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FINAL REPORT: DUAL ALKALI TEST AND EVALUATION PROGRAM
Volume I. Executive Summary

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Volume I. Executive Summary

by

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ABSTRACT

This report presents the results of the Dual Alkali Program conducted by Arthur D. Little, Inc., (ADL) for the Industrial Environmental Research Laboratory, Research Triangle Park (IERL, RTP) of the U.S. Environmental Protection Agency (EPA). The purpose of the program was to investigate, characterize and evaluate the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work was carried out at three levels of investigation:

- Task I - Laboratory studies at ADL and IERL, RTP.
- Task II - Pilot Plant Operations in a 1,200 scfm system at ADL.
- Task III - Prototype Test Program on a 20-megawatt, Combustion Equipment Associates (CEA)/ADL dual alkali system at Plant Scholz, Southern Company Services, Inc./Gulf Power Company.

Various modes of operating dual alkali systems on high- and low-sulfur fuel applications were investigated, including:

- Concentrated and dilute sodium scrubbing systems
- Lime and limestone regeneration
- Slipstream sulfate treatment schemes.

In each mode, the objective was to characterize the dual alkali process in terms of SO_2 removal, chemical consumption, oxidation, sulfate precipitation and control, waste solids characteristics and soluble solids losses.

This is Volume I, the Executive Summary of the final report. Volume II of the final report covers Tasks I and II, the Laboratory and Pilot Plant Programs; Volume III covers the Prototype Test Program, Task III.

VOLUME I

EXECUTIVE SUMMARY

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I. PURPOSE AND SCOPE

This report presents the results of the Dual Alkali Program conducted by Arthur D. Little, Inc., (ADL) for the Industrial Environmental Research Laboratory, Research Triangle Park, (IERL, RTP) of the U.S. Environmental Protection Agency (EPA). The purpose of the program was to investigate, characterize, and evaluate the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work covered a wide range of flue gas conditions, liquid reactant concentrations, and process configurations, including:

- concentrated and dilute mode (dilute sodium scrubbing solutions, active Na^+ concentration below about 0.15M)*
- use of lime and limestone for regeneration
- sulfuric acid treatment for sulfate control.

Each of the modes was evaluated relative to the following performance characteristics:

- SO_2 removal capability
- oxidation and sulfate formation and control
- lime/limestone utilization
- waste solids properties
- sodium makeup requirements and degree of closed-loop operation
- process reliability.

Investigations were carried out at three levels: laboratory, pilot plant and 20-megawatt prototype. Accordingly, the program was divided into three tasks:

- Task I -- Laboratory Program -- In the ADL laboratory program, experiments were performed on the regeneration of concentrated sodium scrubbing solutions using lime or limestone, and the use of sulfuric acid treatment for sulfate removal. Work also

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*See Glossary for dual alkali terminology.

included characterization of the chemical and physical properties of dual alkali solids. Work was performed also at IERL, Research Triangle Park on regeneration using limestone in dilute mode operation.

- Task II -- Pilot Plant Program -- Pilot plant work was conducted at the Combustion Equipment Associates, Inc. (CEA)/ADL pilot facility in Cambridge, Massachusetts. The following modes of operation were investigated in the pilot plant program:

  - concentrated mode using lime for regeneration

  - concentrated mode using lime for regeneration with slipstream sulfuric acid treatment for sulfate control

  - concentrated mode using limestone for regeneration

  - dilute mode using lime for regeneration.

- Task III -- Prototype Test Program -- The test program was conducted on the 20-megawatt CEA/ADL prototype dual alkali system at Gulf Power Company's Scholz Steam Plant in Sneads, Florida, from May 1975 to July 1976. The prototype system used lime in a concentrated mode. The system was operated on flue gas generated from moderately low- to high-sulfur coals, and with varying particulate loads to the system.

This is Volume I, the Executive Summary of the final report. Volume II of the final report covers Tasks I and II of this program; Volume III covers the Prototype Test Program, Task III.

II. DUAL ALKALI CHEMISTRY

The chemistry and terminology of dual alkali systems are briefly described here. A more detailed description is given in Volume II, Chapter III; a glossary of terms is included in each volume and with this Executive Summary.

In the absorption section of sodium-based dual alkali processes, absorption of SO_2 in sodium sulfite solutions occurs to produce a bisulfite scrubber effluent solution according to the overall reaction:

$$Na_2SO_3 + SO_2 + H_2O \rightleftarrows 2NaHSO_3 \qquad (1)$$

Depending upon the dual alkali mode being used, the feed to the absorber may also contain some sodium hydroxide (formed in the regeneration section or used as sodium makeup) and/or some sodium carbonate (used as sodium makeup to the system). Both sodium carbonate and hydroxide form sodium sulfite on absorption of SO_2:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \qquad (2)$$

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad (3)$$

which is used in further absorption to produce bisulfite. The regenerated feed solution to the absorber will also contain some level of sodium sulfate in solution and may contain some sodium bisulfite if neutralization is not completed in the regeneration section. Sodium, identified as associated with anions involved in SO_2 absorption reactions, is referred to as "active" sodium (includes sodium sulfite, bisulfite, hydroxide, carbonate/bicarbonate). The sulfite/bisulfite content of solutions, or total oxidizable sulfur content, is also referred to as TOS.

Some oxidation of sulfite to sulfate occurs in the absorber due to reaction of sulfite with oxygen in the flue gas:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (4)$$

The rate of oxidation or oxygen transfer in the absorber is a function of the absorber design, oxygen concentration in the flue gas, flue gas temperature, and the nature and concentration of the species in the scrubbing solution.

The regeneration of acid sodium sulfite/sulfate scrubber effluent solutions can be considered as a sequential reaction first involving neutralization of the bisulfite using either lime or limestone, to produce a precipitate of calcium sulfite:

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2H_2O\downarrow + 3/2H_2O \quad (5)$$

$$2NaHSO_3 + CaCO_3 \rightleftarrows Na_2SO_3 + CaSO_3 \cdot 1/2H_2O\downarrow + CO_2\uparrow + 1/2H_2O \quad (6)$$

In theory, the lime neutralization reaction should go to completion; complete neutralization of bisulfite is not possible with $CaCO_3$. Using lime, the regeneration can be carried beyond neutralization to generate caustic:

$$Na_2SO_3 + Ca(OH)_2 \rightleftarrows 2NaOH + CaSO_3 \quad (7)$$

to some equilibrium hydroxide concentration. The usual form of calcium sulfite produced is the hemihydrate, $CaSO_3 \cdot 1/2H_2O$.

Depending upon the concentration of sulfite and sulfate and the pH of the solution, the following reaction for sulfate removal also occurs simultaneously with neutralization and regeneration reactions (5)-(7) using either lime or limestone:

$$Ca^{++} + SO_4^{=} \rightleftarrows CaSO_4 \quad (8)$$

The form of this calcium sulfate was investigated and will be discussed later in this report.

Thus, the level of sulfate precipitation in the overall scheme is given by the ratio of calcium sulfate to total calcium/sulfur salts produced:

$$\text{Sulfate Precipitation} = \frac{\text{mols } CaSO_4}{\text{mols } CaSO_4 + \text{mols } CaSO_3}$$

Sulfate precipitation is directly related to the ratio of sulfate/sulfite in solution in the reactor, increasing with the ratio.

If the level of sulfate formation or sulfite oxidation given by:

$$\text{Sulfate Formation} = \frac{\text{mols } SO_3^{=} \text{ oxidized}}{\text{mols } SO_2 \text{ removed}}$$

is matched by the level of sulfate precipitation, then all sulfur removed from the flue gas can leave the system as a calcium salt and no soluble sulfate purge is necessary to maintain a sulfate balance in the system. In practice, even if such a balance is established, the washed calcium

sulfite/sulfate salts will contain some soluble sodium salts as well as soluble fly ash constituents which must be purged and some sodium makeup to the system will therefore be required. Calcium utilization or yield in the overall process is defined as:

$$\text{Calcium Utilization} = \frac{(\text{mols } CaSO_3 + \text{mols } CaSO_4) \text{ generated}}{\text{mol Ca fed}} \times 100\%$$

regardless of whether lime or limestone is used.

Regeneration reactions in the "concentrated mode" produce solutions saturated (or possibly supersaturated) with respect to calcium sulfite; in the "dilute mode" saturation (or possibly supersaturation) is with respect to calcium sulfate (gypsum). For purposes of this program, dilute operating modes are considered to be those involving solutions containing active sodium concentrations less than or equal to 0.15 molar active Na^+, where active sodium is sodium sulfite/bisulfite, carbonate/bicarbonate or hydroxide. Concentrated modes are those involving solutions containing active sodium concentrations greater than 0.15 molar active Na^+. Soluble calcium levels in dilute mode regenerated solutions are quite high compared to levels in the concentrated mode, usually requiring "softening" with carbonate,

$$Ca^{++} + CO_3^{=} \rightleftarrows CaCO_3 \qquad (9)$$

to prevent scaling by precipitation of calcium salts in the scrubber.

