

NO_x Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

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Abstract

This is the sixteenth 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. During an unplanned outage, damage occurred to the electrochemical noise corrosion probes installed at the AEP Gavin plant; testing is expected to resume in August. The KEMCOP corrosion coupons were not affected by the unplanned outage; the coupons were removed and sent for analysis. BYU conducted a series of tests before the ISSR lab was relocated. Ammonia adsorption experiments provided clear evidence of the types of acidic sites present on catalyst surfaces. Data collected this quarter indicate that surface sulfation decreases Lewis acid site concentrations for all catalysts thus far studied, confirming that catalytic activity under commercial coal-based SCR conditions occurs primarily on Brønsted acid sites and would be susceptible to basic impurities such as alkali and alkaline earth oxides, chlorides, and sulfates. SCR activity tests based on MS analysis showed that increasing sulfation generally increases NO reduction activity for both 0% and 1% vanadia catalysts. During this quarter, the slipstream reactor at Rockport operated for 720 hours on flue gas. Catalyst exposure time reached 4500 hours since installation. The reactor is out of service at the Rockport plant and plans are being made to move it to the Gadsden Plant. At Gadsden, modifications have begun in preparation for installation of the slipstream reactor 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 December 31, 2004.

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 boilers;
- impacts of combustion modifications (including corrosion and soot);
- ammonia adsorption / removal from fly ash; and
- 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 an unplanned outage, damage occurred to the electrochemical noise corrosion probes installed at the AEP Gavin plant; testing is expected to resume in August. Preparations were made for replacement of sensor elements.
- The KEMCOP corrosion coupons were not affected by unplanned outage; the coupons were removed and sent for analysis. New coupons were installed.
- Due to a ventilation construction project at BYU, the ISSR lab was shut down and relocated; the CCS lab was also shut down. These events have significantly affected the amount of data that has been generated in the last quarter.
- Experiments completed in the ISSR lab at BYU showed that
 - Vanadia and sulfur preferentially occupy OH⁻ adsorption sites on titania surfaces, indicating that all three prefer acidic sites.
 - NO and NH₃ adsorption, and NO reduction activity experiments were completed as a function of amount of vanadia in the catalyst, the extent of sulfation and temperature. NO adsorption was generally decreased with increasing sulfation, increasing vanadia content, and increasing temperature.
 - Ammonia adsorption experiments provided clear evidence of the types of acidic sites present on catalyst surfaces.
- Data collected this quarter at BYU indicate that surface sulfation decreases Lewis acid site concentrations for all catalysts thus far studied, confirming that catalytic activity under commercial coal-based SCR conditions occurs primarily on Brønsted acid sites and would be susceptible to basic impurities such as alkali and alkaline earth oxides, chlorides, and sulfates.
- SCR activity tests based on MS analysis at BYU showed that increasing sulfation generally increases NO reduction activity for both 0% and 1% vanadia catalysts.
- During this quarter, the slipstream reactor at Rockport operated for 720 hours on flue gas. Catalyst exposure time reached 4500 hours since installation. The reactor is out of service at the Rockport plant and plans are being made to move it to the Gadsden Plant.
- At Gadsden, inlet and outlet ports were installed on Unit 1 for the slipstream reactor during an outage. The slipstream reactor's 9-foot long suction probe has been fabricated

and shipped to Gadsden. Further, gate valves for the inlet and outlet ports have been purchased and shipped to the Gadsden Plant.

Experimental Methods

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

Task 1 - Program Management

During the last performance period,

- Corrosion Probe:
 - Preparations were made for replacement of sensor elements.
 - Damage occurred to the probes installed at Gavin; testing is expected to resume in August.
 - KEMCOP corrosion coupons were removed and replaced.
 - Analysis of removed KEMCOP corrosion coupons begun.
- SCR:
 - During this quarter, the slipstream reactor at Rockport operated for 720 hours on flue gas. Catalyst exposure time reached 4500 hours since installation.
 - The reactor is out of service at the Rockport plant and plans are being made to move it to the Gadsden Plant.
 - At Gadsden, inlet and outlet ports were installed on Unit 1 for the slipstream reactor during an outage. The slipstream reactor's 9-foot long suction probe has been fabricated and shipped to Gadsden. Further, gate valves for the inlet and outlet ports have purchased and shipped to the Gadsden Plant.

Industry Involvement

Results from portions of this research program have been reported to industry through technical presentations at conferences. Two papers were presented at the 29th Coal Utilization & Fuel Systems Conference in Clearwater, Florida, April 18-22, 2004:

- Kevin Davis, Temi Linjewile, David Swensen, Darren Shino, J.J. Letcavits, William Cox and Richard Carr, "A Multi-point Corrosion Monitoring System Applied in a 1300 MW Coal-fired Boiler."
- Constance Senior and Temi Linjewile, "Oxidation Of Mercury Across SCR Catalysts In Coal-Fired Power Plants."

One paper has been accepted for publication in the British Anti-Corrosion Methods and Materials (ACMM) Journal.

- Kevin Davis, Temi Linjewile, David Swensen, Darren Shino, J.J. Letcavits, William Cox and Richard Carr, "A Multi-point Corrosion Monitoring System Applied in a 1300 MW Coal-fired Boiler."

Task 3 - Minimization of Impacts

In May, plans were underway to replace existing electrochemical sensor elements and the EPRI/KEMA screw-in type corrosion coupons (KEMCOP). However, as described below, an emergency outage at the plant had resulted in the electrochemical noise sensors in the probes being damaged by water. The KEMCOP coupons were not damaged and were replaced as planned. The sensor heads for the corrosion probes have since been refurbished and plans are underway to restart testing in August. Given below is the account of the sensor damage incident.

Corrosion Sensor Incident Report

On May 17, 2004 Reaction Engineering International (REI) personnel made a trip to the AEP Gavin station. The original plan called for changing the sensor heads on two of the corrosion probes and updating some of the electronics as part of their OCDO/NETL project. The site visit occurred during an emergency plant outage that resulted in damage to the corrosion probes.

During an initial examination of the equipment, it was noted that moisture had condensed on the outside of the boxes. Further inspection revealed that moisture was present inside the electronics boxes, varying from very little water to pools of water that cover the entire bottom. In addition, air lines, air line filters, and the air control system contained substantial moisture. Furthermore, upon inspection of the corrosion probes, it was observed that the end caps on all four probes had disintegrated by a mechanism involving the formation of large cracks and often with the loss of large sections.

REI engineers inspected the location where the air cooling lines were attached to the plant air to check for moisture in the system. Upon opening a valve to check for moisture, more than 90 seconds were required to remove all of the liquid from the line; note that the valve was set to full open. A second connection point on the fifth floor of the unit (Probe No. 4) required nearly 3 minutes to purge the line of liquid. As a result, all air cooling lines were purged, the filters removed and dried, the electronics in each box were tested (as much as possible while off-line) and all probes were returned to the REI offices in Salt Lake City for repair.

Based on discussions with AEP personnel, this is what appeared to have happened:

1. Gavin Unit 1 went off-line on Friday afternoon, May 14, 2004 due to an emergency outage.
2. At approximately the same time, significant amounts of condensation collected in the plant air supply.
3. Moisture in the plant air system filled much of the plant air system and lines with water (including the area where the corrosion system air lines were connected).
4. The water in the plant air lines was passed into the probe cooling system and entered the probe body while the probe was still at high temperature. The cracking patterns and

sectional loss of material in the probe end caps are consistent with failure due to thermal shock.

