# $NO_x$ Control Options and Integration for US Coal Fired Boilers

**Quarterly Progress Report**

Reporting Period Start Date July 1, 2004
Reporting Period End Date: September 30, 2004

Mike Bockelie, REI
Kevin Davis, REI
Connie Senior, REI
Darren Shino, REI
Dave Swenson, REI
Larry Baxter, Brigham Young University
Calvin Bartholomew, Brigham Young University
William Hecker, Brigham Young University
Stan Harding, N.S. Harding & Associates

October 29, 2004

DOE Cooperative Agreement No: DE-FC26-00NT40753

Reaction Engineering International
77 West 200 South, Suite 210
Salt Lake City, UT 84101

# Disclaimer

# Abstract

This is the seventeenth 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. The SCR slipstream reactor was assembled and installed at Plant Gadsden this quarter. Safety equipment for ammonia had not been installed at the end of the quarter, but will be installed at the beginning of next quarter. The reactor will be started up next quarter. Four ECN corrosion probes were reinstalled at Gavin and collected corrosion data for approximately one month. Two additional probes were installed and removed after about 30 hours for future profilometry analysis. Preliminary analysis of the ECN probes, the KEMA coupons and the CFD modeling results all agree with the ultrasonic tube test measurements gathered by AEP personnel.

# Table of Contents

# 1

# 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 March 31, 2005.

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:

- Additional funding from OCDO and DOE was authorized to help offset the expense of replacing all probes due to the failure that occurred during the last performance period. As part of providing the additional funds, DOE has authorized a three month extension to the project. The cooperative agreement between REI and DOE for this project is now scheduled to be completed on March 31, 2005.
- Four ECN corrosion probes were reinstalled at Gavin and collected corrosion data for approximately one month. Two additional probes were installed and removed after about 30 hours for future profilometry analysis.
- Preliminary analysis of the ECN probes, the KEMA coupons and the CFD modeling results all agree with the ultrasonic tube (UT) test measurement data gathered by AEP personnel.
- The SCR slipstream reactor was assembled and installed at Plant Gadsden; safety equipment for ammonia had not been installed at the end of the quarter, but will be installed at the beginning of next quarter.

# Experimental Methods

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

## Task 1 - Program Management

During the last performance period,

- Additional funding from OCDO and DOE was approved to help offset the expense of replacing all probes due to the failure that occurred during the last performance period. In addition, DOE has authorized a three month extension to the project. The cooperative agreement between REI and DOE for this project is now scheduled to complete on March 31, 2005.

- Corrosion Probe:
  - All recommendations made in the Corrosion Sensor Incident Report included in our previous quarterly report have been completed [Bockelie et al, 2004].
  - Four ECN corrosion probes were installed and two were removed after about 30 hours for future profilometry analysis. Two new probes were installed in their place. Therefore, four ECN probes were installed and collecting data for approximately one month.
  - Preliminary analyses from the EPRI KEMA Chemkop screw-in corrosion coupons were received. The ECN probes, the KEMA coupons and the CFD modeling results all agree with the UT data gathered by AEP personnel.
  - At the end of the last performance period, failures occurred for the probe end-caps. All probes were removed from the boiler and sent to REI for evaluation. The probes are being refurbished and will be reinstalled next quarter.
- SCR:
  - At Gadsden, the SCR slipstream reactor was assembled and installed; safety equipment for ammonia had not been installed at the end of the quarter, but will be installed at the beginning of next quarter. The reactor will be started up next quarter.

During the last performance period, REI was awarded a DOE funded project entitled, "Cyclone Boiler Field Testing of Advanced Layered Technology Approach (ALTA) for NOx Control" from the DOE NETL (DE-FC26-04NT42297). In the project REI will work with AmerenUE and EPRI to demonstrate the ability of the ALTA approach to reduce NOx emissions in a cyclone fired boiler below 0.15 lb/MBtu at less than 75% of the levelized cost of Selective Catalytic Reduction. ALTA combines the use of deep staging with RRI (a NOx control technology evaluated and heavily worked on early in this project) and SNCR in a synergistic fashion to reach very low NOx levels in a cost effective manner. Field testing is expected to commence Spring, 2005. The test site is AmerenUE's Sioux Station near St. Louis, MO.

# 3

## Industry Involvement

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

A paper co-authored by REI and electric utility personnel was presented at a recent engineering conference that highlighted the RRI NOx control technology demonstrated earlier within this project:

- Cremer, M.A., Wang, D.H., Adams, B.R., Boll, D.E., and Stuckmeyer, K.B. "Evaluation of Cost Effective Non-SCR Options For NOx Control in PRB Fired Cyclone Boilers," presented at the 19th International Conference on Lignite, Brown, and Subbituminous Coals, Billings, MT, October 12-14, 2004.

