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Project Summary

Environmental Assessment of a Coal/Water Slurry Fired Industrial Boiler

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This report describes emission results from field testing of an industrial boiler retrofitted to fire a coal/water slurry (CWS). Emission measurements performed included continuous monitoring of flue gas emissions; source assessment sampling system (SASS) sampling of the flue gas, with subsequent laboratory analysis of samples to obtain total flue gas organics in two boiling point ranges, compound category information within these ranges, specific quantitation of the semivolatile organic priority pollutants, and flue gas concentrations of 73 trace elements; EPA Method 5 sampling for particulate; EPA Method 8 sampling for SO_2 and SO_3 emissions; volatile organic sampling train (VOST) testing for volatile organic priority pollutant emissions; gas grab sampling for onsite C_1 to C_6 hydrocarbons emission measurements; gas grab sampling for N_2O emissions measurements; and grab sampling of the CWS fuel for inorganic composition determination.

NO_x, SO_2, SO_3, CO, and total unburned hydrocarbon (TUHC) emissions averaged 510, 450, 2.6, 285, and 1ppm (corrected to 3 percent O_2), respectively, during the 1 day test. Particulate emissions, at 4.3 g/dscm, were high, although expectedly so since the unit was not equipped with a particle control device. Emitted particle size distribution was heavily weighted to coarse particulate. Over half the emitted mass was greater than 10 μm diameter; over 90 percent, greater than 3 μm. Combustibles loss in the particulate was high; the composite particulate was over 40 percent carbon.

Total organic emissions from the boiler were 15 to 17 mg/dscm; of this total, 50 percent were in the C_1 to C_6 boiling point range. Of the semivolatile organic priority pollutants, only naphthalene (at a level less than 5 μg/dscm) was detected in flue gas samples. Of the volatile organic priority pollutants, emissions of several chlorinated C_1 and C_2 aliphatic hydrocarbons, chlorobenzene, benzene, and ethylbenzene were quantitated in the 1 to 20 μg/dscm range.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see Project Report ordering information at back).

Introduction

Coal/water slurries (CWS) have received attention in recent years as an alternative to oil fuels. CWS has the advantage of allowing certain oil-fired boilers to eliminate their oil fuel requirements at modest retrofit cost. Thus, CWS has the potential for conversion of some oil-burning facilities to coal firing, thereby offsetting higher oil prices and (frequently) uncertain supplies. This report gives results of an emission assessment of a CWS-fired industrial boiler.

The boiler tested was a Babcock & Wilcox integral furnace, bent-tube boiler rated at 7.6 kg steam/s (60,000 lb/hr) at 1.2 MPa (175 psig) at the Memphis plant of the E.I. du Pont de Nemours & Company. The unit was originally designed to fire distillate oil, process gas, and natural gas, and had been previously modified to accommodate residual fuel oil.

The unit was most recently modified to allow CWS firing under an Electric Power

Research Institute (EPRI) CWS demonstration program. The tests reported here were performed during the 35-day demonstration burn phase of the EPRI project. A CWS formulation prepared by the Atlantic Research Corporation (ARC-Coal) was being fired during the tests performed for this report.

Summary and Conclusions

Boiler Operation

Table 1 summarizes the boiler operating conditions for the test. As indicated, three of the five available furnaces were fired with the CWS. In addition, about 10 percent of the total heat input to the unit was with natural gas introduced through one burner and through a direct-fired air preheater. Boiler load was slightly greater than 90 percent of rated for the test. Boiler efficiency as calculated by the ASME heat loss method was 72 percent. Table 2 gives the fuel ultimate analysis reported by the host site.

Emission Measurements and Results

The sampling and analysis procedures used in this test program conformed to an extended EPA Level 1 protocol. All flue gas was sampled in a vertical section of breeching, downstream of the units' induced draft fan, but upstream of the breeching transition section to the stack. Emission measurements included:

- Continuous monitoring for O_2, CO_2, NO_x, CO, and TUHC.
- Source assessment sampling system (SASS) for trace elements and semi- and non-volatile organic emissions.
- Volatile organic sampling train (VOST) for volatile organic emissions.
- Combined EPA Method 5/8 for particulate and SO_x emissions.
- Gas grab samples for onsite C_1 to C_6 hydrocarbon measurement.
- Gas grab samples for laboratory N_2O analysis.

