

NOx Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

Reporting Period Start Date April 1 , 2002

Reporting Period End Date: June 30, 2002

Mike Bockelie, REI

Marc Cremer, REI

Kevin Davis, REI

Connie Senior, REI

Bob Hurt, Brown University

Eric Eddings, University of Utah

Larry Baxter, Brigham Young University

July 28, 2002

DOE Cooperative Agreement No: DE-FC26-00NT40753

Reaction Engineering International

77 West 200 South, Suite 210

Salt Lake City, UT 84101

Disclaimer

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

Abstract

This is the eighth 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. CFD modeling studies of RRI in a full scale utility boiler have been performed that provide further insight into the NO_x reduction process that occurs if the furnace is not adequately staged. *In situ* reactivity data indicate thus far that titania sulfates under SCR conditions but there is no indication of vanadia sulfation in agreement with some, but not most literature results. Additional analysis and advanced diagnostics are under way to confirm this result and determine its accuracy. Construction of a catalyst characterization reactor system is nearly complete, with a few remaining details discussed in this report. Shakedown testing of the SCR field reactor was completed at the University of Utah pilot-scale coal furnace. The CEM system has been ordered. Talks continued with American Electric Power about hosting a demonstration at their Rockport plant.

Table of Contents

DISCLAIMER.....	i
ABSTRACT	ii
TABLE OF CONTENTS	iii
EXECUTIVE SUMMARY	1
EXPERIMENTAL METHODS	2
Task 1 Program Management	2
Task 2 NO _x Control	3
Task 3 Minimization of Impacts	na
Task 4 SCR Catalyst Testing.....	7
Task 5 Fly Ash	na
Task 6 Field Validation of Integrated Systems	23
RESULTS AND DISCUSSION.....	24
CONCLUSIONS	25
LITERATURE REFERENCES	26

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:

- CFD modeling studies have been performed to better understand the difference in RRI performance for operating the lower furnace at near stoichiometric conditions as opposed to well below stoichiometric conditions.
- Construction of catalyst characterization reactor system at BYU 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.
- 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.
- Shakedown testing of the field reactor was completed at the University of Utah pilot-scale coal furnace. The CEM system has been ordered. After completion of minor modifications to the reactor, it will be ready to go to the first test site. Talks continued with American Electric Power (AEP). AEP is interested in hosting a demonstration at their Rockport plant.

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

REI has completed Non-Disclosure Agreements (NDAs) with the University of Utah and Brigham Young University for the work to be performed with the SCR catalyst deactivation research to be performed in Task 4.

Industry Involvement

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

- A podium presentation entitled “Evaluation and Design of Rich Reagent Injection in Ameren’s Sioux Unit 1” was provided at the DOE-NETL sponsored 2002 Conference on Selective Catalytic Reduction and Selective Non-Catalytic Reduction for NO_x control, held March 15-16, 2002 in Pittsburgh, PA that highlighted field tests of RRI in the Ameren Sioux Unit #1 boiler that demonstrated RRI can provide up to 30% NO_x reduction with no ammonia slip [Cremer et al, 2002].
- A poster entitled “SCR Deactivation Mechanisms Related To Alkali and Alkaline Earth Elements” was presented at the DOE-NETL sponsored 2002 Conference on Selective Catalytic Reduction and Selective Non-Catalytic Reduction for NO_x control, held March 15-16, 2002 in Pittsburgh, PA that highlighted progress on developing a slipstream reactor and planned field tests [Senior et al, 2002].

Task 2 - NO_x Control – LNFS/SNCR/Reburning

Task 2.2 Evaluation of Integrated System Design for Cyclone Furnace Applications

The first of the two phases of field testing of the RRI process in Ameren's Sioux Unit 1 was completed in August, 2001. This round of testing yielded results that were less than expected, based on the CFD modeling. During the time of the testing, 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. Overall, the results on NO_x reduction were in contrast to the CFD model results that suggested at least 25-30% NO_x reductions were achievable with RRI.

To understand the cause for the apparent discrepancy between the model predictions and the phase I results, additional analyses were performed. Model predictions of OFA in Sioux Unit 1 had indicated that if the lower furnace stoichiometric ratio (SR) was 0.95, then NO_x emissions would be significantly lower than the 0.55 lb/MMBtu levels that were emitted during the phase I testing. This suggested that the unit was not staged as deeply as intended. The CFD modeling to evaluate and design RRI in this unit had been conducted for a lower furnace SR of 0.95.

To understand the dependence of lower furnace SR on RRI performance in this unit, CFD simulations were conducted for a lower furnace SR of 0.99. Table 2.2.1 shows a summary of the results of the predictions. There are two points to be made. First of all, the model predictions showing results with and without RRI are consistent with the observations during the first phase of RRI testing in Sioux Unit 1. With no reagent injection, the field tests showed typical NO_x emissions of 0.55 lb/MMBtu, significantly higher than the expected emissions of 0.40 lb/MMBtu from the model predictions. The model predictions at a lower furnace SR of 0.99 were 0.66 lb/MMBtu, higher than the field results, but indicative of the sharp impact of SR on NO_x emissions at these SRs. Second, the model predictions of RRI performance under these lower furnace conditions indicated little to no NO_x reduction (1% was predicted). Chemical kinetic calculations indicate that at a fully mixed SR of 0.99, significant NO_x reductions would be expected. In reality, an average SR of 0.99 results in a distribution of SRs in which locally, SRs exceed 0.99. In these regions, NO_x formation occurs, which compensates for the local NO_x reduction in the fuel rich regions. This behavior can be seen in Figure 2.2.1 showing the results of the CFD model predictions for a lower furnace SR of 0.99. During the phase I testing, the measured NO_x reductions were very non-reproducible with values varying between 0-20%. In summary, the phase I testing and CFD modeling indicate that during this round of testing, the lower furnace was not adequately staged for effective RRI performance.

In the time period between the first and second phases of testing from August 2001 to March 2002, the operation of the OFA system in unit 1 had been adjusted. During that time period, the NO_x emissions under full load operation dropped from 0.55 lb/MMBtu to approximately 0.40 lb/MMBtu. The current best estimates of air flows as determined by plant personnel suggest that during the first round of testing, the lower furnace SR was approximately 0.99, while during the second phase, the adjusted air flows reduced it to 0.95. Figure 2.2.2 shows the predicted NO_x

distribution with and without reagent injection for a lower furnace SR of 0.95. As shown in Table 2.2.1, the predicted NO_x reduction under these conditions was 31% beyond the predicted NO_x levels of 0.40 lb/MMBtu with OFA. Figure 2.2.3 shows a typical NO_x profile from the continuous emissions monitor (CEM) for the boiler during the second phase of RRI testing, which shows the NO_x emissions to drop to approximately 0.27 lb/MMBtu with RRI under full load conditions.

