

NO_x Control Options and Integration for US Coal Fired Boilers

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Abstract

This is the eleventh 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 boilers 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.

During this quarter, FTIR experiments for SCR catalyst sulfation were finished at BYU and indicated no vanadium/vanadyl sulfate formation at reactor conditions. Poisoned catalysts were prepared and tested in the CCS. Poisoning with sodium produced a noticeable drop in activity, which was larger at higher space velocity. A computer code was written at BYU to predict conversion along a cylindrical monolithic reactor. This code may be useful for monolith samples that will be tested in the laboratory. Shakedown of the slipstream reactor was completed at AEP's Rockport plant. Ammonia was connected to the reactor. The measurement of O₂ and NO_x made by the CEMs corresponded to values measured by the plant at the economizer outlet. Excellent NO_x reduction was observed in preliminary tests of the reactor. Some operational problems were noted and these will be addressed next quarter.

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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, 2003.

Our program contains five major technical tasks:

- evaluation of Rich Reagent Injection (RRI) for in-furnace NO_x control
- demonstration of RRI technologies in full-scale field tests at utility boiler
- 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 successful initial field tests of the RRI technology and the corrosion monitor.

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

- During this quarter, BYU completed *in situ* FTIR experiments indicating no vanadium/vanadyl sulfate formation at reactor conditions.
- Poisoned catalysts were prepared and tested in the CCS. Data were collected from four reactors simultaneously showing the effect of space velocity on apparent catalytic activity. Remarkably high activity (between 17 and 96 mL/g-s) and conversions of 75-100% at very high space velocities were observed for all three catalysts. Poisoning with sodium produced a noticeable drop in activity, which was larger at higher space velocity.
- A computer code was written at BYU to predict conversion along a cylindrical monolithic reactor. This code may be useful for monolith samples that will be tested in the laboratory.
- Shakedown of the slipstream reactor was completed at AEP's Rockport plant. Ammonia was connected to the reactor. The measurement of O₂ and NO_x made by the CEMs corresponded to values measured by the plant at the economizer outlet. Excellent NO_x reduction was observed in preliminary tests of the reactor. Some operational problems were noted and these will be addressed next quarter.
- Mercury speciation measurements were made across the SCR catalyst as part of another DOE-sponsored program.

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

The slipstream reactor designed to test the deactivation of SCR catalysts in the field is operational and collecting data at the AEP Rockport plant. Further details are provided below in the section describing the accomplishments for Task 4.

During the last performance period, a series of measurements for mercury oxidation across the catalyst section within the slipstream reactor were performed with boiler operating at full load. These tests were performed under separate funding from DOE (Cooperative Agreement DE-FC26-03NT41728) and thus the results of these tests will be reported elsewhere.

Industry Involvement

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

- A podium presentation entitled “Application of Soot Model to a Pulverized Coal-fired Boiler,” was presented at the Advanced Combustion Engineering Research Center (ACERC) Conference, held February 20-21, 2003 at Brigham Young University, Provo, Utah, USA. The paper provided detailed explanations of the soot model and implementation of the model into a CFD code. Also included were comparisons between predicted and measured values for soot when firing coal in the University of Utah L1500 (5 mmBtu/hr) Pilot Scale Test Furnace [Shim et al, 2003b].
- Two posters were also presented at the ACERC conference at University of Utah, February 20, 2003:
 - “Sulfation Study of Vanadia Catalyst by In Situ FTIR.” Principal author was Xiaoyu Guo.
 - “BYU SCR Laboratory Poisoning Study of $V_2O_5/WO_3/TiO_2$ Catalyst.” Principal authors were Seth Herring and Aaron Nackos.
- A paper entitled “Modeling The Impacts Of Soot From Low- NO_x Combustion Systems” was presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems, March 10-13, 2003 in Clearwater, Florida, USA [Shim et al, 2003a]. The paper contained an overview of our CFD based model for soot generation and destruction for coal combustion and included a comparison of predicted and measured values for soot in the University of Utah pilot scale test furnace and a study of the impact of including soot in simulations of a full scale coal fired utility boiler that uses a low NO_x firing system.

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- A podium presentation entitled “Selective Catalytic Reduction and Low Rank Fuels” presented at the *EPRI Biomass Interest Group*, held on February 4, 2003, Gainesville, FL, USA. The presentation emphasized the impacts of using low rank fuels for utility boiler applications and included a lengthy discussion of the slipstream reactor that has been developed within this program [Davis, 2003].
- A poster presentation entitled “Improved Rich Reagent Injection (RRI) Performance for NO_x Control in Coal Fired Utility Boilers,” has been accepted for presentation at the 2003 DOE-EPRI-EPA-AWMA Combined Power Plant Air Pollution Control Mega Symposium to be held May 19-22, 2003 in Washington, DC [Cremer et al, 2003]. The poster will highlight the use of RRI for reducing NO_x emissions for coal-fired, electric utility cyclone barrel fired furnaces. Previous demonstrations of RRI have shown 30% NO_x reduction. Recent modeling studies for two furnaces predict 55-60% NO_x reductions are achievable.

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 were described in more detail in the Technical Quarterly Report for July through September 2002. 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 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, *in situ*, spectroscopic experiments partially reported last quarter were completed. The most significant finding of these investigations is a consistent indication that vanadium does not sulfate during SCR activity in the presence of gas-phase SO₂ while both the substrate (anatase) and modifiers (molybdenum) do. In addition, mass-spectroscopy-based analyses of product gases from this reactor system are being completed that will allow analysis of fundamental kinetics and deactivation mechanisms.

FTIR Study of Vanadia Catalyst Sulfation

ISSR Overview

The purpose of the FTIR-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.

Catalyst Sulfation Experiments

FTIR experiments for SCR catalyst sulfation were finished. Some conclusions were made, which were reported in last quarterly report. However, the quality of those figures was not good enough. Therefore, a plot-editing software package called Igor ProTM was learned and applied to the FTIR spectra. The FTIR figures (Figure 1 to Figure 6) edited by Igor are shown below and referenced to experiments listed in Table 1.

A series of twenty-four hour sulfation experiments on titania, a 2% vanadia on titania catalyst, and a 5% vanadia on titania catalyst provided data that are largely consistent with literature data. These experiments focused on the extent of vanadia and titania sulfation in an SO₂-laden, moist environment. All experiments included oxidizing, SO₂-laden environments (nominal 5% oxygen and 0.23% SO₂) and varied from dry to moist (nominal 2.5% moisture) flows. All samples were pre-oxidized in SO₂-free flows. Details of these sulfation experiments are listed in Table 1. Both *in situ* FTIR spectroscopy analyses and XPS analyses provided data regarding the extent of surface sulfation, as summarized in Table 2. In addition, TEM analysis was conducted on the 2% vanadia catalyst, which provided a measure of catalyst particle size.

Sulfation of pure TiO₂ with a moist, SO₂-laden gas under conditions typical of SCR operation provides a baseline comparison for experiments involving sulfation of vanadia catalysts. Based on *in situ*, real-time FTIR analyses, steady-state sulfation was reached in about 5 h at conditions of 35-50 sccm, 370-390°C, and 0.2-0.3% SO₂. Nevertheless, sulfation experiments were continued for an additional 19 hours (a total of 24 h), since literature data for similar catalysts and conditions indicate that 18-24 h may be required for complete sulfation.

IR spectra of the sulfated catalysts include one major sulfate-related feature with a doublet located near 1375 cm⁻¹ (see Figure 1 and Figure 2). It is unclear if these two peaks represent two

different sulfate complexes or two different vibrational/rotational modes for the same complex. Moreover, the peak positions shifted to higher frequencies with increasing time during the sulfation test, indicating increasing sulfate acidity with time/surface coverage.

Table 1. List of Sulfation Experiments

Sample Name	Sample Details	Notes	Gas Stream Composition, %				Flowrate (sccm)	Temp (°C)	Window Type	XPS Sample Type
			He	O ₂	SO ₂	H ₂ O				
V8TH	5% V ₂ O ₅ /TiO ₂	Preoxidation	95	5	0.28	0	50	380	KCl+CaF ₂	Pellet
	24hrs	Sulfation	95	4.8		2.4	52	380		
V8TO	5% V ₂ O ₅ /TiO ₂	Preoxidation	95	5	0.23	0	52	366-380	KCl+CaF ₂	Pellet
	24hrs	Sulfation	95	5.3		0	40	380		
V9TH	2% V ₂ O ₅ /TiO ₂	Preoxidation	90	10	0.23	0	50	377	KCl+CaF ₂	Pellet
	24hrs	Sulfation	93	4.9		2.2	40	380		
V9TO	2% V ₂ O ₅ /TiO ₂	Preoxidation	90	10	0.23	0	50	377	KCl+CaF ₂	Pellet
	24hrs	Sulfation	94	5.3		2.4	40	370-390		
TiO ₂ -H	Pure TiO ₂	Preoxidation	90	10	0.23	0	50	385	KCl+CaF ₂	Pellet
	24hrs	Sulfation	93	4.9		2.2	40	380		
TiO ₂ -O	Pure TiO ₂	Preoxidation	90	10	0.23	0	50	385	KCl+CaF ₂	Pellet
	24hrs	Sulfation	94	5.7		0	40	380		

