RESULTS OF FULL-SCALE UTILITY FGD SO_2 REMOVAL UPGRADE TESTING

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INTRODUCTION

The U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) have contracted with Radian Corporation to conduct full-scale testing, process modeling, and economic evaluations of six utility flue gas desulfurization (FGD) systems. The project objective is to evaluate low capital cost upgrades for achieving up to 98% sulfur dioxide (SO_2) removal efficiency in existing FGD systems. The six systems include a variety of absorber types and FGD operating modes.

The testing is intended to demonstrate that upgrades such as performance additives, mechanical modifications, or a combination of these are viable means of increasing SO_2 removal at low cost. The cost-effectiveness of each upgrade is being evaluated on the basis of test results and/or process model predictions for upgraded performance, and utility-specific operating and maintenance costs. If high SO_2 removal at low cost is successfully demonstrated, SO_2 removal upgrades may be used by utilities with existing FGD systems as an approach for compliance with Phase 2 of Title IV of the Clean Air Act (CAA) Amendments of 1990.

This paper provides an update of the results for efforts completed to date. Results from the first two sites were presented at last year's conference[1], so these sites will not be discussed again. This paper presents results from the third, fourth, and fifth sites. Efforts for the sixth site (NYSEG's Kintigh Station) have not yet begun, so this site is not discussed.

EXPERIMENTAL METHODS

The test program at each FGD system typically consists of three phases. The first phase is baseline testing where the SO_2 removal performance of a single, representative absorber module is measured at normal operating conditions. The baseline tests also measure SO_2 removal efficiencies over a range of conditions, such as varied recirculating slurry pH set points and absorber liquid-to-gas (L/G) ratios, to obtain data to calibrate EPRI's FGDPRISM (FGD Process Integration and Simulation Model) to that system. The calibrated model is then used to predict the SO_2 removal capabilities of the system with upgrades. The best upgrade is selected and a parametric test series is run to verify at full scale the effectiveness of that upgrade. If the upgrade involves performance additives, systemwide additive consumption tests are conducted as the third phase of testing. These results are used to perform economic evaluations of the costs for achieving high SO_2 removal efficiencies with each upgrade. The cost-effectiveness of the upgrades is evaluated by comparing them with the projected market price of SO_2 allowance purchases.

The following describes three of the six full-scale utility FGD systems included in the program, and the testing conducted at those sites. The first two sites tested were described in the paper for the July 1993 conference[1]. No testing has begun at the sixth site.

Southwest Electric Power Company's (SWEPCo) Pirkey Station. The Henry W. Pirkey Station is a 720-MW mine-mouth lignite-fired unit. The FGD system consists of four modules that normally treat approximately 70 to 80% of the flue gas, bypassing the remainder directly to the stack. The amount bypassed is varied to control the outlet emission rate. The UOP dual-loop absorbers have a perforated-plate tray in each upper loop. A flow diagram for the unit is shown in Figure 1. The SO_2 removal across each absorber is typically 90+%. The performance goal for this test program was a systemwide SO_2 removal efficiency of 98%.

Baseline, parametric, and additive consumption tests were conducted at the Pirkey Station. Primary baseline test variables were upper- and lower-loop slurry pH set points. Parametric tests were conducted with both DBA and sodium formate additives. For each additive, test variables included pH set points and additive concentrations. Based on parametric test results and delivered additive costs for this site, DBA was selected over sodium formate as the more cost-effective additive. A systemwide DBA consumption test was subsequently conducted.

PSI Energy's Gibson Station. Unit 5 at PSI Energy's Gibson Station is a 450-MW unit that normally fires a 3.5% sulfur coal. The FGD system is a Kellogg/Weir design where the flue gas flows horizontally through rectangular cross-section absorbers. The recirculating slurry is introduced through spray headers at the top of the absorber; the spray is directed across the flue gas flow. Limestone reagent is used, but dolomitic lime is slaked and mixed with the limestone slurry to introduce magnesium as an additive for enhancing SO_2 removal efficiency. The unit operates in an inhibited-sulfite-oxidation mode; elemental sulfur is added for in situ generation of thiosulfate ion. At full load ,the unit can operate with either four modules in service or with one off-line as a spare. A portion of the flue gas bypasses all four absorbers and goes directly to the stack. A flow diagram illustrating the unit is shown in Figure 2.

The system SO_2 removal efficiency is typically about 80%. The performance goal for this program was to raise the SO_2 removal efficiency to 95%. To achieve this goal, both sodium formate and DBA were tested as a supplement to the magnesium additive.

The baseline test variables included slurry pH set points, absorber flue gas velocity (corresponding to either three or four modules in service at full load), and L/G ratio (varied with flue gas velocity or with either three or four slurry recirculation pumps and spray headers in service per module). Baseline test results were used to calibrate FGDPRISM, which indicated that either sodium formate or DBA additive should allow 95% SO_2 removal to be attained. A parametric test series was conducted with sodium formate additive. Test variables included slurry pH, formate concentration, flue gas velocity, and L/G ratio. Following these tests, a systemwide sodium formate consumption test was conducted. A DBA performance and consumption test was subsequently conducted in February and March 1994.

Duquesne Light's Elrama Station. The FGD system at the Elrama Station treats flue gas from approximately 500-MW of generating capacity firing a 1.9% sulfur coal. The FGD system has five venturi scrubber modules, four of which normally operate at full load. The system uses magnesium-enhanced lime reagent, and operates with inhibited-oxidation by using elemental sulfur to generate thiosulfate ion. Figure 3 is a flow diagram for the system. About 86% overall SO_2 removal is typically achieved. The SO_2 removal is limited by gas/liquid contact unless the venturis are operated at high pressure drop to generate very fine slurry droplets. The performance goal for this program was to raise the SO_2 removal to 95%.

The baseline test variables included slurry pH, venturi pressure drop, and recirculating liquor thiosulfate and magnesium levels. After the baseline tests, the calibrated FGDPRISM model was used to evaluate potential upgrade options. Increased thiosulfate concentrations and increased venturi pressure drop were identified as potentially cost-effective upgrades. These variables were evaluated at normal and low pH set points in parametric tests conducted in March 1994. DBA addition was not predicted to be cost-effective for this system, primarily because it operates with a relatively open water balance (relatively high liquor blowdown rates). The expected high solution loss rates make DBA addition prohibitively expensive.

RESULTS AND DISCUSSION

Test results and the results of economic evaluations of upgrade options are presented and discussed for the Pirkey, Gibson, and Elrama sites. However, some testing at the Gibson and Elrama sites was just completed in March 1994, so not all of these results are available yet.

SWEPCo's Pirkey Station. During baseline tests at the normal pH set points of 5.5 in the lower loop and 6.3 in the upper loop, the average overall SO_2 removal efficiency across the test module was surprisingly high--about 97%. In the DBA parametric tests, the module SO_2 removal efficiency was increased to 98% by adding DBA to a concentration of about 400 ppm in both loops. In the sodium formate parametric tests, equivalent SO_2 removal efficiencies were achieved at similar formate ion concentrations. Both additives had significant beneficial effects on system operation, including increased limestone utilization at a given operating pH and reduced sulfite oxidation percentages. Oxidation percentages were observed to drop from an undesirable level of 15 to 20% to a more desirable 10%. At this lower percent oxidation, the system operates subsaturated with respect to gypsum, reducing the potential for scaling. In fact, during these tests the flue gas pressure drop across the absorbers decreased measurably, presumably due to the dissolution of gypsum scale that had been present in the absorbers.

Because of lower delivered costs for this site, DBA appeared to be the more cost-effective additive, and DBA was evaluated in the subsequent consumption test. The test was conducted at an average DBA concentration of 1100 ppm, which resulted in an average overall system SO_2 removal of 98% at reduced pH set points of 6.0 in the upper loop and 5.2 in the lower loop. Lower pH set points were selected to achieve high limestone utilization (95+%), while maintaining high overall SO_2 removal levels and low sulfite oxidation percentages (<10%) with the DBA additive. To achieve 98% SO_2 removal efficiency across the entire FGD system, the unit was operated with no flue gas bypass. On an SO_2 removal basis, the overall DBA consumption was 10.9 lb/ton of SO_2 removed; 1.9 lb/ton of SO_2 removed was lost with the filter cake liquor; and 9 lb/ton was a nonsolution (degradation and coprecipitation) loss.

In the subsequent economic evaluation, upgrade options considered for the Pirkey FGD system included merely operating without flue gas bypass at normal conditions, or operating without bypass while adding DBA to the system. By just closing the bypass, the Pirkey FGD system could average 98% overall SO_2 removal at an incremental cost of about $42/ton of additional

SO_2 removed. With 500 ppm of DBA additive and the current pH set points, or 1000 ppm of DBA and lower pH set points (6.0 for the upper loop and 5.2 for the lower loop), 99% overall SO_2 removal level could be achieved. For either of these cases, the incremental costs would be approximately $40/ton of additional SO_2 removed. Therefore, all three options could very cost-effectively meet or exceed the target of 98% overall SO_2 removal. However, the cases involving DBA addition would be preferable because of additional benefits from scale-free operation, resulting because of the lower sulfite oxidation percentage during DBA addition.

PSI Energy's Gibson Station. Baseline testing showed that the SO_2 removal across a single module was approximately 86%. This was at the normal recirculating slurry pH set point of 5.3 and for full-load operation with three modules and with all four recirculating pumps and spray headers in service. The unit was firing a coal with lower, 2.5% sulfur content during these tests. During the later sodium formate parametric and consumption tests, a coal with the normal 3.5% sulfur content was fired. These tests showed that 95% SO_2 removal could be achieved with 1500 ppm of formate ion in the recirculating slurry liquor, while operating with the normal pH set point, all four recirculation pumps and headers in service, and four modules in service at full load. A maximum of 97.4% removal was measured with four modules and pumps in service, a higher 5.6 pH set point, and a high 5000 ppm formate ion concentration.

The conditions for the systemwide formate consumption test included four-module operation, a pH set point of 5.6, an 1100 ppm formate ion concentration, and four pumps in service on each module. The system SO_2 removal averaged 93.4%; it is estimated that the SO_2 removal across the absorbers was 96%, but the overall removal was limited by a small amount of flue gas bypass (approximately 3% of total gas flow) due the "open bypass" duct configuration at Gibson. Future improvements in fan controls should lower this minimum bypass amount to about 1%, which should allow 95% overall SO_2 removal at these conditions. The formate consumption rate averaged 9.5 lb/ton of SO_2 removed (as sodium formate). Of this, 64% was solution loss with liquor adhered to the dewatered filter cake; the remaining 36% (3.4 lb/ton as sodium formate) was nonsolution loss (primarily coprecipitation and vaporization).

A DBA additive performance and consumption test was subsequently conducted, at a normal pH of 5.4 and with four modules in service. The average unit load was 540-MW. The overall SO_2 removal averaged 91%, but the average absorber SO_2 removal was estimated at 97%. The overall SO_2 removal was lowered because of approximately 6.5% flue gas bypass. The average total DBA consumption rate was estimated to have been 8.7 lbs of DBA per ton of SO_2 removed. The theoretical (solution) losses from the FGD system were about 28% of the total (2.4 lbs of DBA per ton of SO_2 removed), and the nonsolution losses (primarily coprecipitation and degradation) were about 72% (6.3 lbs of DBA per ton of SO_2 removed).

The economics of achieving 95% or greater SO_2 removal with the Gibson FGD system were evaluated after the sodium formate parametric test series, but have not yet been repeated with the DBA additive consumption test results now available. With sodium formate additive, it was estimated that 95% SO_2 removal could be achieved at an incremental cost of approximately $63/ton of additional SO_2 removed. Similar SO_2 removal performance could be achieved without formate additive with just a higher pH set point. However, limited limestone ball mill capacity at this site makes this a less attractive option. Preliminary economics based on the available results from the DBA consumption test indicate that similar cost-effectiveness could be achieved with DBA additive rather than sodium formate.

Duquesne Light Company's Elrama Station. The baseline tests showed that at normal conditions (pH 7.2, ~170 ppm sodium thiosulfate, 10 in. H_2O venturi pressure drop) and with a 1.5 to 1.8% coal, the test absorber averaged 86.1% SO_2 removal. The SO_2 removal increased to about 90% by raising the pH set point to 8.0, or to 92% at the normal pH by increasing the venturi pressure drop to an indicated 18 in. H_2O. During the parametric test series, at baseline conditions the average SO_2 removal was significantly higher at 90.7% (compared to the previous 86.1%). The increase in removal efficiency between the baseline and parametric tests is believed to be a result of mechanical differences between the two scrubber modules tested, such as relative cleanliness, number of throat dampers working, etc.

During the parametric test series, both increased thiosulfate concentrations and increased venturi pressure drop improved the SO_2 removal efficiency. With a sodium thiosulfate concentration of roughly 1500 ppm, the removal efficiency increased to 92.7%. The increase in removal is actually caused by reduced sulfite oxidation and an increase in dissolved sulfite concentration. However, the sulfite analyses have not yet been completed and the sulfite concentrations achieved are not yet known. Operating at a sodium thiosulfate concentration of roughly 1500 ppm and an increased venturi pressure drop (12 in. H_2O) raised the SO_2 removal efficiency to 94.0%. This represented the highest removal efficiency measured, and was near the target of 95% for the test program.

The economic evaluations completed to date for this site should be considered preliminary. The full-scale tests were only recently completed, and have not yet been used to verify the FGDPRISM model predictions for the effects of the upgrade options considered. The incremental costs for additional SO_2 removal are, in general, higher for this site than for the previous sites. This is because a more expensive reagent is used (magnesium-promoted lime rather than limestone) and disposal costs are higher because of poorer by-product dewatering properties with this reagent. Both of these expenses increase in direct proportion to the quantity of SO_2 removed. Consequently, the minimum cost for additional SO_2 removal by this system (based on increased reagent and waste disposal costs alone) is estimated at $106/ton.

Higher thiosulfate concentrations improve SO_2 removal by reducing sulfite oxidation, which raises liquid-phase sulfite concentrations. The costs associated with this upgrade are minor, as thiosulfate is generated in situ by the addition of elemental sulfur emulsion, a relatively low-cost additive. The preliminary economics for this option indicated that additional SO_2 removed by adding more elemental sulfur emulsion would be achieved at an incremental cost of only $15/ton (in addition to the cost of $106/ton for additional lime and waste disposal).

The effect of higher venturi pressure drop is primarily to produce smaller slurry droplets within the venturi throat, which increases the surface area available for mass transfer. However, increased pressure drop also results in greater fan power consumption. The preliminary economics for this upgrade, based strictly on the FGDPRISM model results, indicate that additional SO_2 removal achieved by raising the venturi pressure drop comes at a cost of about $125/ton (plus the $106/ton for additional lime and waste disposal).

CONCLUSIONS

The results from this program to date show that upgrades to existing FGD systems can be a very cost-effective component of a utility's strategy for complying with the CAA Amendments of 1990. Table 1 provides a summary of these results, including results for the two sites discussed in last year's paper (Big Bend Station and Merom Station). For the first four sites (including Big Bend and Merom), the goal of cost-effectively achieving 95 to 98% overall SO_2 removal has been met. Two sites have exceeded this goal, with 99% overall SO_2 removal appearing to be very cost-effective. DBA and sodium formate additives have been the most effective low-cost upgrade options for these sites. At the fifth site, the goal was nearly met, with a maximum SO_2 removal efficiency of 94% being attained.

The costs for achieving high SO_2 removal levels are very attractive. The incremental costs for the first four sites range from \$50/ton to \$70/ton of additional SO_2 removed. For the fifth site, the costs have not been calculated, but the most cost-effective option will probably show incremental costs in the range of \$125 to \$150/ton. In the first EPA auction for SO_2 allowances, the average successful bid price was \$150/ton. EPRI estimates that at the beginning of Phase 2 for the CAA Amendments (the years 2000 through 2005), SO_2 allowance market prices will range from \$250/ton to \$500/ton of SO_2 in 1992 dollars[2]. Furthermore, we estimate that the cost of generating SO_2 allowances by installing new FGD systems on units firing medium- to high-sulfur coal would be at the upper end of this range. SO_2 allowances generated at a cost of less than \$150/ton in existing FGD systems should be very desirable.

The amount of SO_2 allowances that can be generated by upgrading existing FGD systems can be substantial. At the Pirkey Station, over 21,000 tons/yr of additional allowances can be generated, which would be sufficient to completely offset the Phase 2 SO_2 emissions from a 250-MW unit with no FGD system firing a medium-sulfur coal. At an allowance value of \$250/ton of SO_2, the additional allowances generated by high-efficiency FGD operation at the Pirkey Station would have an estimated net annual value (beyond the cost of generating the allowances) of over \$4,000,000.

These results are very encouraging. Several of the six utilities already plan to implement the optimum upgrade option for their site. The results from these sites may be applicable to a number of other existing FGD systems. Furthermore, the methodology applied in this program can be applied to any FGD system to evaluate the potential for cost-effectively upgrading its performance. DOE and EPRI will cohost workshops (June 94 in Dallas and September 94 in Pittsburgh) to help transfer the findings of this program to the electric utility industry and to help other utilities develop upgrade evaluation programs for their systems.

REFERENCES

1. G. Blythe, J. Lundeen, and J. Phillips, "High-Efficiency SO_2 Removal Testing," paper presented at the Ninth Annual Coal Preparation, Utilization and Environmental Control Contractors' Conference, Pittsburgh, PA, July 19-22, 1993.

2. I. Torrens and J. Platt, "Update on Electric Utility Response to the CAAA," ECS Update, No. 30, p.3, Fall 1993.

Table 1. Summary of SO_2 Removal Upgrade Project Results

Utility	Station (Unit)	Absorber Type	Reagent	Oxidation Mode	Observed Base SO_2 Removal	Upgrade Options	Optimum SO_2 Removal	Estimated Incremental Cost of Additional SO_2 Removed, $/ton	Additional SO_2 Removed, tons/yr
Tampa Electric	Big Bend (#4)	Dual-loop, Packed	Limestone	Forced	94	DBA Additive	99	65	4400
Hoosier Energy	Merom (#1 and #2)	Co-current, Packed	Limestone	Inhibited	83 [1]	DBA Additive	97	61	15,100
SWEPCo	Pirkey	Dual-loop, Tray	Limestone	Inhibited	80 [2]	DBA Additive	99	39	21,200
PSI Energy	Gibson (#5)	Horizontal Spray Tower	Limestone	Inhibited	80 [3]	Sodium Formate Additive [4]	95	63	15,100
Duquesne Light	Elrama	Venturi	Mg-Lime	Inhibited	86 to 91	Increase in Thiosulfate Level, Venturi Pressure Drop	NA	> 106 [5]	NA
NYSEG	Kintigh	Vertical Spray Tower	Limestone	Inhibited	NA	NA	NA	NA	NA

[1] Includes the effects of flue gas bypass; SO_2 removal across the test module was measured at 86 to 90%.
[2] Includes the effects of flue gas bypass; SO_2 removal across the test module was measured at 97%.
[3] Includes the effects of flue gas bypass; SO_2 removal across the test module was measured at 86%.
[4] DBA additive has also recently been tested, and also appears to be an attractive upgrade option.
[5] Assumes that the upgrade option will not measurably affect lime utilization as dewatered byproduct moisture content.

NA = Results not yet available.

Portions of the data obtained at Hoosier Energy's Merom Station are the result of an effort that has been jointly sponsored by the Rural Electric Research Program of the National Rural Electric Cooperative Association and EPRI. Funding for the FGDPRISM portion of this program was provided by EPRI.

