Technical Progress Report

April 1, 2000 – September 30, 2000

"Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control"

Cooperative Agreement No: DE-FC26-99FT40718

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December 1, 2000

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Abstract

This document summarizes progress on the Cooperative Agreement DE-FC26-99FT40718, Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control, during the time period April 1, 2000 through September 30, 2000. The objective of this project is to demonstrate the use of alkaline reagents injected into the furnace of coal-fired boilers as a means of controlling sulfuric acid emissions. The coincident removal of hydrochloric acid and hydrofluoric acid will also be determined, as will the removal of arsenic, a known poison for NO_X selective catalytic reduction (SCR) catalysts. EPRI, the Tennessee Valley Authority (TVA), First Energy Corporation, and the Dravo Lime Company are project co-funders. URS Corporation is the prime contractor.

This is the second reporting period for the subject Cooperative Agreement. During this period, the first of four short-term sorbent injection tests were conducted at the First Energy Bruce Mansfield Plant. This test determined the effectiveness of dolomite injection through out-of-service burners as a means of controlling sulfuric acid emissions from this unit. The tests showed that dolomite injection could achieve up to 95% sulfuric acid removal. Balance of plant impacts on furnace slagging and fouling, air heater fouling, ash loss-on-ignition, and the flue gas desulfurization system were also determined. These results are presented and discussed in this report.

Table of Contents

1.0   Introduction

This document is the semi-annual Technical Progress Report for the project "Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control," for the time period April 1, 2000 through September 30, 2000. The objective of this project is to demonstrate the use of alkaline reagents injected into the furnace of coal-fired boilers as a means of controlling sulfuric acid emissions. The coincident removal of hydrochloric acid and hydrofluoric acid will also be determined, as will the removal of arsenic, a known poison for NO_X selective catalytic reduction (SCR) catalysts. The U.S. DOE National Energy Technology Laboratory is funding the project under Cooperative Agreement DE-FC26-99FT40718. EPRI, the Tennessee Valley Authority (TVA), First Energy Corporation, and the Dravo Lime Company are project co-funders. URS Radian is the prime contractor.

Sulfuric acid is present in most flue gases from coal combustion because a small percentage of the SO_2 produced from the sulfur in the coal (approximately 0.5 to 1.5%) is further oxidized to form SO_3. The SO_3 combines with flue gas moisture to form vapor-phase or condensed sulfuric acid at temperatures below 500^oF.

Besides being a Toxic Release Inventory substance and a potential precursor to acid aerosol/condensable emissions from coal-fired boilers, sulfuric acid in the flue gas can lead to boiler air heater plugging and fouling, corrosion in the air heater and downstream, and the formation of a visible plume. These issues will likely be exacerbated with the retrofit of SCR for NO_X control on some coal-fired plants, as SCR catalysts are known to further oxidize a portion of the flue gas SO_2 to SO_3.

The project is testing the effectiveness of furnace injection of four different calcium- and/or magnesium-based alkaline sorbents on a full-scale utility boiler. These reagents will be tested during four one- to two-week tests to be conducted on a First Energy Bruce Mansfield Plant (BMP) unit. One of the sorbents to be tested will be produced from a wet flue gas desulfurization (FGD) system waste stream, from a system that employs the Thiosorbic Lime$^®$ scrubbing process. The other three sorbents are commercially available in large quantities.

After completing the four one- to two-week tests, the most promising sorbent(s) will be selected for longer-term (30-day) full-scale tests. The longer-term tests will be used to confirm the effectiveness of the sorbents tested over extended operation, and to determine balance-of-plant impacts. Two longer-term tests will be conducted, one on a First Energy unit and the

second on a TVA unit. The units will be selected to represent diverse configurations so as to make the test results applicable to a wide range of utility boilers. If two effective sorbents are identified in the one- to two-week tests, it is possible that both would be tested, one on each host boiler.

At the completion of the project, it is expected that sufficient full-scale test data will be available to design and implement commercial installations of the sulfuric acid control technologies demonstrated.

The remainder of this report is divided into three sections. Section 2 provides an account of progress on the project during the current reporting period, including any problems encountered. Section 3 provides a forecast of plans for the next and future reporting periods, and Section 4 provides a detailed discussion of technical results from the project during the current reporting period.

2.0 Progress during the Current Reporting Period

2.1 Summary of Progress

The current reporting period, April 1, 2000 through September 30, 2000, is the second technical progress-reporting period for this project. October 1, 1999 was the start date for this Cooperative Agreement.

During the current period, a dolomite injection test was conducted at the Bruce Mansfield Plant during the week of April 17. This test evaluated the effectiveness of dolomite injection through out-of-service burners on Unit 2 at lowering flue gas SO_3 concentrations. Balance of plant impacts from the dolomite injection were also determined. After the test was complete, samples collected during the test were chemically analyzed, and sampling and plant data collected were organized, reduced and analyzed. A draft Topical Report for this test was prepared and distributed for review by project team members. Review comments have been received, and a final Topical Report should be issued in the next reporting period. Results from this testing are presented in Section 4 of this Technical Report.

In parallel, considerable efforts continued to design, procure and assemble the sorbent slurry injection equipment that will be used to conduct furnace slurry injection tests. Figure 2-1 illustrates the planned slurry injection system. Major equipment items procured include two 10,000 gallon slurry storage tanks, two air-driven slurry transfer tanks, a day tank to be installed at the slurry injection level, two slurry injection pumps, two magnetic flow meters for measuring injection rates, and slurry agitators for the three tanks. The two air-driven pumps are on loan from team-member TVA, but the other items were purchased for this project. Other equipment items purchased include tank level transmitters, pressure indicators and switches, air regulators and solenoid valves, solid-state controllers, pump skids, hoses, data acquisition equipment, and miscellaneous electrical components, pipe fittings, hand operated valves, and wiring. Most of this equipment was procured, received, assembled and shipped to BMP by the end of the reporting period.

Two related subcontracts were completed to design slurry injection nozzles for the furnace slurry injection tests. GE Energy and Environmental Research Corporation modeled slurry droplet dispersion and evaporation within the furnace, and Ashworth Engineering designed slurry nozzles specifically for this furnace injection application. These subcontracts were completed during the reporting period, and a machine shop in Ohio fabricated the nozzles required for the upcoming slurry injection tests.
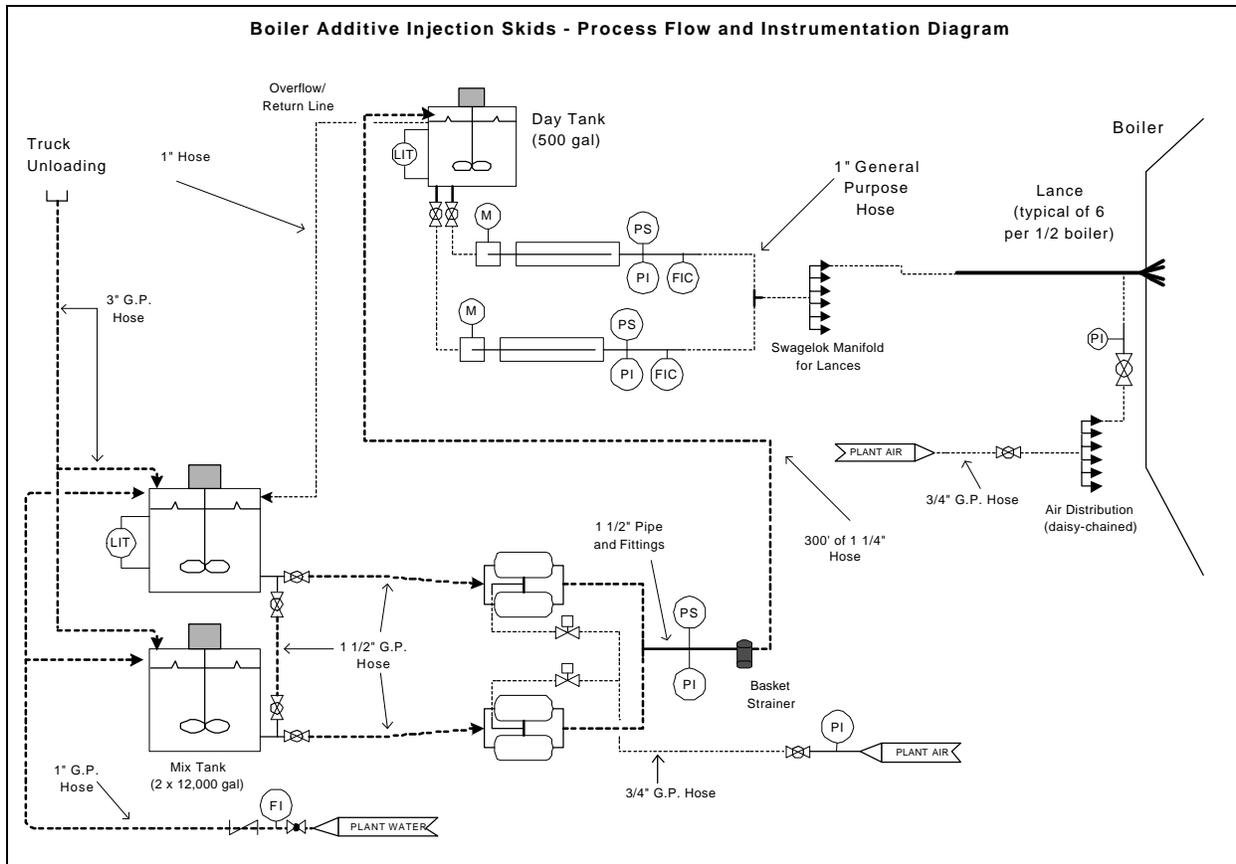
Figure 2-1. Slurry Injection System

A revised test plan was developed and distributed to project team members in September, for upcoming baseline and slurry injection tests to be conducted on BMP Unit 3. A test plan review meeting was held at BMP on September 28. Review comments were received from team members, and a revised test plan was distributed at the end of the month.

2.2   Problems Encountered

As might be expected, a variety of minor problems have been encountered during conduct of the dolomite test on Unit 2 of BMP, and during the design, procurement, assembly, and installation of slurry injection equipment. However, none was so serious as to adversely affect the project objectives, and therefore none warrant reporting here.

3.0   Plans for Future Reporting Periods

3.1   Plans for Next Reporting Period

The next reporting period covers the time period October 1, 2000 through March 31, 2001. Installation of the temporary slurry injection system on BMP Unit 3 should be completed by mid-October. BMP Unit 3 baseline and three short-term (one- to two-week) furnace slurry injection tests are planned, each followed by off-site chemical analyses, data reduction and evaluation, and preparation of a Topical Report. Baseline tests were conducted the week of October 2, and the pressure-hydrated dolomitic lime slurry test was conducted over the time period October 23 through November 3. Based on results from the pressure-hydrated dolomitic lime slurry test, the lime slurry injection test has been replaced with a test of commercially available magnesium hydroxide. This test is scheduled for November 27 through December 8.

The byproduct magnesium hydroxide test is tentatively scheduled for mid-January 2001, and the long-term (30-day) furnace injection test to be conducted at BMP is tentatively scheduled for February or March, 2001.

3.2   Prospects for Future Progress

The only subsequent reporting period for the current period of performance in the Cooperative Agreement is April 1 through June 30, 2001. It is likely that the long-term sorbent injection test at a TVA plant would not occur until May 2001. It may be necessary to request an extension to the Cooperative Agreement beyond the current end date of June 30, 2001, to allow adequate time for data reduction and reporting for the TVA long-term test.

