NOx Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

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Abstract

This is the seventh Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-00NT40753. The goal of the project is to develop cost effective analysis tools and techniques for demonstrating and evaluating low NO_x control strategies and their possible impact on boiler performance for firing US coals. The Electric Power Research Institute (EPRI) is providing co-funding for this program. This program contains multiple tasks and good progress is being made on all fronts. A series of field tests for RRI at the Ameren Sioux Unit #1 have demonstrated that RRI can provide up to 30% NO_x reduction over the use of over fire air in large scale (480MW) cyclone fired utility boilers. The field tests and modeling results are in good agreement. Final data analysis has been completed for tests performed at Eastlake Power Station of a real-time waterwall corrosion monitoring system. The tests demonstrated that corrosion could be measured accurately in real-time in normal boiler operations, and an assessment of waterwall wastage could be made without impacting boiler availability. Detailed measurements of soot volume fraction have been performed for a coal burner in a pilot scale test furnace. The measured values are in good agreement with the expected trends for soot generation and destruction. Catalysts from four commercial manufacturers have been ordered and one of the samples was received this quarter. Several *in situ* analyses of vanadium-based SCR catalyst systems were completed at BYU. Results to date indicate that the system produces results that represent improvements compared to literature examples of similar experiments. Construction of the catalyst characterization system (CCS) reactor is nearly complete, with a few remaining details discussed in this report. A literature review originally commissioned from other parties is being updated and will be made available under separate cover as part of this investigation. Fabrication of the multi-catalyst slipstream reactor was completed during this quarter and shakedown testing was begun at the University of Utah pilot-scale coal furnace. Talks continued with two utilities that have expressed interest in hosting a demonstration.

Table of Contents

DISCLAIMER.....	i
ABSTRACT	ii
TABLE OF CONTENTS	iii
EXECUTIVE SUMMARY	1
EXPERIMENTAL METHODS	3
Task 1 Program Management	3
Task 2 NOx Control.....	5
Task 3 Minimization of Impacts	8
Task 4 SCR Catalyst Testing.....	12
Task 5 Fly Ash	na
Task 6 Field Validation of Integrated Systems	39
RESULTS AND DISCUSSION.....	40
CONCLUSIONS	43
LITERATURE REFERENCES	45
APPENDIX	46

Executive Summary

The work to be conducted in this project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-00NT40753. This project has a period of performance that started February 14, 2000 and continues through September 30, 2002.

Our program contains five major technical tasks:

- evaluation of Rich Reagent Injection (RRI) for in-furnace NO_x control
- demonstration of RRI technologies in utility boiler scale field tests
- impacts of combustion modifications (including corrosion and soot)
- ammonia adsorption / removal from fly ash
- SCR catalyst testing

To date good progress is being made on the overall program. We have seen considerable interest from industry in the program due to our initial successful field tests of the RRI technology and the corrosion monitor.

During the last three months, our accomplishments include the following:

- Completion of successful field tests of RRI at the Ameren Sioux Unit 1. The tests have demonstrated that RRI can provide up to 30% NO_x reduction over the use of only over fire air in a large scale (480MW) cyclone fired utility boiler. Additional modeling studies and further analysis of the phase one set of RRI field tests on the Sioux Unit 1 performed in Fall, 2001 indicated that the boiler was not operating at the correct stoichiometry during the phase one test campaign.
- Completion of all data analysis for field tests performed at Eastlake Power Station of a real-time waterwall corrosion monitoring system. The corrosion tests at Eastlake Power Station provided the first demonstration of real-time high-temperature corrosion assessment in the radiant section of a large coal-fired power generation boiler. The successful completion of the tests demonstrated that corrosion could be measured accurately in real-time in normal boiler operations, and an assessment of waterwall wastage could be made without impacting boiler availability. Good agreement was obtained between the electrochemical noise based corrosion rates predicted by the probe and corrosion rates measured by a surface profilometer.
- Measurements of soot volume fraction have been performed for a coal burner in a pilot scale test furnace. Measurements were performed with a sampling probe and a photoacoustic instrument for burner stoichiometries ranging from 0.75 to 1.05. Measurements were performed at the burner centerline and in the radial direction for selected axial locations. The measured values are in good agreement with the expected trends for soot generation and destruction.
- Sample catalysts have been ordered from four commercial manufacturers of SCR catalysts. One of the commercial catalysts arrived this quarter and the others should arrive in the next quarter
- Several *in situ* analyses of vanadium-based SCR catalyst systems were completed at BYU. These are preliminary data primarily intended as shakedown for the system. Results to date

indicate that the system produces results that represent improvements compared to literature examples of similar experiments (but for different catalyst systems). We have reproduced substantial ammonia and NO adsorption data that are consistent with literature sources. However, we have as yet been unable to reproduce surface sulfation described by some authors in the literature. Construction of the catalyst characterization system (CCS) reactor is nearly complete.

- A literature review originally commissioned from other parties is being updated and will be made available under separate cover as part of this investigation. Permissions to publish some aspects of this survey, specifically those involving field tests, have yet to be granted. However, we are hopeful they will soon be granted.
- The University of Utah completed construction of the multi-catalyst slipstream reactor during this quarter and shakedown testing was begun at the University of Utah pilot-scale coal furnace. Talks continued with two utilities that have expressed interest in hosting a demonstration.

Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the Tasks as outlined in our original proposal.

Task 1 - Program Management

Licensing agreements for Rich Reagent Injection (RRI) have been completed with a second NO_x control equipment implementer – RJM, Inc.. RRI was originally co-developed by EPRI and REI. Through this DOE program, field tests of RRI in cyclone fired utility boilers have been performed that have generated sufficient interest from industry to warrant establishing licensing agreements. REI holds a license from EPRI that allows REI to utilize the RRI technology. Through this license, REI is allowed to enter into sub-license agreements with NO_x control equipment implementers that will in-turn market, design and install RRI technology in utility boilers. REI has completed a sub-license agreement with RJM, Inc.. As reported in our last Quarterly Report, a sub-license agreement has been completed with Fuel Tech, Inc.. Multiple implementers are desired to ensure utilities can install RRI on a cost-competitive basis.

REI has completed Non-Disclosure Agreements (NDAs) with the four commercial vendors of SCR catalysts that will be providing catalysts samples to the project. NDAs between REI and the University of Utah and Brigham Young University are in progress.

Industry Involvement

Results from portions of this research program have been reported to industry through technical presentations at two recent conferences.

- A paper entitled “Unresolved Technical Challenges to NO_x Reduction for Coal-fired Power Generation” that was presented at the 27th International Technical Conference on Coal Utilization and Fuel Systems, held March 4-7, 2002 in Clearwater, FL highlighted our progress on evaluating a corrosion probe for real time monitoring of waterwall wastage, incorporating a soot model into our coal combustion CFD code, experimental results for adsorption of ammonia on to fly ash and an overview of our SCR catalyst evaluation task [Davis et al, 2002]. The Clearwater conference was sponsored by the U.S. Department of Energy, Coal Technology Association, the American Society of Mechanical Engineer and the National Energy Technology Laboratory.
- A condensed article based on a previously published paper “On-line technique for corrosion characterization in utility boilers” [Linjewile et al, 2001] has been selected to be featured in the forthcoming issue of the U.S. DOE-EPRI Newsletter on Materials and Components in Fossil Energy Applications. The newsletter is distributed to approximately 800 researchers and engineers involved in materials applications in fossil fuel-fired processes.

- A paper entitled “Recent Experience with Overfire Air for Cyclone Fired Boilers” that highlights the results of recently completed field tests of RRI in the Ameren Sioux Unit 1 was presented at the 2002 Electric Power Conference, St. Louis, Missouri [Boll et al, 2002]. The paper was presented by personnel from Ameren that have collaborated on portions of the RRI work performed in this project.

Task 2 - NO_x Control – LNFS/SNCR/Reburning

Task 2.2 Evaluation of Integrated System Design for Cyclone Furnace Applications

During the last quarter additional RRI modeling studies have been performed to help analyze the results of previously completed field testing of RRI in Ameren's Sioux Unit 1. This boiler is a 480 MW opposed wall fired cyclone unit, significantly larger than Conectiv's B.L. England Unit 1 (130 MW), the site of the first demonstration of RRI in a cyclone fired unit. The injection system design for Sioux Unit 1 was based on CFD based modeling conducted by REI and includes a total of 20 wall injectors in three elevations between the top row of cyclone barrels and the OFA ports. The first of two phases of field testing of the RRI process in this unit was completed in August, 2001 and yielded results that were less than as expected. During that time, the full load NO_x emissions from the unit had been reduced from the baseline emissions prior to OFA installation of 1.25 lb/MMBtu to approximately 0.55 lb/MMBtu following the OFA installation. At best, RRI was shown to reduce NO_x emissions by an additional 15-20%, lowering NO_x emissions to approximately 0.44 lb/MMBtu. Continuous ammonia measurements showed less than 1 ppm ammonia slip during the first round of testing. These results were in contrast to the CFD model results that suggested at least 25% NO_x reductions were achievable with RRI.