In summary, the RRI testing conducted at Ameren's Sioux Unit 1 demonstrated that RRI in this unit is capable of achieving approximately 30% NO_x reduction beyond the existing NO_x emissions obtained with OFA. The combination of the CFD modeling and the first phase of field testing showed the impact of lower furnace SR on RRI performance. It is not expected that significant NO_x reductions will be obtained with RRI unless the unit is staged to lower furnace SRs of approximately 0.95 or below. The model results have been consistent with the field results and show how the model is an extremely effective tool in understanding furnace operating conditions on RRI performance.

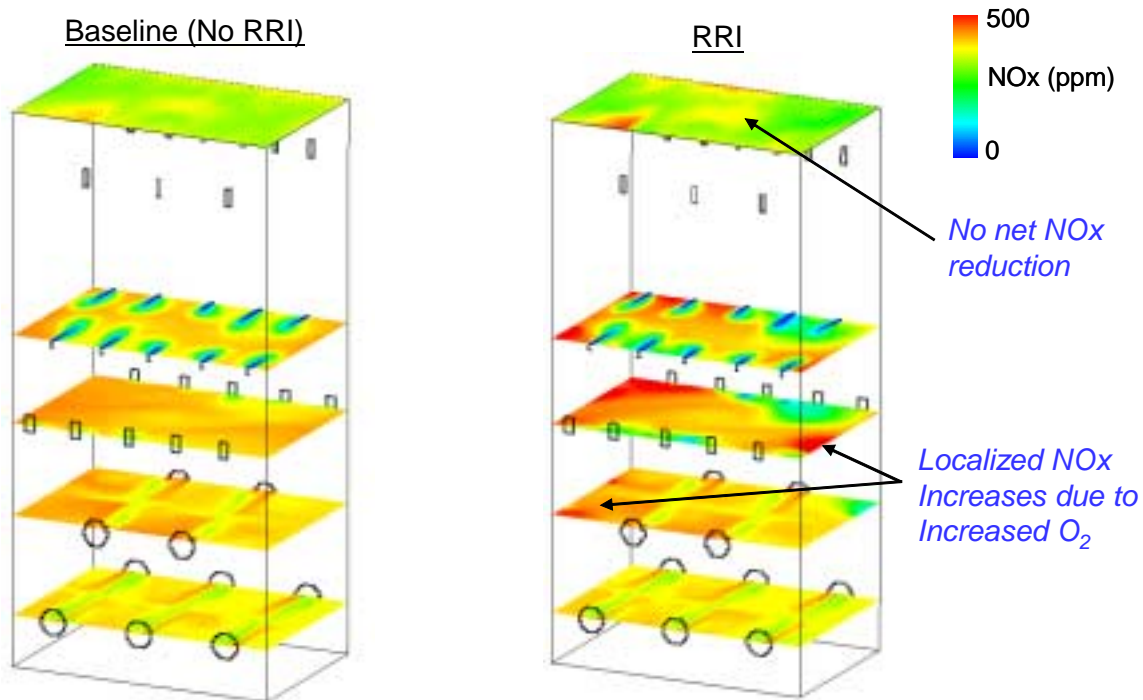


Figure 2.2.1: Predicted NO_x Distribution in the lower furnace of Ameren's Sioux Unit 1 with and without the application of RRI when the lower furnace is staged to stoichiometric ratio of 0.99.

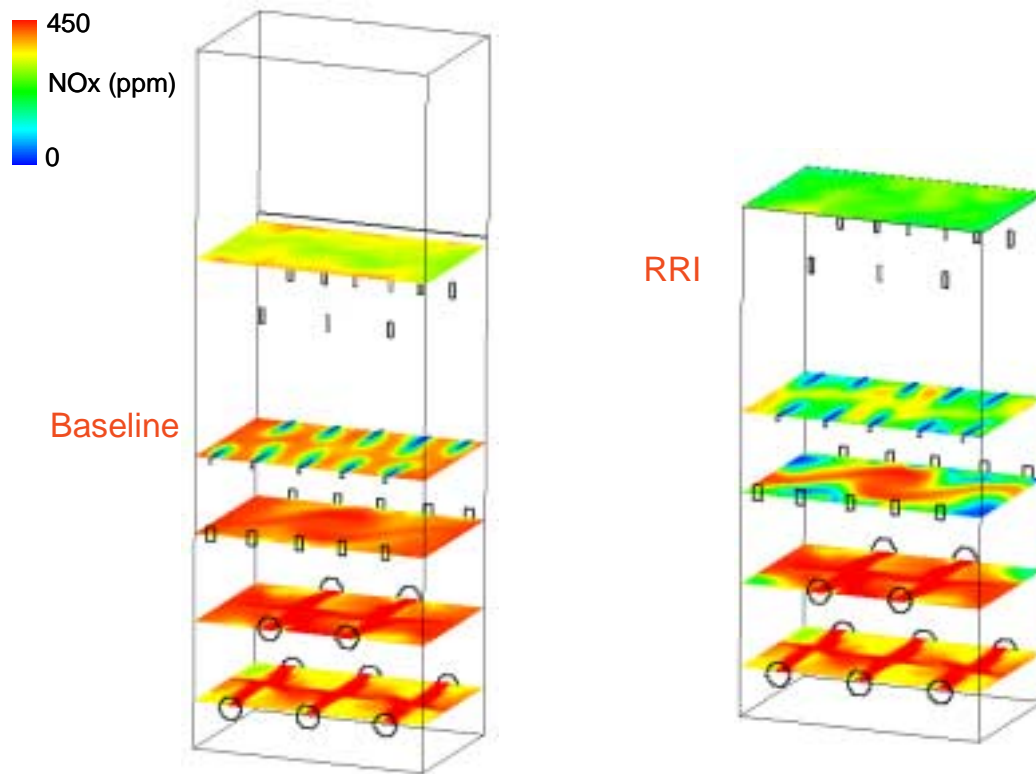


Figure 2.2.2: Predicted NOx Distribution in the lower furnace of Ameren's Sioux Unit 1 with and without the application of RRI when the lower furnace is staged to a stoichiometric ratio of 0.95.

