SOXAL™ PILOT PLANT DEMONSTRATION AT NIAGARA MOHAWK'S DUNKIRK STATION

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INTRODUCTION

The Clean Air Act Amendments of 1990 made it necessary to accelerate the development of scrubber systems for use by some utilities burning sulfur-containing fuels, primarily coal. While many types of Flue Gas Desulfurization (FGD) systems operate based on lime and limestone scrubbing, these systems have drawbacks when considered for incorporation into long-term emissions control plans. Although the costs associated with disposal of large amounts of scrubber sludge may be manageable today, the trend is toward increased disposal costs. Many new SO_2 control technologies are being pursued in the hope of developing an economical regenerable FGD system that recovers the SO_2 as a saleable commercial product, thus minimizing the formation of disposal waste. Some new technologies include the use of exotic chemical absorbents which are alien to the utility industry and utilities' waste treatment facilities. These systems present utilities with new environmental issues. The SOXAL™ process has been developed so as to eliminate such issues.

The objective of the nominal 3 MW SOXAL pilot plant at Niagara Mohawk's Dunkirk Power Station was to demonstrate the technical and economic feasibility of this regenerative FGD process to remove SO_2 from the flue gas of a coal-fired boiler. The key demonstration component was the integration of a bipolar membrane system with proven sodium scrubbing and steam stripping technologies. Previously, bipolar membrane systems had been commercially proven in applications unrelated to flue gas desulfurization.

Sodium alkali scrubbing of the type used in the SOXAL process is an accepted and proven method for removing SO_2 from gaseous streams. It is the system of choice in many industrial applications due to its lower capital requirements, higher SO_2 removal efficiencies, and low maintenance costs. A large number of sodium scrubbers have been operated successfully at industrial and utility sites. The main drawback of such systems is the higher cost of the sodium scrubbing solution versus the reagents required for calcium-based systems. The SOXAL process minimizes the cost of sodium scrubbing by regenerating the scrubbing solution for reuse while simultaneously recovering the sulfur as a saleable product.

PROCESS DESCRIPTION

The SOXAL FGD process has four major unit operations which are illustrated schematically in Figure 1:

1. The prescrubber removes chlorides, fluorides and residual particulates by water scrubbing.
2. The sodium sulfite scrubber removes the SO_2 from the flue gas.
3. The bipolar membrane cell stack regenerates the spent sodium bisulfite solution.
4. The steam stripper removes the SO_2 from the sulfurous acid.

The primary reactions in the sodium sulfite (Na_2SO_3) scrubber are as follows: SO_2 removal is accomplished by the reaction of the SO_2 with Na_2SO_3 in the scrubbing solution to form sodium bisulfite ($NaHSO_3$). In addition, a portion of the Na_2SO_3 in the scrubbing solution is oxidized to sodium sulfate (Na_2SO_4) by reaction with oxygen (O_2) in the flue gas stream. The Na_2SO_4 can be recovered in a saleable crystalline form. Regeneration of the spent scrubbing solution is achieved in the primary bipolar regeneration unit which is shown schematically in Figure 2. Each cell has a bipolar membrane and a cation selective membrane. The bipolar membranes separate the water molecules into hydrogen (H^+) and hydroxyl (OH^-) ions, and $NaHSO_3$ is converted to Na_2SO_3. In addition, sodium ions (Na^{++}) migrate across the cation selective membrane into the base compartment. These become associated with OH^- ions and form NaOH. Most of this NaOH reacts with $NaHSO_3$ to form Na_2SO_3 for recycle to the scrubber. The HSO_3^- anions that remain in the acid compartment associate with H^+ ions from the bipolar membrane to form sulfurous acid (H_2SO_3). The partially saturated H_2SO_3 stream is continuously withdrawn from the cell stack and is subsequently decomposed into SO_2 gas and water molecules in the steam stripper.

