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Project Summary

Environmental Assessment of a Watertube Boiler Firing a Coal/Water Slurry

R. DeRosier and L. R. Waterland

This report describes emission results obtained from field testing of flue gas from a watertube industrial boiler firing a coal/water slurry (CWS). Previously, an emission test of this same unit was made while burning a coal/oil mixture (COM). 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; and grab sampling of fuel and ash for inorganic composition. Two tests were performed firing a CWS containing nominally 60 percent coal by weight: an abbreviated set of tests with flue gas O_2 of about 2.8 percent, and a complete set of tests with flue gas O_2 of about 2.1 percent.

NO_x, SO_2, CO, and TUHC emissions were in the 230-310, 880-960, 170-200, and 1-3 ppm ranges (corrected to 3 percent O_2), respectively, over the two tests. Particulate levels at the boiler outlet (upstream of the unit's particulate control device) apparently increased from 3.5 g/dscm in test 1 to 7.3 g/dscm in test 2. The increase may have been due to increased combustibles loss with the boiler flyash. Coarse particulate predominated: over 60 percent (weight) of the boiler outlet flue gas particulate was greater than 10 μm diameter, almost 70 percent was greater than 3 μm diameter.

Total organic emissions were quite high, almost 50 mg/dscm. About 70 percent of this organic matter was in the nonvolatile (>300°C) boiling point range. The bottom ash organic content was quite high as well, 8 mg/g, with 80 percent of this being in the nonvolatile boiling point range.

Of the polynuclear aromatic hydrocarbons (PAHs) analyzed for, only naphthalene was detected in flue gas samples (on the particulate) with emission levels of 8.6 μg/dscm. Several PAHs were found in the bottom ash, at levels ranging from 0.4 to over 40 μg/g.

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 (see Project Report ordering information at back).

Introduction

Coal/water slurries 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 without completely redesigning the boiler. Thus, CWS has the potential for application as a near-term technology for conversion of certain oil-burning facilities to coal firing and thereby offsetting high oil prices and frequently uncertain supply situations. This report presents the results of an emission assessment of a CWS-fired watertube industrial boiler.

The tests were performed at the Pittsburgh Energy Technology Center's (PETC's) combustion test facility. This facility consists of a 3.0 kg/s steam

(24,000 lb/hr) watertube boiler, an air-cooled steam condenser and deaerator, CWS preparation and storage facilities, and pollution control devices. The boiler is a package, two-drum "D"-type watertube originally designed by Nebraska Boiler Company to fire No. 6 fuel oil. Table 1 summarizes the boiler specifications.

CWS is prepared by charging a predetermined amount of water to a 6,800 L (1,800 gal.) steam-jacketed mix tank with agitator before adding coal through a gravimetric coal feeder. The CWS is then transferred to a 10,600 L (2,800 gal.) holding tank with an agitator and recirculation pump. The CWS is pumped to the burner by a Moyno pump. The original burner was modified for abrasive service.

Table 1. *Boiler Specifications*

Convection heating surface, m^2 (ft^2)	*182 (1,956)*
Radiant heating surface, m^2 (ft^2)	*48 (518)*
Furnace dimension, m (ft)	*1.92 × 4.05 × 2.26 (6.3 × 13.3 × 7.4)*
Design steam capacity, kg/s (lb/hr)	*3.0 (24,000)*
Design pressure, MPa (psig)	*1.7 (250)*
Operating pressure, MPa (psig)	*1.2 (175)*
Soot blower	*One Boyer-type VH valve-in-head*
Year installed	*1978*

Table 2. *Boiler Operating Conditions*

	Test 1	*Test 2*
Steam flow, kg/s	*3.03*	*3.03*
(lb/hr)	*(24,000)*	*(24,000)*
Drum pressure, MPa	*1.3*	*1.3*
(psi)	*(189)*	*(189)*
Furnace draft, Pa	*112*	*116*
(in. H_2O)	*(0.47)*	*(0.466)*
Fuel flow, kg/s	*0.410*	*0.39*
(lb/min)	*(54.2)*	*(51.8)*
Steam temperature, °C	*186*	*188*
(°F)	*(367)*	*(371)*
Boiler feedwater temperature, °C	*101*	*—[a]*
(°F)	*(213)*	*—*
Combustion air temperature, °C	*24*	*28*
(°F)	*(76)*	*(83)*
Flue gas temperature, °C furnace exit	*272*	*291*
(°F)	*(522)*	*(556)*
Excess air, percent[b]	*14*	*11*

[a]Not available.
[b]Calculated from PETC fuel composition and O_2 concentrations.