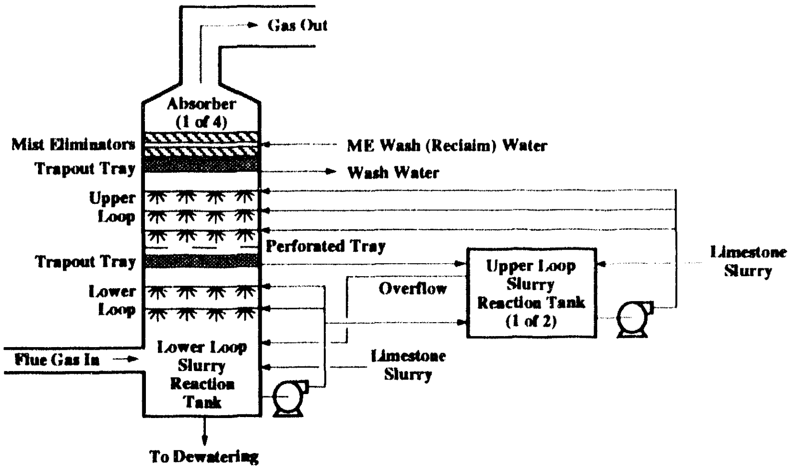

Figure 1. Flow diagram for Southwestern Electric Power Company's Pirkey Station FGD system.

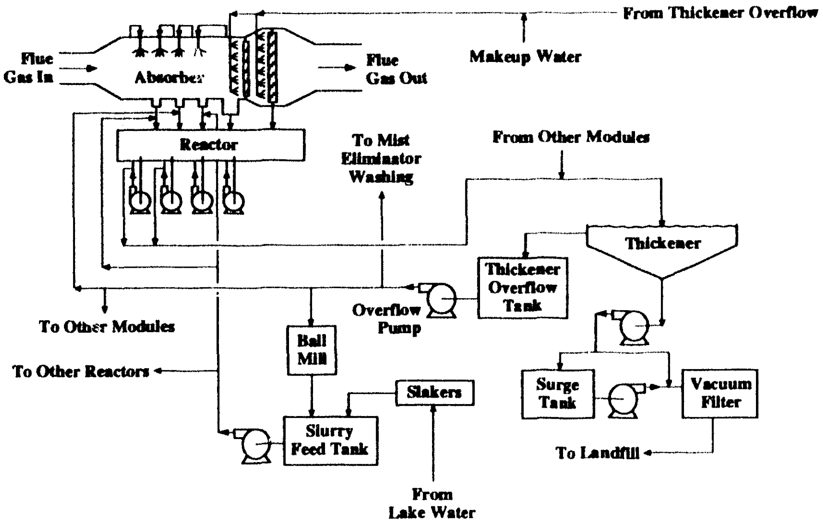

Figure 2. Flow diagram for PSI Energy's Gibson Station Unit 5 FGD system.

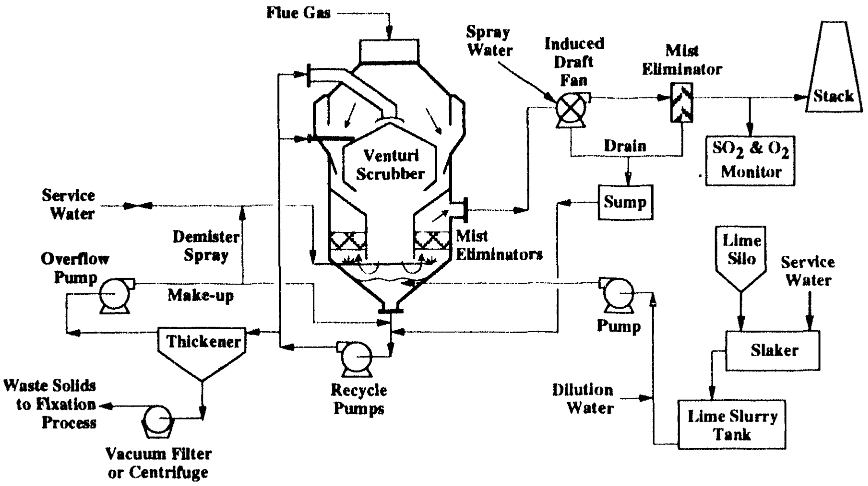

Figure 3. Flow diagram for Duquesne Light Company's Elrama Station FGD system.

DEVELOPMENT STATUS OF ADVANCED SORBENT INJECTION PROCESS FOR SO_2 CONTROL

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ABSTRACT

This paper describes the status of development of an advanced sorbent injection process for the control of SO_2 emissions from coal-fired power plants. The objective of the project is to develop a low-capital-cost process capable of over 90% SO_2 removal as a compliance option for the 1990 Clean Air Act Amendments. A complementary objective is to achieve sufficiently high sorbent utilization so that levelized costs are lower than wet limestone scrubbing costs over a wide range of coal types and plant sizes. The process being developed, referred to as the Advanced Coolside process, involves the use of a contacting device which simultaneously removes fly ash and saturates the flue gas with water vapor. Sorbent is injected into the highly humid flue gas downstream of the contactor and is collected by the existing particulate collector. High sorbent utilization is achieved by optimizing sorbent recycle. The originally established performance targets of 90% SO_2 removal and 60% sorbent utilization were exceeded in 1000 acfm pilot plant operations. The 90% SO_2 removal target was achieved at sorbent utilizations of 70-75%; up to 99% SO_2 removal was attained at over 60% sorbent utilization. An interim process economic evaluation previously reported confirmed the attractiveness of the process and identified specific approaches for process improvement. This paper discusses recent process improvements and the results of a revised economic study which shows that these improvements can substantially reduce cost. Projected capital costs are less than 1/2 of those of wet limestone scrubbing. Levelized SO_2 control cost is 20% lower than wet FGD for a 260 MWe plant burning a 2.6% sulfur coal. The study also indicated areas for future research.

BACKGROUND

Dry sorbent injection technology has been actively developed in the U.S. since the early 1980s. The performance of these processes has been established through the development of the Coolside process (CONSOL)[1-3] and the HALT process (Dravo)[4] and through the DOE duct injection technology development program.[5] In the 105 MWe demonstration of the conventional Coolside process at the Ohio Edison Edgewater Station,[3] an SO_2 removal of 70% was attained at a 2.0 Ca/S mol ratio with sodium-based additive injection at a 0.2 Na/Ca mol ratio. This corresponds to about 32% sorbent utilization efficiency. Process performance data and economic analyses support the attractiveness of duct sorbent injection for a range of retrofit applications.[6] However, the applicability as a compliance option for the Clean Air Act or other regulations can be expanded by increasing SO_2 removals and sorbent utilizations. The performance targets for developing an advanced process (90% SO_2 removal and 60% sorbent utilization) represent a substantial improvement over previous technology.

The Advanced Coolside process is being developed through 1000 acfm pilot plant tests.[7-10] Table 1 shows process performance data previously reported.[8-10] These particular data are from long-term tests simulating SO_2 removal in a retrofit scenario with an existing electrostatic precipitator (ESP). As shown, the 90% SO_2 removal target can be achieved at Ca/S mol ratios as low as 1.2. This corresponds to 75% sorbent utilization, which exceeds the initial target of 60%. At 1.2 Ca/S, the duct and system SO_2 removals were 87% and 90%, respectively, indicating that performance does not depend on high removal in the particulate collector. Tests also have been conducted to simulate SO_2 removal in a plant with a baghouse. These tests indicated that very high removal (up to 99%) is attainable with a baghouse, suggesting that the process may be attractive for high removal efficiency in a new plant application. Although the pilot plant is not of sufficient scale to fully assess process operability, operating experience is a positive indication of the operability and retrofit potential of the Advanced Coolside process. References 8-10 describe pilot desulfurization performance, data reliability, and operability in more detail.

An interim process economic study comparing Advanced Coolside to limestone forced oxidation wet FGD was conducted in early 1993 and was previously reported.[9,10] The study showed that the projected capital cost is 40% lower than wet FGD over the ranges of plant sizes (150 to 500 MWe) and coal sulfur contents (1 to 3.5%) investigated. The study also showed that the levelized SO_2 control cost in \$/ton SO_2 removed is lower than wet FGD over these ranges. The cost differential was about 10% for a 260 MWe plant burning a 2.6% sulfur coal.

The interim economic study identified areas for process improvement with significant potential impact on cost. These included sorbent improvement and equipment cost reduction. Approaches identified for equipment cost reduction were simplification of the contactor, the sorbent recycle system, waste handling systems, and flue gas handling systems. A goal established for further development is to achieve a 20% levelized cost advantage over wet FGD for a wide range of compliance situations, with emphasis on mid-range plant sizes and medium to higher sulfur coals. This cost advantage, in conjunction with the substantial capital cost advantage, would increase the attractiveness of employing this newer, less established technology.

DESCRIPTION OF ADVANCED COOLSIDE PROCESS

Figure 1 shows a schematic of the Advanced Coolside process. The process achieves greater SO_2 removal and sorbent utilization than previous duct sorbent injection processes by operating at a higher flue gas humidity and by more fully exploiting the potential of sorbent recycle. The key to the process is a gas/liquid contacting device downstream of the air preheater. The contactor serves two purposes: to saturate the flue gas with water, and to remove most of the fly ash from the flue gas. The sorbent is injected downstream of the contactor into the highly humid flue gas. Hydrated lime is very active for SO_2 capture near the saturation point. Because the flue gas is already humidified prior to sorbent injection, there is no strict residence time requirement for droplet evaporation, and duct wall wetting and deposition are not serious problems. The heat of reaction between SO_2 and hydrated lime raises the temperature of the flue gas by roughly 8-10 °F for each 1000 ppm of SO_2 removed; therefore, the particulate collector can be operated at an elevated approach to saturation. However, because hydrated lime activity is highly sensitive to the approach to saturation, this reaction heat effect also acts as a limiting mechanism for SO_2 capture.

The spent sorbent is a dry powder which can be disposed of with the wet fly ash. Sorbent recycle is an integral component of the Advanced Coolside process. Laboratory and pilot plant tests have shown that recycle sorbent is quite active for SO_2 capture at high humidity. The potential for recycle is increased because fly ash is removed separately before sorbent injection. Furthermore, recycle sorbent performance can be improved by a simple physical pre-treatment step prior to reinjection. The nature of this pre-treatment step is a proprietary feature of the process.

Design optimization has focused on the contactor. The contactor used in the pilot plant desulfurization testing was a second generation design. It was designed to be compact relative to equipment used in conventional FGD processes. For example, the gas residence time is on the order of 1 s, compared with 8-10 s typical of a spray dryer or an absorber in a wet FGD system. As discussed in this report, a third-generation contactor design is being developed and tested in the pilot plant.

EXPERIMENTAL

The Advanced Coolside process is being developed using a nominal 1000 acfm (0.3 MWe equivalent) pilot plant; over 5000 h of pilot plant testing has been conducted in this program. The pilot plant is discussed in more detail in Reference 7. In addition to the pilot testing, exploratory sorbent studies are being conducted in fixed-bed laboratory reactors.

PROCESS AND EQUIPMENT DESIGN OPTIMIZATION

Improvement of Contactor Design. Since the contactor is the major piece of capital equipment in the process, optimization studies have focused on reducing the cost of the contactor and on reducing the plant footprint to facilitate retrofit application. A third generation contactor design aimed at achieving these goals is being evaluated. The estimated cost of the new contactor is significantly less and it is substantially smaller than the previous contactor.

Pilot plant tests were conducted to confirm the feasibility and to optimize operation of the third generation contactor. The contactor tested was a standard model supplied by a major manufacturer. Therefore, the tests provide data for scale up. Contactor operability has been good in the initial pilot plant testing. Fly ash collection efficiency was over 99% in several tests at different conditions. This is higher than required in the process; about 85-90% collection is needed to keep ash in the recycle loop within reasonable limits. Humidification efficiency was high; the measured approach to saturation ranged from 1 to 3 °F at the contactor exit. This is slightly higher than with the previous contactor (ca. 0 °F), but the difference approaches the accuracy limit of the measurement technique. Tests showed that performance of the pilot contactor (ash removal and humidification) was independent of flue gas flow down to 1/4 of the design flow. This is an important result, because it was assumed in the second interim economic study (discussed below) that two contactors in parallel would be needed to handle load changes. The desulfurization performance with the new contactor is being investigated. Also, tests to optimize operating conditions are ongoing.

Improvement in Solids Handling Systems. Improvements were made in the recycle sorbent handling system and in the waste handling system.

The most significant improvement to the recycle system involves the recycle pre-treatment step, which is a proprietary aspect of the process. The pre-treatment equipment was substantially simplified resulting in reduced capital cost. The feasibility of the modification was confirmed through pilot plant testing using commercial equipment.

The most significant improvement to the waste handling system involves concentration of the fly ash in hydrocyclones instead of a thickener as specified in the original conceptual design (Reference 9). Engineering studies confirmed the feasibility of this change.

SORBENT OPTIMIZATION PROGRAM

Pilot plant tests reported previously were conducted with commercial hydrated lime with no additives. A sorbent optimization test program currently is under way, including work in three areas: a lime hydration study, evaluation of alternative sorbents, and evaluation of additive enhancement.

The objectives of the lime hydration study are to determine the effect of hydration variables on the properties of hydrated lime and to determine the effect of lime properties on desulfurization performance. The hydration study is being conducted in cooperation with Dravo Lime Co. using their continuous pilot (120 lb/hr) hydrator. Preliminary results suggest that hydration variables and quicklime source do not have major effects on process desulfurization performance. The influence of physical and chemical properties of hydrated lime on process performance are being studied.

Evaluation of alternative sorbents includes testing of different commercial hydrated limes and other sorbents, for example, specially prepared high-surface-area hydrated limes. As reported previously,[9,10] limes from different sources and with widely varying surface areas (14 to 40 m^2/g) showed small differences in SO_2 removals in pilot plant tests. This relative insensitivity to surface area and commercial lime source can be an economic advantage, allowing use of the lowest cost sorbent available. Laboratory reactor studies to evaluate other alternative sorbents for the process are continuing.

Previous laboratory studies[7] simulating Advanced Coolside process conditions indicated that sodium-based additives can increase substantially the utilization of hydrated lime (by over 20% absolute). Advanced Coolside pilot plant tests (Table 2) indicate that small amounts of additives added to the recycle sorbent can improve desulfurization performance in a plant with a baghouse. At a fresh Ca/S mol ratio of 1.2, 97 to 99% SO_2 removal was attained using NaCl or $CaCl_2$ at a level of 0.03 mol (Na or Ca) per mol Ca in the fresh lime. This result may be promising for an application where very high efficiency removal is desired, for example, in a new plant. In the tests conducted so far, additives have been most effective in increasing removal in the baghouse; they have not been particularly effective in tests simulating removal in a plant with an ESP.

SECOND INTERIM PROCESS ECONOMIC EVALUATION

A revised process economic study was completed. The purpose was to evaluate the impact of the process equipment improvements described above on the process cost. The following changes were included in the Advanced Coolside conceptual design:

- Use of two contactors (third generation design) in parallel. (It was assumed for this study that two contactors would be needed to handle load changes.)
- Use of a simplified recycle pre-treatment design.
- Use of hydroclones to concentrate the fly ash/water stream before mixing with spent sorbent as waste.

As in the previous study,[9,10] the sorbent was commercial hydrated lime; desulfurization performance was assumed to be the same as in the previous study. As discussed above, desulfurization performance testing with the new contactor is under way in the pilot plant. This performance data will be used in the final process economic study.

Advanced Coolside was compared to limestone forced oxidation wet scrubbing (LSFO). Since the previous study, several modifications were made to the LSFO process design to better reflect current commercial design philosophy. These include a less costly stack design, a less costly dewatering system and use of a blowdown stream to reduce slurry chloride concentration. These resulted in a 6% lower levelized cost for a 260 MWe plant burning a 2.6% sulfur coal.

Technical Assessment Guidelines developed by EPRI were used for the economic analysis. The economic assumptions (Table 3) were the same as used in the previous economic study.

The second interim economic analysis indicated that the process improvements discussed above can reduce the capital cost of Advanced Coolside by 25% and the levelized SO_2 control cost by 15% (for a 260 MW plant and a 2.6% S coal), relative to the Advanced Coolside economics in the previous interim analysis.

Figure 2 shows the capital cost of Advanced Coolside and limestone forced oxidation wet FGD for a 2.6% S coal, based on the recently revised economic study. As shown, the projected capital cost of Advanced Coolside is now less than 1/2 of that of wet FGD over the range of plant sizes evaluated (150 to 500 MWe). Figure 3 shows a comparison of levelized costs on a \$/ton SO_2 removed basis. Advanced Coolside was lower in cost than wet FGD for all cases evaluated. For a 260 MWe plant burning a 2.6% S coal, the relative cost advantage was 20%. This indicates that the process economic target was met for mid-range plant sizes. The goal of ongoing process development is to expand the range of applications over which this target can be attained.

FUTURE WORK

The following work will be conducted to further develop the Advanced Coolside process:

- Further equipment optimization will be explored to reduce process costs. Pilot testing will continue for contactor optimization; a recent contactor design modification will be tested. Engineering studies will be conducted to evaluate process improvements such as on-site lime hydration, use of a single contactor, and optimizing duct layout.

- The sorbent optimization study will be completed.

- A waste disposal/utilization evaluation will be conducted. Properties necessary to evaluate landfill disposal of the combined spent sorbent and fly ash waste will be determined. In addition options for by-product utilization will be explored. An example is use as an aggregate for construction.

- Pilot plant testing and engineering studies will be conducted to optimize the process for new plant applications and for very high SO_2 removal efficiency.

- A long-term pilot plant test will be conducted.

- The potential of the process to remove air toxics will be studied.

A final process economic study will be conducted based on the optimized process configuration. Based on the results of this study, recommendations for any future development or scale up of the technology will be made.

ACKNOWLEDGMENT

This work was conducted under partial sponsorship of the U.S. Department of Energy Contract DE-AC22-91PC90360. The authors are grateful to C. J. Drummond, T. D. Brown, R. E. Tischer, and others at DOE Pittsburgh Energy Technology Center for their support and encouragement of this project.

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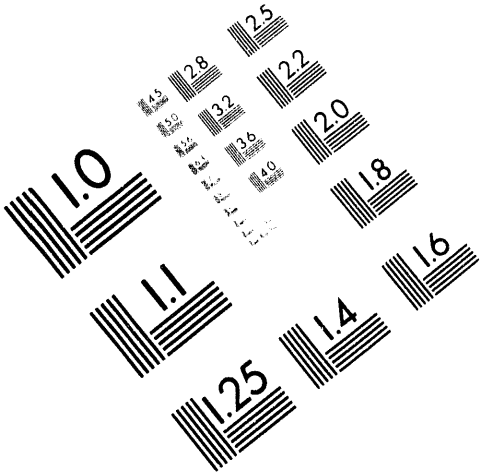
TABLE 1. Advanced Coolside Pilot Plant Recycle Tests at 1500 ppm SO_2 Simulating SO_2 Removal in a Plant With an ESP.

Test	1	2	3	4
Test Duration, hr	36	115	13	73
Process Conditions				
Fresh Ca/S, mol	1.4	1.2	1.5	1.2
Recycle Ratio, lb/lb fresh lime	4.5	6.9	4.4	6.7
Recycle Pretreatment	Yes	Yes	Yes	Yes
Baghouse Approach Temp., °F	23	23	24	22
Hydrated Lime	A	A	A	B
Process Performance				
SO_2 Removal, %, In-Duct	83	87	84	80
System	90	90	90	86
Baghouse	7	3	6	6
Sorbent Utilization, %,	63	75	60	70

TABLE 2. Advanced Coolside Pilot Plant Recycle Tests with Additive Addition Simulating SO_2 Removal in a Plant With a Baghouse at an Inlet SO_2 Concentration of 1500 ppm.

