

INNOVATIVE CLEAN COAL TECHNOLOGY (ICCT)

DEMONSTRATION OF SELECTIVE CATALYTIC REDUCTION (SCR)  
TECHNOLOGY FOR THE CONTROL OF NITROGEN OXIDE (NOx)  
EMISSIONS FROM HIGH-SULFUR COAL-FIRED BOILERS

Technical Progress Report  
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## Section 1 SUMMARY

The objective of this project is to demonstrate and evaluate commercially available Selective Catalytic Reduction (SCR) catalysts from U.S., Japanese and European catalyst suppliers on a high-sulfur U.S. coal-fired boiler. SCR is a post-combustion nitrogen oxide (NO<sub>x</sub>) control technology that involves injecting ammonia into the flue gas generated from coal combustion in an electric utility boiler. The flue gas containing ammonia is then passed through a reactor that contains a specialized catalyst. In the presence of the catalyst, the ammonia reacts with NO<sub>x</sub> to convert it to nitrogen and water vapor.

Although SCR is widely practiced in Japan and Europe on gas-, oil-, and low-sulfur, coal-fired boilers, there are several technical uncertainties associated with applying SCR to U.S. coals. These uncertainties include:

- (1) potential catalyst deactivation due to poisoning by trace metal species present in U.S. coals that are not present in other fuels.
- (2) performance of the technology and effects on the balance-of-plant equipment in the presence of high amounts of SO<sub>2</sub> and SO<sub>3</sub>.
- (3) performance of a wide variety of SCR catalyst compositions, geometries and methods of manufacture under typical high-sulfur coal-fired utility operating conditions.

These uncertainties will be explored by constructing a series of small-scale SCR reactors and simultaneously exposing different SCR catalysts to flue gas derived from the combustion of high-sulfur U.S. coal.

The demonstration will be performed at Gulf Power Company's Plant Crist Unit No. 5 (75 MW capacity) near Pensacola, Florida. The project will be funded by the U.S. Department of Energy (DOE), Southern Company Services, Inc. (SCS on behalf of the entire Southern electric system), and the Electric Power Research Institute (EPRI). SCS is the participant responsible for managing all aspects of this project.

The project is being conducted in the following three phases:

- Phase I - Permitting, Environmental Monitoring Plan and Preliminary Engineering
- Phase II - Detailed Design Engineering and Construction
- Phase III - Operation, Testing, Disposition and Final Report

During this reporting period, detailed design engineering and construction continued. Engineering on the total project is over 90 percent complete. Major equipment delivered to the site during this period included the ammonia storage tank, service water pump, and reactors.

Fabrication of the reactors and transition pieces were begun. Two progress inspection visits to the fabrication shop were made and all the reactors and transition pieces were shipped to the site. The erection of the small reactors upon the support steel structure was begun.

Piping expansion joint bids were issued, bids received and evaluated, and a contract award made. These have been procured and delivered to the site.

Vendor drawings were received and reviewed for the personnel and catalyst hoist. The ductwork expansion joints were designed and an inquiry issued. An award for supply of the ductwork expansion joints was made upon completion of the evaluation of vendor bid submittals.

Additional platforms to provide access to instrumentation were requested based on review by the testing services subcontractor. Design of these platforms was begun. The vendor drawings for the control room elevator were reviewed and approved.

The structural steel painting specification package was prepared and released for bids. Vendor bid evaluation was completed and a contract award was in progress at the end of this reporting period.

With the exception of a few minor items, all the electrical engineering scope has been completed. Instrumentation and Controls personnel completed configuration of the Bailey Control System and check out and testing were in progress at the end of this reporting period. Development of the graphic screens was begun and almost finished. Preparation of the control system was begun for simulation and testing of logic and for operator training during October. Work also started in programming to trend and archive data.

Manufacturing of the gas analysis system continued and an inspection was made by SCS of the first system produced. A final witness test was scheduled for October.

Construction of the Plant Crist SCR demonstration facility continued with the remaining steel fabrication being completed. The structural steel erection was also concluded in September. The construction of the control room building and gas analysis room was started.

The mechanical and insulation contractor mobilized and began work. The large fly ash cyclones, bypass heat exchangers, air preheaters, large reactor fans, and ammonia storage tank were set in place. The cutting of ductwork, piping, structural steel, and cable tray penetrations in asbestos siding was completed. Installation of ductwork commenced and about half of the ductwork from the cyclones to the test facility fans and the ductwork return between these fans and the host unit ducts was erected. Insulation of some installed equipment was begun.

The construction contract for electrical and I&C erection was awarded. The electrical contractor mobilized and began work. Fabrication of cable trays and construction of switchgear foundations was started and completed. Erection of the cable trays and setting of the switchgear was begun.

The operators for the demonstration facility have been selected and they are scheduled to begin training in October. Information and training material were prepared for use by the operators.

Negotiations of terms and conditions for the testing/analytical services were completed and a contract was signed with Southern Research Institute. Development of the data reduction methodology was begun through formulating plans for retrieval and storage of data within the Bailey Control System, transfer of data into a DOS data base format, extraction of data from the gas analysis system, and use of the data in modeling results.

All of the participating catalyst suppliers responded to the revised laboratory testing protocol issued during the previous quarter. In general the laboratory testing protocol is now established. Negotiation of the previously submitted Evaluation Agreement was concluded with the catalyst supplier selected in the evaluation conducted earlier this year (replacing a catalyst vendor who withdrew from the project). The agreement was in the process of being signed by both parties at the end of this quarter.

Weekly coordination meetings were held with Design Engineering. Monthly project review meetings were held between SCS and Gulf Power at Plant Crist. A paper describing the status of

the project and design issues was presented at the First Annual Clean Coal Technology Conference in Cleveland, Ohio, in September. Two of the three U.S. catalyst suppliers were visited to discuss reactor design, catalyst module design, testing protocol, and testing plans.

A Continuation Application and request for additional funds were prepared and submitted to DOE for approval.