During the last performance period, additional analyses were performed in order to better understand the discrepancy between the previously completed CFD model results and the first phase of field testing. First, additional chemical kinetic calculations were completed to evaluate the dependence of RRI performance on the local flue gas temperature and stoichiometric ratio. Second, additional CFD simulations were completed to evaluate the impacts of barrel stoichiometric ratio on RRI performance in Sioux Unit 1.

Figure 2.1 shows the results of chemical kinetic calculations to evaluate the impact of flue gas temperature and stoichiometric ratio on NO_x reduction due to urea. These results are from isothermal plug flow reactor calculations over a fixed residence time, initial NO level and normalized stoichiometric ratio (NSR). This configuration may be interpreted as idealized conditions within the lower furnace of a staged cyclone fired boiler, into which urea is injected. Figure 2.2 shows the residual ammonia (ammonia slip) for the same conditions shown in Figure 2.1.

The results in Figure 2.1 indicate that the local stoichiometric ratio has a very strong impact on NO_x reduction due to RRI at gas temperatures in the vicinity of 1900-2000°F. For example, at a temperature of 1950°F, these calculations suggest that the difference between an average stoichiometric ratio of 0.95 and 0.98 can result in the difference between 40% and 0% NO_x reduction. Thus, for the range of gas temperatures that exist within the lower furnace of a cyclone fired furnace, the difference between an average stoichiometric ratio of 0.95 and 0.98 can dramatically impact RRI performance.

To understand this better, these results need to be discussed within the context of Ameren's Sioux Unit 1. The previously completed CFD modeling of this unit suggested that if the barrels are operated at an average stoichiometric ratio of 0.95, NO_x reductions of 25-30% would be

expected. However, the first phase of field testing was not able to reproduce the predicted NO_x reductions. In addition, the measured NO_x reductions were extremely variable, with certain test

Figure 2.1 Calculated NO_x reduction due to urea in an isothermal plug flow reactor over a range of flue gas temperatures and stoichiometric ratios.

Figure 2.2 Calculated ammonia slip for the same conditions shown in Figure 2.1.

points resulting in anywhere between 0 and 15% NO_x reduction. The explanation for the discrepancy between the original CFD model results and the phase 1 field test results could lie in Figure 2.1, which indicates that the level of lower furnace staging is extremely important. If during the phase 1 testing, the average lower furnace SR were actually 0.98 rather than 0.95, then it is understandable why the predicted NO_x reductions were not achieved. In fact, the

baseline NO_x emissions (OFA, no RRI) from Sioux Unit 1 during the phase 1 testing were 0.55 lb/MMBtu. The previously completed CFD modeling suggested that if the unit were staged to a lower furnace SR of 0.95, then the NO_x emissions would be expected to be approximately 0.42 lb/MMBtu. The higher than expected baseline NO_x emissions also was an indication that the unit was not staged to 0.95, but was higher.

To predict the performance of the installed RRI system in Sioux Unit 1, assuming that the lower furnace was operating at a SR of 0.99 (rather than 0.95), an additional CFD simulation was completed. This evaluation required that a cyclone barrel at SR=0.99 first be simulated. The results of this simulation were then mapped into the Sioux Unit 1 furnace model, where reagent injection was modeled. This evaluation indicated that the identical RRI injection strategy previously modeled for this unit would reduce the furnace exit NO_x emissions by 1%, if the unit were staged to a lower furnace SR of 0.99.

The combination of the chemical kinetics and CFD analyses provided strong evidence that during the first phase of RRI testing in Ameren's Sioux Unit 1, the furnace was not staged deeply enough to result in the NO_x reductions that were expected. The modeling indicated that the unit was likely not staged to a lower furnace stoichiometric ratio of 0.95. By deeper staging, it is expected that both the baseline NO_x emissions would decrease (from 0.55 lb/MMBtu to approximately 0.42 for SR=0.95) and that the performance of RRI would dramatically improve. These simulations provided strong evidence that during the second phase of RRI testing in Sioux Unit 1, the impact of furnace staging should be evaluated.

Task 3 – Minimization of Impacts

Task 3.1 Waterwall Wastage

In this quarter, work on the corrosion probe focused on completion of analysis of data obtained during corrosion measurements at the FirstEnergy Eastlake Power Station, near Cleveland, Ohio. Although much of this work was funded through a grant from the Ohio Coal Development Office, technology development that played a critical role in making this field test possible relied heavily upon this DOE supported task. In view of the completed data analysis, the corrosion probe response to changes in excess oxygen concentration and FEGT at constant boiler load is discussed. To help facilitate technology transfer and more rapidly disseminate the knowledge and experience gained from this project, portions of the completed corrosion work were presented at the 27th International Technical Conference on Coal Utilization and Fuel System in a paper titled “Unresolved Technical Challenges to NO_x Reduction for Coal-fired Power Generation.” Furthermore, a condensed article based on a previously published paper “On-line technique for corrosion characterization in utility boilers” has been selected to be featured in the forthcoming issue of the U.S. DOE-EPRI Newsletter on Materials and Components in Fossil Energy Applications. The newsletter is distributed to approximately 800 researchers and engineers involved in materials applications in fossil fuel-fired processes.

Probe Response to Changes in Excess O₂ Levels and FEGT at Constant Boiler Load

This discussion completes the data analysis pertaining to probe response as a consequence of changes in oxygen concentration in a utility boiler. The occurrence of reducing conditions in the furnace has been blamed for the increased observation of waterwall tube wastage in supercritical boilers; especially those fitted with low-NO_x burner systems or overfire air (OFA) ports. Figure 3.1.1 shows results of the probe’s response during the test, illustrating the relationships between boiler load, corrosion rate, furnace exit gas temperature (FEGT) and excess oxygen concentration. The figure also shows these relationships just prior to the commencement of the test. During tests at Eastlake, the excess oxygen level was about 5.5% at low load and about 2.5-3.0% at full load. The trends in oxygen concentration, boiler load and FEGT showed expected behavior, i.e., an increase in boiler load was associated with an increase in FEGT and a decrease in excess oxygen level.

Prior to the start of the sensitivity tests, the excess oxygen level was decreased to 2.5% as the load was increased from about 325 MW to 600MW. Increasing the load resulted in an increase in corrosion rate to well over 10mils/yr. However, the increase in corrosion activity was not sustained. Once the desired load level was reached, the excess oxygen concentration was increased to 3.5% and maintained there for two hours. As the oxygen concentration was increased from 2.5% to 3.5% at constant load, the corrosion rate dropped, responding to the change in oxygen conditions. The corrosion rate registered a value of about 7 mils/yr during the two-hour test at 3.5% excess oxygen. After the first two hours of testing, the experimental conditions were disrupted by irregularities in coal feed rate. During this period, the boiler load dropped from 600 MW to less than 500 MW. The test was resumed after combustion conditions stabilized and the load increased to 600 MW, and maintained there at an excess oxygen level of 3.0%. Figure 3.1.1 also shows that for the rest of the test, the load remained constant but the FEGT, fluctuated considerably.

Figure 3.1.1 Comparison of trends in excess %O₂ before and during sensitivity tests.

Task 3.2 Soot

During this quarter, progress was made on soot measurement within a pilot-scale test furnace for the purpose of validating the soot model developed previously.

The 5 MMBtu/hr pilot-scale test furnace at the University of Utah Combustion Research Laboratory was operated with various burner stoichiometries while firing Utah coal. The operating conditions and coal properties are shown in Table 3.2.1. Staging air ports were located at 4.48 meter from the burner exit for all operating conditions. Soot volume fractions were measured axially along the centerline and radially at five axial locations using a sampling probe and photoacoustic (PA) instrument [Moosmuller et al., 1998].

Table 3.2.1 Pilot-scale Test Furnace Operating

	case 1	case 2	case 3	case 4	Utah Coal Properties	
Burner Stoichiometry	0.75	0.85	0.95	1.05	As Received, %	
Overall Stoichiometry	1.15	1.15	1.15	1.15		
Coal Feeding Rate [lb/hr]	320	323	323	325		
Air Flow Rate [lb/hr]						
primary	448	449	450	449	C	69.65
secondary	607	693	796	900	H	4.42
tertiary	1211	1382	1592	1805	O	9.16
staging	1197	896	597	383	N	1.25
Exit O ₂ , dry	3.0	3.0	3.0	3.0	S	0.4
					Ash	10.44
					Moisture	4.68
					HHV (BTU/LB)	12303

A water-cooled, air-quenched transpiration probe was used in the experiment. Schematic of the sampling setup is shown in Figure 3.2.1. Various dilution ratios ranged from 400 to 3800 at ambient temperature were employed to measure the soot volume fraction at various sampling locations.