4.0   Technical Results

The technical results for the current reporting period (April 1 through September 30, 2000) are for dolomite injection tests conducted on BMP Unit 2, which was conducted the week of April 17, 2000. The test was the first of several short-term (one- to two-week duration) tests to investigate the effectiveness of alkaline sorbents for sulfuric acid control and the effects of these sorbents on boiler equipment performance. This first short-term test investigated the effect of injecting dry dolomite powder ($CaCO_3 \bullet MgCO_3$), a mineral similar to limestone, into the furnace of Unit 2.

4.1   Test Description

During the test program, various analytical techniques were used to assess the effects of sorbent injection. These primarily included sampling with the controlled condensation system (CCS) for determining flue gas SO_3 content and an acid dew-point (ADP) meter for determining the sulfuric acid dew point (and, indirectly, the concentration of sulfuric acid) of the flue gas. EPA Reference Method 26a was used for determining hydrochloric acid (HCl) and hydrofluoric acid (HF), as well and chlorine (Cl_2) and fluorine (F_2) concentrations in the flue gas. Fly ash resistivity was measured using a SRI point-to-plane resistivity probe, and unburned carbon in fly ash was determined by loss on ignition (LOI). Coal samples were also collected and analyzed for a variety of parameters. Finally, visual observations were made of boiler furnace and convective pass surfaces prior to and during sorbent injection.

Units 1 and 2 at BMP are rated at 780 net MW, and Unit 3 is rated at 800 net MW. Each has an opposed-wall fired, supercritical boiler rated at approximately 6,415,000 pounds of steam per hour at 3785 psig and 1005^oF/1005^oF superheat and reheat temperatures. Each boiler has 16 burners each on the front and back walls of the furnace. Units 1 and 2 have been retrofitted with low NO_X burners and over-fire air. The burners are arranged in four horizontal rows on each wall, with four burners per row. One ball mill pulverizer provides the pulverized fuel for each row. Depending on fuel quality and mill condition, full load can generally be achieved with six of the eight mills in operation (and thus six of eight rows of burners in service).

All three units typically burn 2.0 to 4.5% sulfur coal. Coal blends are typically fired, predominantly blends of a McElroy coal. The facility also has permission to burn up to 20% of the fuel as petroleum coke. During the period of this study on Unit 2, a standard coal blend was used (i.e., no petroleum coke co-firing).

Unit 2 was brought into service in the mid-1970s. The 780-net-MW unit operates as a swing unit to meet the load demands of the grid. The boiler is equipped with two air heaters following the

economizer section. The average flue gas temperature at the outlet of the air heaters is controlled to about 300ºF due to acid dew point considerations.

Figure 4-1 illustrates the flue gas path for Unit 2, and notes the gas sampling locations used during this test. Flue gas from the air heaters passes through six circular ducts to six venturi scrubbers that remove particulate material and SO_2. The six scrubber inlet ducts are labeled A, B, C, D, E, and F from east to west. The scrubbers use a magnesium-enhanced, Thiosorbic® lime slurry reagent and produce a calcium sulfite hemihydrate ($CaSO_3•½H_2O$) byproduct. The flue gas then passes through induced draft fans, one per scrubber module. The six scrubbed flue gas streams are combined in two ducts that each lead to separate flues in the stack. The gas from scrubber ducts A, B, and C combine to go to flue A, and ducts D, E, and F go to flue B.
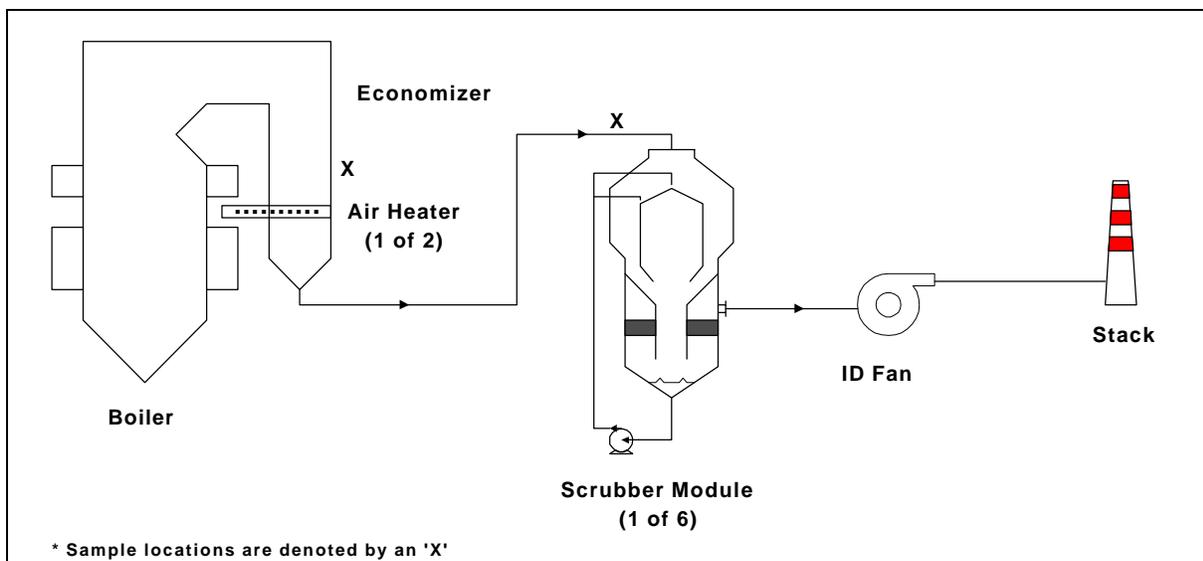
Figure 4-1. Illustration of Flue Gas Path for BMP Unit 2

The concrete stack contains four 19-foot diameter steel flues. Two of the flues are from Unit 1 and two of the flues are from Unit 2. Since the flue gas from two units is combined in one stack, it is difficult to determine if sulfuric acid control measures tested on one unit has had an effect on plume opacity. The flue gas in the stack is saturated at a temperature of about 130ºF. No reheat is used on the stack gas.

During these tests, the top rows of burners on the front and rear walls of the unit were generally out of service. Injection of dolomite was through the top row of burners on the front wall. This was accomplished by charging the coal storage hoppers that feed these burners with dolomite. The limestone was delivered to the coal feeders, fed to the pulverizer, pulverized and blown through the burners into the furnace.

4.1.1 Unit 2 Operating Conditions

Tests were conducted on April 18 through 21, 2000. Dolomite was injected around the clock from 4:20 p.m. on April 18 through 1:00 p.m. on April 21, with one interruption the morning of April 19. Flue gas characterization tests were only conducted during daytime hours each day. During all flue gas testing, the steam generator was at close to full load with two burner rows out of service (typically the top row of burners on the front and rear wall). Overnight the boiler load was sometimes reduced (particularly the evening of April 20 through the morning of April 21), but dolomite injection rates were maintained relatively constant due to minimum flow requirements on the mill used to grind the dolomite. Figure 4-2 illustrates the boiler load and dolomite injection rates over the test period.
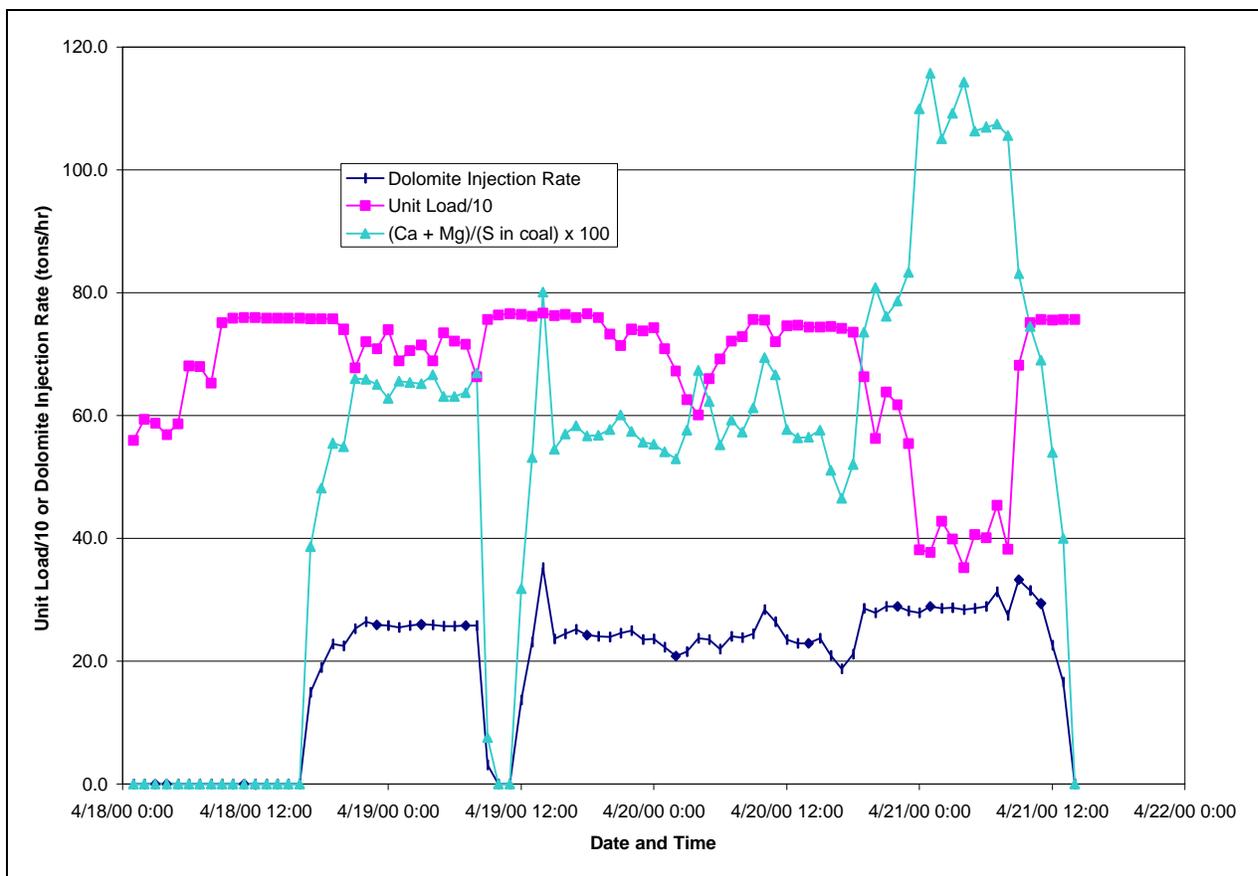
Figure 4-2. Boiler Load and Dolomite Injection Rate during the Test Period

Also shown in the figure is the effective molar ratio of alkalinity in dolomite injected to sulfur in the coal fired. This molar ratio is thought to be an important parameter in the control of sulfuric acid by furnace injection, as it indirectly affects the ratio of dolomite alkalinity to sulfuric acid in the flue gas. For the figure, the alkalinity in the dolomite includes both calciumcarbonate and magnesium

carbonate injected, and the coal sulfur is based on the measured coal feed rates and average coal sulfur analyses.

Flue gas testing conducted on April 18 served as a baseline test and was done with no dolomite being fed to the furnace. The testing conducted on April 19, 20 and 21 included dolomite injection at various flow rates. The dolomite was injected into the furnace through the top elevation of burners on the front wall of the furnace (identified as the "A" burner row). Table 4-1 summarizes the operating conditions during the flue gas test periods.

