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High SO₂ Removal Efficiency Testing

DE-AC22-92PC91338

Technical Progress Report

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INTRODUCTION

This document provides a discussion of the technical progress on DOE/PETC project number DE-AC22-92PC91338, "High Efficiency SO₂ Removal Testing", for the time period 1 April through 30 June, 1993. The project involves testing at full-scale utility flue gas desulfurization (FGD) systems, to evaluate low capital cost upgrades that may allow these systems to achieve up to 98% SO₂ removal efficiency. The options to be evaluated primarily involve the addition of organic acid buffers to the FGD systems. The "base" project involves testing at one site, at the Tampa Electric Company Big Bend station. Up to five optional sites may be added to the program, at the discretion of DOE/PETC. By 30 June, 1993, four of those five options had been exercised. These options include testing at the Hoosier Energy Merom Station (Option I), the Southwestern Electric Power Company Pirkey Station (Option II), the PSI Energy Gibson Station (Option III), and the Duquesne Light Elrama Station (Option IV).

The remainder of this document is divided into four sections. Section 2, Project Summary, provides a brief overview of the technical efforts on this project during the quarter. Section 3, Results, summarizes the outcome from these technical efforts. Results for the base program and for each option in which there were significant technical efforts are discussed in separate subsections. In Section 4, Plans for the Next Reporting Period, an overview is provided of the technical progress that is anticipated for the third quarter of calendar year 1993. Section 5 includes a brief acknowledgment.

2.0

PROJECT SUMMARY

On the base program, testing was completed at the Tampa Electric Big Bend Station in November, 1992. The upgrade option tested was DBA additive. Project efforts during the second quarter of calendar year 1993 primarily consisted of project management activities and reporting. Review comments were received for the draft Technical Note that was submitted last quarter. A paper was prepared summarizing results from this site for presentation at the 1993 SO₂ Control Symposium which is planned for August.

For Option I, at the Hoosier Energy Merom Station, results from another program co-funded by the Electric Power Research Institute (EPRI) and the National Rural Electric Cooperative Association are being combined with results from DOE-funded testing. Three upgrade options have been tested: DBA additive, sodium formate additive, and high pH set point operation. All testing was completed by November, 1992. Project efforts during the current quarter were primarily in data reduction and reporting. The draft Technical Note for the Merom site was submitted in early April, and review comments were received in late May and early June.

Option II involves testing at the Southwestern Electric Power Company Pirkey Station. For this option, baseline testing was conducted in February. The upgrade option scheduled to be tested at this site was sodium formate additive. However, based on interim results from other sites and feedback from the Technology Working Group for this project, it was decided to test both sodium formate and DBA additive at Pirkey. Parametric testing with DBA additive was conducted in March, and parametric testing with sodium formate was conducted in April. Based on the initial results from the parametric test series, DBA appeared to be the more attractive upgrade option for this site. Consequently, a DBA additive consumption test was conducted in May. No sodium formate additive consumption test is scheduled to be conducted at Pirkey, although it now appears that the cost effectiveness of these two additives are closer than

it originally appeared. As for the base site, a paper was prepared summarizing results from this site for presentation at the 1993 SO₂ Control Symposium.

Option III, for testing at the PSI Energy Gibson Station, was exercised by DOE in February. A Categorical Exclusion for this site was approved in April, and baseline testing was conducted in early May. A Test Report summarizing the baseline results was prepared and submitted in early June.

Option IV is for testing at the Duquesne Light Elrama Station. This option was exercised by DOE on March 31st. During the current quarter an Environmental Assessment Questionnaire was prepared and submitted to DOE, and a Categorical Exclusion was approved in mid-June. A site kickoff meeting was held on June 17th, and baseline testing began on June 28th. The baseline test results are not yet available.

3.0 RESULTS

Results from the base program (at the Tampa Electric Big Bend Station) and the first optional site (Hoosier Energy Merom Station) were presented in detail in the previous quarterly report. Consequently, there is only a brief discussion of some new information for the Tampa Electric site, and no discussion of the Merom site in this progress report. There was significant technical activity for the second and third optional sites (the Southwestern Electric Power Company (SWEPCo) Pirkey Station, and the PSI Energy Gibson Station); results for these two sites are discussed in separate subsections below. The baseline testing at the fourth optional site (Duquesne Light's Elrama Station) had just begun at the end of the current quarter. Consequently, no results are available for this progress report. Results for this site will be discussed in the next quarterly progress report.

3.1 Tampa Electric Big Bend Station Results

Details of the results for this site were presented in the previous quarterly report. DBA additive was the upgrade tested at this site, and it was found to be effective at promoting very high SO₂ removal efficiencies (greater than 98%) in a cost-effective manner.

The FGD system at the Big Bend Station operates in a forced-oxidation mode, and produces a wallboard-grade gypsum byproduct. A wallboard manufacturer that regularly uses gypsum from the Big Bend Station FGD system tested a portion of the byproduct from the DBA addition period. The results of this manufacturer's tests became available during the current quarter.

The manufacturer reported that the sample contained no measurable amounts of DBA, which is undoubtedly related to effective washing of the byproduct cake in the Big Bend FGD dewatering system. Physical results such as time to set, and

compressive strength, were found to be equal to the regular gypsum supplied from Big Bend with no DBA in the system, and within acceptable limits for wallboard manufacturing. This is important information, as it suggests that Tampa Electric could implement DBA addition to promote very high SO₂ removal efficiencies, but not jeopardize their ability to utilize the byproduct rather than having to dispose of it.

