



Project Summary

Evaluation of the Limestone Dual Alkali Prototype System at Plant Scholz: Final Report

J. A. Valencia, J. F. Peirson, Jr., and G. J. Ramans

The limestone dual alkali process, developed by Thyssen-CEA Environmental Systems, Inc. (until late 1980 under Combustion Equipment Associates, Inc. ownership) and Arthur D. Little, Inc., was tested at an existing 20 MW prototype facility at Gulf Power Company's Scholz Steam Plant. The intent of the project was to evaluate the technical feasibility of the process at a prototype scale and to develop sufficient technical information leading to the implementation of the process at a full commercial scale.

Due to budgetary considerations, the testing period was reduced from 6 to 2 months. The report gives results obtained during the 2 months of testing—February and March 1981. Excellent SO₂ removal efficiencies in excess of 95 percent were achieved; limestone utilizations were also high, over 97 percent. The solids properties ranged from excellent to poor. The generation of poor solids was the most significant process problem. The solids content in the filter cake was typically 35-45 percent, which was below the anticipated 55 percent. The soda ash consumption of 0.29 moles of Na₂CO₃/mole of SO₂ removed far exceeded the design consumption of 0.04 moles of Na₂CO₃/mole of SO₂. Much of this consumption was due to leaks and other liquor losses in the system. The mechanical performance

of the equipment, recommissioned after 3 years of inactivity, was poor and contributed to the above problems.

Although the technology appears to be technically feasible, further testing is necessary before a conclusive evaluation is made; some refinement of the process is still needed.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of this test program was to evaluate the performance, at a prototype scale, of the limestone dual alkali process developed by Thyssen-CEA Environmental Systems, Inc. (TESI) (initially Combustion Equipment Associates, Inc. (CEA)) and Arthur D. Little, Inc. (ADL). The overall intent of this project, however, was not only to demonstrate the technical feasibility of the process at a prototype level but to supply technical and cost information related to the implementation of the process at a full commercial scale.

The test program was conducted at an existing dual alkali facility at Gulf Power Company's (GPC) Scholz Steam Plant

near Sneads, FL. The 20 MW lime-based dual alkali system was modified for operation with limestone. Following its conversion, the system underwent an evaluation of its performance with regard to:

- SO₂ removal capabilities.
- Raw materials and energy requirements.
- Quality of waste material generated.
- Reliability and ease of operation of the system.

Originally, the formal testing period of the system was to last 6 months; this period was, however, reduced to 2 months due to budgetary considerations.

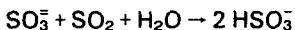
Parallel to this EPA program, the Electric Power Research Institute (EPRI) sponsored a program to study and evaluate the landfill disposal of the waste cake generated by the limestone dual alkali system.

The Scholz Prototype System

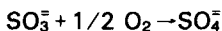
Limestone Dual Alkali Technology

The limestone dual alkali technology is based on the absorption of SO₂ in an alkaline sodium solution, followed by regeneration of the absorbing solution by reaction with a second alkali, calcium. These reactions generate insoluble calcium-sulfur salts which are discharged from the system as a moist cake.

SO₂ is absorbed by contacting flue gas with a sodium sulfite/bisulfite solution. The sulfite reacts with the SO₂ producing additional bisulfite according to the following overall reaction:



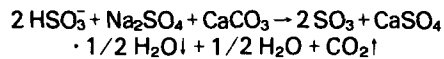
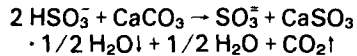
During absorption, and to a lesser extent throughout the remainder of the process, some sulfite is oxidized to sulfate:



The level of oxidation during absorption is generally a function of the scrubber configuration, oxygen content of the flue gas, and the scrubber operating temperature. At excess oxygen concentrations normally encountered in utility power plant operations, the level of oxidation is expected to be 5-10 percent of the SO₂ removed (for medium and high sulfur coal applications).