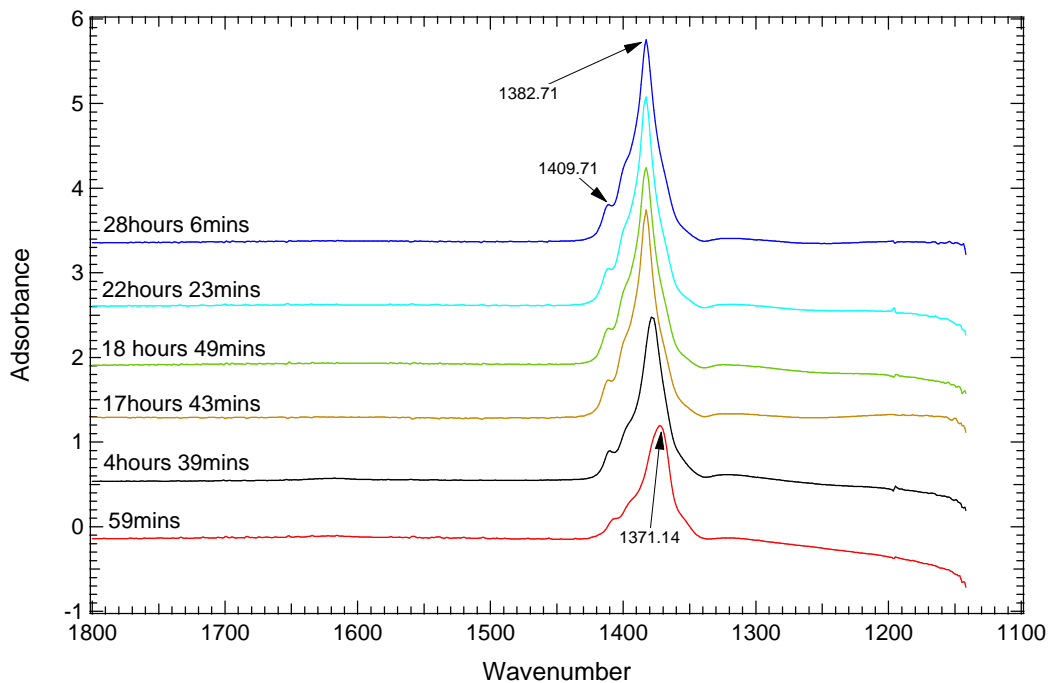


Figure 1. Time-dependent, *in situ* FTIR spectra of an anatase (titanium) substrate exposed to a dry but otherwise typical vitiated gas (see TiO₂-O in Table 1 for details of experimental conditions). Ordinate is offset for each time.

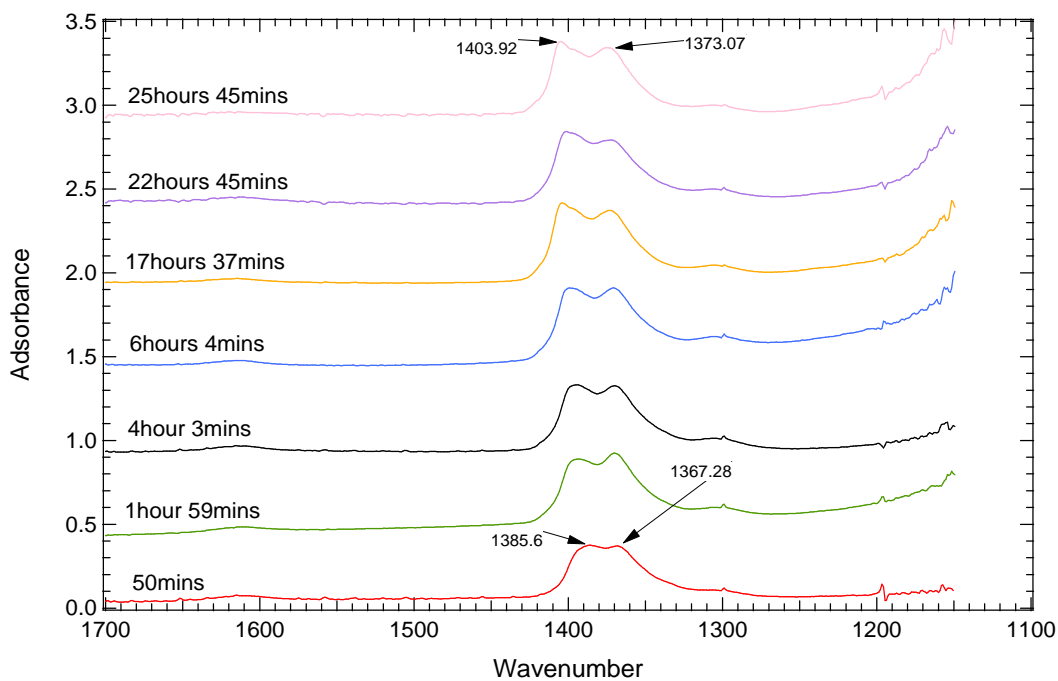


Figure 2. Time-dependent, *in situ* FTIR spectra of an anatase (titanium) substrate exposed to a dry but otherwise typical vitiated gas (see TiO₂-H in Table 1 for details of experimental conditions). Ordinate is offset for each time.

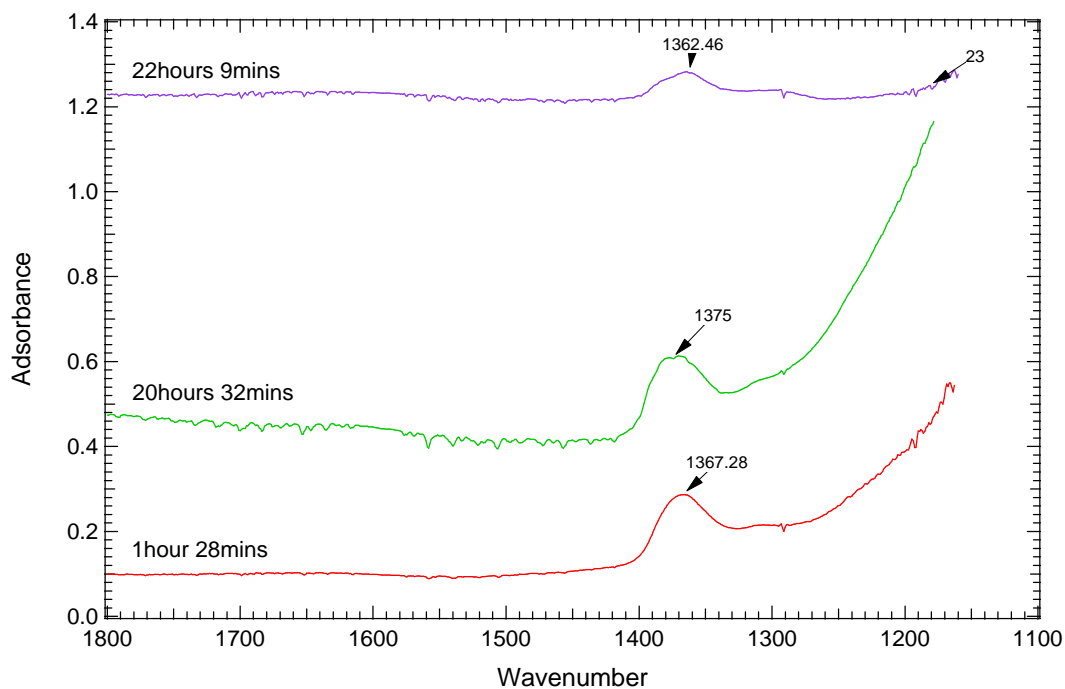


Figure 3. Time-dependent, *in situ* FTIR spectra of a 5% vanadium catalyst exposed to a typical vitiated gas (see V8TO in Table 1 for details of experimental conditions). Ordinate is offset for each time.

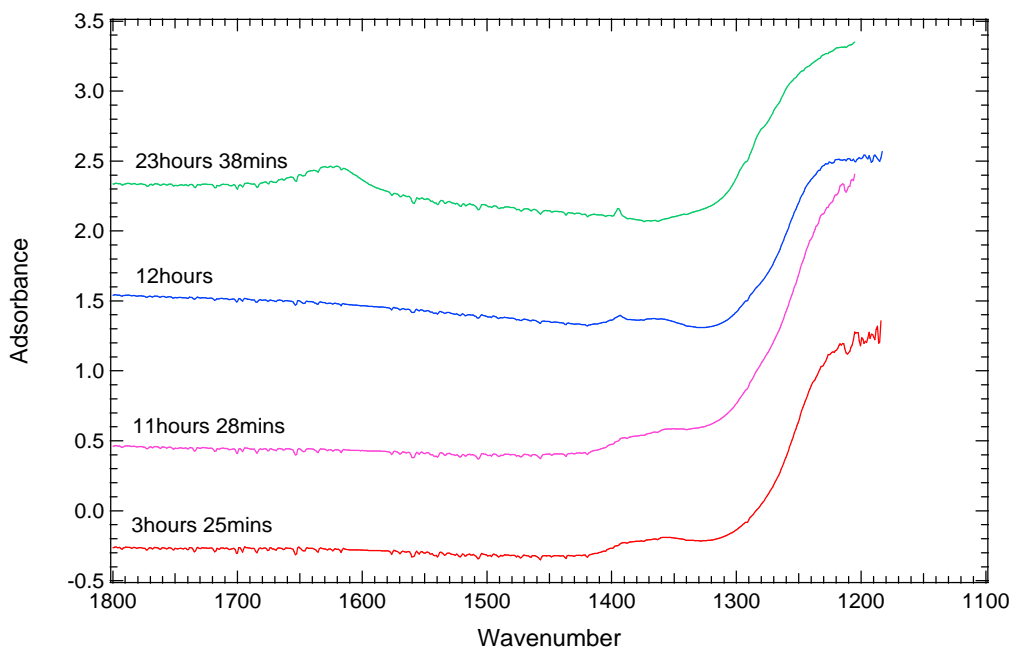


Figure 4. Time-dependent, *in situ* FTIR spectra of a 5% vanadium catalyst exposed to a typical vitiated gas (see V8TH in Table 1 for details of experimental conditions). Ordinate is offset for each time.