PILOT PLANT FACILITIES

The 3 MW SOXAL pilot plant demonstration facility was installed at Niagara Mohawk's Dunkirk Power Station on Lake Erie near Buffalo, NY. This station has two (2) 100 MW and two (2) 200 MW tangential coal-fired boilers. The slip-stream of the flue gas for the 3 MW pilot plant was extracted after the induced draft fan of Unit No. 4. During the demonstration, this boiler was fired with bituminous coal from Pennsylvania and West Virginia which had an average sulfur content of 2.1%, ash content of 7.1%, and heating value of 13,100 Btu per pound. The 3 MW SOXAL pilot plant was located adjacent to Unit No. 4 to minimize the amount of ductwork required to provide the slip-stream of flue gas to the scrubber and to return the processed flue gas back to the station stack. In addition, most of the utilities required for the pilot plant were available with minimal interconnect distances between the station and the pilot plant.

Both the prescrubber and scrubber were designed and supplied by Advanced Air Technology. The water-based prescrubber measured 4.5 feet in diameter by 25 feet in height. It had a Hastelloy quench section, an FRP shell, a six-foot bed of polypropolyene packing, and an FRP mist eliminator. The sodium-sulfite-based scrubber measured 4.5 feet in diameter by 40 feet in height. It had two, six-foot high polypropylene-packed stages. Operation of these units was easy and reliable. No fouling was observed. Considerable particulate matter was removed by the prescrubber, and there was no significant carryover from the prescrubber to the scrubber.

The bipolar membrane cell stack used during the demonstration had 44 two-membrane cells. Each cell included a single bipolar membrane and a cation membrane. Only 176 square feet of cell area was required at the pilot plant, and standard commercial bipolar membranes were used. A DC rectifier provided the energy required to regenerate the absorbent solution. The initial cell stack was operated for over three months with no hardware problems. While some individual membranes occasionally had to be replaced, the overall performance of the stack was well within expectations. At no time was testing delayed due to membrane failures.

The pilot plant steam stripper column measured 16 inches in diameter by 21.5 feet in height. It had a stainless steel shell and contained a six-foot bed or random Kynar packing. A small bed of this same packing material was used as the mist eliminator. Early in the test program, instrumentation failures gave the erroneous impression of low stripping efficiency. However, once these problems were identified and corrected, the steam stripper column operated as designed.

Although some problems were encountered relative to pumps, flow meters, weld leaks, etc., most of these were corrected prior to the main demonstration program. As a result of failure of the continuous SO_2 gas analyzer to operate properly, it was necessary to use an outside testing service during the last four months of the test period in order to obtain accurate and continuous SO_2 measurements. In general, most of the instrumentation installed was reliable and performed up to expectations after initial start-up. The operators found the pilot plant facility to be easy to operate with minimal staffing. Two engineers and four operators manned all shifts, including the 7 days per week, 24 hours per day periods of continuous testing.

TEST DESCRIPTION

The 3 MW SOXAL pilot plant test program took place over a seven-month period and included both continuous operation and parametric tests. Failure of the continuous SO_2 analyzer severely limited the amount of quantitative SO_2 data collected during the first two months of testing. During this time, it was possible to demonstrate continuous operation of the bipolar membrane cell stack in integrated operation with the scrubber and stream stripper systems. The overall process was kept in balance while producing regenerated scrubbing solution and concentrated SO_2.

