SCR CATALYST BLINDING DUE TO SODIUM AND CALCIUM SULFATE FORMATION

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Introduction

Ash-related impacts on selective catalytic reduction (SCR) catalyst performance depend upon the composition of the coal, the type of firing systems, flue gas temperature, and catalyst design (1–5). The problems currently being experienced on SCR catalysts include the following:

- Formation of sulfate- and phosphate-based blinding materials on the surface of catalysts.
- Carrying of deposit fragments, or popcorn ash, from other parts of the boiler and depositing on top of the SCR catalysts.
- Catalyst poisoning from arsenic.

Licata and others (1) conducted tests on a South African and German Ruhr coal and found that the German Ruhr coal significantly increased the pressure drop across the catalyst because of the accumulation of ash. They found that the German coal produced a highly adhesive ash consisting of alkali (K and Na) sulfates. In addition, they reported that the alkali elements are in a water-soluble form and highly mobile and will migrate throughout the catalyst material, reducing active sites. The water-soluble form is typical of organically associated alkali elements in coals. The German Ruhr Valley coal has about 9.5% ash and 0.9% S on an as-received basis, and the ash consists mainly of Si (38.9%), Al (23.2%), Fe (11.6%), and Ca (9.7%), with lower levels of K (1.85%) and Na (0.85%) (2). Cichanosicz and Muzio (3) summarized the experience in Japan and Germany and indicated that the alkali elements (K and Na) reduced the acidity of the catalyst sites for total alkali content (K+Na+Ca+Mg) of 8%–15% of the ash in European power plants. They also found that alkaline-earth elements such as calcium react with SO_3 on the catalyst, resulting in plugging of pores and a decrease in the ability of NH_3 to bond to catalyst sites. The levels of calcium in the coals that caused blinding ranged from 3% to 5% of the ash. FactSage™ calculations indicate that the concentration of potassium and sodium in the gas stream increases more than proportionally with the addition of secondary fuels such as refuse-derived fuel, poultry litter and meat and bone meal (6). Cofiring 25% e/e poultry litter, in particular, increased the gaseous alkali concentrations dramatically.

The mechanisms for this type of low-temperature deposition have been examined and modeled in detail at the Energy & Environmental Research Center (EERC) in work termed Project Sodium and Project Calcium in the early 1990s; however, the focus of those projects was specific to primary superheater and economizer regions of boilers and not SCR systems (4, 7). Deposit buildup of this type can effectively blind or mask the catalyst, diminishing its reactivity for converting NO_2 to N_2 and water and potentially creating increased ammonia slip (1). In examining deactivation mechanisms related to alkali and alkaline earth metals, Senior et al. reported that vanadium tended not to form sulfates on the SCR catalyst in the presence of SO_2(g) but that the catalyst substrate (anatase) and modifiers (molybdenum) do (8).

Arsenic and phosphates, which are not uncommon in low-rank coals, may also play a role in catalyst degeneration. Arsenic is a known catalyst poison (9) in applications such as catalytic oxidation for pollution control. Phosphates can occur in low-temperature ash deposits to create blinding effects. Beck and others (10) found high concentrations of phosphorus compounds as constituents of the bio-residue (sewage sludge) in cofiring with coal to have a significant effect on the rate of catalyst deactivation. Phosphates also occur with arsenic and can cause catalyst poisoning (7). The blinding process involving pyrosulfates has more liquid-phase materials as compared to the calcium sulfate formation processes reported by Siemens (11) who described sulfate materials blocking catalyst pores with 50% catalyst deactivation after 5000 hours for a Powder River Basin (PRB) coal.

The purpose of this research was to obtain fundamental information on the formation of phases and components that comprise SCR blinding deposits. Calcium aluminum phosphate minerals have been observed in North Dakota lignites and PRB coals. Information on how these phosphate-rich phases develop and form will be invaluable for predicting SCR deposition and formulating ash deposit mitigation measures.

