Task 62 – Reducing Power Production Costs by Utilizing Petroleum Coke

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REDUCING POWER PRODUCTION COSTS BY UTILIZING PETROLEUM COKE

1.0 INTRODUCTION

A Powder River Basin subbituminous coal from the North Antelope mine and a petroleum shot coke were received from Northern States Power Company (NSP) for testing the effects of parent fuel properties on coal–coke blend grindability and evaluating the utility of petroleum coke blending as a strategy for improving electrostatic precipitator (ESP) particulate collection efficiency. Petroleum cokes are generally harder than coals, as indicated by Hardgrove grindability tests. Therefore, the weaker coal component may concentrate in the finer size fractions during the pulverizing of coal–coke blends. The possibility of a coal–coke size fractionation effect is being investigated because it may adversely affect combustion performance. Although the blending of petroleum coke with coal may adversely affect combustion performance, it may enhance ESP particulate collection efficiency. Petroleum cokes contain much higher concentrations of V relative to coals. Consequently, coke blending can significantly increase the V content of fly ash resulting from coal–coke combustion. Pentavalent vanadium oxide (V_2O_5) is a known catalyst for transforming gaseous sulfur dioxide (SO_2[g]) to gaseous sulfur trioxide (SO_3[g]). The presence of SO_3(g) strongly affects fly ash resistivity and, thus, ESP performance.

2.0 EXPERIMENTAL

The North Antelope coal, petroleum shot coke, and coal:coke blends of 95:5 and 85:15 (on a weight basis) were selected to investigate the possibility of a coal–coke size fractionation effect. These fuels were pulverized using a Micron Powder Systems Bantam Mill, a small hammer mill. The mill was operated under identical settings typically used to produce a standard coal combustion grind (i.e., 70%–80% −200 mesh). After the fuels were pulverized, sieve analyses were conducted to determine the size distributions of the pulverized fuels. The Ni and V contents of the pulverized products in each of three size fractions (≥200 mesh, <200 mesh but ≥325 mesh, and <325 mesh) were determined using microwave digestion (ASTM D3683) and inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (EPA Method 6010) to assess the preferential partitioning of coal and petroleum coke. Ni and V are significantly enriched in petroleum cokes relative to coals and are, therefore, good tracers for the coke component.

The North Antelope coal and two coal:coke blends of 95:5 and 85:15 were burned in a 40,000-Btu/hr (42-MJ/hr) downfired combustion system shown in Figure 1. Flue gas SO_2 and SO_3 concentrations were measured using an on-line analyzer and a controlled condensation method, respectively, to evaluate V_2O_5 catalytic activity. The controlled condensation method is described by DeVito and Smith (1). In addition, U.S. Environmental Protection Agency (EPA) Method 8 was used during testing of the 85:15 blend to compare SO_3(g) analysis results with the controlled condensation method. SO_3(g) samples were collected from two different locations in