Table 4-1. Summary of Operating Conditions during Dolomite Injection Tests

Date	4/18/2000	4/19/2000	4/20/2000	4/21/2000
Generator load, avg. MW (gross)	758	763	743	754
Steam flow, Klb/hr	5480	5530	5400	5450
Burners out of service	Elevations A and D	Elevations A and D	Elevations A and D	Elevations A and D
Economizer outlet flue gas O_2, vol. % (wet)	3.3-4.1	3.1	3.1	3.0
NO_X, lb/MMBtu	0.34	0.31	0.33	0.35
Fuel flow, avg. Klb/hr	608	634	602	622
Dolomite flow, tons per hour	0-26.5 (dolomite feed started ~1620 hr)	23.1 to 35.2, avg. 25.7	18.8 to 28.4, avg. 23.3	16.6 to 33.2, avg. 25.0
Molar ratio, alkalinity in dolomite injected to sulfur in coal fired	0.0 to 0.66	0.53 to 0.80, avg. 0.65	0.47 to 0.69, avg. 0.62	0.40 to 0.83, avg. 0.64

4.1.2 Test Methods

H_2SO_4 Vapor by Controlled Condensation—Sulfuric acid vapor concentrations were measured at the economizer outlet using the controlled condensation system (CCS). A diagram of this sulfuric acid vapor train is shown in Figure 4-3. Controlled condensation is generally regarded as the most accurate method for measuring sulfuric acid vapor concentrations in flue gas, particularly where the flue gas is above the acid dew point. For these units, this would include flue gas temperatures above about 280°F, or all locations upstream of the scrubbers.

In the controlled condensation system, a sample of flue gas is pulled from the duct through a heated, quartz-lined probe. Particulate material is removed from the sample using a quartz thimble filter. Both the probe and the filter are maintained at about 550°F to ensure that no sulfuric acid vapor condenses in this part of the sampling system. Next, the filtered flue gas sample passes to a glass condenser that is maintained at a temperature of about 150°F by a circulating water bath.
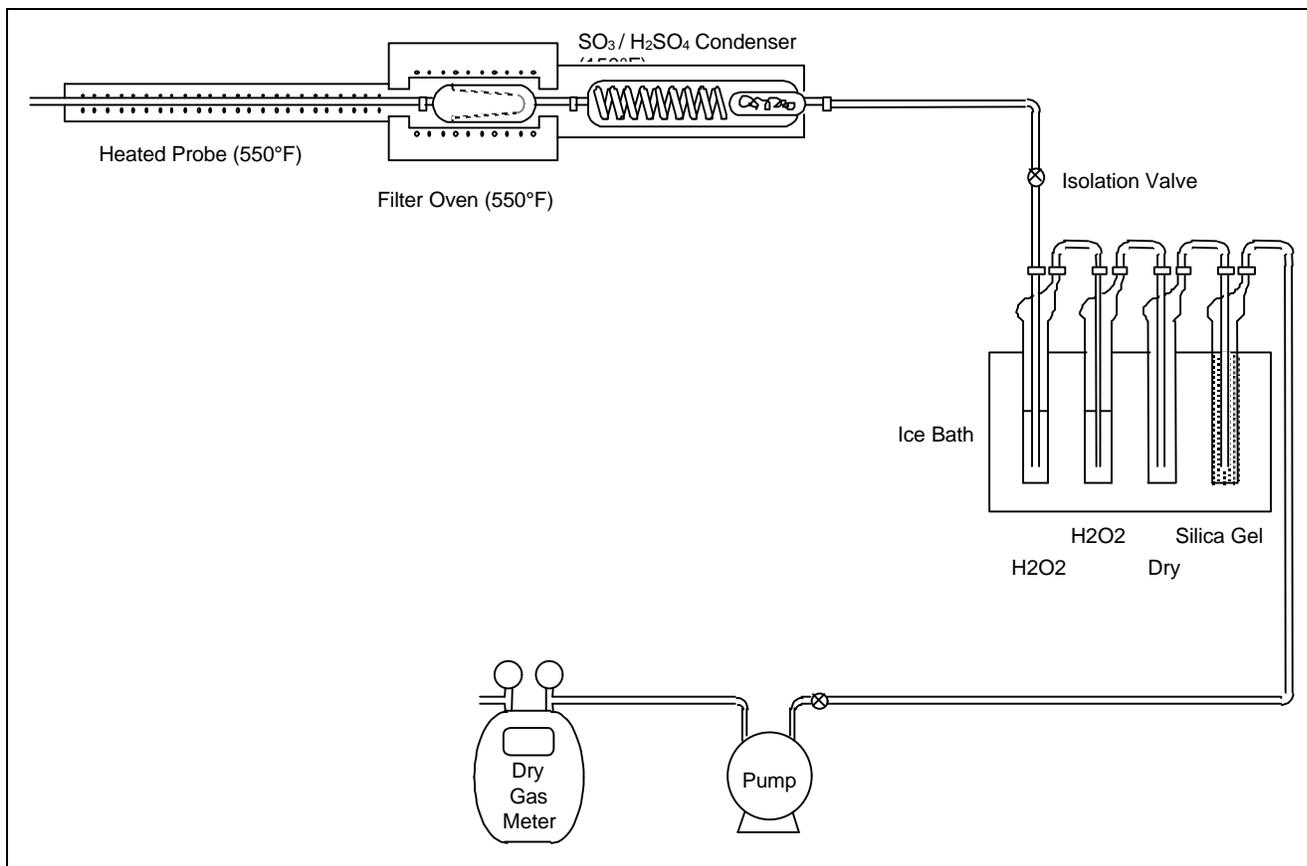
Figure 4-3. Controlled Condensation Sulfuric Acid Vapor Train

This temperature is well below the acid dew point but above the water dew point. The only material in most flue gases that will condense at this temperature is sulfuric acid vapor. Other acid gases have dew points that are much nearer the water dew point. At the completion of a CCS run, the condenser is removed from the sampling system, and a rinse of the condenser is analyzed for sulfate content. By measuring the total volume of flue gas pulled through the system and the amount of sulfate in the condenser, the concentration of H_2SO_4 vapor in the flue gas can be calculated.

Acid Dew Point—A portable acid dew-point meter, manufactured by Land Combustion, was used to determine the acid dew point. These measurements were made at the inlet ducts to the scrubbers where the flue gas temperature is in the range of 280°F to 340°F. The acid dew-point measurement can be used to estimate the flue gas content of sulfuric acid. There are several relationships correlating acid dew point to flue gas sulfuric acid concentration, such as those by Verhoff and Banchero[1]. These correlations are not always in agreement, often yielding results considerably different, especially at high dew points and/or high sulfuric acid concentrations.

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[1] Pierce, Robert R., "Estimating Acid Dewpoints in Stack Gases," *Chemical Engineering*, April 11, 1977, pp 125-128.

Method 26a—Hydrogen Halide and Halogen Emissions (chloride and

Method 26a is the reference EPA test method for determining hydrogen halide and halogen emissions—hydrochloric and hydrofluoric acids, chlorine and fluorine. This method requires isokinetic sample extraction with an apparatus similar to that used in EPA Method 5. An illustration of the Method 26a train is shown in Figure 4-4. Method 26a is different from Method 5 in that it includes an impinger containing sulfuric acid and an impinger containing sodium hydroxide. With the Method 26a sampling train, a flue gas sample is extracted isokinetically, passes through a heated probe and through a particulate filter contained in a heated oven. Following the particulate filter, the gas sample passes through the impinger train where moisture is removed in the first impinger, hydrogen halides (HCl and HF) are dissolved in the second impinger which contains sulfuric acid, and halogens (Cl_2 and F_2) are dissolved in the third impinger which contains sodium hydroxide. The samples collected are analyzed by ion chromatography (IC) or ion specific electrode.

Fly Ash Resistivity—Fly ash resistivity was determined using a point-to-plane in-situ probe. The sampling for fly ash resistivity was conducted at the economizer exit. The resistivity probe and its operator were provided by subcontractor Commercial Testing and Engineering.

Carbon in Ash—The carbon content of the economizer ash hopper ash samples was determined by the LOI method. Samples of ash were obtained from the economizer ash hoppers during each test and later analyzed for LOI using applicable American Society for Testing and Materials procedures. With the LOI method a sample of ash is weighed then incinerated and weighed again. The loss in weight is intended to provide an indication of the amount of combustible material in the ash. However, the method is not specific in that any compound that dissociates at high temperature could lose weight during this procedure (e.g., calcium hydroxide).

4.2   Results

Results from the four-day test are presented and discussed in the following section. First, results of fuel analyses are presented, then the impact of dolomite injection on measured sulfuric acid concentrations, as measured by the CCS and by the acid dew-point meter, is discussed. Next, the hydrogen halide and halogen emissions, as determined by Method 26a measurements, are discussed, followed by a discussion of the effect of dolomite injection on fly ash resistivity. The operation of the steam generating unit itself is next discussed, including ash LOI and observations of slag deposition during the test period. Finally, the observed impacts of the injected sorbent on the downstream flue gas desulfurization (FGD) system are also discussed.
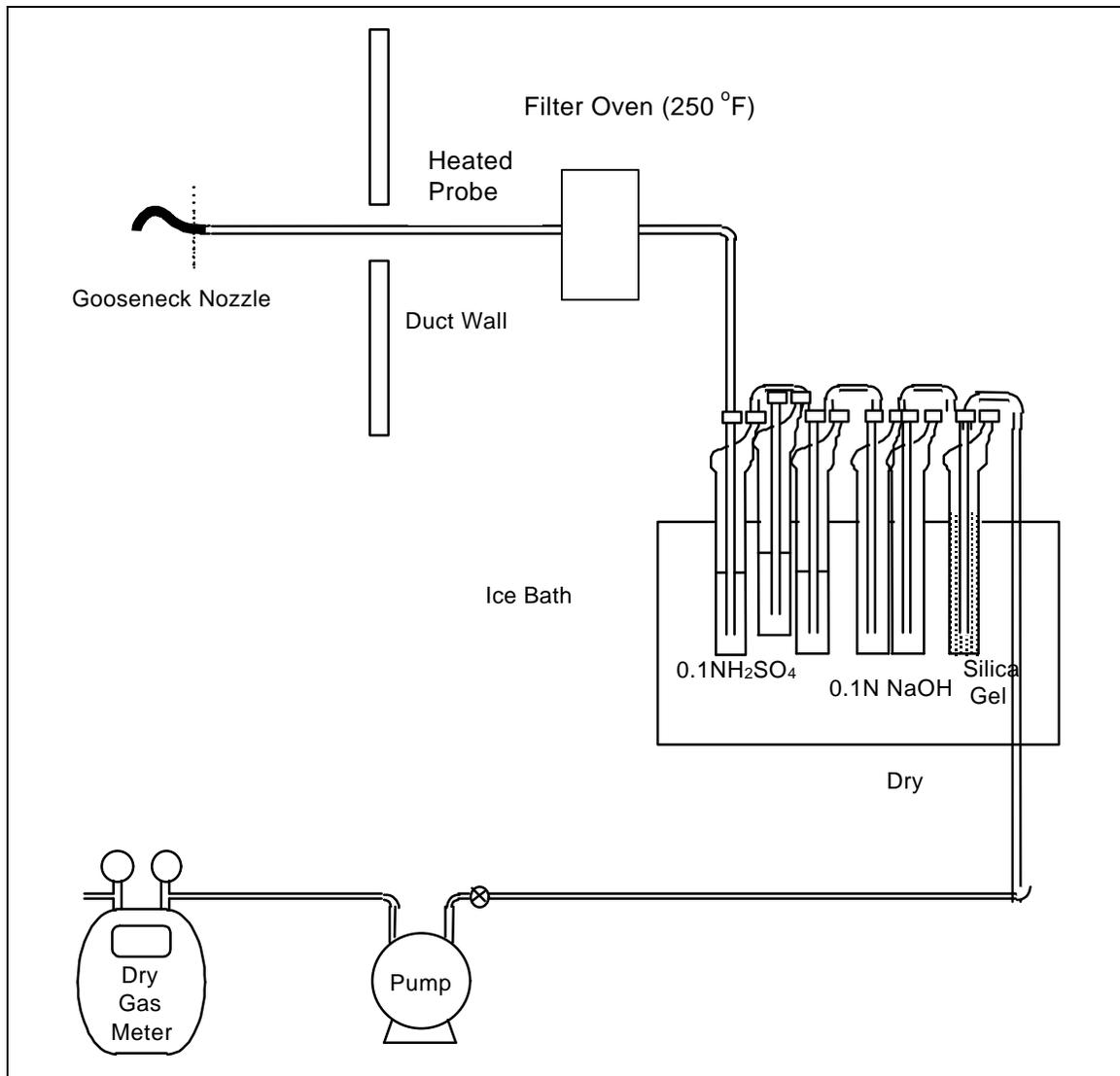
Figure 4-4. EPA Method 5/Method 26a Sampling Train