Fresh Ca/S mol/mol	**Recycle Ratio lb/lb Lime**	**Additive mol/mol**	**Approach**	**SO_2 Removal, %**	
				Duct	**System**
1.0	8.2	0.025 NaCl	22	65	84
1.2	6.8	0.03 $CaCl_2$	11	65	97
1.2	6.8	0.03 NaCl	10	92	99



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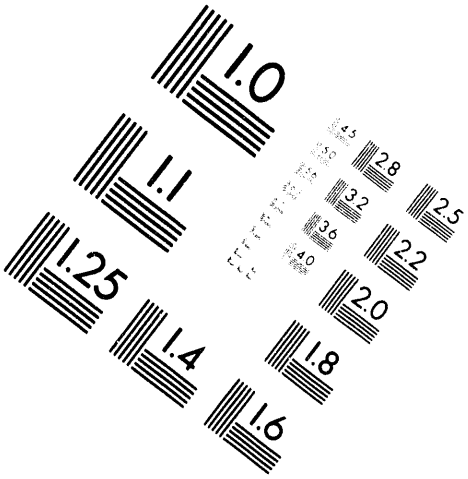

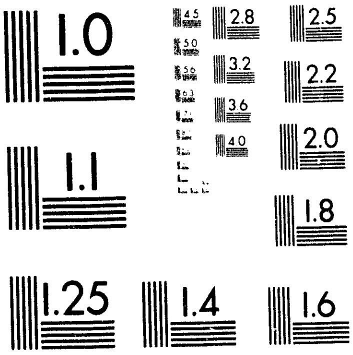

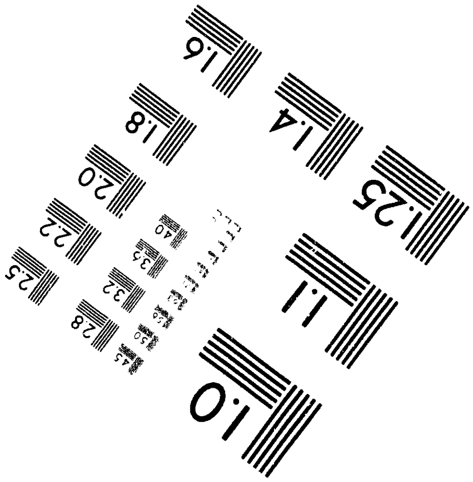

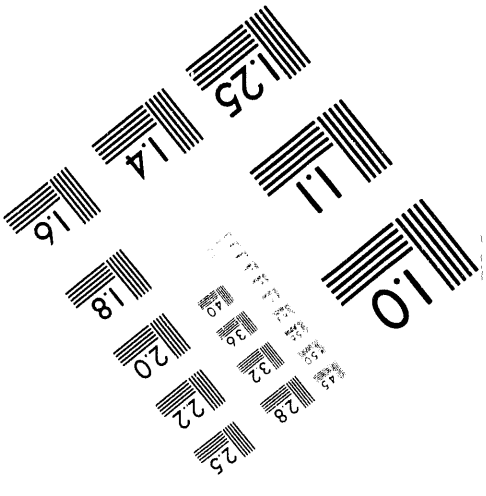

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TABLE 3. Key Assumptions of Second Interim Process Economic Study.

	Advanced Coolside	Forced Oxidation Wet FGD
Delivered Sorbent Cost	$60/ton (hydrated lime)	$15/ton (limestone)
Waste Disposal Cost	$6.50/ton	$6.50/wet ton
SO_2 Removal	90%	90%
Capacity Factor	65%	65%
Capital Life	30 years	30 years
Retrofit Factor	Medium (1.22-1.34)	Medium
Location Factor	1.06	1.06
Design Philosophy	"nth" plant, 18% capital contingency	"nth" plant, 18% capital contingency
Sparing	Auxiliary equip. only, no major equip.	Auxiliary equip. only, no major equip.
Indirect Costs	37.2% of direct	37.2% of direct
Construction	2 years	3 years

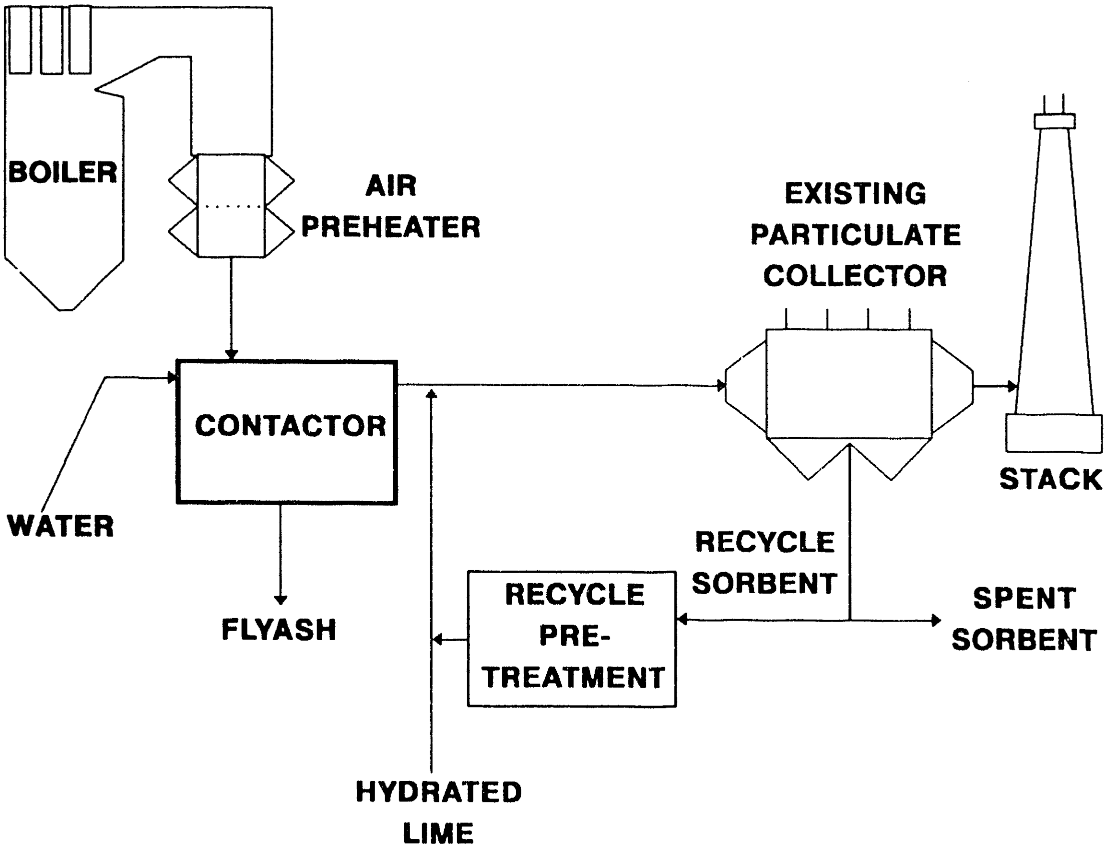

Figure 1. Conceptual Diagram of Advanced Coolside Desulfurization Process.

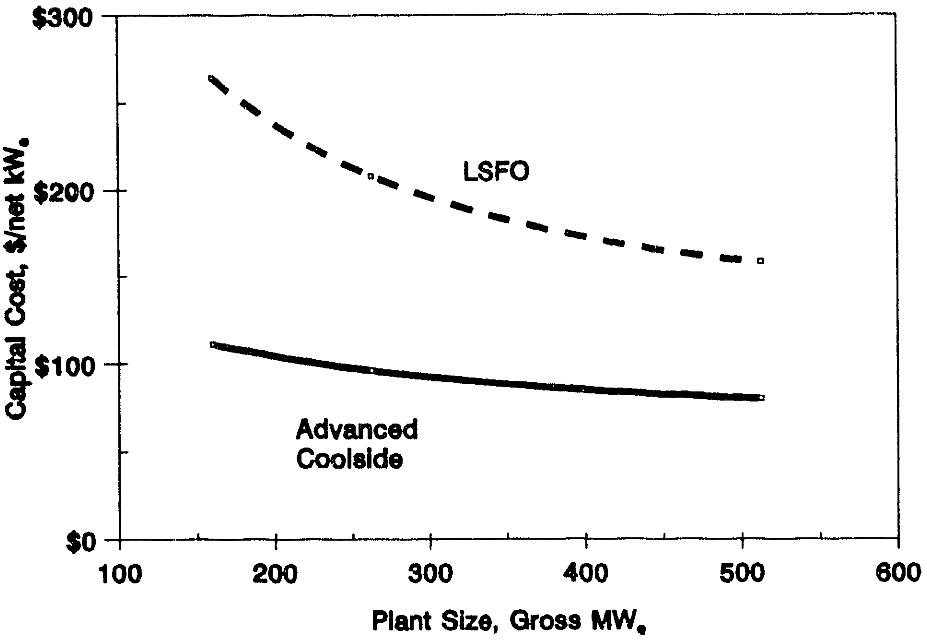

Figure 2. Comparison of Capital Costs for Advanced Coolside and Wet Limestone Forced Oxidation FGD (LSFO) at 2.6% Coal Sulfur Content and Varying Plant Sizes. Based on Second Interim Economic Analysis (1994).

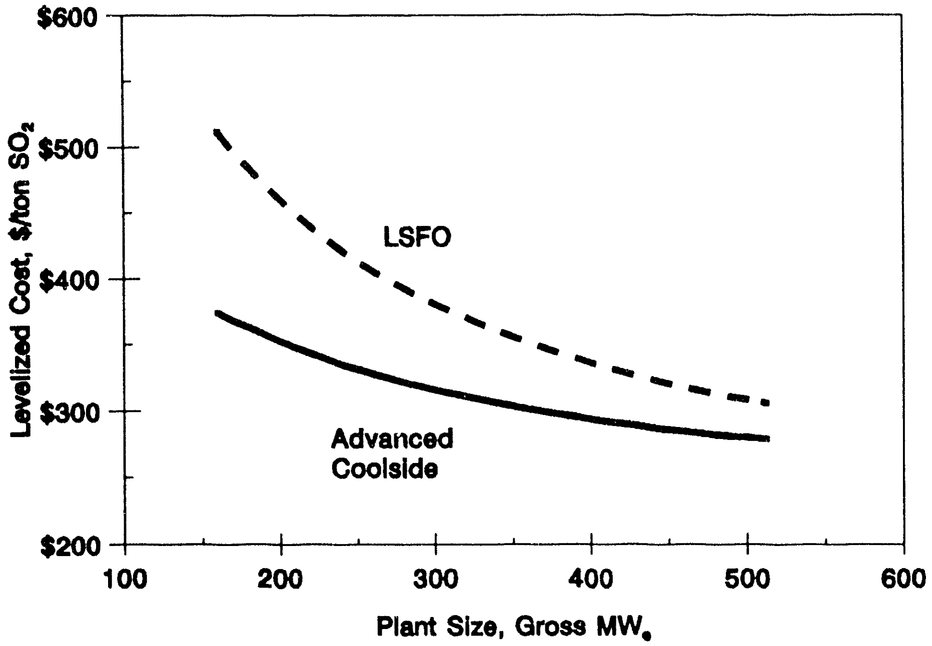

Figure 3. Comparison of Levelized SO_2 Control Costs for Advanced Coolside and Wet Limestone Forced Oxidation FGD (LSFO) for a 2.6% Sulfur Coal and Varying Plant Size. Based on Second Interim Economic Analysis (1994).

OVERVIEW OF RECENT RESEARCH ACTIVITIES AT EPRI'S HIGH SULFUR TEST CENTER - APRIL 1993 TO MARCH 1994

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The Electric Power Research Institute's High Sulfur Test Center (EPRI's HSTC) has been in operation for nearly seven years. During this time, numerous test programs have been performed with the purpose of aiding the utility industry in developing more cost-effective and environmentally sound emission control technologies for use with high-sulfur coals. Funding for the HSTC is provided, in part, by the HSTC cosponsors: New York State Electric and Gas (host utility), Empire State Electric Energy Research Corporation, Electric Power Development Corporation, the U.S. Department of Energy, Babcock & Wilcox, and ABB Environmental Systems.

The overall goals of the HSTC wet flue gas desulfurization (FGD) research program are to investigate ways of reducing the operating costs and improving the reliability of existing lime and limestone wet FGD systems, while also investigating promising new process concepts that can be incorporated into new system designs. Two wet scrubber systems are currently available for testing: a 4-MWe pilot unit and a 0.4-MWe "mini-pilot" unit. The two systems have a common reagent preparation system and upstream particulate control device (ESP or reverse-gas fabric filter). Detailed process descriptions of these systems have been presented previously.

Six EPRI wet scrubber test programs have been completed or are currently underway at the HSTC since March 1993. Test programs completed on the pilot system include Fine Grind Limestone (FGL) tests and Pilot Hydroclone Dewatering (PHD) tests, while the mini-pilot test programs have included two phases of Clear Liquor Scrubbing (CLS) tests, High Calcium Lime with Additives (HCLA) tests, and Liquid Redox Sulfur (LRS) tests. The current test program is the Pilot High Velocity (PHV) test block which began at the end of March 1994. Concurrent with the ongoing wet scrubber tests, an on-line chemical monitoring (OLCM) system is being developed. Over the past two years, this project has involved testing/developing various system components and developing/refining analytical techniques which can be used to provide near continuous measurement capabilities for important slurry chemistry parameters. The remainder of this paper describes the research objectives and summarizes the status and important results for each of these research programs.

Pilot System Test Programs

Fine Grind Limestone Tests

The utility industry has recently shown a preference for wet limestone, forced-oxidation FGD systems for compliance with Phase I of the Clean Air Act Amendment (CAAA) of 1990. Forced-oxidation systems generally provide reliable operation, byproduct solids with good dewatering properties, and the potential for selling the byproduct solids as a useful raw material for the production of wallboard, cement, or other products. Owing to the popularity of this type of system, a test program was performed at the HSTC which investigated the potential benefits of using a finely ground limestone with respect to process performance and reagent costs. Using a very fine limestone grind (100%<325) may allow operation at SO_2 removals above 90% while maintaining a utilization of 95% or greater. A utilization of greater than 95% is desirable because gypsum containing more than 5% limestone cannot be used for wallboard production.

The primary objectives of the Fine Grind Limestone (FGL) test program were to: expand the existing database regarding the effect of limestone grind on forced-oxidation system performance indicators such as SO_2 removal efficiency, utilization, and byproduct solids properties; provide data for FGDPRISM validation over a wide range of limestone particle size distributions; and evaluate forced-oxidation process concepts to improve performance and reduce costs related to limestone grind and limestone use. The first two objectives were achieved during the FGL tests completed to date. Three series of tests were performed with three different limestone grinds: the HSTC baseline grind of 90%<325 mesh, a finer grind of 98%<325 (also produced at the HSTC), and a very fine grind of 100%<325 obtained from a commercial supplier. Upon further review of the data, a second phase of testing may be performed which will test process variations (e.g., modified reaction tank design, lower L/G) designed to reduce costs by taking advantage of the process performance benefits of using a finely ground limestone. Equipment used for producing the fine grind on-site would also be evaluated.

The variables investigated during the 90% and 98% grind tests include three pHs (5.5, 6.0, and 6.1), three calcium concentrations (45, 140, and 250 mM), two solid-phase residence times (6 and 12 hours), and two inlet SO_2 levels (2000 and 2500 ppm). Due to the limited supply of the 100%<325 limestone, fine grind tests were only completed at two calcium levels (140 and 250 mM) and two pHs (6.0 and 6.1). The results of this test program showed that the particle size distribution (PSD) of the 98% grind was finer than the 90% grind; however, the PSDs were not different enough to have a significant effect on limestone utilization at any of the conditions tested. Use of the 100%<325 mesh grind resulted in a substantial increase in limestone utilization for all conditions tested. Compared to the 90% and 98% grind tests, utilization increased from 86% to 96% at the baseline conditions (pH 6.0, 140 mM Ca^{++}); from 55% to 88% at 250 mM calcium; and from less than 75% to 92% at pH 6.1. Finally, during all tests, SO_2 removal efficiency was primarily a function of limestone loading. For a given utilization, SO_2 removal was slightly higher (1% to 3%) with the fine limestone grind due to the higher operating pH.

Pilot Hydroclone Dewatering Tests

Hydroclones will be used for primary dewatering of gypsum in seven of the ten forced-oxidation FGD systems being installed to meet Phase I SO_2 reductions mandated by the 1990 CAAA. Hydroclones separate solids from the feed slurry based on differences in particle size and mass. In a forced-oxidation FGD system, a gypsum-enriched stream (hydroclone underflow) is produced that can be dewatered using a secondary dewatering device, thereby eliminating the need for a thickener. The system can also be designed to produce a limestone-enriched stream (hydroclone overflow) that can be returned to the reaction tank, a processing step referred to as "limestone recovery". This type of system can allow operation with a higher limestone concentration ("loading") in the reaction tank, thereby increasing SO_2 removal while maintaining a high-quality gypsum byproduct and overall high limestone utilization. The hydroclone overflow stream can also be used as a purge stream to control the gypsum chloride concentration. Because the PSD of the overflow solids is finer than the underflow solids, use of a hydroclone can also potentially affect the filtration properties of the byproduct (underflow) solids, depending on the destination of the overflow stream.

Currently, only a limited amount of full-scale performance data are available for FGD systems which use hydroclones for gypsum dewatering. Thus, EPRI sponsored a test program which used the HSTC's pilot system to develop hydroclone performance data for a range of hydroclone operating conditions. The goal of the Pilot Hydroclone Dewatering (PHD) test program was to evaluate the potential for improvements in limestone utilization, SO_2 removal efficiency, solids dewatering properties, and gypsum byproduct quality in forced-oxidation FGD systems which use hydroclones for primary solids dewatering. The variables tested during the PHD test program include dewatering configuration (thickener vs. hydroclone), hydroclone hardware (apex and vortex diameters), feed rate, and feed slurry solids and limestone concentrations. Constant test conditions included the following: 2000 ppm inlet SO_2, 132 gal/macf liquid-to-gas ratio (L/G), 140 mM dissolved Ca^{++}, 85 mM dissolved Mg^{++}, and 90%<325 mesh limestone grind. A total of 26 tests were completed over a 14-week period.

The PHD results showed that the maximum recovery of limestone with the pilot hydroclone dewatering system was about 30% over a wide range of hydroclone operating conditions. (Limestone recovery is defined as the percent reduction in the concentration of limestone in the underflow solids relative to the feed solids.) Comparison of the pilot data with limited full-scale test data shows similar trends with respect to the effects of hydroclone hardware and operating conditions on the maximum recovery, although a higher maximum recovery of about 50% was achieved. The data from both systems suggest that higher recoveries can only be achieved with dramatic shifts in the limestone and gypsum PSDs in the feed slurry. The magnitude of the savings associated with a 30% limestone recovery depends on the reaction tank limestone concentration; when the underflow solids contain less than 5% limestone, the savings represent only a small fraction of the total limestone cost (<3%).

With respect to other process performance results, the relatively low limestone recovery did not allow pilot plant operation at a reaction tank limestone concentration that would result in a significant increase in SO_2 removal without an unacceptable decrease in overall limestone utilization. In addition, the filtration rate of the underflow solids was significantly faster than the reaction tank solids; however, tests may not have been run long enough to reach steady-state with respect to the concentration of fines throughout the system.

Pilot High Velocity Tests

The 1990 CAAA introduced a cap on SO_2 emissions and gave affected electric utilities a set number of emission allowances; however, the CAAA did not mandate specific control strategies. This flexibility allows utilities to develop the most cost-effective compliance strategies using one or more available options. Retrofitting new systems to previously uncontrolled units and using exisiting FGD systems to treat additional gas are two compliance options. Operating FGD scrubbers with higher gas velocities has some potential benefits for both of these options. However, high velocity scrubbers may encounter problems with mist eliminator performance, SO_2 removal efficiency, and absorber scaling.

Since essentially no performance data are available for high velocity scrubber operation, EPRI recently began a test program on the HSTC pilot unit to investigate the effects of higher flue gas velocities (up to 15 ft/s) on process performance in a counter-current spray tower. The variables scheduled for testing include mist eliminator type, spray nozzle type, absorber gas and liquid rates, the effect of absorber internals, and the use of organic additives. Two-stage, high performance mist eliminators were provided by two commercial vendors for use during this test program. Process performance parameters of primary interest include SO_2 removal efficiency, carryover rate, and solids deposition rate (indicated by mist eliminator pressure drop and visual inspection). At the time of this paper, absorber modifications were completed and three baseline tests had been performed. The test program is scheduled to last for a period of five months.