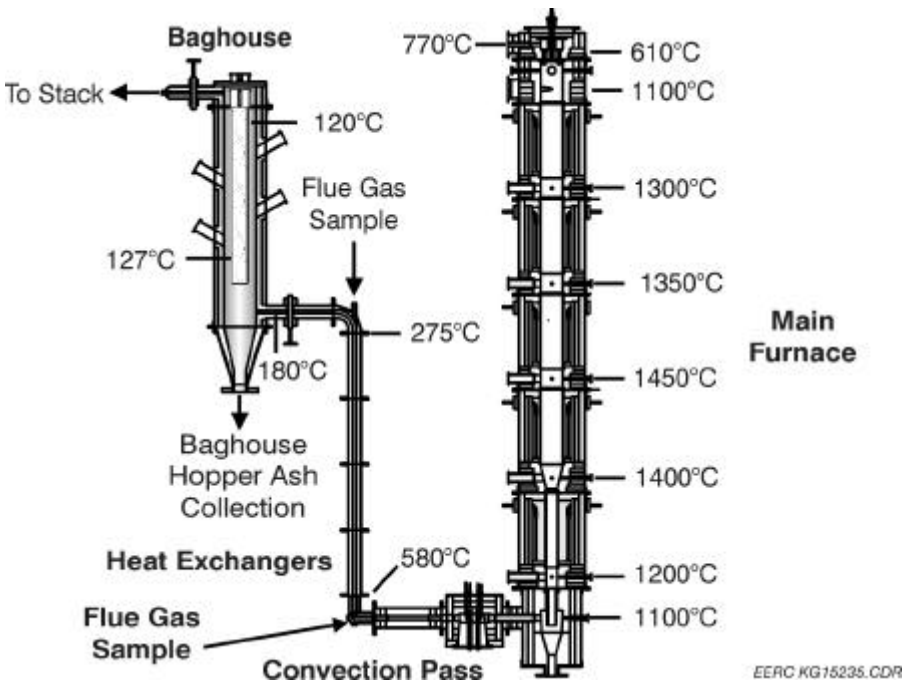

Figure 1. Schematic of the 40,000-Btu/hr combustor showing SO_3(g) sampling locations and temperatures.

the combustor, as indicated in Figure 1, corresponding to temperatures of approximately 275° and 580°C. Fly ash samples were collected from the baghouse after each test and analyzed for major and minor element composition using wavelength-dispersive x-ray fluorescence (WDXRF) spectrometry (ASTM Method D4326). Ni and V concentrations of the baghouse ashes were determined using microwave digestion (ASTM Method D3683) and ICP–AES (EPA Method 6010).

3.0 RESULTS AND DISCUSSION

3.1 Coal–Coke Grindability

Samples of the North Antelope coal, petroleum coke, and coal–coke blends of 95:5 and 85:15 (on a weight basis) were pulverized under identical conditions as described in Section 2.0 of this report. As indicated in Figure 2, Ni and V are significantly enriched in the petroleum coke relative to the coal and are, therefore, good tracers for examining the possibility of a size fractionation effect as a result of the pulverizing process. Seive analyses were conducted on the four fuels to determine their particle-size distributions. As shown in Figure 3, the pulverizer reduced the two parent fuels to approximately the same size, suggesting that the two fuels are very similar in hardness. The pulverized 95:5 blend was significantly finer, whereas the 85:15 blend was significantly coarser relative to the parent fuels. Summations of the Ni and V contents for three size fractions (<45 µm, ≥45 µm but <75 µm, and ≥75 µm) of the fuels are compared in

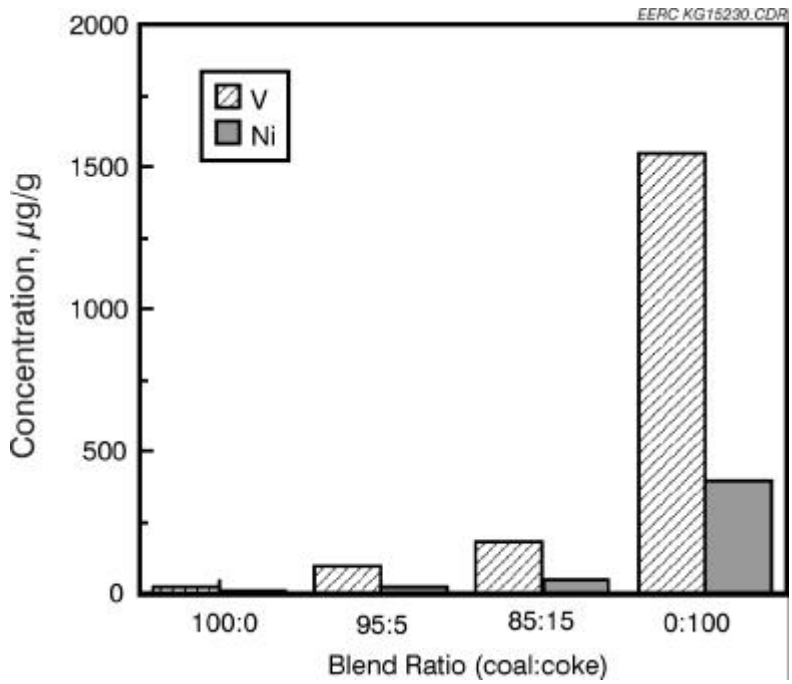

Figure 2. Ni and V concentrations of the coal, coal–coke blends, and coke.