4.2.1 Fuel Analyses

Fuel samples were collected during each day of testing. Two of these samples, from the first day of testing and the last day of testing, were submitted to Commercial Testing and Engineering for a variety of analyses. The results of the analyses are contained in Table 4-2 and, for the most part, show consistency between the properties of the two samples analyzed. The primary differences of the ultimate constituents between the samples from April 18 and 21 were sulfur, which increased by approximately 0.3%, moisture, which decreased by approximately 0.8%, carbon, which increased by approximately 1.6%, and oxygen, which decreased by approximately 1.2% (it is noted that oxygen is determined by difference). The higher heating value was almost 300 Btu/lb (~3%) higher for the April 21 sample. These differences in ultimate constituents and heating value are not considered

Table 4-2. Fuel Analyses

Sample ID	72-431166	72-431165		72-431166	72-431165	
	As Received			**Dry Basis**		
	4/18/2000	4/21/2000	Average	4/18/2000	4/21/2000	Average
Ultimate Analysis, Weight %						
Carbon	65.59	67.24	66.415	70.25	71.37	70.81
Hydrogen	4.36	4.45	4.405	4.67	4.72	4.695
Nitrogen	1.11	1.11	1.11	1.19	1.18	1.185
Sulfur	3.97	4.28	4.125	4.25	4.54	4.395
Oxygen (diff)	4.82	3.62	4.22	5.16	3.85	4.505
Moisture	6.63	5.79	6.21	-	-	-
Ash	13.52	13.51	13.515	14.48	14.34	14.41
Total	100.00	100.00	100.00	100.00	100.00	100.00
Proximate Analysis, Weight %						
Moisture	6.63	5.79	6.21	-	-	-
Ash	13.52	13.51	13.515	14.48	14.34	14.41
Volatile	34.41	36.24	35.325	36.85	38.47	37.66
Fixed carbon	45.44	44.46	44.95	48.67	47.19	47.93
Total	100.00	100.00	100.00	100.00	100.00	100.00
Btu/Lb	11602	11984	11793	12426	12721	12573.5
Sulfur	3.97	4.28	4.125	4.25	4.54	4.395
Alk. as sodium oxide	0.39	0.26	0.325	0.42	0.28	0.35
Btu/lb, MAF	-	-	-	14530	14851	14690.5
Chloride, ug/g coal	-	-	-	1050	590	820
Fluoride, ug/g coal	-	-	-	111	104	107.5
Arsenic, ug/g coal	-	-	-	8	10	9

significant. Because the two coal samples analyzed were relatively consistent with respect to ultimate constituents and heating value, the other two samples from April 19 and April 20 were not analyzed.

The trace constituents determined were chloride, fluoride, and arsenic. The fluoride and arsenic contents of the two samples were fairly consistent. However, the chloride content of the April 18 sample was reported as 1050 ug/g coal while the chloride content of the April 21 sample was reported as 590 ug/g coal. This difference is sizable. It should be noted, however that URS has previously seen a wide range of variability in results of coal chloride content analyses conducted by commercial coal laboratories.

4.2.2 SO$_3$/Sulfuric Acid Measurements

Measurements of SO$_3$ were made at the economizer exit in the east duct. During the test program, two CCS sampling systems were utilized: one sampling system being designated "sampling system '1'" the other "sampling system 'a'". Sampling system "1" had its probe inserted

in the fourth test penetration in the duct (counting east to west) and sampling system "a" had its probe inserted in the sixth test penetration. There are a total of 10 test penetrations across the duct, so both probes were inserted close to the middle of the duct. Sampling system "1" was utilized throughout the entire test program, while sampling system "a" was utilized during the final two days of testing. The purpose of using two sampling systems was to confirm the validity of the data by taking additional measurements (typically simultaneously) at an alternate location in the duct.

Acid dew-point measurements were made with a Land Combustion portable acid dew-point monitor. This device was used at the air heater exit/scrubber inlet location.

The flue gas SO_3 concentrations calculated from CCS data are reported in Table 4-3. Note that there are two values reported for SO_3 concentration by CCS in the table. The first represents the results from on-site titrations of aliquots of the condenser catch from each CCS run, while the second represents the results from off-site ion chromatograph (IC) analyses. The IC results are typically regarded as being more accurate, as the end point for the on-site titration is difficult to see. In most cases, the two values for a given CCS run are very close anyway. Also shown in the table are the results of acid dew-point measurements made by the Land instrument during the corresponding CCS runs, the equivalent sulfuric acid concentrations indicated by the acid dew-point values, and the dolomite injection rate at the time the CCS run was made. The equivalent sulfuric acid concentration values shown are output values from the Land instrument.

The results of the SO_3 and ADP measurements indicate a significant reduction in flue gas SO_3 concentration and acid dew point with the introduction of dolomite into the furnace. Based on the CCS measurements, the flue gas SO_3 concentration dropped by over 60% (from approximately 52 ppm to 19 ppm) within two hours of initiating dolomite injection. On the second day of testing, dolomite injection was interrupted for several hours. Despite this interruption, flue gas SO_3 levels remained relatively low (15 ppm to 18 ppm), indicating a residual effect of previously injected dolomite. As discussed below, this apparent residual effect is most likely the result of dolomite products adhering to heat transfer surfaces and continuing to remove SO_3 from the flue gas stream and/or reducing the amount of SO_2 oxidized to SO_3 in the furnace. As dolomite feed continued, SO_3 removal as measured by both CCS and ADP improved, with measured concentrations dropping to as low as 2 to 4 ppm at times of higher injection rates.

Figures 4-5 and 4-6 provide plots of the CCS data versus time during the week. The data plots show a downward trend in the CCS measurements over the first two days of dolomite injection. Over the last two test days, the measured SO_3 concentrations (by sampling system 1) averaged 7 ppm and ranged from 2 to 12 ppm. Relative to the pre-injection average concentration of 52 ppm, this indicates an average of 86% reduction in economizer outlet SO_3 concentrations. Over this period, the

Table 4-3. Results of CCS and Acid Dew-point Meter Measurements

| Date	4/18/2000							
Dolomite Rate, Tons/hr	0	0	0	0	0	0	22.8	22.5
Test Run – Sample Train 1	1	2	3	4	5	6	7	8
Time Start	941	1023	1057	1138	1214	1421	1815	1853
Time End	1016	1051	1129	1209	1246	1451	1850	1923
SO_3 by Titration, ppm	47.3	54.8	52.5	53.4	33.0	51.4	18.3	16.8
SO_3 by IC, ppm	50.5	58.5	55.5	57.3	34.8	55.6	19.3	17.7
Avg. Acid Dew Point, ^{o}F	299	300	300	300	NA	300	284	280
SO_3 Equivalent, ppm	42	40	42	42	NA	43	18	16
Date	**4/19/2000**							
Dolomite Rate, Tons/hr	0	0	13.7	23.6	24.2	24.5	24.2	24.1
Test Run – Sample Train 1	1	2	3	4	5	6	7	8
Time Start	9:30	1005	1040	1411	1450	1523	1714	1748
Time End	10:00	1035	1115	1445	1520	1556	1744	1818
SO_3 by Titration, ppm	14.3	17.1	16.4	9.5	12.4	15.5	9.0	15.3
SO_3 by IC, ppm	15.1	18.2	17.6	10.1	13.0	16.3	9.4	15.8
Avg. Acid Dew Point, ^{o}F	269	NA	NA	271	273	NA	NA	NA
SO_3 Equivalent, ppm	8	NA	NA	8.8	9.6	NA	NA	NA
Date	**4/20/00**							
Dolomite Rate, Tons/hr	27.4	26.4	23.5	22.9	22.9	23.4	21.2	21.2
Test Run – Sample Train 1 (or a)	1	2	3		4	5	(1a)	(2a)
Time Start	945	1025	1110	1200	1310	1350	1702	1728
Time End	1015	1055	1140	1300	1340	1420	1722	1757
SO_3 by Titration, ppm	2.3	2.1	2.0	NA	10.5	8.0	3.2	20.0
SO_3 by IC, ppm	2.5	2.7	1.6	NA	11.7	9.4	3.5	21.2
Avg. Acid Dew Point, ^{o}F	259	261	273	273	276	278	NA	NA
SO_3 Equivalent, ppm	4.8	5.0	9.6	9.6	11	12	NA	NA
Date	**4/21/2000**							
Dolomite Rate, Tons/hr	33.2	31.5	29.4	29.4	22.5	16.6	16.6	-
Test Run Sample Train 1	1	2	3	4	5	6	7	-
Time Start	830	912	955	1035	1112	1155	1235	-
Time End	900	942	1025	1105	1152	1225	1305	-
SO_3 by Titration, ppm	6.1	3.5	11.1	9.8	5.6	7.2	10.5	-
SO_3 by IC, ppm	7.0	3.7	12.3	10.7	6.2	8.2	11.7	-
Test Run Sample Train a	1a	2a	3a	4a	5a	6a	7a	-
Time Start	840	922	1005	1045	1125	1205	1245	-
Time End	910	952	1035	1115	1155	1235	1315	-
SO_3 by Titration, ppm	5.2	7.9	9.1	7.2	2.9	5.7	12.5	-
SO_3 by IC, ppm	6.2	8.9	10.1	8.2	3.1	6.1	13.3	-
Avg. Acid Dew Point, ^{o}F	253	258	259	267	265	271	277	-
SO_3 Equivalent, ppm	3.5	4.4	4.5	7.5	6.3	8.7	12	-
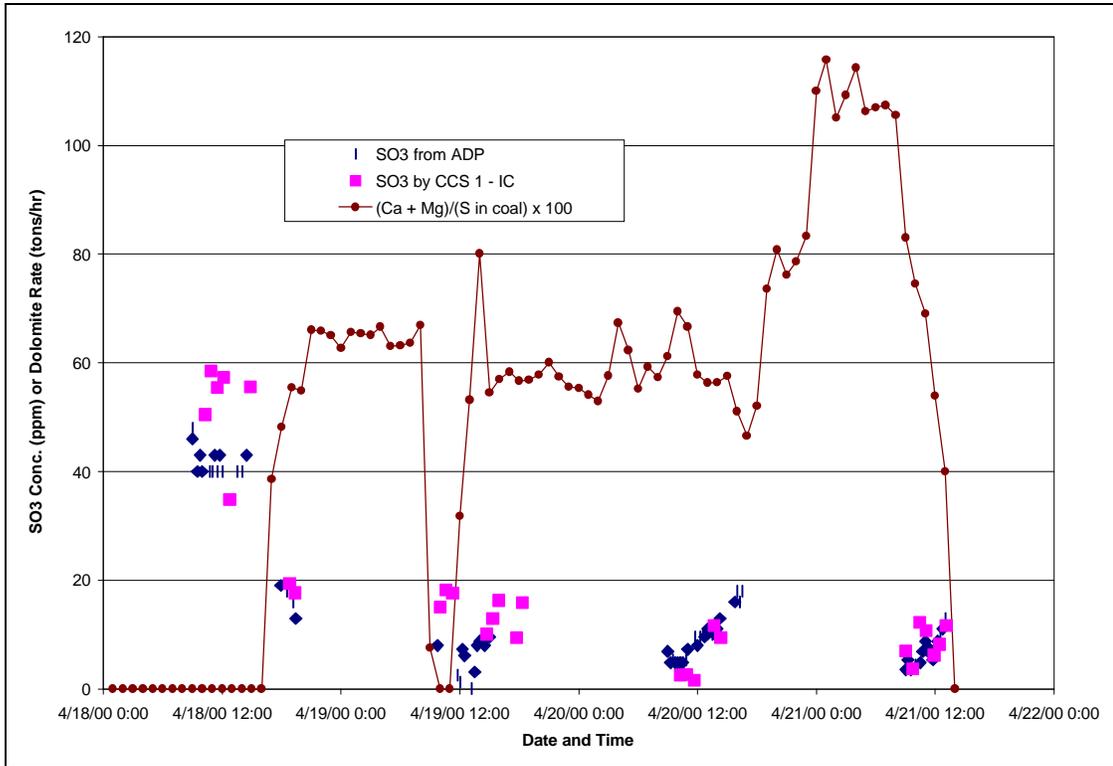
**Figure 4-5. CCS SO$_3$ Measurement Data**
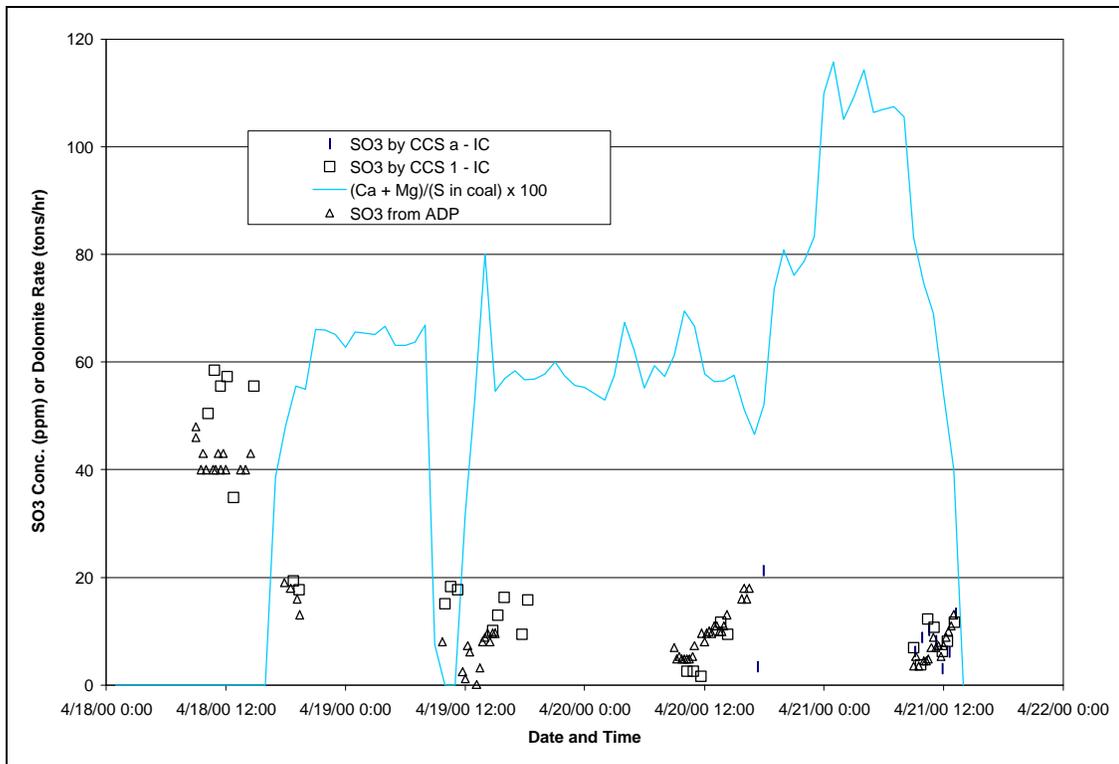
Figure 4-6. CCS SO$_3$ Measurements Compared to Acid Dew-point Measurements