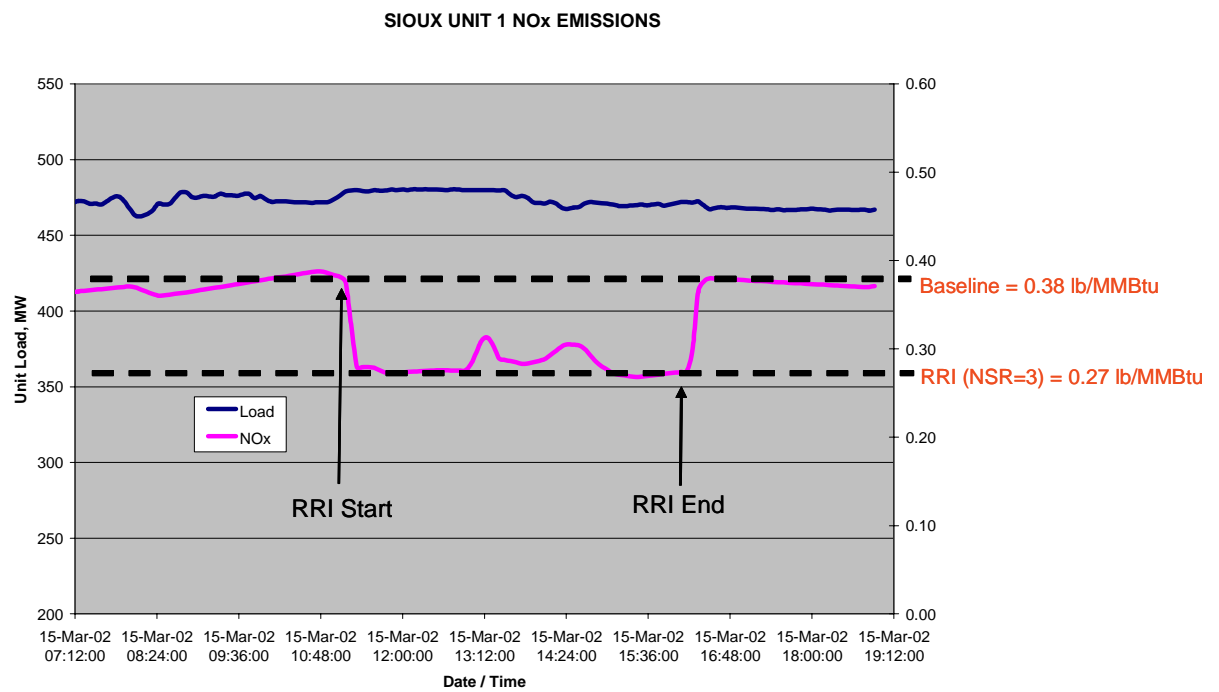


Figure 2.2.3: Typical results from second phase of RRI testing in Ameren's Sioux Unit 1.

Table 2.2.1: CFD Model Predictions showing impact of lower furnace stoichiometric ratio on RRI performance in Ameren's Sioux Unit 1.

Case	Lower Furnace SR	NOx (lb/MMBtu)	NOx Reduction (%)
OFA95	0.95	0.4	-
OFA95+RRI	0.95	0.27	31%
OFA99	0.99	0.66	-
OFA99+RRI	0.99	0.65	1%

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 Topsoe, 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 (Figure 4.1.1) 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. This system was described in detail in previous reports. Here we summarize incremental progress since the last report.

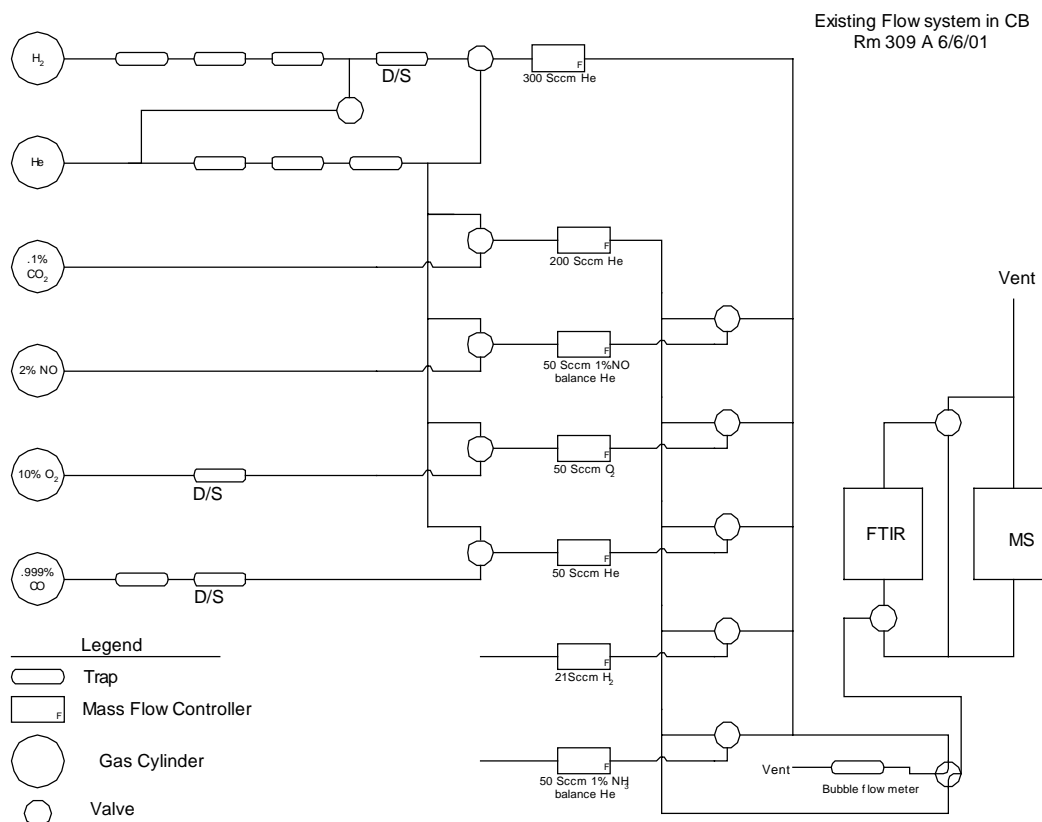


Figure 4.1.1. Overall schematic of the ISSR.

FTIR Investigations

Last quarter we reported preliminary results regarding sulfation of 5% V₂O₅/TiO₂ (by weight) catalyst in three different environments. These environments include:

A: 75 sccm SO₂ (0.5%) + He;

B: 52.5 sccm SO₂ (0.29%) + O₂ (4.8%) + He;

C: 115 sccm SO₂ (0.26%) + O₂ (4.3%) + H₂O (2.8%) + He.

Before each run, all the catalysts were preoxidized.