A paper has been accepted for presentation that will highlight results from measurements of mercury oxidation across the SCR slip stream unit used within this project:

- Senior, C.L., "Understanding Oxidation of Mercury Across SCR Catalysts in Power Plants Burning Low Rank Coals," accepted for presentation at the Power-Gen International Conference, November 29-December 1, 2004, Orlando, Florida

A paper that highlighted our work on water wall corrosion measurements was recently presented:

- Davis, K.A., Linjewile, T., Valentine, J., Swensen, D.A., Shino, D., Letcavits, J.J., Sheidler, R., Cox, W., Carr, R. and Harding, N.S., "On-line Monitoring of Waterwall Corrosion in a 1300 MW Coal-fired Boiler with Low-$NO_x$ Burners", presented at the Combined Power Plant Air Pollutant Control Mega Symposium in Washington, DC, August 30 – September 2, 2004.

A second paper on water wall corrosion measurement was published in a journal for which hardcopies are now available:.

- Davis, K.A., Linjewile, T., Swensen, D.A., Shino, D., Letcavits, J.J., Cox, W., and Carr, R., "A Multi-point Corrosion Monitoring System Applied in a 1300 MW Coal-fired Boiler," British Anti-Corrosion Methods and Materials (ACMM) Journal, Vol. 20, No. 2, 2003.

## Task 3 - Minimization of Impacts

Following the program update meeting in Columbus, OH with OCDO personnel, a plan for reinstallation of the ECN corrosion probes was agreed upon. All items, as presented in the last quarterly report have been accomplished. Specifically, probe cooling has been changed to instrument air, training of AEP personnel has been conducted and refabrication of the probes has been accomplished. In addition, OCDO and DOE have authorized additional funding for the program to help offset the additional costs incurred after the catastrophic probe failures.

## 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 slipstream data and analyses, including computer models that fill this information gap.

Within this task there are for 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. evaluating 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 $SO_2$, and (2) to provide a laboratory-based catalyst test reactor useful for characterization and analysis of SCR deactivation suitable for samples from commercial facilities, slipstream reactors, and laboratory experiments. Two catalysts flow reactors and several additional characterization systems provide the analytical tools required to achieve these objectives. The flow reactors include the *in situ* surface spectroscopy reactor (ISSR) and the catalyst characterization system (CCS), both of which are described in more detail 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%; $NH_3$, 0.1%; $SO_2$, 0.1%; $O_2$, 2%; $H_2O$, 10%; and He, 87.7%. Both custom and commercial catalysts are tested as fresh samples and after a variety of laboratory and field exposures under 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.).

**Tests of Monolith Catalysts from REI Slipstream Reactor**

Initial tests were performed on samples cut out from the commercial monolith catalysts, M1 and M2. The M1 samples were 3.1 cm long and included one section of fresh catalyst, and two sections of catalyst that had been exposed for 2063 hours in the slipstream reactor. The M2 samples were 2.9 cm long and included one section of fresh catalyst and one section of catalyst that had been exposed for 2063 hours in the slipstream reactor (see Table 1). All the samples comprised four channels, in a two by two arrangement.

**Table 1. Samples tested in CCS.**

| SAMPLE | TYPE | TIME EXPOSED | LENGTH |
|---|---|---|---|
| 1 | M1 | 0 hrs | 3.1 cm |
| 2 | M1 | 2063 hrs | 3.1 cm |
| 3 | M1 | 2063 hrs | 3.1 cm |
| 4 | M2 | 0 hrs | 2.9 cm |
| 5 | M2 | 2063 hrs | 2.9 cm |

Each sample was set in the monolith reactor. Airflow through the reactor was set at 1000 scfm and comprised 2% $O_2$, 10 % $H_2O$, 900 ppm $NH_3$, 900 ppm NO, and a balance of He. The reactor temperature was set at approximately 250 $^oC$ and conditions were held constant until temperature and NO level reached steady state. This process was then repeated at approximately 275, 300, and 325 $^oC$ for each sample. **Figure 1** shows a comparison of NO-conversion for the fresh versus exposed M1 catalyst. **Figure 2** shows the same comparison for the M2 catalyst. In both cases, the exposed catalyst had a higher activity than the fresh catalyst for temperatures below 285 $^oC$.