Figure 3.2.1 Schematic of a soot sampling system with a photoacoustic (PA) instrument.

Figure 3.2.2 shows the measured soot volume fraction for case 1 (burner stoichiometry of 0.75) as a function of the axial distance from the burner exit along the centerline and the radial

distance from the side wall. After a peak at about 2 meters from the burner exit, the soot volume fraction decreases with increasing distance as shown in Figure 3.2.2.A.

- The competing nature of two processes, soot formation and destruction can be clearly seen in Figure 3.2.2A. Near the burner, there is significant soot formation from the coal off-gas. After reaching a peak, the soot volume decreases due to oxidation (destruction) of the soot. Soot exists even after additional air introduction from the staging port located at 4.48 meters.
- The radial distribution of soot volume fraction is illustrated by Figure 3.2.2.B. At 0.81 and 2.03 meters, the distributions are similar with a high soot volume fraction at the centerline. However, further downstream the highest soot volume fraction exists at a region close to the side walls. This may be a result of the burner swirl or re-circulation patterns within the furnace.

Figure 3.2.2 Soot volume fraction along furnace centerline and at radial positions.

Figure 3.2.3.A shows the impact of burner stoichiometry on soot volume fraction measured 3.25 m downstream of the burner. As shown in the figure, the soot volume fraction decreases with increasing burner stoichiometry due to increasing oxygen availability for soot destruction (oxidation). Generally, NO_x is expected to decrease as air staging is increased (decreasing burner stoichiometry). This is confirmed in Figure 3.2.3.B, which plots the soot volume fraction as a function of exit NO_x. With increasing NO_x, the soot volume fraction decreases.

Figure 3.2.3 Soot volume fraction measured at 3.25 meters from the burner exit as a function of the radial distance from the side wall for various burner stoichiometries (A) and exit NO_x (B).

Task 4 - SCR Catalyst Performance under Biomass Co-Firing

The purpose of this task is to perform a combination of basic and applied R&D, with heavy focus on laboratory and field tests, to develop a better understanding of the “real” costs associated with using selective catalytic reduction (SCR) for coal-fired boilers using US coals and a coal/biomass blend. Within this task there are four principal sub-tasks:

Task 4.1: Technology assessment on fundamental analysis of chemical poisoning of SCR catalysts by alkali and alkaline earth materials

Task 4.2: Evaluation of commercial catalysts in a continuous flow system that simulates commercial operation

Task 4.3: Evaluation of the effectiveness of catalyst regeneration

Task 4.4: Develop a model of deactivation of SCR catalysts suitable for use in a CFD code

Sub-tasks 1 and 3 are being principally performed at Brigham Young University under the direction of Professors Larry Baxter and Calvin Bartholomew. The work effort for sub-tasks 2 and 4 is being performed by REI, under the supervision of Dr. Constance Senior, with assistance from the University of Utah (Professor Eric Eddings and Dr. Kevin Whitty) on sub-task 2.

Task 4.1 Technology Assessment

The objectives of this subtask are (1) to supplement the largely complete SCR-catalyst-deactivation literature with results from new laboratory-scale, experimental investigations conducted under well-controlled and commercially relevant conditions, and (2) to provide a laboratory-based catalyst test reactor useful for characterization and analysis of SCR deactivation suitable for samples from commercial facilities, slipstream reactors, and laboratory experiments. Two catalysts flow reactors and several additional characterization systems provide the analytical tools required to achieve these objectives. The flow reactors include the *in situ* surface spectroscopy reactor (ISSR) and the catalyst characterization system (CCS), both of which are described in more detail below. The ancillary characterization systems include a temperature-programmable surface area and pore size distribution analyzer, scanning electron microscopes and microprobes, and catalyst preparation systems.

The sample test matrix includes two classes of catalysts: commercial, vendor-supplied SCR catalysts and BYU-manufactured, research catalysts. The commercial catalysts provide immediate relevance to practical application while the research catalyst provides less fettered ability to publish details of catalyst properties. The five commercial catalysts selected for use come from most commercially significant catalyst manufacturers (Cormetech, Haldor Topsøe, Hitachi, and Siemens) and provide a wide range of catalyst designs and compositions. The in-house catalyst allows detailed analysis and publication of results that may be more difficult with the commercial systems. This catalyst suite provides a comprehensive test and analysis platform from which to determine rates and mechanisms of catalyst deactivation. The result of this task will be a mathematical model capable of describing rates and mechanisms of deactivation.

Within the last performance period, construction of the reactor facility was largely completed, as summarized below.

ISSR Overview

The purpose of the ISSR is to provide definitive indication of surface-active species through *in situ* monitoring of infrared spectra from catalytic surfaces exposed to a variety of laboratory and field conditions. The ISSR provides *in situ* transmission FTIR spectrometer measurements of SO₂, NH₃, and NO_x, among other species. Absorption and desorption behaviors of these and other species are monitored. Quantitative indications of critical parameters, including Brønsted and Lewis acidities on fresh and exposed catalysts will be included. Indications of coadsorption of NH₃ and NO_x will help elucidate mechanisms and rates of both reactions and deactivation. The overall flow diagram for the reactor is illustrated in Figure 4.1.1.

The ISSR system is under operation, with preliminary results reported here. The system includes an FTIR spectrometer, two reactor cells (one still under construction), and a flow system. This system is described in more detail, followed by several preliminary results. Results from the following tests appear below: (a) reactor verification and quality control tests; (b) sulfation of vanadia catalyst; and (c) ammonia adsorption, and nitric oxide adsorption on vanadia catalyst.

FTIR Spectrometer A Nicolet, Model 730 FTIR spectrometer provides the *in situ* information in this investigation. This system is illustrated in Figure 4.1.2. The spectrometer is used in transmission mode with a reactor cell designed to provide surface-sensitive, *in situ* data on adsorbed species.

Reactor Cell Figure 4.1.3 presents a schematic diagram of the reactor cell; a photograph is shown in Figure 4.1.4. This cell, which is specifically designed and fabricated for this study, is machined from a 316 SS rod to allow the infrared beam to pass through a catalyst wafer. The wafer is sandwiched between transparent crystal IR windows. The overall length and inside diameter of the cell are 10.9 cm and 2.6 cm, respectively. The catalyst wafer is supported by two aluminum wafer holders to prevent it from being crushed by the tight-fitting crystal windows and to allow the gas stream to enter and pass over the wafer. The gas ports are on opposite sides of the middle section of the reactor to allow continuous flow of reactants or adsorbing gases over the wafer. A thermocouple can be inserted into the reactor so that it just touches the catalyst wafer, providing accurate temperature monitoring. Cooling jackets on the far ends of the tube allow the center of the reactor to be operated at up to 773 K while the ends are kept below the melting temperature of the nitrile or Buna-N and Kalrez O-rings that provide air-tight seals. Reactor preparation involves sliding the KCl circular windows and sample wafer into the tube, positioning the thermocouple into the grooved wafer holder, inserting the O-rings and teflon window holders, and tightening the end caps. The whole apparatus is insulated with high-temperature insulation and aligned in the path of the IR beam so that the beam passes through the reactor and sample wafer.

Figure 4.1.1 Overall schematic of the ISSR.

Figure 4.1.2 FTIR spectrometer with gas cell in sample analysis compartment.

Figure 4.1.3 Schematic diagram of the *in situ* reactor cell used in the FTIR system.

Figure 4.1.4 Photograph of the reactor cell.

Wafer preparation Samples are prepared from powdered catalyst, often with dilution with optical-grade KBr. Typically, a titania (anantase) powder with a specific surface area of approximately $45 \text{ m}^2/\text{g}$ combines with KBr powder at a ratio of 1:10 (titania : KBr). A 0.1 g sample of this material pressed into a 2 cm diameter wafer with 0.4 mm thickness provides a suitable diagnostic reactor volume for this technique. However, dilution with KBr decreases the amount of surface reacting and potentially affects the surface reactivity of the catalyst. The data presented here were obtained with no dilution using a 5 % by weight V_2O_5 mixture with TiO_2 . Fresh catalyst is oxidized prior to testing in the chamber using 5 % by weight O_2 in He at 350°C – 400°C for 4.5 hrs.

The quality control tests involve comparing system performance with known standards. NO adsorption on Rh/ZSM5 provides data to compare with former research results that were obtained with the same FTIR apparatus. The main peaks of NO adsorption on the Rh/ZSM5 catalyst appear at the same spectral position as those observed in the former experiments, as illustrated in Figures 4.1.5 and 4.1.6. The new data report results over a wavenumber range shifted somewhat toward the visible compared with the previous results. The two characteristic NO adsorption peaks at 1869 and 1783 cm^{-1} are even clearer than those in the former results.