Mini-Pilot System Test Programs

Clear Liquor Scrubbing - Phases I and II

The majority of existing wet FGD systems utilize a scrubbing slurry which typically contains between 8 and 14 wt.% solids. The presence of suspended solids in the scrubbing solution impacts maintenance costs and can lead to reliability problems due to equipment erosion and solids deposition. In addition, recirculation of calcium sulfite and/or calcium sulfate crystals through the absorber feed pumps causes the crystals to break up, which serves to deteriorate the solids settling and dewatering properties. A clear liquor scrubbing process addresses both of these operating issues. In a clear liquor process, scrubber effluent is combined with reagent in a reaction vessel, and precipitated solids are separated from the scrubbing liquor prior to recirculation to the absorber. Furthermore, in a clear liquor process, it should be possible to make substantial improvements to the SO_2 removal efficiency and reduce the L/G through the use of packing without the risk of scaling or pluggage, such as exists in a slurry system.

Due to significant progress in the area of scrubber chemistry control, it appears that a limestone-based, clear liquor scrubbing system would be very economical if the concentrations and usage rates of additives required to make the process work were low. To investigate the potential for development of such a process, two phases of Clear Liquor Scrubbing (CLS) tests were performed using the HSTC mini-pilot system. The goal of the mini-pilot CLS test program was to develop a limestone-based, clear liquor scrubbing system with improved costs and performance over existing limestone slurry and dual alkali scrubbing processes.

In Phase I, existing process equipment was used to provide an initial evaluation of the basic chemistry, scrubbing efficiency, and limestone reaction rates for three buffering systems (sulfite, formate, and DBA). Test variables included buffer concentration, pH, process configuration (including packing in the absorber), L/G, solid-phase residence time, and dissolved calcium concentration. Process performance results of primary interest included SO_2 removal efficiency, limestone utilization, solids dewatering properties, additive consumption rates, and system scaling potential. Based on Phase I results, a new Sludge Bed Reaction Tank (SBRT) was designed, fabricated, and installed at the HSTC for Phase II. The tests performed during Phase II were designed to identify the optimum operating set points of the new reactor system. Inhibited-oxidation tests were performed with formate buffer, while several forced-oxidation tests were performed with DBA buffer.

Results from both phases of CLS tests showed that the calcium sulfite relative saturation (R.S.) was an important factor in determining process performance in the inhibited-oxidation system. The best overall performance, with respect to scaling potential, solids dewatering properties, and formate consumption (coprecipitation), was achieved at an R.S. of 4 to 5. Excellent solids properties were achieved for all conditions tested, including thickener unit areas below 2 ft^2/ton/day and filter cake solids concentrations of 65 to 75 wt.%. Also, conditions that allowed scale-free operation in the reaction tank were identified which include 30 to 40 hours solids residence time, a calcium sulfite relative saturation below 5, and 3 to 5 wt.% suspended solids in the reaction zone.

Based on the mini-pilot results, formate is the optimum buffer in a limestone, clear liquor, inhibited-oxidation system, while DBA is the optimum buffer in a forced-oxidation system for the conditions tested. Calcium suppression (by adding magnesium or sodium or by removing HCl from the flue gas) was required to achieve high limestone utilization and low additive coprecipitation in the inhibited-oxidation system, and to achieve a low gypsum scaling potential in the forced-oxidation system. Although excellent solids properties were achieved in the forced-oxidation tests, and SO_2 removal efficiencies were comparable to the inhibited-oxidation tests, the success of this process is dependent on maintaining a low scaling potential in the absorber. Finally, an economic evaluation using EPRI's FGDCOST computer model showed that a limestone-based, clear liquor process could be cost-competitive with conventional limestone slurry processes; the forced-oxidation process using a sludge bed reaction tank design showed the most promise for reducing capital requirements for a new system.

High Calcium Lime with Additives

Lime reagent is currently used in both magnesium-enhanced lime and dual-alkali FGD systems. This reagent has been shown to reliably achieve high SO_2 removal efficiencies at relatively low L/Gs over a range of coal sulfur contents. A primary drawback to the use of Mg-lime reagent, however, is the relatively poor settling and dewatering properties of the solids produced in typical Mg-lime systems. It has been shown that the poor solids properties are due in part to the high dissolved magnesium and sulfite levels in the scrubbing liquor. The main drawback to conventional dual-alkali systems is the high soda ash reagent costs, and occasional excursions in soda ash consumption due to poor process control can be expensive.

The High Calcium Lime with Additives (HCLA) test program was performed on the mini-pilot system to identify promising process concepts using high-calcium lime with organic acid additives to achieve high SO_2 removal efficiency. Potential benefits of scrubbing with this type of reagent include improved solids dewatering properties, higher SO_2 removal at the same L/G (due to lower SO_2 backpressure), operating with in-situ forced oxidation to produce gypsum; and lower pH operation to minimize reagent ratio. The test program consisted of four series of "screening" tests with the following reagents: lime slurry/DBA (natural, inhibitied, and forced oxidation), Mg-lime slurry/DBA (inhibited oxidation), lime clear liquor/formate (natural oxidation), and lime clear liquor/sodium/DBA/magnesium (inhibited oxidation).

The most promising HCLA process tested was the forced-oxidation lime slurry system with DBA addition. Test results showed that SO_2 removal efficiency was insensitive to pH over the range 6.0 to 7.5 (which allowed maximum lime utilization) and was only a function of the DBA concentration and L/G. The dewatering properties of the gypsum solids were excellent, although they deteriorated slightly at very high DBA levels (10,000 ppm). DBA losses were not accurately measured, but rough estimates showed they were low, comparable to limestone slurry forced-oxidation systems.

The solids produced in the inhibited-oxidation lime slurry/DBA tests were very poor, and DBA consumption rates were high, suggesting that this type of reagent is not suitable for use in inhibited-oxidation systems. Addition of 5,000 ppm DBA to a typical Mg-lime slurry (4,000 ppm $SO_3^{=}$) resulted in a slight increase in SO_2 removal, while the solids settling properties improved considerably. This process may be tested further to determine the optimum DBA level required to enhance performance of an existing Mg-lime system. The use of lime reagent in combination with sodium formate is a technically feasible alternative the the standard lime/dual-alkali scrubbing system or a Mg-lime system. However, the estimated formate coprecipiation rate was significant (almost three times higher than in a limestone slurry system), resulting in higher operating costs. Finally, the lime clear liquor/sodium/DBA/magnesium tests demonstrated that some of the sulfite alkalinity required for the dual-alkali process can be successfully replaced with DBA and/or magnesium. However, the DBA coprecipitation rate was relatively high, while substitution of magnesium for sodium resulted in deterioration of solids dewatering properties and process control problems, since the magnesium will precipitate if the regeneration pH drifts above about 10.

Liquid Redox Sulfur

A two-week test program was performed on the mini-pilot system to investigate the potential for substituting liquid redox sulfur (LRS) for commercially available emulsified sulfur as an FGD additive. Over 50 small LRS recovery units are operated by the natural gas industry to remove H_2S by converting it to elemental sulfur. Elemental sulfur is added to FGD systems to generate thiosulfate which inhibits the oxidation of sulfite to sulfate. Identifying uses for the LRS cake is desirable to the gas industry to avoid the costs and environmental implications of landfilling the waste, the normal disposal method. Utilities would benefit from the use of LRS, because it would be a lower cost source of sulfur and would likely generate positive public relations for reusing a waste product.

The objectives of the LRS tests were to: determine the sulfur-to-thiosulfate conversion efficiency; determine if there are any adverse affects on process performance; and evaluate addition of the LRS to the reaction tank with the limestone slurry. During the LRS tests, system operating setpoints were set to simulate the conditions and performance of an FGD system at a utility which fires a lignite coal. This included an adiabatic saturation temperature of about 135°F, an inlet SO_2 concentration of 1600 ppm, and an inlet HCl concentration of about 8 ppm (resulting in roughly 5000 ppm chloride in the slurry).

The overall sulfur conversion efficiency of the LRS to thiosulfate during the two-week test period was between 30% and 50%. This range is typical of emulsified sulfur in previous HSTC tests and in full-scale systems over a wide range of operating conditions. Furthermore, the SO_2 removal efficiency and limestone utilization were typical of what would be expected on the mini-pilot system for the given test conditions. However, sulfite oxidation was lower and solids properties were better compared with a previous lignite simulation test program. While it is unlikely that use of LRS was directly responsible for these effects, this possibility cannot be ruled out. Since these effects are generally beneficial to overall process performance, it was concluded that no detrimental effects will occur if LRS is used to generate thiosulfate in a wet limestone system instead of emulsified sulfur. Results from byproduct solids Toxicity Characteristric Leaching Procedure (TCLP) tests were within the range expected for an unstabilized calcium sulfite sludge. Thus, use of LRS should not affect a utility's ability to landfill stabilized calcium sulfite sludge. Lastly, there were no problems with addition of the LRS to the reaction tank via the ball mill grinding circuit.

On-Line Chemical Monitoring Project

The objective of the on-line chemical monitoring (OLCM) project is to develop a chemical monitoring system for FGD processes which is capable of performing near-continuous measurements of key chemical parameters. Such a system would offer a utility a convenient means of monitoring FGD process chemistry, and the data collected could be used to maximize performance and reduce operating costs. The OLCM system consists of a continuous slurry sampling system, a continuous filtration system with automatic flushing capabilities, a potentiometric analyzer capable of performing automatic titrations to a potentiometric endpoint, and a colorimetric analyzer capable of performing automatic titrations to a colorimetric endpoint. The system can be set up to measure a variety of chemical parameters on either scrubber liquor or slurry samples.

Development of the on-line chemical monitoring system began during the second half of 1992, when two automatic analyzers were installed on the pilot system. Initial activities focused on the design and development of a filtration and slurry sampling system, and on the development and adaptation of analytical methods to measure key FGD chemical parameters. The OLCM was tested during both inhibited- and forced-oxidation pilot tests, depending on the current pilot test program. Chemical parameters that were tested include soluble sulfite, thiosulfate, buffer capacity, organic acid concentration, soluble calcium, soluble magnesium, limestone loading (forced-oxidation slurry), and total alkalinity. A second monitoring system was installed on the mini-pilot system during the second quarter of 1993, and methods development and evaluation continued on both systems.

During the latter part of 1993, work was begun on the development of a prototype OLCM which could be easily taken to utility host sites for testing on full-scale FGD systems. The full-scale prototype was designed to contain all of the systems and components of the OLCM in a weather-proof enclosure. Construction of the prototype was completed early in 1994, and an evaluation of the system was begun. The objective of the current testing is to evaluate the long-term operating reliability and maintenance requirements of the OLCM prototype system and the ability of the system to consistently generate accurate and dependable analytical data. A key focus of the testing is to improve the performance and reliability of the filtration and slurry sampling systems.

FGD WASTE DISPOSAL COST AND SENSITIVITY ANALYSIS

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1.0 INTRODUCTION

Increasing waste disposal charges, resulting from stricter federal and state disposal regulations and reduced landfill availability, are expected to reduce the current economic advantage that the throw-away FGC technologies have over the byproduct-producing processes. The overall purpose of this project is to try to establish realistic FGC waste disposal costs and to estimate their potential impact on the comparative lifecycle economics of several low-cost throw-away FGC processes versus several advanced, regenerable processes that produce marketable byproducts. Most of the project work focused on a review of waste disposal cost estimation for the 16 states with the highest coal-fired generating capacity, and cost projection results out to the year 2010 (and projection methodologies) for future waste disposal charges.

This paper is separated into four major topics: 1) Federal and state fossil fuel combustion (FFC) waste disposal regulations, 2) basic information about disposal technologies and cost of FFC waste disposal systems, 3) comparative analysis of the cost impact of different disposal practices which may be required by current state regulations, and 4) comparative lifecycle cost analysis for competing flue gas cleanup technologies based on the sensitivity to waste disposal charges.

2.0 OVERVIEW OF FEDERAL AND STATE WASTE DISPOSAL REGULATIONS

The primary concerns associated with large-volume power plant solid waste disposal (fly ash, bottom ash, boiler slag, and FGC waste) are the prevention of surface water and groundwater contamination from runoff or leaching of toxic substances (e.g., heavy metals, mercury). The key Federal law regulating large-volume solid waste disposal from power systems is the **Resource Conservation and Recovery Act** (RCRA). The designation of power plant bottom ash, fly ash, boiler slag, and scrubber waste as hazardous or nonhazardous has been one of the most important environmental issues affecting coal-fired power plant operation; in EPA's 1988 report to Congress, these wastes were **provisionally** exempted from regulation under RCRA's **Subtitle C**, pending further study by EPA. Subtitle C establishes the methodology for classifying wastes as hazardous. RCRA **Subtitle D** establishes a management plan, implemented by state and local governments, for the proper handling and disposition of solid wastes categorized as nonhazardous.

After years of waiting, the final U.S. EPA decision was published on August 9, 1993 as required by Section 3001(b)(3)(C) of the Resource Conservation and Recovery Act [1, p. 42466]. It has been concluded that "regulation under Subtitle C of RCRA is inappropriate for the four waste streams that were studied because of the limited risks posed by them and the existence of generally adequate state and federal regulatory programs. The agency believes that the potential for damage from these wastes is most often determined by site- or region-specific factors and that the current state approach to regulation is thus appropriate. Therefore the agency will continue to exempt these wastes from regulation as hazardous wastes under RCRA Subtitle C. However, EPA believes that industry and the states should continue to review the appropriate management of these wastes. EPA will consider these wastes during the agency's ongoing assessment of industrial non-hazardous wastes under RCRA Subtitle D." The effective date for this ruling is September 2, 1993.

Almost all states with the highest coal-firing capacity became more restrictive with utility waste disposal regulations during the period of time from 1983 to 1992. In 1993, SAIC updated previously gathered information regarding state regulatory programs addressing management and disposal of fossil fuel combustion wastes in the 16 States with the highest coal-fired generating capacity [2,3,4]. Based on the individual state waste classification regulations and permit requirements, an overview is presented in

Table 1 for 1) disposal site liner requirements, 2) leachate control requirements, 3) groundwater monitoring requirements, and 3) closure requirements and type of final cover. These data are presented as a system of coefficients with values ranging from 0 to 1; a value of 0 means that the measure is not required in the state, a value of 1 means that the measure is strictly required in the State, and other values indicate the share of facilities where this particular measure is required inside the state. These coefficients can be coupled with the unit cost of any control procedure or measure ($ per ton of disposed waste) to estimate costs for all types of control measures for any particular state.

3.0 BASIC DESIGN AND COST INFORMATION FOR FGC DISPOSAL PRACTICES

General information on design, operation, and maintenance of different types of disposal sites is available from many recent literature sources [5,6,7,8,9]. This information makes it clear that the majority of FFC wastes from electric utilities is disposed of in either landfills or surface impoundments (ponds). Relatively small amounts of the wastes are disposed of at other types of sites, such as old mines. Table 2 presents a comparison of the total estimated costs for basic fossil fuel waste disposal in landfills and impoundments; even though the data source for this cost information, as cited in the 1988 EPA report to Congress [7], is dated June 1985, the data continues to be used as the basis for study assessments (with the use of appropriate escalation factors). However, this cost information does not reflect changes in disposal requirements/practices which have taken place in the states since the early 1980s. On a strictly comparative basis, note the wide range of disposal costs at a specific plant size, as well as the reduction in cost as the size of the facility increases. Also, surface impoundments are significantly more expensive than landfills due to their design and operational differences.

4.0 COMPARATIVE ANALYSIS OF THE COST IMPACT OF DIFFERENT DISPOSAL PRACTICES REQUIRED BY CURRENT STATE REGULATIONS

Relative to the basic disposal practices represented by the cost data shown in Table 2, the current state requirements, as shown in Table 1, can significantly increase the cost of waste disposal for newly designed facilities and, to even a greater extent, for existing waste facilities because the existing sites must be replaced or redesigned to implement some of these measures. Unit costs for these additional measures (in 1991 dollars) are presented in Table 3 [10]. Estimates of the total FGD waste disposal costs which correspond to currently documented regulations in the sixteen largest coal-consuming states are presented in Table 4 for both landfills and impoundments. The total potential costs for FGD waste disposal were estimated as the sum of the basic disposal costs, from Table 2 (escalated to 1991 dollars), and the total incremental costs required for the added waste disposal measures. These values represent the major costs for on-site waste disposal, but do not include some of the additional minor costs, such as cost of permitting, assessments, design work, etc. Based on the potentially high disposal cost estimates shown in Table 3 for the states of Florida, Indiana, Pennsylvania, Ohio, and Wisconsin, the selection of a particular type of FGC system is likely to be significantly influenced by the economic impact of the waste disposal costs. A detailed assessment of individual utility disposal costs would have to be performed to confirm the cost estimates for particular sites, required control/monitoring measures, and waste byproduct types.

5.0 COMPARATIVE COST SENSITIVITY OF WASTE DISPOSAL CHARGES FOR SEVERAL LIME/LIMESTONE THROWAWAY TECHNOLOGIES

Cost comparisons are made for a 300 MW power plant application utilizing a high sulfur Illinois #6 coal (4% sulfur by weight). Control technology costs are based on a previous SAIC study which evaluated a number of ultra-high efficiency combined NO_x/SO_x control options. The cost impact associated with increased waste disposal charges for FGD systems is assessed in Figure 1 based on 30-year levelized costing (current 1991 dollars). The figure compares the constant costs of the advanced Copper Oxide and NOXSO Processes (which produce saleable sulfuric acid and sulfur byproducts) with two throwaway processes (combined with SCR for NO_x control) as the cost of waste disposal is increased from no charge processes (combined with SCR for NO_x control) as the cost of waste disposal is increased from no charge up to $50/ton. As discussed previously, landfill and impoundment costs can range up to more than $40/ton of waste, but are generally found in the $10-$30/ton range. Clearly, the Copper Oxide process becomes much more cost-effective as the disposal charge increases. NOXSO (at $3/Lb sorbent cost and $90/L ton sulfur credit) breaks even with Mag-Enhanced Lime/SCR at a waste disposal charge of about $19/ton and with LDBA/SCR at about $33/ton of waste. If the NOXSO sorbent cost was reduced to $1.50/Lb, breakeven with MgEL/SCR would occur at about $8/ton of waste and with LDBA/SCR at about $15/ton of waste.

6.0 CONCLUSIONS

When assessing the cost-effectiveness of different flue gas emission control processes, both the waste disposal and byproduct credit charges can significantly impact the comparative economics of these technologies. Therefore, appraisal of the current charges and annually projecting them into the future, over the full operating period of a technology application, are important issues involved with technology selection. While the current market valuation of specific FGC byproducts can be estimated based on existing market conditions, projecting the byproduct value into the future is fraught with uncertainty due to changing economic conditions, uncertain future byproduct demand, changing costs of competing materials due to the introduction of FGC byproducts, etc. On the other hand, waste disposal charges should be much easier to evaluate and predict if a relatively stable (or predictable) regulatory environment exists. Unfortunately, because of the diverse regulatory requirements of different states, the site-specific nature of estimating the cost of waste disposal, as well as the alternative methods of waste disposal, a significant range of disposal costs are possible. Landfill and impoundment costs can range up to more than $40/ton of waste, but are generally found in the $10-$30/ton range.

The broad range of the disposal costs and their potentially high values make it clear that more effort must go into defining waste disposal requirements for future FGC system economic assessments. As waste disposal costs increase in value, regenerable processes which produce valuable byproducts become much more cost-effective relative to the throw-away emission control technologies. Of course, as mentioned above, the market value of individual salable byproducts must also be carefully evaluated for a realistic comparative assessment.

LIST OF REFERENCES

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2. ICF Resources Incorporated. *"Coal Combustion Waste Management Study."* For U.S. DOE. February 1993.

3. SAIC. *"Overview of State Regulatory Programs Addressing Management and Disposal of FFC Wastes,"* for Special Waste Branch of Office of Solid Waste, U.S.EPA, March 1993.

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5. National Acid Precipitation Assessment Program. *"Acidic Deposition: State of Science and Technology. Methods for Modelling Future Emissions and Control Costs."* Report 26, December 1990.

6. Environmental Resources Management, Inc. *"The Evaluation of Flue Gas Desulfurization Solid Waste Disposal Alternatives,"* Prepared for Conversion Systems, Inc. January 1992.