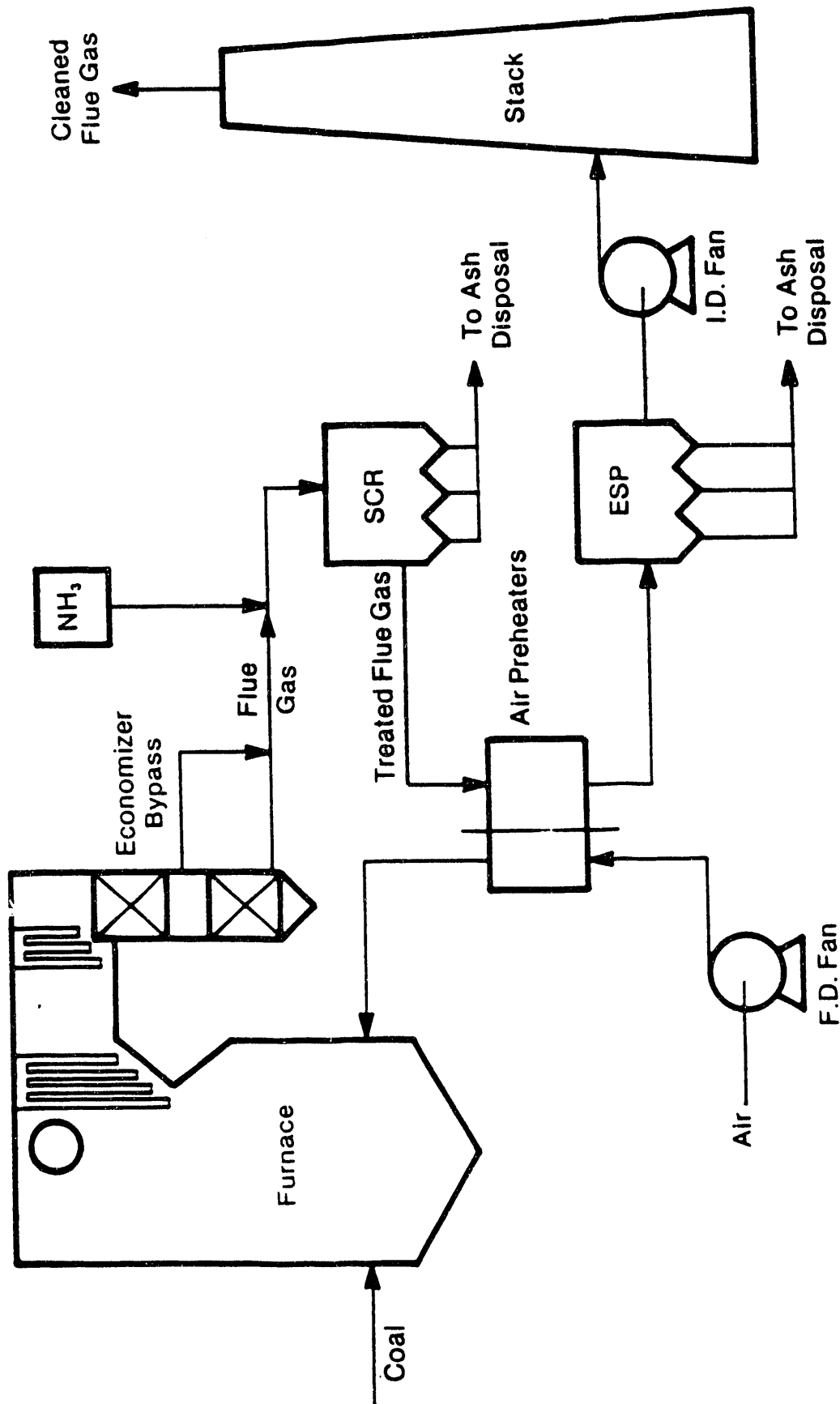
## Section 2 INTRODUCTION

The Innovative Clean Coal Technology (ICCT) Program is designed to demonstrate clean coal technologies that are capable of retrofitting or repowering existing facilities to achieve significant reduction in sulfur dioxide (SO<sub>2</sub>) and/or nitrogen oxides (NO<sub>x</sub>) emissions. The technologies selected for demonstration are capable of being commercialized in the 1990s and are expected to be more cost effective than current technologies.

This ICCT project is jointly funded by the U.S. Department of Energy, the Electric Power Research Institute (EPRI), and by Southern Company Services (SCS) on behalf of the entire Southern electric system. The project's objective is to demonstrate the selective catalytic reduction (SCR) process that removes nitrogen oxides (NO<sub>x</sub>) from the flue gas of boilers that burn U.S. high-sulfur coal. The SCR technology involves the injection of NH<sub>3</sub> into the flue gas and the subsequent catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> to produce molecular nitrogen (N<sub>2</sub>) and water vapor.

A simplified SCR process flow diagram with major equipment is shown in Figure 1. Specifically, hot flue gas leaving the economizer section of the boiler is ducted to the SCR reactor. Prior to entering the reactor, NH<sub>3</sub> is injected into the flue gas at a sufficient distance upstream of the reactor to provide for complete mixing of the NH<sub>3</sub> and flue gas. The quantity of NH<sub>3</sub> can be adjusted and it reacts with the NO<sub>x</sub> from the flue gas. The flue gas leaving the catalytic reactor enters the air preheater where it transfers heat to the incoming combustion air. Provisions are made for ash removal from the bottom of the reactor since some fallout of fly ash is expected. Duct work is also provided to bypass some flue gas around the economizer during periods when the boiler is operating at reduced load. This is done to maintain the temperature of the flue gas entering the catalytic reactor at the proper reaction temperature of about 700°F. The flue gas leaving the air preheater goes to the electrostatic precipitator (ESP) where fly ash is removed. The ESP is part of the existing plant and is generally unaffected by the SCR system except as higher SO<sub>3</sub> content affects the electrical resistivity of the fly ash or if NH<sub>4</sub>HSO<sub>4</sub> co-precipitates with the fly ash.

The SCR technology is in commercial use in Japan and western Europe on gas-, oil-, and on low-sulfur, coal-fired power plants. The first utility applications of SCR catalyst technology started in Japan in 1977 for oil- and gas-fired boilers and subsequently in 1979 for coal-fired boilers. As of 1986, ninety utility boilers in Japan had been equipped with SCR catalyst technology including



**FIGURE 1. BLOCK FLOW DIAGRAM OF SCR INSTALLATION.**



twenty-two coal-fired boilers. These coal-fired boilers represent a combined capacity in excess of 6500 MWe and are typically fired with a low-ash, low-sulfur coal.

In addition to Japanese experience, several countries in western Europe (most notably Germany and Austria) have passed stringent NO<sub>x</sub> emission regulations that have all but mandated the installation of SCR. Prior to commercial SCR installations in Germany, utility companies demonstrated several types of SCR facilities in prototype demonstration programs similar to this ICCT project. Over 50 SCR pilot plants were built and operated in western Europe. These pilot plants ranged from 19 to 6200 scfm and provided the data base that led to commercialization of the SCR technology in western Europe.

Previously completed U.S. work with the SCR process on utility boilers consists of three projects which were carried out in the late 1970s and early 1980s. One of these was carried out on a natural gas-fired boiler by Southern California Edison. Another project consisted of a pilot test conducted for the EPA at Georgia Power's Plant Mitchell. This pilot plant treated a 1000 acfm (0.5 MWe) slip stream of flue gas resulting from the combustion of low-to medium-sulfur coal. A third pilot-scale project, carried out at the Public Service Company of Colorado's Arapaho Station treated a 5000 acfm (2.5 MWe) slip stream of flue gas resulting from the combustion of U.S. low-sulfur coal.

Although SCR is widely practiced in Japan and Europe, there are several technical uncertainties associated with applying SCR to U.S. coals. These uncertainties include:

- (1) potential catalyst deactivation due to poisoning by trace metal species present in U.S. coals that are not present in other fuels.
- (2) performance of the technology and effects on the balance-of-plant equipment in the presence of high amounts of SO<sub>2</sub> and SO<sub>3</sub>.
- (3) performance of a wide variety of SCR catalyst compositions, geometries and methods of manufacture under typical high-sulfur coal-fired utility operating conditions.

These uncertainties will be explored by constructing a series of small-scale SCR reactors and simultaneously exposing different SCR catalysts to flue gas derived from the combustion of high-sulfur U.S. coal.

The first uncertainty above will be handled by evaluating SCR catalyst performance for two years under realistic operating conditions found in U.S. pulverized coal utility boilers. The deactivation rates for the catalysts exposed to flue gas from high-sulfur U.S. coal will be documented to determine accurate catalyst life, and thus, accurate process economics.

The second uncertainty above will be explored by performing parametric testing and through the installation/operation of air preheaters downstream of the larger reactors. During parametric testing, operating conditions will be adjusted above and below design values to observe deNO<sub>x</sub> performance and ammonia slip as functions of the change in operating conditions. Air preheater performance will be observed to evaluate effects from SCR operation upon heat transfer, and therefore, upon boiler efficiency.