The sulfite and sulfate concentrations, besides affecting sulfate precipitation, also have a profound effect on the physical properties of the calcium/sulfur salts and, as a result, on the settling and filtration characteristics of the solids produced in dual alkali modes.

As an alternate approach to operating at decreased active sodium concentrations, high levels of sulfate precipitation can be achieved using sulfuric acid treatment for precipitation of sulfate according to the following equation:

$$Na_2SO_4 + H_2SO_4 + 2CaSO_3 \cdot 1/2H_2O + 3H_2O \rightleftarrows 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O \qquad (10)$$

This reaction is carried out at a low pH (2-3), where sulfite is converted to bisulfite, thereby bringing calcium sulfite into solution and exceeding the solubility product for calcium sulfate. This reaction can be applied on a process slipstream for sulfate precipitation, as required. However, in the overall process this scheme utilizes sulfuric acid, requiring additional lime or limestone for ultimate neutralization of this acidity added to the system and generates an equivalent additional amount of waste calcium/sulfur salts.

III. OVERALL FINDINGS

Based upon results from all three tasks of this program, laboratory experiments, pilot plant operations, and prototype testing, we have concluded that both the concentrated and the dilute modes, using lime for regeneration, can be operated in a closed loop. No purge of soluble solids is required other than solubles in the liquor wetting the washed filter cake. These processes can be applied over a wide range of boiler, fuel, and flue gas design and operating conditions. The concentrated mode is inherently more reliable, less complex and cheaper than the dilute mode, but is limited to situations where oxidation rates will not exceed about 25% of the SO_2 removal rate. The dilute mode can be operated at higher oxidation rates.

The performance of these two modes relative to the important performance characteristics is as follows:

- SO_2 Removal -- These modes are capable of easily achieving over 90% SO_2 removal and approaching 99% removal. SO_2 absorption is easier to control, especially at higher removal efficiencies, in the concentrated mode relative to the dilute mode.

- Lime Utilization -- Utilization easily exceeding 90% and up to 100% can be achieved in either mode. Utilization increases with reactor residence time in both modes, but decreases as regeneration is carried beyond neutralization to the generation of free hydroxide, approaching the reaction equilibrium limits.

- Oxidation and Sulfate Removal -- In the concentrated mode calcium sulfate is coprecipitated with calcium sulfite at rates sufficient to keep up with oxidation levels up to about 25% of the SO_2 removal. The sulfate coprecipitates as a mixed crystal with the sulfite in a manner apparently similar to the coprecipitation observed in direct lime/limestone scrubbing systems. The dilute mode can be operated to precipitate gypsum, equivalent to 100% oxidation in the system.

- Waste Cake Solids Properties -- In the concentrated mode, the insoluble solids content of filter cakes ranges from 45% to 75%. The moisture content increases as the sulfate content in the loop increases, increasing the calcium sulfate content of the cake. Under similar process conditions in the concentrated mode, solids properties are improved using a multistage reactor system. In the dilute mode, insoluble solids content of filter cakes ranges from 60% to 80% when the scrubber effluent is oxidized prior to regeneration to produce gypsum as a waste material.

  The soluble solids content in the cake from either mode can be reduced to the range of 1% to 5% soluble solids (dry cake basis) by washing. The soluble content of the cake decreases as the concentration of total dissolved solids in the dual alkali loop decreases; and as the amount of cake wash water available in the water balance increases (wash

water availability increases with decreasing sulfur content of the fuel).

The solids generated in each of these modes have good dewatering properties and result in a filter cake with good handling properties. The concentrated mode sulfite/sulfate cake has the general consistency of a moist soil-like material. In limited tests it responded similarly to fixation treatment as other sulfite/sulfate waste materials from lime/limestone processes. The dilute mode gypsum material also handled well with a more granular, sand-like consistency.

- Sodium Makeup Requirements -- Since the systems operate in a closed loop, the sodium makeup requirements are equivalent to the sodium losses in the cake and would range from 0.05 mols Na_2CO_3/mol of SO_2 removed down to about 0.01, depending upon the ability to wash the cake in the specific application, as discussed above.

- Power Consumption -- When the dual alkali system is operated for SO_2 removal only, with no simultaneous particulate removal requirement, the overall system power consumption would be about 1% of the generating capacity of the unit being controlled. In a high-sulfur coal application, 95% SO_2 removal can be achieved in an efficient two-stage absorber (e.g. two contact trays) with a total absorber liquid/gas ratio of under 10 gallons/1000 saturated cubic feet. The scrubber system pressure drop should be under 10 inches H_2O.

- Reliability -- Aside from concentration differences, the principal difference in the operating characteristics between dilute and concentrated lime dual alkali systems is that dilute systems operate at or near saturation in calcium sulfate, potentially reducing the reliability and ease of operation of the dilute systems. Dilute systems require the use of carbonate makeup to provide some softening of the regenerated solution prior to recycle back to the scrubber. The concentrated mode is inherently quite reliable and stable requiring no softening for scale control.

No viable approach was developed in this program to enable the use of limestone for regeneration. The problem which remains to be solved is the production of solids with good settling characteristics over a wide range of sulfate, magnesium, and iron concentrations in the scrubbing liquor. These components tend to reduce the rate of reaction of limestone with sodium scrubbing solutions; solids properties tend to deteriorate with a decrease in the limestone reaction rate. However, these problems may be resolvable.

There are considerable economic incentives for the substitution of limestone for lime in dual alkali processes justifying further work in this area. Operating cost savings of about 7¢/10^6 Btu can be realized if limestone is used in lieu of lime in high-sulfur coal applications. These potential savings are equivalent to about 20% of the total annual lime

dual alkali operating cost (with lime at $40/ton, limestone at $5/ton, and including annual capital charges).

The actual performance of any particular dual alkali process will vary depending upon the SO_2 and oxygen concentrations in the flue gas, the design of the system and the concentration of sodium solutions used in the process. Using lime, some version of the dual alkali process can generally be designed to achieve very desirable performance characteristics in most utility applications.

More specific results and conclusions regarding the various dual alkali modes and pilot plant operations are given in following chapters.

IV. FINDINGS - TASKS I AND II, LABORATORY AND PILOT PLANT PROGRAMS

A. PILOT PLANT SO_2 REMOVAL AND OXIDATION-- GENERAL

The pilot plant SO_2 removal and oxidation data are specific to the pilot plant scrubber configuration as influenced by the scrubber operating temperature for the pilot plant flue gas stream. The scrubber operating temperature of 140-150°F is higher than that normally encountered in conventional boiler flue gas applications (120-130°F). The elevated temperature in the pilot plant system tends to decrease SO_2 removal efficiency due to elevated SO_2 partial pressures for any given solution, and tends to increase oxidation rates. However, the purpose of the pilot plant scrubber and its operations was to provide scrubber effluent with an appropriate composition for use in the various dual alkali modes rather than to generate basic data on SO_2 absorption using sodium solutions.

Within the above constraints, the scrubber operations did indicate that SO_2 removal in excess of 90% is easily accomplished over a range of SO_2 inlet concentrations from 700-2,800 ppm by adjusting the scrubber feed stoichiometry. To achieve this removal efficiency, a stoichiometry of 1.1 mols of active Na^+ capacity/mol SO_2 inlet was required at the high inlet SO_2 range; a stoichiometry of 1.3 was required in the lower inlet SO_2 range. In any range of SO_2 concentration, increasing stoichiometry increased the SO_2 removal. There was no important apparent effect of active sodium concentration within a range of 0.2-0.5M or total dissolved solids concentration within a range of 5-15 wt %.

Sulfite oxidation is mass transfer limited at active sodium concentrations above 0.2M with the rate of oxidation increasing with the oxygen content of the flue gas. At lower active sodium concentrations the oxidation rate is roughly proportional to the active sodium concentration. The rate of oxidation decreases with increasing total dissolved solids; by increasing TDS from 8-15 wt % to 25-35 wt %, the oxidation rate would be reduced by a factor of 2-3. At lower total dissolved solids in concentrated active sodium systems (0.3-0.6M active Na^+, 5-15 wt % TDS) sulfite oxidation can be expected to be on the order of 100-300 ppm equivalent SO_2 removal for oxygen concentrations in the flue gas ranging from 4 to 8 vol %.

B. CONCENTRATED MODE WITH LIME REGENERATION

In the concentrated mode using lime for regeneration, calcium sulfate will coprecipitate with calcium sulfite at sulfate precipitation rates equivalent to oxidation rates as high as 25% of the SO_2 removal depending upon the solution sulfate and sulfite concentrations. Solutions remain unsaturated with respect to calcium sulfate and have low soluble calcium concentrations. Process modes can be operated over a wide range of sodium solution concentrations achieving high SO_2 removal (greater than 90%)

producing good quality filter cake (45% solids or greater), and containing low soluble solids (2-5 wt % dry cake basis) with no sulfate purge required. The performance characteristics of concentrated lime regeneration modes are summarized in more detail below.