7. U.S.EPA. *"Wastes from the Combustion of Coal by Electric Utility Power Plants,"* Report to Congress. EPA/530-sw-88-002A. February 1988.

8. Cook-Joyce, Inc. *"Utility Coal Combustion By-Product Storage and Disposal."* Prepared for Edison Electric Institute. December, 1991.

TABLE 1
REQUIREMENTS FOR GROUND-WATER MONITORING, LINERS, CLOSURE, AND LEACHATE CONTROL

State	GW Monitor	Liner Requirement		Liner Type			Type of Cover			Leachate Control
		1 liner	2 liners	Synth	Clay	Soil	Soil	Clay	Synth	
Florida	1	1	0.5	1	0	1	1	0	1	1
Georgia	1	0.5	0	0	1	1	1	0	0	1
Illinois	0	0	0	0	0	0	1	0	0	0
Indiana	1	1	0	1	0	1	1	0	0	1
Iowa	1	1	0	0	0	1	1	0	0	1
Kentucky	1	0.5	0	0	0	0	0	0	0	0.5
Michigan	1	1	0	0	1	1	1	0	0	1
Minnesota	1	1	0	0	1	0	1	0	0	1
Missouri	0.5	1	0	0	1	0	0.5	0	0	1
New Mexico	0	0	0	0	0	0	0	0	0	0
Ohio	1	1	0	0	1	1	1	0	0	1
Pennsylvania	1	1	0	0	0	1	0	1	1	1
Tennessee	1	1	0	1	1	1	1	0	0	1
Texas	0.5	0.5	0	0	0	1	1	1	0	1
West Virginia	1	1	0.5	0	0	1	1	0	0	1
Wisconsin	1	1	0.5	0	0	1	1	0	0	1
Other States	0.8	0.8	0.1	0.2	0.4	0.7	0.8	0.1	0.1	0.8
Total	14	13	2	3	6	12	13	2	2	14

Numbers may not add due to rounding. Due to calculation method, "partial" units are possible.
Numbers in the table are "indicators" of current State requirements.
0 = No requirements applicable in this State facilities will incur the full incremental costs of EPA requirements.
0.5 = Requirements are site specific therefore we assume that 1/2 the units will incur incremental costs.
1 = Mandatory requirements exist in this State, so there will be no incremental cost due to EPA requirements.

Source: SAIC *"Technical Memorandum on Cost Analyses for Large Volume Coal Combustion Waste,"* Submitted for U.S.EPA, Office of Solid Waste. June, 1993.

TABLE 2
RANGES OF AVERAGE TOTAL COSTS FOR COAL-FIRED ELECTRIC UTILITY WASTE DISPOSAL
(4th quarter 1986 dollars per ton)*

Type of Waste	Size of Power Plant			
	100 MW	500 MW	1000 MW	3000 MW
Landfills				
Fly Ash	9-18	6-11	5-9	2-6
Bottom Ash	10-16	5-9	4-8	2-6
FGD Waste	4-10	4-7	3-6	2-4
Surface Impoundments				
Fly Ash	17-31	9-17	8-14	5-8
Bottom Ash	11-26	8-15	7-13	5-8
FGD Waste	8-17	7-13	6-10	5-7

* Dollar per to estimates are based on the amount of waste produced each year. For purposes of this illustration, a power plant is assumed to generate annually 308 tons of fly ash per MW, 77 tons of bottom ash per MW, and 264 tons of FGD waste per MW. Amounts will vary depending on coal quality, FGD technology, and boiler type, among other factors.

Source: SAIC. *"Technical Memorandum on Cost Analyses for Large Volume Coal Combustion Waste,"* Submitted for U.S.EPA, Office of Solid Waste. June, 1993.

TABLE 3
INCREMENTAL COST VALUES FOR COAL-FIRED ELECTRIC UTILITY WASTE DISPOSAL

OPTIONS	INCREMENTAL COST ($/Ton)
Liner	
Single Clay Liner - 3 feet	0.80 - 2.90
Single Synthetic Liner - Unexposable	2.27 - 4.72
Leachate Collection and Treatment	5.34
Groungwater Monitoring	0.07 - 0.14
Site Closure	
Without Liner - 2 feet of soil	0.85 - 1.59
With Liner	2.39 - 5.57

Notes: Costs are presented in 1991 dollars. Costs were escalated to this level based on the GNP price deflator index reported by the U.S. Department of Commerce. The value of this index for 1991 is 131 (1986 was 115.2). Costs shown are incremental costs only; that is, only that portion of the costs in excess of current diposal costs, which result from more stringent regulatory requirements. A power plant is assumed to annually generate 308 tons of fly ash per MW, 77 tons of bottom ash per MW, and 264 tons of FGD waste per MW. (These amounts will vary depending on coal quality, FGD technology, and boiler type, among other factors.) For the purpose of this study, the cost associated with the basic landfill disposal practice for coal combustion waste was determined to be 5.76 - 10.39 dollars per ton of disposed waste based on values in Table 2. This is based on a representative 500 MW plant operating at a 70 percent utilization rate.

Source: Gilbert/Commonwealth, Inc. *"Coal Combustion Waste Dispposal: Update of State Regulations and Cost Data"*, for U.S. DOE, 1991.

TABLE 4
STATE FGD WASTE DISPOSAL INCREMENTAL COSTS[1]

State	Source[2]	Year[3]	Costs for Measures Implementation[4]				Total Incremental Cost for Additional Measures	Total FGD Waste Disposal Cost[5]			
			Liner Requirement	Leachate Control Requirements	Groundwater Monitoring Requirements	Closure Requirements		Size of Power Plant			
								100 MW	500 MW	1000 MW	3000 MW
								Landfills Impoundments	Landfills Impoundments	Landfills Impoundments	Landfills Impoundments
FL	EPRI	1991	0.80-9.44	5.34	0.07-0.14	2.39-5.57	8.60-20.49	13.15-25.04	13.15-28.45	12.01-27.31	10.87-25.04
								17.70-39.82	16.56-35.27	15.42-31.86	14.28-28.45
GA	EPRI	1991	0.40-2.36	2.67	0.07-0.14	00.85-1.59	3.99-6.76	8.54-18.13	8.54-14.72	7.40-13.58	6.26-11.31
								13.09-26.09	11.95-21.54	10.81-18.13	9.67-14.72
IL	EPA	1992	0	0	0	1.28-2.39	1.28-2.39	5.83-13.76	5.83-10.35	4.69-9.21	3.55-6.94
								10.38-21.72	9.24-17.17	8.10-13.76	6.96-10.35
IN	EPA	1992	1.33-14.50	0/5.34	0.07-0.14	2.12-3.97	3.52-23.95	8.07-35.32	8.07-31.91	6.93-30.77	5.79-28.50
								12.62-43.28	11.48-38.73	10.34-35.32	9.20-31.91
IA	EPA	1992	0.85-3.86	5.34	0.07-0.14	1.70-3.18	7.96-12.52	12.51-23.89	12.51-20.48	11.37-19.34	10.23-17.07
								17.06-31.85	15.92-27.30	14.78-23.89	13.64-20.48
KY	EPA	1992	0.40-2.36	2.67	0.07-0.14	0.85-1.59	3.99-6.76	8.54-18.13	8.54-14.72	7.40-13.58	6.26-11.31
								13.09-26.09	11.95-21.54	10.81-18.13	9.67-14.72
MI	EPA	1992	2.67-4.72	5.34	0.07-0.14	0.85-1.59	8.93-11.79	13.48-23.16	13.48-19.75	12.34-18.61	11.20-16.34
								18.03-31.12	16.89-26.57	15.75-23.16	14.61-19.75
MN	EPA	1992	0.26-2.90	5.34	0.07-0.14	0.85-1.59	6.52-9.97	11.07-21.34	11.07-17.93	9.93-16.79	8.79-14.52
								15.62-29.30	14.48-24.75	13.34-21.34	12.20-17.93
MO	GC	1991	0.53-1.93	2.67	0.04-0.07	2.39-5.57	5.63-10.24	10.18-21.61	10.18-18.20	9.04-17.06	7.90-14.79
								14.73-29.57	13.59-25.02	12.45-21.61	11.31-18.20
NM	EPA	1992	0	0	0	0	0	4.55-11.37	4.55-7.96	3.41-6.82	2.27-4.55
								9.10-19.33	7.96-14.78	6.82-11.37	5.68-7.96
OH	EPA	1992	0.80-4.83	5.34	0.07-0.14	2.39-5.57	8.60-15.88	13.15-27.25	13.15-23.84	12.01-22.70	10.87-20.43

TABLE 4 (Continued)
STATE FGD WASTE DISPOSAL INCREMENTAL COSTS

State	Source[2]	Year[3]	Costs for Measures Implementation[4]				Total Incremental Cost for Additional Measures	Total FGD Waste Disposal Cost[5]			
			Liner Requirement	Leachate Control Requirements	Groundwater Monitoring Requirements	Closure Requirements		Size of Power Plant			
								100 MW	500 MW	1000 MW	3000 MW
								Landfills Impoundments	Landfills Impoundments	Landfills Impoundments	Landfills Impoundments
								17.70-35.21	16.56-30.66	15.42-27.25	14.28-23.84
PA	EPA	1992	0.80-4.72	5.34	0.07-0.14	0.85-8.36	7.06-18.56	11.61-29.93	11.61-26.52	10.47-25.38	9.33-23.11
								16.16-37.89	15.02-33.34	13.88-29.93	12.74-26.52
TN	EPA	1992	0.80-2.90	5.34	0.07-0.14	0.85-1.59	7.06-9.97	11.61-21.34	11.61-17.93	10.47-16.79	9.33-14.52
								16.16-29.30	15.02-24.75	13.88-21.34	12.74-17.93
TX	EPA	1992	0.80-2.90	2.67	0.04-0.07	2.39-5.57	5.90-11.21	10.45-22.58	10.45-19.17	9.31-18.03	8.17-15.76
								15.00-30.54	13.86-25.99	12.72-22.58	11.58-19.17
WV	EPRI	1991	0.53-1.93	5.34	0.07-0.14	1.27-2.38	7.21-9.79	11.76-21.16	11.76-17.75	10.62-16.61	9.48-14.34
								16.31-29.12	15.17-24.57	14.03-21.16	12.89-17.75
WI	EPA	1992	1.33-4.83	5.34	0.04-0.14	0.85-1.59	7.56-16.73	12.11-28.10	12.11-24.69	10.97-23.55	9.83-21.28
								16.66-36.06	15.52-31.51	14.38-28.10	13.24-24.69

1. All costs are in 1991 dollars.

2. Sources:
   - EPRI - ICF Resources Incorporated. *"Coal Combustion Waste Management Study."* For U.S. DOE. February 1993.
   - EPA - SAIC.*"Overview of State Regulatory Programs Addressing Management and Disposal of FFC Wastes,"* for Special Waste Branch of Office of Solid Waste, U.S.EPA, March 1993.
   - GC - Gilbert/Commonwealth, Inc. *"Coal Combustion Waste Disposal: Update of State Regulations and Cost Data"*. For U.S. DOE. 1991.

3. All cost data are for the latest year avaylable.

4. These costs are estimated according to each state requirements (Table 1) and costs for additional measures (See Table).

5. Total costs for FGD waste disposal is estimated as a sum of a basic cost from Table reestimated into 1991 dollars and total incremental cost for additional measures. In case if some of additional measures have been already implemented on some particular power plant, the cost of these measures should be subtracted from total disposal cost.

SUPERCLEAN EMISSION & CO_2 CONTROL SESSION

The following manuscript was unavailable at the time of publication.

ELECTROCATALYTIC METHOD FOR SO_2/NO_X CONTROL

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Please contact author(s) for a copy of this paper.

DEVELOPMENT OF A METAL CHELATE ADDITIVE FOR USE IN WET LIMESTONE SYSTEMS TO REMOVE SIMULTANEOUSLY SO_2 AND NO_x FROM FLUE GAS

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INTRODUCTION

The combustion of fossil fuels generates SO_2 and NO_x pollutants which cause acid rain and urban smog[1]. Existing flue gas desulfurization scrubbers involve wet limestone processes which are efficient in SO_2 control but are incapable of removing water-insoluble nitric oxide. Moreover, the current technique for the post combustion control of nitrogen oxides emissions, ammonia-based selective catalytic reduction, suffers from various problems[2]. These include poisoning of the catalysts from flyash rich in arsenic or alkali, disposal of spent toxic catalysts, ammonia slip, and the effects of ammonia byproducts on plant components downstream from the reactor. To circumvent separate control schemes for both SO_2 and NO_x pollutants, we have developed an iron(II) thiochelate complex which promotes the solubility of NO in aqueous solution by rapidly and efficiently absorbing NO to form iron nitrosyl complexes. The bound NO is then converted via electrochemical reduction to ammonia to regenerate the active iron(II) catalyst for continued NO capture. The results suggest that this metal thiochelate-based process can be readily integrated into existing wet limestone scrubbers for the simultaneous removal of SO_2 and NO_x.

EXPERIMENTAL AND RESULTS

We report herein the NO absorption characteristics of a thiolated iron(II) chelate, $Fe^{+2}(DMPS)_2$, where DMPS is 2,3-dimercapto-1-propanesulfonate ($HSCH_2CH(SH)CH_2SO_3^-$).

$$Fe^{+2}(DMPS)_2(aq.) + NO(g) = Fe^{+2}(DMPS)_2(NO)_n(aq.) \quad [n = 1\text{-}2] \qquad (1)$$

Using a bubbling column (50mm i.d. x 420mm) in which simulated flue gas containing 300-600ppm NO is bubbled through a red-colored solution of $Fe^{+2}(DMPS)_2$ (10mM), the NO absorption capacity[3-6] of the resulting scrubber solution has been measured with the aid of a chemiluminescent NO_x analyzer. A typical NO absorption profile for a 10mM $Fe^{+2}(DMPS)_2$ solution under simulated flue gas scrubber conditions, e.g. 580ppm NO, 55 C, and pH 6.6, is shown in Figure 1(a). By graphically integrating the absorption trace, the concentration of the NO adduct is obtained. Thus, 7.5mM of $Fe(DMPS)_2NO$ is produced in Figure 1(a). Since flue gas contains 2-8% O_2, Figure 1(b) shows that the introduction of 5% O_2 reduces the NO absorption capacity of the solution by 44%. For comparison, a 10mM Fe^{+2}(EDTA) solution under similar experimental conditions will produce only 2.6mM of the NO adduct, as shown in Figure 1(c). Introducing 5%O_2 into the flue gas stream results in a 83% reduction in the NO absorption capacity of the Fe^{+2}(EDTA) solution (Figure 1(d)). It is quite clear then, that $Fe^{+2}(DMPS)_2$ possesses a significantly larger NO absorption capacity than Fe^{+2}(EDTA) (2.5 times more, anaerobically and 7.5 times more, in the presence of 5% O_2).

The visible spectrum of $Fe^{+2}(DMPS)_2$ is characterized by a charge-transfer band at 508nm. This band is no longer seen in the NO adduct, $Fe^{+2}(DMPS)_2(NO)$. The infrared data of $Fe^{+2}(DMPS)_2(NO)$ (Figure 2) show a characteristic absorption band for the terminally bound NO at 1702 cm^{-1}. However, at increasingly higher NO concentrations, a new type of nitrosyl complex is formed featuring both terminal NO (1830cm^{-1}) and bridging NO (1560cm^{-1}). There is also a corresponding shift to lower frequency from 2543cm^{-1} to 2426cm^{-1} for the S-H stretching band in the new nitrosyl complex. The S-H bond in the new nitrosyl complex is thus weakened, indicative of the participation of sulfur in bonding to the bridging NO, e.g. a Fe-N(=O)-S three-centered, two-electron bonding framework. The presence of two types of nitrosyl complexes (Figure 2) suggests that equation (1) can be rewritten in terms of two equilibria (K_1 and K_2) associated with the formation of nitrosyl complexes with : (1) only terminally-bound NO at low P_{NO} (< 500ppm) and (2) terminal and bridging NO at higher P_{NO} (>500ppm).

$$Fe^{+2}(DMPS)_2 + NO = Fe^{+2}(DMPS)_2(NO)_1 \tag{1a}$$
$$Fe^{+2}(DMPS)_2(NO)_1 + NO = Fe^{+2}(DMPS)_2(NO)_1(\mu\text{-}NO)_2 \tag{1b}$$

Both K_1 and K_2 have been determined from NO absorption experiments[3] carried out at low and high NO (>500ppm) concentrations, respectively. At 55 C, 75 C, and 95 C, the respective values of K_1 and K_2 (M^{-1}) are $2.1 \pm 0.2 \times 10^7$ and $6.9 \pm 0.1 \times 10^6$, $1.1 \pm 0.3 \times 10^7$ and $3.3 \pm 0.3 \times 10^6$, $6.9 \pm 0.2 \times 10^6$ and $1.8 \pm 0.2 \times 10^6$. For comparison, the equilibrium constant[7-9] for the formation of $Fe^{+2}(EDTA)(NO)$ under typical flue gas scrubber conditions, e.g. 300-600ppm NO, 55 C, pH 6, is $1.0 \times 10^6\ M^{-1}$. The higher value of the equilibrium constant for the formation of $Fe^{+2}(DMPS)_2(NO)_n$ thus provides a good measure of the greater thermodynamic stability of the DMPS-nitrosyl complex, and largely explains the much more efficient absorption of NO by $Fe^{+2}(DMPS)_2$ when compared with $Fe^{+2}(EDTA)$. The enthalpy and entropy for the formation of both types of nitrosyl complexes have been derived. These are, $\Delta H_1^o = -6.9 \pm 0.3$ kcal/mol, $\Delta H_2^o = -9.8 \pm 0.3$ kcal/mol, and $\Delta S_1^o = 8.2 \pm 0.4$ e.u., $\Delta S_2^o = 5.5 \pm 0.4$ e.u..

The presence of bisulfite/sulfite ions in solution did not alter the NO absorption characteristics, suggesting that SO_2 has no effect on the NO absorption capacity of $Fe^{2+}(DMPS)_2$. Unlike $Fe^{+2}(EDTA)(NO)$, $Fe^{+2}(DMPS)_2(NO)$ does not react with bisulfite/sulfite ions to yield undesired nitrogen-sulfur byproducts[10,11].

The clean removal of the bound NO from $Fe^{+2}(DMPS)_2(NO)$ to regenerate $Fe^{+2}(DMPS)_2$ for sustained NO absorption constitutes a critical step in the overall effectiveness of the metal chelate process for the removal of NO from flue gas. Moreover, the oxidation of the SH moiety in DMPS to a disulfide (S-S) linkage must be addressed since the thiol (-SH) group is needed to reduce Fe^{+3} to Fe^{+2} for sustained NO absorption. The electroreduction of a S-S linkage into a S-H bond has been achieved in the transformation of cystine to cysteine[12,13]. In our work, the electrolysis has proved to be well suited to accomplish the dual task involved in the regeneration of $Fe^{+2}(DMPS)_2$: (1) electrochemical removal of the bound NO, and (2) electroreduction of the S-S to the S-H moiety. The following scheme illustrates the chemistry involved:

$$Fe^{+2}(DMPS)_2 + NO = Fe^{+2}(DMPS)_2(NO) \tag{1}$$
$$Fe^{+2}(DMPS)_2(NO) + 5H_2O + 5e^- \text{---->} Fe^{+2}(DMPS)_2 + NH_4^+ + 6OH^- \tag{2}$$

$$Fe^{+2}(DMPS)_2 \xrightarrow{O_2} Fe^{+3}(DMPS)_2 \tag{3}$$
$$2Fe^{+3}(DMPS)_2 + 2DMPSH \text{------>} 2Fe^{+2}(DMPS)_2 + (DMPS)_2[S\text{-}S] + 2H^+ \tag{4}$$
$$(DMPS)_2[S\text{-}S] + 2H_2O + 2e^- \text{------>} 2\,DMPSH + 2OH^- \tag{5}$$

Cyclic voltammetry of $Fe^{+2}(DMPS)_2(NO)$ shows a reversible iron (II/III) redox couple and more significantly, a reduction wave due to NO reduction which can be seen at -0.75V vs. SCE (Figure 3). During controlled-potential electrolysis experiments on the preparative scale, the products from the electroreduction of coordinated NO were collected in a H_2SO_4 trap (100mL of ~0.9M H_2SO_4) and subsequently analyzed by ion chromatography. Results consistently showed the formation of NH_4^+ in quantitative yield. This electrolytic approach leads to the regeneration of

$Fe^{+2}(DMPS)_2$ with no attenuation in its NO removal capacity, as monitored by visible spectroscopy and NO absorption experiments.