Immediately after a previously scheduled one-month boiler outage, parametric testing was initiated in accordance with the following test plan:

Test	Objective
• Initial Baseline Studies	Establish Baseline
• Absorber Parametric Studies	
- Lower Stage pH	Maximize Absorption
- Recycle Rate	Maximize Absorption
- Number of Beds	Minimize Oxidization
- SO_2 Concentration	Minimize Oxidization/Maximize Absorption
• Cell Stack Parametric Studies	
- Base pH	Reduce Flush Cycle
- Recycle Rate	Reduce Cost and Flush Cycle
- Cell Stack Current	Reduce Power Consumption
- Conversion Rate	Reduce Power Consumption
- Cell Stack Temperature	Reduce Power Consumption
• Stripper Temperature Studies	Optimize Efficiency
• Overall Optimized Operation	Maximize Absorption/SO_2 Removal

During the four months of parametric testing, the Dunkirk boiler was operated at a reduced load overnight and was shut down on weekends due to a lack of power demand. As a result, parametric testing was carried out on a "decoupled" basis, five days per week. In other words, when studies were conducted on the absorber, the cell stack unit was shut down, and vice versa. The pilot plant was operated from full storage tanks of either spent or regenerated absorbent. The portion of the process not undergoing testing at any given time was operated overnight to replenish the spent or regenerated absorbent inventory for the next day's testing. The parametric studies were not felt to have been significantly affected by the unanticipated boiler cycling and shutdowns.

TEST RESULTS

The data collected during the demonstration period is summarized in Table 1. During the first two months of testing, the pilot plant was operated continuously. During the last four months of parametric testing after the boiler outage, the pilot plant consistently demonstrated over 98 percent SO_2 absorption as is shown in Figure 3. During this same period, the SO_2 concentration in the flue gas ranged between 1000 and 1500 ppm as is shown in Figure 4. It appears that the same high level of SO_2 absorption was probably achieved during the initial two-month continuous run when the SO_2 analyzer was not operational. The test results also show that when higher inlet SO_2 levels were obtained by recycling some of the recovered SO_2 to the scrubber, SO_2 absorption was enhanced and oxidation of the scrubber solution was reduced. Oxidation of the scrubber solution is an important parameter in the economics of the SOXAL process. Test results showed that total oxidation during SO_2 absorption was well within the design range even without the use of additives or any other attempt to minimize oxidation.

The major parameters associated with the operation of the bipolar membrane cell stack are its power consumption and durability. During the demonstration period, power consumption by the cell stack was consistently in the range of 1100 to 1300 kWh/ton of SO_2 removed as is shown in Figure 5. This is consistent with anticipated power consumption and the value that was used in EPRI's 1990 economic evaluation of the process. During over 2,500 hours of pilot plant operation, the bipolar membranes proved to be extremely durable. An acid wash process was used to minimize fouling of the membranes during the demonstration period, and the optimum operating conditions needed to minimize membrane washing were determined.

CONCLUSIONS

1. Continuous integrated operation of the absorption and regeneration portions of the pilot plant was demonstrated.
2. The ease of independently operating these portions of the SOXAL system was also demonstrated.
3. Over 98 percent SO_2 removal was consistently achieved.
4. Stable bipolar membrane performance was proven.
5. Cell stack power consumption and scrubber oxidation were consistent with plant design expectations.

ACKNOWLEDGMENTS

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Table 1

Summary of Test Data[1]