Our results indicate that sulfation of vanadia catalyst only happens in the presence of water. During this quarter we investigated which sites (Ti, V, or both) sulfate. Our previous results were not definitive regarding the sites where sulfation occurs. Therefore, sulfating tests were carried on pure TiO₂, and 2% w/w V₂O₅/TiO₂. This time experiments were conducted under conditions summarized as B above because literature analyses suggest that sulfations of TiO₂ happens in SO₂ and O₂, even without water. In addition to the spectroscopic analyses, XPS analyses on 5% w/w V₂O₅/TiO₂, 2% w/w V₂O₅/TiO₂, and pure TiO₂ were also conducted. Finally, BET surface area analyses were conducted to give some more information about vanadia catalyst.

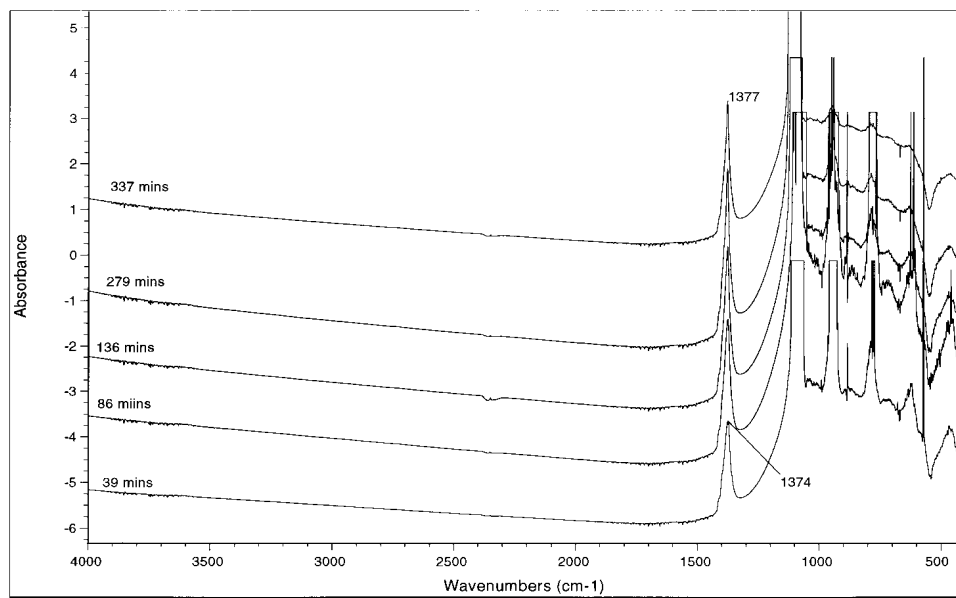


Figure 4.1.2. Results of *in situ* FTIR spectroscopy analyses on pure titania samples under SCR conditions for sulfur-laden, oxidizing flows.

Figure 4.1.2 summarizes results on pure titania. It is very clear that peaks around $1375\text{--}1381\text{ cm}^{-1}$ appear in both spectra, which are reported as the characteristic peaks of sulfate species on vanadia and titania. Moreover, this set of peaks is stronger in pure titania than that in 2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$, and it appears as tiny peak or finally disappears on 5% w/w vanadia catalyst. As the CaF_2 windows were used, which block peaks lower than 1000 cm^{-1} , other peaks can't be clearly detected. These results indicate that vanadia does not sulfate under these conditions. The sulfate formation appears to be limited to the titania surface.

The peaks around 1270 cm^{-1} on 2% w/w vanadia catalyst (Figure 4.1.3) are apparently related to the vanadia species on the catalyst surface, which also appeared on 5% w/w vanadia catalyst. This set of peaks may relate to the SO_3 adsorption peaks on vanadia species, as reported in the literature.

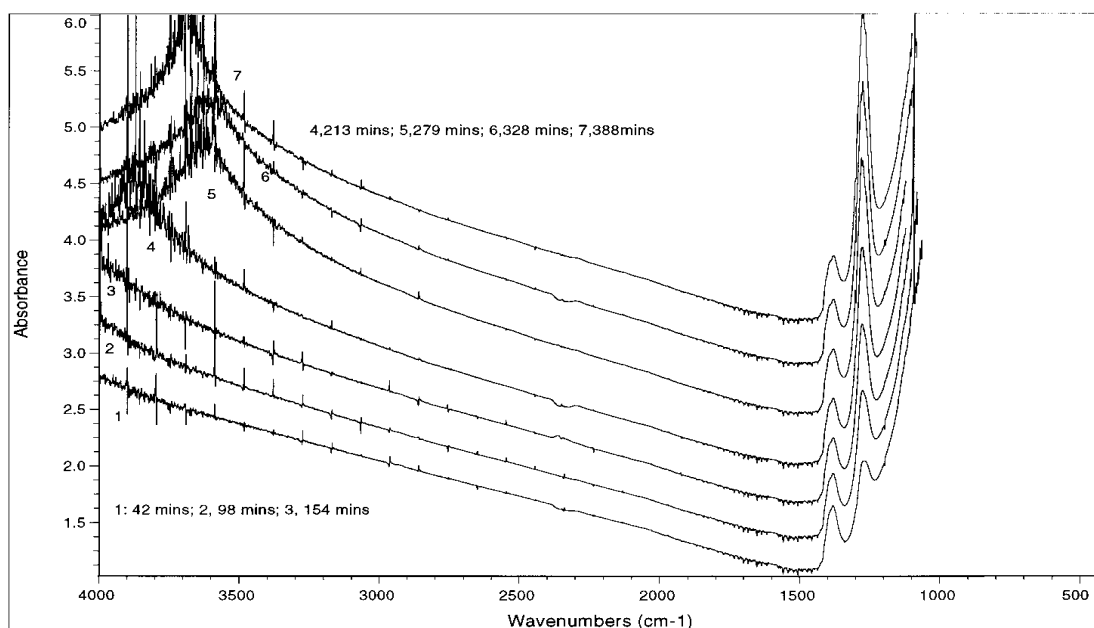


Figure 4.1.3. Results of *in situ* FTIR spectroscopy analyses on 2% vanadia on titania samples under SCR conditions for sulfur-laden, oxidizing flows.

XPS study

XPS analyses of the samples investigated by *in situ* FTIR spectroscopy were also conducted. Figures 4.1.4 through 4.1.6 summarize the results.