5. REI arrived on Monday, May 17, 2004. Inspected damaged probes and investigated moisture accumulation.

Two observations with the corrosion system support this sequence of events:

1. The probe thermocouple data do not indicate any severe spikes in temperature as would have been observed if the air valves had been shut off prior to the outage.
2. The same data show rapid cooling at approximately the outage time that is consistent with the introduction of water.

This was an isolated, unfortunate incident. Under these conditions, there was nothing plant personnel could have done to prevent the catastrophic failure of the probes. However, all team members have discussed plans to get the corrosion system back on-line, how to prevent this type of incident in the future and the status of the data.

Action Plan

The following action plan has been adopted:

1. Re-machine probe caps, refurbish probe bodies and replace sensor elements for the probes.
2. Assemble four corrosion probes and verify all electronics.
3. Install four probes in Gavin Unit 1 and test all four probes for four months.
4. Fabricate additional two probes and verify all electronics.
5. Install final two probes in Gavin and test all six probes for one month.
6. Complete data reduction, modeling, corrosion advisor and profilometry as per original tasks.
7. Prepare final report.

This action plan is shown on the timeline (Figure 1). This allows the project to still be completed within the contract schedule. In addition to the action items noted above, REI will investigate the possibility of obtaining additional funds to repair the damaged probes.

Prevention Plan

To prevent this type of incident in the future, three items were discussed:

1. Change the probe air supply from plant air to dry, instrument air to avoid potential for water reaching the electronics and corrosion sensors.

2. Designate a plant person to provide periodic checks of the corrosion system, using a checklist provided by REI.
3. Train plant personnel on key emergency procedures to minimize the damage resulting from this type of catastrophic event.

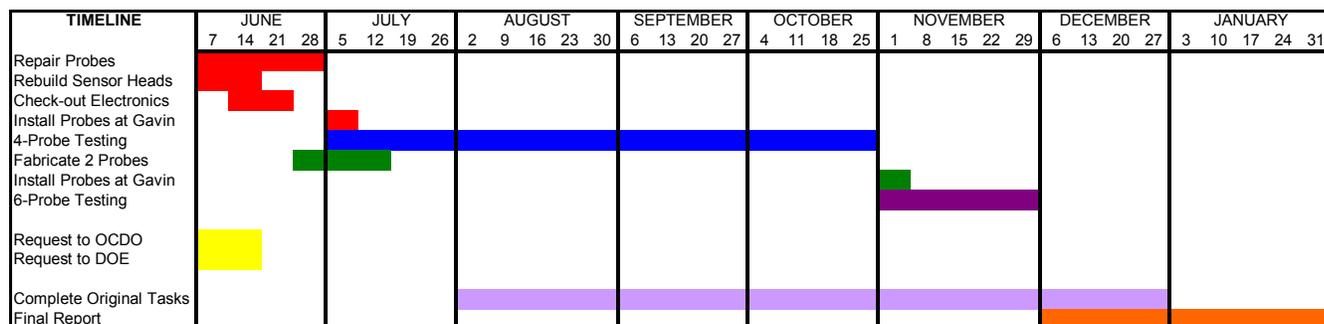


Figure 1. Proposed Timeline for Corrosion Monitoring at Gavin.

Task 4 - SCR Catalyst Testing

Selective catalytic reduction (SCR) represents the only commercially proven technology capable of achieving the relatively large NO_x reductions required to comply with the latest (amended) Clean Air Act requirements. SCR systems are being installed in most large-scale utility boilers. However, most long-term experience with SCR comes from Germany and Japan and most of this is based on high-rank coal combustion. Less experience with low-rank, subbituminous coals specifically Powder River Basin coals, appears in the literature. The literature also provides essentially no US and little foreign experience with systems co-fired with biomass. The purpose of this task is to provide both laboratory and field slip steam data and analyses, including computer models, that fill this information gap.

Within this task there are four principal sub-tasks:

1. technology assessment and fundamental analysis of chemical poisoning of SCR catalysts by alkali and alkaline earth materials;
2. evaluation of commercial catalysts in a continuous flow system that simulates commercial operation;
3. evaluate the effectiveness of catalyst regeneration; and
4. develop a model of deactivation of SCR catalysts suitable for use in a CFD code.

Items 1 and 3 are principally performed at Brigham Young University (BYU) under the direction of Profs. Larry Baxter, Calvin Bartholomew, and William Hecker. The work effort for items 2 and 4 is being performed by REI, with assistance from the University of Utah and BYU. Progress during the last performance period on this task is described below.

Task 4.1 Technology Assessment/Fundamental Analysis

The objectives of this subtask are (1) to supplement the SCR-catalyst-deactivation literature with results from new laboratory-scale, experimental investigations conducted under well-controlled and commercially relevant conditions in the presence of SO₂, 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 in previous reports. Additional characterization systems include a temperature-programmable surface area and pore size distribution analyzer, scanning electron microscopes and microprobes.

The sample test matrix includes two classes of catalysts: commercial, vendor-supplied SCR catalysts and research catalysts synthesized at BYU. The commercial catalysts provide immediate relevance to practical application while the research catalysts provide unfettered ability to publish details of catalyst properties. The five commercial catalysts selected for use come from most commercially significant catalyst manufacturers (Cormetech, Haldor-Topsøe, Hitachi, and Argillon (formerly Siemens)) and provide a wide range of catalyst designs and compositions. The in-house catalysts will be subjected to detailed analysis, activity testing, and characterization, thus providing 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 Studies

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 simulates industrial flows by providing a test gas with the following nominal composition: NO, 0.1%; 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 steady conditions.

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

Work on restoring the gas chromatograph (GC) in the CCS lab has been underway to provide N₂O and N₂ measurement capabilities. This particular device has been used in the past on other NO_x reduction research projects. The valves, flow system, and furnaces/heaters of the GC have

been inspected and are functional. LabVIEW programs to read data from the GC will be completed shortly. Once the thermal conductivity detector is functional, the GC should be in good working condition.

The motor on a pump belonging to the NO_x analyzer was repaired and new pump diaphragms were ordered and received. There has been some confusion regarding the accuracy of the NH₃ concentration labels on our calibration gas cylinder (914 ppm) and/or process gas cylinder (1.01%, or 10100 ppm). Knowing these values accurately is important in analyzing catalyst activity. These gases were measured on a different gas analyzer that belongs to another group. Because the gas analyzer requires special calibration files, the manufacturer has been contacted and is working on providing these items. Results of these measurements await the correct calibration files at the time of this report.

An in-depth review of the literature pertaining to SCR catalyst deactivation, regeneration, and modeling is underway. This review will be submitted as part of this project and as a publication. The BYU College of Engineering began work on laboratory renovations, requiring relocation of several laboratories associated with this project. The CCS lab was not relocated, but the ISSR was moved to the CCS lab. Therefore, the CCS lab has been down because of the renovations involved with the introduction of new equipment. Consequently, no additional data on any catalysts has been produced from the CCS lab.

***In-Situ* Surface Spectroscopy Studies**

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 spectra of SO₂, NH₃, and NO_x, among other species. Adsorption 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, are included. Indications of coadsorption of NH₃ and NO_x help elucidate mechanisms and rates of both reactions and deactivation. Much of the existing literature focuses on SCR reactions in SO₂-free environments. A significant effort in the ISSR laboratory relates to analyzing SCR reactions under coal-relevant conditions (SO₂ laden flows).

1. Most ash-derived contaminants and oxide components of the catalyst are exposed to relatively high concentrations of SO₂ under conditions where coals high in sulfur content are burned (such is the case at many utility boilers in the United States). Sulfates thus formed or deposited on the catalyst surface may profoundly affect surface acidity and hence activity (since the active sites for SCR are thought to include acid functions).
2. Most studies have been conducted either in the absence of SO₂ or under conditions and/or during short periods unfavorable for sulfate formation. Accordingly, it is questionable if these studies are relevant to “realistic” industrial conditions involving long exposures to SO₂ in the presence of water.
3. There are conflicting views in the literature as to whether vanadium species on the catalyst surface are sulfated or not.