Test Code	Test Description	SO_2 Concentration (ppm)	Flue Gas Flow Rate (DSCFM)	SO_2 Absorption (%)	Power Consumed (kWh/ton SO_2)
A	Simultaneous[2] Baseline	916	7,992[3]	98.8	
A	Simultaneous[2] Baseline	1,202		99.3	
A/H1	Simultaneous[2] with 1.25x Feed-to-Base	1,062	5,205	96.3	
A/H2	Simultaneous[2] with 1.5x Feed-to-Base	1,149	7,562[3]	98.9	
A/H2	Simultaneous[2] with 1.5x Feed-to-Base	1,189	7,366[3]	97.2	
B	Absorber Baseline	1,385	5,609	98.7	
B	Absorber Baseline	1,365	5,201	98.8	
B	Absorber Baseline	1,316	5,709	98.4	
C	Cell Stack Baseline				1,122
C	Cell Stack Baseline				1,251
C	Cell Stack Baseline				1,082
D1	Absorber Bottoms at 5:1 Ratio Bisulfite: Sulfite	1,361	5,309	99.6	
D1	Absorber Bottoms at 5:1 Ratio Bisulfite: Sulfite	1,278	5,175	98.9	
D1	Absorber Bottoms at 5:1 Ratio Bisulfite: Sulfite	1,182	5,402	97.7	
D2	Absorber Bottoms at 1:1 Ratio Bisulfite: Sulfite	1,086	5,744	100.0	
E2	Absorber Recycle at 60 gpm	1,146	5,880	97.9	
E3	Absorber Recycle at 45 gpm	1,123	5,771	95.9	
F1	Absorber with One Stage	1,211	5,865	82.7	
G	Absorber with Recycled SO_2	2,141	5,407	99.6	
G	Absorber with Recycled SO_2	2,167	5,394	100.0	
G2	Absorber with Recycled SO_2, 5:1 Ratio Bisulfite: Sulfite	2,228	5,377	99.4	
H2	Cell Stack with 1.25x Feed-to-Base				1,131
I1	Cell Stack at 80 ASF[4]				1,049
I2	Cell Stack at 125 ASF[4]				1,331
J1	Cell Stack at 80% Acid Conversion				1,334
J2	Cell Stack at 120% Acid Conversion				1,292
P	Simultaneous[2] with Recycled SO_2	2,013	4,917	99.6	1,204
P	Simultaneous[2] with Recycled SO_2	2,015	5,108	99.8	1,229
P	Simultaneous[2] with Recycled SO_2	2,155	5,053	99.8	1,238
P	Simultaneous[2] with Recycled SO_2	2,047	5,036	100.0	1,199

Table 1 (Continued)

Test Code	Test Description	SO_2 Concentration (ppm)	Flue Gas Flow Rate (DSCFM)	SO_2 Absorption (%)	Power Consumed (kWh/ton SO_2)
P	Simultaneous[2] with Recycled SO_2	1,865	5,264	99.9	1,215
P1	Simultaneous[2] with Recycled SO_2 at 125 ASF[4]	1,934	4,905	99.7	1,427
P1	Simultaneous[2] with Recycled SO_2 at 112 ASF[4]	2,042	5,268	99.9	1,370
P1	Simultaneous[2] with Recycled SO_2 at 112 ASF[4]	2,023	4,019	99.8	1,242
P1	Simultaneous[2] with Recycled SO_2 at 112 ASF[4]	1,969	5,092	99.9	1,260
U1	Absorber Recycle at 45 gpm; 5:1 Ratio Bisulfite: Sulfite	1,069	5,398	93.6	
U2	Absorber Recycle at 75 gpm; 5:1 Ratio Bisulfite: Sulfite	1,097	5,376	94.3	
V	Cell Stack with 5:1 Ratio Bisulfite: Sulfite Feed				1,152

Notes:

1. Each data point typically represents the average of four measurements taken during an eight-hour test.
2. Simultaneous indicates continuous operation of both absorption and regeneration processes. All other tests were conducted in a "decoupled" mode.
3. These flow rates are in ACFM (actual cubic feet per minute). All others are in DSCFM (standard cubic feet per minute - dry basis).
4. Baseline regeneration tests were performed with 400 amps of operating current. Since the membranes had four square feet of cross-sectional area, this is equivalent to 100 ASF (amps per square foot).