3.2 SWEPCo Pirkey Station Results

3.2.1 System Description

The Henry W. Pirkey Station is a 720-MW mine-mount lignite unit located near Marshall, Texas. The lignite sulfur content ranges from approximately 2 to 10 lbs of SO₂ per 10⁶ Btu. The FGD system typically achieves an outlet emission rate of approximately 1.05 lbs SO₂ per 10⁶ Btu. To achieve this outlet level the four modules in the FGD system normally treat about 80% of the flue gas. The remainder of the flue gas is bypassed directly to the stack, with the amount bypassed being varied to control the outlet emission rate.

Figure 1 is a flow diagram for a single module of the FGD system at Pirkey. The FGD system uses limestone reagent, and operates in an inhibited-oxidation mode. To control sulfite oxidation, elemental sulfur emulsion is added on a continuous basis, and EDTA is added on a batch-wise basis about once per month. The absorber modules are dual-loop absorbers designed by UOP Air Correction Division. The lower loop has two spray headers; slurry is recycled to these headers from an integral reaction tank in the base of the module. The upper loop consists of three spray headers and a perforated plate located below the bottom spray header. Slurry is recycled to the upper-loop headers from a large reaction tank that serves two modules. Vertical-gas-flow mist eliminators are located at the top of each absorber.

Figure 1. Simplified Process Flow Diagram for Pirkey FGD System

Mist eliminator wash water flows to the upper-loop reaction tank. The upper-loop reaction tank feeds the lower loop by gravity overflow, and the lower-loop tank overflows to a waste slurry tank. However, the scheme for controlling slurry level and wt.% solids level in the upper-loop reaction tank calls for feed of slurry from the lower-loop back to the upper-loop reaction tank. This flow scheme results in the two loops having very similar dissolved species concentrations, whereas most dual-loop systems are more concentrated in dissolved species in the lower loop.

The FGD byproduct is dewatered in two parallel thickeners, followed by vacuum drum filters. Filter cake is combined with fly ash in a pug mill, and the mixture is landfilled on site. Thickener overflow and filtrate are reclaimed for mist eliminator wash and for limestone reagent grinding.

3.2.2 Program Description

The program consisted of four separate test periods. The latter two test periods were completed during this quarter. The baseline test period was a week-long effort to determine the SO₂ removal efficiency of the FGD system under normal operating conditions, and to collect the information necessary to calibrate FGDPRISM for this system. Table 1 summarizes the test schedule and nominal operating conditions for the baseline tests. The primary test variables were the pH set points for the upper- and lower-loop slurries. These tests were conducted in February, 1993.

The second test period was a 10-day parametric series of DBA additive tests. Table 2 summarizes the test conditions for the DBA parametric series. The primary test variables were DBA additive level, and pH levels in the upper- and lower-loop slurries. DBA was added to one of the two upper-loop reaction tanks, which meant that half of the FGD system was operated at the desired DBA concentrations, as two of four absorbers share a single upper-loop reaction tank. The performance of only one absorber was tested, though. These tests were conducted in March 1993.

Table 1

Baseline Test Conditions

Test No.	Test Duration (days)	Recirculating Slurry pH		Superficial Flue Gas Velocity, (ft/sec)
		Upper Loop	Lower Loop	
1	2	6.3	5.5	8
2	0.5	5.9	5.2	8
3	0.5	6.1	5.7	8
4	0.5	5.7	5.0	8
5	0.5	6.1	5.2	8
6	0.5	6.3	5.7	8

Table 2

Additive Parametric Test Conditions

Test No.	Test Duration (days)	Recirculating Slurry pH		Superficial Gas Velocity (ft/sec)	Additive Concentration (ppm)
		Upper Loop	Lower Loop		
DBA Parametric Tests					
1	2	6.2	5.6	8	300
2	1	5.7	5.0	8	300
3	2	5.7	4.8	8	600
4	1	6.2	5.5	8	600
5	2	6.3	5.7	8	1300
6	1	5.7	5.0	8	1500
7	1	6.3	5.7	8	2200
Sodium Formate Parametric Tests					
1	2	6.3	5.5	8	500
2	1	5.7	4.8	8	500
3	1	5.7	4.8	8	1000
4	1	6.2	5.5	8	1200
5	2	6.3	5.5	8	2400
6	1	5.7	4.8	8	2800

The third test period was a repeat of the DBA additive parametric test conditions, although with sodium formate additive instead. These test conditions are also summarized in Table 2. The sodium formate series was conducted in April 1993.

The fourth test period was a week-long additive consumption test. DBA additive was selected for the consumption rate testing based on the available results. The performance measured in the parametric test series with the two additives, the delivered additive costs, and the apparent consumption rates of each during the parametric series were all considered in making this selection. During this consumption test, DBA was added to the entire FGD system. The test was conducted in May, 1993.

3.2.3 Test Program Results

Results presented below include measured SO₂ removal efficiencies, a comparison of limestone utilization, sulfite oxidation, and solids dewatering properties for the baseline and parametric tests, and the results of the DBA consumption test.

SO₂ Removal

Baseline Tests--Figures 2 and 3 show the SO₂ removal results for the baseline tests. In these plots, SO₂ removal is expressed in terms of the "number of transfer units" (NTU) which is defined as $\ln(\text{SO}_{2 \text{ inlet}}/\text{SO}_{2 \text{ outlet}})$. For convenience, SO₂ removal is also shown on the figure.

Figure 2 is a plot of NTU versus recirculating slurry pH for the lower loop. The lower-loop SO₂ removal efficiency ranged from about 20% to 60% as the pH increased from 4.9 to 5.7. At the normal upper-loop pH of 6.3, the lower-loop pH ranges from about 5.5 to 5.7, depending on the lignite sulfur content. At these conditions, the lower loop contributes about 25% of the overall mass transfer capabilities of the absorber.

