CLEAR LIQUOR SCRUBBING WITH ANHYDRITE PRODUCTION

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The U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC) and the Electric Power Research Institute (EPRI) are funding this project to develop an advanced flue gas desulfurization (FGD) process that has decreased capital and operating costs, higher SO_2 removal efficiency, and better byproduct solids quality than existing, commercially available technology. A clear liquor process (which uses a scrubbing liquid with no solids) will be used to accomplish this objective rather than a slurry liquor process (which contains solids). This clear liquor scrub-bing (CLS) project will focus on three research areas:

- Development of a clear liquor scrubbing process which uses a clear solution to remove SO_2 from flue gas and can be operated under either forced- or inhibited-oxidation conditions;
- Development of an anhydrite process that converts precipitated calcium sulfite to anhydrous calcium sulfate (anhydrite); and
- Development of an alkali/humidification process to remove HCl from flue gas upstream of the FGD system.

This paper describes the proposed processes and outlines the test approach planned for developing these processes.

Each of the three processes proposed in this program can benefit the power industry individually and are at different stages of development. The proposed program plans to develop each of the processes at the appropriate scale in Phase I. The anhydrite process will be developed beginning with bench-scale testing in the laboratory. After appropriate conditions have been identified which provide adequate kinetics data, the anhydrite process will be tested on a slip stream at the ECTC. The chloride removal process and the CLS process will be developed further using EPRI's Environmental Control Technology Center (ECTC) 4-MW pilot unit. Thus, all three processes will be tested on the pilot unit at the ECTC during Phase I but will not be operated in an integrated, steady-state manner. Approximately three months of test time has been allocated for this Phase I work. If all of the processes continue to appear favorable in Phase I, they will be combined and integrated at EPRI's ECTC during Phase II.

Figure 1 illustrates the basic flow diagram for the CLS process. This figure includes incorporation of the alkali/humidification process for HCl reduction and the anhydrite production process. However, as mentioned above, each of the three processes can be applied independently. Anhydrite laboratory work

has recently begun, but detailed results are not yet available. The three processes to be investigated in Phase I are described below followed by an outline of the Phase I test program approach.

Clear Liquor Scrubbing Process

The basic CLS concept is to recirculate clear liquor which contains a sufficient liquid-phase alkalinity to achieve the desired SO2 removal efficiency without the need for solid-phase alkalinity. The liquor then flows to a limestone reactor and solid-liquid separator which precipitates a calcium-sulfur solid and returns clear liquor to the scrubber. The CLS process can be operated as an inhibited-oxidation system (calcium sulfite production) or as a forced-oxidation system (gypsum production). Either of these two products can then be converted to anhydrite; however, the economics of the anhydrite process are more favorable if calcium sulfite is produced in the CLS system.

To be successful, the CLS process must generate solids that are easily dewatered at high rates so that the high volume of liquor passing through the regeneration system does not require large or expensive tanks and equipment. Other key aspects for the success of the process include low consumption rates of the buffer, low L/G in the scrubber, and control of the chemistry to achieve good utilization and low scaling potential. The CLS process has been developed to date using the 0.4-MW mini-pilot system at EPRI's ECTC.

The CLS process was tested using the mini-pilot system under both inhibited-oxidation and forced oxidation conditions. These tests identified operating conditions that provided the best process performance. Under inhibited-oxidation conditions, a solids residence time of 30 to 40 hours is desirable to minimize scaling potential. The calcium sulfite relative saturation should be 4 to 5.

Based on the previous studies of the CLS process, several issues require further investigation. The first need is to verify the findings observed on the mini-pilot system on the pilot system which is 10 times larger. Full-scale design criteria need to be developed and refined at the 4-MW pilot scale before a full-scale demonstration is attempted. Variables to be tested at the larger scale include residence time, pH, suspended solids concentration, recycle ratio, and degree of agitation. In addition, the potential of combining the CLS process with the anhydrite process needs to be investigated. The high TDS concentration necessary for the anhydrite process may have a negative effect on the calcium sulfite solids properties in the CLS process.

Anhydrite Process

As shown in Figure 1, a process which produces anhydrous calcium sulfate (anhydrite) can be added to the CLS process. The anhydrite process could potentially be added to any conventional FGD system. Potential advantages of crystallizing anhydrite rather than gypsum from solution include the following: saving roughly $10/ton over thermally dehydrating gypsum, producing a material of lesser specific volume than gypsum, potentially displacing gypsum in some commercial applications, and producing a material for different commercial application than gypsum. These potential advantages are somewhat speculative because the anhydrite market is currently small relative to that of gypsum. However, if a relatively cheap source of anhydrite is developed, the use of anhydrite could increase in several different applications.