- SO_2 Removal -- SO_2 removal efficiencies in excess of 90% were easily achieved with the removal efficiency a function of sodium solution feed stoichiometry for any particular absorber design. In all closed-loop runs the feed stoichiometry (scrubber operating pH) was controlled to ensure better than 90% removal. For a given design, a slightly higher feed stoichiometry (or operating pH) was required for high sodium solution concentrations (30-35 wt % sodium salt solutions) than for moderate concentrations (10-15 wt % sodium salt solutions) to achieve this same removal efficiency because of the increase in SO_2 equilibrium partial pressure with the increase in sodium sulfite/bisulfite concentration.

- Lime Utilization -- Lime utilization in the range of 95-100% can be achieved with reactor holdup times of 25 minutes or greater when regenerating to a pH of 8 or higher. High utilizations can be achieved at shorter residence times if the regeneration reaction is not carried beyond neutralization of the bisulfite. Lime utilization decreases if regeneration is carried much beyond a pH of 12.5.

- Oxidation/Sulfate Control -- At active sodium concentrations above about 0.2M, calcium sulfate coprecipitates with calcium sulfite upon reaction of the sodium salt solution with lime. The sulfate/sulfite content of the precipitated calcium salts is related to the sulfate/sulfite concentrations in the reactor liquor by the following relationship:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\substack{\text{reactor}\\ \text{solids}}} = 0.0365 \left(\frac{[SO_4^{=}]}{[SO_3^{=}]}\right)_{\substack{\text{reactor}\\ \text{liquor}}} \qquad (11)$$

This relationship describes the coprecipitation phenomenon over the range of sulfite and sulfate liquor concentrations used in laboratory and pilot plant experiments ($[SO_3^{=}] > 0.2M$, $[SO_4^{=}]/[SO_3^{=}] = 0 - 6$).

This method of sulfate precipitation is effective for oxidation rates up to about 25%. At any given active sodium concentration, high sulfate precipitation appears to be favored by either partial neutralization of the absorbent solution or regeneration to pH's well above neutrality (> 11.5), thereby reducing the sulfite concentration in the reactor liquor and maximizing the sulfate/sulfite ratio in the liquor.

In a properly designed concentrated dual alkali loop, the sulfate/sulfite ratio will self-adjust at steady-state so that the rate of sulfate precipitation equals the rate of sulfite oxidation. It is

possible to achieve this balance over a wide range of active sodium and sulfate concentrations in dynamic response to changes in flue gas rates and oxygen and SO_2 concentrations.

For dual alkali systems operating with high TDS (in the range of 25-30 wt % sodium salt solutions) oxidation rates can be reduced by a factor of 2-3 from those encountered at lower TDS levels (10-15 wt %). At such high TDS levels, the active sodium concentration as well as the sulfate concentration must be elevated in order to promote effective regeneration reactions and production of solids with acceptable dewatering properties. As a result, sulfate precipitation capability is limited.

- Solids Properties -- Single-stage CSTR (continuous stirred tank reactor) and multistage reactor systems can produce solids, over a wide range of process conditions, which settle well and filter to insoluble solids contents of 45 wt % or higher. When using a single CSTR as the regeneration reactor, solids properties deteriorate as the regeneration reaction is carried to a higher pH range with the degree of deterioration increasing from pH 7.5 to pH 12. This effect is worse for reactor holdup times of 60 minutes than for shorter reactor residence times (30 minutes). Using a CSTR, solids properties also decrease as the sulfate/sulfite ratio increases in the reactor liquor (at higher oxidation rates). In a single-stage CSTR, it is difficult to produce solids with acceptable properties (45 wt % insoluble solids) at process conditions consistent with sulfate precipitation and sulfite oxidation rates much beyond 15%.

  Good quality solids can be produced over a wider range of pH and sulfate concentration using a two-stage reactor system, consisting of a short residence time reactor (5-10 minutes) followed in series by a longer residence time second stage (20-40 minutes). This multistage system produces good solids at pH levels up to about 12.5 and at sulfate/sulfite ratios required for sulfate precipitation rates equivalent to about 25% oxidation.

- Sodium Losses -- For a filter cake containing 50% insoluble solids, the soluble solids content of the cake can be reduced to 2-3% (dry cake basis) using the amount of filter cake wash water which would normally be available when operating closed-loop in a high sulfur coal boiler application. At TDS levels in the range of 10-15 wt %, 2 to 3 displacement washes are effective in reducing the soluble content of the cake to 2-3 wt %. Of this material, 0.5-1.0 wt % soluble sodium salts appear to be occluded in the calcium salt crystals and cannot be washed regardless of the amount of wash water used. About 2-3 displacement washes are available for high-sulfur coal applications. At high TDS concentrations (30%), 4 to 5 displacement washes are necessary to reduce solubles to the 2-3% level. With only 3 displacement washes, solubles losses at high TDS concentrations can be expected to be roughly twice those when operating at 10-15 wt % TDS levels in the absorbent solution.

At the lower TDS levels, sodium makeup requirements are on the order of 2-3% of the total alkali requirements (mol basis). That is, roughly 2-3% of the sulfur absorbed from the flue gas leaves the system as sodium salts with the remainder as calcium salts.

From the above considerations, operating a concentrated lime mode with TDS in the range of 10-15%, the single-stage CSTR can produce good quality solids (45 wt % or greater) containing 2-3 wt % solubles at system oxidation rates up to 15%. When using the multistage reactor system the operability of the process is extended to oxidation levels in the range of about 25%. Increasing TDS reduces oxidation but requires more wash water to produce the same cake solubles content. At 2 to 3 displacement washes, the solubles content of the cake is proportional to the TDS levels in the system loop.

- System Operability/Reliability -- In concentrated modes using lime for regeneration, soluble calcium concentrations range from 15-90 ppm with the calcium concentration generally decreasing with increasing sulfite concentration. No scaling or deposition of solids was observed in the scrubber loop during any of the concentrated mode operations. Scrubber operation and SO_2 removal were easy to control. The regeneration reaction is stable and easy to control, but should be kept at a pH below about 8 if operating with a single stage regeneration reactor. Increasing the TDS level in the system raises the sodium salt saturation temperature, increasing the potential for solid sodium salt crystallization in elements of the system which are permitted to cool.

C. CONCENTRATED MODE WITH SULFURIC ACID SULFATE TREATMENT

The sulfuric acid slipstream treatment scheme is a technically feasible and reliable approach for removal of soluble sulfates from dual alkali systems. The basic chemistry of the treatment process is given in the following simplified reaction equation:

$$\begin{aligned} &2CaSO_3 \cdot 1/2H_2O(\text{filter cake}) + Na_2SO_4(\text{system liquor}) \\ &+ H_2SO_4 + 3H_2O \rightarrow 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O \end{aligned} \qquad (12)$$

The treatment produces sulfate in the form of gypsum that can be readily dewatered to 65 wt % insoluble solids or higher. The scheme adds complexity to any dual alkali mode to which it is applied. The complexity is reflected in additional capital costs and in increased operating costs for the sulfuric acid, the additional lime consumed and the additional solid waste produced.

The amount of sulfuric acid required is important since it directly affects the overall lime requirement. As the sulfuric acid addition rate increases, the lime rate must increase accordingly for precipitation of the additional sulfur value added to the system. The maximum efficiency of the treatment

scheme ((mols Na_2SO_4 removed/mols H_2SO_4 fed) x 100%) appears to be practically limited to a maximum in the range of 60-70%. In order to precipitate sulfate at a rate sufficient to keep up with an oxidation rate of 15% (of the SO_2 absorbed), the lime feed requirement will be increased by 25% for a 60% reactor efficiency.

The efficiency of the sulfuric acid treatment is importantly affected by the calcium utilization achieved in the absorbent regeneration reactor in the main dual alkali loop. As calcium utilization decreases in the main loop the efficiency of the sulfuric acid slipstream treatment decreases and acid consumption increases to neutralize unreacted lime in the filter cake. In order to achieve a 50% efficiency in the sulfuric acid treatment system, calcium utilization in the main dual alkali loop must exceed 90%.

Because the use of this sulfuric acid treatment scheme may be costly when applied to systems with high oxidation rates (due to the sulfuric acid and extra lime requirements), it may be more appropriate for systems with intermediate levels of oxidation where the rate of sulfate formation cannot be easily handled in a simpler concentrated sodium mode. The consequences of using the sulfuric acid slipstream treatment approach for sulfate regeneration should, therefore, be carefully evaluated in terms of the overall process operation. In many cases, where oxidation rates are high enough that they cannot be easily handled by normal concentrated mode operation, other dual alkali approaches, such as the dilute lime system, might be more promising than a sulfuric acid treatment scheme.

D. CONCENTRATED MODE WITH LIMESTONE REGENERATION

No viable approach was found for use of limestone in a concentrated dual alkali mode. Through the laboratory and pilot plant efforts allocated to work on the concentrated limestone mode, we were not able to develop process parameters and reactor conditions consistent with good limestone utilization and generation of acceptable quality waste solids. The work did, however, uncover important factors influencing the limestone regeneration reaction that indicated promising areas of future work. Unlike results from work on use of limestone in dilute modes, the potential for technical success argues for additional work on the concentrated limestone dual alkali mode; especially when the economic incentives are considered.