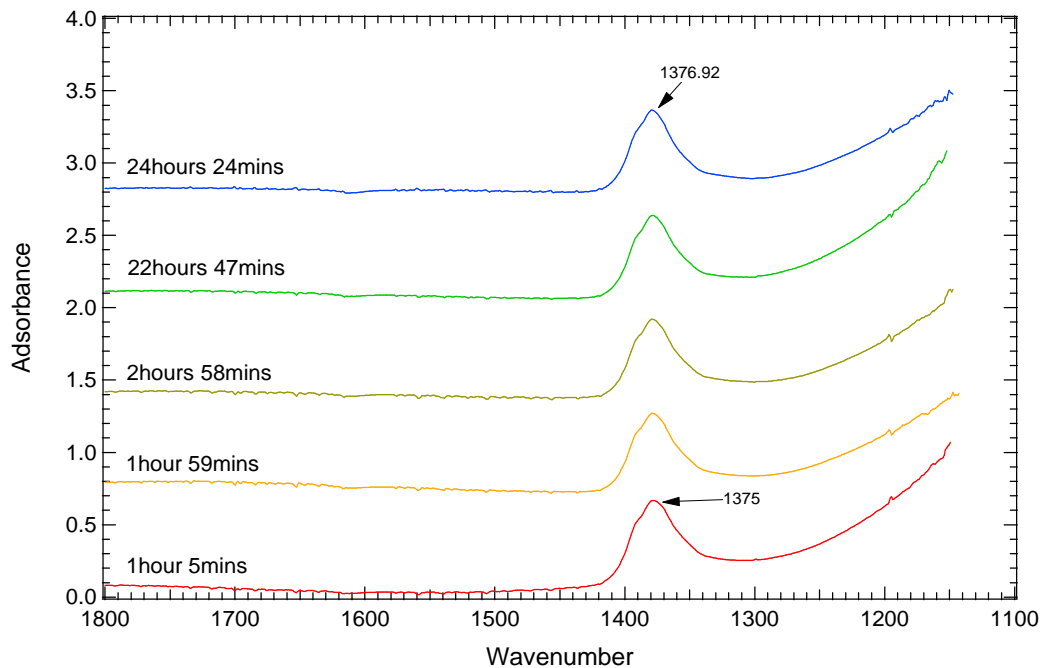


Figure 5. Time-dependent, *in situ* FTIR spectra of a 2% vanadium catalyst exposed to a typical vitiated gas (see V9TH in Table 1 for details of experimental conditions). Ordinate is offset for each time.

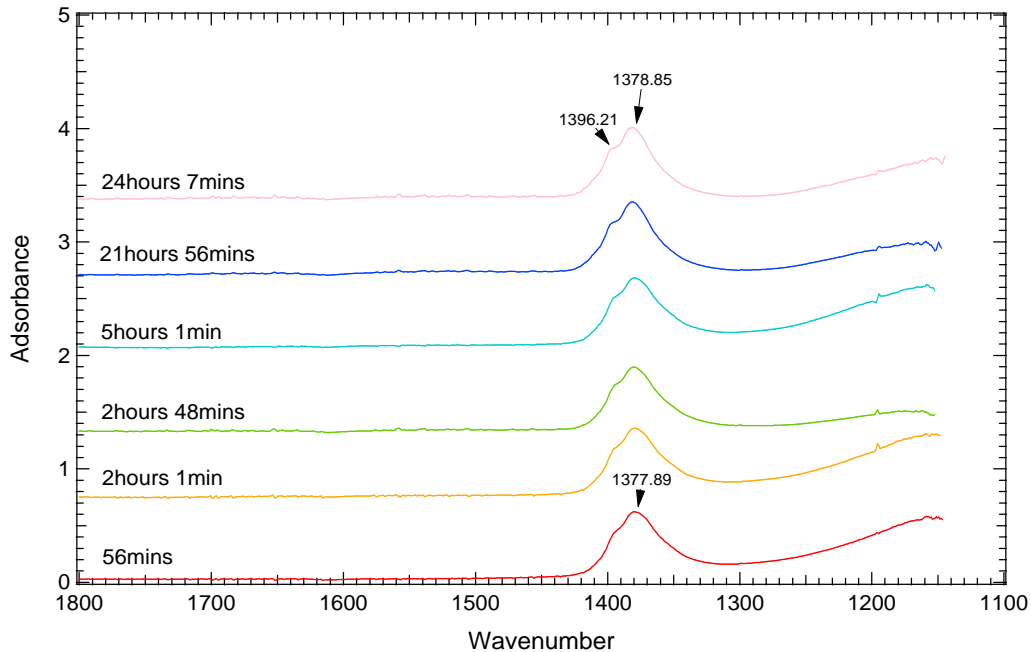


Figure 6. Time-dependent, *in situ* FTIR spectra of a 2% vanadium catalyst exposed to a typical vitiated gas (see V9TO in Table 1 for details of experimental conditions). Ordinate is offset for each time.

The sulfate doublet intensity decreases with increasing vanadia content for all sulfation tests in the range of 0-5% vanadia, including sulfation conducted with no initial gas-phase moisture (compare Figure 1, Figure 3, and Figure 5) and moist sulfation (compare Figure 2, Figure 4 and Figure 6). The feature at 1370-1375 cm^{-1} in the FTIR spectra represents an S=O stretching of sulfate species on the catalysts surface and is only mildly influenced by the cation of the sulfate species.

Others, [Amiridis, Wachs et al. 1996; Dunn, Jehng et al. 1998; Jung and Grange 2000], have observed the same trend of decreasing FTIR intensity with increasing vanadia concentration. Jung suggested that the S=O structure is prerequisite to the generation of acidic sites on sulfate-promoted oxide samples and that a decreasing S=O surface concentration with increasing sulfur content on the surface could be due to the generation of polynuclear sulfate species at the expense of isolated sulfate species. However, further analyses of these same samples indicate that the S=O stretching peak height observed in these FTIR spectra is proportional to sulfur concentrations measured by XPS techniques (see Table 2). Moreover, no other identifiable sulfur forms are detected by IR spectroscopy in our experiments.

Both Dunn and Amiridis indicate that formation of sulfate species on the surface of vanadia catalysts is not favored. Dunn observed that the surface concentration of sulfate species, as reflected by the intensity of the 1373 cm^{-1} band, dramatically decreases with increasing coverage of the surface vanadia species and that the molecular structure of the surface vanadia species was only slightly perturbed by the presence of sulfur. They also concluded that surface sulfate species adsorb on the most basic support hydroxyl species. However, Choo [Choo, Lee et al. 2000] concluded that surface vanadate species titrate both basic and neutral support hydroxyls, forming a complete close-packed monolayer. Amiridis et al. speculated that their observed decrease in sulfate species with surface vanadia concentration might derive from a repulsive interaction between vanadyl and sulfate species. Moreover, their ICP analysis was consistent with a decrease in surface sulfate with increasing surface vanadia.

Results of X-ray photoelectron spectroscopy (XPS - sometimes called ESCA) analyses for six samples after 24-hour exposure to dilute SO_2 (three in the absence and three in the presence of water vapor) appear in Table 2. XPS is an approximately 30-year-old analytical technique that measures photoelectron energies emitted from atoms irradiated with soft X-ray photons (1 - 2 keV). Analytical capabilities of solid-state XPS include high (and variable) structural sensitivity on the outermost solid surface, qualitative chemical characterization of such structures, and reasonable quantitative elemental characterization. XPS provides large quantities of reliable information with straightforward interpretation and represents one of the most fundamental tools of surface science. The third column of the table identifies the element and its electronic orbital analyzed by XPS in these investigations. The table indicates the composition of surface and near-surface layers on the exterior of catalyst particles. The observed surface concentrations of vanadia on the 2% samples of 2.1 and 2.4% are approximately the same as the nominal bulk concentration (i.e., 2%), while surface vanadia concentrations in the 5% samples (3.3% in both cases) are less than in the bulk, although they are still higher than in the 2% vanadia samples. These discrepancies at the 5% level may represent real sulfated surface vs. bulk composition differences or may be instrumental artifacts – an issue still under investigation. However, the conclusions with respect to sulfur are clear.

Table 2. XPS analysis results

	Sample	Elements	B.E.	% Atom
V8TO	5% V Sulfation without water	C-1s	280.623	24.2
		O-1s	529.609	56.0
		S-2p	164.081	1.5
		Ti-2p	453.81	16.5
		V-2p ^{3/2}	512.347	3.3
V8TH	5% V Sulfation with water	C-1s	281.215	5.3
		O-1s	529.601	65.8
		S-2p	164.762	2.8
		Ti-2p	454.354	20.2
		V-2p ^{3/2}	512.892	3.3
V9TO	2% V Sulfation without water	C-1s	281.252	8.3
		O-1s	529.99	67.7
		S-2p	165.225	2.1
		Ti-2p	455.909	20.9
		V-2p ^{3/2}	512.614	1.9
V9TH	2% V Sulfation with water	C-1s	285.23	10.1
		O-1s	530.86	65.2
		S-2p	169.48	2.4
		Ti-2p	458.95	20.2
		V-2p ^{3/2}	517.47	2.1
TiO ₂ -O	Titania Sulfation Without Water	C-1s	280.485	8.7
		O-1s	524.961	66.4
		S-2p	163.95	2.8
		Ti-2p	457.741	23.2
TiO ₂ -H	Titania Sulfation With Water	C1s	280	10.2
		O1s	525.48	70.7
		S2p	164.5	3.4
		Ti2p	458.95	15.6

Surface sulfur concentrations measured by XPS (coverages ranging from 1.5 to 3.3% of the exposed surface) are significant for all 6 samples. However, a general trend of linearly decreasing sulfur coverage with increasing vanadium content is apparent for samples sulfated in the absence and presence of water vapor (with the exception of a slight upturn in sulfur content for the sample of highest vanadium content generated with moist gas). The significantly higher surface sulfur contents for the samples sulfated in the presence of water vapor indicates that water apparently promotes accumulation of sulfur on both the titania support and vanadia catalyst.

Similar samples will be analyzed by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). TOF-SIMS measures atomic and molecular fragments generated by an ion beam tuned to remove as little as a single atomic layer of a solid surface. Secondary ions produced from typically short pulses of ion beams on the surface enter a flight tube of a time-of-flight mass spectrometer. The mass to charge ratio of such secondary ions determine their velocities and hence the residence time in the flight tube. The time-dependent detector signal at the end of the flight tube provides detection capabilities commonly ranging from 0-1000 Daltons (atomic mass units) with a resolution of about 10000. TOF-SIMS generates surface composition maps with submicron (typically 0.15 μm) resolution. Pulsed ion beams permit even dielectric surfaces to lose any accumulated charge between pulses and low-energy beams allow more quantitative and surface-sensitive analyses than is possible from XPS. TOF-SIMS results should be available next quarter for discussion.