Surface OH⁻ group comparison on fresh samples

IR spectra were collected on pure TiO₂ and 1%, and 2% V₂O₅/TiO₂ catalyst wafers run in helium and O₂ at room temperature after pretreatment. During the pretreatment, all the wafers were heated in 5% O₂ and helium for 4 hours at 380 °C. Three major peaks on the spectra located at 3700-3600, 3550-3000, and ~1625 cm⁻¹ appear in Figure 2. They correspond to a free or non-bonded OH⁻ stretch group (3700-3600 cm⁻¹), an H-bonded OH⁻ stretch group (3000-3500 cm⁻¹), and an OH⁻ bend group (~1625 cm⁻¹) (Coates, 2000). Quantitative comparisons of these spectra are difficult in this form. Integration of the peaks determines areas that indicate surface OH group concentration and that provide more meaningful quantitative results, as tabulated in Table 1. The surface OH⁻ concentration decreases upon introduction of vanadia to the titania surface over the range of vanadia concentrations studied (0-2%). This agrees with the suggestion by Topsøe that vanadia interacts with OH⁻ groups present on the titania surface (Topsøe et al., 1995).

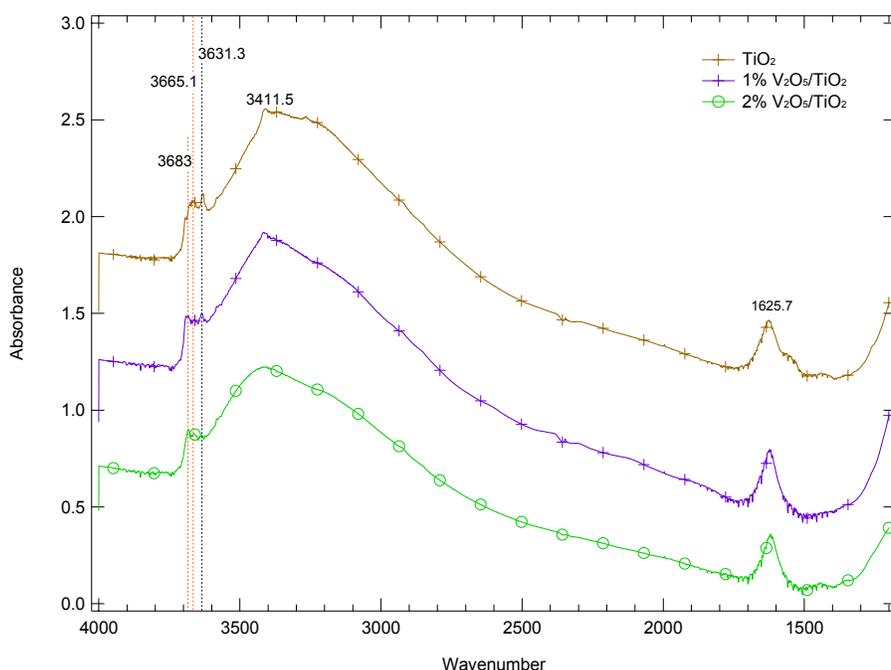


Figure 2. Surface OH⁻ group concentration comparison on fresh TiO₂ and vanadia catalysts at room temperature (RT)

Table 1. Surface OH⁻ group peak area comparison on fresh TiO₂ and vanadia catalysts.

	3720-3600 cm ⁻¹	3550-3000 cm ⁻¹	~1625 cm ⁻¹
	Free OH stretching	H bonded OH stretching	OH bending
Pure TiO ₂	10.62	372.40	21.02
Fresh 1% V ₂ O ₅ /TiO ₂	8.73	314.06	20.68
Fresh 2% V ₂ O ₅ /TiO ₂	4.31	256.02	16.34

NO adsorption

NO adsorption tests conducted with 1000 ppm NO and 5% O₂ in helium at temperatures ranging from 25 °C to 380 °C on various samples provide important information regarding potential active sites for NO reduction on V-Ti SCR catalysts.

Adsorption on fresh, pure TiO₂ and 1% and 2% V₂O₅/TiO₂ catalysts without sulfation

NO adsorption IR bands appear at room temperature on non-sulfated V₂O₅/TiO₂ catalysts with vanadia content ranging from 0-2 %, as illustrated in Figure 3. The NO adsorption bands appear at the same frequencies for all catalysts, suggesting that the same adsorbed NO species form on all samples. These bands correspond to surface nitrate species (Ramis and Busca, 1990).

To verify that the observed peaks correspond to NO and/or NO₂ adsorption, results obtained at BYU were compared to those of previous studies (Ramis and Busca, 1995; Ramis et al., 1990; Hadjiivanov, 2000), as shown in Table 2. The NO adsorption bands observed at BYU are very similar to those noted by the Ramis' study of NO and NO₂ adsorption on pure TiO₂ and a 5% vanadia/titania catalyst, although the BYU data match the results of Hadjiivanov more closely.

The appearance of NO₂ in these spectra indicates that the NO cylinder may contain some NO₂. Accordingly, the NO gas cylinder was replaced and purity of the NO gas will be confirmed with the MS in the future.

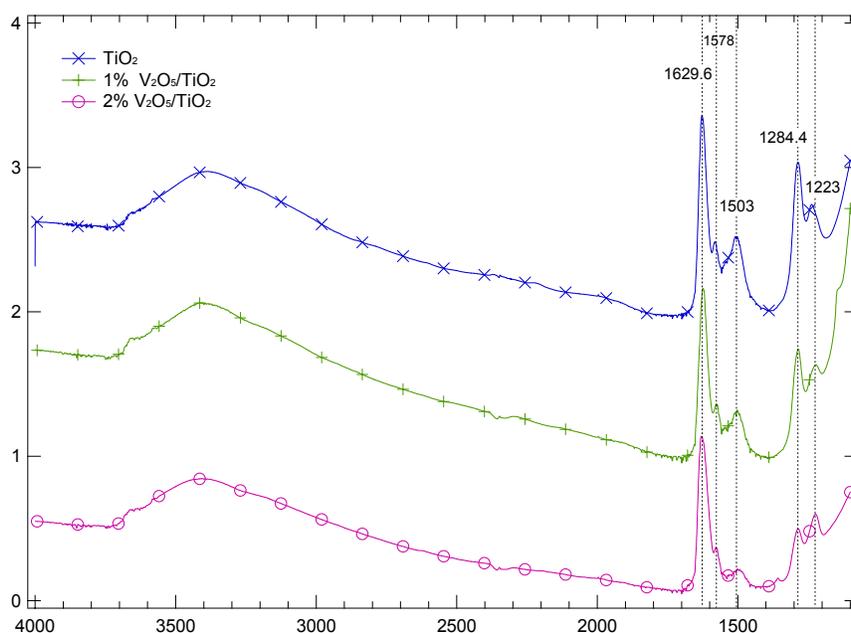


Figure 3. Room temperature NO adsorption comparison on fresh TiO₂ and vanadia catalysts.

Table 2. Comparison of NO and NO₂ adsorption bands from BYU, Ramis, and Hadjiivanov. Highlighted x's indicate similar results.