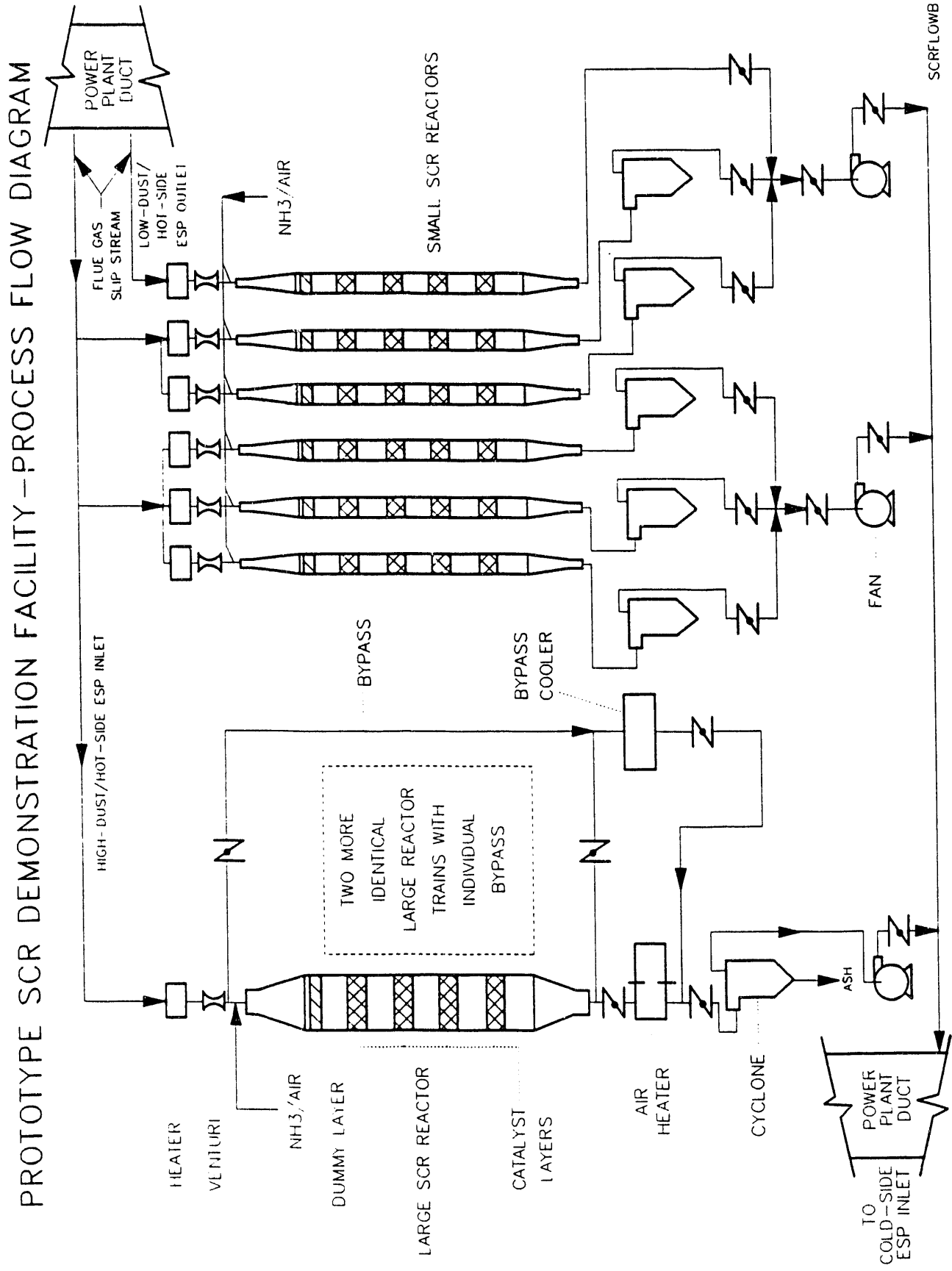
The third uncertainty is being handled by using honeycomb- and plate-type SCR catalysts from U.S., Japan and Europe of various commercial composition. Results from the tests with these catalysts will expand our knowledge of performance on a variety of SCR catalysts under U.S. utility operating conditions with high-sulfur coal.

The intent of this project is to demonstrate commercial catalyst performance, proper operating conditions, and catalyst life for the SCR process. This project will also demonstrate the technical and economic viability of SCR while reducing NO<sub>x</sub> emissions by at least 80%.

The project will be conducted at Gulf Power Company's Plant Crist Unit 5, a commercially operating 75 MW unit, located in Pensacola, Florida, on U.S. coals with a sulfur content near 3.0%. Unit 5 is a tangentially-fired, dry bottom boiler, with hot and cold side ESPs for particulate control. The SCR process to be used in this demonstration will be designed to treat a slip-stream of flue gas and will feature multiple reactors installed in parallel. With all reactors in operation, the maximum amount of combustion flue gas that can be treated is 17,400 standard cubic feet per minute (scfm) which is roughly equivalent to 8.7 MWe.

The SCS facility is a slip-stream SCR test facility consisting of three 2.5 MWe (5000scfm) SCR reactors and six 0.20 MWe (400scfm) reactors that will operate in parallel for side-by-side comparisons of commercially available SCR catalyst technologies obtained from vendors throughout the world. Figure 2 presents a simplified process flow diagram for the proposed facility. The large (2.5 MWe) SCR reactors will contain commercially available SCR catalysts as offered by SCR catalyst suppliers. These reactors will be coupled with small-scale air preheaters to evaluate the long-term effects of SCR reaction chemistry on air preheater deposit formation

Figure 2



and the deposits' effects on an air preheater. The small reactors will be used to test additional commercially available catalysts. This demonstration facility size will be adequate to develop performance data to evaluate SCR capabilities and costs that are applicable to boilers using high-sulfur U.S. coals.

The demonstration project is organized into three phases: (1) Phase I -Permitting, Environmental Monitoring Plan and Preliminary Engineering; (2) Phase II - Detail Design Engineering and Construction; and (3) Phase III -Operation, Testing, Disposition, and Final Report. The cooperative agreement was signed June 14, 1990, and the project completion date is now projected to be mid-1995. The original total estimated project costs are \$15,574,355. The co-funders are SCS (\$6,049,017), DOE (\$7,525,338), and EPRI (\$2,000,000).

**Section 3**  
**PROJECT DESCRIPTION**

Within the three phases of the project, the following tasks will be conducted to effectively demonstrate the SCR process:

**Phase I - Permitting, Environmental Monitoring Plan and Preliminary Engineering**

- Task 1.1.1 - Prototype Plant Permitting Activities**
- Task 1.1.2 - Develop Environmental Monitoring Program**
- Task 1.1.3 - Preliminary Engineering**
- Task 1.1.4 - Engineering and Construction Contracts Scope Development**
- Task 1.1.5 - Project Management and Reporting**

**Phase II - Detail Design Engineering and Construction**

- Task 1.2.1 - Detailed Design Engineering**
- Task 1.2.2 - Construction**
- Task 1.2.3 - Operation Staff Training**
- Task 1.2.4 - Planning for Detailed Testing**
- Task 1.2.5 - Start-Up/Shakedown**
- Task 1.2.6 - Project Management and Reporting**

**Phase III - Operations, Testing, Disposition and Final Report**

- Task 1.3.1 - SCR Demonstration Facility Operations and Maintenance**
- Task 1.3.2 - Process Evaluation**
- Task 1.3.3 - Environmental Data Management and Reporting**
- Task 1.3.4 - Economic Evaluation**
- Task 1.3.5 - Dismantling/Disposition**
- Task 1.3.6 - Project Management and Reporting**

**Section 4**  
**PROJECT STATUS**

Progress during July - September, 1992, is summarized below for each of the on-going tasks in the Scope of Work.

**PHASE I - PERMITTING, ENVIRONMENTAL MONITORING PLAN AND PRELIMINARY ENGINEERING**

**Task 1.1.2 - Develop Environmental Monitoring Program**

A plan to address a fly ash analysis issue, the only remaining issued raised by DOE on the Environmental Monitoring Plan (EMP), was formulated and reviewed internally. The suggested changes regarding fly ash analysis and all other previous comments for incorporation have been forwarded to Radian for modifying the EMP. After incorporation of these changes, and finalization of quality control procedures with the testing and analytical services subcontractor, Radian will submit the EMP to DOE during the next quarter.

**PHASE II - DETAIL DESIGN ENGINEERING AND CONSTRUCTION**

**Task 1.2.1 - Detailed Design Engineering**

The detailed design engineering phase continued during this reporting period with over 90 percent of the total engineering on the project now being completed. Major equipment delivered to the site during this period included the ammonia storage tank, service water pump, and reactors. A summary of equipment ordered and its delivery status is given in Appendix A. Some instruction books for the major equipment already delivered were received and provided to construction and operations personnel.

Based on the previously awarded contract, drawings for the fabrication of the SCR reactors and transition ductwork pieces were received and reviewed. Fabrication of the reactors and transition pieces were begun and a preliminary progress inspection was made. As fabrication neared completion, a final progress inspection was held. All the reactors and transition pieces were shipped to the site. The erection of the small reactors upon the support steel structure was begun.

All mechanical drawings were updated to reflect modifications in design and vendor recommendations since the erection package was issued. Piping expansion joint bids were issued, bids received and evaluated, and an award made to Unaflex, Inc. These have been procured and delivered to the site.