Mass Spectrometer

Considerable energy and time were devoted to improving the sensitivity of the mass spectrometer (MS). The MS was bought about 5 years ago from Pfeiffer Vacuum and had sat unused for more than 1 year. The Pfeiffer QMS 200 includes a quadrupole separator and an EI ion source with both Faraday and SEM detectors. We have encountered problems since we tried to use this instrument to analyze SCR reaction products. Efforts to resolve problems have been made by contacting technical representatives at Pfeiffer and researchers in the Chemistry and Chemical Engineering Departments at BYU.

In our attempts to calibrate for NO, no signal could be detected for NO concentrations lower than 1.4%. However, the detection limit of this MS specified by the manufacture is 20 ppm. After consulting with our technical contact at Pfeiffer Vacuum and with professors and graduate students from Chemistry and Chemical Engineering on this problem, it was suggested that we (1) increase ion source current or the SEM voltage with the N_2 and O_2 signals of MS small than 10^{-7} mA and (2) improve vacuum. Better results were obtained after increasing the ion current from 1mA to 2 mA and SEM voltage from 900 to 1100V, although the MS could still not detect NO below 200 ppm. However, by decreasing the vacuum pressure from 5×10^{-6} Torr to 5×10^{-7} Torr, it was possible to detect about 45ppm of NO. At this point, we are ready to obtain a calibration line for NO.

Another abnormal result observed during MS analysis of NO was an unusually high concentration of N_2 and O_2 with their ratio closes to 4:1. After further comparing with the H_2O signal, which is about 1% of N_2 intensity, it was suggested that there might be a leak in the MS system. Accordingly, leak tests under vacuum conditions were conducted and a significant leak was discovered and fixed.

Mass flow controller calibration

Four mass flow controllers used in the FTIR-MS flow calibration lines were calibrated with a Gilian Gilibrator 2TM calibration device.

Catalyst Reactivity Studies

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. This system, described in detail in our last report, simulates industrial flows by providing a test gas with the following compositions: NO, 0.10%; NH₃, 0.1%; SO₂, 0.1%; O₂, 2%; H₂O, 10%; and He, 87.7%. Both custom and commercial catalysts are tested as fresh samples and after a variety of laboratory and field exposures under both steady and transient conditions.

The purpose of the CCS is to quantitatively determine deactivation mechanisms by measuring specific, intrinsic catalyst reactivity of custom (laboratory) and commercial catalysts under a variety of conditions. These catalysts will be impregnated with a variety of contaminants, including Ca, Na, and K. In addition, the CCS will characterize samples of catalyst from slipstream field tests to determine similar data and changes in characteristics with exposure. This quarter laboratory safety issues have been addressed. Mass flow controllers for the laboratory reactor system have been calibrated and fine-tuned. A computer code was written to predict conversion along a cylindrical monolithic reactor. This code may be useful for monolith samples that will be tested in the laboratory.

Advanced surface and composition analyses will be used to determine composition, pore size distribution, surface area, and surface properties (acidity, extent of sulfation, etc.).

Catalyst Poisoning Experiments

During this quarter, poisoned catalysts were prepared and tested. Data were collected from four reactors simultaneously showing the effect of space velocity on apparent catalytic activity. Reactor one was blank; it had no catalyst in it. Reactors 2, 3 and 4 contained catalyst samples, one fresh and two poisoned with sodium. Remarkably high activity (between 17 and 96 mL/g-s) and conversions of 75-100% at very high space velocities were observed for all three catalysts.

Catalyst Poisoning Procedure

A fresh VO_xWO₃/TiO₂ catalyst (prepared in the last quarter of 2002) was poisoned with sodium at several sodium to vanadium ratios: 0.2:1, 0.4:1, 0.6:1, 0.8:1, and 1:1. The catalyst was poisoned by impregnation according to the following procedure:

1. Weigh fresh catalyst.
2. Place enough sodium carbonate in a beaker to provide the desired weight ratio of sodium to vanadium.
3. Add 0.6 grams water per gram fresh catalyst to the sodium carbonate and stir vigorously until the solid is dissolved.
4. Add sodium carbonate solution drop wise to the fresh catalyst to incipient wetness.
5. Dry the resulting paste for approximately 24 hours at approximately 100 °C.

Preliminary Tests of Poisoned SCR Catalysts

Following the addition of poison to samples of the fresh catalyst, three samples were tested in the reactor system. Reactor 1 had no catalyst in it. Data gathered from Reactor 1 were used to monitor the feed conditions to all four reactors. Reactor 2 was loaded with 0.45 grams of fresh catalyst. Reactor 3 was loaded with 0.45 grams of catalyst poisoned with a sodium-to-vanadium ratio of 0.4:1. Reactor 4 was loaded with 0.45 grams of catalyst poisoned with a sodium-to-vanadium ratio of 0.8:1. All reactors were heated to approximately 350 °C and purged with helium prior to initiation of flow of the reaction gas mixture. When the reactors reached temperature, ammonia, oxygen and nitric oxide were introduced into the gas stream such that the composition was 2% O₂, 1500 ppm NH₃, and 1100 ppm NO. Excess ammonia was injected in order to ensure that NO was the limiting reactant.

The initial volume-based space velocity was 30,000 hr⁻¹ (based on a measured catalyst density of 1.285 g/cm³). After several hours, however, it was observed that the conversion of NO over the fresh catalyst at this space velocity was 100%, and nearly 100% over the poisoned catalyst samples as well. Space velocity was then increased to 45,000 hr⁻¹ in all four reactors. Conversion of NO was still very high over all three catalysts (see Figure 7). Since the flow system was not capable of sustaining higher space velocities in all four reactors simultaneously with the amount of catalyst that was used, space velocity was increased in each of the reactors individually and conversion was recorded.

Figure 7 shows the change in conversion as space velocity was increased for the three catalyst samples. Conversion of NO was 100% over the fresh catalyst until the space velocity reached 80,000 hr⁻¹. The NO conversion over the poisoned catalyst samples was below 100% at a space velocity of 30,000 hr⁻¹ and decreased as space velocity was increased beyond this point.

The data from the reactor with fresh catalyst and the data from the reactor with catalyst that had been poisoned with a 0.4:1 Na:V ratio show reasonable trends. The data from the third reactor, however, shows a sharp drop in conversion when the space velocity reaches 70,000 hr⁻¹. The cause of this drop is unknown, and further work will be conducted to determine if this result is real or simply an anomaly. It is suspected that it is an anomaly and that the trend of the last five points is accurate and that an unknown disturbance was the cause of error in the first three points.

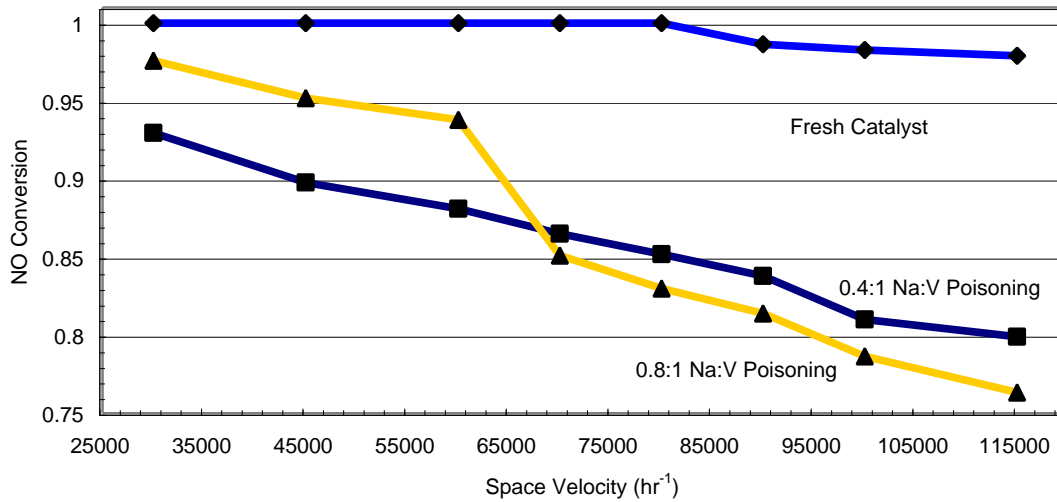


Figure 7. NO conversion over three catalyst samples over a range of space velocities.

The conversion data represented in Figure 7 were used to determine rate constants for the reaction over each of the three catalysts at various space velocities. It was assumed that the reaction was first order with respect to NO concentration and that the reactors behaved as ideal packed bed reactors. Expansion effects were ignored because the gas stream consisted of 97% inert gas. The rate constants were determined according to Equation (1):

$$k' = -\frac{\mathbf{n}_0}{W} \ln(1 - X_{NO}) \quad (1)$$

where k' is the rate constant, \mathbf{n}_0 is the gas flow rate, W is the weight of the catalyst sample, and X_{NO} is the observed conversion of NO. The results of this calculation are summarized in Table 3. The simplicity of the activity model predictably resulted in an increase in apparent rate constant with an increase in space velocity. The real rate constant should be constant with temperature, and a more complex model that accounts for mass transfer effects is being developed to determine catalytic activity with better accuracy.

Table 3. Results of rate constant calculation for catalyst NO conversion.