Figure 4.1.5 NO adsorption from former experiments.

Figure 4.1.6 NO adsorption peaks measured with current system with 20 sccm of 1000 ppm NO at 448 K.

Then sulfation test and reactant gas adsorption test were conducted on self-prepared 5 % (by weight) V_2O_5/TiO_2 catalyst similar to commercial-grade catalyst.

Vanadia catalyst sulfation The sulfation experiment used a 2900 ppm SO_2 , 4.8% O_2 mixture in He at a total flow rate of 52.5 sccm. The temperature ranged from 360 °C to 377 °C for the 6 hr duration of the test.

Several literature sources indicate that the surfaces of the vanadium-based SCR catalysts sulfate in SO_2 -laden flows. The characteristic spectral locations of the surface sulfation and gas-phase adsorption peaks are indicated in Table 4.1.2. The literature indicates that sulfation peaks develop over a period of hours but eventually dominate the surface.

Table 4.1.2. Characteristic spectral location of sulfation and gas-phase adsorption peaks on vanadium-based SCR catalysts.

Species	Spectral Location
Vanadia sulfate	1375 cm^{-1}
Titania sulfate	980,1050,1135,1210 cm^{-1}
SO_2 adsorption	507,539,1133,1164,1344,1350,1360,1372 cm^{-1}
SO_3 adsorption	816,1034,1093,1266 cm^{-1}

Our results show several adsorption peaks, including peaks at 1040, 1070, 1125-1121, 1272, and 1369 cm^{-1} . The peaks at 1040, 1070, and 1275 cm^{-1} increase gradually with time. The 1125 cm^{-1} band first increase, then decrease, with a new peak at 1177 cm^{-1} appearing. The 1369 cm^{-1} bands decrease slowly. If our value is 10 cm^{-1} difference with value reported in the literature, the 1040 and 1125 peaks could be attributed to titania sulfate, while no apparent vanadia sulfate has been observed. None of these peaks can be associated with sulfation, as was confirmed by analysis of the surface for sulfur content using XPS diagnostics.

The results to date do not confirm the literature indications that surfaces of the catalyst sulfate. However, these are preliminary tests and may not have been conducted over a long enough time or at high enough temperatures to promote the reactions. These analyses are continuing.

NH_3 adsorption on vanadia catalyst Adsorption of ammonia on the vanadia catalyst provides similar infrared signatures useful for determining mechanisms of reaction. Additional experiments were performed to explore this reaction. The adsorption gas consists of 0.91 % NH_3 , 9.1% O_2 and He as the balance gas. The total flow rate is 27.5 sccm. The adsorption behavior was tested from room temperature to 352.8 °C. Figures 4.1.7 and 4.1.8 show the adsorption spectra of ammonia.

The adsorption results show that NH_3 has a strong adsorption on vanadia catalyst from room temperature to 200 °C. Then the adsorption tends to decrease with increasing temperature increasing. The main adsorption peaks appeared at the following spectral locations:

- 1221 cm^{-1} . This band is observed after NH_3 adsorption and catalyst was treated with He in room temperature
- 1435 cm^{-1} , NH_4^+ adsorption species: asymmetric bending vibration

- 2800-3100 cm^{-1} , NH_4^+ adsorption species: stretching vibration
- 3100-3400 cm^{-1} , coordinated adsorbed NH_3 , stretching vibration

Peaks at 1282 cm^{-1} and 1119 cm^{-1} have not been clearly indicated in most of the literature, although some authors have reported that 1150-1300 cm^{-1} , 1173 cm^{-1} , and 1220 cm^{-1} bands are coordinated compounds that involve NH_3 . One literature source indicates that 1270 cm^{-1} is $\text{vas}(\text{NH}_3)$ vibration of the coordination-bound ammonia, and 1120 cm^{-1} is $\text{vs}(\text{NH}_3)$ which might be due to NH_3 molecules bound to surface hydroxyl groups. Thus, the 1282 cm^{-1} peak, which in high temperature shifts to lower frequency 1246 cm^{-1} , could be Lewis acid sites, and the 1119 cm^{-1} peak could be Brønsted acid sites.

Two very weak adsorption bands were observed

- 1670 cm^{-1} , NH_4^+ adsorption species: symmetric bending vibration
- 1605-1615 cm^{-1} : coordinated adsorbed NH_3

Therefore, both Brønsted acid sites and Lewis acid sites have been observed, and most of the characteristic bands have been observed.

With the ammonia adsorption, most of the bands shift significantly to lower frequencies. This has been attributed to the interaction of surface vanadia species with the adsorbate. For example, the 1282 cm^{-1} peaks decrease considerably, while the 1119 cm^{-1} peaks grew to a large extent. The data provide definitive evidence that the catalyst surface actively absorbs and (presumably) otherwise interacts with ammonia, with vanadium principally involved. While these data are more consistent with the literature, more investigation is planned for this phenomenon. At high temperatures, all the peaks except the 1119 cm^{-1} band decrease, indicating that ammonia desorption on both Brønsted and Lewis acid sites became more important at high temperatures. This agrees with most literature observations.

NO adsorption on vanadia catalyst After the NH_3 adsorption test, the catalyst was kept in He at room temperature for 12 hrs. Then 1.96 % NO and 9.8 % O_2 with the balance He was introduced to the catalyst. The total flow rate is 12.75 sccm.

New adsorption peaks were obtained only at room temperature (Figure 4.1.9) and were located at 1612 cm^{-1} , which has been assigned to a nitrosyl species. As temperature increased, both ammonia adsorption bands and NO adsorption bands disappeared.

Figure 4.1.7 Ammonia adsorption on a 5 wt % vanadium in titanium catalyst typical of those observed at temperatures below 300 °C.

Figure 4.1.8 Ammonia adsorption on a 5 wt % vanadium in titanium catalyst typical of those observed at temperatures above 300 °C.

Figure 4.1.9 NO adsorption on a 5 wt % vanadium in titanium catalyst as a function of temperature.

CCS Overview The catalyst characterization system (CCS) provides capabilities for long-term catalyst exposure tests required for ascertaining deactivation rates and mechanisms and a characterization facility for samples from the slipstream reactor to determine changes in reactivity and responses to well-controlled environments. Figure 4.1.10 illustrates the essential features of this system up to the analytical train. The analytical train (Figure 4.1.11) is discussed later. This system simulates industrial flows by providing a test gas with the following compositions: NO, 0.10%; NH₃, 0.1%; SO₂, 0.1%; O₂, 2%; H₂O, 10%; and He, 87.7%. Both custom and commercial catalysts are tested as fresh samples and after a variety of laboratory and field exposures under both steady and transient conditions.

The purpose of the CCS is to quantitatively determine deactivation mechanisms by measuring specific, intrinsic catalyst reactivity of custom (laboratory) and commercial catalysts under a variety of conditions. These catalysts will be impregnated with a variety of contaminants, including Ca, Na, and K. In addition, the CCS will characterize samples of catalyst from slipstream field tests to determine similar data and changes in characteristics with exposure. Advanced surface and composition analyses will be used to determine composition, pore size distribution, surface area, and surface properties (acidity, extent of sulfation, etc.).

During this quarter, most of the final designs and specifications were completed and materials were ordered and (mostly) received. Much of the system has been constructed. The various components and their current status are summarized below in the approximate order in which they are encountered by gases flowing through the system.

Helium functions as the carrier gas in this system since molecular nitrogen formed from NO_x is measured as part of the data analysis. NO_x derived nitrogen would represent an insignificantly small fraction of total nitrogen if nitrogen were used as a carrier gas. There is no indication in any literature of which we are aware that substitution of helium for nitrogen in any way alters rates or mechanisms of selective catalytic reduction of NO_x on vanadium-based catalysts.

Figure 4.1.10 Summary schematic diagram of the CCS up to (but excluding) the analytical train.

Figure 4.1.11 Photo of NO_x analyzer (left) and NH_3/SO_2 analyzer for the CCS system. A gas chromatograph has since been added to this system (in the center).

Gas Cylinders and Manifolds Several of the gases used in this experiment are toxic at cylinder concentrations, yet the only feasible storage location of the gases is in the same room as the CCS and, more specifically, the personnel running the CCS. Therefore, standardized gas manifold systems that represent one component for safe handling and use of such gases were developed. Neither BYU nor any of the previous employers of any of the professionals involved in this work publish a standard gas manifold system, so we adapted one used by the PI in similar situations at previous places of employment. The standard system is documented in the Appendix.