Vendor drawings were received and reviewed for the personnel and catalyst hoist. The design of the ductwork expansion joints was completed and an inquiry issued. After review of vendor bid submittals, an award for supply of the ductwork expansion joints was made to Senior Flexonics.

Initial design was completed for instrumentation platforms at elevation 202', economizer bypass support steel at elevation 156'8", walkway and duct support at elevation 141', and additional pipe and support brackets. Additional platforms to provide access to instrumentation were requested based on review by the testing services subcontractor. Design of these platforms was begun.

The structural steel painting package was issued to Gulf Power for release to request bids. Vendor bids were evaluated by SCS Engineering and Gulf Power and a contract award was in progress at the end of this reporting period.

The vendor drawings for the control room elevator were reviewed and approved.

Within the electrical engineering scope, the high voltage system design and procurement of materials was completed. The low voltage system design and procurement of materials is 99% complete. With the exception of a few minor revisions, all electrical drawings have been transmitted to the field.

Instrumentation and Controls personnel completed configuration of the Bailey Control System with check out and testing underway. Development of the graphic screens was begun and almost finished. Manual/auto switches were developed and placed on screen for operator controls. Updating of domestic loop diagrams was initiated. Preparation of the control system for simulation and testing of logic, and for operator training during October, was begun. Work was also started in programming to trend and archive data.

Manufacturing of the gas analysis system continued. A visit was made to inspect the first system produced and the reported inspection results on quality were favorable. A final witness test by SCS was scheduled for October prior to shipment of the system to the site.

Efforts continued to replace Norton, a catalyst vendor who withdrew from the project. Negotiation of the previously submitted Evaluation Agreement were concluded with the supplier selected in the evaluation conducted earlier this year. The agreement is in the process of being signed by both parties.

All of the other participating catalyst suppliers responded to the revised laboratory testing protocol issued during the previous quarter. In general the laboratory testing protocol is now established. Discussions of the laboratory testing protocol were held with the supplier which is now in the process of signing the Evaluation Agreement. This supplier is reviewing the material and will provide comments early in the next reporting period.

#### Task 1.2.2 - Construction

Construction of the Plant Crist SCR demonstration facility continued during this quarter with the remaining steel fabrication being completed. Sequence two was completed in July, sequence three was finished in August, and sequence four was done in September. The structural steel erection also concluded in September. The large crane for steel erection was subsequently moved, providing access to the control room contractor.

The construction of the control room building and gas analysis room was started. The structural steel for each was erected and the concrete slabs were poured. Erection of roof and siding materials was begun.

The mechanical and insulation contractor mobilized and began work. The large fly ash cyclones, bypass heat exchangers, air preheaters, and large reactor fans were set in place. The service water piping, from the pump to the peripheral of the project, and service water filter were installed. The Unit 5 fly ash piping was relocated. The cutting of ductwork, piping, structural steel, and cable tray penetrations in asbestos siding was completed. Fire protection piping work at the 4160V switchgear was completed. Installation of some ductwork commenced. About half of the ductwork runs from the cyclones to the fans and the return ductwork from the fans to the Unit 5 ductwork have been erected. Work on insulating some of the installed equipment was begun. The ammonia storage tank was also set in place.

The construction package contract for electrical and I&C erection was awarded to Red Top Electric. The electrical contractor mobilized and began work. Fabrication of cable trays and construction of switchgear foundations was started and completed. Erection of the cable trays



and setting of the switchgear was begun. Gulf Power substation personnel began their check out of the 115-KV transformer.

#### Task 1.2.3 - Operations Staff Training

The operators for the demonstration facility have been selected from Gulf Power Plant Crist operating personnel. They were scheduled to begin work on the project in October 1992. They have already been provided an SCR information manual and training materials are being gathered and edited for operator use. Training on the data acquisition/distributed control system was scheduled for mid-October. Print and video safety media on ammonia storage and handling was collected on-site for review. The process of securing operating and maintenance manuals on most major equipment was begun.

#### Task 1.2.4 - Planning for Detailed Testing

Negotiations of terms and conditions for the testing/analytical services were completed and a contract was signed with Southern Research Institute. A description of the sampling and analytical methods included in the scope of work are shown in Appendix B.

Development of the data reduction methodology was begun through formulating plans for retrieval and storage of data within the Bailey control system, transfer of data into a DOS data base format, extraction of data from the gas analysis system, and use of the data in modeling results. Data points to be archived, and supplemental trending data, were identified. The frequency of data down-loading and configuration of special calculations (ammonia slip, NO<sub>x</sub> reduction efficiency, etc.) were defined. The concept of modem transfer of data from the site to SCS offices in Birmingham was successfully tested.

#### Task 1.2.6 - Project Management and Reporting

Weekly coordination meetings were held with Design Engineering. The Management Information System, developed for tracking overall budget and schedule information, was used to monitor budget and schedule and to help fulfill DOE reporting requirements. Monthly progress reports were submitted to DOE.

Monthly project review meetings to discuss design and construction status were held between SCS and Gulf Power at Plant Crist. A paper describing the status of the project and design issues

was presented at the First Annual Clean Coal Technology Conference in Cleveland, Ohio, on September 24. Two of the U.S. catalyst suppliers were visited on September 28 and 29 to discuss reactor design, catalyst module design, testing protocol and testing plans.

A Continuation Application and request for additional funds were prepared and submitted to DOE for approval. The Continuation Application requests DOE's approval for matching funds of Budget Period 2 to continue the project to completion. Budget Period 2 provides DOE funding for Phase III, which includes operations, testing, disposition, and final report. Project cost growth has been projected based on improvements to the facility design and additional funding is being requested from DOE in the amount of 25% of DOE's original funding of the project. Funding from other sources is also being solicited to cover the entire cost growth.

**Section 5**  
**PLANNED ACTIVITIES**

During the October-December, 1992 quarter, the following activities are planned:

- Provide remaining detailed engineering to assist completion of construction.
- Complete the following portions of Phase II construction package awards:
  1. Complete mechanical/insulation and electrical/I&C construction work. Install reactors, sootblowers, air compressor, ammonia handling system, control system and instrumentation. Finish installation of ductwork, service water and air piping, electrical systems, fire protection systems, and insulation of equipment and ductwork.
  2. Install personnel/catalyst hoist.
  3. Complete construction of control room and gas analyses system buildings.
  4. Award contract for painting and have painting performed.
  5. Install control room elevator.
- Begin operator training on the control system. Continue training with review of process and equipment; assimilate and modify, as needed, the operating procedures; and inspect equipment and construction.
- Secure signed agreement for selected replacement catalyst supplier.
- Continue developing data reduction methodology.
- Visit remaining U.S. catalyst supplier.
- Hold project review meeting with DOE and EPRI.

## **APPENDIX A**

### **Purchase Order Tracking Report**

PURCHASE ORDER	INQUIRY NO	DESCRIPTION	VENDOR	PO DATE	REQUIRED DATE	PROMISED DATE
C91-000854	SCR-700	HEAT PIPE AIR PREHEATER	ABB AIR PREHEATER	05/17/91	05/01/92	RECEIVED
C91-000855	SCR-701	ROTARY TYPE AIR PREHEATER	ABB AIR PREHEATER	05/17/91	05/01/92	RECEIVED
C91-001152	SCR-702	EXHAUST GAS/COOLING AIR FANS	HOWDEN SIROCCO	06/21/91	07/01/92	RECEIVED
C91-001260	SCR-703	GAS FLOW VENTURIS	FLOW-LIN CORP	07/09/91	06/29/92	RECEIVED
C91-001434	SCR-708	480V MOTOR CONTROL CENTER	SOUTHERN ENGINEER	08/15/91	06/01/92	RECEIVED
C91-001608	SCR-704	DIST CONTROL/DATA ACQ SYSTEM	BAILEY CONTROLS	08/26/91	02/03/92	RECEIVED
C91-001624	SCR-709	FLY ASH CYCLONES	FISHER-KLOSTERMAN	08/28/91	05/15/92	RECEIVED
C91-001672	SCR-706	DUCTWORK HEAT EXCHANGER	XCHANGER, INC	08/30/91	05/15/92	RECEIVED
C91-001673	SCR-707	MISC POWER TRANSFORMERS	ABB POWER T/D	08/30/91	06/01/92	RECEIVED
C91-001707	SCR-705	4KV METAL CLAD SWITCHGEAR	SIEMENS ENERGY	09/06/91	06/01/92	RECEIVED
C91-002003	SCR-710	FLUE GAS/AIR ELECTRIC HEATERS	WATLOW SYSTEMS	10/17/91	06/15/92	RECEIVED
C91-002312	SCR-711	SERVICE/COOLING WATER PUMP	PEABODY FLOWAY, INC	11/27/91	06/01/92	RECEIVED
C91-002553	SCR-712	GAS ANALYZER SYSTEM	LEAR SIEGLER	12/27/91	09/01/92	11/10/92
C91-002554	SCR-712A	OXYGEN ANALYZER SYSTEM	LEAR SIEGLER	12/27/91	09/01/92	11/10/92
			1992			
C92-000039	SCR-714	PLANT AIR COMPRESSOR	HYDROMATICS, INC	01/15/92	06/01/92	RECEIVED