Limestone is substantially less reactive toward sodium salt solutions than is lime, even when reacting with relatively acidic scrubber bleed solutions. The reaction rate of the limestone regeneration reaction is dependent upon:

- nature of the limestone and its particle size;
- reactor temperature and residence time;

- concentrations of soluble reactants (sodium sulfite, sodium bisulfite and sodium sulfate); and

- the presence, at low concentrations, of trace constituents such as magnesium and iron, which influence the reaction rate.

Increase in the reaction rate was generally consistent with improvement in the dewatering properties of the solids produced and with improved utilization of limestone.

Three limestones, with similar particle size distribution, were examined -- Fredonia limestone used in the EPA/TVA Shawnee program; another, locally available, natural limestone; and reagent grade $CaCO_3$. Of these, the Fredonia limestone was amorphous, rather than crystalline in nature, and was considerably more reactive than the other two limestones examined.

The Fredonia limestone, therefore, was used extensively in the laboratory and pilot plant programs.

Laboratory experiments indicated that increasing temperature importantly increased the reaction rate. However, the pilot plant was not equipped for heating the reactors or for heating the reactor feed. As a consequence pilot plant regeneration was performed at a maximum of about 50°C.

The dewatering properties of solids were generally observed to deteriorate as the regeneration reactor residence time was increased. Increasing the reactor residence time results in carrying out the reaction closer to the equilibrium conditions and consequently at a lower driving force and reaction rate. Use of multistage reactor systems, containing several stages with residence times in the range of 15 minutes, were found to produce solids with a quality superior to that of solids produced in fewer reactors with the same total residence time. Recycle of solids, increasing reactor solids concentrations from about 2 wt % to 5 wt %, improved limestone utilization but did not appreciably improve the quality of the solids.

Under controlled conditions, with a multistage reactor system operating at about 50°C, it was possible to produce solids with acceptable dewatering properties (45% insoluble solids) and to achieve limestone utilizations on the order of 75%. However, if the sulfate concentration in the loop rose above 0.7M or if the magnesium concentration rose much above 300 ppm, the reaction rate, and the resulting limestone utilization and solids properties all deteriorated.

Sulfate concentration in the reactor liquor had a much more important, deleterious affect on the reaction rate and solids properties in limestone regeneration reactions than the similar effects of increased sulfate concentration observed in concentrated lime regeneration. As in lime regeneration, the reaction rate is inversely proportional to the ratio of sulfate/sulfite concentrations in the liquor; but the rate drops dramatically using limestone as the sulfate concentration exceeds 0.7M at TOS

levels of 0.3-0.5M. Operation at lower sulfate/sulfite ratios tends to limit sulfate precipitation in this mode and limit the range of oxidation in which limestone regeneration could be operated closed loop.

Calcium sulfate coprecipitates along with calcium sulfite in concentrated limestone regeneration reactions in an analogous fashion to the coprecipitation of calcium sulfate observed in the concentrated lime regeneration. However, pilot plant data indicate that for the same sulfate/sulfite concentrations with the same range of TOS in the feed liquor (i.e., [TOS] of 0.3-0.5M), lower sulfate precipitation occurs when using limestone, as given by the following:

$$\left(\frac{CaSO_4}{CaSO_3}\right)_{\substack{\text{reactor}\\ \text{solids}}} = 0.022 \left(\frac{[SO_4^{=}]}{[SO_3^{=}]}\right)_{\substack{\text{reactor}\\ \text{liquor}}} \qquad (13)$$

The sensitivity of the reaction to high sulfate concentrations and the lower sulfate precipitation rates make limestone regeneration less viable for closed-loop operation than lime regeneration at higher oxidation rates.

The presence of Mg^{++} in solution, introduced into the system in varying amounts depending upon the magnesium content of the limestone, also can retard the limestone regeneration reaction rate, resulting in poor solids quality and limestone utilization. This effect becomes pronounced as the Mg^{++} concentration rises much above a few hundred ppm. Relatively low magnesium limestones, such as Fredonia limestone (1.0-1.5 wt % Mg as $MgCO_3$), would result in concentrations on the order of a few thousand ppm, at steady-state, in a concentrated dual alkali loop.

Laboratory work confirmed that magnesium concentrations could be controlled by reacting part of the process stream with lime to precipitate $Mg(OH)_2$. However, such an approach would reduce operating cost savings, requiring part of the total regeneration to be performed using lime. Use of lime with limestone would increase the complexity and the capital cost, reducing economic incentive.

In pilot plant operations, iron from corrosion of unlined steel equipment was found to have an effect similar to that of magnesium on the limestone regeneration reaction at pH's below about 6. At higher pH's, $Fe(OH)_3$ is highly insoluble, limiting the buildup of iron in solution. By selection of proper materials of construction and linings and by carrying the limestone regeneration beyond a pH of 6, interference by iron can be eliminated in concentrated limestone modes.

Future work on limestone regeneration should be directed at increasing reaction rates at high magnesium levels by increasing sulfite concentrations, reactor temperature and by staging of the reactors.

E. DILUTE MODE WITH LIME AND LIMESTONE REGENERATION

Use of limestone only for the regeneration of solutions in the dilute mode (less than 0.15M active sodium) is not viable. The limestone reaction rate decreases as the ratio of soluble sulfate/sulfite increases in the reactor solutions. At sulfate/sulfite ratios required for adequate sulfate precipitation in the dilute mode, reaction rates are poor resulting in poor limestone utilization and poor solids quality.

Use of lime in combination with limestone in a dilute dual alkali mode was more viable technically. In this approach, the lime regeneration was carried out in a second reaction system to promote sulfate precipitation. The limestone/lime process is more complicated than a simple dilute lime process, resulting in higher projected capital cost. Economic analysis indicated that operating cost savings which could potentially be realized in using limestone for part of the regeneration would not offset the additional capital cost probably required to enable use of the limestone. The dilute lime system, using soda ash for softening, was technically and economically the most viable dilute mode considered. Conclusions based upon laboratory and pilot plant investigations of this mode are given below.

A dilute lime mode can be operated in a closed loop with sulfate precipitation keeping up with any level of system oxidation. The system can be operated with high SO_2 removal (90% or higher) and good lime utilization (90% or higher) to produce high quality solids (60% insolubles or higher) with low soluble sodium losses (2 wt % soluble solids achievable, dry cake basis). The process may be more appropriate for low-sulfur coal applications or in situations where oxidation rates are expected to exceed 25-30% of the SO_2 removal. The dilute lime mode is somewhat more complicated than the concentrated lime mode, involving higher liquid rates and larger reactors and associated equipment. The process is also potentially less reliable than the concentrated lime approach.

The regeneration reaction, carried out at low sulfite levels, results in the precipitation of calcium sulfate (usually gypsum) to produce a regenerated solution of sodium hydroxide and sodium sulfate with soluble calcium levels which are, at best, at the saturation level of about 700 ppm Ca^{++}. Even with moderate amounts of soda ash makeup (and resulting softening by precipitation of calcium carbonate) the solutions have soluble calcium levels in the range of 600-700 ppm with a high potential for scaling in the system. Close control of scrubber pH is required to prevent carbonate or sulfite scaling. High scrubber oxidation rates may create sulfate scaling.

In the dilute mode regeneration reaction, there is a high tendency to produce solutions which are supersaturated in Ca^{++} (with respect to gypsum). Using a single-stage CSTR with no solids recycle, calcium supersaturation levels of 100-200 ppm are easily encountered. Special design precautions must be taken to prevent supersaturation and the resulting scaling throughout the system. Supersaturation can be re-

duced in a number of ways, by reactor system design and by controlling conditions of the regeneration reaction:

- Increased reactor residence time -- Allows time for completion of reaction and desupersaturation. Holdup time of 60 minutes is a minimum; 90 minutes is preferable.

- Solids recycle -- Increases suspended solids concentration and seed crystal concentration for reaction and desupersaturation. Recycle of solids to achieve a concentration of 4% or higher suspended calcium salt solids is required to eliminate supersaturation in the reactor effluent.

- Oxidation of sulfite in scrubber bleed prior to regeneration -- Lowers the concentration of TOS which tends to retard the lime/sulfate reaction when TOS is present in the dilute mode concentration range. Oxidation to TOS concentrations of about 0.02M or lower is desirable.

- Multistage reactor configuration -- Solids generated in a short residence time first stage provide good seeds for completion of reaction in a longer residence second stage. Using a multistage reactor can reduce supersaturation to within about 50 ppm of the saturation level. Solids recycle is required to completely eliminate supersaturation.

Elimination of supersaturation was achieved in the single-stage reactor, with 90 minutes' residence time; using solids recycle to the minimum of 4% suspended calcium salts in the reactor; and with oxidation of the reactor feed solution to TOS levels of 0.02M or lower. Variation in soluble sulfate concentrations in the range of 0.50-0.75M had no apparent effect on the level of supersaturation.