The spent scrubbing solution is reacted with limestone to regenerate the absorbent. The reaction precipitates

mixed calcium sulfite and sulfate solids, resulting in a slurry containing up to 5 wt. percent insoluble solids. The regeneration process involves basically the following overall reactions:



Following regeneration, the insoluble calcium-sulfur salts are separated from the regenerated liquor. After settling in a thickener, the insoluble salts are vacuum-filtered before being discharged as a moist cake. The clarified liquor from the thickener is returned to the scrubber, closing the process liquor loop.

The filter cake is washed to recover most of the soluble sodium salts in the mother liquor. A small portion of the sodium salts, however, remains occluded in the cake and is lost. Thus, some sodium carbonate must be added to the system to make up for these sodium losses. Typically, the Na₂CO₃ makeup should amount to less than 5 mole percent of the SO₂ removed.

The amount of limestone added to the system for absorbent regeneration is reduced slightly due to the soda ash makeup. Under normal conditions, the limestone feed stoichiometry will be slightly less than 1.0 mole of CaCO₃/mole of SO₂ removed.

Description of the Scholz System

The dual alkali system took flue gas from the Scholz Steam Plant Unit No. 1, a 40 MW nominal capacity (47 MW peak capacity) Babcock and Wilcox pulverized-coal-fired power boiler. The flue gas from the boiler passed through a high efficiency, sectionalized electrostatic precipitator (ESP) designed to remove up to 99.5 percent of the particulate matter. Part of the gas discharged from the ESP was directed to the limestone dual alkali system, which was designed to handle flue gas flow rate equivalent to a 20 MW boiler load. The remaining gas was sent directly to the stack.

The limestone dual alkali system at Scholz was a modification of a lime dual alkali system previously installed and operated during 1975 and 1976 for a test program sponsored by Southern Company and jointly funded with EPA. The modified dual alkali system consisted of four sections: absorption,

regeneration, waste solids dewatering and raw materials storage and feed preparation. A process flow diagram for the dual alkali system for Scholz is shown in Figure 1.

The absorption system consisted of venturi scrubber, followed by an absorption tower. An SO₂ injection system was provided to increase, when necessary, the SO₂ concentration in the flue gas entering the dual alkali system by 20 ppm or more.

The variable throat, plumb-bob type venturi scrubber was designed for particulate removal and/or SO₂ absorption. Typically, a dual alkali system taking flue gas from a particulate removal device (e.g., ESP) would not require a venturi scrubber. Such being the case at Scholz, the system in fact did not require the venturi scrubber. Rather than remove it, the venturi scrubber was used primarily for quenching and saturating the flue gas; these operations, which also contribute to the SO₂ removal, would normally be performed in the absorption tower. A booster fan directed the SO₂-rich flue gas exiting the ESP into the scrubber, where it contacted scrubbing liquor flowing at an L/G of 15-20 gal./10⁶ acf.* The liquor was collected at the bottom of the scrubber in an internal recycle tank.

After being quenched and saturated with water, the partially desulfurized gas entered the bottom of the absorption tower. Gas passed upward through two trays and then through a de-entrainment separator. A spray under the bottom tray was used to wet the underside of the tray. The de-entrainment separator was operated dry, without mist eliminator wash water. The scrubbing solution, which was fed to the top tray of the absorber at an L/G of 2-3 gal./10⁶ acf, flowed countercurrent to the gas through the tray system. This counterflow permitted high SO₂ transfer from gas to liquid phase. The liquor was collected at the bottom of the absorber in the internal recycle tank, which served as the supply for the liquor spray under the bottom tray.

A bleed from the absorber liquor recycle line was sent forward to the scrubber recirculation loop where it was used to quench the gas and provide additional SO₂ removal. A bleed stream of spent liquor was drawn from the scrubber recycle line and fed to the absorbent regeneration system.

(*) To convert from British to metric units: multiply gal by 3.79 to yield liters, and multiply cf (ft³) by 0.028 to yield m³.