Experimental

Several coals were selected for testing based on coal type, geographical origin, and phosphorus-mineral-bearing content to obtain a variety of samples types. All test coals were analyzed for proximate, ultimate, heating value, and bulk inorganic composition using standard American Society for Testing and Materials procedures. Among the coals selected for the test matrix were a 48/52 blend of low-sulfur U.S. bituminous and PRB coals (LSUS–PRB) and a 100% PRB coal. Ash from the coals was produced under simulated combustion conditions in the conversion and environmental process simulator (CEPS), a down-fired combustion system that burns 2–4 lb/hr of fuel (Figure 1). The ash was collected and size fractioned using 3-stage cyclone to partition the ash. The 1–3-µm particles were characterized using scanning electron microscopy (SEM) to determine the distribution of elements as a function of particle size and vapor phase.

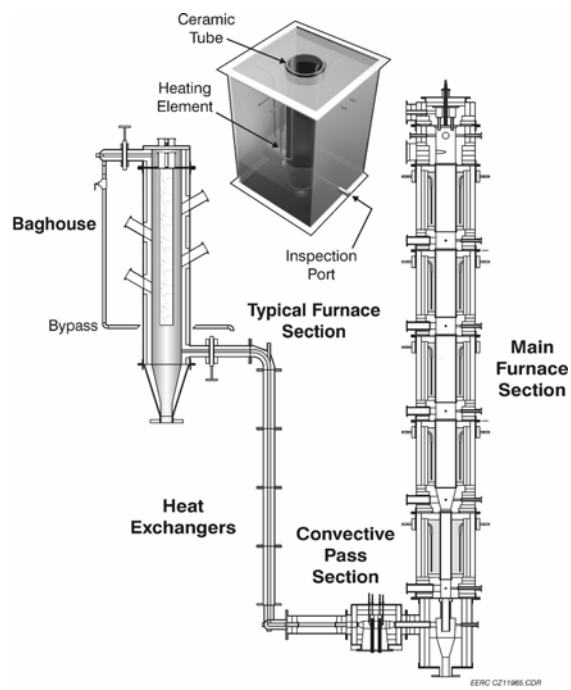

Figure 1. Schematic of the CEPS with furnace section detail.

The impacts of temperature and the presence of the catalyst on the ability of ash to form sulfates were examined. Isothermal tests to develop reaction rate as a function of temperature and gas composition were conducted using thermogravimetric analysis (TGA) with a DuPont model 951 module interfaced to a TA 2100 thermoanalyzer and data processor. The instrument has a 100-mg capacity and a maximum heat-up rate of 100°C/minute. TGA testing was conducted on the 1–3-µm-size fraction of ash produced from the LSUS–PRB and 100% PRB coals and exposing them to vapor-phase sulfur dioxide with and without catalyst at several temperatures. Testing was conducted to determine the weight gain with flue gas containing ammonia. Gas composition for the TGA tests was 74% N_2, 8% H_2O, 14% CO_2, 4% O_2, 100–300 ppm NH_3, 0.04% SO_2, 1–1000 ppm P.

Scanning Electron Microscopy. The SEM method utilizes electron probe microanalysis techniques to chemically analyze individual ash particles. Particles collected in the 3-stage cyclone of the CEPS and exposed in the TGA analyzer were finely dispersed on carbon tape and analyzed for major and minor elements using the ZAF method, which corrects x-ray intensities for differences in the atomic number (Z), absorption (A), and fluorescent (F) effects of the calibration standards relative to the sample. The chemical composition obtained in this manner is semiquantitative at best because of the short x-ray counting time employed (10 s), the use of flat mineral standards for calibration, and the fact that no matrix corrections for particle diameter, shape, or density were applied.