In a solution saturated with calcium and sulfate, anhydrite, rather than gypsum, is the thermodynamically stable form above about 100°F. However, typical forced-oxidation systems operating at 120°F-140°F produce only gypsum. The gypsum product results because the kinetics of gypsum precipitation are very

fast relative to the anhydrite precipitation kinetics. Figure 2 shows the solubility of gypsum and anhydrite as a function of temperature and ionic strength. Both solids become more soluble at lower temperatures, but only gypsum solubility is affected by ionic strength. This property is key to the anhydrite process.

In the proposed process, calcium sulfite produced in the CLS process is converted to anhydrite in a secondary reaction tank by oxidation of sulfite to sulfate and subsequent precipitation of anhy-drite. As discussed above, the kinetics of anhydrite precipitation are relatively slow at typical FGD operating conditions. To increase the precipitation rate of anhydrite, the process must be operated at an elevated temperature (160-180°F) and at a high ionic strength. As shown in Figure 2, gypsum solubility increases with ionic strength while anhydrite solubility does not. Based on information in Figure 2, conditions can be chosen that provide a driving force for anhydrite precipitation while the solution remains subsaturated with respect to gypsum (i.e., gypsum will not be formed). Points A and B in Figure 2 represent such points at lower and higher ionic strengths, respectively. The driving force for anhydrite precipitation is represented by the distance between either Point A or B and the solid line. By increasing the solution ionic strength, the driving force for anhydrite precipitation can be increased without forming gypsum solids.

Since typical systems operate at 120-140°F due to the adiabatic saturation temperature of the flue gas, an outside source of heat must be used to achieve the elevated temperature required for anhydrite production. In the proposed process, the exothermic oxidation of sulfite to sulfate will be used to generate the higher temperature. Gypsum produced in a conventional forced-oxidation system could also be converted to anhydrite; however, since the heat of reaction from sulfite to sulfate is not available in gypsum production, an outside heat source would be required which would affect the process economics.

Previously conducted batch tests determined the precipitation rate of anhydrite at 140°F from a high ionic strength solution. Based on these data, an anhydrite precipitation rate was calculated from the slope of a fitted exponential function. This rate was sufficiently high to warrant further investigation to determine how the rate might be further increased. The success of the anhydrite process depends on finding a set of operating conditions under which the anhydrite precipitation rate is sufficiently fast to yield an economically sized reaction tank and which minimizes gypsum production.

Alkali/Humidification Process

Maintaining a low chloride concentration in a FGD system has potential benefits. Corrosion should be minimized at low concentrations which may allow materials of construction to be cheaper. In limestone systems, the limestone utilization will generally be higher. Finally, the scaling potential is reduced in the CLS process.

EPRI has examined a number of chloride control options including prescrubbing, tail-end separation or concentration, and injection of scrubber blowdown into the flue gas. The first two options are relatively expensive and result in some waste water streams. The last option has been tested with limited success, but chloride removal is limited by off-gassing of HCl in the process of drying the liquid.

The proposed chloride removal process involves injection of an alkaline slurry upstream of an ESP or other particulate removal device. HCl in the flue gas reacts with the alkali to form a solid which is dried by the flue gas and collected in the particulate removal device. EPRI has developed a similar process to react flue gas SO_3 with alkali reagent to mitigate opacity problems and has completed considerable work on the effect of injection on SO_2 removal.

Proposed Test Approach

The general test approaches for the chloride removal process, the CLS process, and the anhydrite process are described below.

Figure 3 illustrates the ECTC process configuration to be used for investigating the chloride control with alkali injection process. Important variables in this process include alkali reagent type (lime or limestone), reagent stoichiometry, approach to saturation temperature (amount of water injection), air-to-slurry ratio (droplet size), and residence time. Each of these variables can be tested using the proposed configuration. The ECTC flexibility also allows the chloride control process to be tested simultaneously with the CLS process.

The chloride removal tests will be conducted for 4 to 8 hours during the day. The ECTC has an on-line HCl analyzer so that the flue gas HCl concentration both upstream and downstream of alkali injection can be easily measured; therefore, HCl removal can be easily measured at a variety of operating conditions. Variations in reagent stoichiometry will occasionally be verified by analytical measurement of calcium and chloride in the spray dryer solids. The gas flow can be adjusted to vary the residence time from about 1 second to 10 seconds. Since lime slurry is known to effectively remove HCl above flue gas temperatures of 200°F, the first test will deter-mine if limestone slurry can achieve similar performance at any approach temperature in the spray dryer (maximum residence time). If limestone is successful in the spray dryer, it will be included in the parametric tests. If not, lime will be the only reagent tested.