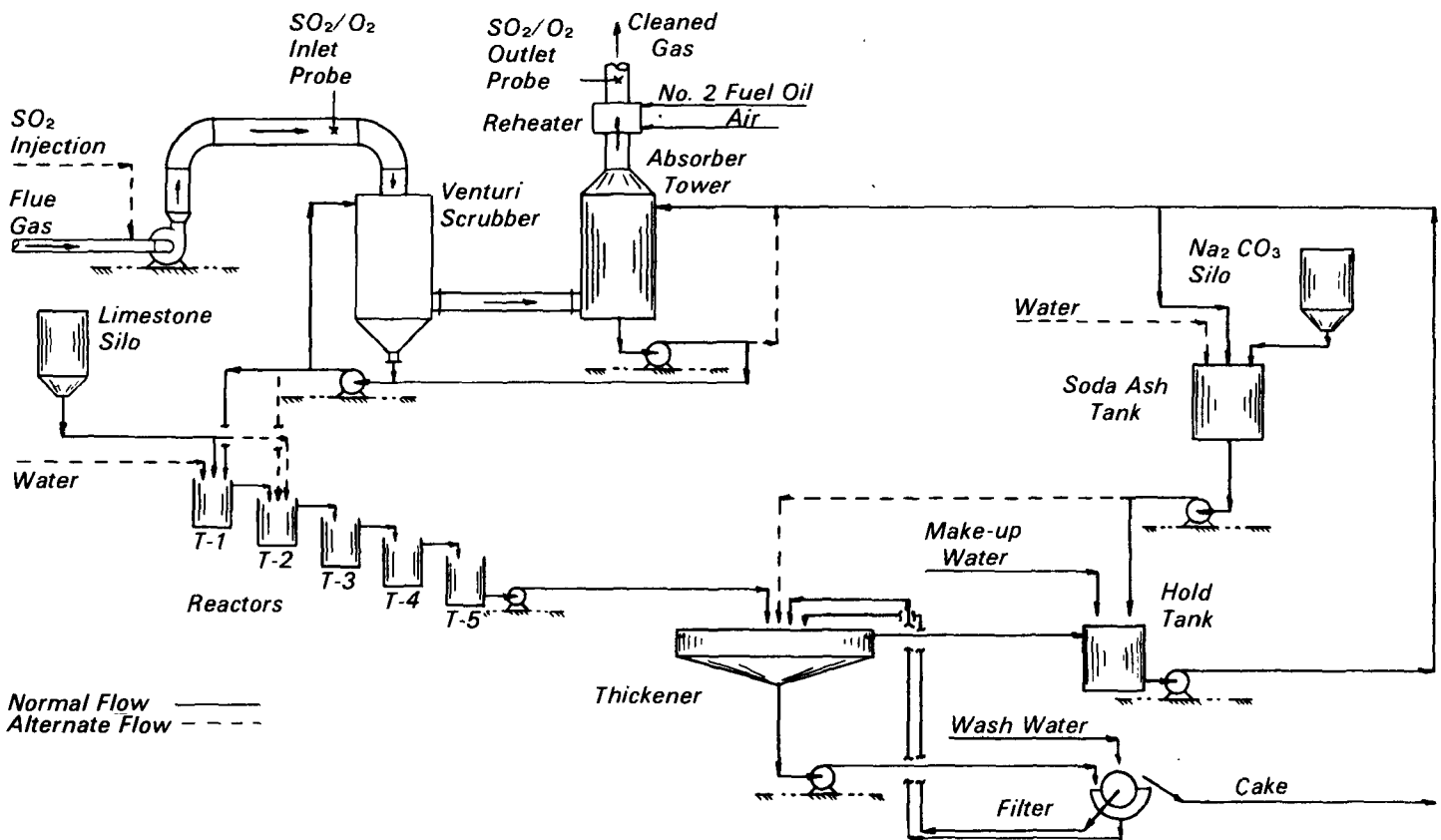


Figure 1. Limestone dual alkali system at Scholz - process flow diagram.