Utilizing these design factors in dilute mode with lime regeneration not only reduces or eliminates supersaturation, but also promotes a good reaction rate which generally improves the overall process performance parameters such as lime utilization, sulfate precipitation and solids properties. More specifically, the performance of the dilute lime mode relative to the important process performance characteristics is given below:

- SO_2 Removal -- SO_2 removal of 90% is easily achieved especially at low to medium inlet SO_2 levels. SO_2 removal is not as efficient as in a concentrated dual alkali mode (with the same scrubber configuration) because of the low active sodium concentration. The scrubber operation is more difficult to control due to the low buffering capacity of the dilute mode liquors. Higher calcium concentrations (in the range of 600-700 ppm Ca^{++}) present potential scaling problems in the scrubbing system. Operation of the scrubber in a high pH range (9-11) to promote good SO_2 removal results in some CO_2 absorption and potential carbonate scale formation. Increasing active sodium concentrations to provide more buffering can result in sulfite scale formation in the pH range of 8-11.

- Lime Utilization -- Lime utilization of 90% or higher is achievable when regenerating to hydroxide concentrations of about 0.1M with solutions containing sulfate in the range of 0.50-0.75M and using reactors with a minimum total holdup time of 60 minutes. Utilization increases as the residence time and sulfate concentration are increased. Solids recycle also helps increase lime utilization. However, TOS levels in the feed to the reactor should be held to 0.02M or less (by deliberate oxidation if necessary) to prevent retarding of the reaction rate by the sulfite.

- Oxidation/Sulfate Control -- Complete sulfate control is possible in this mode of operation at any rate of oxidation in the system. However, at very high scrubber oxidation rates, sulfite/bisulfite buffering is minimal and scrubber pH control becomes difficult. All other aspects of the process operation are improved by high oxidation rates (i.e., minimal TOS concentration in the feed to the regeneration reactor). Deliberate oxidation should be used to maintain TOS levels below about 0.02M. At sulfate concentrations in the range of 0.52-0.75M calcium sulfate (usually gypsum) was produced instead of a mixed calcium sulfite/calcium sulfate crystal, when TOS is maintained at or below 0.02M. At this point the calcium sulfate content of the solids is no longer limited by the apparent maximum content of 25-30% in the mixed crystal; 100% calcium sulfate can be produced.

- Solids Properties -- It is possible to produce excellent quality solids containing 60%-80% insoluble solids. Good solids properties are favored by the following conditions:

  - Low TOS in the reactor feed - less than 0.02M.

  - High sulfate in the reactor feed - 0.50-0.75M (high end of range favored).

  - Solids recycle - improves solids quality but increases the solids load and ultimately the size of the thickener.

  - Multistage reactor system - improves solids quality compared to same total residence time in a single stage.

  - High reactor residence time - 80% insoluble solids can be produced using a 90 minute residence time reactor.

- Sodium Losses -- In any application, increasing the insoluble solids content of the filter cake increases the effective number of displacement washes for any given amount of wash water available. By producing 75% insolubles solids in a high-sulfur coal application, roughly 5 displacement washes are available (as opposed to 2.5 displacement washes at 50% solids) permitting more effective cake washing; in low-sulfur coal applications even more wash water can be available. Consequently, sufficient wash water should be available to reduce the solubles content of the cake to under 2%; and down to the range of

0.5-1.5% solubles in low-sulfur coal applications. In such applications it may be possible to wash the filter cake to loss levels lower than those corresponding to sodium carbonate makeup levels required for softening of the regenerated liquor. A sodium carbonate makeup rate of 2-2.5% of the SO_2 removal rate provides sufficient carbonate to reduce the Ca^{++} concentration in the regenerated liquor by about 50 ppm, providing only minimum softening. Thus, sodium makeup (and ultimately the losses in the cake) may be controlled by softening requirements rather than by wash water availability or cake washability.

- System Operability/Reliability -- The dilute lime mode is inherently less reliable and more difficult to control than the concentrated lime mode. When appropriate care is taken to eliminate supersaturation, the calcium levels in the regenerated solution are in the range of 700 ppm. Only a minimum of softening is provided at low sodium carbonate makeup levels. Potential for scaling exists in the reactor system and associated auxiliaries and piping, and in the absorber. Absorber operation is less effective and more difficult to control than in the concentrated mode.

F. SOLIDS CHARACTERIZATION -- DILUTE AND CONCENTRATED LIME REGENERATION MODES

Limited testing was performed to characterize the basic physical and chemical properties of ash-free waste filter cakes produced in the two most successful dual alkali modes piloted -- concentrated and dilute active sodium modes with lime regeneration. Testing included: analysis of major chemical constituents; crystalline morphology via X-ray diffraction and scanning electron microscopy; unconfined compressive strength compaction moisture/density relationship; permeability; leaching behavior; and the effects of treatment with lime (or portland cement) and fly ash on the physical properties.

The concentrated mode filter cake that was tested was produced in the prototype system using the two-stage reactor. The cake was a mixture of calcium sulfite and sulfate (about 15% calcium sulfate) and contained 55% solids. The crystalline structure of the solids was rosette-like agglomerates of needles characteristic of the concentrated mode operation. X-ray diffraction data and chemical analyses indicate that the calcium sulfite and calcium sulfate were coprecipitated as a mixed crystal of hemihydrate salts. There was no evidence of any appreciable amount of gypsum ($CaSO_4 \cdot 2H_2O$) in the solids.

The dilute mode filter cake was essentially pure gypsum produced in the pilot plant under conditions of intentional oxidation. The solids crystals were monoclinic and the filter cake contained approximately 80% insoluble solids.

The mixed sulfite/sulfate solids had the appearance and physical properties similar to a silt-like soil and handled much like a moist powder.

The gypsum, on the other hand, was much more grainy and had the consistency of a sandy soil. The unconfined compressive strengths of both materials were in the range of typical soils, 10-15 psi; and both had optimum dry densities in the range of 75% solids. The coefficient of the permeability of the compacted sulfite/sulfate solids ranged from about 3×10^{-4} to 5×10^{-5} cm/second. The permeability of dual alkali gypsum was 2×10^{-5} cm/second. These values are within the range of published data on coefficients of permeability of gypsum and sulfite-rich solids produced in FGD systems.[1,2]

The treatment of the sulfite/sulfate filter cake was studied using various mixtures of lime (or portland cement), filter cake, and fly ash. This work showed that the concentrated mode solids could be treated in a fashion similar to the treatment of solids from direct lime and limestone scrubbing systems with similar effects on the mechanical properties. Testing performed on prototype system concentrated dual alkali solids by IU Conversion Systems (IUCS) indicate that the coefficient of permeability of treated filter cake was about 5×10^{-6} cm/second using standard treatment mixes.[2]

Accelerated leaching tests and elutriate analyses performed on untreated samples both at ADL and by IUCS showed that the initial and "steady-state" concentrations of soluble species that can be leached, notably total dissolved solids (TDS) and total oxidizable sulfur (TOS), will be very dependent upon the initial conditions and composition of the solids (as affected by the degree of cake washing, ratio of sulfate-to-sulfite, chloride concentration in the gas, etc.) and the manner of solids handling and disposal. TDS levels in the initial leachate can range from a few thousand ppm to about ten thousand ppm; and "steady-state" concentrations (after the first few pore volume displacements) can vary from a few hundred to approximately two thousand ppm. Similarly, TOS levels can range from essentially nil to up to 50 ppm. These concentrations are consistent with the range of published data for leachates from solids generated in direct lime and limestone scrubbing systems.

Testing performed by IUCS on the treatment of the filter cake indicated significant reductions in both initial and "steady-state" levels of TDS in leachates. Depending upon the type of treatment, reductions of 50% to 80% were observed.

In all physical properties testing performed at ADL, samples were prepared in accordance with standard soil-mechanics testing procedures. These procedures required, as a part of the sample preparation, the drying and rewetting of the filter cake to achieve a desired solids content. While the samples were dried at temperatures of 83°C to prevent loss of water of hydration, there is still concern that the drying/rewetting procedure resulted in some changes in the behavior of the material, particularly in the case of the rosette-like crystals produced in the concentrated mode operation. However, the results of these limited tests are believed to be indicative of the general behavior of the dual alkali solids. More exhaustive testing on both as-received samples and samples prepared in accordance with standard soil testing procedures is required to assess the effects of sample preparation on test results.

V. FINDINGS - TASK III, PROTOTYPE TEST PROGRAM

A. BACKGROUND

The 20-megawatt (nominal capacity) prototype system was designed and built by Combustion Equipment Associates, Inc. (CEA) and Arthur D. Little, Inc. (ADL) for The Southern Company Services, Inc. (SCS) and the Gulf Power Company. The purpose of the test program was to characterize and evaluate the performance of the dual alkali process operating in a concentrated active sodium mode with lime regeneration. The formal test program lasted a total of about 14 months and covered a variety of conditions, including operating with low-, medium-, and high-sulfur coal. The effects of both fluctuating gas loads and simultaneous particulate removal were also tested in conjunction with high-sulfur coal operation.