Summary and Conclusions

Boiler Operation

The test program called for flue gas emission measurements with the boiler operating at constant, near-rated capacity with the CWS fuel. Two tests were performed: test 1 with a 60.9 weight percent coal slurry at 14 percent excess air, and test 2 with a 58.9 percent coal slurry at 11 percent excess air. An abbreviated sampling protocol was completed for test 1; test 2 included the complete, planned comprehensive sampling protocol.

Table 2 lists the boiler operating conditions during both tests. Except for the fraction of coal in the fuel and the excess air, the boiler was operated at essentially the same conditions for both tests. Table 3 summarizes the fuel compositions for both tests.

Emission Measurements and Results

The sampling and analysis procedures used in this test program conformed to a modified EPA Level 1 protocol. All flue gas samples were taken at the boiler outlet, upstream of the unit's particulate control device (baghouse). Emission measurements included:

- Continuous monitoring for O_2, CO_2, NO_x, CO, SO_2, and TUHC
- Source Assessment Sampling System (SASS) for trace elements and organic emissions
- Combined EPA Methods 5/8 for particulate and sulfur oxides
- Grab sample for C_1 to C_6 hydrocarbons by gas chromatography (GC)
- Grab sample for N_2O analysis

In addition, samples of the fuel, bottom ash, and baghouse hopper ash were collected for analysis.

The analysis protocol included:

- Analyzing the fuel, ash, and SASS train samples for 73 trace elements using spark source mass spectrometry (SSMS), supplemented by atomic absorption spectrometry (AAS)
- Analyzing the SASS train and ash 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 and ash extract samples for the 58 semivolatile organic priority pollutants, including many of the PAH compounds of interest from combustion sources
- Performing infrared (IR) spectrometry analysis of organic sample extracts
- Performing liquid chromatography (LC) separation of selected sample extracts with subsequent TCO, GRAV, and IR analyses of LC fractions
- Performing direct insertion probe low resolution mass spectrometry (LRMS) analysis of selected sample extract LC fractions

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

Table 4 summarizes flue gas emissions measured in the test program. Emissions are presented as ng/J heat input and as

Table 3. Fuel Analyses (Percent By Weight)

		CWS (as fired)		
		Test 1	Test 2	
	Coal (dry basis) PETC[a]	*PETC[b]*	*This study[a]*	*PETC[b]*
Carbon	*82.23*	*50.08*	*47.90*	*48.43*
Hydrogen	*5.60*	*3.41*	*3.34*	*3.30*
Oxygen (by difference)	*6.76*	*4.12*	*8.56*	*3.98*
Nitrogen	*1.60*	*0.97*	*1.02*	*0.94*
Sulfur	*1.19*	*0.72*	*0.80*	*0.70*
Ash	*2.62*	*1.60*	*1.93*	*1.54*
Additive	—	*0.50*	—	*0.50*
Water	—	*38.60*	*36.45*	*40.6*
Higher heating value,				
kJ/kg	*34,459*	*20,986*	*21,341*	*20,296*
(Btu/lb)	*(14,829)*	*(9,031)*	*(9,184)*	*(8,734)*

[a]*Measured.*
[b]*Calculated based on coal ultimate analysis and reported proportion of coal, additive, and water in the CWS formulation.*

mg/dscm of flue gas. As a measure of the potential significance of the emissions levels for further analyses, an occupational exposure guideline for most pollutants is also noted in the table. The occupational exposure guideline noted 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-averaged 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 for further analyses. In this respect, pollutants emitted at levels several orders of magnitude higher than their guidelines might warrant further consideration, while species emitted at levels significantly lower than their guidelines might be considered of little potential concern for further analyses. Only elements emitted at levels exceeding their guidelines in these tests are noted in Table 4.

Table 4 shows that several elements were present in the boiler outlet at significant levels. However, flue gas particulate accounts for the major fraction of these elements in the flue gas at this location. Ultimate flue gas discharge concentrations would be significantly reduced after passage through the unit's particulate control device.