The regeneration system consisted of five separate reactors in series with a total design holdup time of approximately 100 minutes. It was designed to provide the capability of operation in various configurations. The bleed from the scrubber system was piped such that it could be fed either to the first or second stage reactor. Similarly, the limestone silo feed chute could feed dry limestone to either of these two tanks. Thus, the modified reactor system was capable of being operated as either four or five reactor tanks in series with dry limestone feed, or as four reactor tanks in series with slurried limestone feed prepared in the first stage reactor. Furthermore, the three intermediate reactors had overflows at two levels to provide the flexibility of varying the holdup time. Due to the shortened testing period, however, the regeneration system was operated in only one mode: five reactors in series with dry limestone feed to the first reactor. The first four reactors operated on overflow (high overflow for the three intermediate reactors), while the last reactor was on

level control so that the effluent could be pumped to the thickener.

Clear liquor overflow from the thickener was collected in the thickener hold tank which acted as surge capacity for the absorbent liquor feed to the scrubber system. Process make-up water was added to this tank to make up for the total water loss due to evaporation in the system and moisture in the cake:

The thickened slurry was fed to a rotary drum vacuum filter. A series of wash sections were used to wash the filter cake in order to recover valuable process liquor. Solids from the filter cake were discharged to a weigh belt conveyor for transport to the waste processing system. The mixed filtrate and wash liquor from the filter were returned to the thickener.

Two raw materials were required for operation of the system—limestone for absorbent regeneration and soda ash to make up for losses of sodium salts in the waste filter cake. Finely ground limestone was received, stored, and fed to the system in a dry form. Dense soda ash was used for the makeup soda ash

solution, which was normally prepared using clarified liquor from the thickener hold tank; occasionally, river water was used for preparing this solution but only when the additional water input did not upset the system volume balance. The makeup soda ash solution was fed back to the thickener hold tank to be mixed with the regenerated scrubbing solution and pumped forward to the absorber.

The waste processing system was installed and operated as part of a separate test program funded by EPRI. It is briefly discussed here to indicate its relation to overall plant operation.

The moist waste cake discharged from the vacuum filter was mixed in a pug mill with fly ash and lime. Fly ash was added at approximately one part of ash per part of dry solids in the cake. Lime was added at a rate of 3-5 wt. percent of the dry solids contained in the mix of cake and fly ash. The mix discharged by the pug mill was trucked to a landfill test area. Mixed material not meeting specifications or untreated filter cake—when the waste processing system was unavailable or inoperative—

were disposed of in a separate "off-spec" disposal area.

Operating History

System design and test program planning began in September 1978, immediately after EPA awarded the contract for the project. Recommissioning and conversion of the existing system to a limestone dual alkali system began in March 1979 and was completed by March 1980.

Process operations were initiated in August 1980. In the interim, the system was operated mechanically to prevent mechanical deterioration of the equipment. This delay was caused by equipment delivery problems encountered in the installation of the EPRI waste disposal system. As the expenses associated with the mechanical operation continued to accumulate, it was decided to start up the system in August even though the EPRI system was not yet completely installed. Formal testing of the dual alkali system did not start until February 1980 when the SO₂ and O₂ monitors were finally placed in operation. During this period—August 20, 1980, to the end of January—the system was operated for about 57 days and was down for about 107 days. Of the downtime in this initial startup and break-in testing period, 43 percent was attributable to mechanical problems (e.g., leak in the thickener tank), 20 percent to process problems (e.g., generation of solids with poor settling characteristics), 26 percent to the time needed to resolve CEA's bankruptcy-related issues*, 7 percent to a lack of raw materials (due to reluctant suppliers in light of the bankruptcy declaration), and 4 percent to miscellaneous causes (e.g., boiler outage).

System tests began on February 2, 1981, and extended until March 28, 1981. During this period, the system was operated for 925 hours (38.5 days) or 71.4 percent of the time, and it recorded one completely uninterrupted period of operation of 431 hours (18 days).