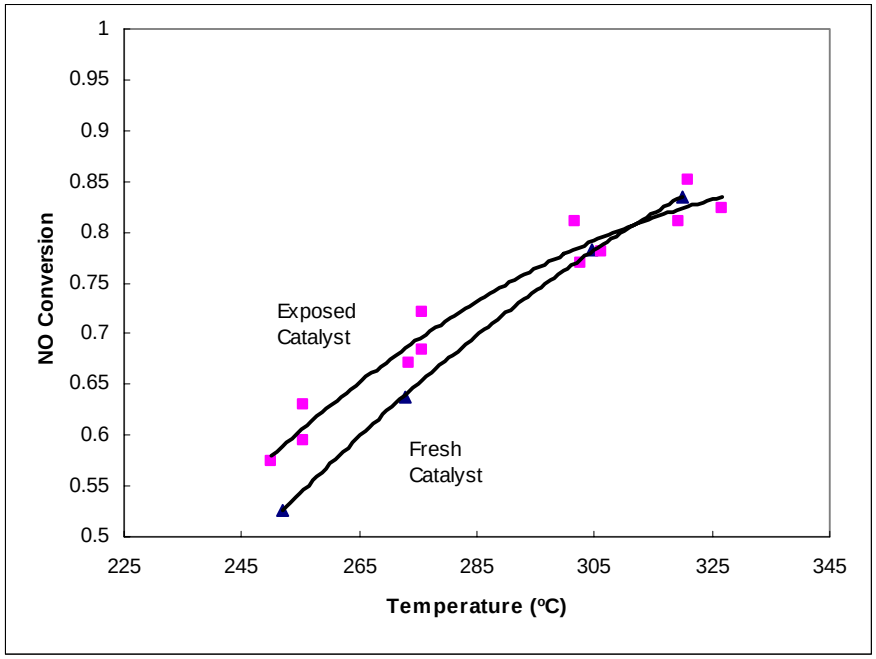



**Figure 1. NO Conversion of M1 over a range of temperatures.**

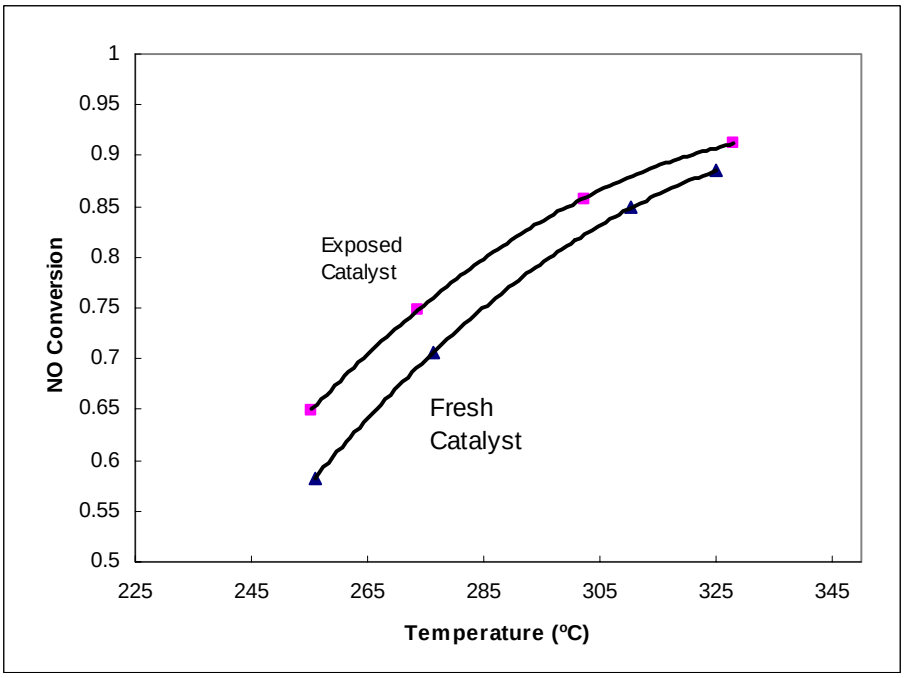



**Figure 2. NO Conversion of M2 over a range of temperatures.**

X-ray photoelectron spectroscopy (XPS) analyses were performed on fresh and exposed M1 and M2 samples to determine which elements were present both inside and outside the catalyst walls. XPS analyses were run at the center and the surface of the wall on M1 and M2 samples (see **Figure 3**). Results of the XPS analyses are shown in **Figure 4** and **Figure 5**.