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dolomite injection rate averaged about 25.7 tons/hr. At this rate, the dolomite injected represents about 8.8% of the coal feed rate. The alkalinity in the dolomite (CaO plus MgO) represents about a 0.7:1 mole ratio compared to the sulfur in the coal fired, and about a 40:1 mole ratio compared to the amount of SO_3 produced under baseline conditions (about 1.7% of the coal sulfur oxidized to the SO_3 form). Note that on those last two days, during the periods when sulfuric acid concentration data were actually being measured, the dolomite alkalinity molar ratio to the coal sulfur was slightly lower, at about 0.62:1, due to the effects of higher unit load during the day.

During the test periods, the dolomite feed rate was adjusted several times in an attempt to establish SO_3 removal as a function of dolomite feed rate. The dolomite feed rate was varied from approximately 16.6 tons per hour to 33.2 tons per hour. However, two effects confounded the ability to establish such a correlation. The dolomite feed rate changes were made relatively frequently, with a stable feed rate often being maintained for just an hour or two at a time. The other effect is that, particularly for the measurements on April 21, low load operation overnight meant that the dolomite was injected at a much higher molar ratio relative to the coal sulfur immediately prior to the testing period (see Figure 4-5).

It is very likely that residual effects of dolomite previously injected into the unit confounded the observed relationship between dolomite feed rate and SO_3 removal on April 21. The effects of alkaline materials injected into a furnace for SO_3 control are thought to be twofold. One is that the alkali calcines in the furnace (evolves CO_2 to form a high-surface-area oxide), and reacts with SO_3 in the furnace gas to produce alkaline sulfate salts. The extent of this reaction, which primarily occurs as a gas/solid interaction in the furnace gas, should change almost immediately with changes in dolomite injection rate. The other effect is that a portion of the alkaline material deposits on heat transfer surfaces in the boiler, where it can continue to participate in the gas/solid reactions described above, and/or reduce the conversion of SO_2 to SO_3 by coating and neutralizing potential catalyst sites. Iron oxide scale on boiler tubes, and iron oxide and vanadium pentoxide in ash deposits are thought to catalyze SO_3 formation. The effects of alkaline materials deposited on boiler heat transfer surfaces are less affected by instantaneous alkali injection rates, and may take hours or even days to reach a steady state level of effect after the injection rate changes. However, the relative contribution to SO_3 control of gas/solid sorbent reactions versus that of sorbent deposits on boiler surfaces can vary from boiler to boiler.

Evidence of residual effects of alkaline sorbents injected into the Unit 2 furnace was shown in Figure 4-5. The morning of April 19, the dolomite injection was stopped for over two hours, yet both CCS and acid dew-point measurements made during the period of no sorbent injection indicated SO_3

concentration reductions of greater than 60% relative to baseline concentrations from the previous day.

During the short-term variations in dolomite feed rates, particularly during the daytime hours on April 20 and the morning of April 21, there was a clear response of measured SO_3 concentrations by CCS and acid dew point to dolomite feed rate. Increased dolomite feed rates resulted in lower measured values, and vice versa. However, in most instances the feed rates were changed too rapidly to establish an SO_3 concentration that could be considered representative of a given dolomite feed rate.

There were two periods where the injection rate was held at a relatively constant value for two or more hours during which CCS runs were made. Late in the afternoon of April 19, the injection rate averaged 24.4 tons per hour, and CCS runs over that period averaged 14 ppm of SO_3. This indicates an average removal percentage of about 74% relative to baseline at a mole ratio of dolomite injected to coal sulfur of 0.57:1. On the morning of April 20, the dolomite injection rate averaged 27.4 tons per hour over a two-hour period. CCS runs during that period averaged about 2.6 ppm of SO_3, indicating a sulfuric acid removal rate of about 95% relative to baseline. The mole ratio of dolomite injected to coal sulfur during this period was about 0.68:1.

It would take longer duration at a given dolomite injection rate and unit load to determine a steady state (or near steady state) SO_3 removal level. A full day or more at each injection rate and unit load combination would provide more representative SO_3 removal percentages.

The equivalent SO_3 concentrations determined from ADP measurements were in fairly good agreement with the CCS results. This comparison can be made from the data in Table 4-3 and is illustrated in Figure 4-5. Before dolomite injection began, the ADP measurements indicated substantially lower SO_3 concentrations than did the CCS results, with the two differing by as much as 15 ppm. During dolomite injection, though, the two measurement techniques typically differed by 2 to 3 ppm or less. During the last two days of the test, the SO_3 concentrations indicated by the ADP measurements were, with few exceptions, bracketed by the CCS results.

The data plotted in Figure 4-6 compare the results from the measurements with the two sampling trains, "1" and "a." The plot shows good comparison between the measurements at two locations in the duct except for relatively low value of 3.5 ppm followed by a much higher value of 21 ppm from the "a" sample train the evening of 4/20. There are no corresponding CCS run data for sampling system "1" during the sampling system "a" measurements that day. However, the high value follows a trend for increasing SO_3 concentrations previously that afternoon, as indicated by the acid dew-point values, during a period of relatively low dolomite injection rate. From this standpoint,

the 21-ppm measurement seems consistent with the other data, while the measurement of 3.5 ppm that immediately preceded the 21-ppm measurement by the "a" sampling train is most likely erroneous.

4.2.3   Method 26a—Hydrogen Halide and Halogen Concentration Results

The flue gas hydrogen halide and halogen content was determined by conducting the EPA Method 26a test procedure. The samples collected with this sampling train were analyzed for chloride and fluoride content. A summary of these analyses is presented in Table 4-4, reported on the basis of milligrams per sample for chlorides and fluorides. The flue gas concentrations of these components are calculated from these values divided by the quantity of flue gas sampled during each test run. The concentrations of each chlorine and fluorine species are shown in the table in terms of ppmv on a dry flue gas basis.

The injection of dolomite into the Unit 2 furnace did not appear to have a noticeable affect on the measured concentrations of HCl or HF. The measured HCl and HF concentrations actually averaged about 15 to 20% higher during dolomite injection than during the baseline period. However, some reduction in the mass emission rate of chlorine and fluorine was seen, with the values measured during dolomite injection averaging about 1/3 of the baseline average for chlorine and ¼ of the baseline average for fluorine. Samples of the dolomite were not analyzed for chloride or fluoride, so any contribution to the measured concentrations from the dolomite is unknown. It is assumed that this contribution is negligible, though.

Table 4-5 presents these data in terms of calculated mass rates of hydrogen halides, halogens and total chloride and fluoride as measured by Method 26a. The concentrations of chloride and fluoride in the fuel samples submitted for analysis were shown in Table 4-2 and are repeated in Table 4-5. Also shown are calculated mass rates of chloride and fluoride fed into the furnace with the fuel, based on measured coal feed rates and the two fuel analyses.

The fuel sample obtained during the first day of testing contained approximately twice the concentration of chloride as the sample from the final day of testing, while the two fluoride analyses yielded similar concentrations. The Method 26a results agree reasonably well with the coal chloride content reported for the sample from 4/21. For the sample from 4/18, though, the mass rate of chloride entering the furnace with the coal based on that day's analysis was more than twice what was measured in the flue gas by Method 26a. This makes the coal chloride analysis for 4/18 suspect. URS Radian's experience has been that coal chlorine analyses for concentrations in the range of 1000 ppm or lower can show quite a bit of variability, so this suspect analysis is not surprising.