Figure 4 illustrates the ECTC process configuration for the CLS process without anhydrite production. The detailed gas flow and absorber configuration was shown in Figure 3. This CLS configuration separates the limestone and solids reactor from thickener/clarification operations so that important design information can be developed for each. Phase I testing will focus on the sizing criteria for a commercial solids reactor/clarifier and on identifying the higher ionic strength operating conditions required for the anhydrite process. A reactor which incorporates crystallization and dewatering in a single vessel and full integration of the anhydrite process will be included in Phase II.

Testing with the forced-oxidation ECTC process will focus on the solids properties produced and the optimum reaction-clarification vessel characteristics. Test variables will include residence time (by varying both the system volume and solids concentration), degree of agitation, and pH. Analytical measurements will be taken to ensure that appropriate conditions are being maintained throughout each test. After steady-state is achieved (three solid-phase residence times), three sets of final samples will be taken to allow statistical analyses to be performed with the results. Final samples include complete solid and liquid analyses (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_3^{2-}, SO_4^{2-}, and CO_3^{2-}), settling rate (to determine unit area), and filtration rate. Scaling coupons will be used to directly measure the scaling tendency of various operating conditions.

Following gypsum testing, the inhibited-oxidation CLS process will be tested with the ionic strength required for the anhydrite process. The focus will be on achieving good solids properties with the more elevated sulfate concentrations caused by oxidation in the anhydrite process. Residence time, suspended solids concentration, and recycle rate will be adjusted to achieve clear liquor scrubbing solution and concentrated underflow slurry. During Phase II, both the gypsum and sulfite CLS processes will be integrated with the anhydrite process to determine the optimum process for commercialization.

Development of the anhydrite process will begin with a series of batch and flow-through reactor tests in

the laboratory. The objective of these tests will be to provide kinetic data over a range of operating conditions. Laboratory batch tests have recently been completed; however, interpretation of the data is not yet complete. Test variables included solution ionic strength, temperature, and initial liquid-phase calcium-to-sulfate ratio. These tests were conducted by generating the desired initial solution composition with reagent grade chemicals and seeding the batch reactor with anhydrite. The anhydrite seed material was generated in the lab by thermally converting gypsum in a high ionic strength solution at 80-90°C. Complete conversion of the gypsum to anhydrite was confirmed using thermal gravimetric analysis (TGA) and Infrared (IR) spectroscopy. During each batch test, the liquid calcium and sulfate concentrations were measured with time by analyzing liquid samples with either atomic absorption spectroscopy (AA) or ion chromatography (IC). Changes in the calcium and/or sulfate concentration with time yield the anhydrite precipitation rate. Solids collected at the end of each test were analyzed using TGA and IR to con-firm that no gypsum was generated.

Based on the batch test results, laboratory flow-through reactor tests will be conducted at the most promising conditions. Variables to be tested include temperature, ionic strength, residence time, solids loading, and seed crystal size. These tests will provide data to determine the rate form of the precipitation kinetics and the optimum conditions for pilot-scale testing. Liquid flow-through tests generally provide more realistic kinetic data than batch tests since the data is generated at a constant liquid composition (i.e., constant anhydrite relative saturation).

Figure 5 illustrates the configuration to be used during the flow-through tests. The desired solution composition will be established, and a known charge of anhydrite seed material will be added to the reactor at the beginning of each test. Throughout each test, liquid will be filtered from the reaction vessel while “fresh” solution, saturated with respect to gypsum, is added to the reaction vessel. In this way, these experiments will approach steady-state with respect to the solution chemistry. Provided the charge of seed material is large relative to the mass of anhydrite precipitated during the test, the change in solid surface area should be small, and changes in the soluble species concentration should also be small. The rate of reaction can be determined by a liquid-phase material balance between the inlet and outlet streams. The weight percent solids will be measured at the beginning and end of each test to confirm the liquid-phase measurements, although the error in the solid-phase balance will be much larger given the relatively small change in suspended solids concentration.

Provided that each of the three processes continues to show promise after Phase I testing is complete, the three processes will be integrated during Phase II testing. This testing will be completed at EPRI’s ECTC using the 4-MW pilot unit. Based on the CLS results and anhydrite kinetic results, appropriately sized equipment will be designed for these tests.

Graphics and diagrams are to be entered at a later date

Figure 1 Clear Liquor Scrubbing with Anhydrite Production

Figure 2 Calcium Sulfate Solubility Data

Figure 3 ECTC Pilot Wet FGD Gas Path

Figure 4 Separate Reactor CLS Process Flow Diagram

Figure 5 Bench-Scale Flow-Through Crystallizer