The data in Table 4 show that emissions of the vapor phase pollutants NO_x, SO_2, CO, and TUHC were essentially equivalent in both tests performed. However, particulate emissions approximately doubled in test 2. This test was run at slightly lower excess air than test 1: flue gas O_2 of 2.1 percent in test 2 and 2.8 percent in test 1. Also, the CWS in test 2 had slightly more water (less coal) than in test 1. Both of these would be conducive to poorer combustion efficiency. This, in turn, could lead to increased particulate mass emissions as the combustibles losses in the flyash increased. Indeed, the baghouse hopper ash from test 2 was found to contain over 60 percent carbon (dry basis). Unfortunately, no such carbon content data were taken for the test 1 flyash; although, it is interesting that complete emissions of all the ash content of the fuel fired would result in particulate emissions of about 3.1 g/dscm. This is just below the measured value in test 1, but less than half that measured in test 2.

The size distribution of test 2 boiler outlet particulate favored coarse particulate as shown in Table 5. Over 60 percent (weight) of the flue gas particulate was greater than 10 μm diameter; almost 70 percent was greater than 3 μm diameter.

Table 4 shows that total organic emissions (C_1 to C_6, TCO, and GRAV) were quite high, at 48 mg/dscm. The nonvolatile (GRAV) boiling point range accounted for most of the organics measured.

SASS train and ash extract samples for the semivolatile organic priority pollutant species, a grouping which contains several polynuclear aromatic hydrocarbon compounds, were analyzed. Results of these analyses are summarized in Table 6. As noted, only naphthalene and several phthalates (which are suspected contaminants) were found in SASS train samples.

The bottom ash extract contained the greatest number and concentration of the priority pollutants sought. This is consistent with the very high total organic (TCO plus GRAV) content of this sample (8 mg/g). As with the SASS train samples, most of the total organics in the bottom ash (80 percent) were in the nonvolatile (GRAV) boiling point range.

The SASS train organic module extract and the bottom ash extract samples were subjected to liquid column chromatography (LC) separation, with TCO, GRAV, IR, and LRMS analyses of eluted fractions, in an attempt to elucidate the chemical character of the organic material in these samples. These analyses suggested that the flue gas organic consisted largely of oxygenated organics such as carboxylic acids. Oxygenated organics and alkyl aromatics were suggested in the bottom ash extract.

Bioassay tests were performed on the SASS train and ash stream samples. The health effects bioassay tests performed were the Ames mutagenicity assay, and the CHO cytotoxicity assay. The results of these assays, summarized in Table 7, suggest that the flue gas was of low to moderate toxicity and low mutagenicity. The ash streams were of low to moderate toxicity and nondetectable mutagenicity.

The positive Ames response of the XAD-2 extract is typical of such extracts from SASS tests of combustion sources. Current studies sponsored by EPA's Air and Energy Engineering Research Laboratory 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.

Results of several quality assurance (QA) activities performed in these tests are discussed in Volume I of the full report. Most analysis precision determinations achieved project QA objectives. However, two precision challenges and one accuracy challenge failed project QA objectives (one only marginally). Discussion in the report indicates that these failures have no effect on conclusions derived from data obtained in these tests.

Table 4. *Summary of Exhaust Gas Emissions*[a]

Compound	Test 1 (ng/J heat input)	Test 1 (mg/dscm)	Test 2 (ng/J heat input)	Test 2 (mg/dscm)	Occupational exposure guideline (mg/dscm)[b]
SO_2	786	2,580	680	2,480	5
SO_3	0.86	2.8	<0.5	<2	1
NO_x (as NO_2)	136	448	172	624	6
N_2O	18	58	41	148	[d]
CO	62	202	66	239	55
TUHC (as CH_4	0.2	0.73	0.53	1.9	[d]
Solid particulate	1,064	3,485	1,991	7,255	10[e]
Total volatile organics (C_1 to C_6)	4.3	14.0	2.5	9.1	[d]
Total semivolatile organics (TCO)	—[c]	—	1.6	5.9	[d]
Total nonvolatile organics (GRAV)	—	—	9.1	33.1	[d]
Trace Elements					
Iron, Fe	—	—	55	201	1
Phosphorus, P	—	—	3.6	13.2	0.1
Aluminum, Al	—	—	82	297	2
Arsenic, As	—	—	0.3	1.06	0.01[f]
Silicon, Si	—	—	148	537	10[e]
Vanadium, V	—	—	0.46	1.67	0.05
Chromium, Cr	—	—	0.33	1.19	0.05
Beryllium, Be	—	—	0.01	0.045	0.002
Copper, Cu	—	—	0.56	2.03	0.1[f]
Lead, Pb	—	—	0.23	0.85	0.05[f]
Barium, Ba	—	—	2	7.95	0.5
Nickel, Ni	—	—	0.37	1.33	0.1
Calcium, Ca	—	—	6.9	25.3	2
Lithium, Li	—	—	0.07	0.27	0.025
Potassium, K	—	—	5.3	19.3	2[g]
Cobalt, Co	—	—	0.17	0.64	0.1
Titanium, Ti	—	—	5.4	20	10[e]
Uranium, U	—	—	0.02	0.09	0.05[f]
Magnesium, Mg	—	—	4.1	15	10