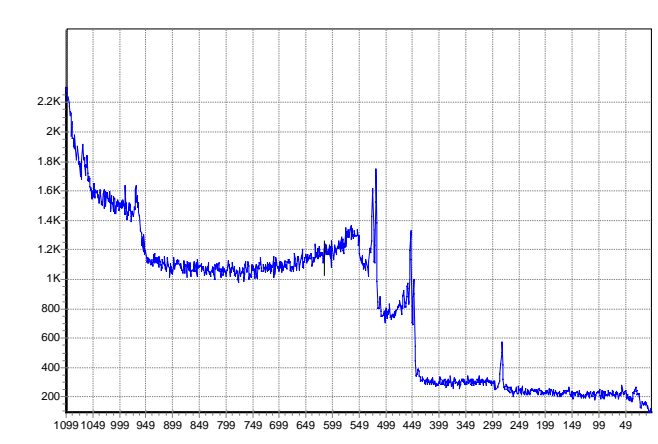


Figure 4.1.4. XPS analysis of pure TiO_2 sample exposed to sulfur-laden gases under SCR conditions.

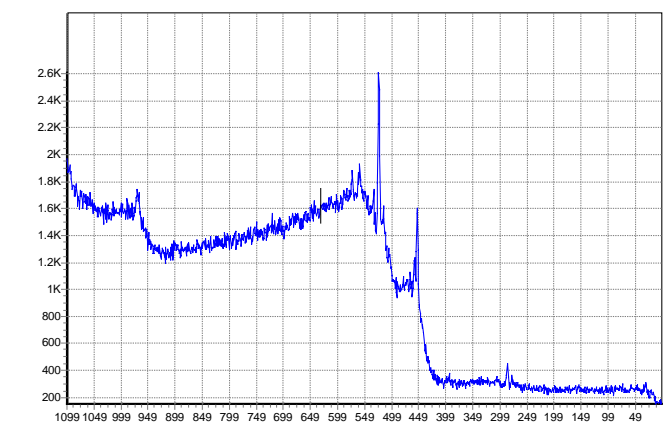


Figure 4.1.5. XPS analysis of 2% w/w vanadia sample exposed to sulfur-laden gases under SCR conditions.

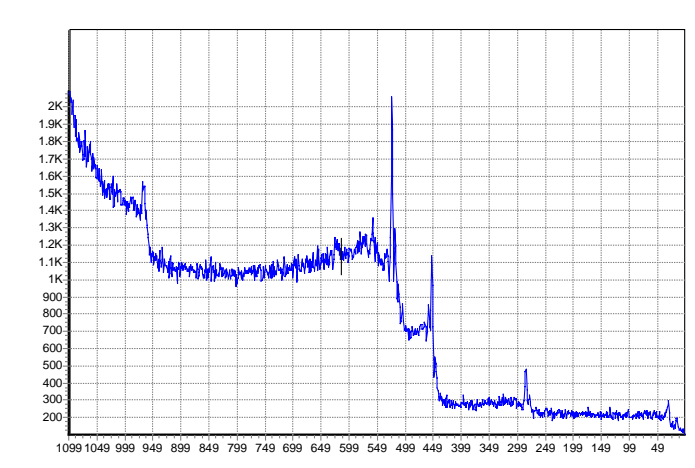


Figure 4.1.6. XPS analysis of 5% vanadia sample exposed to sulfur-laden gases under SCR conditions.

These XPS analyses indicate no sulfur peaks can be detected. This may be due to the sample preparation method. Samples tested were first ground to powder. This may sufficiently dilute the surface-exposed material with bulk material that the sulfur concentration drops below the detection limit (about 1 % sulfur). These tests will be repeated next quarter with a modified sample preparation procedure that does not involve grinding the sample.

FTIR-MS and TPD systems

The FTIR-MS system is completed and we are currently interfacing the system with a TPD system. Results from these two systems will be presented in the next quarter.

BET surface area analysis

BET surface area analyses for pore size distribution were conducted on three homemade samples: densified TiO_2 , 2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$, and 5% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$. The results were shown in Table 4.1.1.

Table 4.1.1. BET surface area and pore sizes for BYU samples

	Pure TiO_2	2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$	5% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$
BET surface area	27.9 m^2/g	15.4 m^2/g	18.6 m^2/g
Surface area of pores	37.19 m^2/g	16.98 m^2/g	19.25 m^2/g
Mean pore size	39.30 nm	32.41 nm	26.61 nm

The mean pore size decreases with increasing vanadia content on the catalyst surface. This is due to pores filled or blocked with vanadia particles. However, the surface area of 2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$ is less than that of 5% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$. This is in the same trend with the surface area of pores, where 5% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$ has a larger pore area than that of 2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$. From the pore size distribution it is observed that small pores still exist on 5% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$, where for 2% w/w $\text{V}_2\text{O}_5/\text{TiO}_2$, there are almost no small pores on this catalyst, thus it has smaller surface area.

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 4.1.7 illustrates the essential features of this system up to the analytical train. The analytical train is discussed later. This system simulates industrial flows by providing a test gas with the following compositions: NO , 0.10%; NH_3 , 0.1%; SO_2 , 0.1%; O_2 , 2%; H_2O , 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.).

A detailed description of the CCS was provided in the last report. During this quarter, construction of the CCS was essentially completed. Specific activities are summarized below.