In addition, samples of the fuel were collected for analysis. The analysis protocol included:

- Analyzing the fuel and SASS train samples for 73 trace elements using spark source mass spectrometry (SSMS), supplemented by atomic ab-

Table 2. *CWS Fuel Composition*

Component	*Percent by weight (dry basis unless noted)*
Moisture[a]	*29.7*
Solids[a]	*70.3*
Carbon	*83.3*
Hydrogen	*5.1*
Oxygen[a,b]	*5.0*
Nitrogen	*1.4*
Sulfur	*0.6*
Ash	*4.6*
Higher heating value, MJ/kg	*34.374*
(Btu/lb)	*(14,810)*

[a]*As fired.*
[b]*By difference.*

Table 1. *Boiler Operating Conditions*

Parameter	*Range*	*Average*
Steam flow, kg/s (10^3 lb/hr)	*6.89 to 7.13 (54.6 to 56.5)*	*7.01 (55.5)*
Steam pressure, MPa (psig)	*1.19 to 1.21 (173 to 176)*	*1.21 (175)*
CWS flow, l/s (gpm)[a]	*0.60 to 0.61 (9.5 to 9.7)*	*0.61 (9.6)*
Natural gas flow to burner No. 4, scm/min (10^3 scfh)	*1.39 to 1.79 (2.94 to 3.79)*	*1.48 (3.14)*
Natural gas flow to air heater, scm/min (10^3 scfh)	*1.58 to 1.76 (3.35 to 3.73)*	*1.68 (3.55)*
Inlet air temperature, °C (°F)	*29 to 39 (85 to 102)*	*36 (96)*
Windbox air temperature, °C (°F)	*274 to 283 (525 to 542)*	*279 (535)*
Windbox air pressure, kPa (in. WC)	*279 (11.2)*	*279 (11.2)*
CWS heater temperature, °C (°F)	*37 to 38 (98 to 101)*	*38 (100)*
CWS strainer discharge pressure, MPa (psig)	*1.35 to 1.38 (196 to 200)*	*1.37 (198)*
Feedwater temperature, °C (°F)	*129 (265)*	*129 (265)*
Stack gas temperature, °C (°F)	*293 to 304 (559 to 580)*	*299 (571)*
Atomizing air pressure, MPa (psig)		
Burner No. 2	*1.41 to 1.42 (204 to 206)*	*1.42 (206)*
Burner No. 3	*1.42 to 1.43 (206 to 208)*	*1.43 (208)*
Burner No. 4	*1.41 to 1.42 (204 to 206)*	*1.42 (206)*
CWS burner pressure, MPa (psig)		
Burner No. 2	*1.13 to 1.16 (164 to 168)*	*1.14 (166)*
Burner No. 3	*1.12 to 1.14 (162 to 166)*	*1.14 (165)*
Burner No. 4	*1.16 to 1.23 (168 to 179)*	*1.21 (176)*
Furnace pressure, Pa (in. WC)	*−77 to −37 (−0.31 to −0.15)*	*−60 (−0.24)*
Excess air (percent)[b]		*45*
Boiler efficiency (percent)[c]		*72*

[a]*Average of two flowmeters installed; one magnetic and one mass.*
[b]*Calculated from flue gas composition.*
[c]*Calculated using "ASME test form for abbreviated efficiency test."*

sorption spectrometry (AAS) and other techniques.

- Analyzing VOST traps for the volatile organic priority pollutants.
- Analyzing the SASS train organic extract samples for total organic content in two boiling point ranges; 100 to 300 °C by total chromatographable organics (TCO) analysis, and >300 °C by gravimetry (GRAV).
- Analyzing the SASS train extract samples for the 58 semivolatile organic species, including many of the polynuclear aromatic hydrocarbon (PAH) compounds.
- Performing infrared (IR) spectrometry analysis of organic sample extracts.

Bioassays were also performed on SASS train and ash samples to estimate their potential toxicity and mutagenicity.

Table 3 summarizes flue gas emissions measured in the test program. Emissions are presented as nanograms per Joule heat input and as milligrams per dry standard cubic meter of flue gas. As a measure of the potential significance of the emission levels for further analyses, an occupational exposure guideline for most pollutants is also noted in the table. The occupational exposure guideline is either the time-weighted-average Threshold Limit Value (TLV) established by the American Conference of Governmental Industrial Hygienists, or the 8-hr time-weighted-average exposure limit established by the Occupational Safety and Health Administration (OSHA). These are noted only to aid in ranking the potential significance of the emission levels. In this respect, pollutants emitted at levels several orders of magnitude higher than their occupational exposure guideline might warrant further consideration, while pollutants emitted at levels significantly lower than their occupational exposure guideline might be considered of little potential concern. Only elements emitted at levels exceeding 10 percent of their occupational exposure guideline in these tests are noted in Table 3.