OSHA-compliant gas cylinder mounting racks and separations are being installed in the laboratory. The College Safety department is involved in reviewing all installations and procedures.

The major issues remaining to be resolved in the CCS do not represent a major roadblock for our program. A leak in one regulator was discovered after it was installed. All regulators associated with toxic or corrosive gases were sent to a local company to be inspected and repaired. After many weeks the local company indicated they were unable to do the work, so the regulators are being sent to a second company for refurbishment. We anticipate these regulators will be returned early in May.

The flow systems are in shakedown using inert gases (helium). We are resolving issues with the mass flow controllers and one of the modules in the field point control system. The remaining components of the flow system appear to be working well.

The bubblers are essentially complete, except for welding metal frits in the end of the tubes being inserted into the water.

We anticipate several issues will arise after the complete flow system is functioning. In particular, the tuning of flow controllers and calibration and operation of the analyzers cannot be completed until the remaining portions of the flow system are installed and functioning. The analytical system is in place but has yet to be tested under real flow conditions.

We are resolving heat-tracing issues with several moisture-carrying lines. The ammonia/SO₂ analyzer is designed to work with moisture-laden flows, but the remaining analyzers (NO_x and GC) are not.

Mass Flow Controllers and Solenoids Mass flow controllers (MFCs) meter a total of five gases, with controllers adapted to specific properties of gases being used where necessary. Solenoids provide automated gas line actuation after the controllers and are part of both the control and the safety system. The controllers allow for both manual and computer interfaces. All require dry gases for accurate control. The MFCs are the first major control component in the flow line. A picture of the current installation is indicated in Figure 4.1.12. The MFCs and much of the tubing between them and the remaining system are installed. Stainless tubing and Swagelock™ fittings are used for most flow systems.

Figure 4.1.12 Mass flow controllers for the CCS.

Bubblers Coal combustion stack gases typically contain about ten percent water vapor. A water bubbler maintains similar water concentrations in the CCS (Figure 4.1.13). The constant-temperature, heated aluminum block of the bubbler determines the water concentration in the exit stream, assuming equilibrium conditions prevail. Each of the four reactor flow lines within the CCS includes an independent bubbler.

NO, NH₃, and SO₂ streams bypass the bubbler since water absorbs each of these gases and they are present in small quantities. Furthermore, moisture in gases compromises both the accuracy and the durability of the mass flow controllers, so the bubblers appear downstream of all flow controllers. Helium and oxygen, which comprise the overwhelming fraction of the total gas flow, bubble through the water. The water content of the He/O₂ stream must exceed ten percent for the final concentration to be on target.

The bubbler design pressure is 34.5 kPa (5 psig) and 70 °C. Each bubbler consumes about 34 ml of water per day. Gravity-driven fill tanks maintain water levels in each bubbler. All tubes downstream of the bubbler are heat traced to prevent water vapor from condensing in the lines.

Figure 4.1.13. Schematic diagram of constant-temperature bubblers installed in the CCS.

Reaction Chambers The four reactor lines in the CCS simultaneously characterize up to four catalysts, one in each of up to four reaction chambers. The CCS includes two types of reaction chambers. The reactor chamber for laboratory samples comprises a 3/8" tube that houses a powdered catalyst sample. A second reactor chamber provides a site suitable for characterization of the samples from the slip-stream field reactor. The second chamber includes a 5.7 cm (2.25 in) square cross section to match the size of the monolith samples from the slipstream field reactor. The plate-type samples will be cut to fit these dimensions.

Two furnaces control the temperatures in two reactors apiece. The furnaces have aluminum inserts that enclose the reactor tubes to facilitate uniform heating. These furnaces have been purchased and installed. They have been mounted vertically, and have digital temperature control.

Filters Two sintered metal filters in series follow each reaction chamber. The filters remove particles larger than 15 microns and 5 microns, respectively. The filters protect the downstream analytical equipment. Both catalyst attrition particles and ammonium bisulfate will collect in the filters. Each filter element is replaceable to allow easy maintenance and diagnosis of particulates in the line.

Analyzer Subsystem The analyzers at the end of the sample train (Figure 4.1.14) provide quantitative data regarding feed streams and products from the four reaction chambers. The analyzers and ancillary equipment are described in the following section.

Figure 4.1.14 CCS analyzer subsystem flow diagram.

Ten-way Selector Valve A computer-addressable, ten-way selector valve provides analyzer access to each of the four reaction chamber inlets and each of the four outlets. All streams not directed to the analyzers are combined in a single line that is treated and vented. The valve is installed and interfaced with the computer and control system.

NH₃/SO₂ Analyzers The NH₃/SO₂ analyzer system is installed (see Figure 4.1.11). The analyzer appears to be fully functional but has yet to be tested under full reactor conditions. Issues of primary concern include (a) dead space/time lags in analyzer performance, (b) flow-rate compatibility between the several analyzers and the experiment, and (c) ability of the heat-traced lines in the analyzer to avoid problems with condensation.

Condenser Design The condenser dries the sample stream before passing it to the gas chromatograph and NO_x analyzer. The condenser cools the gas in an ice bath to near 0° C. The

condensate periodically drains through a ball valve. The condenser will be installed after completion of the analyzer installation.

Gas Chromatograph System The gas chromatograph (GC) works in parallel with the NO_x analyzer since neither requires high flow rates. The GC quantitatively analyzes for N_2 , O_2 , and N_2O using helium as a carrier gas. The GC system is installed and awaiting shakedown with the remaining analyzer systems.

NO_x Analyzer The Thermo Environmental Instruments Model 42H chemiluminescence NO_x analyzer quantifies the NO and NO_2 concentrations in a sample stream. The NO_x analyzer is installed and awaiting shakedown with the remaining analyzer systems.

Data Acquisition and Control Systems The CCS is designed to allow manual control of all components. However, computer-based data acquisition and control provide more convenient and possibly more reliable means of collecting data during the long-terms tests for which the CCS is designed. National Instruments™ LabVIEW™ software provides the data acquisition and control platform for the CCS. The relatively recent FieldPoint™ technology is used to manage the acquisition and control signals, providing several operational and reliability advantages.

Fourteen FieldPoint™ modules acquire the data on our system. The modules are networked as shown in Figure 4.1.15.

Figure 4.1.15 FieldPoint™ module network scheme (cross reference with Appendix).

FP-1000 represents the base FieldPoint™ module. It connects to the computer through a serial cable. The speed of the protocol through the serial cable is sufficient for the needs of this experiment. The FP-1000 uses an Optimux protocol to communicate with the other modules on the network. The relays (RLY-420), digital input (DI-330), and thermocouple modules attach to the main terminal. This allows optimal placement for the RLY and DI to control the multi-position valve actuator after the reactors and gather data from the thermocouples, but will require the extended wiring of the RLYs to the solenoid valves. The networked FP-1001 controls the mass flow controllers (MFCs) and resides close to the MFCs. However, since the analytical system requires wiring to the AI, the dual control module (which allows control of the analytical devices) is placed on this module sequence as well. All of the channels on all modules are summarized in Appendix 1.

Wiring is considered second in priority to instrumentation placement. Lengths of wires that carry analog signals are minimized while those that carry digital signals or only voltage don't matter. For this reason, solenoid valves were wired across the system to a power supply placed out of the way on a shelf high above the insulated furnaces. The solenoid valves are wired especially to allow either manual control or computer control. To avoid confusion they are first wired to a master toggle switch that controls whether manual or FieldPoint™ will actuate the solenoid valves.

The solenoid wiring and control scheme (Figure 4.1.16) provides safety and operational control for the gases used in the CCS, several of which are toxic at gas cylinder concentrations. A representative wiring diagram for this system is summarized in Figure 4.1.16. Both manual and automated switching of individual solenoids is provided with manual switching overriding the automated system. A master manual switch is provided primarily for safety (emergency shutdown) reasons. To avoid clutter, only three of sixteen wiring and control loops are illustrated.

Figure 4.1.16 Schematic wiring and control diagram for solenoid operation in the CCS.