Sample	Space Velocity (hr ⁻¹)	Flow Rate (cm ³ /hr)	Conversion k' (cm ³ /gm/sec)	
Fresh	90,000	3.15x10 ⁴	0.987	84.49
	100,000	3.50x10 ⁴	0.983	88.08
	115 000	4.03x10 ⁴	0.979	96.04
Na:V, 0.4:1	30,000	1.05x10 ⁴	0.9296	17.21
	45 000	1.58x10 ⁴	0.8978	22.19
	60,000	2.10x10 ⁴	0.881	27.61
	70,000	2.45x10 ⁴	0.865	30.30
	80,000	2.80x10 ⁴	0.852	33.04
	90,000	3.15x10 ⁴	0.838	35.41
	100,000	3.50x10 ⁴	0.81	35.90
	115 000	4.03x10 ⁴	0.799	39.89
	Na:V, 0.8:1	30,000	1.05x10 ⁴	0.976
45 000		1.58x10 ⁴	0.952	29.54
60,000		2.10x10 ⁴	0.938	36.07
70,000		2.45x10 ⁴	0.851	28.81
80,000		2.80x10 ⁴	0.83	30.64
90,000		3.15x10 ⁴	0.814	32.72
100,000		3.50x10 ⁴	0.7864	33.37
115 000		4.03x10 ⁴	0.7634	35.83

Mass Flow Controller Performance Assessment

The performance of the CCS mass flow controllers (MFC's) was analyzed by measuring their actual flow rates with a Gilian GilibratorTM bubble column. At the same set points, actual flow rates were found to be somewhat inconsistent from MFC to MFC; Figure 8 and Figure 9 display these results. Since there are four MFC's in parallel feeding four reactors, inconsistencies in their actual flow rates introduce variations in the concentrations of reactants fed into the reactors and compromise validity of the data. In order to conveniently monitor actual MFC flow and perform necessary calibrations, a LabviewTM program was written that automates valve switching, converts flow rates from standard to ambient conditions, etc. The front panel of this program is shown in Figure 10.

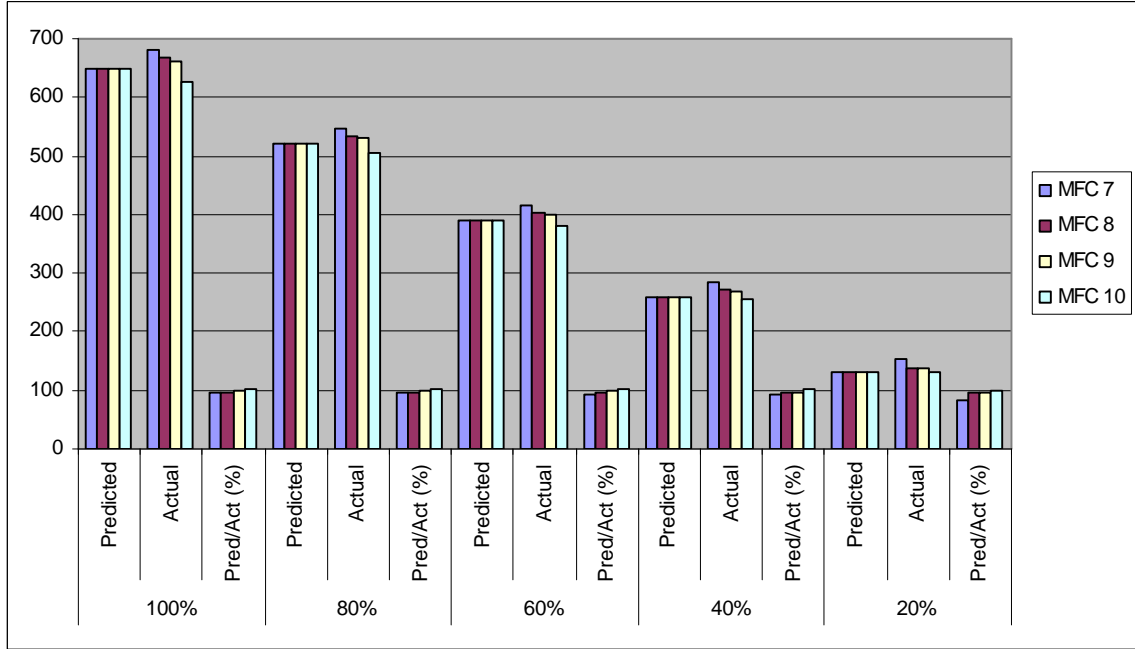


Figure 8. Deviations of MFC 7-10 flow rates from their set points at various rates of flow.

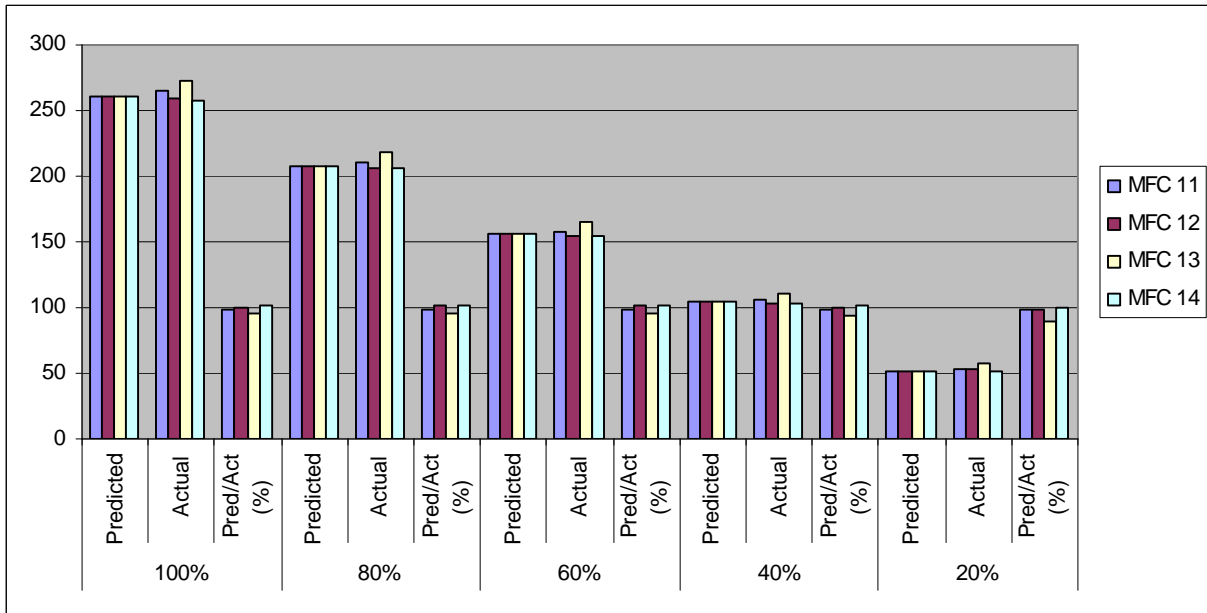


Figure 9. Deviations of MFC 11-14 flow rates from their set points at various rates of flow.

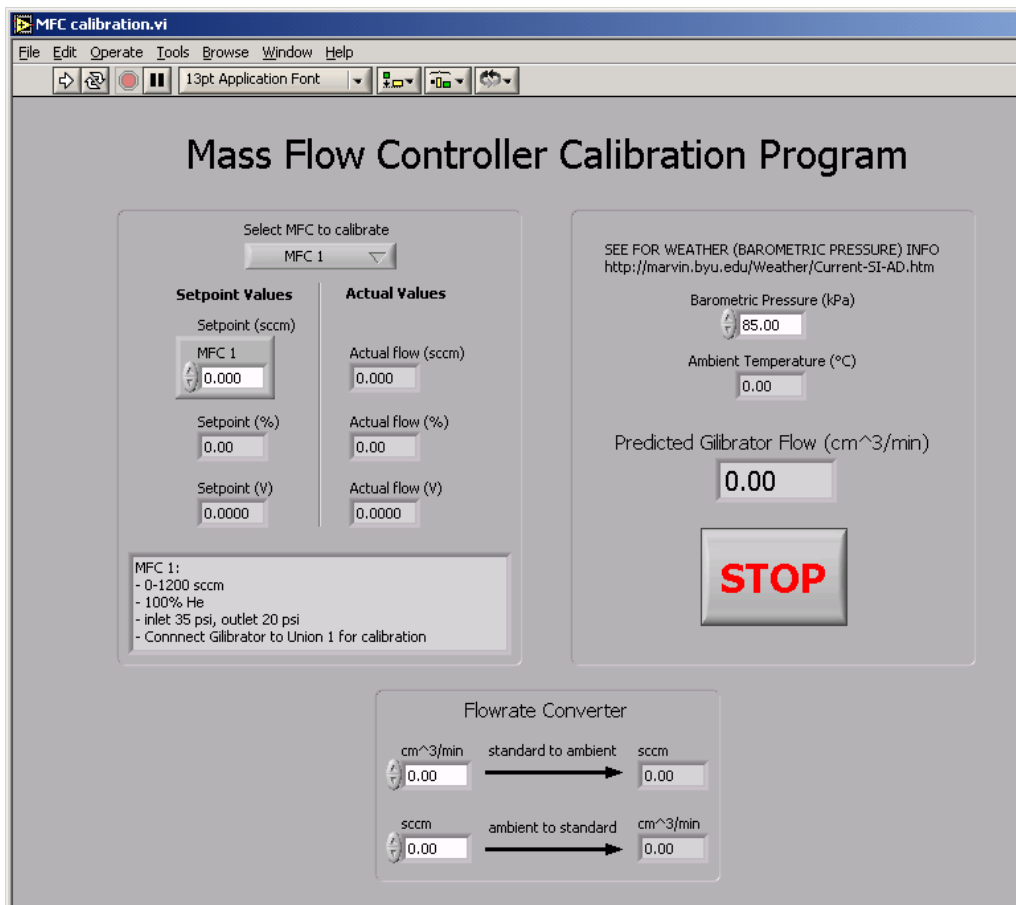


Figure 10. Screenshot of the front panel of the Labview™ MFC calibration program.

Literature Sorting and Organizing

Over the years the catalysis research group has accumulated many papers and other literature pertaining to SCR and SCR-related issues. Efforts to sort these papers according to categories or otherwise have been confusing as often an article may fall into several categories.