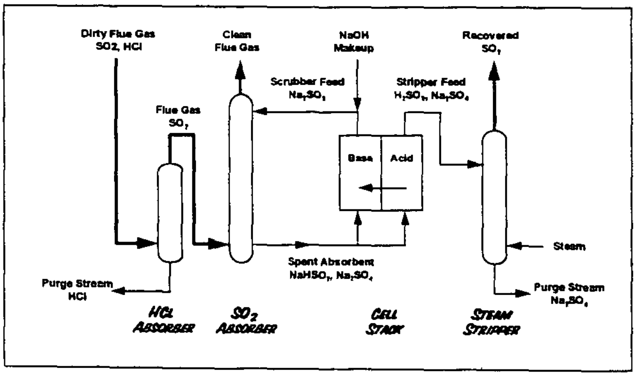

Figure 1
SOXAL Process Flow Sheet

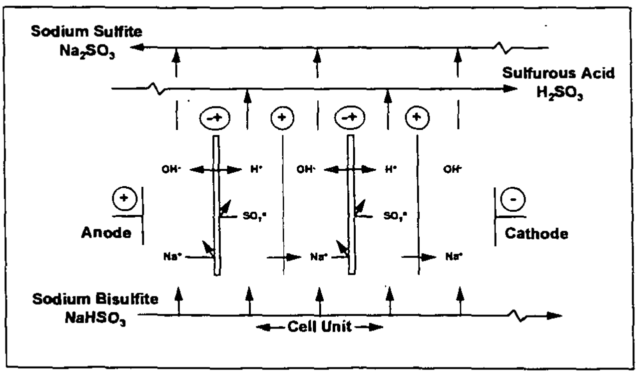

Figure 2
Schematic of Bipolar Membrane Regeneration Unit

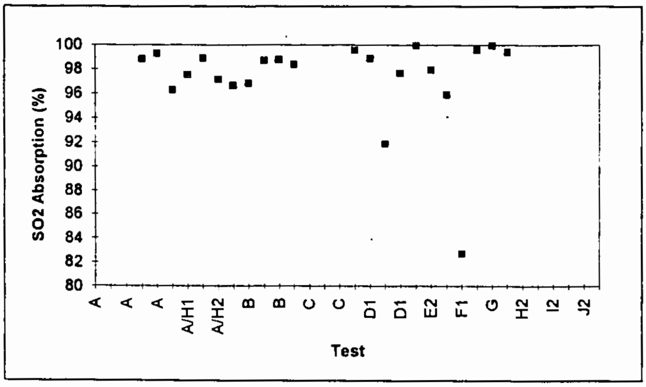

Figure 3
SO_2 Absorption Efficiency

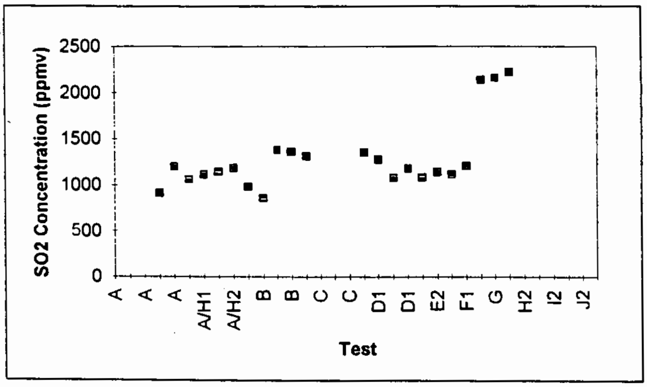

Figure 4
Inlet SO_2 Concentration

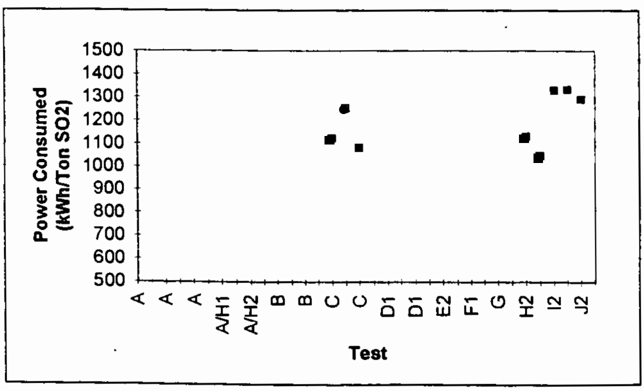

Figure 5
Cell Stack Power Consumption