Gases pass through the solenoids and mass flow controllers into bubblers (He and O₂ only) and mixing plenums, eventually arriving at the reaction chambers. The reaction chamber control system provides, as currently configured, three types of actions. The logic diagram for these actions indicates automated control sequences for purging, conditioning, and running each reaction chamber. These conditions combine with conditions with the reactor off and the furnace door open to define the five current computer-controlled operating conditions of the system. Specifically, these conditions are as follows:

1. Reactor Purge This function serves the purpose of not only clearing the lines to the reactor, but also clearing the gas in the catalyst. The following logical steps are required to purge the reactor:
 - a. Communicate to the multi-position valve actuator to skip over both the feed and the reactor exhaust because it does not need to be analyzed. This will increase the amount of analysis on the other reactor during this time.
 - b. Switch the 3-way solenoid valve 5, 6, 7, or 8 away from water bubbler. (Which solenoid switched depends, of course, on which reactor has been selected to purge. Reactor 1 purge will require 3-way solenoid 5 to be switched etc.)
 - c. Set MFC 7, 8, 9, or 10 to zero. The purge gas will be a He/O₂ - only mixture. (Again, set the MFC that corresponds with the appropriate reactor. Reactor 1 purge will require MFC 7 to be set to zero.)
 - d. Switch 2-way solenoid valve 1, 2, 3, or 4 closed. This will be closed to prevent back flow and increase safety while this line is not in use.
 - e. Recalculate MFC 3, 4, 5, & 6. The flow rate needed from these will decrease because this gas mixture is no longer needed through the reactor.
 - f. Recalculate MFC 1 & 2. These values will probably not change, but it is good practice to recalculate all initial MFC set points for any experimental changes.

2. Reactor This function serves the purpose of possibly studying catalyst
Conditioning activation. Also, to obtain optimal results we will want to condition the catalyst before every run. The following steps are required to condition the reactor:
 - a. Check multi-position-valve to vent? (It is to take data points to analyze the changes in concentration during a conditioning run. If so, the feed and reactor exhaust are directed to the analyzers rather than vented.)
 - b. Switch 3-way solenoid valve 1, 2, 3, or 4 from SO₂.
 - c. Open 2-way solenoid valves 1&5, 2&6, 3&7, or 4&9.
 - d. Switch 3-way solenoid valve 5, 6, 7, or 8 to bubbler (It is unclear at this point if water is desired during condition of catalyst.)
 - e. Calculate MFC 7&11, 8&12, 9&13, or 10&14.

- f. Recalculate MFC 1 through 6.
3. Run Catalyst Test This is the central function of the reactor and main purpose for building this reactor system. It will involve the full capacity of the analytical system and will, of course, require the most precise programming. The following basic steps will be required.
- Confirm that Purge and Conditioning has been performed.
 - Open 2-way solenoid valves 1&5, 2&6, 3&7, or 4&9.
 - Switch 3-way solenoid valve 5, 6, 7, or 8 to bubbler.
 - Switch 3-way solenoid valve 1, 2, 3, or 4 from NO_x.
 - Calculate MFC 7&11, 8&12, 9&13, or 10&14.
 - Recalculate MFC 1 through 6.
 - Allow multi-position valve to choose for analysis.
 - Set NH₃/SO₂ Analyzer controls and acquire data.
 - Set G.C. Analyzer controls and acquire data.
 - Set NO_x Analyzer controls and acquire data.
4. Reactor Off Currently, there are two reactor in one furnace. The procedure if this option is selected will be to:
- Purge the reactor for a specific amount of time.
 - Switch 2-way solenoid valves 1&5, 2&6, 3&7, or 4&8 closed.
 - Set MFC 7&11, 8&12, 9&13, or 10&14 to zero.
 - Recalculate MFC 1 through 6.
5. Open Furnace Door This is a function separate from the turning the reactor off, because of the fact that each reactor shares the furnace with another reactor. If the door were to be opened prematurely noxious and hot gas would be released into the room. This function ensures that the furnace door is safe to open. It only requires two time consuming steps:
- Run reactor off function for reactor selected.
 - Check and make sure companion reactor is off.

The computer interface for the Data Acquisition and Control system was reviewed and substantially modified. Several components of the system have been checked with those components of the CCS that are functional. We anticipate significant effort to be required to tune the controllers and acquisition system to deal with pressure transients, dead space, etc. in the system, but none of these issues should add delay to construction of the laboratory.

Figure 4.1.17 Reaction chamber process control summary.

Catalyst Preparation BYU is preparing catalyst for use in the slip-stream reactor built by the University of Utah. This sample is one of six total samples to be included in the reactor and provides baseline data from which all details of catalyst and its performance can be published. Proprietary bars prevent some details of commercially supplied catalysts from being included.

The BYU SCR group is therefore preparing a catalyst for which all findings can be reported. This catalyst will be installed and tested in the field reactor as well as in the BYU laboratory. The catalyst will be prepared to simulate the performance of a typical industrial catalyst. It will be a Ti-W-V type catalyst. The catalyst will consist of: 90 wt% TiO_2 , 9 wt% WO_3 , and 1wt% V_2O_5 . The raw materials used to produce these species are: P-25 anatase TiO_2 powder from Degussa, ammonium metatungstate, and ammonium metavanadate.

Two types of catalyst will be prepared, a catalyst powder and a catalyst coated monolith. The powder catalyst will simply be the anatase form TiO_2 impregnated by a solution containing the ammonium metatungstate and ammonium metavanadate. The impregnated powder will then be dried and calcined in air. This will result in the metal oxide catalyst.

Dow Corning has provided ceramic monoliths that will be used to prepare the wash-coated catalyst. These coated monoliths will be installed in the SCR field reactor. The Titanium dioxide powder from Degussa needs to be modified in order to create a stable washcoat. Without modification the powder severely cracks and does not adhere to the monolith. A densification procedure outlined in the literature will be used to decrease cracking. The densification procedure simply includes mixing the powder with water to form a paste, then drying and calcining the paste. The densified titanium dioxide will then be crushed and ball milled to a fine powder.

Adhesion to the monolith will be improved by adding 2 wt% colloidal silica, Ludox®, to the dense titanium dioxide powder. The following is an outline of the monolith catalyst preparation procedure:

1. Cut the monolith into pieces suitable to fit into the field reactor (approx 2.25" squares).
2. Immerse the monolith pieces into an acid bath to roughen the surface.
3. Grind some of the TiO_2 to a particle size suitable to form a composite.
4. Prepare a slurry of the dense TiO_2 and Ludox®. A 50 wt% slurry of solids has an appropriate thickness and viscosity.
5. Dip and dry the monolith repeatedly in the slurry to reach the desired weight percent of TiO_2 .
6. Measure the liquid uptake of one monolith piece.
7. Prepare a solution of the tungsten and vanadium so that one dip will yield the desired catalyst composition.
8. Dip and dry the monolith in the tungsten and vanadium solution.
9. Calcine the monolith in air at 550 °C to leave only the desired metal oxides in the wash coat.

The catalyst preparation is underway. The monoliths have been cut and prepared. We have encountered some problems with stability of the washcoat layers of anatase, with poor adhesion to the monolith surface during temperature cycles. We can resolve the issue using additional materials to promote adhesion, but many of these include Ca or other compounds known to deactivate vanadium-based SCR catalysts. We have contacted commercial vendors for advice on improving adhesion properties and have developed a method we hope will resolve this issue. Once it is resolved, the catalysts preparation will be complete and the catalysts will be shipped to REI/University of Utah for installation in the slipstream reactor.

Task 4.2 Evaluation of Commercial Catalysts for Power Plant Conditions

The objective of this task is to evaluate SCR costs at a deeper level and to improve estimates of actual costs. One of the prime motivations for this program is to look at the influence of the alkali and alkaline earth elements in biomass and how those affect SCR catalyst when biomass is co-fired with coal.

Design of the multi-catalyst reactor was described in the previous quarterly report. During this quarter, the reactor was assembled by the University of Utah at their L1500 combustion facility. The L1500 is a 3m x 3m x 13m pilot scale furnace. Pilot plant and ancillary equipment include:

- 5 MMBtu/hr dual-swirl coal-fired burner.
- Air preheat system to heat secondary and tertiary combustion air to 800°F.
- Solid feeding system for pulverized coal including: feeders, hoppers, and eductors.
- Opto 22 distributed control system.
- Continuous emissions monitoring equipment for real time measurement of O₂, CO₂, CO, NO_x, and THC emissions.
- 6500 CFM wet venturi scrubber for abatement of SO₂ and particulate emissions
- 400 ton cooling tower and shell and tube heat exchanger for indirect cooling of flue gases.

The reactor has been installed at the end of the shell and tube heat exchanger using a 4-inch flexible steel pipe. Figure 4.2.1 shows the reactor, which is installed vertically. Gases flow downward through the catalyst chambers as installed. The catalyst chambers consist of square aluminum tubing; surrounding the catalyst chambers are heated and insulated steel panels (not shown in the figure). Below the catalyst chambers are the venture flow meters and eductors that meter and control the flow through individual chambers. There are also sampling ports located at the exit of each chamber. After the eductors, the gases are combined into a 6-inch exhaust pipe. The reactor exhaust is fed back into the main flue gas stream.

Figures 4.2.2 and 4.2.3 show the hardware for the control system, which resides in two electrical boxes. The main control functions reside on an embedded controller (seen in Figure 4.2.2) that communicates with a PC via an Ethernet connection. The host PC can be accessed over the internet to download data or change control set points. Another box (Figure 4.2.3) contains pressure transducers and relays.

