity of the slurry liquid that makes contact with the flue gas. Adding an organic acid to the system expands the capacity of the liquid to absorb SO_2 by buffering the pH in the absorber. These are the reactions that take place:

Sulfur dioxide + Water $\rightleftarrows$ Acidity (H^+) + Sulfites (1)

Organic buffer anion (carboxylate ion) + Acidity (H^+) $\rightleftarrows$ Organic acid (2)

As the buffer reacts with the acidity formed in the SO_2 absorption reaction, a weak organic acid is formed (Reaction 2). The buffer is regenerated in the reaction tank by adding limestone:

Organic acid + Sulfites + Limestone $\rightarrow$ Organic buffer anion + Calcium sulfite solids + Carbon dioxide (3)

Adding organic buffers can result in increased SO_2 removal, a decreased risk of chemical scaling, potentially decreased limestone consumption, and potentially reduced mist eliminator fouling because of increased utilization of limestone.

When EPA engineers realized that organic buffers could possibly be used to solve some of the maintenance and cost problems that utilities were experiencing with their lime/limestone FGD systems, the Agency began an extensive research program designed to provide a thorough evaluation of various organic acid additives and how they can be used to improve lime/limestone scrubbing. It consisted of four phases--laboratory, pilot, prototype, and commercial scale.

The EPA began its research by sponsoring theoretical and laboratory investigations of a number of different acids. As a result of these studies, adipic acid appeared to be the most promising buffer candidate because of its solubility in water, low volatility, chemical stability, non-toxicity, high availability, and low cost. Also, the region of maximum buffering for adipic acid, between pH 4 and 6, is ideal for limestone FGD systems.

Two full-scale test programs were also sponsored by EPA to demonstrate the technical and economic viability of this approach on operating utility and industrial FGD systems. Results of both of these demonstration programs verified the viability of organic-acid-enhanced operations.[1]

TECHNICAL AND ECONOMIC ANALYSES OF OPERATING SYSTEMS

Technical and economic analyses were made for four FGD installations to determine the nature and cost of converting each to an organic-acid-enhanced limestone scrubbing system. The four installations are: City Utilities' Southwest Power Plant, Central Illinois Light Company's Duck Creek Station, San Miguel Electric Cooperative's San Miguel Station, and Big Rivers Electric Corporation's R. D. Green Station. The first three installations are limestone scrubbing systems, and the fourth installation is a limebased FGD system.

The approach used in conducting these process evaluations was basically the same for all systems. First, typical process operating conditions for each system were identified through a series of questionnaires and meetings with plant personnel. Baseline operating parameters such as pH, limestone (or lime) utilization, liquid-to-gas (L/G) ratios, and SO_2 removal were recorded for each system to document pretest process conditions and operating costs. Next, technical evaluations were made to identify any process modifications that would be required to convert each system to an organic-acid-enhanced system, and to establish organic acid makeup requirements. Finally, the capital investment costs for all required process modifications and the annual operating costs of organic-acidenhanced operations were determined. The results for each system are summarized below.

CITY UTILITIES--SOUTHWEST POWER PLANT (1)

City Utilities' (CU) major interest in converting their system to an organic-acid-enhanced limestone scrubbing system was to improve the SO_2 removal performance so that it could comply with the applicable SO_2 removal requirements. Several process alternatives were considered, each of which had the potential for achieving the utility's goal of increased SO_2 removal. The process alternatives considered included: increasing the L/G ratio to the tray tower, adding adipic acid, and adding a mixture of by-product organic dibasic acids (DBAs). The DBA used at CU is a by-product of adipic acid production and consists of a mixture of adipic, glutaric, and succinic acids. The higher L/G option represented a capital cost intensive solution; whereas, the adipic id and DBA options had lower capital costs but higher annual operating costs. A esent worth analysis was performed using escalation factors consistent with CU's long range planning activities. The escalation of adipic acid and DBA closely approximated CU's assumed escalation rate of fuel oil, and the escalation of cost of electricity (production costs only) closely approximated CU's assumed coal escalation rate. The discount factor for the analysis was assumed to be equal to the general inflation rate.

The results of the present worth analysis are shown in Figure 1. Note that the adipic acid option is a lower cost option than increased L/G for about 6 years. The technical uncertainties in making the L/G modification, coupled with the demonstrated adipic acid system flexibility, make the adipic acid option a good choice. However, the DBA option remains the best choice economically through more than 15 years. Consequently, City Utilities elected to convert their FGD system to DBA-enhanced operations in December 1981. The excellent results of the first 2 years of operation of that system are reported later in this paper.

CENTRAL ILLINOIS LIGHT COMPANY—DUCK CREEK STATION (2)

As was the case at City Utilities, Central Illinois Light Company's (CILCo) main interest in considering a conversion to an organic-acid-enhanced limestone scrubbing system was related to improving the system's performance so that it would achieve compliance with the applicable SO_2 regulations. As with City Utilities, several process alternatives were considered. The options identified for CILCo to achieve compliance included:

- constant DBA feed,
- intermittent DBA feed,
- intermittent DBA feed plus recycle,
- constant magnesium oxide feed,
- intermittent magnesium oxide feed, and
- intermittent magnesium oxide feed plus recycle.