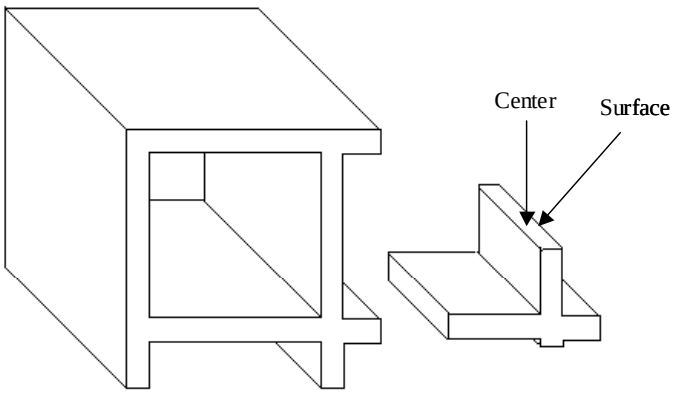
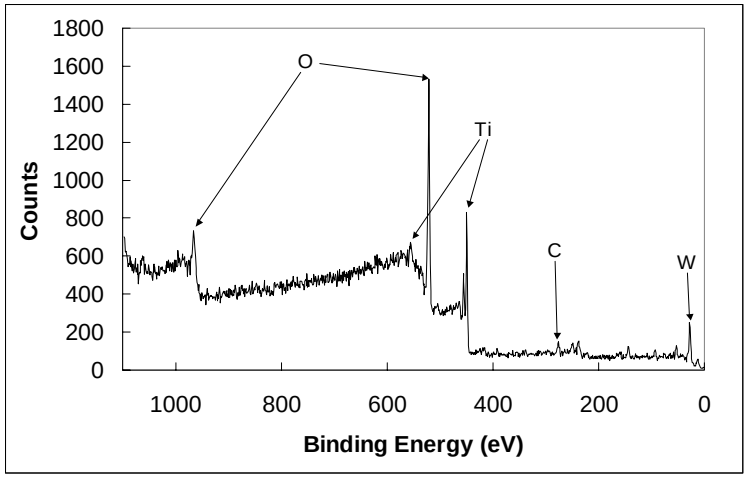
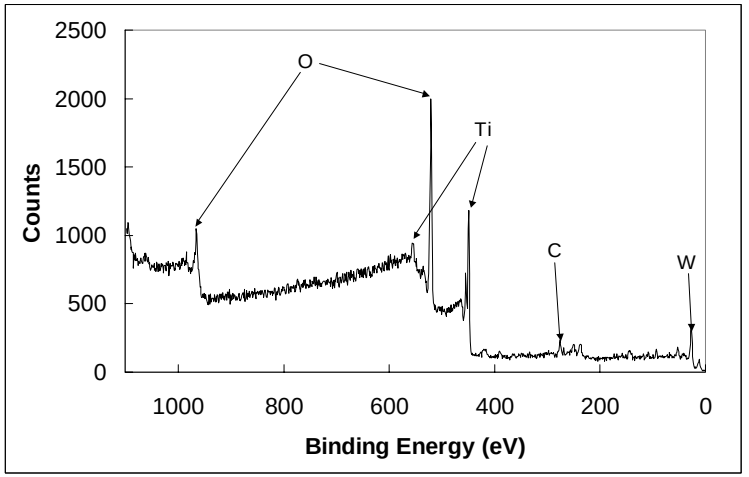