Table 3. *Summary of Flue Gas Emissions*

Component	*Emission concentration (ng/J heat input)*	*Emission concentration (mg/dscm)*	*Occupational exposure guideline[a] (mg/m³)*
Major constituents			
Particulate	2,510	4,310	10[b]
SO_2	540	930	5.0
SO_3	3.9	6.7	1.0
NO_x (as NO_2)	440	760	6.0
CO	150	260	55
N_2O	57	98	—[c]
Total volatile organics (C_1 to C_6)	8.8	15.1	—[c]
Total semivolatile organics (TCO)	0.03	0.05	—[c]
Total nonvolatile organics (GRAV)	0.2	0.3	—[c]
Trace Elements			
Beryllium	0.25	0.43	0.002
Aluminum	160	270	2.0
Iron	47	80	1.0
Chromium	1.3	2.3	0.050
Silicon	225	385	10[b]
Sodium	28	48	2.0[d]
Phosphorous	1.1	1.9	0.10
Potassium	16	28	2.0[d]
Nickel	0.67	1.2	0.10
Lithium	0.15	0.26	0.025
Vanadium	0.26	0.44	0.050
Calcium	7.5	13	2.0
Arsenic	0.032	0.056	0.010[e]
Lead	0.097	0.17	0.050[e]
Copper	0.19	0.33	0.10[e]
Barium	0.74	1.3	0.50
Titanium	9.7	17	10[b]
Cobalt	0.070	0.12	0.10
Magnesium	4.5	7.7	10
Zinc	0.25	0.43	1.0
Silver	0.0024	0.0041	0.010
Selenium	0.018	0.031	0.20
Bromine	0.063	0.11	0.70
Yttrium	0.082	0.14	1.0

[a] *Time-weighted-average TLV unless noted.*
[b] *For nuisance particulate.*
[c] *No occupational exposure guideline applicable.*
[d] *Ceiling limit.*
[e] *8-hr time-weighted-average OSHA exposure limit.*

As noted in Table 3, particulate emissions from the boiler were quite high (about 4.3 g/dscm). This is not unexpected, however, since the unit had no particulate control device. The emission levels for NO_x, SO_2, SO_3, CO, and N_2O correspond to 510, 450, 2.6, 285, and 70 ppm (corrected to 3 percent O_2), respectively. The NO_x level noted is in the range typical for coal-fired sources. The SO_x (SO_2 and SO_3) levels correspond to what would be expected from this source burning a 1 percent (dry basis) sulfur fuel. The analysis summarized in Table 2 indicates less sulfur in the fuel. However, an independent analysis cited by the host site suggests that the fuel sulfur content could have been above 0.9 percent. The ratio of SO_3 to total SO_x, at 0.6 percent, is lower than the typical 2 to 5 percent range for coal fired sources.

Table 3 notes that several trace elements were emitted at levels significantly higher than their occupational exposure guideline. In fact, two elements were emitted at levels over a factor of 100 times their occupational exposure guideline and another eight at levels greater than 10 times their guideline. Again, however, this is largely the result of the absence of a particulate control device on the boiler for these tests. In fact, five of the first eight elements noted in the table (aluminum, iron, silicon, sodium, and potassium) are major constituents of the ash fraction of the CWS fuel. For further comparison, the criterial pollutants NO_x and SO_2 (in addition to particulates) were also emitted at levels over 100 times their occupational exposure guidelines.

The size distribution of emitted particulate was heavily weighted toward coarse particulate, as noted in Table 4. Over half of the emitted particulate mass had diameters greater than 10 μm; over 90 percent had diameters greater than 3 μm. Combustible losses in the particulate were quite high as noted in Table 5. Composite particulate had a carbon content of about 40 percent which, with the hydrogen noted, would give a particulate higher heating value of 13.7 MJ/kg (5,920 Btu/lb).

Table 3 noted that total organic emissions from the unit were about 15.5 mg/dscm, comprised chiefly (over 95 percent) of compounds in the volatile (boiling point less than about 100 °C) category. Emissions of both total semivolatile organics (boiling point between 100° and 300 °C) were 0.05 mg/dscm; of nonvolatile organics (boiling point greater than 300 °C) were 0.3 mg/dscm.

Analysis of SASS train samples for the semivolatile organic priority pollutants showed that only naphthalene was present in the flue gas at detectable levels; naphthalene emissions were less than 5 μg/dscm.