The goals of the shakedown testing are as follows:

1. Check for leaks (cold)
2. Check for leaks (hot and after thermal cycling)
3. Verify ability of control system to monitor all inputs

4. Verify operation of flow control loops
5. Develop start-up and shut down procedures
6. Verify all emergency shutdown procedures
7. Test data-logging system
8. Test mass flow controller operation
9. Test sootblowing system and pressure drop control loop

During most of this testing, natural gas will be fired in the furnace. For a limited series of tests, coal and coal-sawdust blends will be fired in the furnace. Data will be collected on the fine particulate produced during coal-biomass co-firing. Little pilot-scale work has been done in the US on the fine particulate produced from biomass-coal co-firing. Much work has been done in Europe, but the biomass fuels used may not be typical of what would be used in the US. Therefore, the data would be valuable for understanding mechanisms of fine particle formation relevant to US practice for co-firing.

Figure 4.2.1 Multi-catalyst slipstream reactor with outer doors removed to show catalyst chambers.

Figure 4.2.2 Control box for the slipstream reactor, which contains the Fieldpoint bus with embedded controller (the black strip at the top) plus power conditioning and relays. The embedded controller runs the reactor and communicates with a PC via an Ethernet link.

Figure 4.2.3 Electronics box for the slipstream reactor.

This quarter discussions continued with Allegheny Energy regarding testing at Albright Station. This plant burns a mixture of Pittsburgh bituminous coal and sawdust. Albright has a planned outage for September 2002, and thus may not be the best candidate for the first field test. Due to the plant's schedule, we will try to find another utility for the first field test and follow that with testing at Albright. A number of utilities were contacted about hosting the second test, which is to be at a boiler firing a PRB coal. American Electric Power (AEP) expressed interest in having the testing take place at one of their units that fires a blend of PRB and bituminous coal. During the next quarter, more specific discussions will take place with AEP.

Task 4.3 Evaluation of Catalyst Regeneration

The focus of this sub-task is to evaluate the effectiveness of commercially viable catalyst regeneration techniques. Regeneration of catalysts used in Subtask 2 will be investigated at BYU using water and solvent washing techniques. At a minimum, two regeneration techniques will be used: water and sulfuric acid washing. Additional regeneration techniques may be attempted, depending on the success of these two. Catalyst activity before and after each rinsing will be reported.

Within the last performance period, mechanisms of catalyst reactivation have been explored based on both literature results and experience of other, mostly European, institutions. Several promising reactivation mechanisms have been established. However, serious investigation of these will await the results of the deactivation mechanisms within this project.

Task 6 – Field Validation of Integrated Systems

Field Tests

During this performance period, a second set of field tests of RRI in Ameren's Sioux Unit 1 were performed. As previously reported, the first phase of testing of RRI in Ameren's Sioux Unit 1 was completed in August, 2001. The results were quite unexpected, with measured NO_x reductions due to RRI underachieving the expected reductions. As discussed above in the Task 2 summary, additional analyses were completed during this quarter to better understand the discrepancy between the test results and the previously completed CFD model results. These analyses indicated that it was likely that during the first phase of testing, the boiler was not sufficiently staged. During that time, the OFA system had only recently been installed, and sufficient testing of the OFA system had not been completed to optimize its operation prior to the RRI field testing. Baseline NO_x emissions (OFA only) during the phase 1 testing were approximately 0.55 lb/MMBtu, whereas the CFD modeling indicated that if the furnace were staged to SR=0.95, the NO_x emissions would be approximately 0.42 lb/MMBtu.

The second phase of RRI testing in Sioux Unit 1 was conducted during March, 2002. These test results confirmed our suspicions regarding the lower furnace stoichiometry. Baseline NO_x emissions (without RRI) were approximately 0.4 lbs/MMBtu throughout the second phase of testing. Boiler air flow measurements and the lower baseline NO_x emissions both showed the lower furnace to be more deeply staged during this phase of testing. As a result, RRI alone was able to consistently reduce NO_x emissions by an additional 30%, lowering NO_x emissions to 0.25 lb/MMBtu. As per the first phase of testing, no ammonia slip was observed. These results are in excellent agreement with previously completed CFD model predictions of RRI performance for this furnace. In addition, both the test results and the model predictions have shown that sufficient air staging is required for RRI to be effective. Short term testing at 80% of full load showed that the same NO_x reduction was achievable under that condition.

Results and Discussion

RRI: Field tests at the Ameren Sioux Unit 1 have demonstrated that RRI can provide up to 30% NO_x reduction with no ammonia slip. The RRI performance demonstrated in the field tests are in good agreement with the original CFD modeling results. Additional modeling studies and a review of the initial RRI field tests performed in Fall, 2001 indicate that the boiler was not operated at the desired stoichiometry of 0.95 during the first set of field tests. Furthermore, the additional modeling effort indicated very little NO_x reduction is achieved if the boiler is not operated well below stoichiometric conditions. The measured performance in Sioux Unit 1 was similar to that previously achieved in Conectiv's B.L. England unit 1, a three barrel, 138 MW cyclone fired furnace. In both cases, the field tests confirmed the CFD model predictions and demonstrated the importance of accurate CFD modeling to a successful RRI design. The results of these demonstrations suggest that similar performance could be expected in a wide range of OFA-equipped cyclone boiler types over a wide range of sizes and firing configurations. Results of the RRI field tests have been reported to industry by Ameren personnel through a presentation at the recent American Power Conference [Boll, 2002]. A paper describing the CFD modeling to develop the RRI design at Sioux Unit 1, including comparisons of the model predictions with the field test results, will be presented at the upcoming DOE sponsored SCR/SNCR conference [Cremer, 2002].

Corrosion Probe: The analysis of results of a study on the application of the electrochemical noise (ECN) corrosion probe for real-time monitoring of corrosion in the radiant section of a utility boiler has been completed. It has been demonstrated that corrosion in a full-scale plant could be accurately measured in real-time and waterwall wastage could be determined immediately following changes in boiler operation. Some concerns on the effect of ash deposits on probe response were raised. The field test results showed that with the passage of time, ash deposits tended to accumulate on the probe face. This is not inappropriate, as ash is also present on the boiler tubes and for corrosion behavior to be representative of the furnace tubes, the sensor should be allowed to achieve a similar condition to that of the wall tubes. The build-up of an ash layer on the probe face will modify the probe's response to a corrosive environment. On the one hand, high temperature ash may improve the electrical conductivity of deposits on the probe face. This is a desirable effect because enhanced deposit conductivity increases cell efficiency causing an increased sensitivity of the sensor, thereby making it more representative of conditions experienced by the boiler tubes. However, the ash build-up also may hinder the diffusion of reactive gaseous species to the metal substrate, thereby preventing access to the fresh metal surface underneath. A thick layer of ash or clinker may either act as a protective blanket, which effectively modifies the sensor temperature response, or may provide an aggressive molten salt condition under which the tube material is attacked. It is important, therefore, for the surface condition on the sensor to mirror as closely as possible the condition on the surfaces of tubes on which the corrosion behavior is being investigated. Recent work (Kung and Bakker, 2000; Bakker et. al., 2001) has shown that FeS-rich deposits may cause high rates of corrosion. This effect is enhanced when unburned carbon is also present in the deposit. FeS deposits form when pyrite in coal is not oxidized completely. It is postulated, as a result of the present study, that, under oxidizing, mildly reducing and alternating oxidizing and reducing conditions, FeS in the deposits can decompose releasing corrosive sulfur species, including elemental sulfur, SO₂ and H₂S, in close proximity to the boiler tubes. Although ash deposits may

affect probe response in a variety of ways, changes in the flue gas from reducing to oxidizing conditions are known to cause an immediate response in measured corrosion rate because such changes rapidly affect the gaseous environment in the deposit. Moreover, as long as the probe is experiencing the same deposit formation behavior as the adjacent waterwall tubes, then the measured corrosion rates are representative of the accurate corrosion behavior in the boiler. It should be noted that real-time electrochemical measurements offer the capability to improve operational control, extend tube service life, reduce maintenance and non-availability and avoid the risk of high temperature corrosion damage. If used in conjunction with CFD-based combustion optimization modeling, the approach should also allow combustion conditions to be managed in real time, thereby minimizing the cost and impact of NO_x reduction techniques such as staged combustion and catalytic de-NO_x requirements.