PURCHASE ORDER	INQUIRY NO	DESCRIPTION	VENDOR	PO DATE	REQUIRED DATE	PROMISED DATE
C92-000043	SCR-713	BULK AMMONIA SYSTEM	LAROUCHE INDUSTRIES (Lease Contract)	01/15/92	05/31/92-TANK 11/01/92-AMMON	TANK RECD
C92-000047	SCR-1018-01	DAMPERS/ACTUATORS	PRECISION ENG PROD	01/16/92	06/01/92	RECEIVED
C92-000051	SCR-1018-02	SOOTBLOWERS	COPEES-VULCAN, INC	01/17/92	07/31/92	RECEIVED
C92-000201	SCR-1113-01/01A	LOW VOLTAGE TRANSFORMERS	GRAYBAR ELECTRIC	02/05/92	04/01/92	RECEIVED
C92-000241	SCR-715	STRUCTURAL STEEL/GRATING	STEEL SYSTEMS	02/12/92	06/01/92	RECEIVED
C92-000301	SCR-0220-01	125 VOLT DC BREAKER	MCCOMBS BROS ELECT	02/21/92	03/25/92	RECEIVED
C92-000336	SCR-0123-01	BARGRAPH INDICATORS	DIXSON INSTRUMENTS	02/26/92	04/01/92	RECEIVED
C92-000337	SCR-0114-04	PRESSURE SWITCHES	AWC	02/26/92	08/01/92	RECEIVED
C92-000342	SCR-0114-01	GAS FLOW CONTROLLER	SIERRA INSTRUMENTS	02/28/92	06/01/92	RECEIVED
C92-000380	SCR-0114-03	PRESSURE TRANSMITTERS	TECHNICAL SPEC	03/05/92	08/01/92	RECEIVED
C92-000570	SCR-0114-02	THERMOCOUPLES	JMS SOUTHEAST, INC	04/01/92	08/01/92	RECEIVED
C92-000618	SCR-1223-01	SEGREGATING VALVES	JOY ENVIRON EQUIP	04/07/92	07/01/92	RECEIVED
C92-000620	SCR-0124-01	WEAR RESISTANT PIPE/FITTINGS	ULTRA TECH	04/07/92	07/01/92	RECEIVED
C92-000623	SCR-0131-01	480V CONTROL PANEL	INSTRUMENT CONT SVC	04/07/92	08/01/92	RECEIVED
C92-000624	SCR-1217-01	ROTARY VALVES	ROTOLOK, INC	04/08/92	07/01/92	RECEIVED
C92-000629	SCR-0123-04	KNIFEGATE VALVES	DEZURIK	04/08/92	07/01/92	RECEIVED
C92-000630	SCR-0123-03	PLUG/CHECK VALVES	PIPING & EQUIPMENT	04/08/92	07/01/92	RECEIVED
C92-000636	SCR-0401-01	UDS MODEMS	HALL-MARK ELECTR	04/09/92	ASAP	RECEIVED

PURCHASE ORDER	INQUIRY NO	DESCRIPTION	VENDOR	PO DATE	REQUIRED DATE	PROMISED DATE
C92-000643	SCR-0123-05	CS TRANSITION PIECES	CMC CORPORATION	04/10/92	07/01/92	RECEIVED
C92-000818	SCR-0123-02	MASS FLOW METERS	SIERRA INSTRUMENTS	05/14/92	08/01/92	RECEIVED
C92-000894	SCR-0428-01	SERVICE WATER STRAINER	VOIGT-ENGLAND CO	05/29/92	07/15/92	RECEIVED
C92-000965	SCR-0512-01	3/C 250 MCM CABLE	OKONITE CO	06/10/92	09/01/92	RECEIVED
C92-001034	SCR-716	PERSONNEL HOIST	USA HOIST	06/18/92	09/01/92	11/15/92
C92-001068	SCR-717	HEACT/TRANS DUCTWORK	CENTRAL ALABAMA FAB	06/26/92	START - 09/01/92	RECEIVED
C92-001152	SCR-0410-02	BALL VALVES	GULF COAST MARINE S	07/10/92	07/31/92	RECEIVED
C92-001154	SCR-0610-01	THERMOCOUPLES	JMS SOUTHEAST, INC	07/10/92	07/31/92	RECEIVED
C92-001156	SCR-0410-01	GLOBE VALVES	MASONIELAN	07/10/92	08/01/92	PARTIAL
C92-001285	SCR-2606-01	EXPANSION JOINTS	UNAFLEX, INC	08/03/92	08/03/92	RECEIVED
C92-001334	SCR-0207-01	SAFETY RELIEF VALVES	INDUSTRIAL VALVE	08/14/92	09/30/92	RECEIVED
C92-001407	SCR-2807-03	SOLENOID VALVES	GULF COAST MARINE	09/21/92	09/30/92	RECEIVED
C92-001548	SCR-2508-02	TRANSMITTER/TWO WIRE	ROMAN ENGINEERING	09/22/92	10/15/92	RECEIVED
C92-001550	SCR-2508-03	WINDSOCK	ARADYNE PRODUCTS	09/22/92	10/15/92	RECEIVED
C92-001551	SCR-2508-01	LEAK DETECTOR	MITCHELL INSTRUMENT	09/22/92	10/15/92	RECEIVED
C92-001552	SCR-2807-02	CHAIN HOISTS	PENSACOLA MILL SUP	09/22/92	10/15/92	RECEIVED
C92-001577	SCR-033002	INTEGRAL ORIFICE PLATES	TECHNICAL SPECIALTIE	09/22/92	11/15/92	PARTIAL
C92-001567	SCR-2807-01	FIRE PROTECTION EQUIP	FIREMASTER	09/24/92	10/30/92	RECEIVED

PURCHASE ORDER	INQUIRY NO	DESCRIPTION	VENDOR	PO DATE	REQUIRED DATE	PROMISED DATE
C92-001576	SCR-718	DUCTWORK EXPANSION JOINTS	SENIOR FLEXONICS	09/25/92	10/16/92	RECEIVED
C92-001707	SCR-VERB	APARTMENT RENTALS	J M. ENDRY REALTY	10/22/92	10/22/92	RECEIVED
C92-001792	SCR-VERB	MISC TEST EQUIP (SRI)	MILLIPORE PRODUCTS	10/28/92	12/01/92	AS REQ
C92-001799	SCH-2110-07	MISC TEST EQUIP (SRI)	MICRO FILTRATION	10/28/92	12/01/92	AS REQ
C92-001802	SCR-2110-08	MISC TEST EQUIP (SRI)	MERIAM INSTR	10/28/92	12/01/92	AS REQ
C92-001826	SCR-1510-01	MISC TEST EQUIP (SRI)	BYTE SIZE COMP	10/31/92	11/15/92	AS REQ
C92-001827	SCR-2110-03	MISC TEST EQUIP (SRI)	BAXTER SCIENTIFIC	10/31/92	11/30/92	AS REQ
C92-001842	SCR-2110-04	MISC TEST EQUIP (SRI)	DWYER INSTR	11/04/92	11/15/92	AS REQ
C92-001843	SCR-2110-05	MISC TEST EQUIP (SRI)	GEORGE S. EDWARDS	11/04/92	11/15/92	AS REQ
C92-001860	SCR-VERB	SUBSTRATE MATERIAL	CORNING, INC	11/04/92	11/15/92	12/15/92
C92-001861	SCR-0311-02	MISC TEST EQUIP (SRI)	SOUTHERN RESEARCH I	11/04/92	12/01/92	AS REQ
C92-001863	SCR-VERB	SOFTWARE/DATA BACKUP	SOFTWARE CITY	11/04/92	11/15/92	AS REQ