The CILCo system is significantly different than the other systems evaluated in that a waste disposal pond is used for solids disposal. Since a slurry waste stream of approximately 10 percent solids is sent to the disposal pond, the DBA or magnesium oxide makeup requirements would be significantly increased. For this reason, a process alternative, which included recycle by the addition of a hydroclone to concentrate the blowdown stream to 40 weight percent solids and thus reduce the additive losses, was also examined.

Results of the present worth analysis over a 15-year period are shown in Figure 2. These results show that the DBA options cost significantly less than the magnesium oxide addition options, except for the case in which recycle is used to reduce the amount of scrubber blowdown sent to the waste disposal pond. Although the process options using the hydroclone for recycle showed cost advantages, the use of a hydroclone has not been demonstrated at CILCo; thus, technical uncertainties associated with its use in this application exist. For this reason, CILCo has elected to convert its process to a DBA-enhanced limestone scrubbing system with intermittent feed controls so that DBA is added only during high load operations.

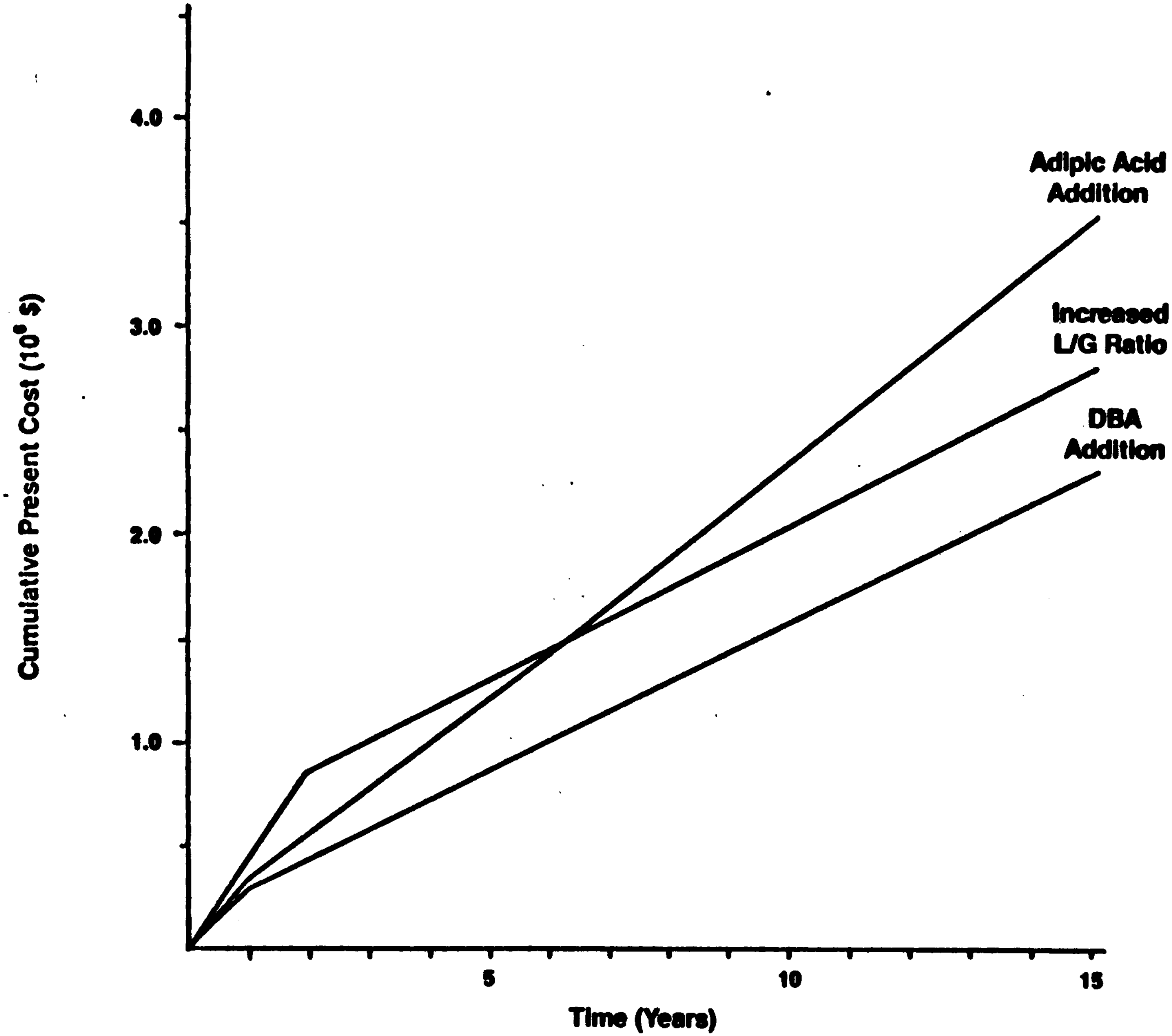

Figure 1. Cumulative Present Cost for Southwest Power Station

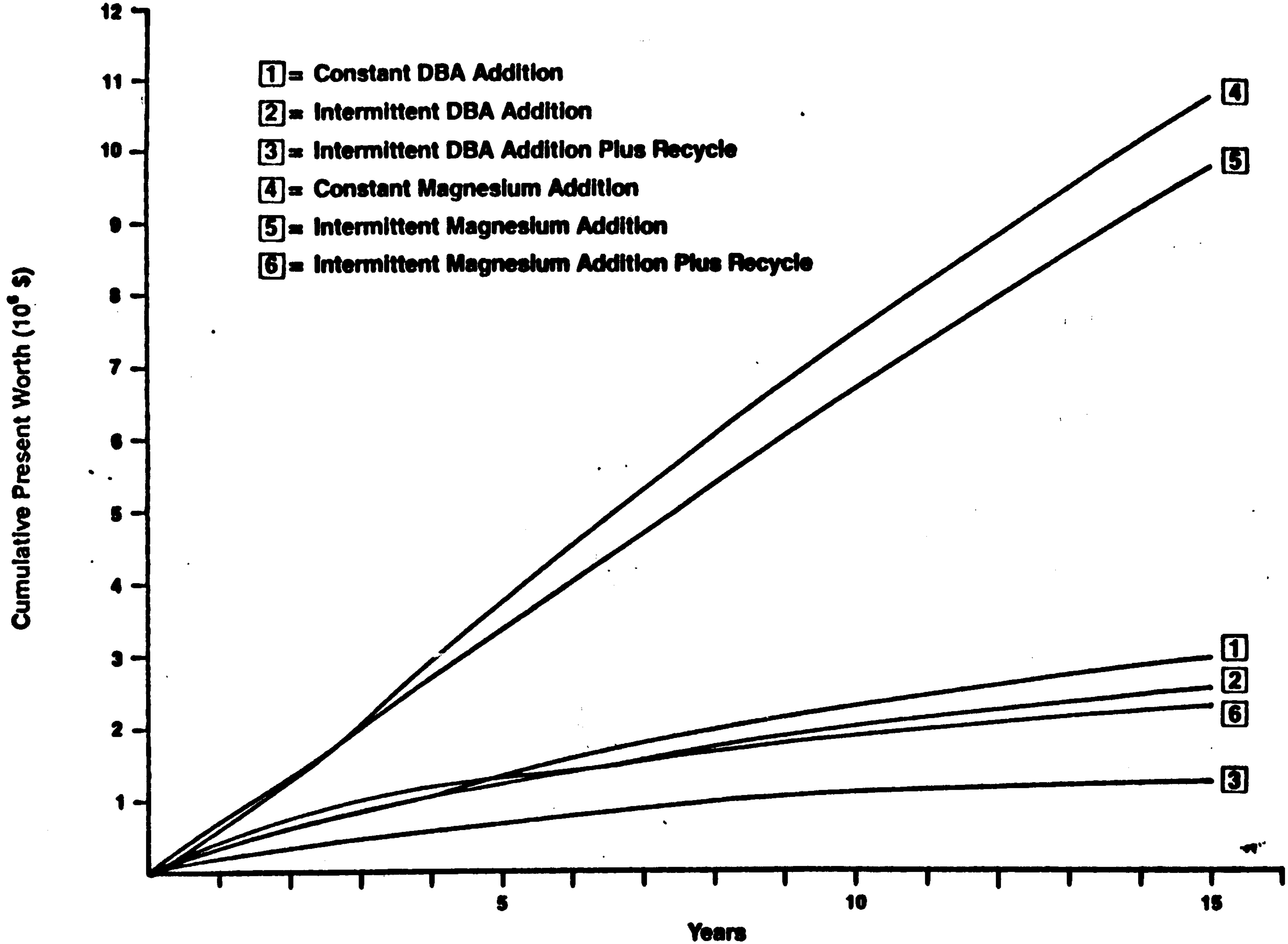

Figure 2. Cumulative Present Worth of Converting CILCo's Duck Creek Station

SAN MIGUEL ELECTRIC COOPERATIVE (3)

San Miguel's interest in converting their system to an organic-acid-enhanced system stemmed primarily from a desire to reduce their FGD operating costs rather than from regulatory pressures. Normal operating conditions at San Miguel required the use of fairly high limestone reagent ratios (greater than 1.4) in order to meet compliance. Besides the obvious costs associated with excess limestone use, San Miguel also experienced chemical scaling in their absorber tower which was probably related, at least in part, to the excess limestone present in the system.

In 1982, San Miguel participated in a program with EPA to evaluate the costs associated with converting their system to organic-acid-enhanced operations. Results of the economic analysis indicated that over a 15-year period, costs of organic-acid-enhanced operations could range from an increase of $657,000 to a savings of $1,550,000 in terms of net present worth. This range in costs was a result of uncertainties in both the organic acid consumption rate and the estimated improvement in limestone utilization which could be achieved with organic acid addition. Because of the potential savings associated with organic acid addition, San Miguel agreed to participate with EPA in a program to gather actual field test data at the San Miguel plant to verify the results of this engineering evaluation.

