

NOx Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

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Abstract

This is the ninth 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.

Various subsystems of BYU's Catalyst Characterization System (CCS) were upgraded this quarter. Work on the CCS hardware and software will continue in the coming quarter. A preliminary test matrix of poisoning experiments in the CCS has been drafted that will explore the effects of at least three poisons: sodium, potassium and calcium. During this quarter, we attempted to resolve discrepancies in previous *in situ* measurements of catalyst sulfation. Modifications were made to the XPS analysis procedure that allowed analyses of uncrushed samples. Although the XPS and FTIR results are now more consistent in that both indicate that the surface is sulfating (unlike the results reported last quarter), they disagree with respect to which species sulfates. The CEM system for the multi-catalyst slipstream reactor arrived this quarter. Minor modifications to the reactor and control system were completed. The reactor will be shipped to AEP Rockport plant next quarter for shakedown and installation. In a parallel effort, we have proposed to make mercury oxidation measurements across the catalysts at the start of the field test. Pending approval from DOE, we will begin the mercury measurements next quarter.

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.....	na
Task 3 Minimization of Impacts	na
Task 4 SCR Catalyst Testing	3
Task 5 Fly Ash	na
Task 6 Field Validation of Integrated Systems	na
RESULTS AND DISCUSSION	20
CONCLUSIONS.....	21
LITERATURE REFERENCES	22
APPENDIX.....	23

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:

- Various subsystems of BYU's Catalyst Characterization System (CCS) were upgraded this quarter. Work on the CCS hardware and software will continue in the coming quarter.
- A preliminary test matrix of poisoning experiments in the CCS has been drafted that will explore the effects of at least three poisons: sodium, potassium and calcium. We may also explore the effect of arsenic, if this can be carried out in a safe manner. The full design will consist of 64 experiments, requiring approximately 15 weeks to complete.
- Previous *in situ* reactivity data indicated that titania sulfates under SCR conditions but there was no evidence of vanadia sulfate forming based on the peaks reported in the literature as indicative of vanadium sulfation. During this quarter, we attempted to resolve these issues. Modifications were made to the XPS analysis procedure that allowed analyses of uncrushed samples. Although the XPS and FTIR results are now more consistent in that both indicate that the surface is sulfating (unlike the results reported last quarter), they disagree with respect to which species sulfates.
- We also noted that the FTIR signal from a surface compound thought to be the product of sulfation of vanadium was sensitive to the presence of water in the gas stream; there appeared to be reversible adsorption/desorption of water occurring at this sulfate site.
- The CEM system for the multi-catalyst slipstream reactor arrived this quarter. Minor modifications to the reactor and control system were completed. The reactor will be shipped to AEP Rockport plant next quarter for shakedown and installation. In a parallel effort, we have proposed to make mercury oxidation measurements across the catalysts at the start of the field test. Pending approval from DOE, we will begin the mercury measurements next quarter.

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

Industry Involvement

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

- A podium presentation entitled “Demonstration of Rich Reagent Injection for NO_x control in Ameren’s Sioux Unit 1” was provided at the 19th Annual International Pittsburgh Coal Conference, held September 24-26, 2002 in Pittsburgh, PA that highlighted modeling and field tests of RRI in the Ameren Sioux Unit #1 boiler that demonstrated RRI can provide NO_x reductions of 30% from full load baseline emissions with OFA of approximately 0.4 lb NO_x/mmBTU with no ammonia slip [Cremer et al, 2002].
- A podium presentation entitled “Evaluation of an On-line Technique for Corrosion Characterization in Boilers” was provided at the *3rd International Workshop on Life Cycle Issues in Advanced Energy Systems* held June 10-12, 2002 in Woburn, England that highlighted the combined use of CFD modeling and a corrosion probe to develop a corrosion monitoring system [Davis et al, 2002a].

A podium presentation entitled “Prediction and Real-Time Monitoring Techniques for Corrosion Characterization in Furnaces” was provided at the 19th Annual International Pittsburgh Coal Conference, held September 24-26, 2002 in Pittsburgh, PA that highlighted CFD modeling to predict water wall corrosion and field test results that measured water wall corrosion in a PC fired boiler [Davis et al, 2002b].

Task 4 - SCR Catalyst Testing

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 catalyst 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.

Catalyst Characterization System

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. A detailed description of the CCS was provided in the April through June 2002 quarterly report.

During this quarter, various subsystems of BYU's Catalyst Characterization System (CCS) were upgraded. A preliminary test matrix of poisoning experiments in the CCS was drafted that will explore the effects of at least three poisons: sodium, potassium and calcium.

Control System The SCR test reactor system was designed to test four catalyst samples simultaneously, which has required the construction of a considerably complex system of various pieces of hardware that control gas flow rates and gas mixtures. (A detailed description of this system has been included in previous reports and is not given here.) The system allows for automatic or manual control. Originally, it was intended that the system would be run manually until the computer programming was completed so that data could be obtained as soon as possible, although in a limited manner. In addition to the setbacks that have precluded any type of operation at all (i.e. heat-tracing lines and testing with water), problems have occurred if manual operation is utilized only.

Although four catalyst samples can be run simultaneously under test conditions, the effluent of only *one* sample may be sampled at a time if the system is started and left unattended. Complete manual operation of the reactor system that would test four samples simultaneously would require that a person be available to manually switch the valve that selects which of the four reactor's effluents to sample once every fifteen minutes or so—hardly a desirable task for an operation that runs continuously for days at a time. In addition, the operator would need to either change or annotate the file to which the computer logs data during the simultaneous runs in order to indicate which reactor is being sampled.

The above circumstance has necessitated extra attention to computer automation control, which has been done with National InstrumentsTM LabVIEWTM software. Although the student who had done most of the LabVIEWTM programming on the reactor system left for graduate school, his programs have served as the basis for progress on the current program and the reactor system is almost to the point where it is functional in a practical way.

Currently, the computer allows a user to specify inlet reactor concentrations and flow rates based on GHSV (gross hourly space velocity), catalyst density, and catalyst weight. It also switches the multi-port selector valve at a regular time interval (specifiable by the user) so that each reactor may be sampled in turn in order to obtain NO conversion data. It allows for the operation of a reactor with or without water. It displays all pertinent process data including inlet pressures; temperatures of the bubblers, furnaces, and heating tapes; analyzer outputs (in ppm); and individual mass flow controller set point and flow rate values. Figures 1 through 4 illustrate various parts of the program, as it now exists. Although the appearance and arrangement of the controls and indicators displayed will change, the functionality will remain mostly as it is. A brief explanation of each figure is now included.