Figure 2. Pirkey Baseline Tests: Lower-Loop NTU vs. Lower-Loop pH

Figure 3. Pirkey Baseline Tests: Overall NTU vs. Upper-Loop pH

Figure 3 shows the overall removal data versus the upper-loop slurry pH. The overall removal efficiency ranged from about 85% to 97% as the upper-loop pH increased from 5.7 to 6.3.

Parametric Tests--Figure 4 shows the lower-loop SO₂ removal data for both the DBA and formate parametric tests. Two curves are plotted for each of the additives: a low-pH curve and a high-pH curve. Also shown on this figure are baseline results (at zero additive concentration) interpolated from Figure 3. In this figure, the sodium formate additive concentration is expressed in terms of formate ion concentrations, not as sodium formate.

The average molecular weight of DBA, a dicarboxylic acid that is a mixture of adipic, glutaric, and succinic acids, is about 130. The molecular weight of formate ion, a monocarboxylic acid, is 45. Given the differences in molecular weight and number of functional units per molecule, if the buffering capacity of DBA and formate were fully used as the FGD slurry absorbs SO₂, the buffering capacity per unit mass of formate should be nearly 50% higher than that of DBA. In practice, however, because the two additives buffer over different pH ranges, the relative effectiveness of DBA and formate is a complex function of the absorber configuration and the operating pH.

The results in Figure 4 suggest that formate may be slightly less effective than DBA in the lower loop at the higher pH level. However, much of this difference can be accounted for by the difference in lower-loop pH between the DBA and formate parametric tests. The high-pH formate tests were conducted with a lower-loop pH range from 5.4 to 5.5, while the DBA test pH range was 5.5 to 5.7. A single data point from one formate test, in which the lower-loop pH was increased from 5.5 to 5.74, is also shown in Figure 6. Formate performance for this test was much nearer that of DBA. At the lower pH level, the DBA and formate performance data were comparable.

Figure 4. Pirkey Parametric Tests: Lower-Loop NTU vs. Additive Concentration

Figure 5. Pirkey Parametric Tests: Overall NTU vs. Additive Concentration

Figure 5 shows the overall SO₂ removal efficiency for the module plotted versus the upper-loop additive concentration for the DBA and formate parametric tests. High-pH and low-pH curves are again shown separately. The results in this figure show that formate is comparable to DBA at the lower pH level, but may be slightly less effective than DBA at the higher pH level. The difference is not large, however.

The results in Figure 5 show that at the normal upper-loop set point of 6.3, overall SO₂ removal levels of 98% to 99.5% were achieved as the DBA concentration was raised from about 500 ppm to nearly 2400 ppm. With sodium formate additive, overall removal levels of 98% to over 99% were achieved with formate ion concentrations in the same range. This is not a large increase over the baseline level of 97% at this pH set point. However, when the data are compared on the basis of NTU, the additives improved the overall mass transfer capability of the absorber by approximately 10 to 30%. Also, as will be discussed in the next subsection, corresponding limestone utilizations were higher during the additive tests.

The low-pH test results in Figure 5 show that with a pH set point of 5.7 in the upper loop, and a corresponding pH of 4.7 to 5.0 in the lower loop, overall removal levels of 97% were achieved with a DBA concentration of about 1500 ppm. Similar performance was achieved with sodium formate additive, although at a higher formate additive concentration of about 2500 ppm.

Limestone Utilization

Baseline Tests--The baseline SO₂ removal data plotted in Figure 3 show that overall SO₂ removal within the target range for this project (95% to 98% removal) could be achieved by the Pirkey FGD system with no upgrade. At the normal operating condition, with a pH of 6.3 in the upper loop, the results for the test module showed that an overall SO₂ removal level of 97% could be achieved if no flue gas were bypassed.

However, at these conditions the limestone utilization values measured were relatively low. The observed baseline test series limestone utilization values are plotted in Figures 6 and 7 for the upper and lower slurry loops, respectively. For a pH value of 6.3, the limestone utilization in the upper loop was measured at only 65%. The blowdown from the absorbers to dewatering is actually from the lower loop. At the corresponding normal lower-loop pH of 5.5 to 5.7, the utilization in that loop ranges from about 80% to 85%. Thus, there is a financial incentive, in terms of reduced limestone consumption, for an additive that would allow overall SO₂ removal levels of 95% to 98%, but at higher limestone utilization values of 95% or greater.

Parametric Tests--The limestone utilization values measured during the DBA and sodium formate parametric tests are plotted in Figures 8 and 9, for the upper loop and lower loop, respectively. The corresponding baseline limestone utilization values from Figures 6 and 7 are represented in Figures 8 and 9 by a curve fit to those data. To simplify the figure, the DBA and formate parametric test data are not plotted as a function of additive concentration. No discernable trends for concentration effects were noted.

The results show that limestone utilization at a given pH increased during both the DBA and formate parametric test series. In general, this appears to be attributable to the lower sulfite oxidation percentages that resulted when these additives were used in the Pirkey FGD system. This observed effect is discussed further in the next subsection. At lower oxidation percentages, the liquid-phase calcium concentration is correspondingly reduced, due to lower liquid-phase sulfate concentrations. This in turn lowers the calcium carbonate relative saturation and increases limestone dissolution at a given pH level.

The data plotted in Figures 8 and 9 show that for an upper-loop pH value of approximately 6.3, the limestone utilization values improve from approximately 65% with no additive, to greater than 80% with either additive. At the corresponding lower-

Figure 6. Pirkey Baseline Tests: Upper-Loop Limestone Utilization vs. Upper-Loop Slurry pH

Figure 7. Pirkey Baseline Tests: Lower-Loop Limestone Utilization vs. Lower-Loop Slurry pH

loop pH of approximately 5.5 to 5.7, lower-loop limestone utilization values were slightly higher than for the baseline tests, at approximately 83 to 88%. Correspondingly, at these normal pH values, both the DBA and sodium formate additive were observed to increase overall removal across the test module from 97% to 98% and greater.