Results and Discussion

Table 1 contains the proximate and ultimate analysis of the selected test materials. The 100% PRB coal had twice the moisture (24.1 vs. 12.9 wt%) of the LSUS–PRB blend. It also contained about 14 wt% more oxygen and 7.5 wt% fixed carbon. Hydrogen and nitrogen content were similar between the coals. The percent ash of the LSUS–PRB blend was about 3.5 wt% higher than the 100% PRB. The sulfur content was also higher (8.3 vs. 5.6 wt% of the ash). Table 2 shows the ratio of mineral constituents in the as-received coals. The 100% PRB coal ash has a higher proportion of Ca than Al and Si. The ashed coal also contained S, Mg, Fe, and small amounts of Ti, Na, and K. The P content was less than 1%. The greatest change resulting from the blending of the PRB with LSUS was the aluminosilicate nature of the ashed blend. The Ca content was one third that of the 100% PRB, and the Mg was half the PRB content. The rest of the elements were present in similar proportion to the 100% PRB coal ash

Table 1. Proximate and Ultimate Analysis of Coal, as received

	100% PRB	LSUS–PRB
Air Dry Loss, %	17.58	9.86
Moisture, %	24.1	12.9
Volatile Matter, %	35.6	35.72
Fixed Carbon, %[1]	36.03	43.59
Ash, %	4.27	7.8
H, %	6.19	5.44
C, %	52.06	62.48
N, %	1.26	1.61
S, %	0.24	0.65
S, % of mineral constituents	5.6	8.3
O, %[1]	35.99	22.03
Calculated Calorific Value	8904	10,830

[1] By difference.

Table 2. SEM Analysis of the Mineral Content of the Coals

Oxide content, SO_3 free	100% PRB	LSUS–PRB
Al_2O_3	32.0	48.3
CaO	20.3	29.7
Fe_2O_3	7.1	5.3
K_2O	1.7	1.8
MgO	1.1	0.4
Na_2O	28.5	9.5
P_2O_5	7.6	2.9
SiO_2	1.1	0.8
TiO_2	0.5	1.3
Al_2O_3	32.0	48.3

The aim of the TGA testing was to determine the potential of the formation of sulfates to cause particle-to-particle bonding that leads to the formation of deposits in the temperature range where SCR catalysts are used. The TGA testing is focused on determining the reactivity of the 1–3-µm ash produced from the LSUS–PRB and 100% PRB coals to sulfur dioxide and gas-phase phosphorus species as a function of temperature. Testing was conducted to determine the weight gain with flue gas containing ammonia. The impact temperature on the weight gain due to the formation of sulfates for the LUSU–PRB blend is shown in Figure 2. The rates of sulfation were found to increase with increased temperature. The increase in the weight gains was magnified when ammonia and phosphorus were added. Ground catalyst was mixed with the 100% PRB ash in the TGA. Increases in weight gain were observed when catalyst was added as compared to baseline cases for 100% PRB, as shown in Figure 3. The presence of catalyst enhances the formation of sulfates.

The ash exposed in the TGA was examined using the SEM. Figure 4 shows the LSUS–PRB blend. The analysis included points at the margins of the spheres to identify coating elements and points in the center of the large spheres to excite as much of the underlying particle as possible. A comparison of the coating and ash particle composition (Table 3) shows higher Ca and S content in the coating material, supporting evidence of sulfate—as $CaSO_4$—formation on the ash particles under SCR reactor conditions.

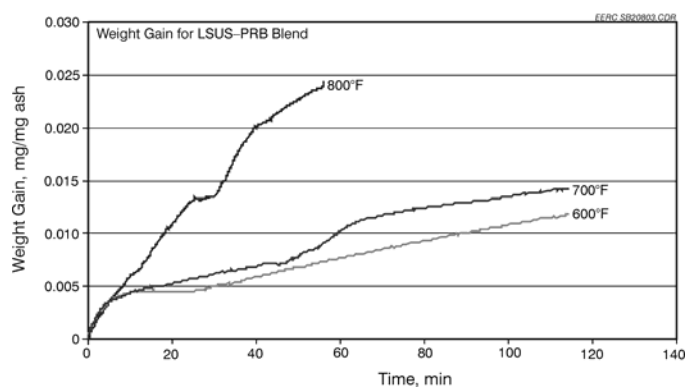

Figure 2. Weight changes for LSUS–PRB coal ash exposed to simulated flue gases and ammonia at three temperatures.