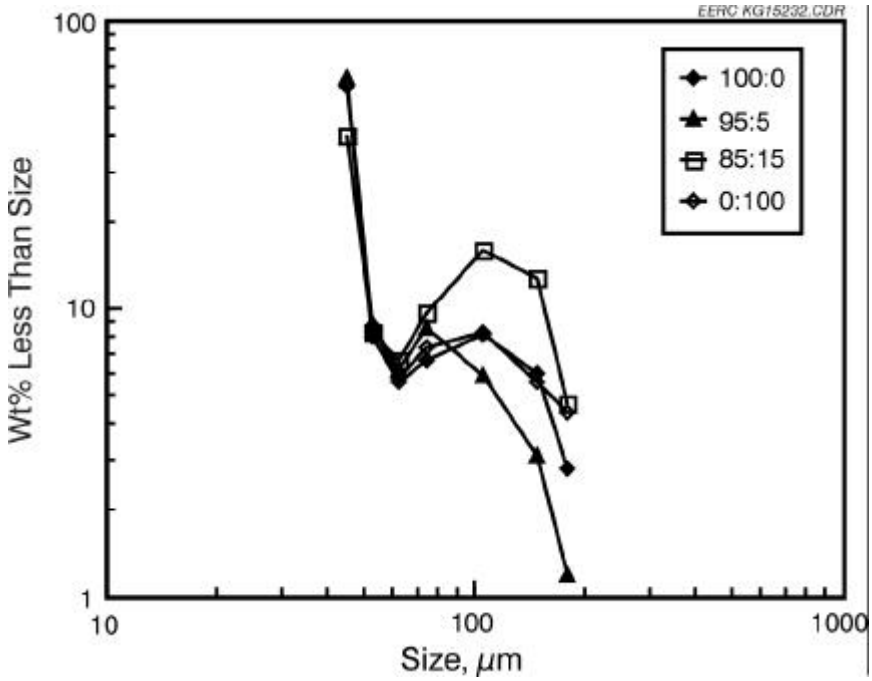

Figure 3. Size distributions of the fuels as a function of blend ratio (coal:coke on a weight basis).

Figure 4. The finest particle-size fraction of the petroleum coke is significantly enriched in V and Ni relative to its coarser size fractions. In contrast, V and Ni are uniformly distributed among the three particle-size fractions of the pulverized North Antelope coal. The finest particle-size fractions of the coal–coke blends are only slightly enriched in V and Ni relative to their coarser size fractions because of the relatively low proportions of petroleum coke that were blended with the coal. Based on this comparison, the size fractionation effect hypothesized in Section 1.0 of this report is not very significant for these fuels at relatively low coke blend proportions.

3.2 Vanadium Catalysis of SO_2(g) Oxidation

Proximate and ultimate analyses of the North Antelope coal and petroleum coke fuels are presented in Table 1. The analysis results in Table 1 compare favorably, with relative percent differences of generally <10, to yearly average values for moisture, ash, calorific value, and sulfur provided by NSP. The flue gas compositions resulting from burning the North Antelope coal and two coal–coke blends in the 40,000-Btu/hr combustion system are presented in Table 2. Mass balance calculations, based on the fuel compositions in Table 1 and fuel feed rates, were used to estimate the inorganic sulfate (SO_4) composition of the flue gas. As expected, the primary effect of petroleum coke blending on flue gas composition is a significant increase in sulfur concentration. Sulfur speciation analyses indicate that although SO_2(g) concentrations increase significantly with increasing coke blending, the SO_3(g) remains undetectable. Mass balance calculations suggest that increasing coke blending promotes the conversion of fuel sulfur to inorganic SO_4 compounds in the fly ash. Chemical analyses of fly ashes collected in the