Figure 1 shows the controls and displays corresponding to one of four reactor states (OFF, Purge, Condition, and Reaction). Note that individual reactor temperature, pressure, and water bubbler feed temperature are displayed. Also note that water may be turned on or off at the command of the operator by pressing the "RCTR _ Water?" buttons at the bottom of the figure. At present, the temperatures of the bubbler and reactors (furnaces) are controlled manually, but this may be automated in the future.

Catalyst and Reactor Information:

	RCT-1	RCT-2	RCT-3	RCT-4
Reactor Function	OFF ▾	Purge ▾	Condition ▾	✓ OFF Purge Condition Reaction
GHSV (hr ⁻¹)	30000	30000	30000	
Amount of Catalyst (g)	0.500	0.500	0.500	0.500
Catalyst Bulk Density (g/cm ³)	0.800	0.800	0.800	0.800
Flow into Each Reactor to Achieve GHSV (sccm)	312.50	312.50	312.50	312.50
Reactor Pressures (PSI gauge)	-0.038	-0.021	-0.019	-0.054
Reactor Temperatures (°C)	24.288	23.105	24.288	22.981
	RCTR 1 Water?	RCTR 2 Water?	RCTR 3 Water?	RCTR 4 Water?
Bubbler Temperatures (°C)	22.016	24.879	21.984	24.848

Figure 1. Display of individual reactor condition controls.

Figure 2 shows the input fields for gas cylinder concentrations (left), which can be easily adjusted as new cylinders of potentially different concentrations are received. Also displayed are the mixtures of gases corresponding to the reactor states mentioned in the previous paragraph.

Gas Cylinder Information:

Gas	Conc. gas in cylinders (%)	Conc. into Reactors (%)		
		Purge	Condition	Reaction
NO	0.7500	0.00	0.00	0.10
NH3	1.0000	0.00	0.00	0.10
SO2	3.0000	0.00	2.40	0.10
O2	100.0000	30.00	20.00	2.00
He	100.0000	70.00	77.60	87.70
H2O*	100.0000	0.00	0.00	10.00

Figure 2. Gas cylinder concentration inputs and reactor function concentrations.

Figure 3 is a display of the mass flow controller (MFC) set points, which are calculated based on the settings displayed in Figures 1 and 2. The actual flow rates are also displayed so that a quick visual check can be made to ensure correct operation.

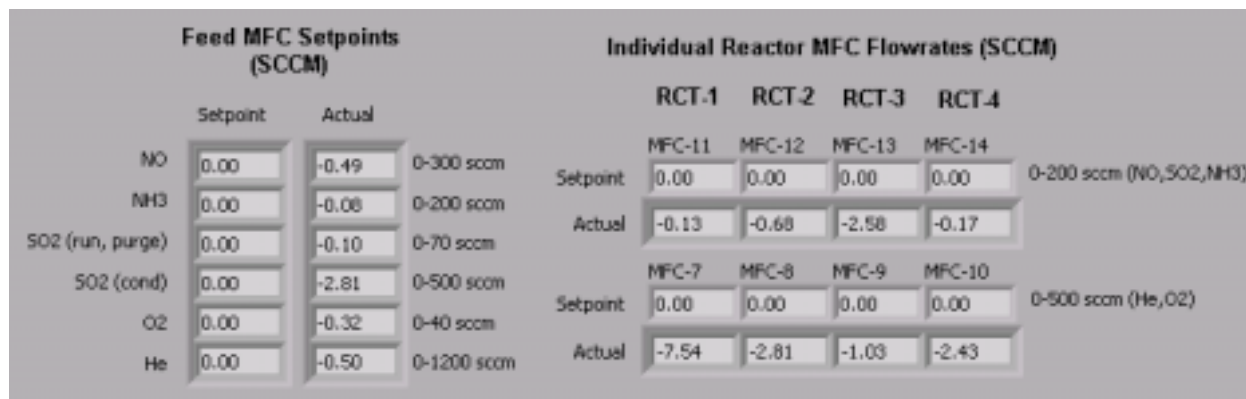


Figure 3. Mass flow controller setpoint and actual flowrate indicators.

Figure 4 includes several items. The temperatures of 16 thermocouples placed at various locations on heating tapes are displayed. The reactor that is being sampled is indicated by the light under the “Valve Switch Time,” which is the time interval in between the changing of the multi-port selector valve. The concentration outputs of analyzer data (in ppm) are displayed. Finally, the STOP button is the part of the program that halts its execution.

Again, the program will be enhanced so that the user can input file names where data will be logged and it will record data pertaining to each reactor to a separate file.

One crucial issue that needs to be addressed before serious data may be taken is the calibration of the mass flow controllers, thermocouples, etc. This will be performed by defining standards against which to compare the values and then adding correction factors to the computer programs.

When the control program is complete and functional (probably within several weeks), it will allow the user to input a file name (for a total of 4) corresponding to each catalyst sample. As a reactor is being sampled, the computer will log data to the file that corresponds to that reactor, switching between files automatically.

Ultimately, controls for the periodic sampling of reactor feed streams will be incorporated into the sampling scheme (as opposed to reactor product streams only). In addition, the reactor control system will need to be configured for compatibility with the gas chromatograph (GC). Specifically, subroutines will need to be written that switch the GC valves that control gas sample injection into the GC at regular intervals (see below also). Also, a subroutine needs to be written to record the GC output so that a curve may be formed for integration. Ultimately, LabVIEW™ may even be programmed to perform this integration automatically. Obtaining the best GC column temperatures and GC valve timing schemes will involve trial and error, but these schemes can be written into the control code.