To address this problem, this research group has decided to store articles in a central location, sorting them by the first author's last name. The group has also adopted EndNote™, a software package that will store information about articles, reports, books, etc. Although the main purpose of EndNote™ is to create and format bibliographies automatically in a word processor document, it also doubles as a searchable database of the literature that we have. Additionally, the software can store electronic files, so that a hard copy need not be utilized. This group's literature information is currently being entered into EndNote™ as articles are utilized in papers. It is thus anticipated that over time many, if not most of our articles will be entered into an EndNote™ library.

Simple Computer Code to Model NO_x Conversion

Many models for selective catalytic reduction of NO_x can be found in the literature (Buzanowski and Yang 1990; Beeckman and Hegedus 1991; Tronconi and Forzatti 1992; Tronconi, Forzatti et al. 1992; Svachula, Ferlazzo et al. 1993; Andersson, Gabriellsson et al. 1994; Beretta, Orsenigo et al. 1998; Fu and Pereira 1998; Koebel and Elsener 1998; Roduit, Baiker et al. 1998; Snyder and Subramaniam 1998; Tronconi, Cavanna et al. 1998; Khodayari and Odenbrand 1999; Chae, Choo et al. 2000; Fontes, Byrne et al. 2003). These models vary in their levels of complexity as each treats the kinetics and mass transfer in different ways.

For purposes of contributing to the goals of this catalyst deactivation project, BYU has developed a simple computer code to predict conversion of nitric oxide through a cylindrical, single-channel of a monolithic catalyst whose inside wall is coated with an active catalytic phase. The code assumes that the conversion performance of a heterogeneous vanadia/titania monolithic catalyst can be closely approximated by a cylindrical monolith, whose geometry and transport properties are readily available and substantiated (See Figure 11). The model functions by dividing the cylinder length into multiple nodes (each is a shorter cylinder with the same diameter). It is assumed that each node behaves as a perfectly mixed chemical reactor (commonly referred to as a continuously-stirred reactor, or CSTR). The CSTR performance equation is given in Eq. (2), where W is the weight of catalyst, F_{A0} is the initial reactant feed rate (moles/time), $X_{A,out}$ and $X_{A,in}$ are dimensionless outlet and inlet reactant conversions of each node, and r_A is the reaction rate equation (moles/catalyst weight/time). The program solves for the outlet conversion ($X_{A,out}$) for each node, the final of which is the outlet conversion of the monolith. The model can accommodate expressions that relate catalyst deactivation to time as well as to position along the length of the catalyst. In this manner, the performance of the catalyst (including ammonia slip and NO conversion) can be predicted.

$$\frac{W}{F_{A0}} = \frac{X_{A,out} - X_{A,in}}{-r_A} \quad (2)$$

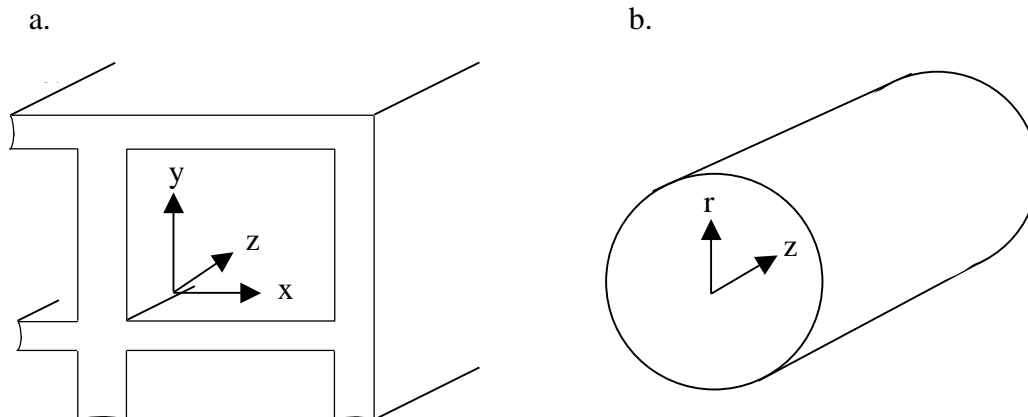


Figure 11. Cross-section view of a (a) monolithic catalyst (Farrauto and Bartholomew 1997) and (b) cylindrical approximation of a monolithic catalyst.

Advantages of this code include its simplicity and fast computer run time. Currently, it is written in MathcadTM and is thus easily altered. The code utilizes, however, many simplifying assumptions. Perfect radial mixing along the monolith is assumed. This is only true for highly turbulent flows, which are not present in the gas flow through actual monoliths. However, since diffusion of gases at high temperatures is fast on the small scale, this assumption may prove to be valid to some degree.

Task 4.2 Evaluation of Commercial Catalysts for Power Plant Conditions

The objective of this task is to evaluate SCR costs 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. This will be accomplished using a multi-catalyst slipstream reactor designed by the University of Utah. During this quarter, the slipstream reactor was started up at AEP's Rockport plant.

In January, following a meeting between REI and AEP plant officials, several issues were identified relating to ammonia safety training, the role of AEP plant personnel in the test program, insurance certificates, employee health and safety, subcontractor insurance, SCR reactor operating procedures and Host Site agreement. All the issues were resolved to the satisfaction of both AEP and REI and the Host Site agreement was signed.

In February, SCR reactor shakedown tests commenced. Some of the questions that needed to be answered during the shakedown tests were:

- Does the flue gas heat up the SCR sufficiently?
- Do the SCR heaters provide adequate heating?
- Can the SCR reactor maintain temperature at the set point value?
- Do we get the same NO_x and O₂ readings at the inlet and the outlet of the SCR?
- How do the analyzer readings compare with plant CEMs?
- How does the flow control perform at low flow rates?
- Is the ammonia manifold leak-proof?
- Are all the ammonia safety precautions in place?

The tests started with heating up the SCR reactor using the electrical heaters mounted around it. In stage one of the heat-up procedure, the SCR was heated electrically to 500°F with the flue gas inlet gate valve closed. The temperature of the flue gas at the economizer intake was 720°F. Upon opening the gate valve, the temperature of gases at the inlet of the SCR just before catalysts was 149° F. The unit was left running overnight. In spite of this, the temperature before catalysts did not improve. Initially it was thought that the flue gas temperature dropped due to heat losses to the 6" schedule 80 carbon steel standpipe leading into the SCR. It was then decided to troubleshoot for causes of the temperature drop using a variety of approaches. It was later discovered that the flue gas intake line to the SCR unit was blocked with ash in the duct wall region. This occurred after the plant was shut down for an outage, allowing ash to consolidate in the suction probe. Measures were taken to clear the blockage and flue gas flow into the SCR was established.

Other problems encountered during the shakedown tests included CEMS not receiving sample gases from the SEQUENCER, difficulties in controlling low flow rates through the SCR unit, blockage of the SCR chambers with ash at very low flow rates, leakage of the SCR unit at the top flange and plugging of sample line filters with ash. A summary of the shakedown test plan implemented is presented in the Appendix.

In March, most of the problems plaguing the SCR unit were resolved to make it operational for the planned catalyst deactivation tests and Hg tests. With most of the problems resolved, the ammonia supply system was turned on and tested. Figures 12 and 13 show the ammonia tanks being prepared for installation and their location in the Fan room after they have been connected to the ammonia manifold. By the end of March, initial tests with ammonia flow were conducted and mercury oxidation tests in the SCR were completed. The main catalyst deactivation tests will be continued in the next quarter. Efforts to settle some unresolved problems related to sealing of the SCR top, sample filter blockage and operation of the control system will also be continued in the next quarter.



Figure 12. Ammonia cylinders being prepared for hauling to the installation site.



Figure 13. Four 150-lb ammonia cylinders connected to the ammonia supply manifold in the Unit 1 Fan room.

Initial testing on the reactor focused on the ability to measure NO_x and O_2 using the CEM system. During these tests, Unit 1 was operating near full load and load was stable. Figure 14 compares data reported from the plant PI database (three-minute averages) of oxygen at the economizer outlet as compare with the inlet sample from the reactor CEM. Multiple oxygen probes are located in the economizer outlet ducts; we have chosen two for this comparison. The reactor CEM measurement, which is reported on a dry basis, has been corrected to 10% water. The reactor CEM measured O_2 concentrations that corresponded well to the plant PI data.

3/27/03 (00:00-12:00)

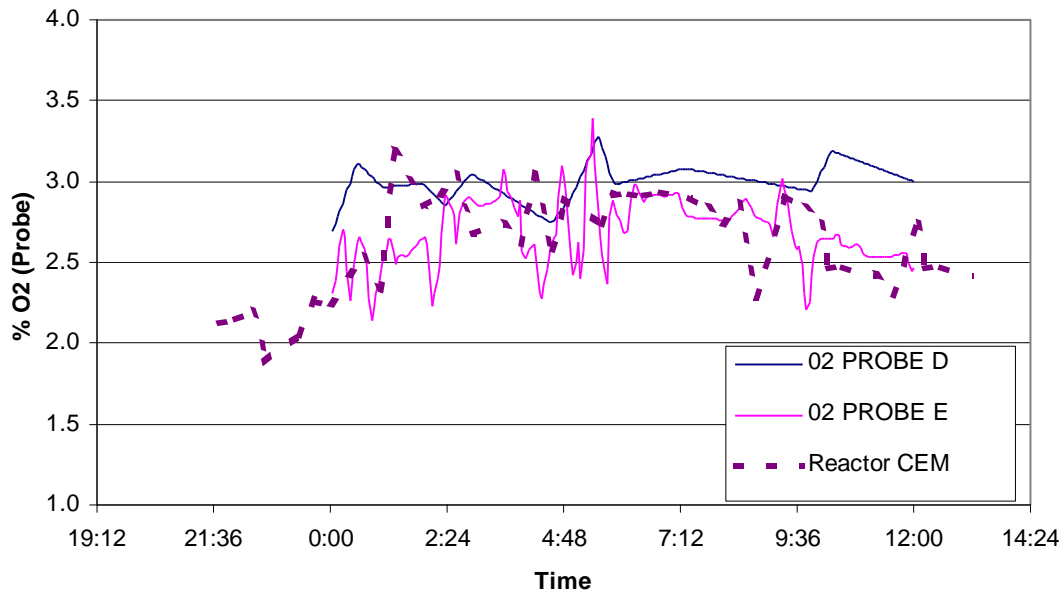


Figure 14. Oxygen at economizer outlet, Unit 1: Plant measurements (Probes D and E) compared with inlet value measured by SCR reactor CEM.