*On October 20, 1980, CEA filed a petition for financial reorganization pursuant to Chapter 11 of the U.S. Bankruptcy Code. Thyssen-CEA Environmental Systems, Inc. (TESI) bought the CEA Air Pollution Division and administered this EPA contract starting in early December 1980, assuming financial responsibilities retroactive to October 21, 1980. The EPA contract for this project was formally assigned to TESI in April 1981. CEA is referenced in this report to maintain historic integrity.

Outages during the test period were due primarily to mechanical problems (filter repairs) which accounted for 63 percent of the downtime, and to process problems (resuspension of solids left in thickener while repairing the filter) which accounted for 30 percent of the downtime.

System Performance

Given the limited tests performed, due to the reduction of testing from 6 to 2 months, a final and conclusive evaluation of the technology, leading to its full-scale commercialization, cannot be made at this time. Nevertheless, a number of very encouraging qualities of this technology have been clearly identified. Problem areas that will require further refinement have been identified as well.

SO₂ Removal

The SO₂ removal capability was excellent. During the tests, the system averaged an SO₂ removal efficiency of 95.8 percent. SO₂ removal efficiencies were easily controlled by simply adjusting the pH of the scrubber bleed liquor. SO₂ removal efficiencies greater than 90 percent were obtained by maintaining a scrubber bleed pH of at least 5.5. Outlet SO₂ concentrations of less than 100 ppm were obtained at scrubber bleed pH's higher than 5.7; concentrations less than 50 ppm were obtained at a pH of 6.0. Inlet SO₂ concentrations during this period ranged from 1460 to 3240 ppm and averaged slightly over 2000 ppm.

Limestone Utilization

Limestone utilization by the dual alkali system was very good. During the test period, utilizations in the reactor train effluent were 85-95 percent of the available CaCO₃ in the raw limestone. As the reaction with limestone continued in the dewatering system, the final system utilizations, determined from chemical analyses of the filter cake, were 93-100 percent, averaging 97.5 percent.

Oxidation and Sulfate Precipitation

About 18 percent of the SO₂ removed by the scrubbing solution was oxidized to sulfate as it passed through the system. As anticipated, most of this oxidation, as much as 90 percent, took place in the absorber/scrubber section. The capabilities of the system to coprecipitate calcium sulfate along with

calcium sulfite were adequate to remove the sulfate formed. The soluble sulfate concentration in the system achieved a steady level about 1 M. Although liquor losses (due to leaks, spills, and purges to maintain the liquor volume balance in the system) contributed to the removal of sulfate from the system, the sulfate concentration in a tight closed-loop operation is not expected to rise above 1.2 M, which appears to be within the sulfate coprecipitating capabilities of the system.

Waste Solids

The generation of solids with good settling characteristics was the most significant process limitation encountered at Scholz. It essentially accounted for all of the process-related outages. Throughout December and February, solids with excellent settling characteristics were generated. In contrast, poor solids were generated in January. The good settling solids were agglomerates, roughly spherical in shape; whereas, the poor solids were fine, needle-shaped solids. These fine solids, whenever carried over in the thickener overflow in noticeable amounts (>1000 ppm), promoted the formation in the reactors of more fine and difficult-to-settle solids. While on some occasions, the formation of these fine solids was stopped by process changes, in others it simply continued to deteriorate, forcing interruptions in system operation. Although some mechanical problems intensified the difficulties in the settling of solids, the fundamental physical and chemical reasons for the formation of poor settling solids are not clearly understood, and therefore require further investigation.

The solids appeared, in general, to have good dewatering characteristics; nevertheless, the typical solids content in the cake was 35-45 wt. percent, far below the anticipated 55 wt. percent. Severe mechanical problems with the filter and associated pumps and piping were the major factors in this shortcoming. Closely associated with this problem were the high sodium losses in the waste filter cake.