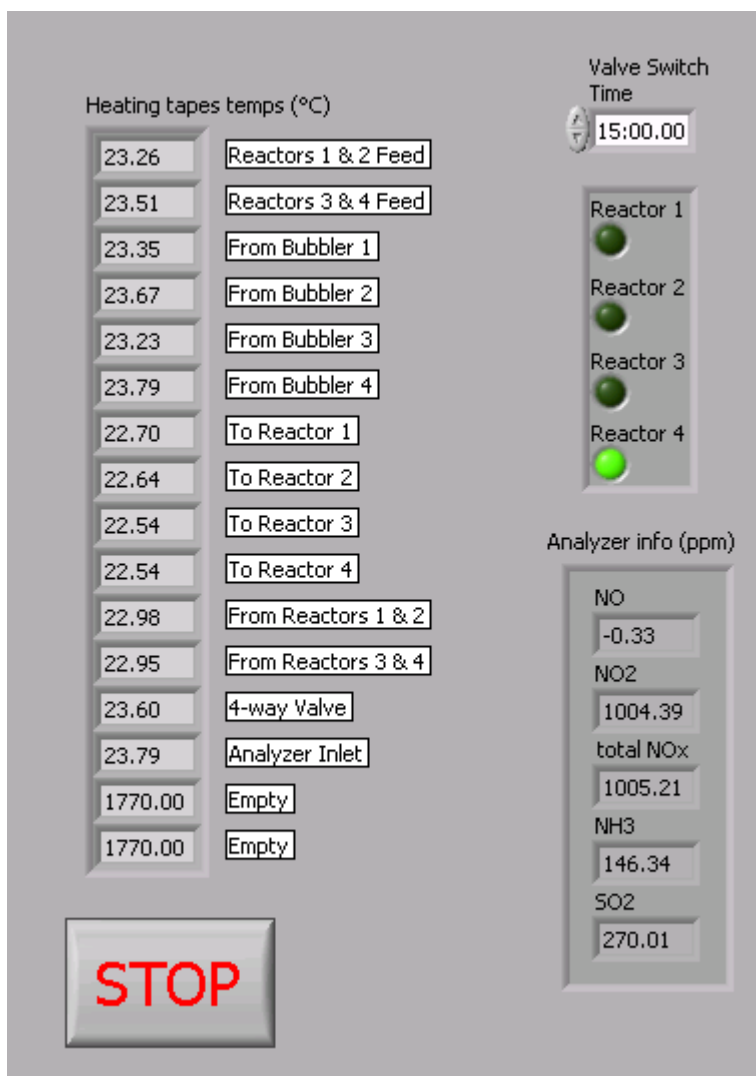


Figure 4. Temperature, valve position, and analyzer concentration displays.

Gas Chromatograph The gas chromatograph (GC) is the last piece of equipment that is not entirely functional. The exact work that needs to be done is somewhat unknown as the GC is quite old and may need new column(s) installed and/or other new parts or repairs. Progress has been made with the valves that control the injections of samples into the GC. These valves are controlled pneumatically via compressed air, which is delivered by solenoid valves. These solenoid valves have recently been configured so that they are computer controllable.

Calibration System During several tests, we have noticed that the ammonia analyzer exhibits about 30 ppm of drift in about a week. This necessitates frequent calibration of the equipment. In order to facilitate this calibration, a new calibration system has been installed. The previous means of calibration required several hours because there is so much volume in the reactor system. The new calibration system provides a much shorter route to the analytical equipment,

allowing calibration to be completed in just a few minutes. Another benefit of the new system is that it allows the reactor gases to be bypassed in order to calibrate the equipment in the middle of a run, if necessary.

Water Condenser The NH_3/SO_2 analyzer is the only instrument that can tolerate water vapor. Thus, the water is to be condensed downstream of this piece of equipment (but upstream of the gas chromatograph and the NO_x analyzer). The current method of water knockout is a condenser that consists of a 150 cm^3 stainless steel vessel (submerged in an ice bath) through which gas is flowed before entering the GC and NO_x analyzers. Some concern exists as to how much the dead volume in this container will affect the system. Furthermore, it is not known how much product gas will be absorbed by condensed water. Significant delays have already been observed due to effects attributed to delay times produced by long tubing runs, and a condenser such as this one will only exacerbate the problem. Other methods of water knockout such as a water trap similar to that underneath a household sink coupled with a shell-and-tube type heat exchanger may be considered if the current condenser is problematic.

Water Content The bubbler that was installed to introduce water to the gas stream has now been tested. We tested it by bringing it to a steady-state temperature, putting a desiccant (calcium sulfate) in one of the reactor tubes, and turning on the gas flow to that reactor. We found that the water partial pressure developed in the bubbler was slightly less than the equilibrium vapor pressure.

Table 1 summarizes the results. The departure from equilibrium concentrations increases with increasing temperature, indicating that the contact time of the air in the bubbler may be too limited or the bubbles may be too large at the higher temperatures. These results represent serviceable performance from the bubblers, but we hope to decrease the differences between partial and vapor pressures to improve the repeatability and precision of the system.

Table 1. Actual water compositions and predicted water compositions at different temperatures and flow rates.

400 sccm			500 sccm		
T/°C	mol% H_2O	Predicted	T/°C	mol% H_2O	Predicted
60	19.6%	19.9%	60	19.3%	19.9%
65	22.6%	24.9%	65	20.7%	24.9%
65	21.3%	24.9%			
70	28.5%	31.1%	70	25.5%	31.1%
70	27.9%	31.1%			

Ammonia Analyzer We initially observed signal overshoot from the ammonia analyzer at the beginning of a high-concentration test. The ammonia concentration reported by the analyzer was

actually higher than the concentration in the gas cylinder (See Figure 5). After calibrating the analyzer, the overshoot discussed above was not observed and it has not since returned.

When lower concentrations were run in step tests, a small bump was exhibited upon initial ammonia detection, but during later steps, the analyzer otherwise behaved as expected (See Figure 6). The step-tests represented by Figure 6 were performed by running a constant helium flow rate and varying the flow rate of ammonia. Upon increasing the flow rate of ammonia, the concentration of ammonia at the analyzer quickly reached an elevated value, but continued to gradually increase. When the flow rate was decreased to a smaller, non-zero value, the concentration at the analyzer dropped quickly and remained fairly constant. When the flow rate of ammonia was decreased to zero, the concentration dropped to a small, non-zero value and gradually fell to zero. This behavior seems to indicate adsorption of ammonia on the stainless steel tubing used in the construction of the reactor system. When flow rate is increased, partial pressure of ammonia is increased, and ammonia coverage of the stainless steel must increase to achieve equilibrium. Significant time is required to achieve this equilibrium. When flow is decreased, the ammonia desorbs and equilibrium is achieved quickly. When the flow of ammonia is stopped, it takes a while for all of the ammonia to desorb and the concentration to reach zero. Additional work is necessary to quantify this absorption, but the evidence that it occurs is compelling.

Turning off the helium and leaving the ammonia flowing caused the first large spike on the graph. Troubleshooting a valve upstream of the mass flow controller caused the spikes at the end of the test. These apparent abnormalities are the expected cause of our actions, and are, therefore, not cause for concern.