Table 4-4. Summary of Method 26a Data

Date	Test	Sample Gas Volume, dscf	Hydrogen Halides				Halogens			
			Chloride, mg/sample	Fluoride, mg/sample	HCl, ppmv (dry basis)	HF, ppmv (dry basis)	Chloride, mg/sample	Fluoride, mg/sample	Cl_2, ppmv (dry basis)	F_2, ppmv (dry basis)
4/18/00	1	48.458	57.45	15.40	28.4	14.2	0.883	0.162	0.22	0.075
4/18/00	2	43.486	56.10	12.83	30.9	13.2	0.749	0.166	0.21	0.085
4/18/00	3	42.185	43.90	13.24	24.9	14.0	2.028	0.117	0.58	0.062
4/19/00	4	42.261	61.15	16.62	34.6	17.6	0.535	0.071	0.15	0.037
4/19/00	5	42.081	60.00	17.69	34.1	18.8	0.627	0.039	0.18	0.021
4/19/00	6	39.829	53.15	15.46	31.9	17.3	0.608	0.047	0.18	0.027
4/20/00	7	42.193	63.50	18.23	36.0	19.3	0.073	0.016	0.02	0.008
4/20/00	8	43.196	59.80	17.89	33.1	18.5	0.002	0.028	0.00	0.014
4/20/00	9	57.203	67.60	18.74	28.3	14.6	0.313	0.026	0.07	0.010
4/21/00	10	42.644	62.15	16.91	34.9	17.7	0.009	0.017	0.00	0.009
4/21/00	11	44.496	42.95	11.34	23.1	11.4	0.953	0.016	0.26	0.008

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Table 4-5. Hydrogen Halide and Halogen Mass Rates

Date	Test	Hydrogen Halides		Halogens		Total		Fuel Data			
		HCl, lb/hr as Chloride	HF, lb/hr as Fluoride	Cl_2, lb/hr as Chloride	F_2, lb/hr as Fluoride	Chloride Emission, lb/hr	Fluoride Emission, lb/hr	Fuel Chloride Content, ug/g	Fuel Fluoride Content, ug/g	Approximate Input Rate of Chloride from Fuel, lb/hr	Approximate Input Rate of Fluoride from Fuel, lb/hr
4/18/00	1	295	79	4.5	0.83	300	80	1050	111	672	71
4/18/00	2	321	73	4.3	0.95	325	74				
4/18/00	3	259	78	12.0	0.69	271	79				
4/19/00	4	360	98	3.2	0.42	363	98				
4/19/00	5	355	105	3.7	0.23	358	105				
4/19/00	6	332	97	3.8	0.30	336	97				
4/20/00	7	375	107	0.4	0.09	375	108	590	104	378	67
4/20/00	8	345	103	0.01	0.16	344	103				
4/20/00	9	294	82	1.4	0.11	295	82				
4/21/00	10	363	99	0.05	0.10	363	99				
4/21/00	11	240	63	5.3	0.09	246	64				

The Method 26a results for total fluoride in the flue gas showed about 30% more fluoride accounted for than was indicated in the fuel. This apparent measurement bias was seen for both coal analyses.

4.2.4 Fly Ash Resistivity Measurement Results

Fly ash resistivity tests were conducted on the first two days of testing: April 18 with no dolomite injection and then with dolomite injection late in the day; and, April 19 with dolomite injection. Due to a miscommunication amongst the sampling team, these measurements were erroneously taken at the economizer outlet, where the flue gas temperature was approximately 700°F. It was intended that these measurements instead be taken at the air heater outlet, where the flue gas temperature was between 280 and 340°F. The latter is more representative of the flue gas temperature at the inlet to a "cold-side" electrostatic precipitator (ESP), which is the most common form of particulate control for utility boilers that are fired with bituminous coals.

Fly ash resistivity is a function of flue gas temperature. Therefore, the resistivity values reported from these tests are different than what would be expected if the sampling had been done at the lower, air heater outlet temperature. The results of the fly ash resistivity tests are reported in Table 4-6, but are of little value for the intended purpose of quantifying the effects of dolomite injection on fly ash resistivity at the inlet to a cold-side ESP. They would be relevant, though, for a plant that has a hot-side ESP for particulate control.

Each resistivity reading shown in the table is an average of four individual readings taken over a 45-minute time frame. It is noted that the temperatures reported by Commercial Testing and Engineering were in the 550°F range, while plant instrumentation and other test instrumentation measuring the flue gas temperature indicated temperatures closer to 700°F. The temperatures reported by Commercial Testing and Engineering are considered to be incorrect.

Fly ash resistivity is generally dominated by bulk particle resistivity at higher temperatures (e.g., 700°F) while surface resistivity effects become important at lower temperatures (e.g., 300°F). The intent of this resistivity testing was to determine whether a reduction in flue gas sulfuric acid concentrations during dolomite injection would adversely affect (raise) fly ash surface resistivity values. Sulfuric acid adsorption is known to lower fly ash surface resistivity in this temperature regime, and removal of sulfuric acid upstream of the air heater may negate this effect. While the measurements reported in Table 4-6, from upstream of the air heater, do not provide useful information about effects on surface resistivity, it is interesting to note that the bulk resistivity of the particles appeared to decrease with dolomite

Table 4-6. Fly Ash Resistivity Measurement Results

Date	Time	Flue Gas Temperature, °F	Resistivity, Ohm-cm	Dolomite Injection Rate, TPH
April 18, 2000	09:00-09:45	537	1.670 E 16	0
	10:00-10:45	539	1.601 E 16	0
	11:00-11:45	541	1.525 E 15	0
	12:00-12:45	544	1.570 E 15	0
	13:15-14:00	544	1.539 E 15	0
	14:15-15:00	545	1.495 E 15	0
	15:15-16:00	542	1.511 E 15	0
	16:15-17:00	540	0.155 E 12	14.9
	17:15-18:00	546	0.145 E 12	19.0
	18:15-19:00	553	0.148 E 12	22.8
April 19, 2000	09:00-09:45	553	0.138 E 12	0
	10:00-10:45	559	0.140 E 12	0
	11:00-11:45	559	0.135 E 12	13.7
	13:45-14:30	567	0.135 E 12	29.4
	14:45-15:30	565	0.326 E 12	24.1
	15:45-16:30	551	0.435 E 12	24.9
	16:45-17:30	550	0.331 E 11	24.6

injection. This is most likely because the magnesium oxide content of the dolomite has a lower
bulk resistivity than the normal fly ash.

It would be desirable to collect resistivity data at the air heater outlet during any future
dolomite injection tests conducted by BMP.

4.2.5 Economizer Ash Loss on Ignition Results

Two ash samples were obtained from the economizer hoppers, one from each side of the
unit (east and west), during each day of testing. Each sample was analyzed in duplicate for
apparent combustibles content using the LOI test method. The results of the LOI tests are
reported in Table 4-7. The LOI result is indicative of unburned combustible matter in the ash,
typically carbon, which is a source of energy loss.

With the injection of dolomite, which adds calcium and magnesium oxides to the ash, it
is possible that hydroxides could form as the ash cools in the presence of humid air. Hydroxides
in the ash could show up as LOI in the ash sample. However, this effect is expected to have been
minimal in the samples collected during this test, as the samples were sealed in plastic bags
shortly after they were removed from the economizer hoppers.

Table 4-7. Loss on Ignition Data

Date	Sample Identification	Initial Vessel + Sample (g)	Final Vessel + Sample (g)	Mass Lost (g)	Init. Ash LOI (%)	LOI Avg. (%)
4/18/00	4-18E	13.1926	13.1962	-0.0036	-0.2979	0
4/18/00	4-18E	11.8627	11.8641	-0.0014	-0.1397	
4/18/00	4-18W	13.1480	13.1441	0.0039	0.3798	0.37
4/18/00	4-18W	12.6095	12.6058	0.0037	0.3611	
4/19/00	4-19E	13.0966	13.0610	0.0356	3.4600	3.42
4/19/00	4-19E	12.3881	12.3513	0.0368	3.3824	
4/19/00	4-19W	12.0549	11.9707	0.0842	8.1361	8.14
4/19/00	4-19W	12.6092	12.5229	0.0863	8.1454	
4/20/00	4-20E	13.0504	13.0363	0.0141	1.3554	1.38
4/20/00	4-20E	12.8215	12.8076	0.0139	1.4015	
4/20/00	4-20W	12.5032	12.4730	0.0302	2.9760	2.97
4/20/00	4-20W	10.7327	10.7030	0.0297	2.9549	
4/21/00	4-21E	18.1721	18.1380	0.0341	3.3749	3.39
4/21/00	4-21E	17.8907	17.8476	0.0431	3.4009	
4/21/00	4-21W	16.7747	16.7059	0.0688	6.6972	6.67
4/21/00	4-21W	16.4713	16.4034	0.0679	6.6497	

During the test program, the only significant operating parameter that changed from day to day was the introduction of dolomite into the furnace. Dolomite or limestone injected into the furnace absorbs heat as it goes through the calcination process (an endothermic reaction). However, the relatively small quantity of dolomite injection into the furnace was not expected to significantly affect the quantity of unburned carbon. It is somewhat surprising, therefore, that the results in Table 4-7 show a considerable variation of LOI: from 0 to 3.4 wt% on the samples from the east side of the unit and 0.4 to 8.1 wt% on the west side of the unit.

The baseline samples collected on 4/18 showed very low LOI values of 0.0 to 0.4 wt%, on the east and west sides, respectively. These values are lower than would be expected for this unit in the operating mode during the baseline test. The higher values, ranging from 1.4 to 3.4 wt% on the east side and 3.0 to 8.1 wt% on the west side, were all collected during dolomite injection.

Boiler CO values were compared to see if they showed any indication of less complete combustion, and hence higher carbon content in the fly ash during dolomite injection. CO values averaged about 47 ppm during operation at about 750 MW on April 18, and about 24 ppm during operation at 750 MW on April 21 during dolomite injection. These are both relatively low CO concentrations, not typically associated with high LOI in the ash.

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It is also noted that the LOI results from the west-side samples were roughly double the magnitude of the east samples. It is not surprising to see side to side differences in fly ash LOI for various reasons. Most fossil fired steam generating units have side to side air and fuel flow imbalances that can result in one side of the unit having less excess air than the other, resulting in higher LOI on one side. It is also common for a single burner to be malfunctioning to the point where its air to fuel ratio or air-fuel mixing results in excessive unburned carbon. A single malfunctioning burner can result in excessive LOI results.

It is also possible that the anomalous results for the LOI analyses could be due to the quality of the samples. The economizer ash samples were grab samples collected from economizer hoppers. As such, there are no assurances that the small sample collected each time was representative of the bulk of the material collecting in the economizer during that period of operation.

4.2.6 Unit Performance, General Observations and Slag Formation Observations

Other than FGD impacts, which are discussed in the following section, there were no remarkable events with respect to unit operation that appeared to have been directly or indirectly related to injection of dolomite into the furnace. There were several occurrences of equipment failure but these events were not out of the ordinary and were not related to dolomite injection.

Observations of slag accumulations were made on a daily basis to assess if slag build-up on heat transfer surfaces was affected by dolomite injection. Observations were made primarily in the upper furnace where the partial-division-wall superheater and pendant superheater sections could be observed. Furnace slag accumulations were not the focus of attention because injection of dolomite was through the top elevation of burners and furnace observation ports are primarily located at or below that elevation. Soot blowing schedules and procedures were not altered from the normal during these tests. The soot blowers on this unit do not have a significant affect on the slag accumulation in the area observed. Prior to injection of dolomite, the upper furnace side walls, partial division walls and pendants had very little slag accumulations, with perhaps ½" to 1" of slag build-up. This amount of accumulation is fairly typical, although it is not uncommon to observe large local accumulations of slag, known as "clinkers", in this area of the unit. After three consecutive days of injecting dolomite, the slag accumulations on the side wall varied from 0" to 2" in thickness, accumulations on the partial division walls were between 1" and 2" and the pendant superheaters had between 2" and 4" of slag accumulation. There did not appear to be any bridging of flue gas flow passages; however, visibility in the upper furnace was limited by a

hazy appearance, presumably caused by injection of the dolomite (the visibility was not as limited when no dolomite was being injected).