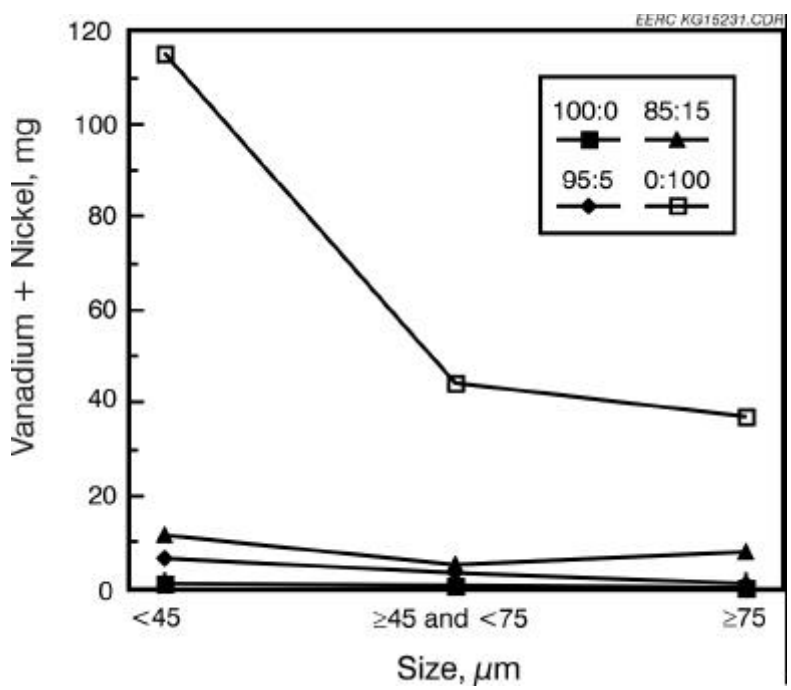

Figure 4. V + Ni contents for three size fractions of the fuels as a function of blend ratio (coal:coke on a weight basis).

baghouse, presented in Table 3, confirm the direct relationship between coke blending and sulfation of the fly ash. In addition to sulfur, the V concentrations of the ashes increase significantly with increasing coke blending, suggesting that V_2O_5-catalysis of SO_2(g) oxidation is responsible for the increase in fly ash sulfation.

Essentially all of the sulfur in the North Antelope coal and coal–coke blends is released as SO_2(g) during combustion. A fraction of the SO_2(g), however, is probably oxidized downstream of the combustion zone to SO_3(g), which reacts with water vapor to form sulfuric acid (H_2SO_4[g, l]). Recent experimental tests by Graham and Sarofim (2) indicate that submicrometer ash is important in controlling the fate of sulfur in combustion flue gas because it contains known catalytic species for SO_2(g) oxidation, generally contributes >90% of the total aerosol surface area, and is intimately mixed with the flue gas. Therefore, both the amount of sulfur released and the fraction of SO_2(g) converted to SO_3(g) and H_2SO_4(g, l) depends strongly on the composition of the submicrometer ash. The submicrometer ash produced from burning subbituminous Powder River Basin coals, such as the North Antelope coal, is generally enriched in alkaline species such as lime (CaO) that readily react with SO_2(g), SO_3(g), and H_2SO_4(g, l) (3, 4). Therefore, petroleum coke blending with the North Antelope coal may promote ash fouling and not the desired effect of generating SO_3(g) to improve ash resistivity characteristics.

TABLE 1

Proximate and Ultimate Analysis Results of the North Antelope Coal and Petroleum Coke Fuels, wt% as-received unless otherwise noted

Parameter	North Antelope Coal	Petroleum Coke
Moisture	26.6	6.00
Volatile Matter	34.4	8.60
Fixed Carbon	34.9	84.8
Ash	4.14	0.60
Calorific Value, Btu/lb	9355	14,280
Hydrogen	6.85	4.00
Carbon	51.8	83.3
Nitrogen	0.64	1.49
Sulfur	0.26	6.14
Oxygen	36.3	4.44

TABLE 2

Flue Gas Compositions, Mean Values of Five Analyses with 95% Confidence Limits (±2σ)

Blend Ratio (Coal:Coke):	100:0	95:5	85:15
CO_2, mol%	14.8 ± 0.2	15.4 ± 0.2	15.4 ± 0.2
CO, ppmv	<3	<3	<3
Excess O_2, mol%	4.2 ± 0.2	4.0 ± 0.2	4.0 ± 0.2
NO_x, ppmv	1185 ± 15	1080 ± 70	1090 ± 70
SO_2, ppmv	251 ± 5	451 ± 6	790 ± 30
SO_3, ppmv	<0.5	<0.4	<0.5
Inorganic SO_4, ppmv[1]	<5	54	180

[1] Estimated based on mass balance calculations.

TABLE 3

Chemical Compositions of the Baghouse Ashes

Blend Ratio (Coal:Coke):	100:0	95:5	85:15
SiO_2, wt%	27.8	28.4	25.4
Al_2O_3	20.1	20.0	18.7
Fe_2O_3	7.2	6.8	6.9
TiO_2	1.6	1.6	1.6
P_2O_5	1.6	1.5	1.5
CaO	29.1	27.9	28.6
MgO	6.7	6.5	6.4
Na_2O	1.5	1.5	1.5
K_2O	0.3	0.3	0.3
SO_3	2.9	4.1	7.4
Ni	0.012	0.036	0.090
V	0.033	0.165	0.531

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