DISCUSSION

The commercial viability of this metal thiochelate-based process has been considered and the following practical and economic analyses suggest that the process represents a strong case for further industrial scale-up.

The NO absorption rate in metal chelate solutions has been found to be a liquid film mass transfer control process[8,14,15]. The effectiveness of gas liquid contact is critical to achieve 80% NO removal, which is the target for NO removal processes. A Thiosorbic® lime pilot plant test[15] with 10-15mM $Fe^{+2}(EDTA)$ showed that NO removal was about 30% at a flue gas velocity of 2.5 m/sec and a L/G of 4.4 liter/m^3. The rate equations suggest that the absorption efficiency is improved[8,14] with an increase in the equilibrium constants for NO absorption. Moreover, the absorption efficiency as transfer units[15] increases in direct proportion to the gas-liquid interfacial area and to absorber height. With the increase of L/G, installation of sieve trays, and/or use of a turbulent contact absorber[16] to increase the interfacial area by a factor of about 4.5, the absorption rate of NO should reach 80%. The NO absorption rate of more than 80% efficiency by $Fe^{+2}(EDTA)$ has been demonstrated[17] at the pilot plant stage with an L/G of about 14 liter/m^3. Preliminary bench-scale experiments indicated that the reaction rate of NO with $Fe^{+2}(DMPS)_2$ was comparable to that with $Fe^{+2}(EDTA)$. Pilot plant tests are needed to determine the NO removal efficiency by $Fe^{+2}(DMPS)_2$ under realistic operating conditions.

In a preliminary economic evaluation of material costs, a fair estimate of \$1.00/lb DMPS is assumed. This estimate was derived[18] based on the synthesis of DMPS from allyl chloride, sodium sulfite, chlorine, and sodium hydrosulfide. We have considered reagent loss due to water entrainment in solid wastes. Under natural oxidation conditions where solid precipitates (filter cake of a mixture of calcium sulfite and sulfate) may occlude as much as 50% by weight of liquors, a wet limestone scrubber that removes 90% SO_2 from flue gas containing 2000ppm SO_2 in a 500MW coal-fired power plant would consume 2.7 ST of DMPS/day due to entraiment, assuming the scrubbing liquors contain 10mM $Fe^{+2}(DMPS)_2$. If the addition of this metal thiochelate results in the removal of 80% NO from flue gas containing 375ppm NO (i.e. 22.5 ST NO/day), then the DMPS loss is US\$158/ton NO_x removed. This loss may be reduced by washing the filter cake to recover the reagent. Under forced oxidation conditions where gypsum is precipitated, the reagent loss due to entrainment is about US\$31.6/ton NO_x removed, because the gypsum precipitates occlude only 10% by weight of liquors. However, aeration under forced oxidation conditions would accelerate the oxidation of $Fe^{+2}(DMPS)_2$. To get around this problem, the forced oxidation aeration may be performed after the extraction of entrainment liquors (Figure 4).

As illustrated in eq 2, five electrons are needed to regenerate the spent scrubber solution. While oxidation of the sorbent will actually require a total of nearly nine electrons to achieve the electroregeneration, we have found that addition of a five-fold molar excess of sodium thiosulfate will significantly slow down the oxidation of the chelate such that effectively, only six electrons are required for the regeneration. Based on the electricity cost of \$0.05/kw-hr, the electricity requirement for the process to absorb 300ppm NO and convert it to NH_3 suggests a cost of \$390/ton NO_x removed. With nominal costs expected for additional equipments, this cost should compare favorably to the cost of \$2000-\$4000/ton NO_x removed by the selective catalytic reduction (SCR) process[19]. More realistic cost evaluations of this new process can not be done until the completion of a pilot plant test.

PLANS

Bench-scale tests of this new metal chelate process using a 4 inch-diameter turbulent contact absorber are in progress.

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FIGURE CAPTIONS

Figure 1. NO absorption profiles for: (a) 10mM $Fe^{+2}(DMPS)_2$ + 580ppm NO + 0%O_2 (at 55 C and pH 6) -----> 7.5mM $Fe^{+2}(DMPS)_2(NO)$; (b) 10mM $Fe^{+2}(DMPS)_2$ + 580ppm NO + 5%O_2 (at 55 C and pH 6) ------> 3.3mM $Fe^{+2}(DMPS)_2(NO)$; (c) 10mM $Fe^{+2}(EDTA)$ + 575ppm NO + 0%O_2 (at 55 C and pH 5.9) ------> 2.6mM $Fe^{+2}(EDTA)(NO)$; (d) 10mM $Fe^{+2}(EDTA)$ + 550ppm NO + 5%O_2 (at 55 C and pH 5.8) ------> 0.44mM $Fe^{+2}(EDTA)(NO)$.

Figure 2. Infrared data for: (a) $Fe^{+2}(DMPS)_2$ + 300ppm NO (KBr pellet): 2543cm^{-1} (S-H), 1702cm^{-1} (NO), 1420cm^{-1} (C-H bend), 1191cm^{-1} and 1132cm^{-1} (S=O). (b) $Fe^{+2}(DMPS)_2$ + 100% NO (KBr pellet): 2426cm^{-1} (S-H), 1830cm^{-1} (NO), 1560cm^{-1} (bridging NO), 1385cm^{-1} (C-H bend), 1202cm^{-1} and 1137cm^{-1} (S=O). Note: † due to CO_2, * due to H_2O.

Figure 3. Cyclic voltammogram of $Fe^{+2}(DMPS)_2(NO)$ at 25 C and pH 6.0 (0.1M Na_2SO_4 supporting electrolyte; $[Fe^{+2}(DMPS)_2]$ = 10mM; glassy carbon working electrode; Pt wire counter electrode, SCE reference electrode; scan rate 50mV/s).

Figure 4. Conceptual flow diagram of a metal thiochelate-based process for flue gas cleanup. The coordinated NO is electrically reduced to produce NH_4^+, which may be separated from the liquors by heating. The NH_3 produced may be injected into the boiler to reduce the concentration of NO_x based on the principle of selective noncatalytic reduction (SNCR).

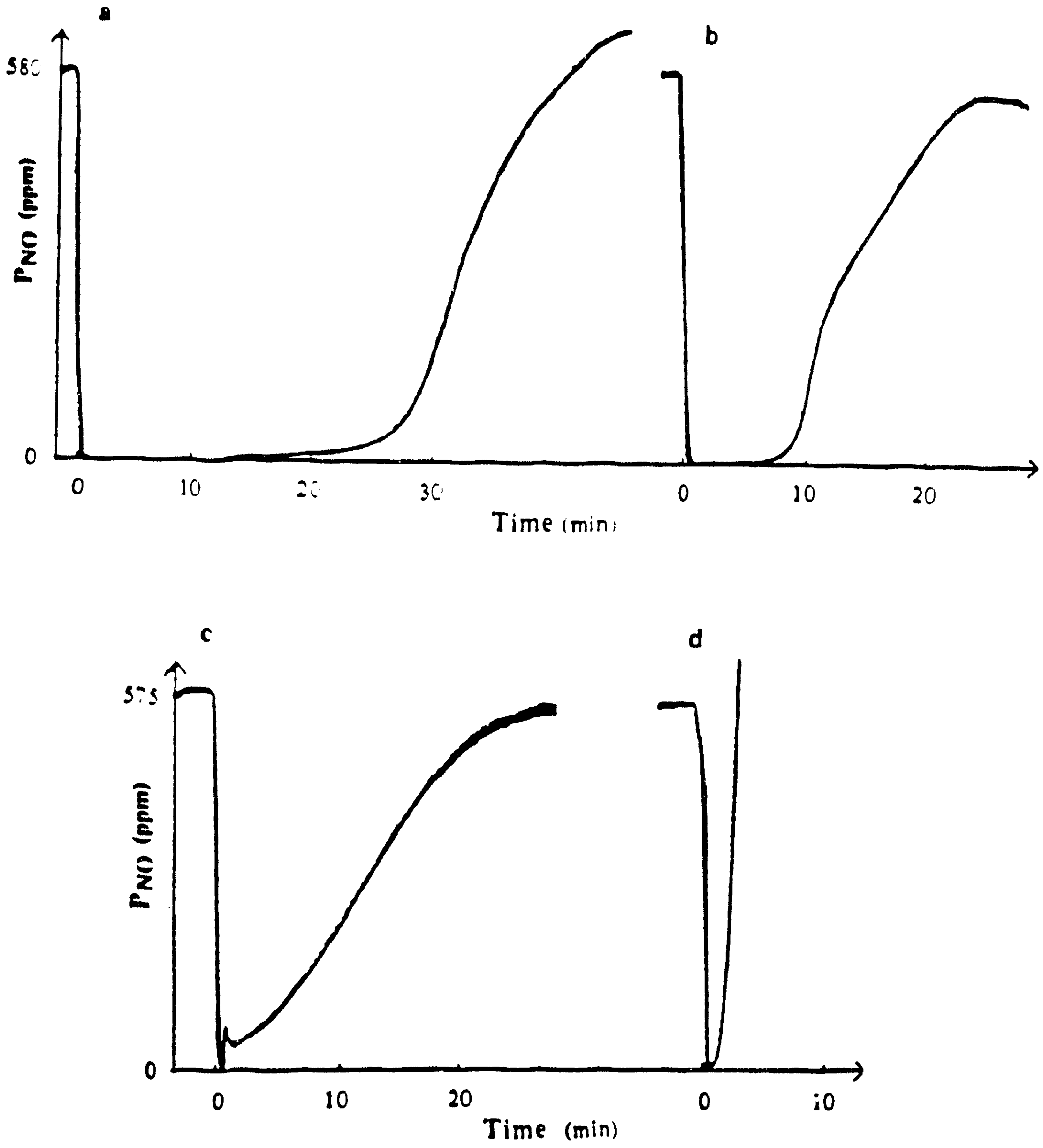
a
b
580
P_{NO} (ppm)
0
0
10
20
30
0
10
20
Time (min)
c
d
575
P_{NO} (ppm)
0
0
10
20
0
10
Time (min)

Figure 1

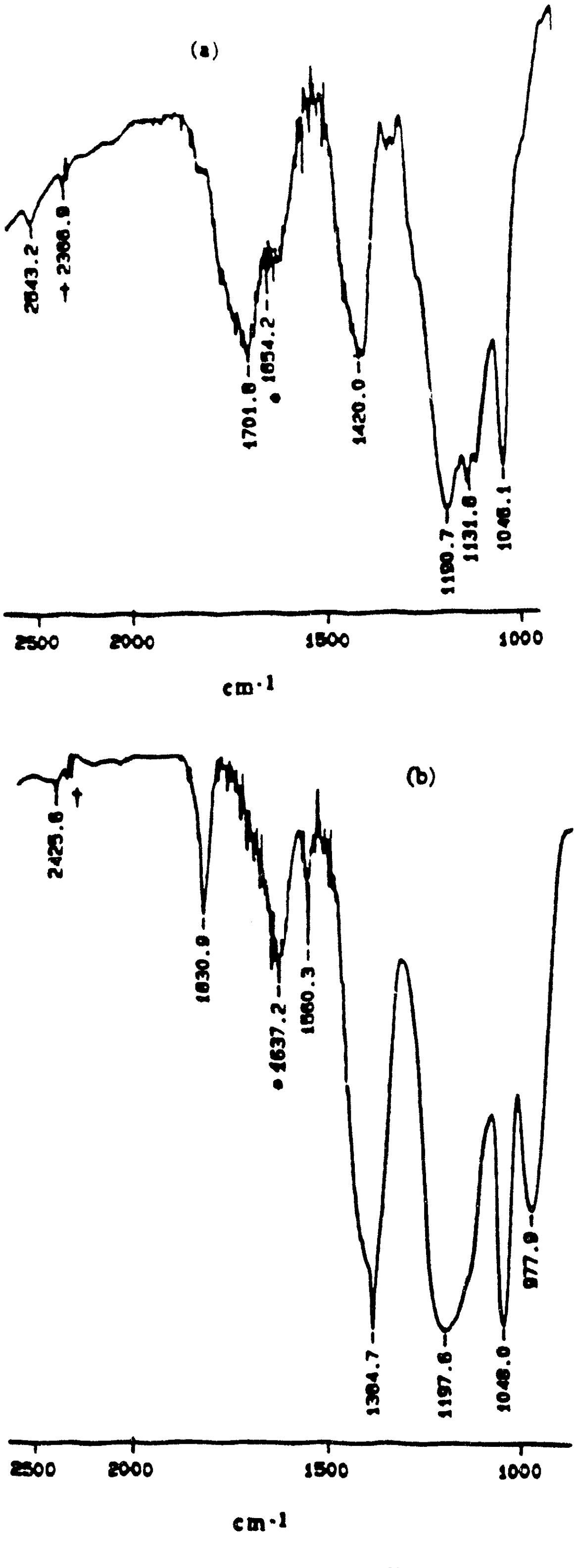

Figure 2

XBL 938-1218

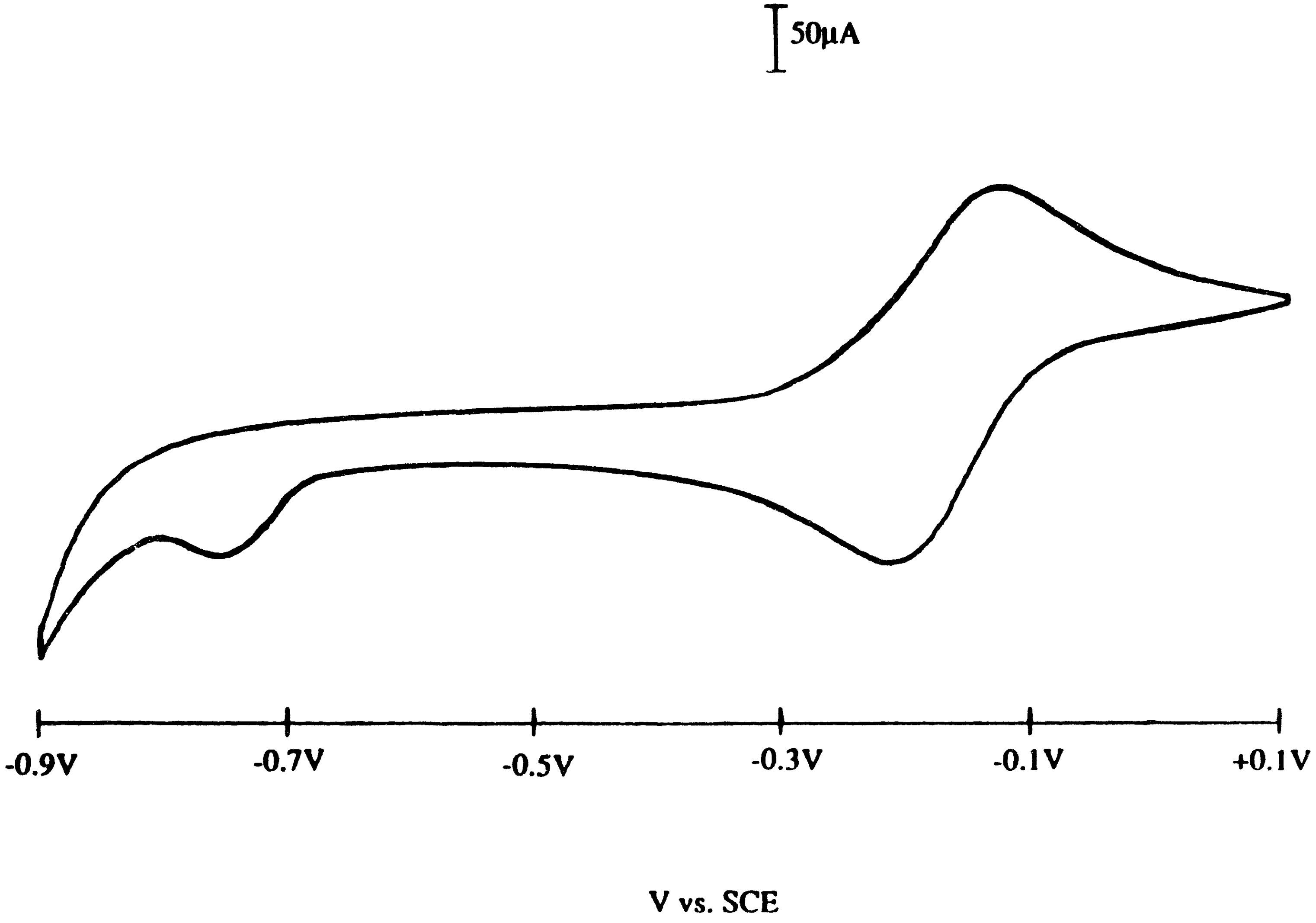

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Figure 3

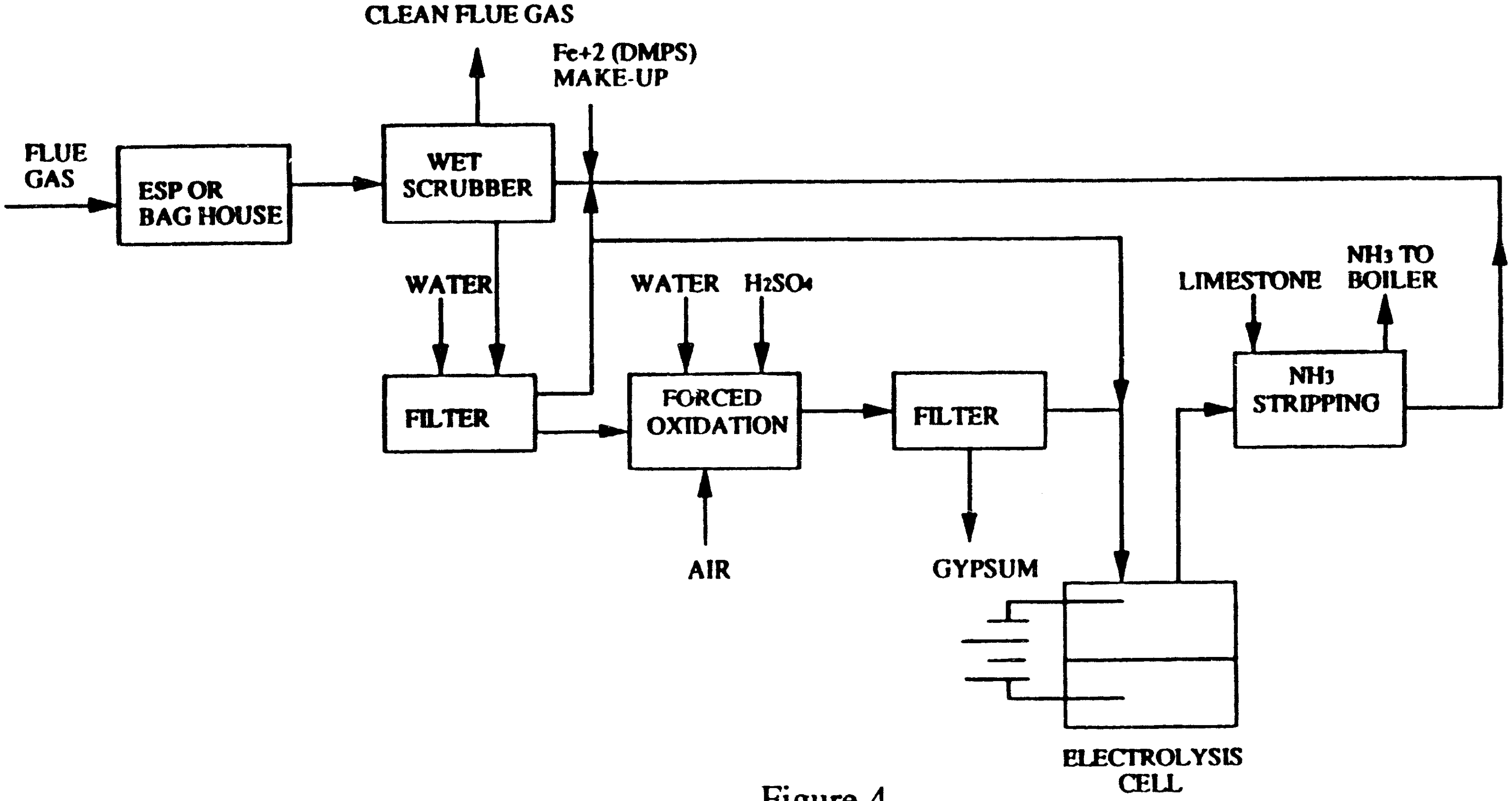
CLEAN FLUE GAS
Fe+2 (DMPS) MAKE-UP
FLUE GAS
ESP OR BAG HOUSE
WET SCRUBBER
WATER
FILTER
WATER
H2SO4
FORCED OXIDATION
AIR
FILTER
GYPSUM
LIMESTONE
NH3 TO BOILER
NH3 STRIPPING
ELECTROLYSIS CELL

Figure 4

The following manuscript was unavailable at the time of publication.