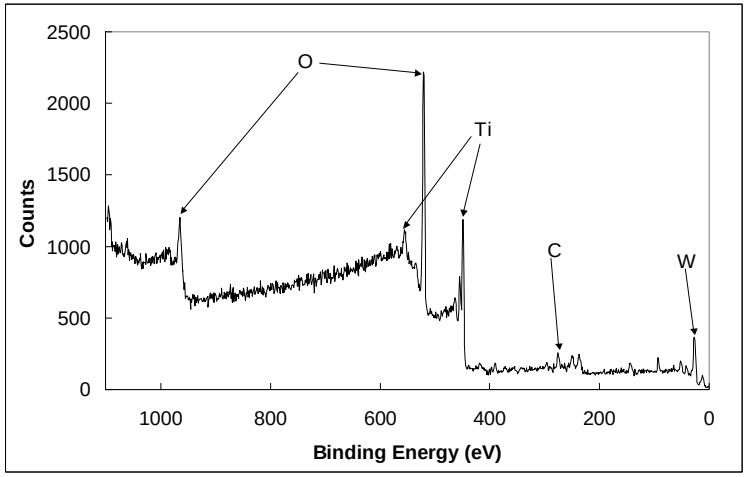

**Figure 3. Sites of XPS Analyses of the Monolith Catalysts.**



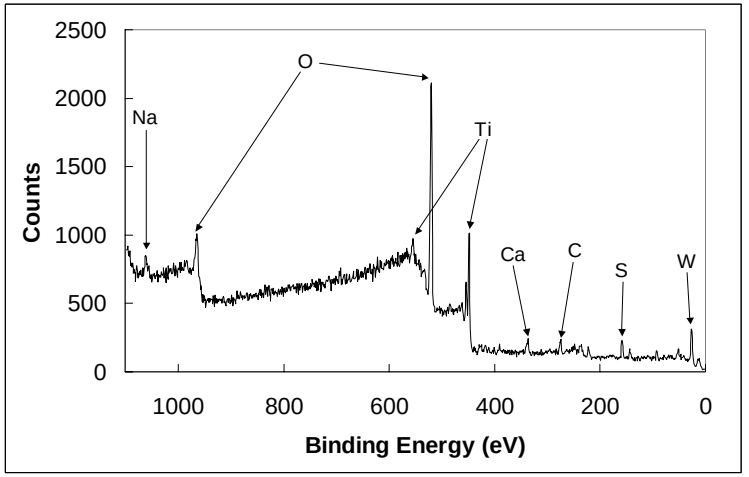

**(a) Center of Fresh M1**




**(b) Center of Exposed M1**

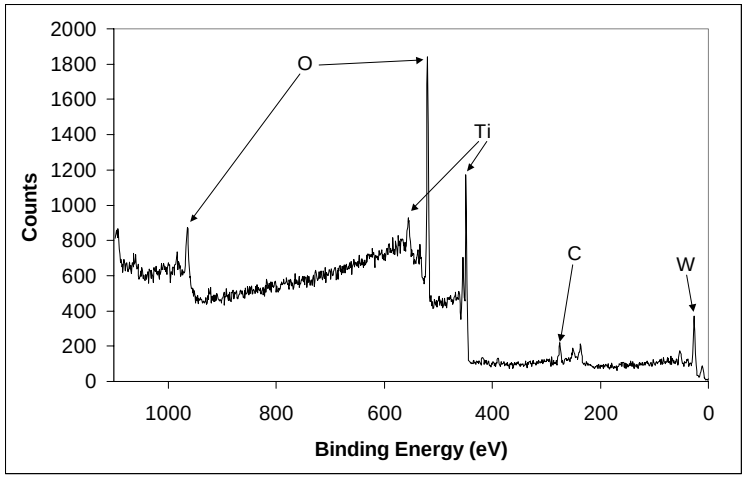



(c) Edge of Fresh M1

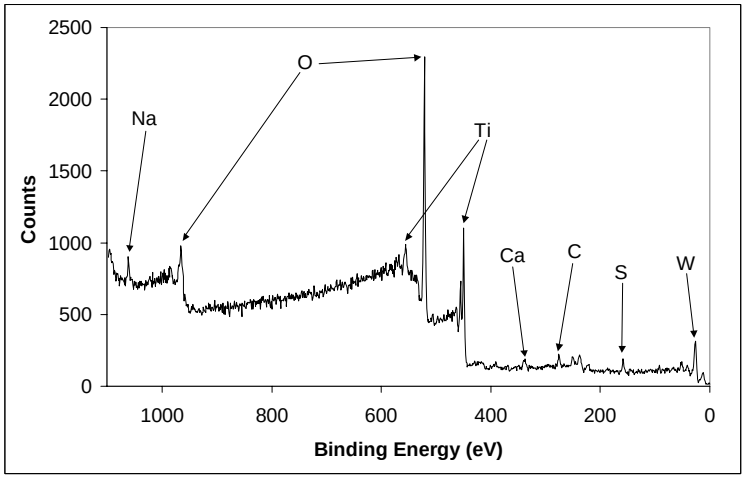



(d) Edge of Exposed M1

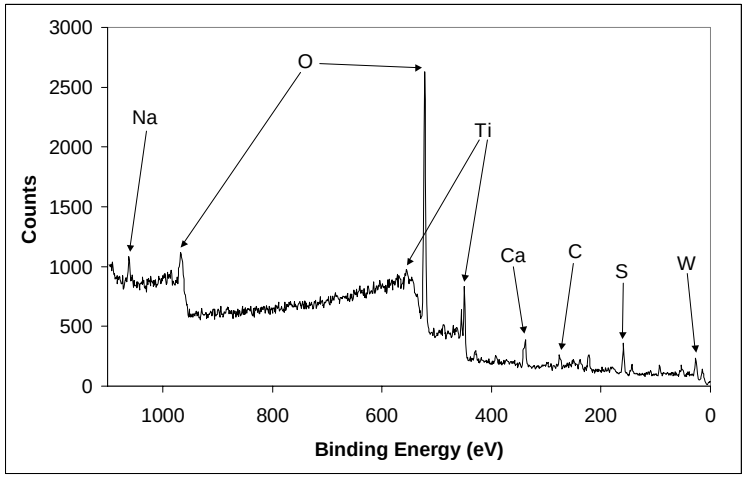
**Figure 4. XPS analyses of M1.**



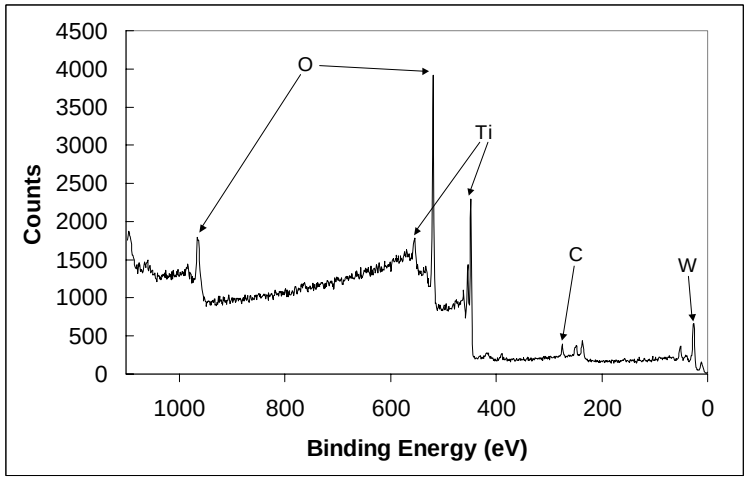

**(a) Center of Fresh M2**




**(b) Center of Exposed M2**




(c) Edge of Fresh M2




(d) Edge of Exposed M2

**Figure 5. XPS Analyses of M2.**

To analyze the XPS results, the experimental C peak was first identified on each graph. The binding energy at this peak was then subtracted from the standard binding energy peak of C (285 eV). The other peaks' binding energies were then adjusted by adding this difference to their respective experimental binding energies. The characteristic peaks of certain elements were identified by comparing the adjusted peak binding energies to those found in literature [Moulder, 1995] (see **Table 2**).