NO_x is not measured routinely by the plant at the economizer outlet. Plant PI data contain NO_x measured at the stack. The NO_x in the stack was lower than the NO_x measured by the reactor CEM by about 100 ppm (Figure 15). Previous testing at the plant of NO_x levels at the economizer outlet duct under full load conditions showed higher levels of NO_x , similar to the CEM values; these are also shown on the figure. Perhaps there is some stratification in the NO_x exiting the furnace. In any case, the reactor CEM produced NO_x measurements that corresponded to measurements made at the economizer outlet duct, even though these did not match the stack NO_x measurements.

3/27/03 (00:00-12:00)

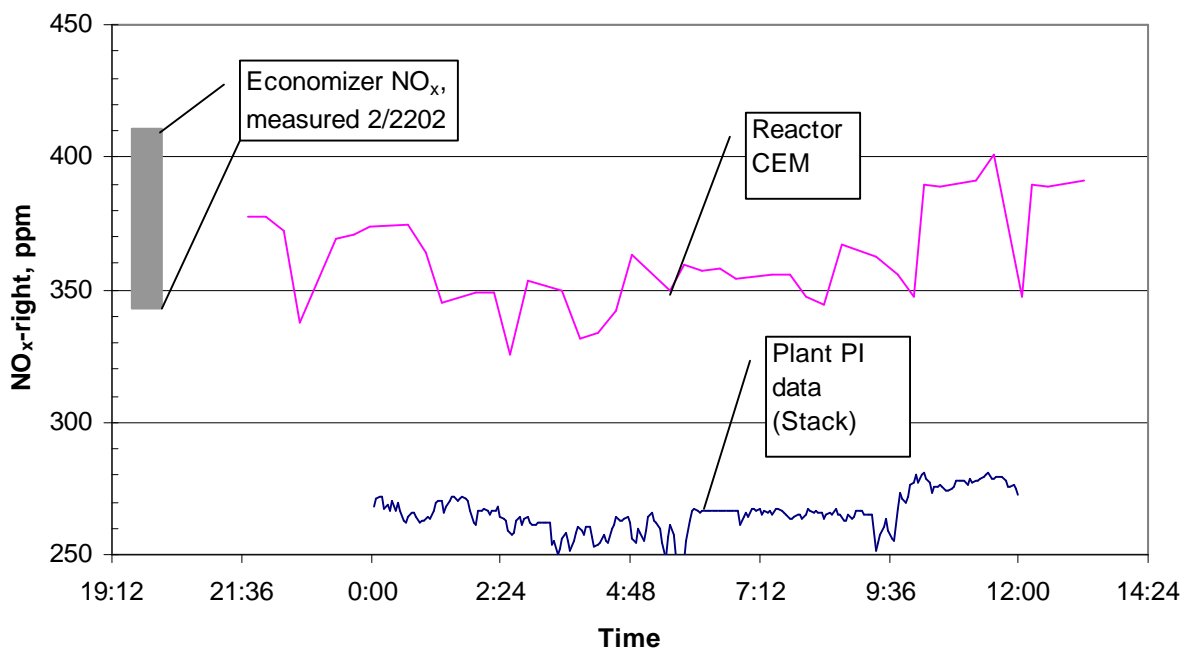


Figure 15. NO_x, Unit 1: Plant measurements at the stack compared with inlet value measured by SCR reactor CEM.

During the period March 25-April 3, 2003 specialized measurements were carried out on the reactor on mercury speciation, as reported in the quarterly technical report on another DOE program (Cooperative Agreement DE-FC26-03NT41728). At the conclusion of these tests, the CEM was brought on-line again to begin long-term deactivation testing.

Figure 16 shows the O₂ measured at the inlet sample line and at the outlet of each catalyst chamber. The O₂ is now on a dry basis. With the exception of sample line 5, the oxygen concentration at the outlet of the sample chamber matched that at the inlet. For sample line 5, there was probably a small leak in the sample line; NO_x values will be corrected back to 4% O₂ for this sample line.

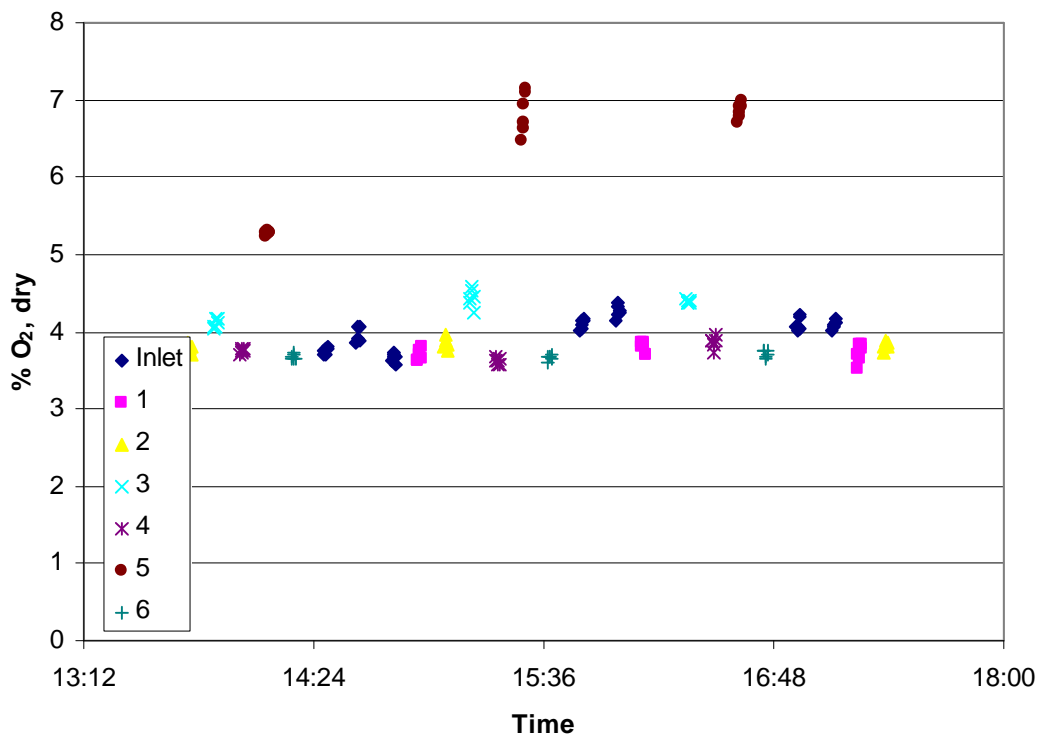


Figure 16. Dry O₂ versus time for all reactor sample lines (4/4/02)

Figures 17 and 18 show the NO_x and calculated NO_x reduction, respectively. The Chamber 5 value has been corrected to 4% O₂ (dry basis). The average chamber temperature was 650°F (344°C). Chambers 1 through 4 experienced problems with flow; we were not able to get to the desired flow rates (space velocities). There seemed to be some plugging of the chambers; this will be addressed next quarter.

The NO_x reductions are generally higher than expected. However, the space velocities are also lower than originally planned.

Catalyst	Space Velocity, hr ⁻¹	Space Velocity Target, hr ⁻¹	Average NO _x Reduction*	Comment
1	13,938	25,603	65.1%	BYU catalyst (Monolith)
2	8,091	13,965	84.9%	Monolith
3	7,333	15,362	93.7%	Plate catalyst
4	7,172	15,362	94.6%	Plate catalyst
5	17,821	30,724	91.3%	Monolith
6	18,242	30,724	81.0%	Monolith