At the low pH set points for the parametric tests, of 5.7 in the upper loop and 4.7 to 5.0 in the lower loop, the data show very high limestone utilizations, with values in the range of 96% to 98% for the upper-loop samples, and 97% to 99% in the lower-loop samples. These utilization values are only a few percentage points higher than the baseline test results at similar pH set points.

However, the comparison between the baseline and parametric results is much more dramatic when SO₂ removal results are also considered. At the low pH set points, the baseline SO₂ removal results showed only 85 to 87% overall removal. With the additives, overall SO₂ removal levels of 97% could be achieved at these same pH set points. In the baseline tests, 97% overall SO₂ removal was measured when the pH set point was 6.3 for the upper loop, and the lower loop was maintained at a pH of 5.5 to 5.7. The corresponding limestone utilization in the lower loop (and hence in the blowdown slurry) was approximately 80% to 85%. Thus, with additives and the low pH set point of only 5.7 in the upper loop, the same 97% overall SO₂ removal level could be achieved, but at a limestone utilization value of approximately 98%.

Sulfite Oxidation Percentage

Baseline Tests--During the baseline tests, sulfite oxidation percentages in samples from both the upper and lower loops of the test module were measured in the range of 14% to 20%. The corresponding liquid-phase gypsum relative saturation values ranged from slightly subsaturated (0.8 to 0.9) to supersaturated (1.1 to 1.3). The highest supersaturation value of 1.3 was near the point where rapid scale formation may occur due to gypsum particles nucleating from the liquor, rather than precipitating on existing

gypsum crystal surfaces. These liquor gypsum relative saturation values agree well with the observed solid-phase sulfite oxidation percentages.

These data illustrate the difficulty SWEPCO sometimes faces in controlling sulfite oxidation percentages below 15% in the Pirkey FGD system. This percentage is typically the maximum at which subsaturated gypsum operation can be sustained. As mentioned in the system description, the difficulty in controlling sulfite oxidation percentages is thought to be related to the higher FGD liquor temperatures in the lignite flue gas application, among other factors, and aggravated by lower load and lower lignite sulfur content.

The relatively high pH set points in the Pirkey FGD system upper and lower loops during normal operation are primarily to help control sulfite oxidation. In general, higher pH operation tends to lower liquid-phase bisulfite ion (HSO_3^-) concentrations, and bisulfite is believed to be a reactant in the sulfite oxidation reaction chain.

Surprisingly, the oxidation percentages observed in the baseline tests appeared to be relatively independent of the pH set point. However, most of the baseline tests were too short in duration for the solid phase present in the recirculating slurries in the test module to come to steady state at each condition. Longer tests at each pH set point would be required to establish a relationship between pH set point and sulfite oxidation percentage for this FGD system.

Parametric Tests--Figures 10 and 11 show the effects of the DBA and formate additives on sulfite oxidation percentages in the upper- and lower-loop slurry solids, respectively. Both additives were observed to have a significant affect -- lowering oxidation from the baseline range of 14 to 20%, to about 10%. The beneficial effects of combining sodium formate additive with sulfur addition, in achieving lower sulfite oxidation percentages than can be achieved with sulfur addition alone, has been previously documented (Burke et al., 1990 SO_2 Control Symposium). A similar beneficial

Figure 10. Upper-Loop Oxidation vs. Additive Concentration

Figure 11. Lower-Loop Oxidation vs. Additive Concentration

effect of DBA additive on sulfite oxidation has been observed previously by Radian for other FGD systems. There are several possible explanations for such benefits. One is that the additive lowers the pH drop as the recirculating slurry flows through the countercurrent absorber vessel. A lowered pH drop would have a similar benefit to sulfite oxidation as raising the recirculating slurry pH set point.

This lower oxidation percentage is an important result for the Pirkey site because low oxidation percentages have been difficult to maintain using the conventional elemental sulfur additive to generate thiosulfate, even with EDTA addition as well to chelate transition metal oxidation catalysts. As described above, low oxidation percentages permit operation in a sub-saturated mode with respect to gypsum, preventing scale formation. In fact, during the DBA parametric tests, existing scale deposits in the system appeared to dissolve during the tests. This was indicated by decreasing module pressure drop over the course of the parametric test series at given gas velocity. For example, the overall pressure drop across the test module was lowered from 5.6 in H_2O to 4.2 in H_2O , at a controlled flue gas superficial velocity through the absorber of 8 ft/sec. This lower pressure drop was maintained during the subsequent sodium formate parametric tests.

The liquid-phase results for samples collected during the DBA parametric tests all show gypsum relative saturations in the subsaturated region and show a steady decrease as the concentration of DBA in the system increased. As the DBA tests proceeded, gypsum relative saturation fell to 0.2 in the upper loop, as the sulfite oxidation percentage was lowered to about 10%. Corresponding lower-loop gypsum relative saturations were in the range of 0.3 to 0.4.

In general, the liquid-phase gypsum relative saturation results for the formate parametric tests were significantly higher than those for the DBA tests. During the high formate concentration, normal pH set point test, lower-loop gypsum relative saturation values were calculated to be in the range of 0.3 to 0.8, whereas in the corresponding DBA tests the values had ranged only from 0.3 to 0.4.