REGENERATION KINETICS OF CuO/ALUMINA SORBENT

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The following manuscript was unavailable at the time of publication.

IEA PROGRAM ON CO_2 CONTROL

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POTENTIAL FOR TERRESTRIAL DISPOSAL OF CARBON DIOXIDE IN THE U. S.

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ABSTRACT

Abandoned oil and natural gas reservoirs and deep aquifers were investigated as potential disposal sites for CO_2. Currently abandoned oil and gas reservoirs could hold approximately 2.9 Gt of CO_2. Since the annual CO_2 emissions from utility power plants is 2 Gt, these reservoirs would be filled in less than 1.5 years. The volume corresponding to ultimate reserves of oil and gas would hold roughly 100 Gt of CO_2. Therefore, the ultimate capacity for CO_2 storage is approximately 50 years. Over half of the CO_2 is emitted east of the Mississippi River, and most of the potential disposal sites are west of the Mississippi. Because of the high cost of transporting CO_2 by pipeline over long distances, only a small fraction of the reservoir capacity would be useful.

The capacity of deep aquifers for CO_2 disposal is highly uncertain. A rough estimate for the U.S., derived from global estimates, is 5-500 Gt of CO_2.

INTRODUCTION

One of the options proposed for reducing the buildup of greenhouse gases in the atmosphere is to collect CO_2 from point sources, such as utility power plants, and dispose of the CO_2 by injection into underground structures, such as, abandoned oil and natural gas reservoirs or deep aquifers. This paper describes the first steps toward systematically locating disposal sites and evaluating their suitability for CO_2 storage.

Information on the location and size of abandoned oil and natural gas reservoirs in the United States was extracted from a Petroleum Information, Inc., (PI) database. The locations of utility power plants and CO_2 emissions from each were taken from a Utility Data Institute (UDI) database. An estimate of aquifer disposal capacity was taken from recent International Energy Agency (IEA) reports.[1,2,3]

POWER PLANT SOURCES OF CO_2

If CO_2 concentration in the atmosphere must be reduced in the future, the most promising place to capture CO_2 is at utility power plants burning fossil fuels. An estimated 33 percent of U.S. anthropogenic CO_2 emissions originate from these sources.[4] Large amounts of CO_2 in relatively high concentrations are present in the flue gas of these plants. Other CO_2 sources are more diffuse, such as the transportation sector, which accounts for roughly 30 percent of total CO_2 emissions.[4] Collection of CO_2 from these sources would be more difficult to implement.

CO_2 emissions from utility power plant CO_2 sources in the United States were calculated by using data on fuel type and annual consumption at each power plant. An average carbon content was used for each fuel type. The CO_2 emissions for 1990 are shown by state in Table 1. The states with the highest CO_2 emissions are Texas (the largest emitter), Alabama, Georgia, Florida, and a belt of states extending across the upper Midwest from Missouri to New York. These 13 states (see Figure 1) generate almost 60 percent of U.S. power plant CO_2 emissions. The total CO_2 emissions from all power plants in 1990 was 2 Gt (giga tonnes, billion metric tons). This estimate compares well with Energy Information Administration (EIA) calculations yielding 1.8 Gt CO_2.[5]

DISPOSAL OF CO_2 IN ABANDONED OIL AND GAS RESERVOIRS

Evaluating the technical and economic aspects of this option requires knowledge of the status and capacities of abandoned reservoirs. The approach taken in this study is to identify those reservoirs where no production has been recorded for the past 3 to 12 months. The assumption is that these reservoirs have been abandoned as uneconomical, at least in the near term. The information on abandoned oil and gas reservoirs came from a PI database and shows that the empty volume is equivalent to 2.9 Gt of CO_2. Table 1 shows how abandoned reservoir volumes are distributed among the states.

A number of states, for example, Ohio and West Virginia, have significant oil and natural gas production but no easily accessible record of abandoned reservoirs. For these and several other states, a complete listing of abandoned reservoirs with cumulative production volumes is not yet available. Insufficient information about individual reservoirs makes identification and sizing of abandoned reservoirs uncertain. The majority of currently abandoned reservoirs are relatively small in volume and not good candidates for disposal.

Calculation Procedures

Estimated reservoir volumes were derived from cumulative oil, natural gas, and water production figures for each reservoir. Since the data were reported at ambient conditions on the earth's surface, the volumes of products were adjusted to account for increased temperature and pressure at reservoir depth. The reservoir volume was taken as the total adjusted volumes of products. The amount of CO_2 to fill this space at reservoir conditions was calculated using average underground pressure and temperature gradients and known CO_2 properties data. This correlation is recognized to be imprecise, but it is judged adequate for this preliminary analysis.

In calculating the adjusted hydrocarbon liquid and gas volumes, it was assumed that the liquids removed are incompressible, the gas behaves as a perfect gas at the pressure of the reservoir, and the volumes of the liquid and gas phases are additive.

Other Disposal Capacity Estimates

Other authors have estimated disposal capacity by other means. Total cumulative production of oil and natural gas would be another means of estimating disposal capacities. The underground volume corresponding to cumulative oil and gas production would hold approximately 70 Gt of CO_2. Not all this volume is available for disposal today. It will become available as the individual reservoirs are abandoned. The IEA has estimated global capacity by taking the ultimate reserves of oil and natural gas in the world. This capacity will be available at some distant time in the future. The ultimate capacity for CO_2 disposal in the U.S. equals approximately 100 Gt of CO_2.[7,8]

Comparison of Sources and Sinks

Most of the 48 contiguous states have insufficient abandoned reservoir capacity to dispose of the CO_2 generated by their power plants in one year. Table 1 gives the power plant CO_2 emissions, abandoned reservoir capacity, and ultimate reserves, along with the time in years to fill the reservoirs with CO_2. In this table, 14 states plus the District of Columbia (from CT to WI) have no oil or natural gas production. Without reservoirs, their CO_2 would have to be transported out of state for disposal. Fourteen states (from FL to WV) have oil or gas production, but their records are not sufficiently complete to allow identifying and sizing of abandoned reservoirs. Therefore, the amount of CO_2 that could be disposed of within each state is not well known at this time. None of these states is likely to have even one year's disposal capacity. Fifteen other states (excluding Alaska and Hawaii) would fill their abandoned reservoirs in less than one year. This leaves only five states that can dispose of their annual power plant CO_2 emissions for more than one year -- Mississippi, Texas, California, Oklahoma, and Louisiana. The data in Table 1 show that the total tonnage of power plant CO_2 emissions in the U.S. would fill the total capacity of abandoned reservoirs in approximately 1.4 years and the ultimate reserves in approximately 50 years.

Shallow reservoirs, less than 900 meters (3,000 feet), have too low a pressure to hold CO_2 in a dense, super-critical phase. Sequestering CO_2 becomes uneconomical because of inefficient storage. Approximately 10 percent of abandoned reservoirs are in this category.

For deep reservoirs, CO_2 compression costs will become prohibitive beyond some pressure. This pressure was arbitrarily assumed to be 345 Bar (5,000 pounds per square inch absolute) at a corresponding depth of 3,300 meters (11,000 feet). An economic analysis will be required to determine this cutoff pressure and depth.

The bulk of future disposal capacity is west of the Mississippi River. Almost 90 percent of domestic oil and gas is produced in seven states -- Texas, Louisiana, Oklahoma, New Mexico, Kansas, Wyoming, and California. The other 41 contiguous states, therefore, will never have large abandoned reservoir capacity, unless, of course, future oil and gas discoveries are made and utilized. Thus, if the CO_2 emitted by power plants in these 41 states is to be sequestered, it will have to be transported to one of the seven states where significant future abandoned reservoir capacity exists, and substantial costs will be incurred. Texas is a special case, because it is both the largest CO_2 emitter and has the largest volume of abandoned reservoirs and excess storage capacity.

Figure 1 shows the largest CO_2 emitting states and the seven states with the largest future abandoned reservoir capacity. It shows that total sequestration of CO_2 will require major pipeline networks stretching possibly to 2,500 Km (1,500 miles) and more. The cost of CO_2 pipeline construction is expected to be similar to natural gas pipelines. The cost of laying a natural gas pipeline is roughly \$1 million to \$1.5 million per mile,[9,10] including compression costs and right-of-way costs and depending on terrain and population density along the route. Securing permits for pipeline construction is becoming increasingly difficult, especially in populated areas. Legal battles could drag on for years, if the pipeline must go through highly built-up areas such as suburbs and industrialized areas.

The total volume of abandoned reservoirs will increase as currently producing reservoirs become exhausted. The next step is to estimate the timing of abandonment to determine the earliest date at which CO_2 disposal could begin in these reservoirs. This is not easy because the production histories for individual reservoirs are not readily accessible, and future production is difficult to predict. To fully evaluate this disposal option, better cost estimates and time schedules for commencement and continuation of disposal in oil and gas reservoirs should be developed. Refining of cost estimates requires knowledge of the size and location of both individual reservoirs and utility sources of CO_2. To optimize transportation costs, which appear to be a significant portion of the total cost of CO_2 disposal, an estimate of when individual reservoirs will be abandoned and available is necessary.

DISPOSAL OF CO_2 IN AQUIFERS

Aquifers can be divided into two categories - freshwater aquifers (with less than about 1000 to 3000 mg/L of dissolved solids) and brackish or saline aquifers. The former are sources of drinking water and are well protected by very stringent controls of the federal Safe Drinking Water Act. It is highly unlikely that CO_2 would ever be injected into or near these aquifers. Furthermore, freshwater aquifers are mainly at shallow depths, where pressures are too low for economic storage of CO_2 as a high density fluid.

Uncertainties Regarding Capacity Estimates.

The aquifers most suitable for disposal of CO_2 will be the deeper saline aquifers. These aquifers have not been studied as extensively as either the freshwater aquifers or hydrocarbon reservoirs because interest has been much less. The capacity of saline aquifers for disposal is difficult to estimate because of a dearth of data.

The potential aquifer volume available for disposal of CO_2 has been estimated by a number of authors, the range of global totals corresponding to 100-10,000 Gt of CO_2. A recent IEA report discusses these estimates in detail[1] and also gives results of studies in three geographical areas, namely, 1) the Alberta Basin in Western Canada, 2) Senegal in Western Africa, and 3) East Midlands in the UK. The wide range of estimates shows the huge uncertainties involved. Many aquifers in the world are not close to power plants or other sources of CO_2 and cannot be used for storage. The IEA study team concluded that extrapolation of the limited data available to predict global potential was not reasonable at this time.

Prorating the range of capacities above, using relative land areas, gives an estimated disposal capacity in the U.S. of 5-500 Gt of CO_2. Aquifer capacity appears to be at least equal to the capacity of ultimate oil and gas reserves and could be much greater. Further studies to determine aquifer capacity are obviously required.

Unfavorable CO_2 Flow Patterns

Super-critical CO_2, with a density of approximately 0.6 the density of typical brines, would be expected to rise to the top of a formation because of buoyancy. Also, since CO_2 at prevailing underground pressures and temperatures often has a lower viscosity than water, viscous fingering would occur, that is, channeling and accelerated flow of the CO_2 phase relative to the native fluid. The CO_2 would tend to travel along the upper surface of the formation, moving rapidly in a geometry resembling fingers of flow out from the injection well and leaving behind pockets of the aqueous phase. Only a fraction of the native fluid in the aquifer would be displaced, and, thus, only a fraction of the aquifer volume would be filled by CO_2. The CO_2 would be expected to fill any trap (a stagnant pocket above the normal flow path) it might encounter, since the CO_2 is lighter than the formation water. Eventually, the CO_2 would continue on and reach the edge of the formation and escape earlier than the time calculated for the native fluid. It has been estimated that possibly only 2-4 percent of the total volume of an aquifer would be filled with CO_2 because of these unfavorable properties.[7]

Other Uncertainty Factors

Some authors have stated that geologic traps will be required for CO_2 disposal.[1] If this is the case, only a fraction of the aquifer volume would be available for disposal. Aquifers would be filled much sooner than if the whole aquifer could be used. Traps have not been identified in aquifers to the extent that they have in oil and natural gas containing structures. If traps are required, extensive drilling of test wells could be required to locate them. However, current practice in underground disposal of hazardous and nonhazardous industrial waste in the U.S. does not require injecting into a trap. Obtaining a permit can be based on modeling studies which show that the injected waste will not escape from the confining formation for at least 10,000 years. Very slow movement of the native fluid in the formation, sometimes as low as a few centimeters per year, would give a retention time long enough to provide confinement for the required period. Hazardous and nonhazardous industrial wastes in the U.S. are currently being disposed of by underground injection at the rate of approximately 75 million cubic meters per year (20 billion gallons per year). This volume corresponds to about 0.05 Gt of CO_2 or 1/40 the rate of CO_2 emissions from utility power plants.

Chemical reactions between the injected CO_2 and the reservoir rock can take place in some instances. Disposal capacity could be either reduced or increased depending on chemical reactions involved.

Different procedures and policies among various states can affect usable storage capacity. Title 40 of the Code of Federal Regulations, Parts 144-149, contains the regulations for underground injection control (UIC). It establishes minimum requirements for states to set up a UIC program and to obtain primary enforcement authority. Each state can adhere to the federal regulations or impose more stringent rules. Pennsylvania, for example, does not issue permits for underground injection at this time. Other states may have taken this position as well, either because their procedures have not yet been approved by the U.S. Environmental Protection Agency, or because of their policy position. A particular state may allow disposal of wastes in an aquifer, while an adjacent state does not issue permits for the same aquifer. Therefore, the presence of a suitable aquifer may not necessarily lead to approval for CO_2 disposal.

The agency issuing disposal permits is concerned about the fate of the waste material, the time required for the material to travel to the edge of the disposal zone and a number of other issues. What happens to the native fluid is also important. The injected waste will displace the brine and may increase its flow velocity, resulting, for example, in increased rate of discharge into a lake or stream, which could handle the previous lower flow safely. Or the higher velocity may cause the brine to discharge along new paths into different zones, for example, mixing into drinking water aquifers that it previously bypassed. Also, if modeling shows that CO_2 injection would accelerate the movement of hazardous and nonhazardous wastes injected in the past, states might limit or prohibit CO_2 injection into these aquifers, further reducing available capacity.

Several state agencies have reported growing resistance from the public to underground disposal of wastes. Permits are becoming harder to obtain. Acceptance of large-scale disposal of CO_2 by underground injection will require much more intensive research to minimize the technical uncertainties and risks.

CONCLUSIONS

Despite the fact that large quantities of oil and natural gas have been extracted from reservoirs, the total volume of identifiable abandoned oil and natural gas reservoirs available for immediate disposal is relatively small, offering only enough capacity to dispose of power plant CO_2 emissions for about 1.5 years. New storage capacity will be added as currently producing reservoirs are depleted and abandoned. The timing of these additions is uncertain but is an important factor in evaluating future strategies for sequestering CO_2 in these reservoirs. Ultimate capacity for disposal is approximately 50 years, if all reservoirs could be used. This is highly unlikely.

Transportation costs will be high because of the vast distances in the U.S. between CO_2 sources and potential disposal sites. Except for Texas, which has a relatively large volume of abandoned reservoirs and high CO_2 emissions, the bulk of power plant CO_2 is emitted in industrialized states remote from potential disposal sites. Therefore, only a small fraction of abandoned reservoir capacity will ultimately be used to store CO_2.

This method of disposal will make sense in certain localities where large abandoned reservoirs and power plants are in close proximity, such as along the Texas Gulf Coast. However, disposing all of the CO_2 from utility power plants in abandoned reservoirs will not be practical.

The potential for CO_2 disposal in aquifers is very difficult to estimate from the information available. Disposal capacity is probably as great or greater than the capacity in oil and gas reservoirs. Many power plant CO_2 sources are closer to potential aquifer disposal sites than to large oil and gas reservoirs.

Based on this work, additional effort should be directed toward the following:

- Developing better methods for predicting the number of years remaining in the active life of producing oil and gas reservoirs.

- Searching oil and gas production records of individual state agencies to obtain current information on abandoned reservoirs.

- Obtaining more reliable cost estimates relating to reservoir development and maintenance costs and CO_2 transportation costs. Predicting reservoir acquisition and permitting procedures and costs.

- Locating and characterizing candidate aquifers to determine their potential for CO_2 disposal.

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Table 1. Years of CO_2 Storage Capacity in Oil and Gas Reservoirs by State.