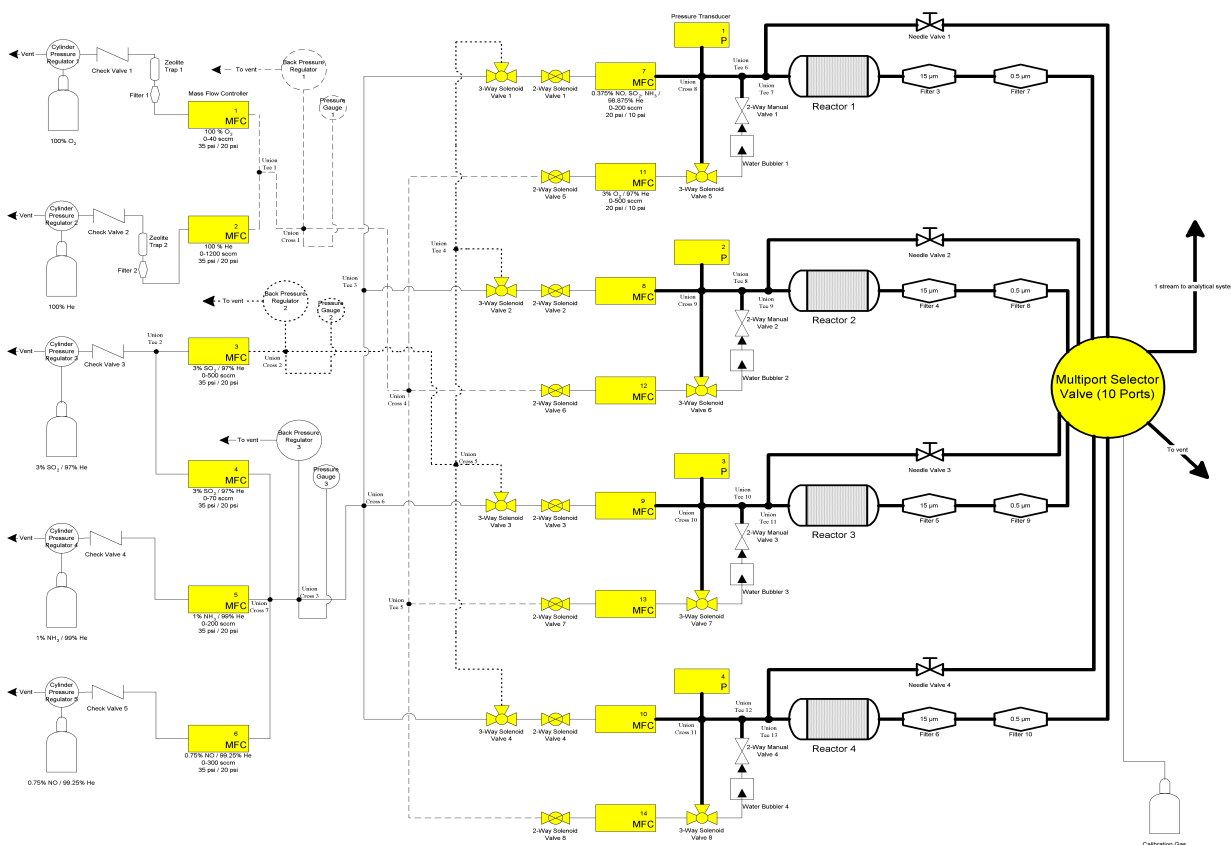


Figure 4.1.7. Summary schematic diagram of the CCS up to (but excluding) the analytical train

Gas Manifold System

We have virtually completed assembly of the gas manifold system. Specific accomplishments include replacement of several faulty check valves on the low-pressure part of the corrosive manifolds, installation of check valves at each cylinder to prevent back-flow of gases, the receipt of repaired corrosive gas pressure regulators (which were nonfunctional at the writing of the last progress report), and the installation of a high-pressure helium line. This high-pressure helium line is connected to the high-pressure inlet of each corrosive gas pressure regulator. It will be used to check the integrity of corrosive gas pressure regulators each time a gas cylinder is replaced, as well as to purge the system of any corrosive gases flow, which may remain without needing to remove or adjust fittings.

Gases

Two cylinders of each type of corrosive gas have been ordered from Airgas. Of each pair, one cylinder is of low concentration (~1000 ppm) and is used for instrument calibration, while the other cylinder is for actual run concentrations (0.75%, 1%, and 3% for NO, NH₃, and SO₂, respectively, with the balance being He).

Mass Flow Controllers

One significant setback that has finally been resolved is regarding the mass flow controllers (MFC's). Much troubleshooting was done to uncover the cause of erratic MFC behavior. Even after uncovering several problems with the external computer connections, it was found that three of the fourteen cables had faulty internal wiring. These cables were returned to the manufacturer and were recently received.

Pressure Transducers

The insulation of the wiring on the pressure transducers was chafed. The wiring has been replaced and modified to avoid this problem.

Heating Tape

This reactor system is designed to allow for the introduction of water vapor. In order to prevent water vapor from condensing inside tubing, areas where water vapor will be present (essentially, every piece of tubing downstream of the water bubbler) must be heat-traced. This will be accomplished with insulated electric heating tape wrapped around the tubing. This heating tape has recently been received and is to be installed soon. This will require some additional wiring and the use of six power supplies as it is desired to be able to heat and cool various isolated sections of tubing.

Bubbler

It has been difficult to construct inexpensive level indicators for the four columns of water in the bubbler. One design suggests attaching thin glass capillary tubes to a float. The water level in each column can be read from the floating capillary tubes. The capillaries can be seen inside a glass tube that is attached to the top of the bubbler column. Originally Styrofoam or cork was going to be used for the float. However when the capillary gets wet it sticks to the inside of the glass tube, and the float can be left suspended above the water level. Using a heavier float solved this problem. A float made from a 3/8" polyethylene tube is heavy enough to overcome the attraction of the wet capillary tube to the larger glass tubing. The ends of the polyethylene tubing was sealed with epoxy glue and attached to the capillary tube. Figure 4.1.8 is a depiction of the level indicator currently being used in the bubbler.

The bubbler has been installed into the rest of the test reactor system. Water vapor cannot be added to the gas stream, however until the tubing in the reactor system has been heat traced with heating tapes.

Analytical System

With the flow system fully operational, the analytical system can be checked and calibrated. Cylinders of calibration gas have been received of NO and SO₂. The concentrations of these gases are 990 ppm and 940 ppm, respectively. The instruments have been calibrated. Interferences, drift, and stability of the instruments will be assessed in the next quarter.

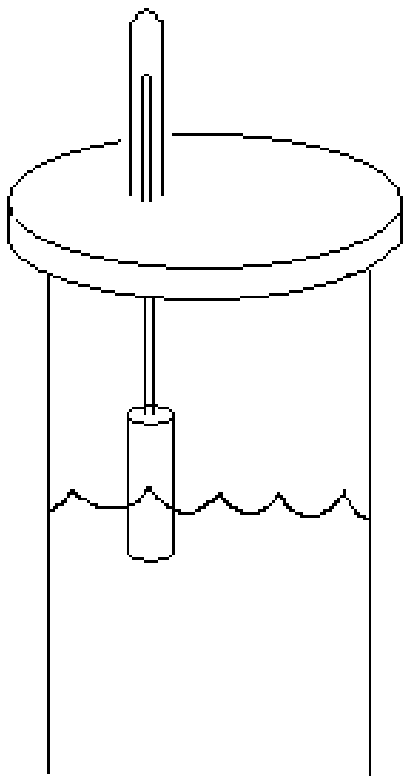


Figure 4.1.8. Bubbler Level Indicator

Computer Control Program

It has been our intention to control the gas flow rates and sampling cycles of four reactors in parallel with a computer in order to reduce operator labor and to avoid mistakes or inconsistencies between runs. Additionally, the computer system will be used to log data to an Excel or equivalent file for future analysis.

A student (who unfortunately just graduated and left for home) has been writing the computer code in Labview. Although his work represents considerable progress and has functionality, it remains incomplete. A document left by him summarizes his work and is being used in order to finish the computer code.