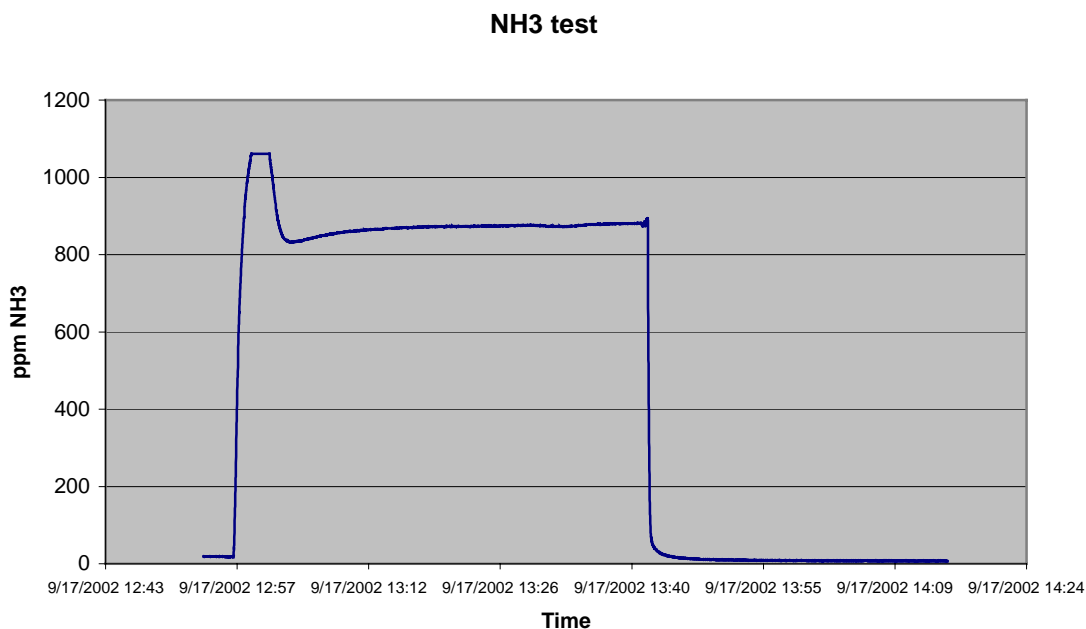


Figure 5. The concentration of ammonia reported by the analyzer initially jumped to about 1070 ppm, more than 150 ppm above the source concentration of 914 ppm.

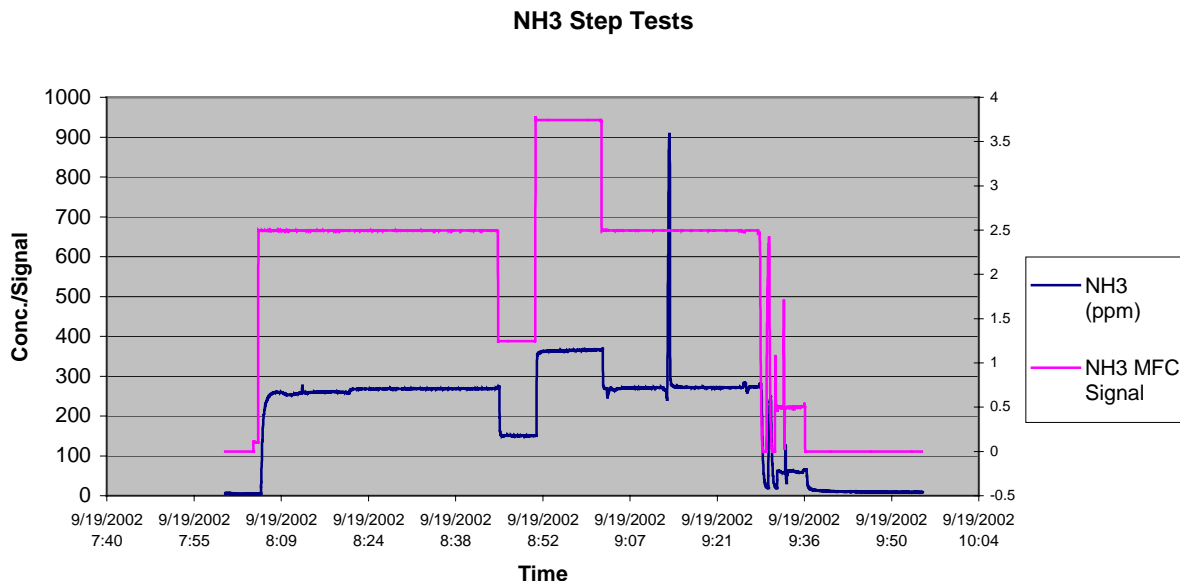


Figure 6. The concentration of ammonia (lower line, left axis) and ammonia mass flow controller signal (top line, right axis) show no anomalies in the step test.

Experimental Design/Future Plans Our experimental design will allow us to explore the effect of each poison, multiple poisons, and temperature on catalyst performance (See Appendix). Temperatures and poisoning levels have not yet been determined. They will be specified after several preliminary runs have been conducted which will establish baseline performance of the clean catalyst. The run order has been randomized in order to eliminate time bias in the research. During our experiments we will explore the effects of at least three poisons: Sodium, Potassium and Calcium. We may also explore the effect of Arsenic, as indicated in the experimental design. This will be dictated by safety conditions. The catalyst will be tested at four different levels of poisoning with each metal, and two temperature at each poisoning level. It will also explore the arsenic-calcium and arsenic-potassium interactions at a single temperature. The full design will consist of 64 experiments, requiring approximately 15 weeks to complete.

***In Situ* Spectroscopy Reactor**

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 co-adsorption of NH₃ and NO_x will help elucidate mechanisms and rates of both reactions and deactivation.

During this quarter, we attempted to resolve discrepancies in previous *in situ* measurements of catalyst sulfation. Modifications were made to the XPS analysis procedure that allowed analyses of uncrushed samples. Although the XPS and FTIR results are now more consistent in that both

indicate that the surface is sulfating (unlike the results reported last quarter), they disagree with respect to which species sulfates.

FTIR test---Sulfation of TiO_2 , 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ Previously reported *in situ* FTIR sulfation experiments that were conducted at 380 °C for six hours using TiO_2 , 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, and 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts indicated that the amount of sulfate species, as represented by an infrared peak at 1375 cm^{-1} , is directly proportional to the titania content and inversely proportional to the vanadia content. That is, there was no evidence of vanadia sulfate forming based on the peaks reported in the literature as indicative of sulfation. Also, after six hours of pure vanadium catalyst exposure to SO_2 -laden flows, a new peak at about 1270 cm^{-1} that is possibly associated with sulfates appeared. However, no sulfur was detected on such samples from XPS analysis, a possible result of sample preparation methods. Samples were crushed during preparation for the XPS analysis, generating largely unsulfated surfaces, which could explain the lack of sulfate found. During this quarter, we attempted to resolve these issues.