For both additive types, the gypsum relative saturation data were found to be pH dependent, particularly for the lower-loop samples. For example, at a 1500 DBA concentration, with the lower-loop pH set point in the range of 5.5 to 5.7 the gypsum relative saturations were calculated to range from 0.2 to 0.5. At the lowest pH set point of 4.7 to 5.0, the gypsum relative saturation values ranged from 0.7 to 0.9. A somewhat surprising result is the increase in gypsum relative saturation into the scaling regime, at 1.7 to 1.8 in the lower loop, during the final formate test. This was a low-pH test, but at a formate ion concentration of greater than 2500 ppm.

The solids analyses did not indicate that oxidation was greater than 15% in this test, as would be expected due to the supersaturated gypsum condition. However, the gypsum saturation results in general appear to be a more sensitive indicator of oxidation rate than the solids analyses. This is not unexpected, because the solid-phase residence time can be much longer than the elapsed time for the one-day pH change tests, especially at the low inlet SO_2 concentrations seen during the formate tests. This is probably why the sulfite oxidation percentage values plotted in Figures 10 and 11 did not show a pH dependence. The change in liquid-phase chemistry with pH is much faster.

At first glance, the liquid-phase gypsum relative saturation data seem to indicate that DBA is a more effective oxidation inhibitor than formate in the Pirkey FGD system. However, there were differences in both average unit load and inlet SO_2 content that could have affected this comparison. During the DBA tests, the inlet SO_2 ranged from 1200 to 1700 ppm compared to 800-1200 ppm during the formate tests. The unit load ranged from 460 to 690 MW during the DBA tests compared to 290-610 MW during the formate tests. Higher oxidation percentages are favored by both lower inlet SO_2 concentrations and lower unit loads. Therefore, the difference in gypsum saturation between the DBA and formate tests cannot be attributed solely to differences in the additive type.

Solids Dewatering Properties

Settling tests conducted on site indicated that DBA addition greatly increased the slurry settling rate, relative to baseline rates, while formate addition did not. This is consistent with observed changes in the crystal morphology between the three test periods, as discussed below.

Samples were collected for slurry form filtration rate determinations during the baseline tests and the parametric tests for both additive types. These results are not yet available.

Scanning electron microscope photos of solids samples from the baseline, DBA, and formate tests show that differences in crystal size and morphology are readily apparent. In the baseline tests, the crystals are thin platelets with a length-to-width ratio (L/W) of about 2:1. The DBA test solids have an L/W of 3:1 or 4:1 and are much thicker. The formate test solids are nearly square (L/W = 1) and do not show the increased thickness of the DBA solids. These crystal size and morphology indications agree well with the on-site settling rate results, which showed the slurry samples from the DBA parametric test series to settle more rapidly than those from the baseline and sodium formate parametric tests.

3.2.4 DBA Consumption Test Results

A DBA consumption test was completed in mid-May of 1993. DBA was first added to the system by spiking the upper-loop reaction tanks and thickeners. The next day, the first DBA inventory was completed. Continuous addition to both upper-loop reaction tanks was then used to maintain the DBA concentration at a steady-state level.

As discussed previously, the current operating strategy for the Pirkey FGD system is to maintain relatively high pH set points in an attempt to inhibit oxidation to the extent possible. This strategy yields high SO₂ removal (about 97%) in the individual modules, but at the expense of lower limestone utilization (about 85% or lower). To meet the required emissions limit (1.2 lb SO₂ per million Btu heat input) at Pirkey, typically only 70% removal efficiency is required. Therefore, some flue gas is usually bypassed to the stack.

The objective of the consumption test was to measure the DBA addition rate required to maintain overall system SO₂ removal at 98% without flue gas bypass. This would be the desired operating mode to earn excess SO₂ allowances under the provisions of the 1990 Clean Air Act amendments. Target DBA concentration (1000 ppm) and pH set points (6.0 upper loop, 5.2 lower loop) were selected based on the results of the DBA parametric tests. These conditions were expected to yield the desired SO₂ removal performance while maintaining high limestone utilization (95+%) and a low sulfite oxidation percentage.

Even though the selected pH set points were maintained in the control room, local pH measurements showed that the actual module pH values were typically about 0.2 pH units higher than the set points during the consumption test. On-site DBA measurements by buffer capacity titration showed that the actual DBA concentration averaged about 600 ppm, which is well below the target value of 1000 ppm.

The DBA consumption rate was determined by an overall FGD system material balance for the test period:

$$\text{DBA consumption (lb)} = \text{DBA added} - \text{Change in DBA inventory}$$

The DBA consumption term was separated into "solution loss" and "non-solution loss" to facilitate application of the results to other process conditions. The solution loss is DBA

lost with the liquor leaving the system in the byproduct filter cake. The non-solution loss includes all other losses. Based on previous studies at EPRI's High Sulfur Test Center, the non-solution losses for DBA in an inhibited-oxidation system are primarily due to inclusion of DBA in the calcium sulfite crystal lattice. Some oxidative degradation also occurs.

The material balance can be written in terms of the different loss mechanisms as follows:

$$\begin{aligned} \text{DBA non-solution loss (lb/ton SO}_2 \text{ removed)} = \\ (\text{DBA added (lb)} - \text{DBA inventory change (lb)} - \text{DBA solution loss (lb)}) \\ / \text{Total SO}_2 \text{ removed during the test (tons)} \end{aligned}$$

An FGD system material balance spreadsheet that was developed for the parametric tests was used to track the DBA consumption on site. The amount of DBA added was determined by gauging the tanker trailer(s). The inventory change was measured by sampling each vessel in the system for DBA concentration. DBA was measured on-site by buffer capacity titration and will be determined off-site by ion chromatography as for the parametric tests. The DBA solution loss was estimated using the filter cake belt scale totalizer along with an assumed value for the cake moisture content and a measured DBA concentration in the filtrate. The total tons of SO₂ removed was estimated from the limestone belt scale totalizers using an assumed value for utilization. All of the assumptions inherent in the on-site DBA material balance will eventually be updated using actual data from the off-site analyses.