Currently, work is being done to finish this program. However, small programs which will allow the logging of some data that can only be taken by computer will be written and used in the meantime in order to run the system manually.

Catalyst Preparation

Industrial SCR catalysts are commonly made of titanium dioxide of the anatase phase impregnated with the oxides of vanadium and tungsten. As part of a larger study of the deactivation of SCR catalysts, Brigham Young University has prepared a monolithic catalyst where the active catalyst has been wash-coated onto a cordierite monolith support.

The primary obstacle in preparation of the wash-coated monolithic involved development of robust surfaces. Aqueous slurries of titania crack as they dry, resulting in thin films that do not adhere to the monolith. After many consultations with experts and a search of the literature, a combination of additives and procedures produced a stable titania washcoat suitable for the basis of an SCR catalyst.

Materials The following raw materials were used in the preparation of the BYU SCR catalyst.

Monolith

1. 19 pieces of cordierite monolith each approximately 2 1/8" x 2 1/8" x 6", containing 1/4" square channels

Ingredients used in Titania washcoat

1. P25 Titania from Degussa
2. Ludox® AS-40 colloidal silica from Grace Davison
3. Certified A.C.S Barium Nitrate (crystal)
4. Reagent Grade Sulfuric Acid

Ingredients used during Impregnation of Active Metals

1. Laboratory Grade Ammonium Metavanadate
2. Anhydrous Crystal, Reagent Oxalic Acid
3. AMT-1 Grade Ammonium Metatungstate

Procedure The monolith pieces were immersed in an aqueous 1 M nitric acid solution for 30 min at 80 °C. The acid bath roughens the surface of the cordierite and improves washcoat adhesion. Following the acid treatment, the monolith pieces were rinsed with distilled water and dried at 120 °C overnight.

The P25 Titania from Degussa was treated with a densification procedure similar to one from the literature. The titania was mixed with distilled water at a ratio of 1:1.75 by weight. The paste that was produced was dried at 120 °C for 24 hours. After drying, the titanium dioxide was crushed with a mortar and pestle. The crushed titanium dioxide was calcined at 600 °C for 4h.

The calcined titanium dioxide was then mixed with distilled water at a 1:1 ratio by weight and poured into a ball mill. The resulting slurry was ball milled at 45 rpm for 90 min. The ball-milled slurry product had a bimodal particle size distribution with major peaks at 2 microns and 20 microns. This particle sizing produces a tough, non-cracking coating.

Ludox® AS-40 was added to the ball milled slurry. Ludox® AS-40 contains 40 weight percent silica. Enough of this colloidal silica was added to create a 9:1 ratio of titanium dioxide to silica by weight.

Barium sulfate can be added to the SCR catalyst support as a binder according to U.S. Patent 4,975,256.

Barium nitrate was dissolved into the ball-milled titania slurry such that the resulting ratio of barium sulfate to titanium dioxide would be 1:9 by weight. Reagent-grade sulfuric acid was then added at 5% excess to precipitate virtually all of the barium, to barium sulfate.

The resulting slurry was thinned with a small amount of distilled water so that the dry coating would account for 20% of the total mass of the coated monolith. The monolith pieces were dipped in the titania slurry and compressed air was used to blow out the passages of the monolith. The coated monoliths were then dried for 15 hours at 120 °C followed by calcining at 600°C for 4 hours. Table 4.1.2 below shows the change in mass due to the addition of the titania washcoat.

Table 4.1.2. Monolith and Washcoat Weights

	Monolith alone (g)	with TiO ₂ coat (g)	wt% TiO ₂
	191	231	17.3%
	193	238	18.9%
	193	245	21.2%
	195	247	21.1%
	197	248	20.6%
	198	251	21.1%
	200	255	21.6%
	201	255	21.2%
	203	263	22.8%
	203	263	22.8%
	205	264	22.3%
	205	265	22.6%
	207	268	22.8%
	208	271	23.2%
	211	275	23.3%
	213	275	22.5%
	218	282	22.7%
	220	289	23.9%
	224	294	23.8%
Average	204.47	262.05	21.9%
Standard deviation	9.5	16.8	1.7%

The pore volume of the coated monoliths needs to be known before an appropriate impregnation solution can be prepared. The coated monolith pieces were dipped into distilled water. The excess water was blown off with compressed air, and the monolith pieces were weighed to determine the water uptake. On average, a coated monolith piece had an uptake of 45 grams of water.

The desired amount of active metal for one monolith piece needs to be dissolved in 45 mL of solution. The impregnation solution was prepared by dissolving the ammonium metavanadate and oxalic acid in warm water, dissolving the ammonium metatungstate in the solution, and finally adding enough water to dilute to the desired concentration.

After the impregnation solution was prepared, each titania-coated piece of monolith was immersed in the solution, and then the excess was blown off with compressed air. The impregnated monoliths were then dried at 120° for 15 hours followed by calcination at 550° for 5 hours.

Table 4.1.3 below shows the weights and approximate composition of the catalyst. This procedure yields a suitable V₂O₅/WO₃/TiO₂ catalyst washcoated on a cordierite monolith.

Table 4.1.3: Weight and composition of final catalyst

	monolith (g)	w/ TiO ₂ coat (g)	wt% TiO ₂	w/ W and V	wt% W & V wrt Ti
	191	231	17.3%	235	12.5%
	193	238	18.9%	241	8.3%
	193	245	21.2%	250	12.0%
	195	247	21.1%	251	9.6%
	197	248	20.6%	252	9.8%
	198	251	21.1%	255	9.4%
	200	255	21.6%	261	13.6%
	201	255	21.2%	260	11.6%
	203	263	22.8%	268	10.4%
	203	263	22.8%	268	10.4%
	205	264	22.3%	269	10.6%
	205	265	22.6%	269	8.3%
	207	268	22.8%	273	10.2%
	208	271	23.2%	276	9.9%
	211	275	23.3%	279	7.8%
	213	275	22.5%	280	10.1%
	218	282	22.7%	288	11.7%
	220	289	23.9%	295	10.9%
	224	294	23.8%	299	8.9%
average	204.4736842	262.0526316	21.9%	267	10.3%
standard deviation	9.5	16.8	1.7%	17.3	1.5%

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 previous quarterly reports. During this quarter, shakedown testing of the reactor was completed by the University of Utah at their L1500 combustion facility. The L-1500 is a 4-ft by 4-ft by 40-ft 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 was installed at the end of the shell and tube heat exchanger using a 4-inch flexible steel pipe. 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 was fired in the furnace. For a limited series of tests, coal and coal-sawdust blends were fired in the furnace. Data were collected on the fine particulate produced during coal-biomass co-firing; analysis of these is not complete and will be reported in a subsequent quarterly report.