Flue gas temperatures at the economizer exit and the air heater exit were examined to determine if solids buildup adversely affected heat transfer in the boiler and back pass. Adverse effects would be seen as temperature increases at these locations. Temperature increases were, in fact, seen over the course of the test. When compared at a gross unit load of approximately 760 MW, the average economizer outlet temperature increased from about 706°F to 731°F and the average air heater exit temperature increased from 314°F to 322°F, both over the time period April 18 through April 21. These temperature increases suggest that dolomite injection had an adverse effect on unit heat rate. It is difficult to quantify this effect from these short-term test results, though. The best way to quantify such an effect would be to track air heater exit temperature versus time of operation, starting with a clean air heater, for baseline operation versus extended operation with dolomite injection.

If dolomite injection does result in a measurable increase in air heater exit gas temperature, this could represent a substantial operating cost impact. EPRI heat rate documents show an industry average of 2.7 Btu/kW-hr-^{o}F increase in exit gas temperature (corrected to zero air inleakage). For a unit the size of Unit 2, an 8°F increase in air heater exit temperature would correspond with about $200,000 in fuel cost increase annually.

4.2.7 Scrubber Performance Results

Results from the analyses of a number of slurry samples collected before and during dolomite injection on Unit 2 are summarized in Tables 4-8 and 4-9. Table 4-8 summarizes slurry solid phase analyses, and Table 4-9 summarizes liquid phase analyses. Collection and analysis of these samples and review of the results proved to be very interesting, because it is a truly unique situation to have calcined dolomite added to a magnesium-enhanced, lime-based scrubber as a dry powder. Such a situation may have never been encountered before on a full-scale, coal-fired utility unit.

Special precautions had to be made in sampling the scrubber slurry. In normal FGD situations, whole slurries can be collected in a sealed bottle and the solid phase analyzed later, as so little material is present in the liquid phase that any dissolution or precipitation would not measurably affect the solid phase composition. However, in this situation, the possibility existed for oxides in the solid phase to hydrate over time. Therefore the solids were separated from the liquor in the slurry samples immediately after the samples were collected, and dried to halt any ongoing hydration reactions.

Table 4-8. Unit 2 FGD Slurry Solids Analyses

Description	2B	2C	UF	2B	2C	2E	UF
Date	18-Apr-00	18-Apr-00	18-Apr-00	21-Apr-00	21-Apr-00	21-Apr-00	21-Apr-00
Time	11:30	11:30	-	-	-	-	-
Ca, mmole/g	4.39	4.31	4.73	3.81	3.89	3.80	4.33
Mg, mmole/g	0.281	0.208	0.286	0.967	0.880	0.960	1.10
SO_3, mmole/g	3.53	3.52	3.95	3.09	2.97	2.84	3.04
SO_4, mmole/g	0.745	0.720	0.906	0.771	1.043	0.993	1.051
CO_3, mmole/g	0.338	0.311	0.321	0.156	0.103	0.145	0.326
Inerts, wt%	33.32	38.12	30.26	33.27	36.12	37.94	30.86
Solids, wt%	14.24	9.58	NR	NR	NR	NR	NR
pH	7.4	7.93	NR	NR	NR	NR	NR
Temp, ^{o}C	42.3	47.3	NR	NR	NR	NR	NR
Reagent Util, %							
Ca-Independent	92.7	93.2	93.8	96.1	97.5	96.4	92.6
SO_4- Independent	92.8	93.1	93.6	96.7	97.8	97.0	94.0
CO_3- Independent	91.4	93.7	96.9	80.8	84.3	80.6	75.5
Reagent ratio							
Ca- Independent	1.08	1.07	1.07	1.04	1.03	1.04	1.08
SO_4- Independent	1.08	1.07	1.07	1.03	1.02	1.03	1.06
CO_3- Independent	1.09	1.07	1.03	1.24	1.19	1.24	1.33
Oxidation, %	17.4	17.0	18.6	20.0	26.0	25.9	25.7
Solid solution, wt%	54.5	54.4	61.1	47.7	46.0	43.9	47.0
Gypsum, wt%	2.1	1.7	3.6	3.9	8.9	8.5	8.8
$CaCO_3$, wt%	3.4	3.1	3.2	1.6	1.0	1.5	3.3
Inerts, wt%	33.3	38.1	30.3	33.3	36.1	37.9	30.9

NR – Not reported.

Table 4-9. FGD Slurry Liquor Analyses

Description	2B	2B	2B-2	2B	2B	2E
Date	18-Apr-00	19-Apr-00	19-Apr-00	20-Apr-00	21-Apr-00	21-Apr-00
Time	11:30	16:00	17:30	12:15	10:30	12:30
Ca, mmole/L	2.52	3.25	1.64	2.11	2.17	6.07
Mg, mmole/L	172.95	257.4	287.0	269.1	324.8	195.1
Na, mmole/L	5.32	5.12	5.14	4.25	3.86	3.48
Cl, mmole/L	32.09	28.62	0.0	23.60	24.77	18.70
CO_3, mmole/L	2.42	1.44	0.0	1.32	2.75	1.96
SO_3, mmole/L	38.01	78.27	71.07	82.89	113.96	25.10
SO_4, mmole/L	114.03	185.38	192.96	186.31	213.23	167.38
pH	~7	~7	~7	~7	~7	~7
Temp, ^{o}C	~50	~50	~50	~50	~50	~50
Relative saturation						
Gypsum	0.12	-	-	-	0.09	-
$CaSO_3 \cdot$ ½ H_2O	3.69	-	-	-	4.63	-
$CaCO_3$	0.16	-	-	-	0.09	-

Based on the results summarized in Table 4-8, the calcium content of the dolomite appears to be highly utilized in the wet scrubber. The analytical results for April 21 suggest that about 96 to 97% of the CaO in the calcined dolomite slakes in the scrubber and replaces a portion of the normal slaked lime feed. This calculation is made by comparing the moles of calcium to the moles of sulfite, sulfate, and carbonate in the solid phase, and assuming that none of the latter are present in the solid phase as magnesium salts. Magnesium sulfate and sulfite are much more soluble than the corresponding calcium salts, and would be expected to have been in the liquid rather than the solid phase. At the dolomite injection rate the morning of April 21, 96 to 97% of the calcium in the dolomite would represent (and offset) about one-third of the normal scrubber lime makeup.

The magnesium content of the dolomite does not appear to be as highly utilized. About half of the magnesium appears to be passing through the scrubber as relatively unreactive MgO, which remains in the scrubber solids. This is seen as an increase in the magnesium content of the scrubber solids, but no corresponding increase in the amount of sulfite, sulfate, and/or carbonate in the solids beyond that which can be accounted for as calcium salts.

The other half of the magnesium in the dolomite appears to end up in the liquid phase in the scrubber. On module 2B, the liquid-phase magnesium concentrations doubled from baseline values over the time period April 18 through April 21; the baseline (April 18) magnesium concentration was about 4200 ppm, and the April 21 value was about 7900 ppm. The liquid phase magnesium increase also doubled the amount of sulfite and sulfate in the liquid phase, so this magnesium should also go towards offsetting lime consumption (i.e., more of the sulfur species removed were leaving the scrubber in the liquid phase). Based on an approximate material balance, 50% utilization of the magnesium in the dolomite injected should offset another 15 to 20% of the lime consumption at the dolomite injection rate of April 21 a.m. Thus, the calcium in the dolomite and half of the magnesium in the dolomite should offset a total of about half of the normal (no dolomite injection) lime flow to the scrubbers.

Note that the 15 to 20% offset by dissolving magnesium would likely diminish with time, as the FGD liquor will eventually become saturated with respect to magnesium sulfite, and limit the amount of dolomite magnesium that can dissolve in the scrubbers. It would take a longer test period to determine what this steady state magnesium dissolution level would be.

The dolomite that is not reactive in the scrubber seems to continue to react over the extended solids residence time in the thickener. This ongoing reaction is seen in measurements of the thickener influent pH, and of thickener overflow and underflow sample pH. The thickener

influent pH values were observed to increase within hours after dolomite injection began the afternoon of April 18. On April 17 and 18, prior to the onset of dolomite injection, the thickener influent pH ranged from 6.3 to 6.7. By 9:00 p.m. on April 18, this pH had increased to 7.2, and ranged from 7.2 to 7.9 over the next two days. During the period of low overnight load the morning of April 21, the thickener influent pH increased further to 8.2. Over this entire period, the pH values for individual scrubber slurries remained in the normal range of nominally 6.5 to 7.0. The higher pH of the thickener influent stream appears to indicate that magnesium oxide dissolution and hydration was occurring between the scrubbers and the thickener influent pH measurement point.

Samples of the thickener overflow and underflow streams showed even further pH increases over the residence time in the thickener. On April 21, the thickener overflow was at a considerably higher pH than either the FGD blow down or the thickener influent, at pH 8.70, and the underflow was even higher at 9.33. Fortunately, the thickener overflow pH was not high enough to precipitate magnesium sulfite, as the overflow solids content was quite low (0.002%).

Magnesium sulfite precipitation in the thickener overflow could be a potential problem in longer runs with dolomite injection. It will depend on the plant water balance (magnesium blowdown in liquor versus magnesium entering scrubber with dolomite and Thiosorbic$^®$ lime) as to whether the steady state magnesium levels will be high enough where magnesium sulfite precipitation becomes a problem.

Plant operators did report an apparent thickener operating problem during the dolomite injection period. The evening of April 19, after more than 24 hours of dolomite injection, thickener bed level measurements indicated that the bed height increased abruptly from about 6 ft to 9 ft. Over the morning of April 20, this level indication dropped to 7 to 8 ft, and by April 21 the level indication was down to about 5 to 6 ft. It is not be surprising that the thickener bed properties changed during dolomite injection, as the chemical composition of the scrubber blow down solids clearly changed. An abrupt change in bed height the evening of April 19 might have been a transient effect as the bed solids properties changed from normal operation to the new composition reflecting operation with dolomite injection. Similar transient effects have been seen in other FGD systems when scrubber blow down solids properties change, such as due to changes in sulfite oxidation percentage. Since the bed height was restored to normal values as dolomite injection continued, this is not considered to be a long-term issue for dolomite injection on Unit 2.

On first review of the scrubber solids data, the high magnesium levels appeared to have promoted higher sulfite oxidation percentages, which could also change solids settling properties. This apparent oxidation increase could have resulted because so much of the sulfur species remain in the liquid phase at these very high magnesium concentrations, where they can continue to undergo oxidation reactions. The baseline (April 18) samples showed 17 to 19% oxidation, and the April 21 samples showed 20 to 26% oxidation. All of these percent oxidation values are above the desired level of less than 15% oxidation, below which all of the sulfate formed by sulfite oxidation will co-precipitate as a "solid solution" with the normal calcium sulfite hemihydrate ($CaSO_3 \cdot \frac{1}{2}H_2O$) FGD byproduct. In most wet scrubber applications, as the sulfite oxidation increases above 15%, not all of the sulfate can be co-precipitated, and high gypsum relative saturations result in the FGD liquor. As the gypsum relative saturation levels increase, the likelihood of gypsum scaling increases dramatically. At approximately 20 to 25% oxidation, gypsum scale formation at some locations in the scrubbers is almost a certainty.