Several sulfation tests were repeated on TiO_2 , 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, and 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts to obtain a more complete, representative sample suite for the XPS analysis. Table 2 summarizes the test conditions. Table 3 provides a summary of the peaks and peak-strengths identified in these experiments.

The FTIR spectra of TiO_2 qualitatively mimicked the earlier results in all tests with respect to the peak at $1374\sim 1377\text{ cm}^{-1}$, generally consisting of one large peak at $1374\sim 1377\text{ cm}^{-1}$ that decreased in magnitude as TiO_2 decreased or V_2O_5 increased. Furthermore, the peak heights, which approximately correspond to the surface sulfate concentrations, appear to saturate after a few hours of exposure. That is, the peak heights do not change with increasing time except during the first few hours. However, no peak was observed around 1277 cm^{-1} for the 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, as illustrated in Figure 7.

Modifications were made to the XPS procedure that allowed analyses of uncrushed samples. Such analyses are designated as "pellet" analyses in Table 2. XPS analyses of uncrushed wafers or pellets renders clear indications of sulfation in all cases, qualitatively consistent with the FTIR results. However, the XPS-indicated fractions of vanadium, sulfur, and titanium on the surface are only qualitatively consistent with the bulk analyses. For example, increasing the bulk vanadium concentration from 2% to 5% increased the indicated surface concentration of vanadium atoms by less than 20%, from 5.9 to 7 %.

Table 2. Summary of *in situ* FTIR test conditions for sulfation of vanadium-based catalysts.

Date	Sample	Sample	Notes	Process go through, %					Flow rate	Temp	Windows	XPS
	Name			He	O ₂	SO ₂	NH ₃	NO	H ₂ O	sccm	°C	sample
1-Jul	TiO3 (1-5)	Pure TiO ₂	Preoxidation	95	5				0	49.75	380	KCl+CaF ₂
		6 hrs	Sulfation	94.954	4.76	0.286			0	52.5	380	KCl+CaF ₂ Pellet
3-Jul	TiO3 (6-9)	2% V ₂ O ₅ /TiO ₂	Preoxidation	95	5				0	49.75	380	KCl+CaF ₂
		6 hrs	Sulfation	94.954	4.76	0.286			0	52.5	380	KCl+CaF ₂ Pellet
11-Jul	V7TH	5% V ₂ O ₅ /TiO ₂	Preoxidation	95	5				0	49.75	380	KCl+CaF ₂
		24 hrs	Sulfation	94.954	4.76	0.286			2.4	52.5	380	KCl+CaF ₂ Pellet
29-Jul	V8TO	5% V ₂ O ₅ /TiO ₂	Preoxidation	95	5				0	52.5	366-380	KCl+CaF ₂
		24 hrs	Sulfation	94.48	5.29	0.23			0	39.69	380	KCl+CaF ₂
10-Sep	TiO4	Pure TiO ₂	Preoxidation	90	10				0	50	385	KCl+CaF ₂
12-Sep		24 hrs	Sulfation	94.06	5.69	0.23			0	36.89	380	KCl+CaF ₂
13-Sep	V9TO	2% V ₂ O ₅ /TiO ₂	Preoxidation	90	10				0	50	377	KCl+CaF ₂
14-Sep		24 hrs	Sulfation						0		370-390	KCl+CaF ₂
Now	V9TH	2% V ₂ O ₅ /TiO ₂	Preoxidation	90	10				0	50	377	KCl+CaF ₂
		24 hrs	Sulfation									KCl+CaF ₂

Table 3. Results of XPS analyses of vanadium-based catalysts after exposure to SO₂-laden flows.

		TiO ₂		2% V ₂ O ₅ /TiO ₂		5% V ₂ O ₅ /TiO ₂	
XPS Line	Peak ID	Norm Area	Atom %	Norm Area	Atom %	Norm Area	Atom %
Ti 2p3	Pk01	110.752	6.162	96.762	5.384	79.448	4.42
S 2p3	Pk01	6.153	0.342	3.872	0.215	7.237	0.403
V 2p3	Pk01			10.588	0.589	12.5	0.695

The highest sulfur content was acquired on the 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, but this sample was exposed for 24 hours, four times as long as the other two pellet samples. The sulfur content will eventually saturate, but we do not yet know at what level that happens. Therefore, results to date are preliminary pending additional tests. The XPS and FTIR results are now more consistent in that both indicate that the surface is sulfating (unlike the results reported last quarter). However, they disagree with respect to which species sulfates. The *in situ*, time-resolved FTIR results suggest that the surface concentration of sulfates decreases with increasing vanadium and saturates after a few hours. The XPS results, which are neither *in situ* nor time resolved, indicate that sulfur concentration increases with increasing vanadium content and/or with increasing time beyond the first 6 hours up to 24 hours.

The sulfate peak we are analyzing at 1375 cm^{-1} corresponds to a sulfur-oxygen stretch in anionic portion of a sulfate salt. Its position should be only weakly affected by the nature of the cation. Therefore, it would be most unlikely that a vanadium or vanadyl sulfate peak would lie in a region significantly removed from 1375 cm^{-1} . However, if this were the case, it would resolve the apparent disagreement between the various analyses. For reasons that we are still investigating, the sulfur content of the catalyst surface as measured by XPS is not proportional to the 1375 cm^{-1} peak in the FTIR spectrum for 5% $\text{V}_2\text{O}_5/\text{TiO}_2$. The existence of a different sulfate peak for vanadium/vanadyl sulfates is one hypothesis, but we propose alternative hypotheses to explain these data below, which we believe to be better.

In order to get comparable data on all samples, twenty-four hour sulfation tests were also conducted on TiO_2 and 2% $\text{V}_2\text{O}_5/\text{TiO}_2$. FTIR spectrums of TiO_2 were similar to those obtained before, as shown in Figure 8. The 1375 cm^{-1} peak is still present in the spectrum of the 2% $\text{V}_2\text{O}_5/\text{TiO}_2$, although new peaks around $1151\sim1157\text{ cm}^{-1}$ instead of peaks at 1277 cm^{-1} appear, as shown in Figure 9. A small peak at 1375 cm^{-1} appeared only in the spectrum of 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ where sulfation was carried without water and disappeared on the one where sulfation was carried with water (Figures 10 and 11). However, a 1278 cm^{-1} peak for 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ appeared after the water treatment (Figure 11). XPS results were delayed because the equipment was down for repair.