This paper presents a brief summary of the results achieved from the field test program (4). The objective of the test program was to evaluate two sources of DBA at three different concentrations in the recirculating slurry. The DBA sources were:

- A DBA solution supplied by DuPont Petrochemicals of Victoria, Texas, and
- A DBA mixture supplied by Badische Corporation of Freeport, Texas.

The initial phase of the test program using the DuPont-supplied DBA was carried out as scheduled. However, the tests using the Badische acid were terminated after the first test because of severe foaming in the absorber and quench recirculation tanks which made it very difficult to operate the FGD system. After this test, the program was modified to include tests not originally scheduled. The new tests included:

- Testing of an organic-acid by-product stream consisting primarily of maleic acid which was supplied by Badische Corporation, and
- Testing of manganese addition (as $MnSO_4$) to the FGD system to reduce DBA consumption.

A present worth analysis was performed based upon San Miguel's long-term escalation and market interest rate assumptions and is presented in Figure 3. Taking into account the initial capital investment for the DBA system, the cost savings for the three organic acids that were tested were estimated over a 15-year period to range from $2.9 to $7.2 million. Note that no credit for increased reliability was assumed in any of the cost calculations. For San Miguel, which has experienced chemical scaling problems, the savings could be very significant. Because of the expected cost savings and performance improvements associated with the use of an organic-acid-enhanced system, San Miguel has permanently converted their FGD system to organic-acid-enhanced operations.

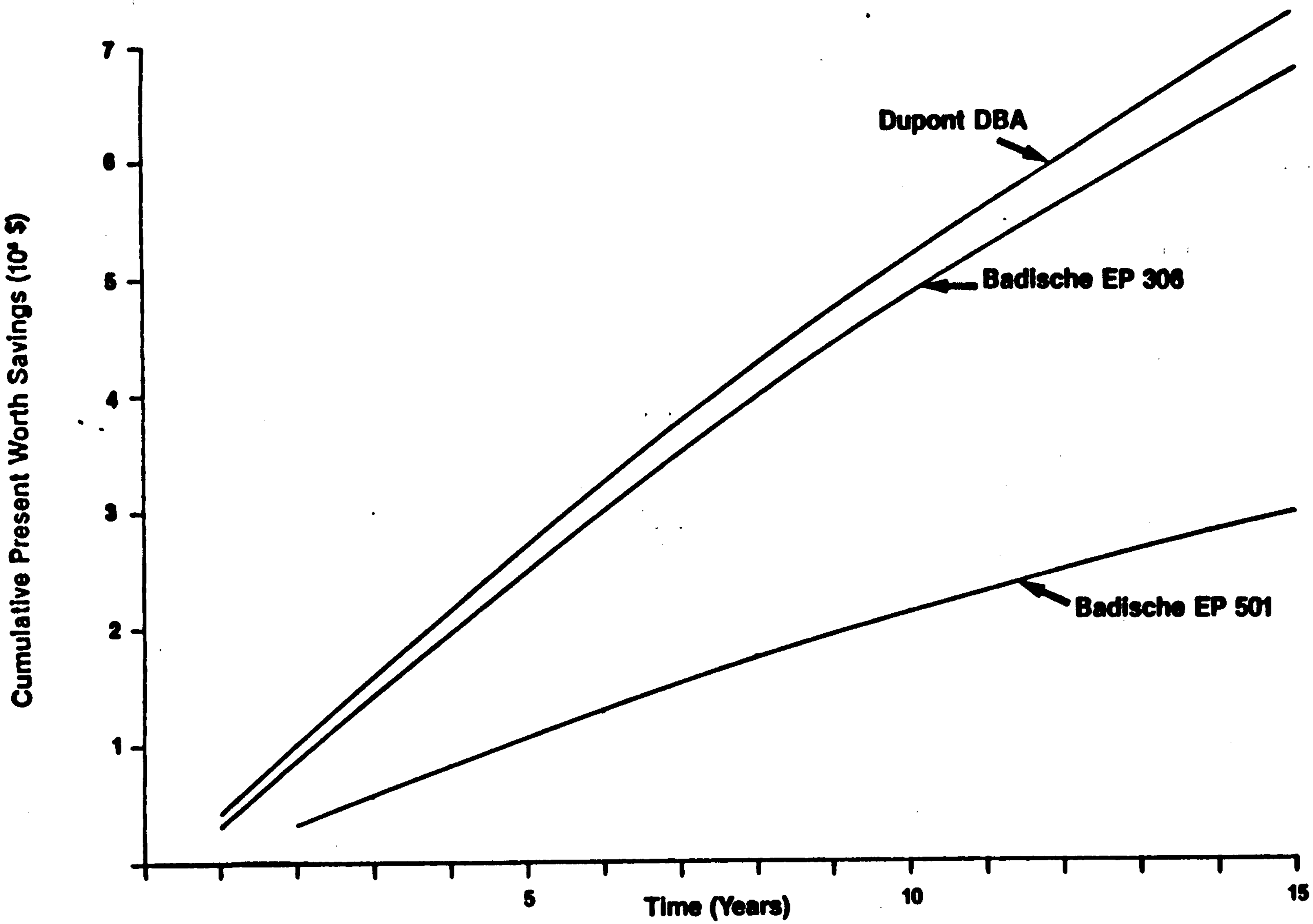

Figure 3. Cumulative Cost Savings of Converting San Miguel's FGD System to Organic Acid Operations