## **APPENDIX B**

### **Description of Sampling and Analytical Methods**

## Section 2

### DESCRIPTION OF SAMPLING AND ANALYTICAL METHODS

#### DETERMINATION OF PARTICULATE CONCENTRATION AND PARTICLE SIZE

Several methods are available for measurement of mass concentration and particle size distribution. For measurement of mass concentration at the various sampling locations within the Unit 5 and pilot plant ducting, Methods 5 and 17 promulgated by the U.S. Environmental Protection Agency can be used. In the Method 5 arrangement the particulate matter is collected on a filter mounted in a heated enclosure outside of the stack or ducting. In Method 17 the filter holder is located in the gas stream at the end of the sampling probe. Method 17 is generally preferred because it eliminates problems associated with particle loss in the probe. Method 17 sampling equipment (Nutech Model 220) will be used for the proposed work.

Particle size distribution of the particulate matter in the flue gas streams can be determined either in the laboratory using samples of particulate matter collected during the measurements of mass concentration described above, or, alternatively, by use of cascade impactors sampling flue gas in situ. While the in situ measurements using cascade impactors result in a more accurate representation of the particle size distribution, the expense of obtaining these data can be excessive. The laboratory technique is much less expensive and is considered the method of choice for the proposed work in which a large number of sample streams must be characterized.

Laboratory determination of the particle size distribution of collected particulate samples will be performed with a Shimadzu Model FACP-4 Particle Classifier. This instrument provides particle size data in the range of 0.1 to 100 microns, while only requiring a small test sample (0.1 to 0.2 grams). The instrument characterizes particle size using an aerodynamic sedigraph (centrifugally-enhanced settling in liquids of various viscosities) technique. In assessing the quality assurance of the laboratory measured particle size distributions, cascade impactor tests are recommended on a very limited scale to demonstrate the relative accuracy of the laboratory technique.

Cascade impactors are the most common technique for measuring particle size in situ. The instruments are small, compact, provide for particle fractionation in up to 13 size ranges (0.5 to 10 microns), and can be inserted directly into the flue gas stream. Quartz fiber substrates are used as

microns), and can be inserted directly into the flue gas stream. Quartz fiber substrates are used as collection media. Particle size distributions are calculated using computer data reduction programs written by SRI.

## **DETERMINATION OF ASH MINERAL COMPOSITION AND TRACE METAL CONCENTRATIONS**

The samples of fly ash to be subjected to analysis will be obtained by use of one of three types of sampling devices: 1) a Method 17 (ceramic filter) sampling train, 2) a set of cyclones in series, and 3) a sampling train consisting of a Method 5 particulate filter, followed by a set of impingers containing aqueous solutions to collect vapors that penetrate the filter.

The particulate matter collected in the Method 17 ceramic thimbles will be subjected to mineral analysis. The constituents of the ash that make up the so-called mineral analysis are, in the context of this proposal, those oxides that usually make up 98-100% of fly ash:  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{SO}_3$ .

Size-specific trace metals concentrations can be important factors in determining the cause of catalyst deactivation. Fly ash samples collected with a set of cyclones in series will be subjected to a trace metals analysis to address this issue. The size cutpoints in the six-stage cyclone set with back-up filter are approximately 10.0, 6.0, 3.0, 1.5, 0.8, and 0.6  $\mu\text{m}$ . After the series cyclone samples are weighed, as an additional quality assurance check of the particle size distribution determined in the laboratory, the fly ash in each particle size range will be subjected to a trace metals analysis as described below.

For collecting trace metals, the U.S. EPA has sanctioned the use of a Method 5 filtration device and back-up impingers; two filled with nitric acid and hydrogen peroxide and two filled with potassium permanganate and sulfuric acid. The combination of a particulate filter and the back-up impingers provides a convenient way to collect the trace elements in fly ash and flue gas that are of paramount concern. The trace elements that occur as components of the fly ash are collected on the filter, except from the fractions of certain metals (such as As and Se) that may occur partly in the vapor state. These partly volatile metals are collected in the  $\text{HNO}_3/\text{H}_2\text{O}_2$

impingers. The element Hg is usually completely in the vapor state even at 300°F and will surely be almost exclusively in the vapor state above 600°F in the SCR reactors. Hg is collected from the vapor state in the  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  impingers.

Routinely, the analysis defined above as ash mineral analysis will be performed by dissolving the ash in concentrated mineral acids and performing a screening analysis by Inductively Coupled Argon Plasma (ICAP) emission spectrometry. This method yields concentrations on the elements other than silicon and sulfur whose oxides make up most of the composition of fly ash (Li, Na, K, Mg, Ca, Al, Fe, Ti, and P). This method also can be made to yield the concentrations of trace elements, if desired, and will be employed for that purpose in trace metal analysis. The other two major components of fly ash,  $\text{SiO}_2$  and  $\text{SO}_3$ , will be determined separately.  $\text{SiO}_2$  will be determined by dissolving the ash in fused NaOH and will be determined colorimetrically with molybdate.  $\text{SO}_3$  will be extracted in water and determined as sulfate ion by ion chromatography.

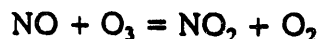
The method used to perform a trace metal analysis depends upon the elements one is concerned about. We presume that, in general, the trace elements that cause adverse effects in an SCR reactor are not yet known (we presume that indications of elements that cause adverse effects will come from this project), although at least arsenic must be regarded as a threat. Our plan, in consonance with EPA's recommendations, is to follow a method that, with relatively little difficulty, allows determination of a wide spectrum of elements. The ICAP method mentioned above will do that. It will give the concentration of As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, and V, among others (this specific list includes those now of concern to EPRI in its PISCES investigations). ICAP may require auxiliary determination of As and Se by atomic absorption with the elements converted to the hydrides if improved sensitivity to these elements is required. ICAP will definitely require use of a second method -- cold-vapor atomic absorption -- for Hg.

## DETERMINATION OF INDIVIDUAL COMPONENTS OF THE FLUE GAS

Nitrogen Oxides ( $\text{NO}$  and  $\text{NO}_2$ ).

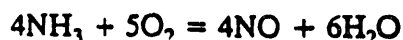
Southern Company Services (SCS) will have the main responsibility for determining oxides of nitrogen and will do so by use of a set of chemiluminescence monitors. In the so-called "NO

mode," this type of analyzer responds only to nitric oxide (NO); the response is due to the emission of light from a reaction cell in which NO from the flue gas is converted to nitrogen dioxide (NO<sub>2</sub>) with ozone that is generated within the analyzer. The equation is as follows:



In the "NO<sub>x</sub> mode," the analyzer responds to the combination of NO and NO<sub>2</sub> from the flue gas. It gains sensitivity to NO<sub>2</sub> from the flue gas by thermally decomposing or converting NO<sub>2</sub> to NO. Southern Research Institute will on occasion use a similar portable monitor (specifically the Thermo Electron Model 10) for verifying the data obtained with the SCS monitors. We may also have occasion to use the manual phenol disulfonic acid method for reference. Flue gas is collected in an evacuated bulb that contains an oxidizing solution of hydrogen peroxide and sulfuric acid. Nitrogen oxides are converted to nitric acid, which then is reacted with phenol disulfonic acid to produce a colored compound that is measured colorimetrically.