	2300-2230	1914, 1900	2200-1800 ^b	1630	1608	1586	1500	1291	1250	1222
BYU NO adsorption				x		x	x	x		x
Ramis NO ₂ on TiO ₂			x	x	x	x	x	x	x	x
Ramis NO on TiO ₂	x	x		1622		1545		1322		1190
Ramis NO ₂ on V ₂ O ₅ /TiO ₂			x	x		x		x		x
Ramis NO on V ₂ O ₅ /TiO ₂		1898	x	x	1615	x		x		x
NO ₍₂₎ /TiO ₂ from Hadjiivanov				x	x	x	x	x		x

b: broad

Upon NO adsorption, the band intensities of the free surface OH⁻ stretch groups (3720 – 3600 cm⁻¹) significantly decreased for all samples (compare Figure 2 to Figure 3). This indicates that NO interacts with surface OH groups, which are the same sites that vanadia displaces on the titania surface, as shown in Figure 2. On the other hand, the amount of adsorbed NO, which is proportional to NO adsorption peak area, decreases with increasing vanadia content on the titania surface, as shown in Table 3. It seems that addition of vanadia species suppresses NO adsorption, which may be explained by vanadia's occupation of the same surface OH⁻ groups that NO adsorbs on.

Table 3. Room temperature NO adsorption peak area comparison on fresh TiO₂ and vanadia catalysts.

	1630-1570 cm ⁻¹	~1500 cm ⁻¹	1285-1220 cm ⁻¹
Pure TiO ₂	45.41	15.19	48.14
Fresh 1% V ₂ O ₅ /TiO ₂	43.29	9.78	24.23
Fresh 2% V ₂ O ₅ /TiO ₂	43.64	2.46	17.3

In conclusion, our observations indicate that NO does not interact with vanadia species, but rather with the OH⁻ groups on the titania surface.

Adsorption on sulfated TiO₂ and 1% V₂O₅/TiO₂ catalysts

The fresh wafers described above were sulfated at two SO₂ exposure times (30 minutes and 24 hours) and the results of NO adsorption were compared to those for the non-sulfated (fresh) samples. All the NO adsorption studies in this series of tests proceeded at room temperature. NO

adsorption on fresh, lightly sulfated, and 24-hour sulfated TiO_2 are shown in Figure 4, where it is clear that all the NO adsorption bands gradually decrease with increasing sulfation time. Therefore, surface sulfates suppress NO adsorption. Several authors (Choo et al., 2000; Dunn et al., 1998) suggested that sulfates interact with the same surface titania OH^- groups with which the NO and vanadia species interact. This is confirmed by our results, as shown in Figure 5. The IR spectra OH^- groups are strong on fresh TiO_2 , but very weak on both lightly and 24-hour sulfated TiO_2 .

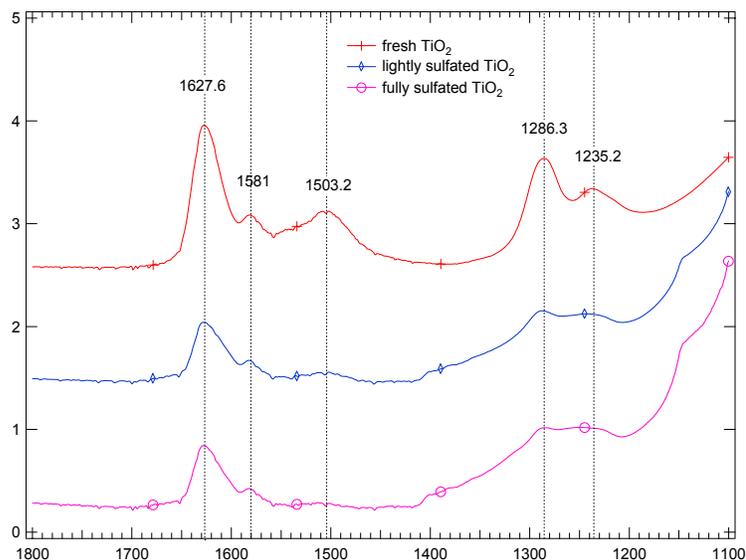


Figure 4. Comparison of NO adsorption on fresh, lightly sulfated, and 24-hour sulfated TiO_2 (TiOA).

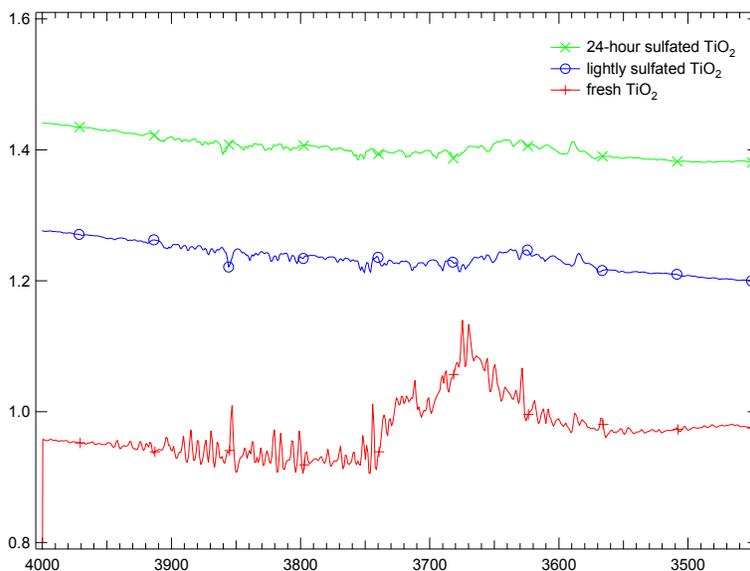


Figure 5. Surface OH^- group comparison on fresh, lightly sulfated, and 24-hour sulfated titania.

Similar results were obtained on fresh, lightly and 24-hour sulfated 1% V_2O_5/TiO_2 catalysts, as shown in Figure 6. NO adsorption peaks on the fresh 1% V_2O_5/TiO_2 catalyst are intense, but decrease with increasing sulfation time. This observation further confirms that sulfate species present on both pure titania and vanadia/titania catalysts suppress NO adsorption by occupying surface OH^- groups.

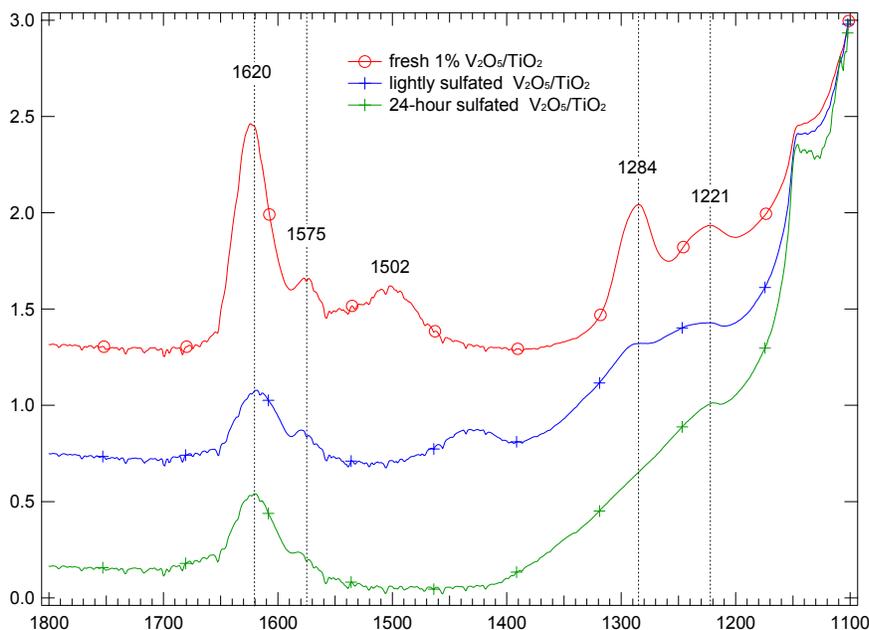


Figure 6. Comparison of NO adsorption on fresh, lightly sulfated, and 24-hour sulfated 1% V_2O_5/TiO_2 (VTOL).