An important observation is that the 1375 cm^{-1} peak on all samples disappears when the samples are exposed to a room environment, accompanied by the appearance of a new peak at $1620\sim1630\text{ cm}^{-1}$. However, the 1375 cm^{-1} peak reappears after samples are reheated. This phenomenon may be related to water adsorption/desorption. As a test of this hypothesis, during the sulfation test of TiO_2 , on which the 1375 cm^{-1} was still present and the temperature was about 375°C , water was introduced. In this situation, the 1375 cm^{-1} peak disappeared while the 1620 cm^{-1} peak appeared, (Figure 12). Thus, the surface species corresponding to 1375 cm^{-1} peak in the FTIR spectrum may react with water reversibly. It is unlikely that water would be directly adsorbed as water of hydration at these temperatures, but it is probable that water would adsorb and decompose to form adsorbed surface species. In any case, water, which is an integral part of the SCR reaction, clearly has a major affect on the sulfate peak heights. This is important for future interpretation of FTIR spectra but it is not an explanation for the anhydrous data in which increasing vanadium concentrations decreased sulfate peak height. This latter trend may be explained by the next series of experiments.

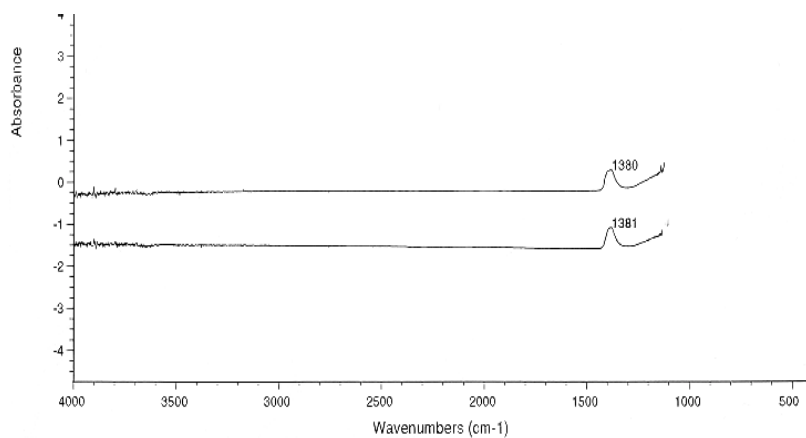


Figure 7. Six hour sulfation test on 2% V_2O_5/TiO_2 (TiO3(6-9); see Table 2).

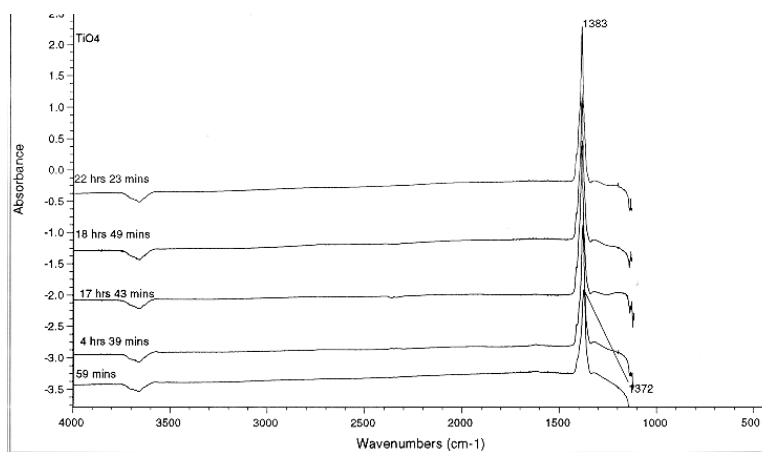


Figure 8. Twenty-four hour sulfation test without H_2O on TiO_2 (TiO4; see Table 2).

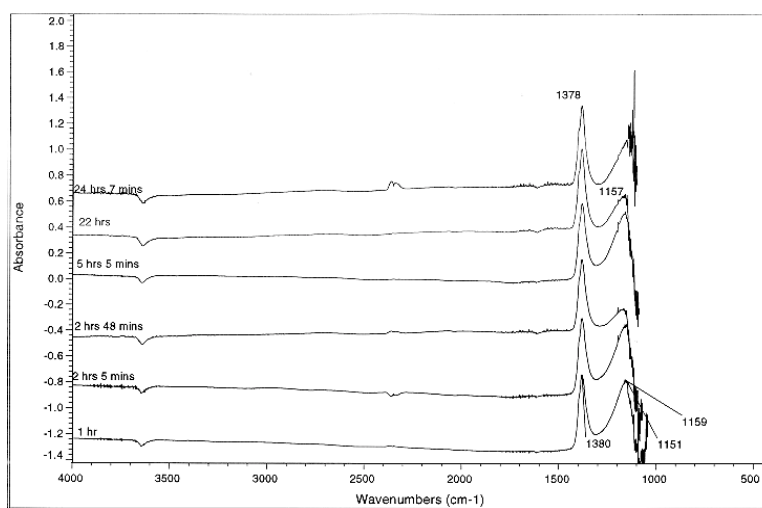


Figure 9. Twenty-four hour sulfation test without H_2O on 2% V_2O_5/TiO_2 (V9TO; see Table 2).

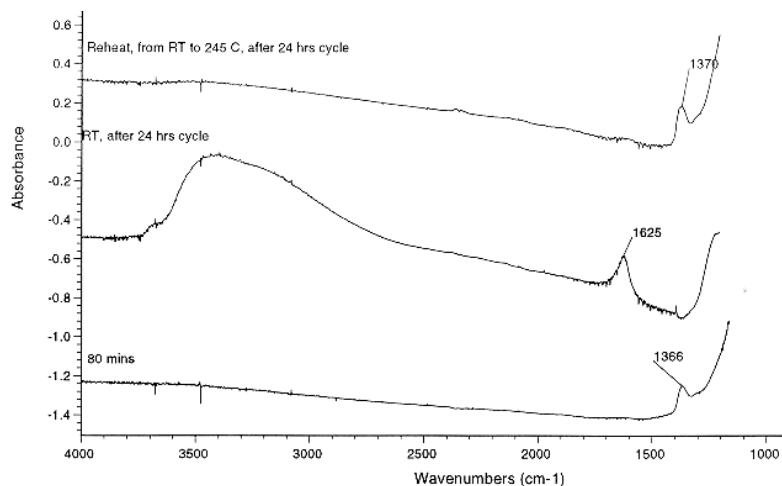


Figure 10. Twenty-four hour sulfation test without H_2O on 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ (V8TO; see Table 2).