There is the possibility or even the likelihood that the chemiluminescence analyzers will give an unwanted response to NH<sub>3</sub>. This gas may be oxidized to NO in the thermal converter for changing NO<sub>2</sub> to NO. The equation for the oxidation process is as follows:



In the event that this reaction occurs, the concentration of NO<sub>x</sub> will include NH<sub>3</sub> in addition to NO and NO<sub>2</sub>. Whether this occurrence can be tolerated will depend upon the relative concentrations of NH<sub>3</sub> and NO<sub>2</sub>. We expect to find around 20-40 ppm of NO<sub>2</sub> if the total NO<sub>x</sub> concentration is about 400 ppm as expected. Only at the outlet of the SCR reactors will the concentration of NH<sub>3</sub> be negligible in comparison to that of NO<sub>2</sub>; even there, it will be negligible only for low slippages of NH<sub>3</sub> through the reactors.

For routine purposes, the response to NH<sub>3</sub> may be disregarded. Generally, only the concentration of NO may be required, and that parameter will not be affected by NH<sub>3</sub>. When the interference from NH<sub>3</sub> must be overcome, it may be accomplished by drawing the sample gas stream through an acid-packed absorption tube ahead of the analyzer. A tube packed with a silica support for sodium bisulfate, NaHSO<sub>4</sub>, should effectively remove NH<sub>3</sub>.

## Nitrous oxide (N<sub>2</sub>O).

Whereas most of the oxides of nitrogen issuing from the coal-fired combustor will be NO and NO<sub>2</sub>, some small part of the oxides will occur as nitrous oxide, N<sub>2</sub>O. This oxide contains nitrogen in the +1 state, in contrast to the +2 and +4 states normally produced in a combustor. Even more of the N<sub>2</sub>O oxide may be produced in a SCR reactor. SCS does not plan to maintain a CEM for N<sub>2</sub>O. SRI on the other hand, plans to recommend for purchase an instrument of the NDIR type for determining N<sub>2</sub>O. At least two commercial vendors supply NDIR analyzers for N<sub>2</sub>O. We have investigated the Horiba VIA-510 dual beam analyzer and believe it may be the instrument of choice. We will keep abreast of new instrument developments, however, and may choose another at the time a purchase is to be made. There has been a great deal of activity on development of analyzers for N<sub>2</sub>O in the recent past; thus, there may soon be significant new improvements offered.

## Ammonia (NH<sub>3</sub>).

Sample collection. NH<sub>3</sub> will be collected by drawing a stream of flue gas through a heated probe and a heated particulate filter and then through an air-cooled condenser and a series of bubblers filled with dilute sulfuric acid. A substantial part of the NH<sub>3</sub> that gets through the filter will condense, along with water vapor, in the air-cooled condenser as the result of the low-temperature reaction of NH<sub>3</sub> with HCl or SO<sub>3</sub> to produce NH<sub>4</sub>Cl, NH<sub>4</sub>HSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

Temperatures at which the probe and filter are to be controlled will have to be determined after the operating conditions (duct temperatures and flue gas concentrations) are better known. Attempts will be made to retain on the filter any particulate matter that contains NH<sub>3</sub> (which may be fly ash with adsorbed NH<sub>3</sub> or aerosol particles of ammonium sulfate and bisulfate). Ideally, the probe and filter would be operated at the temperature of the duct being sampled; in this way, in principle, the distribution of NH<sub>3</sub> between the solid phases and the gas phase would not be disturbed. Both NH<sub>3</sub> retained in particles on the filter and collected in the condenser and bubblers would be analyzed separately. In practice, however, some shift in temperature away from that in the duct may prove desirable when tests are conducted at the air heater outlets

downstream of the large reactors. As the following discussion will illustrate, the need for a shift in temperature to cope with solids containing  $\text{NH}_3$  will be more likely at the outlet of the air heater than at locations upstream from the air heater.

At high temperatures ahead of the catalyst, there is only a remote possibility that ammonium sulfate or bisulfate aerosol particles will be formed. Actually, the possibility of the sulfate forming can be disregarded and only the possibility of the bisulfate forming need be considered. The equilibrium constant for the formation of ammonium bisulfate has been given by Matsuda et al (Ind. Eng. Chem. Prod. Res. Dev. 21, 48 (1982)) as  $1.14 \times 10^{12} e^{-53000/RT} \text{ atm}^2$  (where R is the ideal gas constant and T is the absolute temperature). If at the inlet of the catalyst the concentration of  $\text{NH}_3$  has been brought up to 500 ppm, the concentration of  $\text{SO}_3$  (or  $\text{H}_2\text{SO}_4$  vapor) must exceed some threshold value before ammonium bisulfate formation can occur:

Temperature, °F	ppm $\text{SO}_3$
800	78,900
700	2,950
600	59.3

It is unlikely that the  $\text{SO}_3$  from the boiler will exceed any of the above concentrations; thus, there is little likelihood of the formation of ammonium bisulfate ahead of the catalyst if the sampling train duplicates the duct temperature.

At the outlet of the catalyst, where the temperature has not changed appreciably, the concentrations of  $\text{NH}_3$  and  $\text{SO}_3$  are more likely to be of similar magnitude. If it is assumed for illustration that they are precisely equal, the concentrations that will just permit ammonium bisulfate formation to occur are these values:

Temperature, °F	ppm $\text{NH}_3$ and $\text{SO}_3$ (equal)
800	6,280
700	1,210
600	172

The figures above imply that ammonium bisulfate formation in the sampling train will not be a problem at the catalyst outlet, just as it is not at the catalyst inlet, if the sampling temperature is kept at the duct temperature.

In the temperature range below 600 °F, the formation of ammonium bisulfate and, ultimately, ammonium sulfate will take place. Extending the prediction of equal concentrations of NH<sub>3</sub> and SO<sub>3</sub> that are thresholds for the formation of ammonium bisulfate, the following results are obtained at temperatures of 500 and 400 °F:

Temperature, °F	ppm NH <sub>3</sub> and SO <sub>3</sub> (equal)
500	16.25
400	0.855

Surely below 400 °F and maybe even above, the more stable solid will be the normal sulfate rather than the bisulfate. In this lower temperature range, the only gaseous species expected to penetrate a filter at duct temperature will be the species in stoichiometric excess. This may be NH<sub>3</sub> if NH<sub>3</sub> is in excess of that reacting to produce a solid, or it may be SO<sub>3</sub> if that species is in excess.

One reason that the experimentalist may choose to depart from the duct temperature insofar as the filtration temperature is concerned is that, on occasion, penetration of gases through the filter may not follow the prediction of chemical equilibrium in terms of the sulfate and the bisulfate. For example, the species in excess may not penetrate the filter because of physical adsorption. Under circumstances such as this, one may choose to raise the temperature to such a point (above 600 °F) that no formation of these salts is possible and all of the NH<sub>3</sub> present is collected behind the filter. With accurate data on both NH<sub>3</sub> and SO<sub>3</sub> concentrations in all forms, one may decide how the two species are most likely distributed between solid and gaseous phases using available equilibrium constants for the formation of the solids.

Sample analysis. A simple method for determining NH<sub>3</sub> that is collected as the chloride or as a sulfate salt is to make the solution alkaline (converting NH<sub>4</sub><sup>+</sup> ion to free NH<sub>3</sub> in solution) and measure the concentration with an ammonia-selective electrode, associated with a reference electrode and attached to a pH meter. The voltage output of the pH meter, ΔE, is used to calculate the concentration of NH<sub>3</sub> as follows:

$$\ln [\text{NH}_3] = (\Delta E)/RT + C$$

where R is the ideal gas constant, T is the absolute temperature, and C is a calibration constant.



While convenient, the electrode does not give a linear relationship between the  $\text{NH}_3$  concentration and the parameter measured. Two other instrumental methods will give linearity and are thus preferred. One of the methods involves a chemical reaction between  $\text{NH}_3$  and other reagents to give a colored product. Another involves a reaction that produces a fluorescent product. Both methods are reported to detect  $\text{NH}_3$  at lower concentrations in the dissolved state than the electrode and are to be preferred for this additional reason. Our present plan is to use the fluorometric method; for this purpose, we are recommending the purchase of a fluorometer.

On occasion, when  $\text{NH}_3$  as a component of the particulate matter suspended in the flue gas must be determined, the sample retained on a filter will be analyzed. The filter cake will be extracted with a dilute solution of  $\text{H}_2\text{SO}_4$ ; the extract will then be processed as described for samples containing the gaseous fraction.