So far, our findings indicate that NO, sulfate species, and vanadia species interact with the same surface OH^- group on the titania surface.

NO adsorption at different temperatures

Figure 7 and Figure 8 illustrate the effect of temperature on *in situ* IR spectra taken during NO adsorption on 24-hour sulfated TiO_2 and fresh 1% V_2O_5/TiO_2 . Here, temperature ranged from 25 to 380 °C. On both samples, the NO adsorption peaks at 1626.7, 1582.3, and 1286.3 cm^{-1} gradually decreased with increasing temperature. In the case of NO adsorption on 24-hour sulfated TiO_2 , bands at 1286.3 and 1582.3 cm^{-1} disappeared from the IR spectra at 150 °C, while the NO adsorption band at 1626.7 cm^{-1} remained until 250 °C. In the case of fresh 1% V_2O_5/TiO_2 , NO adsorption bands at 1623 and 1575 cm^{-1} disappeared from the IR spectrum at 300 °C, while no band at 1285 cm^{-1} could be observed after the temperature reached 200 °C. Since both samples contained different amounts of vanadia and sulfates, different NO desorption temperatures were obtained.

Most researchers have observed NO adsorption on pure TiO_2 and on reduced vanadia catalysts, but not on fully oxidized vanadia catalysts (Topsøe et al., 1995; Yang et al., 1998; Ozkan et al., 1994). The 1% V_2O_5/TiO_2 used in this experiment had been preoxidized at 400 °C for 4 hours

before NO adsorption; therefore, the vanadia valence should be 5^+ . Thus, we not only observed NO adsorption on fresh or sulfated titania and vanadia catalysts, but at higher temperatures up to 300 °C.

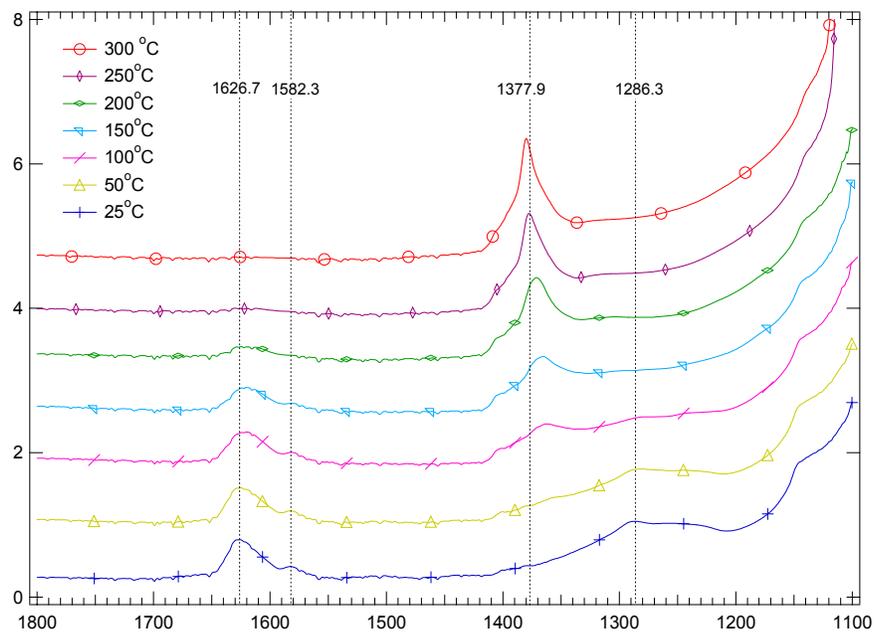


Figure 7. NO adsorption on 24-hour sulfated TiO₂ at different temperatures. (TiOA).

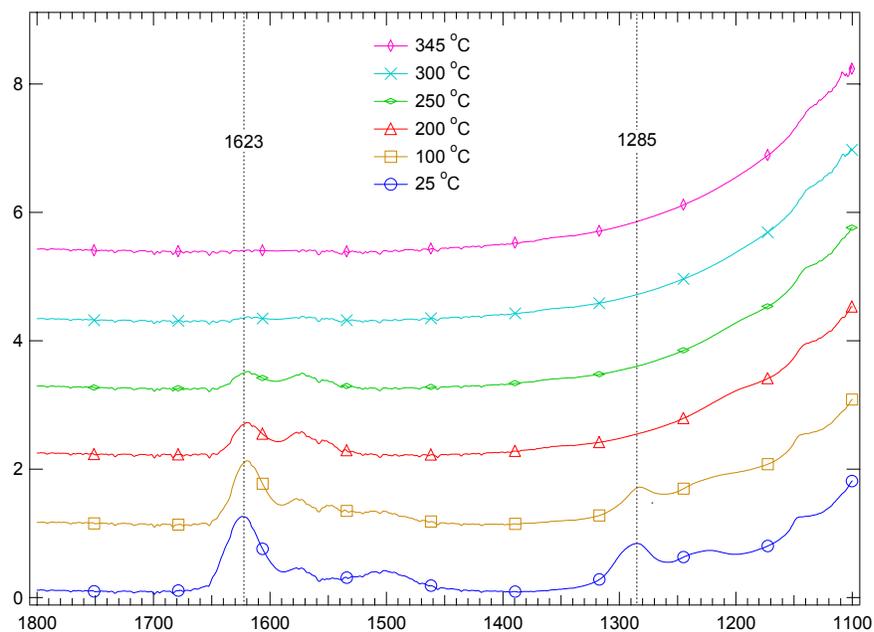


Figure 8. NO adsorption on fresh 1% V₂O₅/TiO₂ at different temperatures. (VTOL).

Ammonia adsorption

Ammonia adsorption was conducted with 1000 ppm NH₃ in helium at room temperature. *In situ* IR spectra were collected during ammonia adsorption on fresh and sulfated TiO₂, 1%, and 2% V₂O₅/TiO₂ catalysts.

Adsorption on fresh (unsulfated) TiO₂, 1%, and 2% V₂O₅/TiO₂ catalysts

Results from ammonia adsorption at room temperature on fresh TiO₂, 1%, and 2% V₂O₅/TiO₂ catalysts appear in Figure 9. Ammonia adsorbed on Lewis acid sites appears at 1602 and 1301.7 cm⁻¹, while NH₃ adsorbed on Brønsted acid sites appears at 1444 cm⁻¹. Adsorption on Lewis acid sites occurs most prominently for the fresh TiO₂ and to significantly lower extent on 1% V₂O₅/TiO₂ catalysts. There is no indication of adsorption on Lewis sites in the 2% sample. However, all three samples show substantial adsorption on Brønsted sites. Moreover, an adsorption peak at 1568.8 cm⁻¹, which is assigned to amide (–NH₂) species, was observed on titania, but not on 1% and 2% vanadia catalysts.

These results illustrate that commercial, non-sulfated catalysts (typically about 1% vanadia) exhibit primarily Brønsted acid activity with respect to ammonia adsorption.