Note that it was intended that no flue gas be bypassed during the consumption test, so that the system SO₂ removal performance would represent the average performance of the four absorber modules. In practice, the system could not be operated continuously without bypass due to problems with the stack condensation drain. The stack drain was plugged, and operation without bypass caused condensation to

collect in the base of the stack. With time, the condensed moisture would overflow into the bypass duct. This situation is undesirable for a number of reasons, particularly concerns over accelerated corrosion in the bypass duct. To avoid overflow of condensed moisture, the bypass dampers were periodically opened to dry out the stack. The data averages for the test were computed only for periods of zero-bypass operation.

In spite of the absorber DBA concentrations averaging only 600 ppm rather than the target value of 1000 ppm, the target SO₂ removal efficiency of 98% was met or exceeded throughout the test. This excludes the periods when the system bypass dampers were briefly opened.

The estimated overall non-solution loss rate was measured at 11.5 lb DBA per ton of SO₂ removed, and the corresponding overall consumption rate was measured at 12.4 lb/ton. These values will be refined as the results of off-site analyses become available, but are not expected to change markedly. This non-solution loss rate is about double that measured for DBA at the Tampa Electric Big Bend site, and about 60% higher than the DBA rate measured at the Hoosier Energy Merom site. The differences in non-solution loss rate are due to specifics of FGD system chemistry, absorber type, oxidation mode, DBA concentrations, etc.

The site-specific non-solution loss rates measured during this project will be used to supplement data from the EPRI High Sulfur Test Center to improve the predictive capabilities of the FGDP_{PRISM} model. The fact that a fairly wide range of non-solution loss rates has been measured at the first three sites in this DOE program underscores the importance of evaluating performance additives at each particular site where they are being considered, rather than applying conclusions from other sites.

3.2.5 Economics

Because the field testing at this site was just completed in mid-May, a detailed evaluation of SO₂ removal upgrade economics has not yet been conducted. A cursory evaluation of DBA addition at this site is discussed below, though.

The baseline and parametric test results for this site indicate that a system-wide SO₂ removal level of 97%, which is within the target for this project of 95% to 98%, could be achieved with no additives by operating at the current upper- and lower-loop pH set points and closing the system bypass damper. A repair to the stack drain would be required. The primary costs for this upgrade would be the limestone required to remove this additional SO₂, and the additional fan power required for the additional gas flow through the absorbers.

An alternate approach would be to employ an additive, also with the bypass damper closed, and operate the system at lower pH set points in both the upper and lower loops. This would allow 97% SO₂ removal to be achieved at a limestone utilization of 95% or greater, rather than at the current utilization of about 85%. Preliminary economics indicate that the cost of the DBA additive required is less than the value of the limestone reagent saved by this approach. The economic benefits of this approach relative to the "no additive" approach will depend largely on the value assigned to the expected lower sulfite oxidation percentage with DBA additive. Potential benefits might include reduced manpower for absorber scale removal during outages, and reduced fan power requirements due to lower module pressure drop. These issues will be resolved when the detailed economics for the various upgrade options are developed.

Similarly, DBA and/or sodium formate addition could be employed to achieve system SO₂ removal efficiencies greater than 97%. The cost effectiveness of employing additives to achieve higher SO₂ removal percentages, relative to the market value for SO₂ allowances, will also be determined in the detailed economics.

Finally, it should be noted that the selection of DBA versus sodium formate additive for the additive consumption test was based on a review of field data and a limited amount of analytical results from the parametric tests. At this point, with consumption results for DBA additive alone, it is only this additive for which accurate upgrade economics can be developed. As more results become available, the differences in cost effectiveness between DBA and sodium formate additive for this site are less than it first appeared. However, DBA still appears to be slightly more cost effective.

3.3 PSI Energy Gibson Station Results

3.3.1 System Description

PSI Energy's Gibson Generating Station is located in Gibson County near Owensville, Indiana. Figure 12 presents a simplified process flow diagram for a single scrubber module at the Gibson Unit 5 FGD system. Flue gas exits the boiler and passes through the ESP for particulate control. From the ESP, the flue gas passes through ID fans and booster fans and then into the FGD system. Four modules treat flue gas from the 650-MW unit.

The absorber modules are of the Kellogg/Weir horizontal configuration. In this configuration, flue gas flows horizontally through a rectangular cross-section absorber vessel, and recirculating slurry is introduced through spray headers at the top of the absorber. There are four spray headers on each absorber, with one slurry recirculation pump per header. At full-load and high-sulfur-coal operation, all four pumps and spray headers are normally operated. Flue gas exiting the absorber section flows through a two-stage horizontal gas flow mist eliminator to the stack. A portion of the flue gas bypasses all four absorbers and goes directly to the stack. The amount bypassed varies with unit load, coal sulfur content, and absorber operating conditions. The FGD system is normally controlled to achieve an SO₂ emission rate of 1.00 lb SO₂/MMBtu, but no greater than 1.10 lb SO₂/MMBtu.

After contacting the flue gas, the recirculating slurry drains to a rectangular reaction tank below the absorber. Waste slurry is bled to dewatering from the first recycle pump discharge. Fresh limestone reagent slurry is fed to the opposite end of the tank.