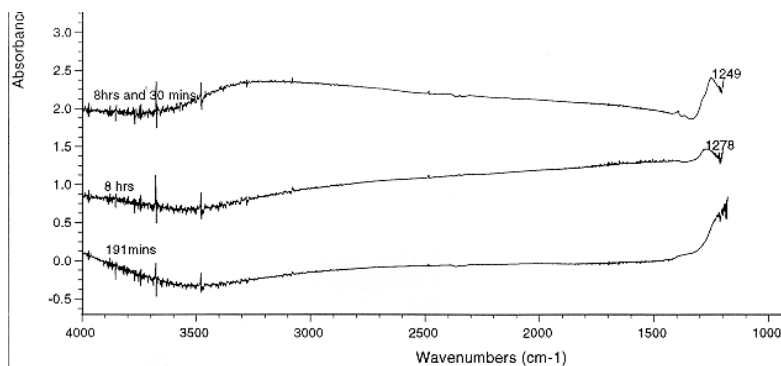


Figure 11. Twenty-four hour sulfation test in presence of H_2O on 5% $\text{V}_2\text{O}_5/\text{TiO}_2$ (V7TH; see Table 2).

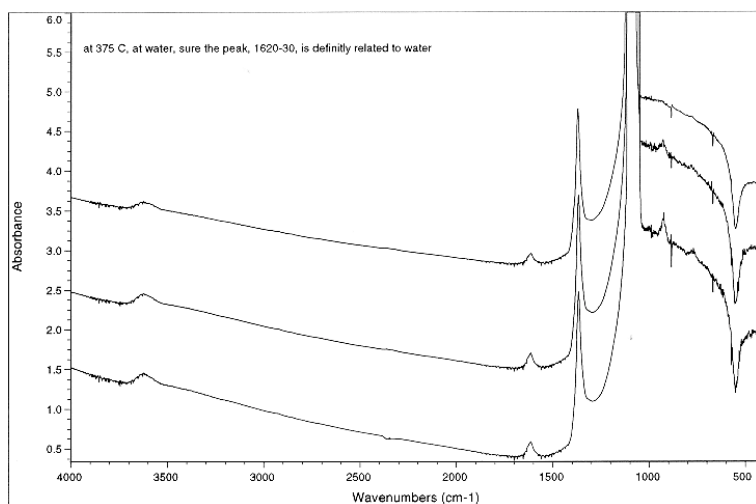


Figure 12. Test of 1375 cm^{-1} peak changes to 1620 cm^{-1} peak in presence of water.

Vanadyl Sulfate and Vanadium Sulfate Reference spectra of two likely sulfate species of vanadium (vanadyl sulfate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$) and vanadium (III) sulfate ($\text{V}_2(\text{SO}_4)_3$)) provide information on peak location and its sensitivity to vanadium oxidation state/sulfate structure. Literature spectra for pure samples of these compounds provide ambiguous results, including inconsistencies between figure labels and compound formulas. Therefore, we obtained reagent grade materials of pure components and developed our own reference spectra.

Pure vanadyl sulfate spectra as measured by our system appear in Figure 13. No peak appears at 1375cm^{-1} , although a peak at $\sim 1670\text{cm}^{-1}$ is detected, which is $\sim 50\text{cm}^{-1}$ higher than the 1620cm^{-1} which has been correlated with the 1375cm^{-1} peak in our previous reports. While these results are preliminary, the early indication is that vanadyl sulfate compound predicted by bulk equilibrium to be the most stable under these conditions does not have a peak at 1375cm^{-1} . If this is the compound that forms on the surface in the presence of SO_2 , this observation resolves the apparent discrepancies between the XPS and FTIR results. In addition, the $\text{V}=\text{O}$ overtone bands at 2025cm^{-1} and 1995cm^{-1} were detected, although they are not strong, which could indicate that the vanadium is not entirely sulfated in this reagent-grade material.

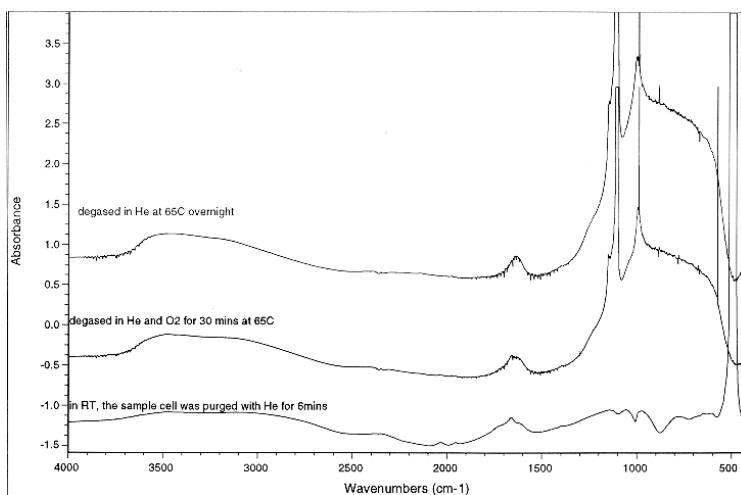


Figure 13. Spectrum of vanadyl sulfate.

Similar tests on pure vanadium (III) sulfate are currently underway and are expected to render a classical sulfate peak at 1375cm^{-1} .

Mass Spectroscopy A power surge in the building rendered the mass spectrometer inoperable. The spectrometer was not protected by a surge protector, which has since been corrected. The mass spectroscopy detector was checked by the manufacture. No damage was found although contamination was observed. The equipment has been returned and reinstalled and is currently operable again.

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.

The CEM system ordered from Horiba Instruments arrived this quarter. The system is designed around a seven-point sequential monitoring system to measure ppm levels of NO_x and percent levels of O₂ at selectable points on the SCR reactor. Each sampling point is 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 exits the heated valve module and enters 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 control system.

AEP Rockport has agreed to host the first test. In a parallel effort, we have proposed to make mercury oxidation measurements across the catalysts at the start of the field test. Pending approval from DOE, we will begin the mercury measurements next quarter.

The Rockport plant consists of two 1300 MW_e B&W opposed wall-fired boilers. These are supercritical boilers that burn a blend of bituminous and subbituminous coals. The average mix is 87% Powder River Basin sub-bituminous and 13% bituminous coal. 100% PRB is burned during off-peak periods and on weekends when the unit is not expected to be required to operate at full load. The bituminous coal is expected to be primarily from East Kentucky area although Colorado/Utah coal may be purchased if the economics are favorable.

During this quarter, the plant installed inlet and outlet ports for the reactor on Unit 1. The inlet port is located just upstream of the air heater. The outlet port is located downstream of the air heater.