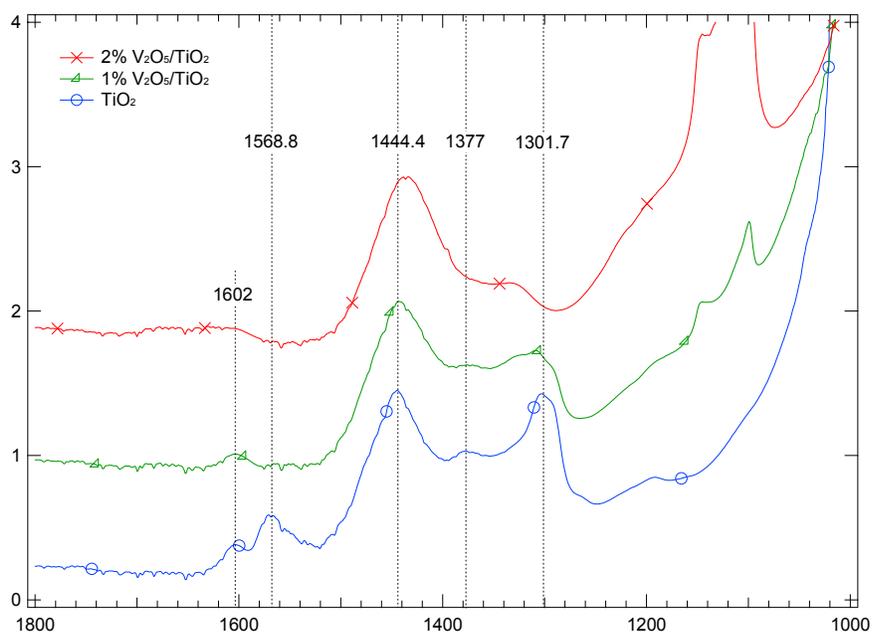


Figure 9. Comparison of NH₃ adsorption on fresh TiO₂, 1%, and 2% V₂O₅/TiO₂.

Adsorption on sulfated TiO₂ and 1% V₂O₅/TiO₂

IR spectra of ammonia adsorption at room temperature on fresh and sulfated TiO₂ are shown in Figure 10. On fresh titania, four major ammonia adsorption peaks appear. Peaks at 1601 and 1302.7 cm⁻¹ correspond to coordinately adsorbed ammonia on Lewis acid sites, the peak at 1440 cm⁻¹ is due to ammonia chemisorbed on Brønsted acid sites, and the peak at 1569.8 is from amide (–NH₂) species. On lightly sulfated titania, a trace of coordinately adsorbed ammonia appears at 1302 cm⁻¹, while on 24-hour sulfated titania, only chemisorbed ammonia on Brønsted acid sites at 1444 cm⁻¹ can be seen. Therefore, sulfation reduces the number of Lewis acid sites on the titania surface. It is possible that sulfate species transform Lewis acid sites into Brønsted

acid sites on the titania surface, which would explain why sulfated catalysts exhibit higher NO reduction activity than do non-sulfated catalysts (discussed in next section). However, the only definitive indication from these experiments is that surface sulfation decreases the amount of Lewis-active sites for ammonia adsorption. Similar results were observed by comparing ammonia adsorption on fresh and sulfated 1% V_2O_5/TiO_2 , as shown in Figure 11. Weakly coordinated adsorbed ammonia appears on fresh 1% V_2O_5/TiO_2 , while only chemisorbed ammonia appears on the same catalyst sulfated for 24 hours, further confirming that sulfates reduce Lewis acidity.

Previously reported results indicate that vanadia does not sulfate. Those results, combined with these results, indicate that surface sulfation decreases Lewis acid site concentrations for all catalysts thus far studied, confirming that catalytic activity under commercial coal-based SCR conditions occurs primarily on Brønsted acid sites and would be susceptible to decrease by basic impurities such as alkali and alkaline earth oxides, chlorides, and sulfates.

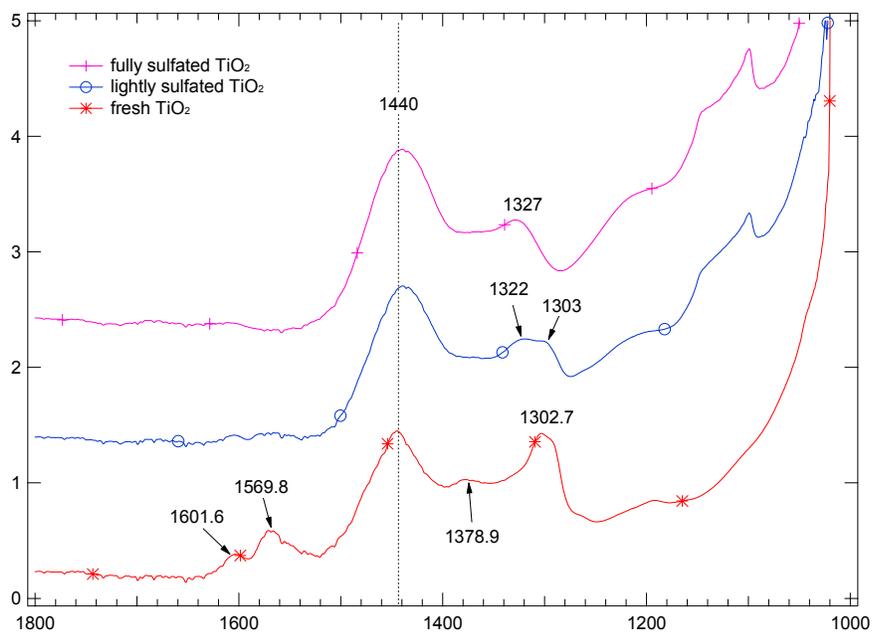


Figure 10. Comparison of NH_3 adsorption on fresh, lightly sulfated, and 24-hour sulfated TiO_2 (TiOA).