* NH₃/NO=1.1

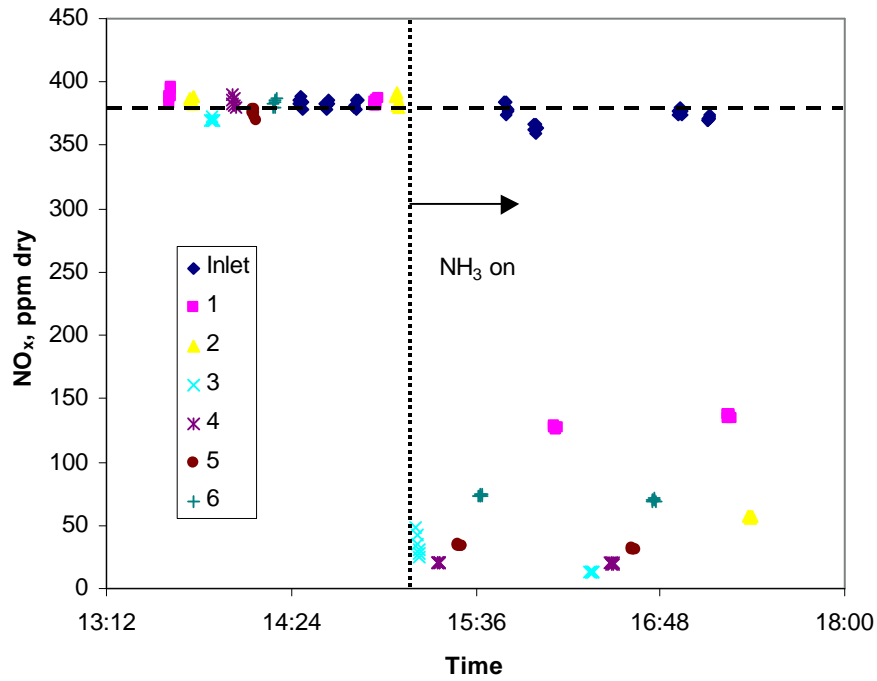


Figure 17. Dry NO_x versus time for all reactor sample lines (4/4/02),

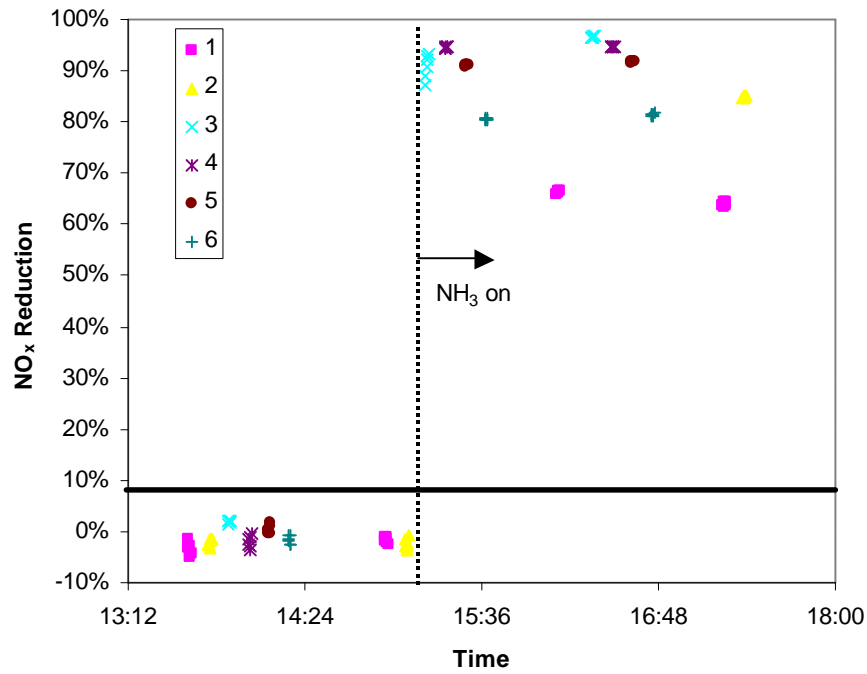


Figure 18. NO_x reduction versus time for all reactor sample lines at NH₃/NO=1.1 (4/4/03).

Results and Discussion

During this quarter, FTIR experiments for SCR catalyst sulfation were finished at BYU and indicated no vanadium/vanadyl sulfate formation at reactor conditions. Considerable energy and time were devoted to improving the sensitivity of the mass spectrometer used with the FTIR, particularly to increase its sensitivity to NO. Mass flow controllers for the laboratory reactor system have been calibrated and fine-tuned.

Poisoned catalysts were prepared and tested in the CCS. Data were collected from four reactors simultaneously showing the effect of space velocity on apparent catalytic activity. Reactor 1 was blank; it had no catalyst in it. Reactors 2, 3 and 4 contained catalyst samples, one fresh and two poisoned with sodium. Remarkably high activity (between 17 and 96 mL/g-s) and conversions of 75-100% at very high space velocities were observed for all three catalysts. Poisoning with sodium produced a noticeable drop in activity, which was larger at higher space velocity.

A computer code was written at BYU to predict conversion along a cylindrical monolithic reactor. This code may be useful for monolith samples that will be tested in the laboratory.

Next quarter, BYU plans complete TOF-SIMS analyses of catalysts generated in the ISSR. Also planned is construction of a reactor with modular inserts that fit each type of monolith/plate catalysts to be tested. Shakedown and fine-tuning of the SCR test reactor system that has already been assembled will be completed. Several other items require action for the coming quarter. First, the catalyst poisoning data presented here must be replicated and a more comprehensive model must be developed to more accurately determine rate constants. Second, fresh catalyst must be poisoned with potassium and calcium and combinations of the poisons to determine how the different poisons affect the powder catalyst. Finally, a larger reactor must be designed to accommodate monolith catalysts that are currently in the slipstream reactor.

During this quarter, shakedown of the slipstream reactor was completed at AEP's Rockport plant. Ammonia was connected to the reactor. We verified that the CEMs were able to sample the inlet and outlet of all chambers. The measurement of O₂ and NO_x made by the CEMs corresponded to values measured by the plant at the economizer outlet. Excellent NO_x reduction was observed in preliminary tests of the reactor.

The catalyst chambers experienced plugging problems sometimes. When this occurred, the pressure drop across the chamber increased. This was manifested in an inability to obtain high flow rate through the chamber. Next quarter, we will change the reactor operating procedure in order to reduce the likelihood of excessive ash build-up in the reactor, which we believe is responsible for the inability to get high flows.

Occasionally one or more of the sample lines appeared to leak; this may have been caused by ash build-up on the sintered metal filter at the start of the sample line, which would cause a high pressure drop across the filter. This would make it difficult for the sample pump to pull enough flow from the reactor and might exacerbate small leaks in the sample line. The filters will be replaced by filters with a larger pore size.

Conclusions

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

- During this quarter, FTIR experiments for SCR catalyst sulfation were finished at BYU and indicated no vanadium/vanadyl sulfate formation at reactor conditions.
- Poisoned catalysts were prepared and tested in the CCS. Data were collected from four reactors simultaneously showing the effect of space velocity on apparent catalytic activity. Poisoning with sodium produced a noticeable drop in activity, which was larger at high space velocity.
- Shakedown of the slipstream reactor was completed at AEP's Rockport plant. Ammonia was connected to the reactor. The measurement of O₂ and NO_x made by the CEMs corresponded to values measured by the plant at the economizer outlet. Excellent NO_x reduction was observed in preliminary tests of the reactor. Some operational problems were noted and these will be addressed next quarter.

During the next quarter,

- TOF-SIMS analyses of catalysts generated in the ISSR will be completed
- The data presented here must be replicated and a more comprehensive model must be developed to more accurately determine rate constants.
- Fresh catalyst must be poisoned with potassium and calcium and combinations of the poisons to determine how the different poisons affect the powder catalyst.
- A larger reactor must be designed to accommodate monolith catalysts that are currently in the slipstream reactor,
- Testing catalyst in monolithic and plate form will be performed. This requires construction of a reactor with modular inserts that fit each type of monolith/plate catalysts to be tested.
- Modifications will be made to the SCR reactor currently located at Rockport to eliminate or reduce ash plugging problems, and then the long-term testing will commence.

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APPENDIX

SCR Reactor Shakedown Schedule at Rockport

SCR Reactor Shakedown Schedule at Rockport

Test Item	Objectives and Test Plans	Schedule
SCR heat up and running	<p>Objectives</p> <ul style="list-style-type: none"> • Effect of flue gas flow rate on ability to control SCR temperature • Flue gas and SCR heaters combined ability to hold SCR reaction temperature (700°F) • Establish time required to heat up the SCR • Familiarize plant personnel with the taking of daily data logs and running of the SCR <p>Plans</p> <ul style="list-style-type: none"> ○ Monitor temperatures for several days with control on ○ Vary flow rate and monitor temperatures ○ Make routine data logs specified for plant personnel in the operating manual <p>Note: This test took one week longer than planned due to blockage of the suction probe with ash at the boiler intake port.</p>	Feb 5 – 28, 2003
Inlet and Outlet NO _x and O ₂ readings	<p>Objectives</p> <ul style="list-style-type: none"> • Analyzer performance and cal gas reliability in providing meaningful readings <p>Plans</p> <ul style="list-style-type: none"> ○ Troubleshoot inlet NO_x line leaks ○ Change cal gas value on analyzer to reflect new sample gas (219.5ppm) ○ Take NO_x and O₂ readings from all sample lines ○ Compare NO_x and O₂ measurements with plant CEMs readings ○ Compare inlet and outlet NO_x and O₂ readings taken in the absence of ammonia injection 	Feb 17 – 19, 2003
Low-flow Control	<p>Objectives</p> <ul style="list-style-type: none"> • Ability to hold low flow rates for Hg tests <p>Plans</p> <ul style="list-style-type: none"> ○ Gradually close the SCR outlet gate valve to restrict flow into the SCR ○ Determine the lowest controllable flow rate 	Feb 18 – 19, 2003
Sootblowing and sample line blowback	<p>Objectives</p> <ul style="list-style-type: none"> • Verify that sootblowing operates correctly • Verify sample line blowback works correctly <p>Plans</p> <ul style="list-style-type: none"> ○ Implementation of sootblowing schedules ○ Resolve clock issues for automatic sootblowing 	Feb 5 – 21, 2003

Ammonia	<p>Objectives</p> <ul style="list-style-type: none"> • Leak testing of ammonia manifold and lines • Review ammonia safety <p>Plans</p> <ul style="list-style-type: none"> ○ Test safe operating procedures for ammonia cylinder connection and disconnection ○ Checking ammonia flow control at operating conditions ○ Check whether ammonia safety interlocks are effective ○ Identify any overlooked ammonia safety measures ○ Run the SCR with ammonia and check the NO_x and O₂ readings 	Feb 24 – Mar 24, 2003
Data Acquisition	<p>Objectives</p> <ul style="list-style-type: none"> • To check if all data needed is collected as specified. • Make sure ammonia usage information is logged <p>Plans</p> <ul style="list-style-type: none"> ○ Review data files 	Feb 5 – 28, 2003
Data Analysis	<p>Objectives</p> <ul style="list-style-type: none"> • Establish a data analysis protocol <p>Plans</p> <ul style="list-style-type: none"> ○ Create a file naming convention ○ Check whether the data transfer procedures work well ○ Set up procedures for data analysis ○ Prepare daily ammonia usage logs ○ Prepare daily calibration logs 	Feb 10 – 28, 2003
Preparations for Hg Tests	<p>Objectives</p> <ul style="list-style-type: none"> • What are the logistics of setting up the Hg sample train? • What special considerations need to be made in docking the sample train to the SCR? <p>Plans</p> <ul style="list-style-type: none"> ○ Two days of SCR/Hg sample train hook-up and shakedown scheduled for week of February 24 – 28 ○ Test configuration of the software for Hg tests ○ Resolve any testing related problems 	Feb 17- Mar 24, 2003