[a] Exhaust O_2 and CO_2 levels averaged 2.76 and 14.9 percent, and 2.08 and 15.7 percent, respectively for the two tests.
[b] Time-weighted-average TLV unless noted.
[c] Double dashes indicate that sample was not obtained; abbreviated test.
[d] No occupational exposure guideline applicable.
[e] For nuisance particulate.
[f] 8-hr time-weighted-OSHA exposure limit.
[g] Ceiling limit.

Table 5. *Flue Gas Particulate Size Distribution*

Particle Size	Emission Rate (g/dscm)	Emission Rate (ng/J)	Emission Rate (percent of total)
>10μm	4.34	1,190	63.6
3 to 10μm	0.38	100	5.6
1 to 3μm	1.19	330	17.4
Filter (<1μm)	0.91	250	13.4
Total	6.82	1,870	100.0

Table 6. *PAH and Other Semivolatile Organic Priority Pollutant Species Detected*

	Sample						
	10 + 3 µm particulate		1 µm + filter particulate		XAD + condensate extract	Bottom ash	Baghouse ash
Species	(mg/kg)	(µg/dscm)	(mg/kg)	(µg/dscm)	(µg/dscm)	(mg/kg)	(mg/kg)
PAHs							
Acenaphthene	--[a]	--	--	--	--	1	--
Acenaphthylene	--	--	--	--	--	2	--
Anthracene	--	--	--	--	--	1	--
Benz(a)anthracene	--	--	--	--	--	0.4	--
Benzo(j+k)fluoranthenes	--	--	--	--	--	0.4	--
Chrysene	--	--	--	--	--	0.8	--
Fluoranthene	--	--	--	--	--	2	--
Fluorene	--	--	--	--	--	2	--
Naphthalene	0.2	0.9	3.7	7.7	--	42	0.3
Phenanthrene	--	--	--	--	--	11	--
Pyrene	--	--	--	--	--	2	--
Other priority pollutants							
Bis(2-ethylhexyl)phthalate	<0.15	<0.7	3.4	7.2	7.8	84	0.3
Butylbenzylphthalate	<0.07	<0.3	0.2	0.4	2	120	0.08
Diethylphthalate	--	--	0.4	0.8	--	--	0.04
2,4-dimethylphenol	<0.2	<0.9	<0.4	<0.8	<7	5	<0.2
Detection limit	0.05	0.2	0.05	0.1	1.1	0.4	0.04

[a] Double dashes denote less than detection limit noted.

Table 7. *Bioassay Results*

Sample	Ames mutagenicity	CHO clonal toxicity
10 + 3 µm particulate	ND[a]	L/M
1 µm + filter particulate	ND	ND/L
XAD-2 + organic module condensate total extract	L[b]	U[c](L)
Bottom ash	ND	L/M[d]
Baghouse ash	ND	L

[a] No detectable mutagenicity/toxicity.
[b] Low mutagenicity/toxicity.
[c] Undetermined toxicity. Exact toxicity range could not be determined due to insufficient amount of sample. Test results indicate low toxicity or less.
[d] Moderate mutagenicity/toxicity.

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R. DeRosier and L. R. Waterland are with Acurex Corp., Mountain View, CA 94039.
***Robert E. Hall** is the EPA Project Officer (see below).*
The complete report consists of two volumes, entitled "Environmental Assessment of a Watertube Boiler Firing a Coal/Water Slurry:"
"Volume I. Technical Results," (Order No. PB 86-159 845/AS; Cost: $11.95)
"Volume II. Data Supplement," (Order No. PB 86-183 308/AS; Cost: $16.95)
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The EPA Project Officer can be contacted at:
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U.S. Environmental Protection Agency
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