Dolomitic lime is slaked and mixed with the limestone slurry to introduce magnesium as an additive to increase SO₂ removal efficiency. Gibson Unit 5 operates in an inhibited sulfite oxidation mode. This was the first limestone FGD system to add elemental sulfur for in-situ generation of thiosulfate to inhibit sulfite oxidation.

Waste slurry blowdown from the absorber is fed to either of two thickeners. The overflow from the thickeners flows to a reclaim water tank, while the underflow sludge is pumped to a surge tank and then to vacuum filters for secondary dewatering. The filtrate is sent to the reclaim water tank, and the filter cake is sent to pug mills and blended with fly ash for on-site disposal. Reclaimed water from the thickeners and vacuum filters is used for limestone grinding, mist eliminator wash, and FGD system makeup.

The system normally achieves approximately 87% SO₂ removal. The normal sulfur content of the coal fired in Unit 5 is approximately 3.5%. However, currently, an alternate coal is being fired in Unit 5. The sulfur content of this coal averages approximately 4.5 lbs of SO₂ per 10⁶ Btu of heat input, or approximately 2.5% to 3% sulfur.

3.3.2 Test Approach

The baseline tests were conducted on Module A. Each of the four modules has a separate inlet booster fan. During the course of the baseline tests, the flue gas volume treated by Module A was held constant by keeping the A booster fan power demand constant (110 amps for normal gas flow, 91 amps for low gas flow). The

remainder of the flue gas was treated by the other three absorbers in service. By operating in this manner, Module A test conditions were maintained independent of boiler load.

The baseline test plan is shown in Table 3. Independent test variables include reaction tank pH, number of recycle pumps in operation, and absorber flue gas velocity. The high absorber gas velocity conditions are representative of three module operation and the low absorber gas velocity is representative of four-module operation. For each test, the desired conditions were set by PSI Energy operators with the concurrence of the Radian lead engineer. After a period of stable operation (defined by steady control room pH readings), testing began.

The inlet and outlet flue gas was sampled for SO₂ concentration by EPA Reference Method 6. The inlet SO₂ concentration was measured at a single point, but the outlet SO₂ concentration was measured across 18 traverse points to account for potential stratification of SO₂ and gas flow in the duct.

During a typical test, flue gas velocity and SO₂ concentration were measured simultaneously at the scrubber outlet by a pitot tube traverse and Method 6 sampling train. Two Method 6 traverses were done at the module inlet sample location and module outlet sample location during each test. The flue gas velocity was measured at the scrubber inlet by pitot traverse as part of the preliminary testing and during Tests 5 and 7. The inlet flue gas velocity was measured twice during the baseline testing because the outlet flue gas flow rate measured was greater than the inlet flue gas flow rate on a standard, dry basis. The difference in gas flow measurements may be due in part to obstructions in the outlet ductwork just upstream of the sample location. The results of inlet flue gas measurements are consistent with historical gas flow data as a function of booster fan amps. Radian is currently trying to determine the explanation for this discrepancy.

Table 3
Revised Baseline Test Schedule for Gibson Station

Test	Objective	Performance Indicators	Duration (Days)	Reaction Tank pH	Recycle Pumps in Service	Absorber Gas Velocity
1	Characterize baseline performance under normal conditions	SO ₂ Removal Utilization Oxidation Solids Dewatering Relative Saturation	2	5.3	4	High
2	Characterize performance versus L/G with high pH	SO ₂ Removal Utilization Relative Saturation	0.5	5.5	4	High
3			0.5	5.5	3	High
4	Characterize performance versus L/G with low pH	SO ₂ Removal Utilization Relative Saturation	0.5	5.1	4	High
5			0.5	5.1	3	High
6	Characterize performance versus L/G and absorber gas velocity with normal pH	SO ₂ Removal Utilization Relative Saturation	0.5	5.3	3	High
7			0.5	5.3	3	Low

Flue gas samples for Orsat analyses were also obtained during each test at both sample locations. Recirculating slurry samples were obtained concurrently with the Method 6 traverses. Slurry flow rate measurements for each of the absorber recycle pumps were also made during the tests using a portable ultrasonic flow meter.

3.3.3 Test Results

Test results available to date are presented below. SO₂ removal efficiency results are based on field data. Previous experience has shown close agreement between the Method 6 field titration results and subsequent laboratory ion chromatograph data results.

SO₂ Removal Efficiency

Figure 13 summarizes the SO₂ removal performance data collected during baseline testing. The figure is a plot of NTU versus absorber slurry pH. In the figure, data for tests at different L/G's and/or gas velocities are indicated. With 4 pumps in service and with a superficial gas velocity through the absorber of 25 ft/sec, the NTU averaged about 2 at the base pH condition, or about 85 to 86% removal. At the high pH value of 5.6 to 5.7, the removal was in the range of 2.3 to 2.4 NTU, or about 90 to 91% SO₂ removal. At the lower pH of approximately 5.1, only 76 to 78% SO₂ removal was achieved.

At the 25 ft/sec velocity, but with only 3 pumps operating, the SO₂ removal levels varied from 66% (1.1 NTU) up to 83% (1.75 NTU) over this same pH range.

Absorber SO₂ removal performance can be approximately described by the following expression:

$$\text{Number of Transfer Units (NTU)} = \ln (\text{SO}_{2 \text{ in}} / \text{SO}_{2 \text{ out}}) = K A / G$$

Figure 13. Absorber NTU vs. Absorber pH

where: $\text{SO}_{2\text{ in}}$ and $\text{SO}_{2\text{ out}}$ = inlet and outlet SO_2 concentrations;
 K (lb/hr-ft²) = average overall gas-phase mass transfer coefficient;
 A (ft²) = total interfacial area for mass transfer; and
 G (lb/hr) = total gas flow rate.