It appears that both of these problems—low solids content of the cake and high sodium losses—are not inherent to the limestone dual alkali technology, but were rather caused by the mechanical condition of the equipment used.

Soda Ash Consumption

Soda ash consumption was excessive, amounting to about 0.29 mole of Na_2CO_3 /mole of SO_2 removed, far above the design value of 0.04 mole of Na_2SO_3 /mole of SO_2 removed. Soda ash is fed to the system to make up for normal sodium losses in the liquor entrained in the filter cake. At Scholz, however, not only were the sodium losses high in the filter cake, but much sodium was lost through leaks, spills, and liquor purges needed to maintain the liquor volume balance in the system. (Large amounts of seal water were needed to keep worn out pumps in operation which, coupled with heavy rains, were very taxing on the limited surge capacity available.)

Again, this excessive soda ash consumption problem does not appear to be inherent to the limestone dual alkali technology.

Power Consumption

Power consumption ranged from 2.5 percent (0.53 MW)—at flue gas rates equivalent to a boiler load of 21 MW—to 5.3 percent (0.42 MW)—at an equivalent load of 8 MW. In a typical limestone dual alkali application, where flue gas is taken from an ESP and the use of a venturi is not required, one would expect the power consumption to be much lower—more like 1-1.5 percent of the power generated at full boiler load.

Process Operability

Process operability, unlike equipment or mechanical operability, refers to: the ease with which the system can be operated and controlled, the ability of the system to adequately respond to varying conditions, and the ability of the system to tolerate upsets in process chemistry due to mechanical problems or operator oversight.

In general, process operability was good after the first 2 or 3 days of stable operation. It was during these initial days, following any restart of the system, that problems with process operability were encountered. All of these related to the generation of solids with poor settling characteristics.

Once the system reached a stable operation, such as during December or February, process operability was very good. The system was able to easily accommodate variations in inlet SO_2 concentrations of as much as 500 ppm, by simply adjusting the feed forward rate of regenerated solution to the absorber/scrubber to maintain a con-

stant bleed pH. Variations in boiler load and thus in the amount of gas processed were accommodated in the same fashion.

Upsets to process chemistry were also handled well by the system. These upsets included the carryover of fly ash in the flue gas due to a malfunction in the ESPs, the gross overfeeding of limestone due to operator oversight, and occasional limestone and soda ash outages lasting from 1 to 5 hours.

Mechanical Performance

The mechanical performance of the equipment and its associated instrumentation represented a major source of problems at Scholz: 43 percent of system downtime during the start-up and break-in and 59 percent of the downtime during testing were due to mechanical problems. Not only was system availability affected by these mechanical problems, but also system operating conditions were affected. An example of these limitations was the inability of undersized thickener underflow pumps to handle slurry with more than 15 wt. percent solids, which required the dilution of the 20-25 percent thickener underflow slurry. Although some of the problems were caused by the limited capacity of an existing piece of equipment, most of the mechanical problems were due to equipment failures. The age of the equipment and its condition, even after recommissioning, were, undoubtedly, primary causes of these failures.

Conclusions

System performance, summarized above, leads to the following conclusions:

- The limestone dual alkali process appears to be technically feasible.
- Further testing is required to reinforce the above conclusion and to develop sufficient process information needed for full-scale commercialization.

It is also recommended that laboratory or small pilot plant tests, to better understand the generation of solids with good settling characteristics, be performed prior to any further prototype scale testing.

J. Valencia and J. Peirson are with Arthur D. Little, Inc., Acorn Park, Cambridge, MA 02140; G. Ramans is with Thyssen-CEA Environmental Systems, Inc., 555 Madison Avenue, New York, NY 10022.

Norman Kaplan is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of the Limestone Dual Alkali Prototype System at Plant Scholz: Final Report," (Order No. PB 82-110 685; Cost: \$12.00, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Project Officer can be contacted at:

*Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335



Official Business
Penalty for Private Use \$300

PS 0000329
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604