**Table 2. XPS Summary.**

| Catalyst* | Wall Location | C peak | Adjustment | Experimental Peaks (eV) | | | | | | Adjusted Peaks (eV) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | Na | O | Ti | Ca | S | W |
| M1 F | Center | 276 | 9 | --- | 521 | 449 | --- | --- | 27 | --- | 530 | 458 | --- | --- | 36 |
| M1 F | Surface | 276 | 9 | --- | 521 | 449 | --- | --- | 27 | --- | 530 | 458 | --- | --- | 36 |
| M1 E | Center | 276 | 9 | --- | 521 | 450 | --- | --- | 27 | --- | 530 | 459 | --- | --- | 36 |
| M1 E | Surface | 276 | 9 | 1062 | 520 | 448 | 337 | 159 | 27 | 1071 | 529 | 457 | 346 | 168 | 36 |
| M2 F | Center | 275 | 10 | --- | 520 | 449 | --- | --- | 27 | --- | 530 | 459 | --- | --- | 37 |
| M2 F | Surface | 275 | 10 | --- | 520 | 448 | --- | --- | 26 | --- | 530 | 458 | --- | --- | 36 |
| M2 E | Center | 276 | 9 | 1062 | 521 | 450 | --- | 159 | 26 | 1071 | 530 | 459 | --- | 168 | 35 |
| M2 E | Surface | 276 | 9 | 1062 | 522 | 449 | 338 | 159 | 27 | 1071 | 531 | 458 | 347 | 168 | 36 |

*F = Fresh

*E = Exposed

Characteristic peaks for O, Ti, and W were present in all the samples. Characteristic peaks for Na, Ca, and S were present on the wall surface of exposed M1, and the wall center and surface of exposed M2. The reason these species penetrated the center of M2 and not M1 might be due to the thinner walls of M2 (0.77 mm vs 1.20 mm).

## Task 4.2 Evaluation of Commercial SCR Catalysts for Power Plant Conditions

**Biomass Co-firing Tests at Gadsden**

The Gadsen Plant (Figure 6) is located in Gadsden, Alabama, and has two 70 MWe 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.

**Figure 6. Plant Gadsden.**

The difficulty in running switchgrass for extended periods of time on Unit 2, prompted Southern Company and REI to condsider firing sawdust on Unit 1 by co-milling sawdust at about 5% weight basis. The plant personnel 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, installation of the slipstream reactor was begun at Gadsden. Work with plant engineers identified a location for the reactor on Unit 1. Figure 7 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).