BIG RIVERS ELECTRIC CORPORATION (5)

In 1982-83, Peabody Process Systems, Inc. (PPSI) conducted a series of pilot plant tests at the R. D. Green Station of Big Rivers Electric Corporation (BREC). A portion of these tests included comparisons of the operating costs of a lime-based FGD system to a retrofit limestone system enhanced with DBA or adipic acid. The potential cost savings from a conversion of a lime system to an organic-acid-enhanced limestone system stem primarily from reduced reagent costs that result from replacing lime with limestone.

This paper presents a summary of the results of an evaluation of the capital and operating cost changes that would result from converting the BREC system from lime operations to organic-acid-enhanced limestone operations. The cost estimates reported in this paper are specific to the BREC system and may differ for other lime-based FGD systems due to differing process modifications that may be required to convert from lime operations to organic-acid-enhanced limestone operations.

Capital cost estimates for the BREC conversion were based on using as much existing equipment as possible. For this system no changes to the absorption portion of the process were required, and the major capital cost items were ball mills and an organic acid feed system. No capital costs were included for an electrical substation to provide power to the ball mills since BREC indicated that sufficient electrical capacity was available from existing equipment.

A comparison of annualized operating costs of the existing lime-based system to DBA-enhanced limestone operations and adipic-acid-enhanced limestone operations is shown in Table 1. The capital cost portion of the annualized costs was estimated using a fixed capital recovery factor of 20 percent. Operating costs were based on the typical BREC operating load of 75 percent. Results of these cost estimates, shown in Table 1, indicate a yearly savings of $2,642,000 for an adipic-acid-enhanced limestone system and $3,153,000 for a DBA-enhanced system.

RESULTS OF THE FIRST TWO YEARS OF COMMERCIAL OPERATION OF AN ORGANIC-ACID-ENHANCED FGD SYSTEM (6)

In 1980, Radian Corporation and City Utilities of Springfield, Missouri, entered into an agreement to participate in a demonstration project which was sponsored by U.S. EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina. Adipic acid and DBA were tested as buffering agents in the Southwest Power Plant's Unit 1 limestone scrubber to determine their effectiveness in increasing utilization and SO_2 removal. This testing was conducted during 1981 and verified the effectiveness of organic acid buffers in a commercial limestone scrubber. This section of the paper describes the results of the first 2 years of DBA operations.

DBA FEED SYSTEM

A temporary DBA feed system was installed in late December 1981 to add the DBA solution on a continuous basis. This temporary system used a 26,000 ℓ (6,000 gal.) stainless steel tank truck equipped with thermal jacketing as a storage vessel. Two residential-sized electrical water heaters provided a source of hot water at ~ 60°C (140°F) for

TABLE 1

ANNUALIZED COST SUMMARY
FIRST YEAR COSTS OF BASE CASE SYSTEM
COMPARED WITH ORGANIC ACID ALTERNATIVES

Cost Items	Base Case Lime System (10^6\$)	Adipic-Acid-Enhanced Limestone System (10^6\$)	DBA-Enhanced Limestone System (10^6\$)
New Capital Investment	-	0.898	0.900
Alkali/Additive			
Lime	5.856	-	-
Limestone	-	1.222	1.222
Additive	-	0.931	0.418
Utilities	0.215	0.378	0.378
Total Annualized Cost	6.071	3.429	2.918
Annualized Cost Savings	-	2.642	3.153
(mills/kWh)		0.927	1.106

circulation through the thermal jacket of the truck. The heater return lines were run in parallel with the DBA feed line through a 10-cm (4-in.) PVC conduit in order to prevent feed line cooling. Maintaining high DBA temperatures was a major concern because DBA tends to easily precipitate out of aqueous solution. As an example, a 20 percent solution of DBA will begin to show crystal formation at 22°C (72°F); higher concentrations require even higher temperatures to keep the DBA in solution. The entire temporary system was assembled on-site and tied into the scrubber system in a few days.

Initially, DBA was pumped from the tank truck to the ball mill sump. The feed rate was set manually. After the DBA was mixed with the freshly ground limestone slurry from the ball mills, the mixture was pumped to the limestone storage tank. Since the limestone handling equipment was common to both scrubber modules, both scrubbers operated with the same DBA concentration. Late in September, the DBA feed system was modified to allow DBA to be fed separately into the reaction tank of either scrubber. (7)

SO_2 REMOVAL

Results of 2 year's worth of testing using DBA as an FGD additive were consistent with those anticipated based on the demonstration project conducted in 1981. On the whole, FGD performance was enhanced to such an extent that Southwest Power Plant consistently operated in compliance with the 1.2 lb $SO_2/10^6$ Btu (516 ng/J) federal emission limitation. The few emission exceedances experienced were generally associated with start-ups, shutdowns, and other periods of allowable operational curtailment.