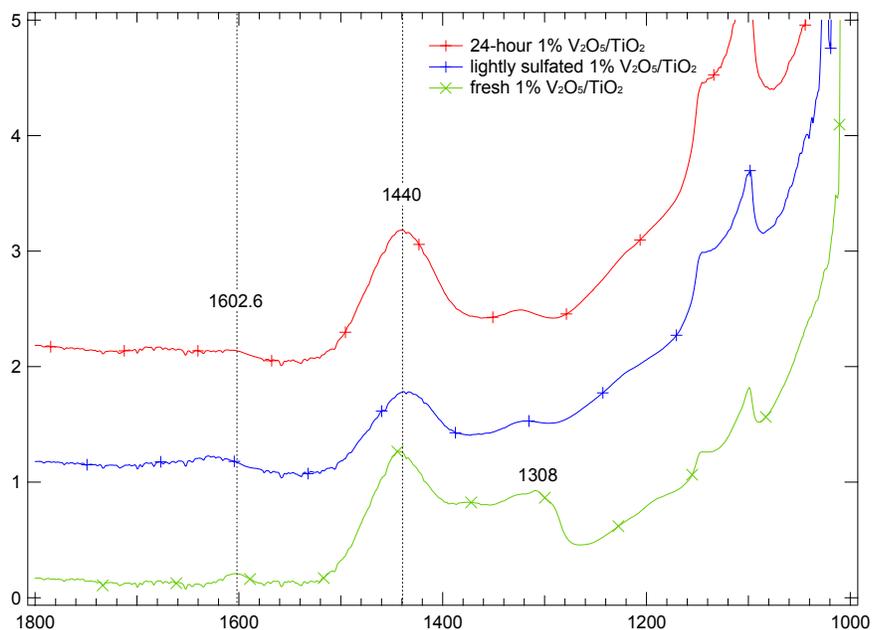


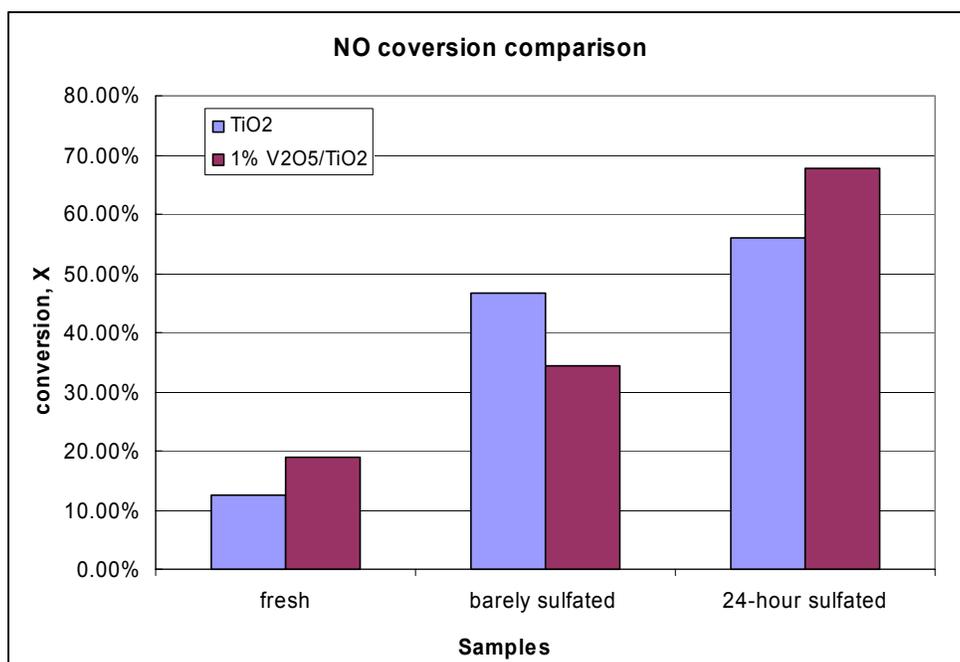
Figure 11. Comparison of NH_3 adsorption on fresh, lightly sulfated, and 24-sulfated 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ (VTOL).

NO reduction activity study

NO reduction experiments by ammonia at 380 °C on fresh, lightly, and 24-hour sulfated TiO_2 and 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ indicate the role of surface sulfation on SCR activity. The reactant gas passing over both sides of the catalyst wafer in the IR cell at ambient pressure consisted of 1000 ppm NH_3 and NO, 5% O_2 , and helium at a GHSV of about 100,000 hr^{-1} . The NO conversion results are shown in Table 4 and displayed graphically in Figure 12. A comparison of observed conversion shows that 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ has a higher NO reduction capability than does TiO_2 under fresh and 24-hour sulfated conditions while lightly sulfated 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ has a lower NO reduction activity than does lightly sulfated TiO_2 . For both pure titania and 1% $\text{V}_2\text{O}_5/\text{TiO}_2$, NO conversion increases with increasing degree of sulfation. This indicates that surface sulfation enhances NO reduction activity of both the titania support and the vanadia catalyst. The trend of increased activity with increased degree of sulfation seems well established. The details under barely sulfated conditions are unexpected (pure titania being more active than 1% vanadia loading) and may be an artifact. Statistical error bars on these results will be developed based on replicated experiments to confirm whether this initial trend observation is important.

Table 4. NO conversion on fresh, lightly and 24-hour sulfated TiO₂ and 1% V₂O₅/TiO₂.

	NO conversion, %	
	TiO ₂	1% V ₂ O ₅ /TiO ₂
Fresh	12.50	18.90
Lightly sulfated	46.73	34.47
24-hour sulfated	56.10	67.85

**Figure 12. Comparison of NO conversion on TiO₂ and 1% V₂O₅/TiO₂.**

Task 4.2 Evaluation of Commercial SCR Catalysts for Power Plant Conditions

Catalyst Exposure to Flue Gas

In this quarter the slipstream reactor was operational in the month of April only after which there was an outage at the plant. The reactor was exposed to flue gas for an additional 720 hours and at shutdown, total exposure time since installation reached 4500 hours. Figure 13 shows the steady build up of reactor operating time accrued this year. The slipstream SCR reactor is currently shutdown and plans are underway to dismantle it and ship it to the Gadsden Plant in the next quarter.

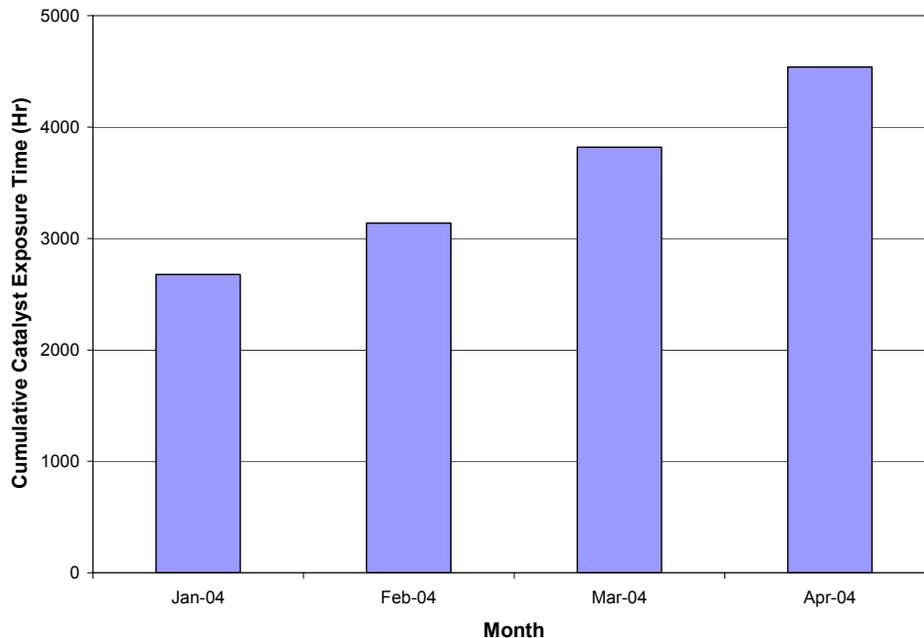


Figure 13. Cumulative catalyst exposure time this year before shutdown in April 2004.

Biomass Co-firing Tests at Gadsden

The Gadsden Plant has two 70 MW tangentially fired boilers. It has been burning biomass as part of a three-year DOE program. Currently the plant fires switchgrass seven to eight hours per day, five days a week, in Unit 2. The switchgrass is ground and fed pneumatically into two corners of the boiler, just below the topmost coal port. The switchgrass is fired at 2.5 tons per hour, or about 5% on an energy input basis.

There is a keen interest on Southern Company's part in better understanding catalyst deactivation by biomass. They suggested two different ways to go for long-term testing:

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- Switchgrass firing on Unit 2, collecting data 7-8 hours per day as with the existing slipstream reactor.
- Sawdust firing on Unit 1 by co-milling sawdust at about 5% weight basis.

They believe that they could co-mill 5% sawdust twenty-four hours per day. This would have the advantage of longer exposure times for the catalysts to biomass and a fairly steady fuel source. The disadvantage is that the amount of biomass would be small (2-3% of the fuel on an energy basis).

During this quarter, inlet and outlet ports were installed on Unit 1 for the slipstream reactor during an outage. The slipstream reactor's 9-foot long suction probe has been fabricated and shipped to Gadsden. Further, gate valves for the inlet and outlet ports have been purchased and shipped to the Gadsden Plant.

Work with plant engineers this quarter has identified a location for the reactor on Unit 1. Figure 14 shows a sketch of the piping required to bring flue gas (upstream of air heater) to the slipstream reactor and return the flue gas (downstream of the air heater).