The operation of the system was evaluated with regard to the following performance characteristics used to evaluate all dual alkali modes, as discussed in Chapter I. While the overall operability and reliability were a principal concern, the system was not intended to be a demonstration unit to test the ultimate availability of such systems in full-scale applications. The test program was focused on evaluating the viability of the process technology and defining process capabilities and limitations. The process reliability and operability were, therefore, of importance primarily as they reflected process chemistry and operational problems related to process chemistry.

B. PROGRAM DESCRIPTION

1. System Design

The 20-megawatt prototype system was installed at Plant Scholz on Unit No. 1, a 40-megawatt (nominal capacity) Babcock and Wilcox pulverized-coal-fired power boiler. The boiler is equipped with a high-efficiency, sectionalized electrostatic precipitator. The system consisted of basically three process sections: scrubbing; absorbent regeneration; and waste solids dewatering. The scrubbing system contained a venturi followed by an absorption tower with two trays and a demister. The scrubber system was designed with the flexibility of operating either in a direct lime or limestone scrubbing mode as well as dual alkali. The venturi was included for testing simultaneous particulate and SO_2 removal. Modifications to the scrubber system following startup of the system provided for operation of the venturi alone by bypassing regenerated liquor around the absorber.

The regeneration system consisted of the CEA/ADL two-stage reactor system. Provisions were made for feeding dry or slurried hydrated lime to either or both reactors.

The waste solids dewatering system consisted of a thickener and a single rotary drum vacuum filter equipped with wash sprays. The thickener was

sized to handle 40 megawatts of capacity in contrast to the scrubbers, reactor and filter, which were designed for 20 megawatts.

The system was designed to operate in the concentrated active sodium mode on medium- and high-sulfur coal. In this mode, sulfate removal cannot be accomplished by precipitation of gypsum ($CaSO_4 \cdot 2H_2O$); rather, calcium sulfate is precipitated along with calcium sulfite, resulting in a mixed crystal of the two salts.

2. System Operation

The prototype system was started up on February 3, 1975 and was operated over a period of 17 months, through July 2, 1976. The EPA test program formally began in May 1975 and was completed in July 1976, after which the system was shut down. This report covers the entire 17 months of operation, including system startup and shakedown.

The operation of the system can be logically broken down into three discrete periods as defined by coal composition, flue gas conditions, and the characteristics of the system operation. The first period, from February through July 1975, covered system startup and shakedown. During these first six months of operation the boiler burned low-sulfur coal (average sulfur content corresponding to approximately 2.6 lbs SO_2/MM Btu). Sulfur dioxide concentrations in the flue gas averaged 1,050 ppm (range = 600-1,550 ppm) and oxygen levels averaged 7.5% (range = 5.0-11.0%), conditions well outside the range for which the process was originally designed. This represented a difficult test for a system operating in the concentrated active sodium mode because of the rich levels of oxidation experienced.

In the second operating period, lasting from September 1975 through early January 1976, the system was tested under relatively stable load conditions with the boiler firing a combination of medium- and low-sulfur coals (the average sulfur content of the coal fired corresponded to approximately 3.1 lbs SO_2/MM Btu). During this period the electrostatic precipitator was maintained in full service. Repairs to the boiler combustion air preheater and better control of combustion resulted in improved flue gas conditions in comparison to operations in Period 1. SO_2 levels in the flue gas during Period 2 averaged 1,250 ppm (range = 800-1,700 ppm), and oxygen concentrations average 6.0% (range = 4.5-9.5%).

In Period 3, which lasted from March through early July 1976, the system was tested on high-sulfur coal (average sulfur content in the coal corresponding to about 5.7 lbs SO_2/MM Btu). Flue gas SO_2 levels averaged about 2,250 ppm (range = 1,500-2,800 ppm), and oxygen concentrations averaged about 6.5% (range = 4.5-9.0%).

In addition to 10 weeks of operation at relatively stable load, testing during Period 3 consisted of three weeks of operation at fluctuating gas loads and two weeks of particulate testing. The fluctuating load

testing involved adjusting the gas flow to the system to four different levels according to a prearranged schedule roughly representative of the normal load swings of the Scholz boilers. The average gas rate handled during fluctuating load testing was 65%, as compared with 85-90% during the stable load periods. Particulate testing was performed during the last two weeks of the program to evaluate the effects of fly ash on the system performance (SO_2 removal, scale formation, oxidation, and waste cake properties) and to assess particulate removal efficiency and mist eliminator performance. During these two weeks the operation of the precipitator ranged from fully activated to completely deactivated.

C. SYSTEM PERFORMANCE

Overall, the performance of the system was excellent. The system demonstrated high SO_2 removal efficiency, high lime utilization, excellent waste cake properties, and very good overall availability. The various aspects of system performance are discussed below.

1. SO_2 Removal

SO_2 removal efficiencies at Plant Scholz confirm the high SO_2 removal capability of sodium solution scrubbing in the concentrated active sodium mode. With sodium solution scrubbing, achieving a given outlet SO_2 level (within the limit of the number of contact stages used) is essentially a matter of adjusting the operating pH of the scrubber system (by adjusting the feed forward rate or regenerated liquor pH). Over the 15 months between April 1975 and July 1976, the average SO_2 removal using both the venturi and absorber (with two trays) was 95.5% (for low-, medium-, and high-sulfur coal); with the venturi alone (low-sulfur coal only) SO_2 removal efficiency averaged 90.7%.

For the most part, when both the venturi and absorber were operated together, the venturi was used principally for quenching the gas, and the venturi pressure drop was maintained in the range of 4.5 to 7 inches of water. Under these conditions the pH of the venturi bleed liquor was maintained between 4.8 and 5.9 to ensure better than 90% SO_2 removal. With the low inlet SO_2 levels of Periods 1 and 2 (600-1,700 ppm) this resulted in outlet SO_2 levels generally ranging from 15 to 100 ppm. At the higher inlet SO_2 levels of Period 3 (1,500-2,800 ppm), the outlet SO_2 typically ranged from 25 to 150 ppm.

When the venturi alone was used (10-16 inches of water pressure drop), the bleed liquor was generally maintained at a pH above 5.7 to keep outlet SO_2 levels below 100 ppm.

2. Particulate Removal

The particulate removal capability of the scrubber system was tested with the venturi operated at both 12 and 17 inches of water pressure drop followed by the absorber containing two trays. Three ranges of inlet particulate loadings were tested (by partially or wholly

deenergizing the precipitator): 0.015-0.025 grains/standard cubic foot dry; 0.030-0.085 grs/scfd; and 2.3-3.6 grs/scfd. In general, outlet particulate loadings increased slightly with increasing inlet loadings, as would be expected. Outlet loadings ranged from 0.010-0.015 grs/scfd at the lowest inlet loadings to 0.024-0.037 grs/scfd at the highest inlet loadings. However, there was no statistical difference in outlet loadings between operations at 12 inches and 17 inches of pressure drop across the venturi throat (undoubtedly due, at least in part, to the two trays).

At these high venturi pressure drops, the SO_2 removal increased to an average of about 98% for the particulate test period (using high-sulfur coal).

3. Oxidation/Sulfate Control

a. Oxidation

Oxidation rates experienced in the prototype system were slightly lower than those observed in the pilot plant under similar conditions. As in the pilot operation, though, oxidation in the scrubber circuit accounted for 80-95% of that throughout the system. The principal variable affecting oxidation was the oxygen content of the flue gas, although the flue gas rate and the type of coal fired also had some effect.

With the low- and medium-sulfur coals fired in Periods 1 and 2, oxidation rates in the scrubber system ranged from about 180 ppm equivalent SO_2 ($\sim$230 ppm in the entire system) at 5% oxygen in the flue gas to about 370 ppm equivalent SO_2 ($\sim$420 ppm in the entire system) at 9% oxygen in the flue gas. The total system oxidation rates correspond to a range of 20% to 45% of the SO_2 removed for the average inlet levels for these periods. However, there was considerably more gas/liquid contacting provided in the scrubber system (venturi + two trays) than would normally be incorporated in an absorption system for a low sulfur coal application. This not only resulted in very low outlet SO_2 levels (typically less than 50 ppm) but also unnecessarily high rates of oxidation (as a percentage of SO_2 removed).

With the high-sulfur coal in Period 3, the absolute rate of oxidation in the scrubber system increased slightly. At 5% oxygen in the flue gas, oxidation in the scrubber system averaged about 200 ppm equivalent SO_2 ($\sim$250 ppm throughout the system); and at 9% oxygen, oxidation in the scrubber ran slightly over 500 ppm ($\sim$550 ppm throughout the system). These higher oxidation rates, though, represent lower percentages of oxidation in terms of SO_2 removed. For the average SO_2 removal in Period 3 these oxidation rates correspond to about 10% and 25% of the SO_2 removal, respectively.