Results and Discussion

SCR Catalyst: Various subsystems of BYU's Catalyst Characterization System (CCS) were upgraded this quarter. A new calibration system for the CEMs was installed, allowing for faster calibration and, it is hoped, reduction of drift in the ammonia analyzer. The valving on the gas chromatograph has been updated, but more work may have to be done. The control system for the CCS is in the process of being modified. Work on the CCS hardware and software will continue in the coming quarter. A preliminary test matrix of poisoning experiments in the CCS has been drafted. Temperatures and poisoning levels have not yet been determined, but will be specified after several preliminary runs have been conducted which will establish baseline performance of the clean catalyst. During our experiments we will explore the effects of at least three poisons: sodium, potassium and calcium. We may also explore the effect of arsenic, if this can be carried out in a safe manner. The full design will consist of 64 experiments, requiring approximately 15 weeks to complete.

Previous *in situ* reactivity data indicated that titania sulfates under SCR conditions, but there was no evidence of vanadia sulfate forming based on the peaks reported in the literature as indicative of vanadium sulfation. During this quarter, we attempted to resolve these issues. Modifications were made to the XPS analysis procedure that allowed analyses of uncrushed samples. XPS analyses of uncrushed wafers or pellets rendered clear indications of sulfation in all cases, qualitatively consistent with the FTIR results. However, the XPS-indicated fractions of vanadium, sulfur, and titanium on the surface were only qualitatively consistent with the bulk analyses. Although the XPS and FTIR results are now more consistent in that both indicate that the surface is sulfating (unlike the results reported last quarter), they disagree with respect to which species sulfates. We also noted that the FTIR signal from a surface compound thought to be the product of sulfation of vanadium was sensitive to the presence of water in the gas stream; there appeared to be reversible adsorption/desorption of water occurring at this sulfate site. Water is an integral part of the SCR reaction, and clearly has a major affect on the sulfate peak heights. This is important for future interpretation of FTIR spectra but it is not an explanation for the anhydrous data in which increasing vanadium concentrations decreased sulfate peak height. This latter trend may be explained by the next series of experiments.

The CEM system for the multi-catalyst slipstream reactor arrived this quarter. Minor modifications to the reactor and control system were completed. The plant installed inlet and outlet ports for the reactor. The reactor will be shipped to AEP Rockport plant next quarter for shakedown and installation. In a parallel effort, we have proposed to make mercury oxidation measurements across the catalysts at the start of the field test. Pending approval from DOE, we will begin the mercury measurements next quarter.

Conclusions

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

- Various subsystems of BYU's Catalyst Characterization System (CCS) were upgraded this quarter. Work on the CCS hardware and software will continue in the coming quarter.
- A preliminary test matrix of poisoning experiments in the CCS has been drafted that will explore the effects of at least three poisons: sodium, potassium and calcium. We may also explore the effect of arsenic, if this can be carried out in a safe manner. The full design will consist of 64 experiments, requiring approximately 15 weeks to complete.
- Previous *in situ* reactivity data indicated that titania sulfates under SCR conditions, but there was no evidence of vanadia sulfate forming based on the peaks reported in the literature as indicative of vanadium sulfation. During this quarter, we attempted to resolve these issues. Modifications were made to the XPS analysis procedure that allowed analyses of uncrushed samples. Although the XPS and FTIR results are now more consistent in that both indicate that the surface is sulfating (unlike the results reported last quarter), they disagree with respect to which species sulfates.
- We also noted that the FTIR signal from a surface compound thought to be the product of sulfation of vanadium was sensitive to the presence of water in the gas stream; there appeared to be reversible adsorption/desorption of water occurring at this sulfate site.
- The CEM system for the multi-catalyst slipstream reactor arrived this quarter. Minor modifications to the reactor and control system were completed.

Plans for the next quarter include: completion of modifications to the CCS at BYU and the beginning of poisoning experiments; continuation of *in situ* studies of surface compounds on SCR catalyst; completion of the control system of the field reactor, shipment to the Rockport plant and shakedown in the field. In a parallel effort, we have proposed to make mercury oxidation measurements across the catalysts at the start of the field test. Pending approval from DOE, we will begin the mercury measurements next quarter.

Literature References

Cremer, M.A., Adams, B.R., Boll, D., O'Connor, D., and Slaff, R.D., "Demonstration of Rich Reagent Injection for NO_x control in Ameren's Sioux Unit 1", presented at the 19th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 24-26, 2002.

Davis, K.A., Linjewile, T. and Cox. W., "Prediction and Real-Time Monitoring Techniques for Corrosion Characterization in Furnaces", presented at the 19th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 24-26, 2002.

Davis, K.A., Linjewile, T. and Cox. W., "Evaluation of an On-line Technique for Corrosion Characterization in Boilers" presented at the *3rd International Workshop on Life Cycle Issues in Advanced Energy Systems* held June 10-12, 2002 in Woburn, England.

Appendix: SCR CCS experimental design

T1 and T2 indicate two different (as yet undetermined) temperatures. Poisons and poisoning levels are similarly abbreviated.

Run Number	Temperature	Poison/Level	Poison/Level	Run Number	Temperature	Poison/Level	Poison/Level
1	T1	As1	Na1	33	T1	As4	Na4
2	T1	K1		34	T2	Na3	
3	T2	Na1		35	T1	As1	Ca2
4	T1	As4	Ca3	36	T1	As1	
5	T2	Na2		37	T1	As3	Ca4
6	T1	As3	Ca2	38	T1	Ca3	
7	T1	As1	Ca4	39	T1	As1	Ca1
8	T1	As2	Ca2	40	T2	As2	
9	T1	As3		41	T1	As2	Ca4
10	T1	As2	Na2	42	T1	As4	Na2
11	T1	As3	Ca3	43	T1	As1	Na4
12	T1	Ca4		44	T1	As1	Na3
13	T2	Ca1		45	T1	As2	
14	T1	As2	Na3	46	T2	As3	
15	T1	As1	Na2	47	T1	As1	Ca3
16	T1	Na2		48	T1	K2	
17	T2	K1		49	T2	Ca3	
18	T1	As4	Na1	50	T1	As4	
19	T1	As4	Ca1	51	T1	As3	Ca1
20	T1	Na3		52	T1	As3	Na1
21	T1	As2	Na3	53	T2	Na4	
22	T2	K2		54	T2	Ca4	
23	T1	Ca2		55	T1	As2	Ca1
24	T2	Ca2		56	T1	Na1	
25	T1	As3	Na2	57	T2	K4	
26	T1	As2	Ca3	58	T1	As4	Ca4
27	T1	K4		59	T1	As4	Na3
28	T1	As3	Na4	60	T2	As4	
29	T1	Na4		61	T1	K3	
30	T1	Ca1		62	T1	As2	Na4
31	T1	As4	Ca2	63	T2	As1	