Results of VOST testing for volatile organic compounds are summarized in Table 6, which shows that several chlorinated C_1 and C_2 aliphatic hydrocarbons, chlorobenzene, benzene, and ethylbenzene were emitted at levels in the 1 to 20 μg/dscm range. Such levels of benzene and ethylbenzene are common in combustion source flue gas. The chlorinated compounds also arise whenever chlorine-containing fuels are burned. Although not noted in Table 2, an independent host site analysis suggests that the chlorine content of the CWS burned was 0.1 percent.

Bioassay tests were performed on the SASS train organic sorbent module extract and two particulate size fractions. The health effects bioassays performed were the Ames mutagenicity assay, and the CHO cytotoxicity assay. The results of these assays are summarized in Table 7. The results suggest that the sorbent module extract was of moderate toxicity and mutagenicity and both particulate size fractions were of nondetectable mutagenicity and low toxicity.

Table 4. *Particle Size Distribution*

Size range	Weight percent of particulate in size range
>10 μm	51.4
3 to 10 μm	40.4
1 to 3 μm	7.8
>1 μm	0.4

Table 5. *Particulate Carbon and Hydrogen Content*

Size range	Carbon content (weight percent)	Hydrogen content (weight percent)
>3 μm (10 μm + 3 μm cyclone catch)	42.67	0.13
<3 μm (1 μm + filter catch)	13.13	0.09
Composite	40.19	0.13

Table 6. *Stack Gas Volatile Organic Compound Concentrations*

	Stack gas concentration[b,c] (μg/dscm)						
	Trap set 1			Trap set 3			
Compound[a]	Tenax trap	Tenax/ charcoal trap	Total	Tenax trap	Tenax/ charcoal trap	Total	Average total
Chloromethane	0.4	27.6	28	<0.3	12.8	13	21
Vinyl chloride	<0.3	5.2	5.2	<0.3	8.3	8.3	6.8
Chloroethane	<0.3	8.2	8.2	<0.3	12.9	12.9	11
1,2-dichloroethane	0.4	<0.3	0.4	<0.3	<0.3	<0.3	0.4
Benzene	20.9	<0.3	21	25.4	<0.3	25	23
Chlorobenzene	<0.3	<0.3	<0.3	1.5	<0.3	1.5	0.9
Ethylbenzene	<0.3	2.4	2.4	<0.3	1.1	1.1	1.8

[a]*Bromomethane, chloroethane, methylene chloride, 1,1-dichloroethylene, 1,1-dichloroethane, t-1,2-dichloroethylene, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, dichlorobromomethane, 1,2-dichloropropane, t-1,3-dichloropropene, trichloroethylene, 2-chloroethyl vinyl ether, bromoform, tetrachloroethylene, 1,1,2,2-tetrachloroethane, toluene, allyl chloride, ethylene oxide, propylene oxide, and 2-nitropropane were also analyzed for and not detected above a detection limit of 0.3 μg/dscm.*
[b]*Field blank corrected.*
[c]*Triplicate sets of traps samples; trap set 2 not analyzed.*

The positive Ames responses for the sorbent module extracts noted above are typical for such extracts from SASS tests of combustion sources. Current studies are investigating if such bioassay responses are due to artifact compounds formed when combustion product gas containing NO_x is passed over XAD-2 resin.

Quality assurance (QA) was performed for these tests to establish the precision and accuracy of several laboratory analyses. The precision of the TCO analysis met the project QA goal for this procedure. However, only 70 percent of the C_1 to C_6 GC measurements met the QA objective for this procedure compared to a project completeness objective of 90 percent. Deviations occurred in the C_1 and C_3 quantitations. Since negligible amounts of C_1 hydrocarbons were detected in these tests, this deviation had no effect on project conclusions. The deviations in the C_3 measurement may introduce factor of 2 differences in cited C_3 emissions, which would introduce factor of 30 percent differences in total C_1 to C_6 hydrocarbon reported. Such differences would not significantly alter test conclusions regarding total organic emission dominated by the volatile (C_1 to C_6) fraction.

Table 7. *Bioassay Results*

	Bioassay	
Sample	Ames[a]	CHO[b]
XAD-2 extract:	M	M
<3 μm particulate (1 μm + filter)	ND	L
>3 μm particulate (3 μm + 10 μm)	ND	L

[a]*Mutagenicity test*
[b]*Toxicity test*
M: Moderate, L: Low,
ND: Nondetectable

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"Volume I. Technical Results," (Order No. PB 86-183 795/AS; Cost: $11.95)
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