As would be expected, the absolute rate of oxidation (mols/min) decreased with reductions in gas flow, although the percentage of SO_2 oxidized increased slightly. No effect of fly ash on oxidation was apparent during the particulate testing period.

b. Sulfate Precipitation

Precipitation of calcium sulfate measured in the reactor system showed that calcium sulfate could be coprecipitated with calcium sulfite at levels as high as 25% of the total calcium sulfur salts, indicating that the system was capable of keeping up with such levels of oxidation. The correlation of sulfate/sulfite content of the precipitated calcium salts to sulfate/sulfite concentrations in the reactor liquor was found to be:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\text{reactor solids}} \simeq 0.031 \left(\frac{[SO_4^{=}]}{[SO_3^{=}]}\right)_{\text{reactor liquor}} \qquad (14)$$

This degree of sulfate coprecipitation corresponds to about 85% of that observed in the pilot plant.

There was also a slight decrease in the calcium sulfate/sulfite ratio in the filter cake in comparison with that in the reactor product solids. The data indicate about a 15% decrease in the sulfate content between the reactor and filter. This is probably due to some dissolution of calcium sulfate during the long holdup in the thickener.

Overall, the sulfate formation oxidation/sulfate precipitation data show that the system is capable of keeping up with oxidation rates of up to 25% of the SO_2 removed--oxidation rates much higher than those anticipated for most medium and high sulfur coal applications. And the operation at the widely fluctuating conditions demonstrated the stability of the system chemistry and its ability to "self-adjust" to handle any oxidation rate up to 25% without operator intervention. As oxidation changed, the ratio of sulfate to active sodium in the liquor changed accordingly to increase or decrease the amount of calcium sulfate precipitated.

4. Waste Cake Properties

a. Solids Content

The solids content of the waste filter cake varied from 41% to 77% of the total cake weight. In general, the solids content of the cake varied with calcium sulfate content (decreasing with increasing calcium sulfate levels) and with variations and upsets in the filter operation. During stable load conditions the average solids content of the filter cakes produced in each successive operating period increased from 48% in Period 1 (low-sulfur coal) to 54% in Period 3 (high-sulfur coal). The inclusion of fly ash during simultaneous particulate removal in Period 3 increased the average solids content to about 57%. These averages include periods of minor filter upsets and partial loss of vacuum.

Under most all conditions the cake had the appearance and handling properties of a moist soil.

It was easily transferred from the storage pile to dump trucks using a front-end loader for transfer to the disposal pit.

b. Solubles Content

Wash efficiency tests performed on the prototype filter verified pilot plant results regarding the washability of the cake. The results show that the soluble solids levels in the cake can be readily reduced to 2-3% (dry cake basis) under controlled filter conditions using a wash ratio of about 2.5 (gals wash water/gal water occluded in the cake). The solubles level actually achieved on a continuous basis, though, were higher due to the limited capacity of the spray nozzles, system upsets, and inadequate operator attention to cake washing. Soluble solids levels in the cake throughout the program ranged from as low as 1.2% to as high as 12% of the dry cake weight, depending upon the degree of washing and the solids content of the filter cake. The average losses estimated for each operating period based upon cake analyses and overall material balances ranged from 4% (Period 2) to as high as 8% (estimated, Period 1). The average solubles losses, though, were biased upward by the fluctuating wash conditions. Long periods of adequate cake washing were more than offset by short periods of poor cake washing (due to occasional high rates of cake withdrawal required with the single filter to compensate for filter downtime, and inattention to wash water rates).

5. Sodium Makeup

The rate of sodium makeup to the system in comparison to the estimated sodium value losses in the filter cake provide a measure of the degree of closed-loop operation (as well as accountability in the overall material balances). Soda ash feed rates were closely monitored only during Periods 2 and 3. During Period 2 soda ash makeup rates represented about 8% of the total SO_2 removal (mols Na_2CO_3/mol ΔSO_2) compared with about 4.5% soda ash requirements based upon cake losses. The difference is attributed to pump seal leaks, a small thickener leak that developed during Period 2, and errors in the overall material balance. Entrainment losses of sodium (in entrained liquor) were negligible. As measured in both December 1975 and June 1976, entrainment losses were equivalent to less than 0.1% of the ΔSO_2 (as soda ash required). During Period 3 the material balance on sodium was almost completely closed. The soda ash required to makeup for cake losses was about 7% of the SO_2 removal (using an average wash ratio of 1.8) versus a soda ash feed rate of 8% of the SO_2 removal.

While soda ash requirements were slightly higher than desired due primarily to inadequate control of the filter operation, the relatively small soda ash requirements and the degree of closure in the soda ash material balance reflect a tight, closed-loop operation.

6. Power Consumption

Since the process included a venturi scrubber as well as additional pump capacity for operation in a direct lime or limestone mode, the power consumed in the dual alkali mode was greater than that which would be consumed in a system designed specifically as a dual alkali system. When operating at or near design gas flow, the system power consumption averaged 2.5-3.0% of the boiler output. Correcting for the additional pressure drop included with the venturi and the unnecessary pump capacity, the power consumed by the equipment actually required for this application was about 1.0% of the capacity of the boiler.

7. Operability/Reliability Potential

a. Availability

While the system was not operated for the purpose of achieving a high availability figure, the availability record of the system is impressive. Over the 17 months of operation the system logged more than 7,100 hours of operation, which corresponded to an overall availability of slightly higher than 70%. Most of the downtime occurred between the operating periods and resulted from equipment problems of a mechanical nature or problems caused by operation of the system well outside the design condition. The availability during the operating periods averaged about 90%. This availability is impressive, particularly in light of the fact that the only spare equipment was pumps (and replacement parts for unspared equipment were minimal); and that the system was called upon to operate about 70% of the time at conditions outside those for which it was designed.

The longest single outage (1,460 hours) occurred between Periods 1 and 2. During the end of Period 1, oxygen levels in the flue gas were running in the range of 8-10%, with inlet SO_2 levels depressed to 850-950 ppm. Because of the resulting high oxidation levels (as a percentage of SO_2 removal) the system was allowed to drift into a dilute active sodium mode, a mode for which it was not designed. The result was precipitation of gypsum and formation of some gypsum scale in the reactor tanks and piping. At the same time, mechanical problems in the scrubber required a shutdown of the system, and it was decided to await repair of the preheater and higher sulfur coal prior to restart of the system. There was also some delay in replacement parts, so the system remained down from mid-July through mid-September 1975. Such delays would not normally be encountered in full-scale applications with adequate sparing of equipment and maintenance of a reasonable inventory of spare parts.

Between Periods 2 and 3 the boiler was shut down for scheduled maintenance. The system remained out of service an additional month following boiler startup, again due to delays in shipments of replacement parts and equipment being overhauled.

b. Equipment Performance

Most of the problems encountered with equipment and instrumentation during the course of the test program were mechanical in nature and reflected design or fabrication oversights commonly associated with a prototype system. All but a few were resolved during the course of the test program by simple operational adjustments and/or equipment modifications.

Equipment

The most significant equipment problems encountered in the system involved the filter, vessel linings, scrubber control and block valves, and solids buildup in the first-stage reactor. Collectively, these accounted for the bulk of mechanical-related downtime and maintenance.

- The filter was the largest source of problems in the prototype system, but the problems resulted in few system outages due to the solids holdup capacity in the thickener, which allowed sufficient time for most filter-related maintenance work. Normally, filters do not require an inordinate amount of maintenance. However, a large part of the filtration equipment in the prototype system was fabricated out of fiberglass and plastic both because of the anticipated corrosion problems from the high chloride levels achieved in the tight, closed-loop operation (3,500-11,000 ppm Cl^-), and to minimize the cost for the short-term prototype test program. Fiberglass is not as sturdy as stainless steel, and there were failures at stress points in the construction as well as erosion of some of the plastic and fiberglass parts. Most of the problems occurred during Period 1 and the early part of Period 2. Modifications of the filter drum and tub by plant personnel, and overhaul of the filter drum by the manufacturer between Periods 2 and 3 either eliminated the problems or reduced them to routine, low-level maintenance.

- Erosion, cracks and pinholes occurred in glass flake linings various vessels in the system. Cracks and pinholes occurred in the absorber recycle tank and the thickener floor and walls. These were patched during interim periods and did not recur during the remainder of the test program. Erosion of lining occurred beneath the agitator in the second-stage reactor vessel and on the liquor redistribution shelf in the venturi. These linings were also patched in the interim between Periods 2 and 3, and the venturi tangential nozzles modified. No further erosion at either location was observed. There was also deterioration of the lining in the area of the quench zone at the gas inlet to the venturi. The cause of the failure may have been a combination of factors including poor application, inadequate surface preparation, and

severity of temperature and chemical attack. This failure suggests that corrosion-resistant metal alloys may be most suitable in such areas.