As a result of shakedown testing, the control system software was completed with the exception of the subsystem that interfaces with the CEM system, discussed below. Computer-controlled operation of the reactor can be carried out remotely, either over an Ethernet cable or over the internet.

The reactor was checked for leaks and partially insulated for the shakedown tests. The flow meters were calibrated and automatic control of the flow through individual catalyst chambers was verified. As a result of the shakedown testing, various items were identified as needing replacement or redesign. That work will be finished in the next quarter.

After discussions with the University of Utah and vendors, it was decided to purchase a continuous emission monitor (CEM) system rather than to lease one. The former turned out to be the least expensive option. After reviewing several bids, a CEM system was ordered from Horiba Instruments. The system is designed around a seven-point sequential monitoring system to measure ppm levels of NO_x and percent levels of O_2 at selectable points on the SCR reactor. Each sampling point will be connected to a heated sample valve module via individual sections of heated Stainless Steel sample line. The heated valve module is a Nema 4 enclosure containing the valving for sample sequencing, sample point back purge, and calibration gas injection. Hot sample gas will exit the heated valve module and enter into a close-coupled sample preconditioner containing a thermo-electric cooler for first stage removal of water vapor from the sample gas.

The partially prepared sample gas exits the preconditioner module and is directed to a NEMA 4 air conditioned enclosure containing a Horiba Sample Conditioner Model ES-C510, a Horiba Model CLA-510 Chemiluminescent NO-NO_x Analyzer and a Horiba Model MPA-510 Magnetopneumatic Paramagnetic Oxygen Analyzer. The resulting clean dry sample gas is analyzed and an analog signal is sent to the customer supplied PLC to record the ppm concentrations of NO_x and percent levels of oxygen. A terminal strip at the rear of the analyzer will connect to the control system to enable remote range changing capability.

American Electric Power (AEP) expressed interest in having the testing take place at their Rockport plant, which fires a blend of PRB and bituminous coal. During the past quarter, a visit was made to the plant to view the site. A suitable site was found at the plant. The plant is interested in working with REI on conducting the tests. In the next quarter, technical specifications will be discussed with the plant, leading to installation of the reactor at Rockport, tentatively in August-September 2002, assuming that the final modifications on the reactor can be completed. Allegheny Energy's Albright station will be available for testing in late winter, 2003.

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

The second phase of RRI testing in Sioux Unit 1 was conducted during March, 2002. Preliminary results of the field tests were included in our previous quarterly report. However, the plant has not completed their final report documenting the field test results in detail. Shown in Figure 2.2.3 is a typical NO_x profile from the continuous emissions monitor (CEM) for the unit during the second phase of RRI testing. This figure illustrates that the NO_x emissions drop from about 0.38 lb/MMBtu to approximately 0.27 lb/MMBtu with RRI under full load conditions. These results are in good agreement with our CFD model predictions.

Results and Discussion

RRI: Field tests at the Ameren Sioux Unit 1 demonstrated that RRI can provide up to 30% NO_x reduction with no ammonia slip. The RRI performance demonstrated in the field test is in good agreement with the original CFD modeling results. To better understand the dependence of the lower furnace stoichiometric ratio on RRI performance in this unit, additional CFD modeling studies were conducted for operating the furnace at a stoichiometric ratio of 0.99 and 0.95. The modeling results indicate that operating the furnace at a stoichiometric ratio of 0.99 results in localized pockets of fuel rich and fuel lean conditions. When using RRI, reagent entering the fuel rich pockets results in NO_x destruction but reagent entering the fuel lean pockets results in NO_x production. For these operating conditions, the net result is that RRI provides only a minor NO_x reduction overall. When operating at a stoichiometric ratio of 0.95, the fuel lean pockets are fewer and smaller. As such, the use of RRI creates less (localized) NO_x production and more NO_x destruction, resulting in noticeably greater NO_x reduction. These additional modeling studies provide insight aid in understanding the RRI field test results, and provide further guidance on how to use the modeling tools to create RRI designs.

SCR Catalyst: During this quarter, several *in situ* analyses of vanadium-based SCR catalyst systems were completed. These are preliminary data with which to compare results from literature investigations. Results of sulfation tests thus far indicate that titania sulfates under SCR conditions but there is no indication of vanadia sulfation. This is in agreement with some, but not most literature results. Additional analysis and advanced diagnostics are under way to confirm this result and determine its accuracy. 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.

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.

Shakedown testing of the field reactor was completed at the University of Utah pilot-scale coal furnace. The CEM system has been ordered. After completion of minor modifications to the reactor, it will be ready to go to the first test site. Talks have continued with American Electric Power (AEP). AEP is interested in hosting a demonstration at their Rockport plant.

Conclusions

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

- Field tests completed earlier this year at the Ameren Sioux Unit 1 demonstrated that RRI can provide up to 30% NO_x reduction with no ammonia slip when appropriate furnace staging is employed. CFD modeling studies have been performed that indicate the noticeable improvement in RRI performance for operating the lower furnace at a stoichiometric ratio of 0.95 rather than 0.99 is due to the presence of fewer fuel lean pockets in the lower furnace where reagent is injected.
- Preliminary data from BYU on reactivity of vanadia and titania thus far indicate that titania sulfates under SCR conditions but there is no indication of vanadia sulfation. This is in agreement with some, but not most literature results. Additional analysis and advanced diagnostics are under way to confirm this result and determine its accuracy.
- Construction of the CCS reactor system is nearly complete, with a few remaining details discussed in this report.
- Shakedown testing of the field reactor was completed at the University of Utah pilot-scale coal furnace. The CEM system has been ordered.
- Talks continued with American Electric Power (AEP). AEP is interested in hosting a demonstration at their Rockport plant.

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 and preparation to ship it to a plant for installation.

Literature References

Cremer, M.A., Adams, B.R., Boll, D., O'Connor, D., and Slaff, R.D., "Demonstration of Rich Reagent Injection in Ameren's Sioux Unit 1", presented as at the DOE 2002 Conference on Selective Catalytic Reduction and Selective Non-Catalytic Reduction for NO_x Control, Pittsburgh, PA, May 15-16, 2002.

Senior, C.L., Davis, K.A, Bockelie, M.J., Baxter, L., Bartholemew, C., Whitty, K., Eddings, E., "SCR Deactivation Mechanisms Related To Alkali and Alkaline Earth Elements", poster presented at the DOE 2002 Conference on Selective Catalytic Reduction and Selective Non-Catalytic Reduction for NO_x Control, Pittsburgh, PA, May 15-16, 2002.