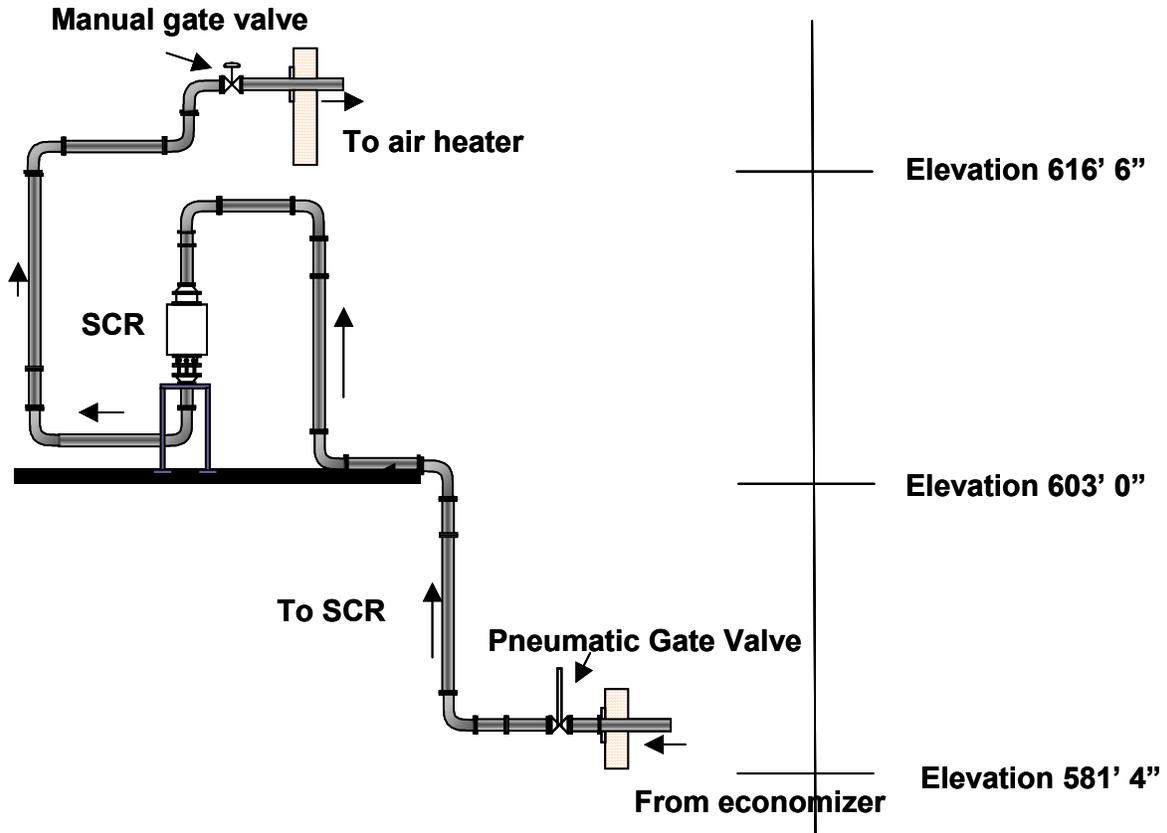


Figure 14. Proposed SCR layout at Gadsden.

Results and Discussion

Discussion of the Corrosion Monitoring Study

Due to the incident that destroyed the probes, there are only corrosion measurements made with the probes - comparisons between profilometry results and probe results can not be performed. However, in February the main corrosion probe element was removed for profilometry evaluation. This will provide a comparison from November 2003 to February 2004.

Additional comparisons will be made on all probes once they are reinstalled and operated for a four-six month period. During this time additional operating data will be collected from the plant to provide comparisons between corrosion occurrence and boiler conditions.

Discussion of the Catalyst Activity Study

A series of tests was completed before the ISSR lab was relocated. Hydroxyl adsorption spectra indicate that vanadia and sulfur preferentially occupy OH⁻ adsorption sites on titania surfaces, indicating that all three prefer acidic sites. NO and NH₃ adsorption, and NO reduction activity experiments were completed as a function of amount of vanadia in the catalyst (0%, 1%, and 2% V₂O₅/TiO₂), extent of sulfation (no sulfation, 30-minute slight sulfation, and 24-hour complete sulfation), and temperature. NO adsorption was observed to varying degrees on the catalysts under investigation, generally decreasing with increasing sulfation, increasing vanadia content, and increasing temperature. Ammonia adsorption experiments provide clear evidence of the types of acidic sites present on catalyst surfaces. Data collected this quarter indicate that surface sulfation decreases Lewis acid site concentrations for all catalysts thus far studied, confirming that catalytic activity under commercial coal-based SCR conditions occurs primarily on Brønsted acid sites and would be susceptible to basic impurities such as alkali and alkaline earth oxides, chlorides, and sulfates. SCR activity tests based on MS analysis showed that increasing sulfation generally increases NO reduction activity for both 0% and 1% vanadia catalysts.

Conclusions

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

- Corrosion testing is expected to resume in August after replacement of sensor elements due to damage incurred during an unplanned outage at the AEP Gavin plant.
- The KEMCOP corrosion coupons were not affected by unplanned outage; the coupons were removed and sent for analysis. New coupons were installed.
- Due to a ventilation construction project at BYU, the ISSR lab was shut down and relocated; the CCS lab was also shut down. These events have significantly affected the amount of data that has been generated in the last quarter.
- Experiments completed in the ISSR lab at BYU showed that
 - Vanadia and sulfur preferentially occupy OH⁻ adsorption sites on titania surfaces, indicating that all three prefer acidic sites.
 - NO and NH₃ adsorption, and NO reduction activity experiments were completed as a function of amount of vanadia in the catalyst extent of sulfation and temperature. NO adsorption was generally decreased with increasing sulfation, increasing vanadia content, and increasing temperature.
 - Ammonia adsorption experiments provided clear evidence of the types of acidic sites present on catalyst surfaces.
- Data collected this quarter at BYU indicate that surface sulfation decreases Lewis acid site concentrations for all catalysts thus far studied, confirming that catalytic activity under commercial coal-based SCR conditions occurs primarily on Brønsted acid sites and would be susceptible to basic impurities such as alkali and alkaline earth oxides, chlorides, and sulfates.
- SCR activity tests based on MS analysis at BYU showed that increasing sulfation generally increases NO reduction activity for both 0% and 1% vanadia catalysts.
- During this quarter, the slipstream reactor at Rockport operated for 720 hours on flue gas and catalyst exposure time reached 4500 hours since installation.
- The reactor is out of service at the Rockport plant and plans are being made to move it to the Gadsden Plant.

Plans for Next Quarter

Corrosion probe activity for the next quarter will focus on the following:

- Review of the probe damage due to water.
- Refurbishing and assembly of the probes.
- Installation of instrument air supply for the probe cooling.
- Continued testing at Gavin.
- Analysis of the KEMCOP coupons will be reported.

Activity at BYU next quarter will focus on the following:

- An undergraduate student who can work on the project will be hired. The CCS lab's functionality will be restored.
- A review of the SCR catalyst deactivation literature will be finished.
- All non-chemical characterization of the exposed industrial catalyst samples will be completed (SEM, BET surface area, microprobe, etc.).
- Based on the literature and communication among involved parties, appropriate models for reaction and mass transfer models will be explored and selected, and tests on monolith catalyst performance will commence.
- The ISSR reactor system will be made operational in its new location ; NO and NH₃ adsorption studies will resume.

SCR slipstream activity for the next quarter will focus on the following:

- Removal of the reactor from Rockport and shipment to Plant Gadsden.
- Installation of the reactor at Plant Gadsden.

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