Soot: The soot volume fraction was measured axially along the centerline and radially at selected axial locations in a 5 MMBtu/hr pilot-scale coal fired test furnace (with staging air ports) for burner stoichiometries ranging from 0.75 to 1.05. The soot volume fractions were measured using a sampling probe and photoacoustic (PA) instrument. The measurements show good agreement with the expected trends based on theoretical considerations. In particular, the competing nature soot formation and destruction process is clearly seen in the measured values. Near the burner, there is significant soot formation from the coal off-gas. After reaching a peak, the soot volume decreases due to oxidation (destruction) of the soot. Soot continues to exist even after additional air introduction from the staging port. The test results also show that the amount of soot generated by the burner decreases as the burner stoichiometry is increased.

SCR Catalyst: Six SCR catalysts will be tested under Task 4, four monolith and two plate. Four commercial manufacturers agreed to provide samples to the program. Five of the catalysts to be tested will come from catalyst manufacturers. The sixth catalyst will be a generic vanadia-titania catalyst formulated at BYU. One of the commercial catalysts arrived this quarter and the others should arrive in the next quarter

During this quarter, several *in situ* analyses of vanadium-based SCR catalyst systems were completed. These are preliminary data primarily intended as shakedown for the system. Results to date indicate that the system produces results that represent improvements compared to literature examples of similar experiments (but for different catalyst systems). Investigations of surface chemistry specific to vanadium-based SCR catalysts shows mixed results. We have as yet been unable to reproduce surface sulfation described by some authors in the literature. However, we have reproduced substantial ammonia and NO adsorption data that are consistent with literature sources.

Construction of the CCS reactor system is nearly complete, with a few remaining details discussed in this report.

A literature review originally commissioned from other parties is being updated and will be made available under separate cover as part of this investigation. Permissions to publish some aspects of this survey, specifically those involving field tests, have yet to be granted. However, we are hopeful they will soon be granted.

The University of Utah completed construction of the multi-catalyst slipstream reactor during this quarter and shakedown testing was begun at the University of Utah pilot-scale coal furnace. Talks continued with two utilities that have expressed interest in hosting a demonstration. The first test was tentatively scheduled to begin over the summer at Albright Station. However, a planned outage at the plant for September will make that difficult. Another utility (AEP) is interested in hosting a test at a plant burning PRB coal. At this time, it seems likely that the PRB test will take place first.

Conclusions

Good progress has been made on several fronts during the last three months. In particular:

- Field tests completed in the last quarter at the Ameren Sioux Unit 1 have demonstrated that RRI can provide up to 30% NO_x reduction with no ammonia slip. The RRI performance demonstrated in this field test is in good agreement with the original CFD modeling results. Additional modeling studies and a review of the initial RRI field tests performed in Fall, 2001 indicate that the boiler was not operated at the desired stoichiometry of 0.95. In addition, the modeling studies indicate very little NO_x reduction is achieved if the boiler is not operated well below stoichiometric conditions.
- The waterwall corrosion study was completed in this quarter. Conclusions include:
 1. The corrosion tests at Eastlake Power Station provided the first demonstration of real-time high-temperature corrosion assessment in the radiant section of a large coal-fired power generation boiler. The successful completion of the tests demonstrated that corrosion could be measured accurately in real-time in normal boiler operations, and an assessment of waterwall wastage could be made without impacting boiler availability.
 2. Examination of the plant data revealed that corrosion rate was strongly linked with the boiler load. The higher the boiler load, the higher the rate of corrosion. A strong correlation between corrosion rate and heat flux at the radiant section membrane tube wall was also demonstrated.
 3. The performance of the probe settled some previously unresolved technical issues, notably its capability to operate in a particulate-laden combustion environment. Additionally, it was observed that the sensor was not adversely affected by high-pressure water washing of the surrounding boiler tubes, though in general this is not considered a desirable operational circumstance.
 4. Laboratory data, obtained under carefully-controlled test conditions, showed that stoichiometry (CO concentration), flue gas concentration (H₂S and HCl) and probe operating temperature all could affect the measured corrosion rate on plain carbon steel of similar composition to radiant section membrane tube material. As the stoichiometric ratio was reduced, the concentrations of acid gases increased, the probe sensor temperature increased, and the measured corrosion rate also increased.
 5. The corrosion results from the Eastlake tests show good agreement between the cumulative corrosion rate obtained from the electrochemical instrumentation and high-precision metrology. This combination of methods provided firm evidence that the on-line instrumentation offers a reliable method of high temperature corrosion assessment and on-line combustion management.
- Measurements of soot volume fraction have been performed for a coal fired burner in a pilot scale test furnace. The burner was operated at both fuel rich and fuel lean conditions. The measured values are in good agreement with the expected trends for soot generation and destruction.
- Sample catalysts have been ordered from four commercial manufacturers of SCR catalysts. One of the commercial catalysts arrived this quarter and the others should arrive in the next quarter

- Several *in situ* analyses of vanadium-based SCR catalyst systems were completed at BYU. Results to date indicate that the system produces results that represent improvements compared to literature examples of similar experiments. Construction of the CCS reactor system is nearly complete, with a few remaining details discussed in this report. A literature review originally commissioned from other parties is being updated and will be made available under separate cover as part of this investigation.
- The University of Utah completed construction of the multi-catalyst slipstream reactor during this quarter and shakedown testing was begun at the University of Utah pilot-scale coal furnace. Talks continued with two utilities that have expressed interest in hosting a demonstration.

Plans for the next quarter include: additional CFD modeling studies to study injection strategies for using RRI in tangentially fired furnaces; comparisons of the measured soot volume fractions with values predicted by a CFD based model for soot generation/destruction; completion of the shakedown testing for the SCR catalyst test reactor.

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APPENDIX

UNIT	Ch	Device
Analog Input		
FP-AI-110, 8 channel isolated input		
#1	1	MFC - 1
	2	MFC - 2
	3	MFC - 3
	4	MFC - 4
	5	MFC - 5
	6	MFC - 6
	7	MFC - 7
	8	MFC - 8

UNIT	Ch	Device
Analog Output		
FP-AO-210, 8 Channel analog output		
#1	1	MFC - 1
	2	MFC - 2
	3	MFC - 3
	4	MFC - 4
	5	MFC - 5
	6	MFC - 6
	7	MFC - 7
	8	MFC - 8

UNIT	Ch	Device
Relay		
FP-RLY-420, 8 SPST relays (250V @ 3A)		
#1	1	2-way Solenoid 1
	2	2-way Solenoid 2
	3	2-way Solenoid 3
	4	2-way Solenoid 4
	5	2-way Solenoid 5
	6	2-way Solenoid 6
	7	2-way Solenoid 7
	8	2-way Solenoid 8

UNIT	Ch	Device
Thermocouple Input		
FP-TC-120, 8 Channel TC input X3		
#1	1-8	All for 24 Thermocouples
#2	1-8	
#3	1-8	

**these use TB-3 base

#2	1	MFC - 9
	2	MFC - 10
	3	MFC - 11
	4	MFC - 12
	5	MFC - 13
	6	MFC - 14
	7	NH3/SO2 Analyser
	8	NH3/SO2 Analyser

#2	1	MFC - 9
	2	MFC - 10
	3	MFC - 11
	4	MFC - 12
	5	MFC - 13
	6	MFC - 14
	7	
	8	

#2	1	3-way Solenoid 1
	2	3-way Solenoid 2
	3	3-way Solenoid 3
	4	3-way Solenoid 4
	5	3-way Solenoid 5
	6	3-way Solenoid 6
	7	3-way Solenoid 7
	8	3-way Solenoid 8

Digital Input (For Valve read)		
FP-DI-330, 8 Channel Digital Input X1		
#1	1	1 - black wire
	2	2 - brown wire
	3	4 - red wire
	4	8 - orange wire
	5	10 - yellow wire
	6	
	7	
	8	

#3	1	Press Trans 1
	2	Press Trans 2
	3	Press Trans 3
	4	Press Trans 4
	5	Press Trans 5
	6	NOx Analyzer
	7	NOx Analyzer
	8	NOx Analyzer

For Multi-selector valve actuator (VALCO)		
#3	1	1 - brown wire
	2	2 - red wire
	3	4 - orange wire
	4	8 - yellow wire
	5	input enable - green wire
	6	10 - blue wire
	7	home - violet wire
	8	step - gray wire

Dual Channel I/O Module		
FP-DO-DC60, Dual Channel Base		
card # 1	1	GC Switch 1
	2	GC Switch 1
card # 2	1	GC Switch 2
	2	GC Switch 2

#4	1	Gas Chromatograph
	2	MFC - 15
	3	
	4	
	5	
	6	
	7	
	8

* Diameter of line to vent must be equal to or greater than that of process line in order to ensure safe pressure relief.

† Pressure relief valve must be able to accommodate the same volumetric flow rate as a failed regulatory process line.

Minimum: 3/8" Adjustable Pressure Relief Valve

NPT Fitting

Swagelock Fitting