Figure 4 displays a monthly history of FGD performance, expressed as overall SO_2 removal efficiency, for the 1982 and 1983 calendar years. Missing SO_2 removal data fr 1983 indicate a boiler outage period which occurred from December 1982 through May 1983. It can be seen that efficiencies were consistently greater than the approximately 82 percent removal generally required at the Southwest Power Plant to maintain compliance. For comparison, Figure 4 also displays the performance history for calendar year 1980, where removal efficiencies were erratic and averaged only 26.0 percent. Figure 5 shows these data in terms of average monthly emission rates. This figure illustrates the significant improvement in the ability of the system to comply with the regulatory emission standard after the conversion to a DBA-enhanced system. (6)

The addition of DBA also improved the system's ability to respond to various operational changes. During a 2-week period in March, the coal supplied to the system contained 4.5 percent sulfur instead of the 3.5 percent sulfur coal for which the system was designed. During this period, the unit was able to maintain an in-compliance status by increasing the amount of DBA feed to the system (7). The average coal sulfur content for the remainder of the 2-year period was 3.7 percent.

RELIABILITY

The overall reliability of the system was also increased significantly in 1982 and 1983 in comparison with other years. Figure 6 shows the monthly average FGD reliability for organic-acid-enhanced operations compared with the average reliability for

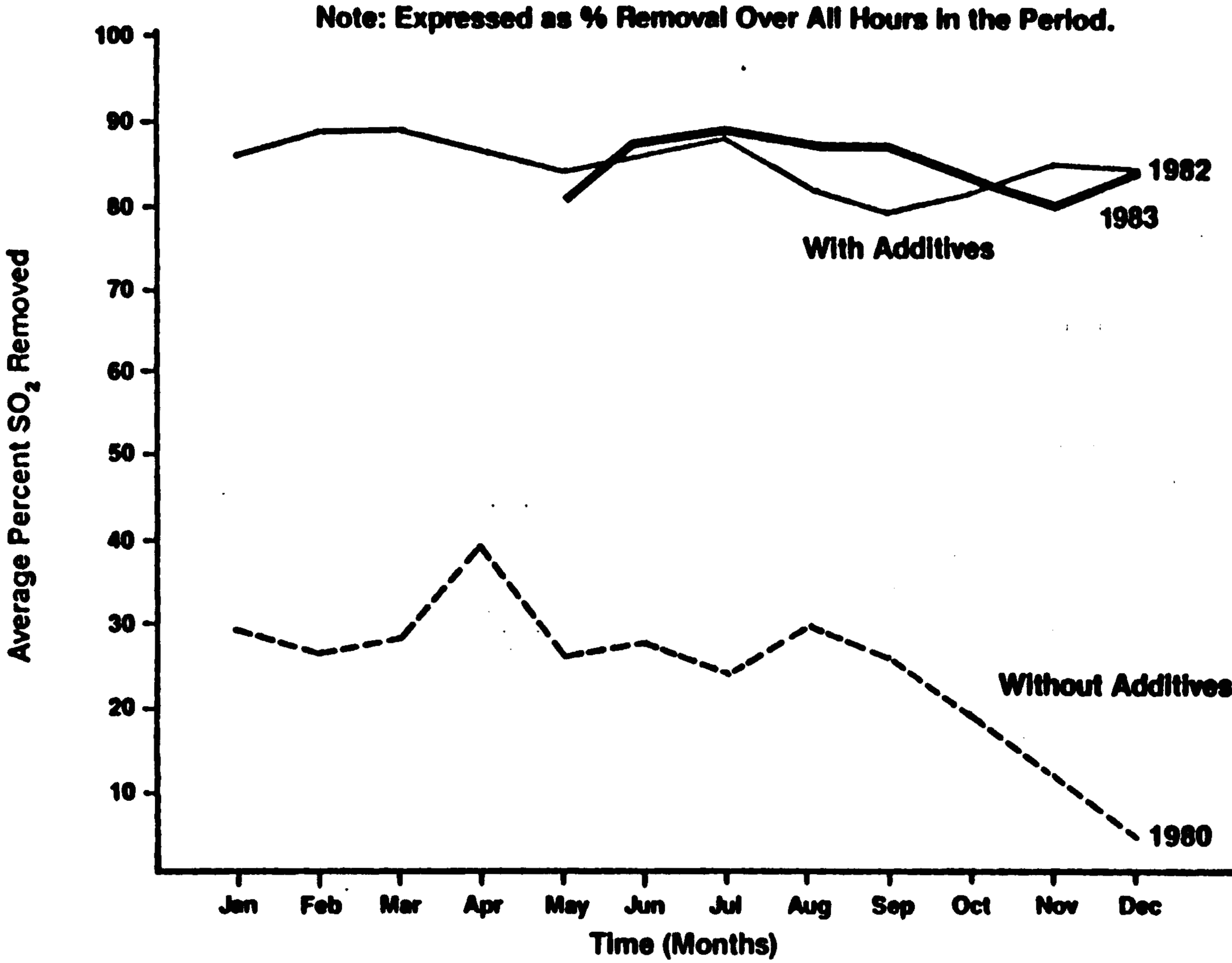

Figure 4. Comparison of Southwest Power Station SO_2 Removal Efficiencies with and without Organic Acid Additives