- Erosion and "debonding" of rubber linings occurred in control and block valves in the scrubber system. These failures were traced to the high degree of throttling to the control flow. (The valves were sized to accommodate the higher flows associated with direct lime slurry scrubbing.) These valves were replaced with 316 stainless steel valves prior to Period 3 and no further erosion or debonding occurred in the valves. There was also no corrosion or erosion of the 316 after the three and one-half months of service in Period 3.

- Buildup of product solids occurred in the first reactor throughout the test program. Through adjustments made to the reactor system and simulation of the operation in the ADL pilot plant, the cause of the problem was traced to poor agitation and operation during severe upset conditions (e.g., gross overfeeding of lime). While the buildup was never serious enough to cause a shutdown, it did require occasional cleaning. Improved agitation and better process control should reduce such buildup to, at worst, a semi-annual maintenance item. Such maintenance would not require system shutdown in large-scale systems where parallel reactor trains can be used, or the first reactor temporarily bypassed.

Instrumentation

Instrumentation problems primarily involved pH units, level transmitters, and the soda ash feed solution control system.

- The flow-through pH probes originally installed in the system were prone to plugging and/or erosion and failure of probe tips. The flow-through unit in the reactor system was replaced with an immersion unit, which proved to be much more reliable. Modification of take-off lines for flow-through units in the scrubber system and increasing the flow rate minimized problems with these units.

- The level transmitters originally installed were unreliable and required an inordinate amount of instrument maintenance. These were eventually replaced with Foxboro units, which proved to be much more reliable and less prone to failure of critical parts.

- A number of difficulties were encountered with the soda ash feed control system, some of which were related to the wide turndown range for which it was designed. None of the problems affected the operability of the system, since continuous, accurate control of makeup soda ash is not required to replace

the small sodium losses in the cake. The principal impact of the difficulties in the feed control system were in the accuracy of the material balances on sodium.

c. Ease of Operation

Ease of system operation was assessed throughout the program either during planned tests of system capabilities under differing conditions or indirectly through inadvertent process upsets and equipment malfunctions. The planned testing included:

- stable operation with low-, medium-, and high-sulfur coal;
- fluctuating load testing (30-100% of design gas rate) with high-sulfur coal; and
- simultaneous particulate removal with high-sulfur coal.

The results of this testing have been discussed.

Indirect measures of the system operability were also obtained during upset conditions. Upset conditions encountered included:

- wide, short-term fluctuations in inlet SO_2;
- wide swings in inlet oxygen concentration;
- inadvertent substitution of limestone for lime in the chemical storage silo;
- gross under- and overfeeding of lime; and
- short-term outages of the filter, first-stage reactor and various instruments with continued operation.

Operation during both the planned variations in system conditions and upsets served to demonstrate the basic stability of the system and the inherent ability of the concentrated lime mode dual alkali technology to withstand sudden (and extended) changes in operating conditions without loss of performance. Of particular note is the fact that close control of pH throughout the system is not required to ensure high SO_2 removal efficiency and prevent scaling. In fact, during some extended periods lasting up to a few days in length the system flows and makeup chemical feed rates were set by inlet and outlet SO_2 and trimmed according to pH's of samples taken from the reactor and scrubber twice per shift.

As oxidation rates changed (due to changes in inlet SO_2 or oxygen concentration of the flue gas), the system chemistry adjusted accordingly. The ratio of sulfate-to-active sodium in the system liquor simply shifted to effect the appropriate rate of calcium sulfate precipitation required (up to about 25% oxidation).

Similarly, operator errors in setting system flows or makeup chemical feed rates rarely had any immediate effect on system performance, and the effects were usually completely reversed simply by re-establishing proper system conditions.

d. Scale Potential

Due to the low calcium concentrations maintained throughout the system, there was little potential for scale formation. Other than the deposition of solids in the first-stage reactor (previously discussed) the only occurrence of scale formation in the system was the precipitation of calcium carbonate in the absorber during two extended periods when the scrubber system was inadvertently operated well outside the specified pH range. The calcium carbonate was completely dissolved within a few hours by returning the system to normal operating conditions and had no effect on system performance in any way.

The low scale potential, particularly in the scrubber system, is evidenced by the operation of the mist eliminator in the absorber. The mist eliminator was operated without any wash sprays (fresh water or liquor) for the last two operating periods (4,600 hours). No deposit of solids or scale of any form could be found on the mist eliminator following completion of the test program. Similarly, there was no deposit of solids on the reheat gas distributor downstream of the mist eliminator.

REFERENCES

1. Leo, P. P., and J. Rossoff. Control of Waste and Water Pollution from Power Plant Flue Gas Cleaning Systems: First Annual R&D Report, EPA-600/7-76-018, October, 1976.

2. Edwards, R. Personal Communication. I.U. Conversion Systems to Reed Edwards of the Southern Company Services, Inc., April, 1976.

GLOSSARY

Active Sodium - Sodium associated with anions involved in SO_2 absorption reactions and includes sulfite, bisulfite, hydroxide and carbonate/bicarbonate. Total active sodium concentration is calculated as follows:

$$[Na^+]_{active} = 2 \times ([Na_2SO_3] + [Na_2CO_3]) + [NaHSO_3] + [NaOH] + [NaHCO_3]$$

Active Sodium Capacity - The equivalent amount of SO_2 which can be theoretically absorbed by the active sodium, with conversion to $NaHSO_3$. Active sodium capacity is defined by:

$$[Na^+]_{active} \text{ capacity} = [Na_2SO_3] + 2 \times [Na_2CO_3] + [NaOH] + [NaHCO_3]$$

Calcium Utilization - The percentage of the calcium in the lime or limestone which is present in the solid product as a calcium-sulfur salt. Calcium utilization is defined as:

$$\text{Calcium Utilization} = \frac{\text{mols } (CaSO_3 + CaSO_4) \text{ generated}}{\text{mol Ca fed}} \times 100\%$$

Concentrated Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing $CaSO_3 \cdot \frac{1}{2}H_2O$ or a mixed crystal containing calcium sulfite and calcium sulfate hemihydrates, but not containing gypsum. Active sodium concentrations are usually higher than 0.15M Na^+ in concentrated mode solutions.

CSTR--Continuous Stirred Tank Reactor - A well-agitated, baffled reactor vessel having a uniform concentration of species throughout. At any time the concentrations in the effluent from a CSTR are equivalent to those within the vessel.

Dilute Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing gypsum ($CaSO_4 \cdot 2H_2O$). Active sodium concentrations are usually lower than 0.15M Na^+ in dilute mode solutions.

Sulfate Formation - The oxidation of sulfite. The level of sulfate formation relative to SO_2 absorption is given by:

$$\text{Sulfate Formation} = \frac{\text{mols } SO_3^{=} \text{ oxidized}}{\text{mol } SO_2 \text{ removed}} \times 100\%$$

Sulfate Precipitation - The formation of $CaSO_4 \cdot XH_2O$ in soluble solids. The level of sulfate precipitation in the overall scheme is given by the ratio of calcium sulfate to the total calcium-sulfur salts produced:

$$\text{Sulfate Precipitation} = \frac{\text{mols } CaSO_4}{\text{mol } CaSO_X}$$

TDS--Total Dissolved Solids - Equivalent to the sum of all soluble species.

TOS--Total Oxidizable Sulfur - Equivalent to the sum of all sulfite and bisulfite species.

APPLICABLE CONVERSION FACTORS

ENGLISH TO METRIC UNITS

British	Metric
5/9 (°F-32)	°C
1 ft	0.3048 meter
1 ft^2	0.0929 $meters^2$
1 ft^3	0.0283 $meters^3$
1 grain	0.0648 gram
1 in.	2.54 centimeters
1 in^2	6.452 $centimeters^2$
1 in^3	16.39 $centimeters^3$
1 lb (avoir.)	0.4536 kilogram
1 ton (long)	1.0160 metric tons
1 ton (short)	0.9072 metric tons
1 gal	3.7853 liters
1 Btu	252 calories

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16. ABSTRACT Volume I of the report is an executive summary of the results of a three-task program to investigate, characterize, and evaluate the basic process chemistry and the various operating modes of sodium-based dual alkali scrubbing processes. The tasks were: I, laboratory studies at both Arthur D. Little, Inc. (ADL) and IERL-RTP; II, pilot plant operations in a 1200 scfm system at ADL; and III, a prototype test program on a 20 MW dual alkali system at Plant Scholz. Dual alkali system operating modes on high and low sulfur fuel applications investigated included: concentrated and dilute dual alkali systems, lime and limestone regeneration, and slipstream sulfate treatment schemes. For each mode, the dual alkali process was characterized in terms of SO2 removal, chemical consumption, oxidation, sulfate precipitation and control, waste solids characteristics, and soluble solids losses.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Calcium Oxides	Air Pollution Control	13B	
Alkalies	Limestone	Stationary Sources	07D	08G
Sodium	Sulfates	Dual Alkali Process	07B	
Scrubbers	Tests	Plant Scholz	07A	14B
Desulfurization	Pilot Plants			13I
Sulfur Dioxide	Prototypes			

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