Parenthetically, it can be suggested that  $\text{NH}_3$  is unlikely to appear on the solid matter unless a strong acid is initially present on the solid matter.  $\text{H}_2\text{SO}_4$  adsorbed on the solid is the most probable acid for picking up  $\text{NH}_3$  from the gas phase; it is the strongest acid that is likely to be present. Even the reactivity of  $\text{H}_2\text{SO}_4$  toward  $\text{NH}_3$  is limited at SCR temperatures above  $600^\circ\text{F}$ , however. This is shown by the fact that  $\text{NH}_4\text{HSO}_4$  is not likely to be deposited from the gas phase unless the temperature reaches the lower range found on air heater surfaces.

We concur with the viewpoint in the Request for Proposal that a manual determination of  $\text{NH}_3$  is preferred to an instrumental method. None of the detection principles that might be used (chemiluminescent detection of  $\text{NO}$  produced from  $\text{NH}_3$  or absorption of UV or IR radiation) overcomes the inherent difficulty of maintaining  $\text{NH}_3$  in the gaseous state if a gas stream containing  $\text{HCl}$  and  $\text{SO}_3$  is cooled to normal measurement temperatures.

Hydrogen chloride ( $\text{HCl}$ ).

$\text{HCl}$  will be collected by drawing flue gas through a heated probe and a particulate filter and then through an air-cooled condenser and a series of bubblers filled with dilute  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  solution. In principle, the sampling train is the same as the one for  $\text{NH}_3$ , except that the

absorbent solution contains a base rather than an acid. The resulting solution containing NaCl will be analyzed by ion chromatography.

HCl may react with  $\text{NH}_3$  to produce  $\text{NH}_4\text{Cl}$  solid, but we believe this unlikely at the gas temperatures to be encountered.  $\text{NH}_4\text{Cl}$  is similar to the sulfate and bisulfate discussed above but is much less stable and much less likely to form except at relatively low temperatures. If  $\text{NH}_3$  is collected in the condenser as  $\text{NH}_4\text{Cl}$ , this salt will be rinsed into the base-containing bubblers and transformed to NaCl. The  $\text{NH}_3$  thus released will not interfere in the determination of the chloride ion.

Sulfur trioxide ( $\text{SO}_3$ ) and sulfur dioxide ( $\text{SO}_2$ ).

Sample collection.  $\text{SO}_3$  in the flue gas will be collected by the controlled condensation method. The flue gas is sampled with a train consisting of a heated quartz-lined probe, a quartz-fiber filter supported on a frit in a heated quartz filter holder, and finally a Pyrex condensing element maintained around 160° F. The condenser may be a spiral of tubing surrounded by a jacket of heated water; alternatively, as in the sampling train we have used for many years, the condenser may be a bulb with connections on both ends, which contains a packing of glass wool and maintains its temperature with a heated water jacket.

When the gas stream is lowered from a duct temperature in excess of 600° F, the  $\text{SO}_3$  present begins to undergo a hydration reaction with the water vapor that is present, making  $\text{H}_2\text{SO}_4$  as the product. Depending upon the even lower temperature reached subsequently, the  $\text{H}_2\text{SO}_4$  and the water vapor in excess begin to condense concurrently to produce a condensate of concentrated aqueous  $\text{H}_2\text{SO}_4$  (perhaps 80% acid by weight). If the concentration of  $\text{SO}_3$  ( $\text{H}_2\text{SO}_4$ ) is about 75 ppm, condensation will commence around 300° F; it will be essentially complete, leaving a residual vapor concentration well below 1 ppm, when the temperature reaches 160° F.

It will be obvious that the interaction of  $\text{NH}_3$  and  $\text{SO}_3$  introduces the same problems in regard to solids formation whether the sampling is for one gas or the other. Thus, the same considerations apply with  $\text{SO}_3$  as were discussed with  $\text{NH}_3$ . With  $\text{SO}_3$  there is the added problem of tenacious adsorption of  $\text{SO}_3$  on even inert filter materials, such as quartz. This problem led several researchers who worked toward the development of the controlled condensation method to

recommend a filter temperature of 500-550 °F, regardless of the temperature in the duct being sampled. This is never an altogether satisfactory procedure, because it causes the risk of vaporizing SO<sub>3</sub> from condensed matter. If the duct temperature is low, there will be an aerosol of sulfuric acid in the duct, but it will be vaporized to SO<sub>3</sub> on the filter. If the duct contains NH<sub>3</sub> in the form of the sulfate or bisulfate, thermal decomposition to the gases at a high filter temperature is likely to occur. Our strategy in the past in field sampling of SO<sub>3</sub> in the presence of NH<sub>3</sub> has been to collect samples at various filter temperatures, ranging from 550 °F, where complete volatilization of the sulfate or bisulfate should occur, to the actual duct temperature, and to attempt to apportion SO<sub>3</sub> between the solid and gaseous phases on the basis of simultaneous measurements of NH<sub>3</sub> and deductions from the measured concentrations and the literature values of equilibrium constants for the sulfate and bisulfate.

We understand that one practice in Europe is to remove NH<sub>3</sub> from a gas stream with an oxalic acid filter before any attempt is made to sample other gases that react with NH<sub>3</sub>. The information we have suggests that the oxalic acid filter must be maintained between the water dew point (about 125 °F) and the decomposition temperature of ammonium oxalate (not specified). We cannot, on the basis of the limited information we have, recommend this approach in regard to the SO<sub>3</sub> sampling problem, because there is the possibility that NH<sub>3</sub> will react with SO<sub>3</sub> before the gas stream is cooled sufficiently for NH<sub>3</sub> to react with oxalic acid. One literature article we have consulted states that the decomposition temperature of ammonium oxalate is lower than the decomposition temperature of ammonium sulfate, which would prevent the oxalic acid filter from having the desired effect.

Sample analysis. When SO<sub>3</sub> is collected in the manner described, SO<sub>2</sub> is usually collected in a bubbler downstream (between the condenser and the pump) in a aqueous solution of hydrogen peroxide. Peroxide oxidizes SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. Thus, two solutions of H<sub>2</sub>SO<sub>4</sub> are collected – one a very concentrated solution of limited amount containing the original SO<sub>3</sub> and one a relatively weak solution in far greater amount containing the original SO<sub>2</sub>.

Determination of H<sub>2</sub>SO<sub>4</sub> in both collectors allows one to express the concentrations of both SO<sub>3</sub> and SO<sub>2</sub> in the flue gas. In a laboratory suitably equipped, as planned for this investigation, the most convenient determination of the sulfate ion in H<sub>2</sub>SO<sub>4</sub> is by ion chromatography.

We know of only one possible instrumental analyzer for SO<sub>3</sub>. That is the SSL Monitor originally developed by the CEGB in Great Britain. We have made a side-by-side comparison of the

instrument with the manual controlled-condensation method on more than one occasion. Our opinion is that the instrument requires too much attention to be regarded truly as an automatic analyzer and we cannot recommend that it be used during this project.

#### Oxides of carbon (CO and CO<sub>2</sub>).

SCS plans to use NDIR analyzers for determining the concentrations of CO and CO<sub>2</sub>. We know of no portable analytical instrument of comparable accuracy that can be used for readings at the several sampling ports of interest. We can only suggest a non-instrumental Fyrite analyzer for verifying the instrumental readings for CO<sub>2</sub>. We believe that color-indicating tubes can be used for CO but will have to make a study of other possibilities that may be more attractive.

#### Oxygen (O<sub>2</sub>).

The fixed monitors for O<sub>2</sub> will be based upon ZrO<sub>2</sub> sensing elements. For validation of the data from the fixed CEMs, we will use a portable Teledyne O<sub>2</sub> analyzer that is described as a fuel cell device. The specific operation principle is not distinctly described by the manufacturer's literature, however, the detector is an electrochemical cell in which the measured O<sub>2</sub> is reduced at the cathode and some unidentified material is oxidized at the anode. The Teledyne device operates over a wide concentration of O<sub>2</sub>, up to 21% in air.

**END**

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