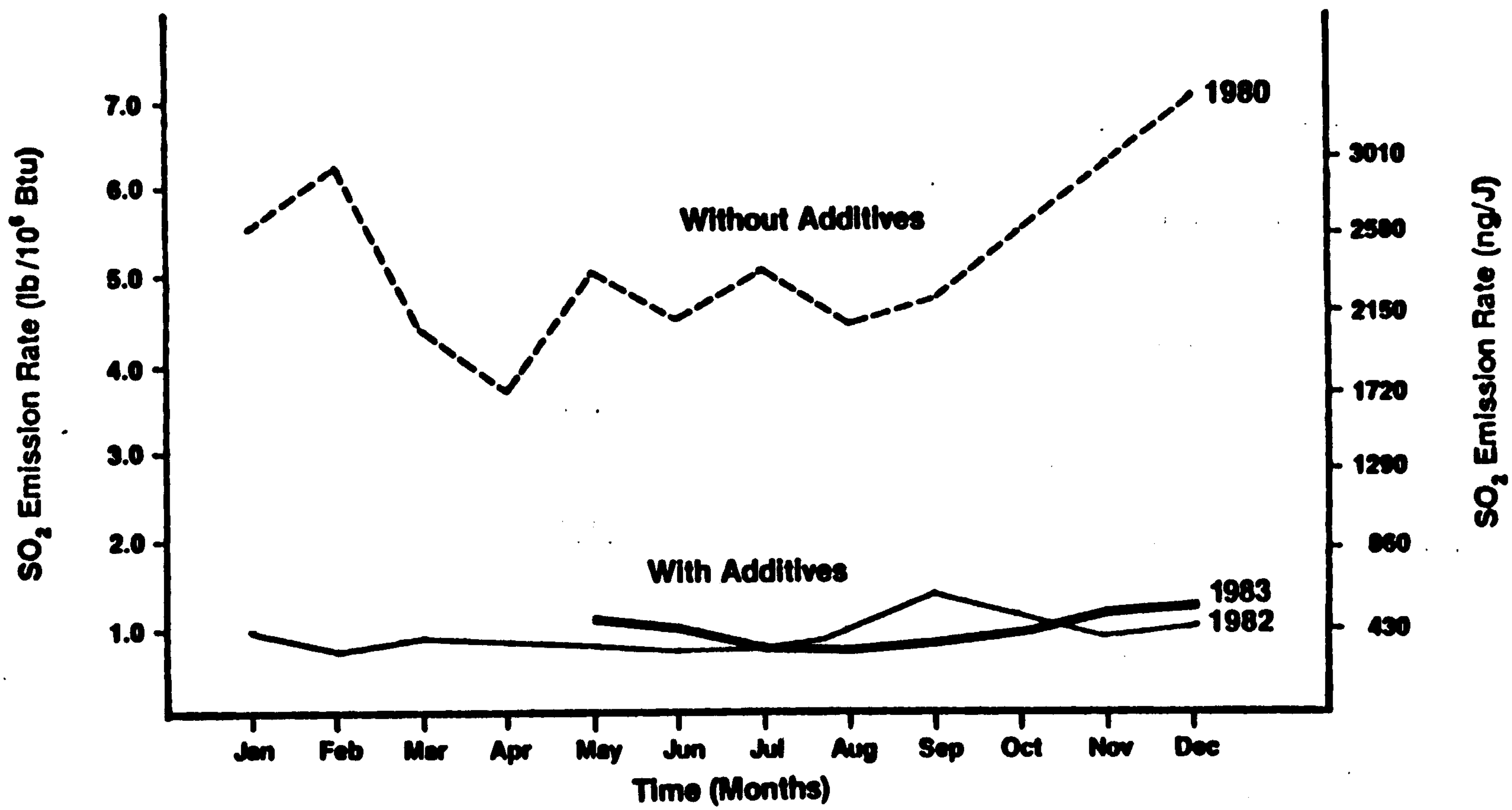

Figure 5. Comparison of Southwest Power Station Monthly Average SO_2 Emission Rates with and without Organic Acid Additives