It is assumed in the above expression that the equilibrium partial pressure of SO_2 above the FGD liquor is small compared to the inlet and outlet concentrations.

The overall coefficient K can be expressed as a function of two individual coefficients, k_g and k_l , that represent mass transfer rates across the gas and liquid films, respectively:

$$1/K = q/k_g + H/k_l\phi$$

where H is a Henry's law constant, and ϕ is the liquid-film "enhancement-factor." For a given absorber operating at constant gas and liquid flow rates, the NTU will be a function of slurry pH because of the effect of pH on the liquid film enhancement factor. Equation 1 also shows that NTU should be inversely proportional to gas flow rate (if K and A are independent of gas velocity) and proportional to liquid flow rate (if A is proportional to liquid flow rate).

The data plotted in Figure 13 show that the overall scrubber performance can be approximately correlated with absorber slurry pH and L/G ratio. At a given L/G (e.g. 4 pumps and 25 ft/sec flue gas velocity) the NTU plot in a smooth curve as a function of absorber slurry pH over the range tested. It is for this reason that it is convenient to plot absorber performance in terms of NTU.

Note in Figure 13 that the data points for Test 7, conducted at the lower gas velocity but with 3 pumps in service, had an SO_2 removal approximately equal to that measured at the higher gas velocity and 4 pumps, which is essentially the same L/G . If

K and A in Equation 1 are independent of gas velocity and A is proportional to the absorber slurry rate, then SO₂ removal should not be affected by gas velocity at constant L/G. These results suggest that these assumptions are valid.

Slurry Flow Rate Measurements

Slurry flow rate measurements were conducted on the spray headers twice during the baseline tests using an ultrasonic Doppler flow meter. This instrument processes a signal from a pair of transducers placed on the pipe. The recommended location for the transducers is on opposite sides of the pipe, away from turbulent flow. Radian experienced problems getting stable readings when the transducers were located in this manner. In order to get stable flow readings, it was necessary to place the transducers on the same side of the pipe. Each measured flow rate was based on the totalized flow measured over a 5 minute period.

The average flow rate for each slurry recycle pump was approximately 12,500 gpm. Based on these measured slurry flow rates, an L/G ratio of approximately 75 gal/macf is achieved when four recycle pumps are in service at the baseline operating gas velocity. When three recycle pumps are in service, the operating L/G drops to 56 gal/macf. During Test 1, at a lower gas flow and with three pumps in service, the operating L/G was approximately 75 gal/macf.

Slurry Sample Chemical Analyses

For Test 1 at normal baseline operating conditions, three complete sets of slurry and slurry filtrate sampled were collected. For Tests 2 through 7, three slurry samples and one set of slurry filtrate samples were collected. Of the three slurry samples, one was completely analyzed, and the other two were analyzed for solids content and solid carbonate only. The results of sample analyses are not available at this

time, but will be included in the technical note to be prepared and issued after the parametric testing.

Settling Rate Tests

Settling rate tests were performed to evaluate baseline solids dewatering properties. Three test measurements were performed during baseline testing, two during Test 1 and one during Test 4. Since it takes several solid-phase residence times in the reaction tank for solids properties to reach steady state, test measurements were not made during the tests of short duration. However, during the course of baseline testing, the Mg concentration ranged from a higher-than-normal concentration of 12,000 ppm, to an average concentration of 8,000 ppm. As a result, a third settling rate test was performed during Test 4 to determine if the high Mg levels measured during Test 1 had an effect on the solids settling properties. For Test 1, the thickener unit area required to achieve an underflow solids concentration of 30 percent was approximately 15 ft²/ton/day. For Test 4 the required thickener unit area was approximately 11 ft²/ton/day. The final underflow concentration was 43.4± 1.2 percent solids by weight. Although Test 4 was not conducted long enough to achieve steady-state with respect to solids properties, it appears that the elevated Mg levels may have negatively impacted the solids settling properties.

4.0

PLANS FOR THE NEXT REPORTING PERIOD

Technical progress during the third quarter of calendar year 1993 will involve efforts for all five sites. The first three sites, for the base program and Options I and II, are in the final reporting phases. For the both the base program at the Big Bend site, and Option I at the Merom site, the final version of the Technical Notes and draft version of the Topical Reports for these sites will be prepared. For the SWEPCo Pirkey site, efforts at the first of the quarter will involve completing and submitting the draft Technical Note. As review comments are received, the Topical Report for this site may be prepared later in the quarter.

At the PSI Energy Gibson Station, efforts during the quarter will involve conducting the parametric test series, most likely with sodium formate additive, then conducting an additive consumption test with the same additive. This parametric testing was scheduled to have begun on July 12th. However, a coal miners' strike has caused an interruption in supply of the normal coal to this plant. Consequently, this testing may be delayed for some time.

We currently anticipate conducting an additional, week-long performance and additive consumption test with DBA additive at this site. This additional test will provide comparison data for the two additives for this site as well.

The Technical Note for this site is currently scheduled to be submitted to DOE and to the host utility by the end of the third quarter of calendar year 1993. However, the delays in conducting the parametric tests, as discussed above, will likely delay this report until the fourth quarter of the calendar year.

Baseline testing at the Duquesne Light Elrama site (Option IV) was conducted the week of June 28th. Correspondingly, a Test Report for the baseline tests is scheduled to be submitted by late July. Parametric testing at that site will likely not

be conducted until late in the third quarter of calendar year 1993, or early in the fourth quarter.

Option IV, for testing, was just exercised by DOE/PETC at the end of the first quarter of calendar year 1993. The schedule for the testing efforts at this site has not been set. However, it is anticipated that the baseline testing at this site will be completed by the end of the quarter.

5.0

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