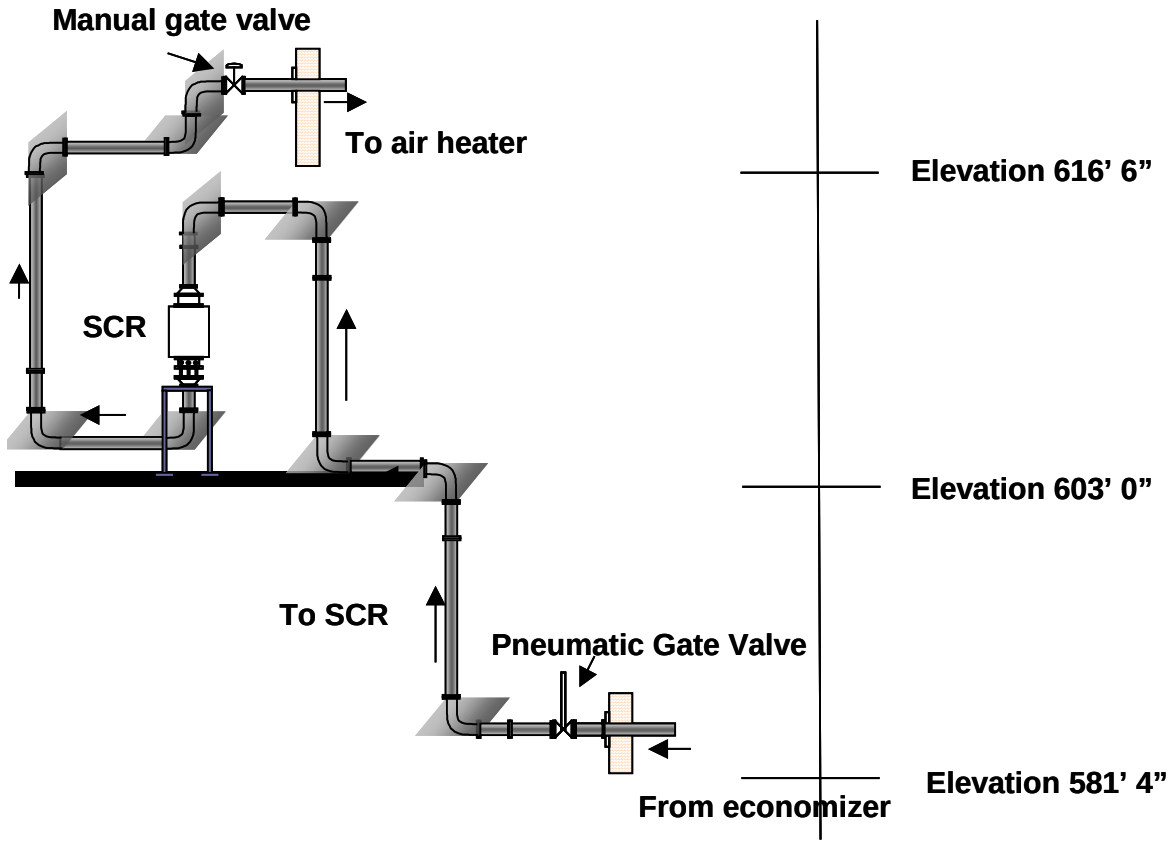



**Figure 7. SCR layout at Gadsden**.

During August and September, the reactor was assembled at Gadsden. Most of the components had been shipped to the plant from Rockport in the previous quarter. Certain components were fabricated in Salt Lake City and shipped to the plant, while other components were fabricated on-site. During this time, Unit 1 was not operating because the plant was idled during ozone season (which ended at the end of September).

The reactor was assembled (Figure 8). After assembly, electrical and plumbing connections were made. The heaters and flow system were tested, and then the reactor was insulated (Figure 9). As at Rockport, the Control Box and CEM sequencer cabinet were located next to the reactor (Figure 10).

An Ethernet cable was run from the Control Box to the control room and connected to the host PC. After several false starts, a modem connection was established over a dedicated phone line, allowing REI to download information (although at a low data transfer rate).

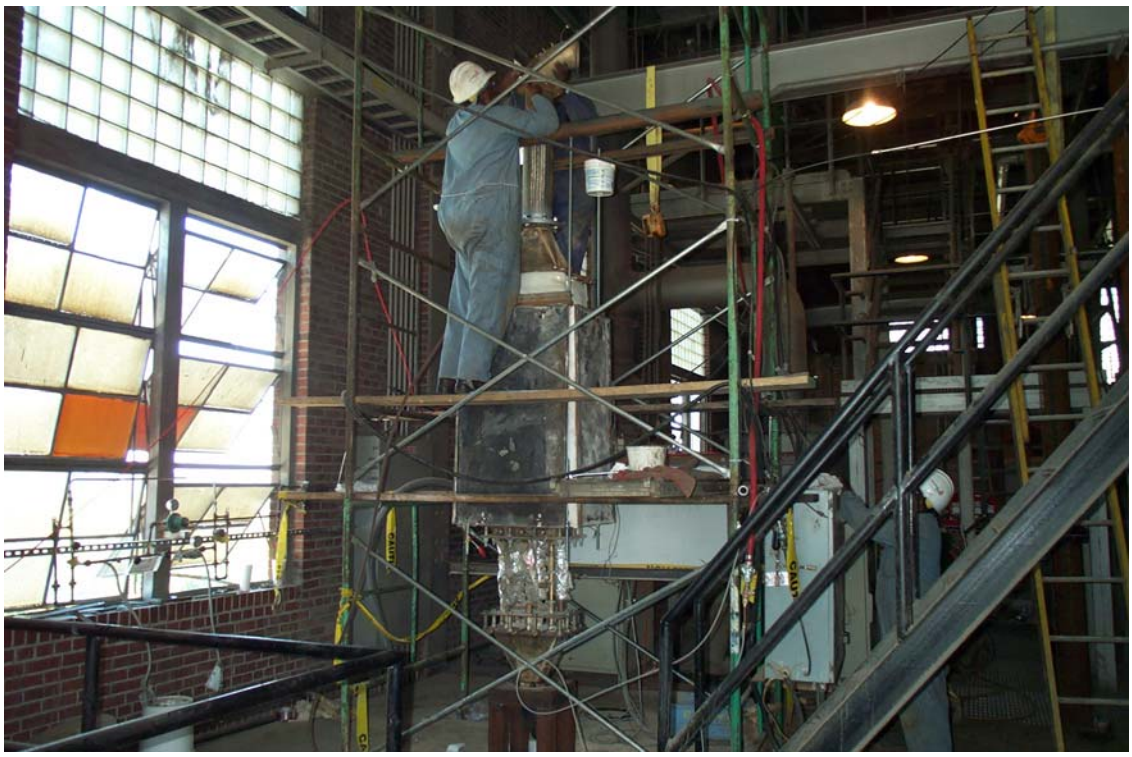


**Figure 8. Assembly of slipstream reactor.**

**Figure 9. Slipstream reactor after insulation.**


**Figure 10. Control Box and Sequencer.**

As can be seen from Figure 7, there is a considerable amount of piping needed to connect the slipstream reactor to the boiler. Last quarter the inlet and outlet gate valves were installed. This quarter, piping was run from the inlet (Figure 11) to the reactor and then to the outlet (Figure 12). The inlet and outlet ports are located upstream and downstream of the air heater, respectively.