State	Power Plant Emissions,* Million tonnes CO_2/yr	Abandoned Oil and Gas Reservoir Capacity,** Million tonnes CO_2	Storage Capacity Today, Years	Ultimate Reserves, Equivalent Capacity,*** Billion tonnes CO_2	Ultimate Storage Capacity, Years
AK	0.7	10	15.0	2.7	3,900
HI	7.6	None	0	None	0
AL	54.2	4	0.1	0.3	5
AR	27.9	0	0	1.0	34
AZ	39.8	0	0	-	-
CA	24.3	160	6.4	6.0	250
CO	36.9	9	0.2	1.2	33
IL	64.7	1	0	-	-
IN	107.2	0	0	-	-
KS	34.6	2	0	4.5	130
KY	72.5	0	0	0.6	8
LA	37.6	58	1.6	15.0	400
MI	75.6	11	0.2	0.6	8
MS	11.6	230	20.0	1.2	100
MT	22.7	3	0.2	0.4	16
NE	17.4	8	0.5	-	-
NM	30.8	11	0.4	6.1	200
OK	41.3	140	3.5	10.0	250
PA	109.0	22	0.2	1.4	13
TX	233.0	2,100	9.2	38.0	160
UT	32.1	22	0.7	0.6	19
WY	49.3	27	0.6	3.2	66
FL	87.8	N/A	-	0.1	1
IA	33.7	N/A	-	-	-
MD	29.1	N/A	-	-	-
MO	60.9	N/A	-	-	-
ND	43.3	N/A	-	0.3	7
NV	18.6	N/A	-	-	-
NY	67.2	N/A	-	-	-
OH	123.5	N/A	-	0.9	7
OR	0.7	N/A	-	-	-
SD	5.0	N/A	-	-	-
TN	48.6	N/A	-	-	-
VA	24.2	N/A	-	-	-
WA	11.7	N/A	-	-	-
WV	79.9	N/A	-	2.0	25
CT	14.5	None	0	None	0
DC	0.8	None	0	None	0
DE	7.8	None	0	None	0
GA	64.3	None	0	None	0
ID	0.0	None	0	None	0
MA	29.1	None	0	None	0
ME	3.2	None	0	None	0
MN	39.7	None	0	None	0
NC	49.2	None	0	None	0
NH	6.0	None	0	None	0
NJ	14.3	None	0	None	0
RI	0.5	None	0	None	0
SC	24.2	None	0	None	0
VT	0.0	None	0	None	0
WI	42.7	None	0	None	0
Misc States+	-	-	-	0.85	-
Totals	2,061	2,870	1.4	100	50

* Source: Utility Data Institute (1990)

** Source: Petroleum Information, Inc. (1992)

*** Source: Energy Information Administration (1988)

\+ Including: AZ, IA, IL, IN, MD, MO, NE, NV, NY, OR, SD, TN, VA, WA

N/A: Not Available

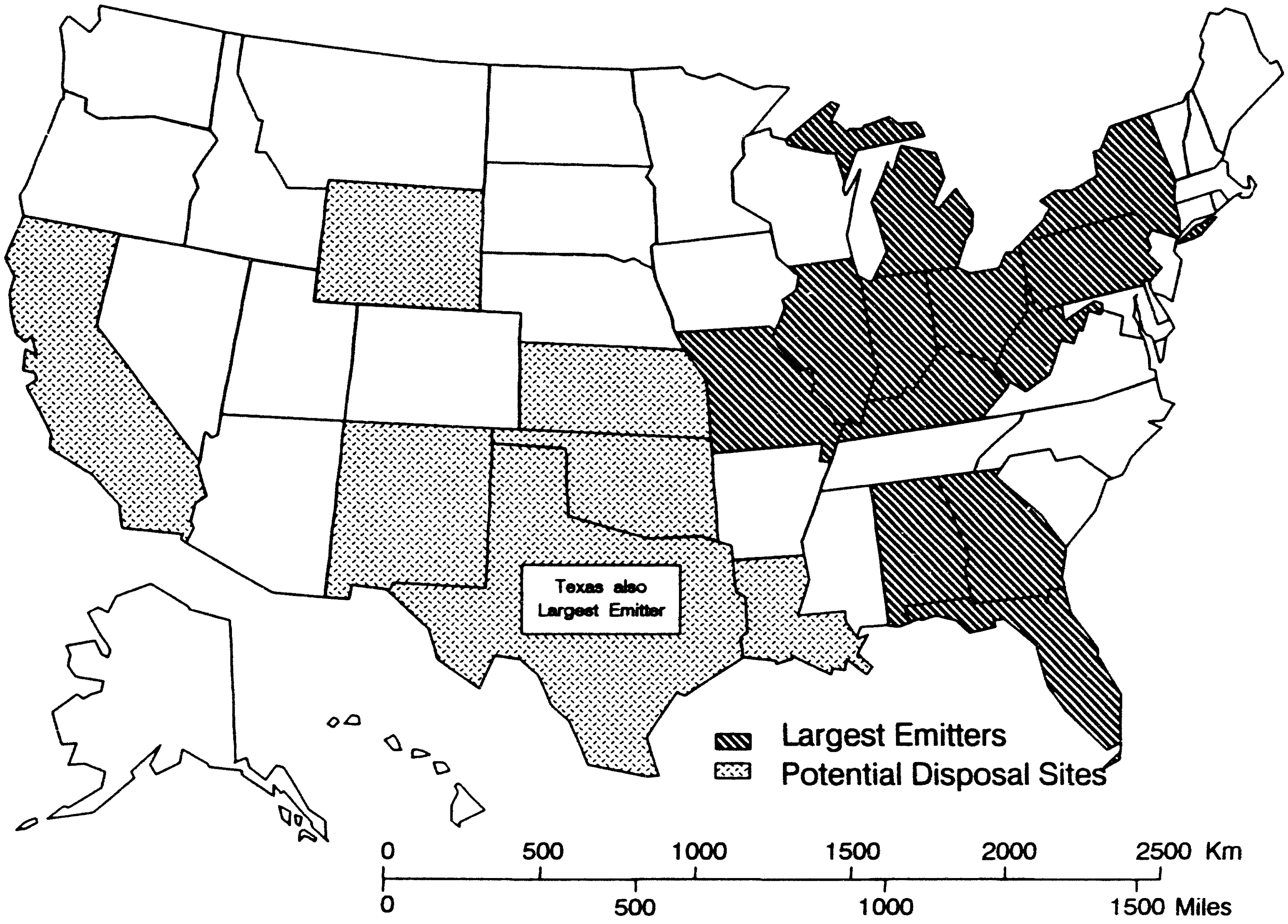

Figure 3. CO2 Sources and Potential Disposal Sites.

AN OVERVIEW OF CO_2 RECOVERY TECHNOLOGIES

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Abstract

Growing concerns about global climate change may prompt regulators to limit the emissions of CO_2 from poer plants. Efficiency Improvements and fuel switching, although helpful can have only a limited impact. It may therefore become necessary to remove CO_2 from flue gas and to recover it for long term storage or disposal. Several technically viable technologies exist , but all are expensive and require large amounts of parasitic power. The most energy efficient system is estimated to use 35% of the host plant's power.

Introduction

In recent years there has been a growing concern that human activities are contributing to global climate change through the emission of certain gases to the atmosphere. These gases are referred to as "greenhouse gases. Of those gases, carbon dioxide is generally of the greatest concern due to the massive quantities emitted. It has been estimated that in the United States alone, 2 billion tons are emitted from fossil fuel-fired power plants with similar quantities being emitted by mobile sources and by residential/commercial users of fossil fuels.

Numerous studies and research projects are underway for ways to reduce CO_2 emissions. The most straightforward approach is to improve the efficiency of the various CO_2 sources or to switch to fuels with a lower carbon content. However, the potential impact of these techniques is very limited. Another approach is to capture, recover and use or sequester the CO_2.

This paper will present a summary of the state-of-the-art in the capture and recovery of CO_2. Current work in this area deals essentially with fossil fuel-fired power plants since these are the largest single-source emitters of CO_2.

Summary

There are several processes which have been studied as potential means to capture and recover CO_2. These include

- Absorption/Stripping
- CO_2/O_2 replacing air to combustors
- Membrane separation of flue gas
- Molecular Sieves
- Cryogenic Techniques

Unfortunately, all these techniques, at their present state of development, require large amounts of parasitic power and money. It is clear that significant improvements are needed for all these techniques if their costs and energy consumption are not going to constitute a severe burden to the electric industry and its customers.

Discussion

Each of the techniques will be briefly discussed and costs/parasitic power requirements, as obtained from the literature, will be presented.

Scrubbing

There are numerous processes capable of removing CO_2 from flue gas streams. All of these processes contact the flue gas with a liquid reagent which absorbs the CO_2. The solution is then regenerated and the CO_2 is released for reuse or disposal. Among the reagents used are aqueous solutions of:

- Monoethanol Amine
- Diethanol Amine
- Di-isopropanol Amine
- Na_2CO_3 with Arsenites or Arsenates
- K_2CO_3
- Methyl Diethanol Amine
- Na_2CO_3

Most of the current attention is being paid to the processes based on monoethanol amine (MEA) and diethanol amine (DEA).

A simplified process flow diagram for an MEA system is shown in Figure 1. In a typical coal-fired installation, the CO_2 recovery system would be located downstream of the FGD system.

The flue gas enters the system through the flue gas cooler where cooling water is used to reduce the temperature of the flue gas to 10 to 40 °C, the operating range for these types of systems. The flue gas then enters the base of the scrubber where it is contacted countercurrently with a solution of MEA. The solution strength typically ranges from 10 to 30 % MEA. The clean flue gas leaving the top of the stripper is washed with water to minimize amine losses. The rich solution leaving the bottom of the stripper is heated by heat interchange with hot, lean solution returning from the stripper. The heated rich solution enters the top of the stripper where it flows downward while being stripped of CO_2 by hot vapors rising upward. The stripper overheads are passes through a cooler to condense the water and amine vapors. The vapor/liquid mixture is separated in the overhead separation drum. The amine solution is returned to the stripper while the CO_2 is rejected.

A portion of the lean hot solution leaving the bottom of the stripper is passed through the reboiler where it is vaporized to provide the energy for the stripper. Periodically, a portion of the stripper bottoms are treated in a reclaimer to reverse the reactions that occurred with SO_2 and to remove other impurities from the system.

The bulk of the stripper bottoms are pumped through the lean/rich solution interchanger, then through a solution filter, then through a lean solution cooler before being returned to the scrubber to contact the flue gas.

The CO_2 product would, at a minimum, need to be compressed since these systems typically operated at near-ambient pressure. In addition, residual water vapor would normally be removed before the CO_2 is sent to either disposal or reuse.

The MEA systems are capable of achieving high removal levels of CO_2 (typically 90+ %) and can produce a product of well over 99 % purity. Based on a study by Smelser and Booras (1990) the cost of CO_2 recovery using MEA is in the $39-41 per short ton. The following data, presented by Sander and Mariz (1992) are for a 200 tonne/day CO_2 production facility and are generally indicative of MEA-based CO_2 recovery systems.

Capital Cost (1990)	$12,000,000
Steam	16.2 tonne/hr
Power	80 KWH/tonne of CO_2
Cooling Water	165 m^3/tonne of CO_2
Operating Labor	1 full-time, 1 part-time per shift
Annual Maintenance	2-3 % of Capital
Reagents	$4-5/tonne of CO_2

In addition to the monetary cost, a major drawback is that these systems use about 35% of the utility plant production as parasitic power. Thus, a plant that had been 40% efficient would be reduced to an efficiency of less than 30 %. The major reason for the large reduction is the steam required for the reboiler.

There is some potential for improvement in this type of process. Optimizing integration with the host power plant, as opposed to retrofit application, might offer some efficiency improvement. It seems, however, that reducing steam to the reboiler is the area that could have the most impact. This might be accomplished by improvements in heat exchanger design, ways to increase solvent loading or the development of better solvents.

O_2/CO_2 Pulverized Coal Boilers

Another concept (Figure 2) that has been given quite a bit of consideration is that, instead of separating CO_2 from the nitrogen in the flue gas we can fire a boiler using coal and a mixture of CO_2 and oxygen. This would result in a flue gas with only small amounts of nitrogen and oxygen, thus greatly reducing or eliminating the need to separate the flue gas components.

In this technique a mixture of nearly pure oxygen is mixed with recycled CO_2 from the flue gas. It is necessary to use the mixture since combustion of coal with pure oxygen would result in unacceptably high temperatures and would also result in significant performance problems due to altered heat transfer patterns. The altered heat transfer is caused by the differences in temperature and the different specific heats and emissivities of CO_2 and N_2 as well as greatly reduced flue gas volumes.

The major expense and utility requirements for this CO_2 mitigation technology are due to the air separation plant. If a relatively impure CO_2 product is unacceptable, then additional cost and utility consumption penalties would be incurred.

This process consists simply of mixing a portion of the flue gas with oxygen in proportions that best imitate air in the boiler. Only ducting, valves and controls are required to provide the CO_2/O_2 mixture once the O_2 is obtained from the air separation plant.

Oxygen is provided by a conventional air separation which compresses air in several stages with cooling of the air by cooling water after each stage of compression. The air is further cooled after the last stage by a refrigeration system. The air is then expanded and cooled to its condensation point by the Joule-Thompson effect. Separation of nitrogen, oxygen and argon (optional) is accomplished by low temperature distillation.

The major drawback to this technique is the energy penalty associated with the air separation plant. Ref 1 reports that parasitic power would be 55 % compared to 35 % for the amine-based technology. Ref 1 indicates that costs are expected to be higher than for an amine system while Nakayama et. al. indicate that the CO_2/O_2 option would cost less per year than an amine system. They also indicate slightly lower parasitic power requirements. These differences are largely attributable to whether or not SO_2/NO_x removal are required and whether or not credits are taken for their removal. Currently, there is some debate on whether SO_2 and NO_x can be disposed of with the CO_2. Depending on the answer to this question and on assumptions made regarding credits for avoiding SO_2 and NO_x reductions, costs and utility estimates for this technology could vary widely.

Problems associated with applying this technology, aside from cost and parasitic power, are associated with preventing air in-leakage to the boiler system. Since utility boilers tend to allow significant quantities of air to leak into the system, it is difficult to keep N_2 levels acceptably low.

In addition to refining boiler operation on the O_2/CO_2 mixture, the major area where improvement is needed is in reducing parasitic power requirements in the air separation plant. Since cryogenic air separation plants have been widely used for many years, large improvements are unlikely. Several chemical base separation processes have been developed - barium oxide/peroxide and the Molton (TM) processes. Both react O_2 from the air with their reagents and then apply heat to reverse the reactions. As stand-alone processes, these also tend to be high energy users. However, there appears to be considerable potential to reduce their energy requirements by careful integration into the power cycle.

Cryogenic Separation

Cryogenic separation entails separating the flue gas components at the very low temperatures where they are in the liquid or solid state. Cryogenic processes have been developed to separate CO_2 from hydrocarbons. These processes would have to be adapted to separating CO_2 from the other flue gas components. This cryogenic technique is similar to that used to produce the oxygen in the boilers where coal is combusted by an O_2/CO_2 mixture.

Two of the normal components of flue gas present problems for the conventional cryogenic system and must be removed to very low levels upstream of the cryogenic process. One is that particulate matter found in coal-derived flue gas can cause excessive wear in the compressors used in cryogenic processing.

The presence of water vapor in the flue gas is also a serious problem since, at the conditions at which the flue gas components are to be separated, the formation of CO_2-water solids (clathrates) or of the formation of ice can cause serious operating problems.

After particulate removal, the flue gas is treated by conventional means (cooling/condensation) to remove the bulk of the water vapor. It must then be treated by desiccants to remove the water vapor to extremely low levels.

Following dehydration, the flue gas is compressed in several stages, with cooling by water cooled heat exchangers following each stage. Additional cooling is provided by a refrigeration system following the last stage of water cooling. The gas is then expanded to achieve cooling to its condensation temperature. Separation of the nitrogen and residual oxygen is then accomplished by conventional cryogenic separation. SO_2 and NO_x would remain with the CO_2 unless their removal was required. This system would be used with an air fired boiler or with one where coal is burned in an O_2/CO_2 mixture if the impurities are unacceptable in the CO_2.

As with all CO_2 recovery processes as they exist today, the major objections are cost and energy requirements. Energy requirements have been estimated at more than 50 % of the power plant output and costs are greater than for amine-based systems.

Due to the large amounts of mechanical energy required to compress the total volume of flue gas it is not likely that this type of process can be improved sufficiently to greatly reduce its energy demand, although some improvements are possible.

Membrane Technologies

Two types of membranes are applicable to recovering CO_2 from flue gases - gas separation membranes and gas absorption membranes.

Gas separation membranes are typically polymers. The gas mixture, under pressure is passed over one side of the membrane and the gases diffuse through the membrane to the low pressure side at different rates. The rate at which each gas diffuses through the membrane is determined by its partial pressure and the permeability of the gas. The permeability of a gas is the product of its solubility and its diffusion coefficient. The ratio of the permeabilities of two gases is defined as the membrane's selectivity for that gas pair. Selectivities of several suitable polymers, as presented by Feron, et al., are shown below:

Polymer	CO_2-N2 Selectivity
Polyphenylene-oxide	19
Cellulose Acetate	66.5
Polysulfone	30
Polyimide	23.3

In its simplest form, a single staged separator, compressed flue gas would be passed over a membrane and the CO_2 rich portion would be sent to disposal while the CO_2-free portion would be discharged. Unfortunately, this simple system results in low recovery and low purity. Better results are achieved in a two stage system as shown in Figure 4. While purity and recovery are adequate, the cost of CO_2 recovery reaches $71/tonne (Van Der Sluus, el al, 1992). The major technical drawback is that the required flue gas compression uses more than half the electricity produced. Improved selectivity of membranes could improve this situation. Several authors have estimated that CO_2-N2 selectivity needs to be about 200 in order to make membranes competitive with MEA systems.

Gas absorption membranes are a relatively new development. These are permeable, hydrophobic materials. (Figure 5.) Flue gas is passed on one side and the absorbing solution is held on the other by the hydrophobic nature of the membrane. The use of these membranes allows for efficient, compact absorber design (e.g., in an MEA system). Currently, operation is limited to near atmospheric pressure. Future development of these membranes might make them useful in improved absorbers. Unfortunately, the major costs associated with scrubbers are the gross energy requirements associated with solution regeneration.

Membranes are not currently suited to separating CO_2 from power plant flue gas. Development of gas separation membranes with selectivities of 200 or above and gas absorption membranes capable of operating above atmospheric pressure might make these technologies more competitive.

Physical Adsorption

In physical adsorption systems, gases are separated by selectively adsorbing one component onto a high-area solid sorbent. When the sorbent becomes "full" the sorbent is regenerated by either raising the temperature (temperature swing) or lowering the pressure (pressure swing adsorption).

In a typical pressure swing application (Figure 6) the flue gas would be cooled and compressed then passed over the adsorbent bed where CO_2 would be retained. When the sorbent approached saturation, the flue gas flow would be shifted to the second bed and the first bed would be regenerated, with the CO_2 product being compressed for transport. Typical sorbents and their potential CO_2 capacity are (8):

Adsorbent	Capacity (wt %)
Zeolite	6-16
Activated Alumina	2
Activated Carbon	5-7
Silica Gel	3

It can be seen that the capacity of these adsorbents is rather low. Thus large quantities of sorbent and/or frequent recharging would be required. These systems are modular and are generally considered to be best suited to applications smaller than utility plants. Compression and regeneration energy requirements are quite high (80 % of power plant capacity). Therefore, these systems are not competitive with MEA scrubbers.

Conclusions

Table 1, from Ref 1, summarizes the key characteristics of each technology.

Several technologies (MEA scrubbers, O_2/CO_2 combustion, and cryogenic separation) are technically ready to remove CO_2 from flue gas and to recover a relatively pure byproduct. Solid adsorbents and membranes still require development work to be used a power plant scales. When examining costs and parasitic power requirements, it becomes obvious that all these technologies are extremely expensive and gross users of energy. By way of comparison, a well designed and operated flue gas desulfurization unit will use 2 or 3 % of the power plant output, while the least energy intensive CO_2 recovery system uses in excess of 30 %.

Attributes of CO_2 Capture Technologies

Attribute	Chemical	Cryogenic	Membranes	Adsorption
Capture efficiency, %	90	90	80-90	90
Net CO_2 Reduction, %	84	78	60-80	50
Cost, $/Tonne Avoided	61	*	*	*
Developmental Feasibility ^{O}	5	3	3	3
Energy Consumption, % of Net Power Product	35	55	50	80
Environmental Impact $^{+}$	1	2	3	3
Potential Barriers $^{+}$	3	3	1	1
By-Product Credits $^{+}$	1	1	1	1

* Not reported, but expected to be greater than conventional amine technology.

^{O} Scale 0 (concept) to 5 (existing technology).

$^{+}$ 0 (major barriers, impacts, no credits) to 3 (minimal barriers, impacts, high credits).

It must be noted that SO_2 removal technologies are mature and that great improvements in efficiency, performance and reliability have taken place. However, at this point in time, the energy and money required to recover CO_2 from flue gas are exorbitant. Therefore, it must be concluded that no practical, economical way exists today to remove and recover CO_2. Much more research is needed.

Recommendations

There are several areas in which continued work might lead to significant improvements in CO_2 recovery technologies.

All technologies should benefit from optimizing their integration into the power cycle. Scrubbers and chemical O_2 separation for O_2/CO_2 firing seem to be particularly amenable to improvement by this technique. These technologies would also benefit greatly from the development of reagents which require greatly reduced energy to regenerate.

Gas separation membranes are currently non-competitive with scrubbing systems and are likely to remain so for some time to come given that a three fold increase in selectivity is needed for them to "catch up" to where scrubbers are today. Research in this area is recommended since a major breakthrough could result in a simple effective technique to separate CO_2.

Membrane separation, CO_2/O_2 combustion and cryogenic separation would all be helped by improvements in compressor efficiency. Equipment manufacturers already work on this area and additional research is not recommended specifically for CO_2 recovery systems. In addition, improvements are likely to come slowly and major improvements are needed.

In general, it is recommended that R & D be continued to develop CO_2 recovery systems that are far less dollar and energy intensive so that, if the need to recover CO_2 is established, these systems will not place an undue burden on the world's economy.

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