However, the corresponding liquid phase analyses, summarized in Table 4-9, do not show the expected high gypsum relative saturation values. In fact, the samples from both baseline operation (April 18) and at the end of dolomite injection (April 21) show low gypsum relative saturation values of about 0.1. This means that the FGD liquor would tend to dissolve gypsum rather that precipitate gypsum scale; precipitation requires FGD liquor relative saturation values above 1.0.

In reviewing both the solid and liquid phase results, we identified two technically feasible explanations for the low FGD liquor gypsum relative saturation values on April 21, while the apparent oxidation values are in the range of 20 to 26%. One, if the calcium oxide in the dolomite reacts with SO_2 in the flue gas to achieve approximately 10% SO_2 removal as the gas flows from the furnace to the FGD system, about 10% of the total sulfur "removed" in the scrubber will be in the form of anhydrite ($CaSO_4$) solids that are physically scrubbed in the venturi. The anhydrite would be relatively unreactive, not tending to dissolve or hydrate to form gypsum ($CaSO_4 \cdot 2H_2O$) in the scrubber.

Thus, the SO_2 removed from the gas phase in the scrubber could be oxidized at less than 15%, meaning that all of the sulfate formed in the scrubber would be coprecipitated with the calcium sulfite hemihydrate, and the gypsum relative saturation would be less than 1.0. The apparent oxidation would be in the range of 20 to 26% because of the anhydrite also present in the slurry, having been physically scrubbed from the flue gas as particulate matter.

Said another way, the scrubber bulk solids analyses indicate that the sulfite oxidation was in the range of 20 to 26%, which would lead us to believe the sulfur species in the slurry were present as "solid solution" (a mixture of calcium sulfite hemihydrate and calcium sulfate hemihydrate) and gypsum. If this were the case, the FGD liquor should be supersaturated with respect to gypsum, which the liquor analyses do not show. However, it is possible that the sulfur species were present as a mixture of solid solution and anhydrite that was formed by gas/solid reactions upstream of the scrubber. In this case, the scrubber liquor could be subsaturated with respect to gypsum, as the liquor analyses indicate.

A second possible explanation is seen in reviewing the unit load profile the day of the April 21 solid sample. The unit load dropped below 400 MW overnight, and had only been increased above 700 MW for a couple of hours when the slurry sample was collected. At low load, the furnace typically operates at higher excess air levels, raising the ratio of oxygen to SO_2 in the flue gas entering the scrubber. This, in turn, can raise the sulfite oxidation percentage in the scrubber. The actual economizer oxygen concentrations were about 4.2% overnight, at 3.0% the morning of April 21 after the boiler load was increased. While this is not a large change in excess air levels, it is possible that the scrubber solids sample was representative of overnight operation at a higher oxidation. It would take a number of hours to purge these solids from the scrubber, due to the solids residence time in the scrubber recycle loop. The gypsum relative saturation in the liquor would change rapidly with the load increase. Therefore it is possible that the solids were not representative of the liquor conditions at the time the samples were taken.

The latter scenario could also explain why the baseline liquor sample from April 18 appeared to be subsaturated with respect to gypsum in spite of the sulfite oxidation being in the range of 17 to 19%. On April 18, the overnight hourly-average economizer oxygen concentrations ranged between 3.8 and 4.2%. However, by the time the liquor sample was taken from module 2B, the economizer oxygen concentration had been lowered to an hourly average of 3.3%. Again, this is not a large change in excess air levels, but this change could help explain the presence of solids showing greater than 15% sulfite oxidation, yet a liquor that is subsaturated with respect to gypsum.

There is one other concern about gypsum scaling in the scrubbers during dolomite injection. That is the possibility of scale formation at the wet/dry interface in the scrubber, where the flue gas is first contacted with the recycle slurry. As excess calcium oxide in the calcined dolomite solids dissolves into the liquor to hydrate, it is possible that localized gypsum relative saturation values could increase above 1.0, potentially causing gypsum scale formation in this

portion of the scrubber. It may require scrubber inspection before and after an extended period of dolomite injection to determine whether or not this occurs.

4.3   Summary and Conclusions

A test was conducted with pulverized dolomite being injected into the furnace of Unit 2 at the Bruce Mansfield Plant to lower flue gas sulfuric acid (or SO_3 at higher flue gas temperature) concentrations. The unit typically operated at about 750 MW (gross) during the day, with lower loads overnight. Dolomite was injected almost continuously over a period of 93 hours (there was one interruption of almost 2 hours early in the injection period).

The dolomite was injected in place of coal through the top row of burners on the front wall of the boiler. The injection rate was approximately 8 to 9% of the coal feed rate to the unit. The coal fired had an average sulfur content of 4.1 wt%. The resulting flue gas prior to dolomite injection had an SO_3 concentration that averaged 52 ppm as measured by the Controlled Condensation method at the east economizer outlet location. This corresponds with approximately 1.6 to 1.7% of the SO_2 in the flue gas being oxidized to SO_3. The molar ratio of alkalinity in the dolomite (calcium plus magnesium) to sulfur in the coal fired averaged 0.6:1 to 0.7:1. The molar ratio of alkalinity in the dolomite injected to SO_3 in the baseline flue gas was about 40:1.

The dolomite was effective in greatly reducing flue gas SO_3 concentrations. Over the last two days of the test, the SO_3 concentrations at the economizer outlet showed an average of 7 ppm, or an 86% reduction from the baseline concentration average of 52 ppm. As mentioned above, this was at an average molar ratio of total alkalinity in the dolomite (calcium plus magnesium) to sulfur in the coal of 0.6:1 to 0.7:1.

During the test, the dolomite injection rate was varied in an attempt to determine SO_3 removal as a function of dolomite rate. In general, the injection rate changes were too rapid to ensure that representative SO_3 removal performance was measured at each rate. However, during two periods where the injection rate was held at a value long enough to perhaps measure representative performance, SO_3 removal was quite sensitive to dolomite injection rate. At a molar ratio of dolomite alkalinity (calcium plus magnesium) to coal sulfur of 0.57:1, the apparent SO_3 removal was 74%, while at a molar ratio of 0.68:1, the apparent removal improved to 95%.

Dolomite injection had little effect on the concentrations of two other acid gases in the flue gas. No removal of HCl or HF from the flue gas was measured. Some removal of chlorine

and fluorine from the flue gas was observed, but the uncontrolled concentrations of these gases were already quite low (less than 1 ppm).

There was a concern about the effects of dolomite injection on the performance of cold-side (downstream of the air heater) electrostatic precipitators (ESPs) used for particulate control. Adverse effects are possible due to the increased particulate loading and potentially lower ash resistivity during dolomite injection. Unit 2 does not have an ESP; it has wet scrubbers for combined SO_2 and particulate control. Although Unit 2 does not have an ESP for particulate control, ash resistivity measurements were made to determine the effects of dolomite injection on this parameter. Due to a miscommunication between sampling team members, the ash resistivity measurements were made at the economizer outlet rather than at the air heater outlet on Unit 2. The latter better represents the flue gas temperature at cold-side ESP conditions. Because fly ash resistivity is strongly a function of flue gas temperature, the measurements made at the economizer outlet do not provide useful information about potential effects of dolomite injection on ESP performance. Thus no conclusions can be made about potential effects of dolomite injection on a cold-side ESP.

LOI measurements of fly ash samples collected from the economizer outlet location indicated that LOI values increased from less than 1% under baseline operation to as high as 8% during dolomite injection. LOI measurements were conducted to provide an indication of unburned carbon in the fly ash, which is a measure of the boiler combustion efficiency. It would be expected that significant increases in fly ash LOI would correspond with higher boiler flue gas CO concentrations; however, this was not the case. Although the LOI results suggest an adverse effect of dolomite injection on unburned carbon concentrations, there is some question as to how representative of current operating conditions each of the economizer ash grab samples might have been. No firm conclusions can yet be made about the effects of dolomite injection on coal combustion efficiency as determined by LOI content in the fly ash.

Another concern about dolomite injection in the furnace was the potential for increased slagging in the upper furnace. Prior to injection of dolomite, the upper furnace side walls, partial division walls and pendants had very little slag accumulations, with ½" to 1" of slag build-up. After nearly four consecutive days of injecting dolomite, the slag accumulations on the side wall varied from 0" to 2" in thickness, accumulations on the partial division walls were between 1" and 2" and the pendant superheaters had between 2" and 4" of slag accumulation. There did not appear to be any bridging of flue gas flow passages. Dolomite injection did appear to have an adverse effect on unit heat rate, as the average air heater exit temperature at a load of 760 gross MW was observed to increase by 8°F over the duration of the test.

Because Unit 2 does not have an ESP for particulate control, the entrained, partially utilized dolomite was removed from the flue gas as particulate matter in the wet-lime FGD scrubbers. Chemical analyses of the scrubber solids indicate that virtually all of the calcium content of the dolomite and about half of the magnesium content was used to react with SO_2 removed in the scrubbers. Between the two components, nearly half of the normal FGD system lime slurry makeup should have been offset (replaced) by the injected dolomite. The contribution from the magnesium content was due to magnesium dissolving into the liquid phase of the scrubber slurry. With time, FGD liquor magnesium concentrations would tend to increase due to cycling up of the magnesium dissolving from the dolomite. Solubility limits may begin to reduce the amount of magnesium in the dolomite utilized in the scrubber.

There were concerns about two potential adverse effects of injected dolomite on the FGD system. One is that magnesium oxide not utilized in the scrubber would continue to hydrate and dissolve in the thickener, to the point where magnesium sulfite might precipitate in the thickener. Although the pH of the thickener underflow and overflow did increase above the scrubber pH set points, indicating further magnesium oxide hydration there, no magnesium sulfite precipitation was observed. This may become an issue as the liquor magnesium concentration cycles up.

The other concern was about the potential for gypsum scaling in the scrubbers. Analyses of the recycle liquor did not indicate an increase in gypsum scaling potential during dolomite injection. However, it remains possible for scaling at localized areas of the scrubber, such as around the wet/dry interface.

Overall, dolomite injection into the furnace appears to be an effective approach for lowering flue gas sulfuric acid concentrations by up to 95%, particularly on Unit 2 (or Unit 1) where the dolomite injected actually offsets the consumption of more expensive lime reagent in the FGD system. As described above, though, there are a few technical uncertainties that require additional testing to resolve.

Although furnace injection of dolomite shows promise as a sulfuric acid control technology for Units 1 and 2, we recommend that BMP conduct at least one additional, longer-term dolomite injection test on one of these units. If possible, the test should be several weeks or longer in duration. The objectives of this test would be to:

- Provide an opportunity to measure SO_3 removal as a function of dolomite injection rate, with longer periods of operation at each rate (one to two days each rate) so as to ensure steady state SO_3 removal performance at that rate.

- Provide more information about the effects of dolomite injection on combustion efficiency and fly ash LOI.

- Allow an extended period to observe the effects of dolomite injection on slagging and fouling in the furnace and back pass of the boiler, and on air heater performance, to determine whether the buildup seen in this 93-hour test represents a steady-state condition or whether the buildup would continue to grow with time.

- Allow longer-term effects of dolomite injection on the FGD system to be evaluated, such as evaluating steady-state magnesium ion concentrations in the FGD liquor, determining whether magnesium sulfite precipitation in the thickener will become a problem, and determining effects of gypsum scale formation in the scrubbers. For the latter, we recommend trying to inspect one or more scrubber modules immediately before and after the dolomite test to try to quantify scale buildup.

Such a longer-term test would also provide the DOE project with an opportunity to measure the effects of dolomite injection on fly ash resistivity at air heater outlet temperatures.

We also recommend that in future tests, BMP try varying the dolomite injection rate with boiler load and coal sulfur variations. It may be possible to maintain low SO_3 concentrations in the flue gas by lowering the dolomite injection rate in proportion with overnight load reductions and/or at lower coal sulfur contents.