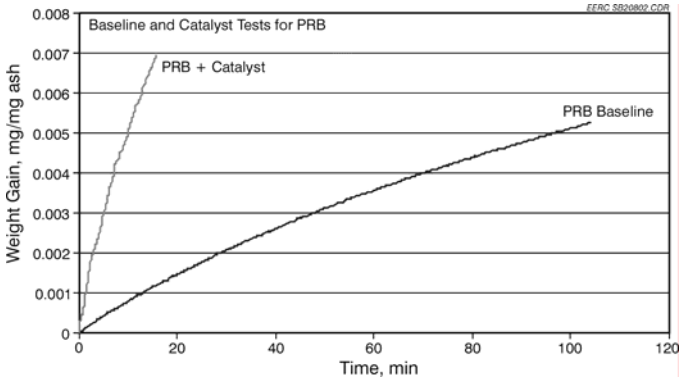

Figure 3. Weight changes for 100% PRB coal ash exposed to simulated flue gases and ammonia as with and without SCR catalyst present at 800°F.

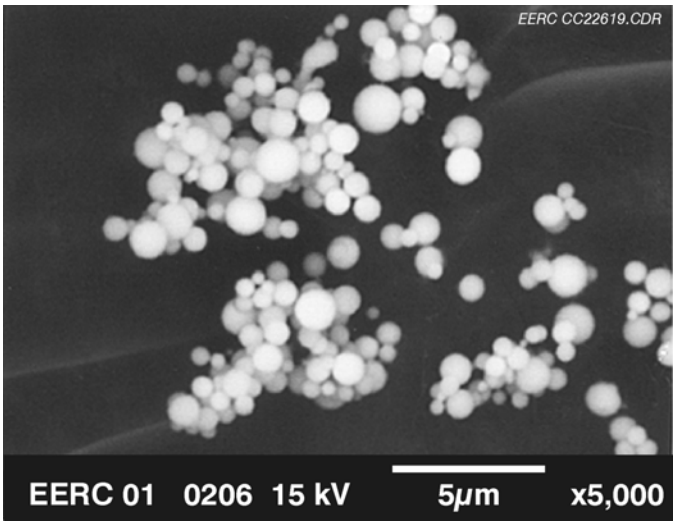

Figure 4. SEM micrograph of LSUS–PRB-blend coal ash exposed to simulated flue gases and ammonia at 800°F (no catalyst present).

Table 3. SEM Analysis of the LSUS–PRB Ash Exposed to Simulated Flue Gas, Ammonia, and Phosphorus in the TGA

Elemental Content	Coating, wt%	Particle and Coating, wt%
Al	15.9	12.6
Ba	0.0	1.0
Ca	20.0	10.6
Cl	0.1	0.0
Cr	0.0	0.0
Fe	4.9	5.6
K	1.7	1.0
Mg	2.1	3.1
Na	0.4	0.5
P	2.0	4.0
S	1.0	0.0
Si	14.5	21.8
Ti	0.9	3.0
O	36.4	36.5

Conclusions

The following observations were noted from the bench-scale phase of this research:

- PRB and lignite coals have the potential to blind SCR catalysts.
- A high blinding potential exists for LSUS–PRB blends.
- The addition of ammonia, phosphorus, and catalyst enhances the formation of phosphates and sulfates.
- Morphology analysis of fly ash exposed to SO_2, ammonia, and P in the TGA shows that sulfates and phosphates accumulated on the surface of the ash.

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