The ammonia delivery manifold had to be refabricated this quarter because the black iron pipe used for the manifold had rusted. The manifold was refabricated out of stainless steel. The ammonia tanks could not be installed this quarter because an eyewash and shower had not yet been installed in the fan room, where the ammonia will be located. The eyewash and shower will be installed early next quarter.

**Figure 11. Inlet port located upstream of air heater.**

**Figure 12. Outlet port located downstream of air heater.**

# Results and Discussion

## Discussion of the Corrosion Monitoring Study

At the start of the last performance period, four of the corrosion probes were reinstalled at Gavin using instrument air and began recording data. After approximately 30 hours, two of the ECN probes were removed for future profilometry analysis. The remaining two new probes were installed in their place. All four probes were on-line and collecting data.

Preliminary analyses from the EPRI KEMA Chemkop screw-in corrosion coupons were received. These data showed extremely large corrosion rates (+50 mils/yr) at the coupon by the center ECN probe and much lower corrosion rates at the coupons on the side of boiler. These data are consistent with the ECN measurements. Therefore, the ECN probes, the KEMA coupons and the CFD modeling results all agree with the ultrasonic tube thickness (UT) measurement data gathered by AEP personnel.

During the last performance period AEP personnel conducted routine checks of the probes on a daily basis. During one of these inspections, it was noted that communication had been lost with probe 5 (center probe on North side of boiler). During the week of September 21, 2004, personnel from the REI team traveled to Gavin to correct the situation and determined that the other three probes were also malfunctioning. The probes were removed and it was discovered that the probe caps had warped and ruptured. Examination of these caps showed that the metal thickness on the caps was too thin. All probes were removed and sent to REI for evaluation. After a review of the probe status, all ECN probe caps are being machined using thicker metal to prevent warpage. Probe bodies and sensor heads are being refurbished while the end caps are being machined.

## Discussion of the Catalyst Activity Study

Fundamental tests conducted by BYU demonstrate that surface sulfation increases catalyst activity, consistent with our observations from these commercial catalysts exposed to $SO_2$-laden environments. The laboratory tests also show that alkali significantly poisons catalysts when intimately associated with the catalyst material. Measurements from the commercial catalysts in the slipstream reactor show significant amounts of sodium on the surface and, in one case, in the catalyst interior after exposure. However, there was not associated decrease in activity. We conclude that while sodium-containing fume (likely sodium sulfate) appears to have permeated the entire catalyst in one case and a portion of it in the second case, in neither case did it have a significant impact on catalyst activity. In fact, catalyst activity actually increased with exposure, due mainly to the sulfation. This indicates that such lightly attached alkali-containing particles are not sufficiently associated with the catalyst surface to act as poisons. We speculate that if the catalyst were to become wet, which would dissolve the alkali materials and probably plate it out on the surface, activity may be more significantly impacted.

There does appear to be a drop in catalyst activity measured in the field data. These results suggest that such drops are primarily caused by plugging passages or fouling the catalyst surface, but not by chemical interactions between the catalyst and the fly ash. More tests will be run to more accurately determine the variability of NO conversion of the catalysts and elements present on the wall centers and surfaces.

# 17

# Conclusions

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

- Two ECN corrosion probes were installed and removed after approximately 30 hours for future profilometry analysis.
- The ECN probes, the KEMA coupons and the CFD modeling results all agree with the ultrasonic wall thickness data gathered by AEP personnel showing the areas of high corrosion in the boiler.
- Work has begun on remachining the ECN probe caps to make them thicker to prevent warpage and failure.
- Surface sulfation increases catalyst activity, consistent with our observations from these commercial catalysts exposed to $SO_2$-laden environments.
- Measurements from the commercial catalysts in the slipstream reactor show significant amounts of sodium on the surface and, in one case, in the catalyst interior after exposure. However, there was not associated decrease in activity.
- The SCR slipstream reactor was assembled and installed at Plant Gadsden; safety equipment for ammonia had not been installed at the end of the quarter, but will be installed at the beginning of next quarter.

## Plans for Next Quarter

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

- Complete refurbishing of all ECN corrosion probes with thicker end caps.
- Reinstall all probes in Gavin and continue corrosion measurements.
- Perform profilometry analysis on selected sensor elements.
- Begin ECN corrosion data analysis.
- Continue analysis of the KEMA coupons.

Activity at BYU next quarter will focus on the following:

- A more in depth XPS analysis will also be performed in order to determine relative amounts of the elements found at the surface and center of the walls.

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

- Hook up ammonia to slipstream reactor at Gadsden, complete shakedown on flue gas, and commence running the reactor.

# 18

# References

Bockelie, M. J., Davis, K. A., Linjewile, T. M., Senior, C. L., Eddings, E. G., Whitty, K., Baxter, L., Bartholomew, C., Hecker, W., Harding, N. S. “NOx Control Options and Integration for US Coal Fired Boilers”, Technical Progress Report No. 16, DoE Cooperative Agreement No. DE-FC26-00NT40753, July 30, 2004.

Moulder, Stickle, Sobol, & Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, MN: Physical Electronics, Inc, 1995