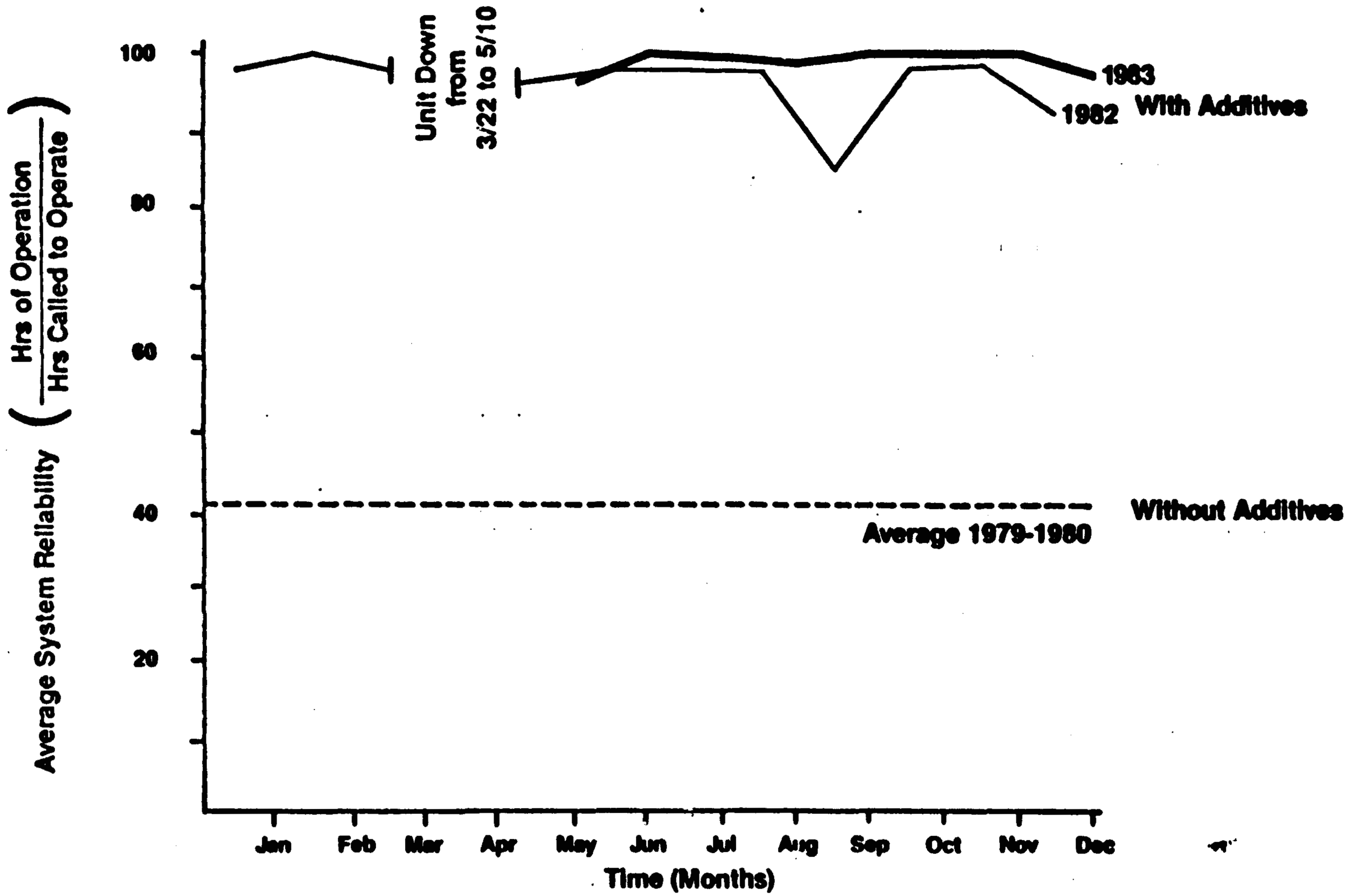

Figure 6. Comparison of Southwest Power Station Process Reliability with and without Organic Acid Additives

1979 and 1980 (8). This reliability increase may have resulted in part from DBA addition, but it was also related to a number of process improvements made during 1981 and 1982, such as the conversion from turbulent contact absorption towers to tray towers.

DBA CONSUMPTION

During the last half of 1982 the DBA consumption rate increased to nearly twice that observed during the 1981 demonstration tests. The increased DBA consumption was due to two main factors: changes in the recycle slurry pH and deterioration of the slurry recycle pumps. Slurry pH was decreased in 1982 from 5.4 to 5.1 to improve limestone utilization in an attempt to improve mist eliminator reliability. (Mist eliminator performance has been greatly improved by this technique and by washing with greater amounts of fresh water.) While the lower pH does improve limestone utilization, a higher concentration of DBA is required to achieve the desired SO_2 removal. (7)

The deterioration in the recycle slurry pumps resulted in an actual L/G ratio less than indicated. In order to maintain the same SO_2 removal at a decreased L/G, the concentration of DBA was increased. The pumps underwent a complete overhaul at the plant's scheduled outage in early 1983 to correct this problem.

Several operational improvements were implemented during the 1983 extensive maintenance outage. Examples are limestone classification system and a permanent DBA addition system. The limestone classification system was added to produce a finer grind limestone which would allow improved limestone utilization at a higher pH and result in reduced DBA consumption. This change has reduced the DBA consumption rate about 20 percent over that experienced in 1982.

CONCLUSION

The use of organic acid additives in commercially operating limestone FGD systems has resulted in improved SO_2 removal, reliability, system performance, and cost effectiveness. Exploration of additional applications of the technology in new and existing limestone FGD systems should further extend its commercial viability.

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