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Project Summary

Environmental Assessment of a Firetube Boiler Firing Coal/Oil/Water Mixtures

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This report describes emission results from sampling of flue gas from a firetube boiler burning a coal/oil/water (COW) mixture and the same mixture with soda ash (sodium carbonate) (COW+SA) added to control SO_2 emissions. Measurements included continuous monitoring of flue gas emissions; source assessment sampling system (SASS) sampling of the flue gas with subsequent laboratory analysis of samples to give total flue gas organics in two boiling point ranges, specific quantitation of the semivolatile organic priority pollutant species, and flue gas concentrations of 73 trace elements; Method 5 sampling for total particulate; and controlled condensation system sampling for SO_2 and SO_3 emissions.

Flue gas SO_2 emissions decreased almost 99 percent with soda ash addition from 1,089 to 13.6 ppm (3 percent O_2). NO_x emissions decreased slightly from 477 to 427 ppm, while CO emissions increased significantly from an average of 25 to 426 ppm (all at 3 percent O_2). Particulate loading at the boiler outlet almost doubled (from 1,970 to 3,715 mg/dscm) with the additive. The size distribution of particulate also shifted to a much smaller mean diameter. Total organic emissions increased from 6.7 to 13.1 mg/dscm, attributed to increased nonvolatile (C_{16+}) organics. Volatile (C_1 to C_6) organic emissions remained relatively constant; semivolatile organics (C_7 to C_{16}) were not detected in either test. Of the semivolatile organic priority pollutant species, only fluoranthene and phenanthrene were detected with the COW fuel at levels of 0.05 and 0.1 μg/dscm, respectively. Only phenanthrene was present in the COW+SA flue gas sample, though at significantly increased concentration (0.7 μg/dscm).

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

Introduction

Coal/oil mixtures (COM), coal/oil/water (COW) mixtures, and coal/water slurries (CWS) have received attention in recent years as alternatives to oil fuels in oil-fired combustion equipment. These mixtures have the advantage of allowing an oil-fired boiler to reduce its oil requirements without completely redesigning the boiler. Thus, these fuels have a potential for application as near-term technologies for conversion of oil-burning facilities to partial coal firing, thereby partially offsetting higher oil prices and frequently uncertain supply situations. This report gives results of an emissions assessment of a COW-fired firetube industrial boiler with and without the sorbent soda ash (sodium carbonate) added to the fuel to control SO_2.

Boiler Description and Fuel Properties

A Cleaver Brooks CB400-350 firetube boiler rated 4.1 MW (14 million Btu/hr) heat input was used for the tests. At rated capacity, the unit produces 1.5 kg/s (12,000 lb/hr) of saturated 1,030 kPa (150 psig) steam. The unit uses a four-

pass design, with tube cross-sectional area decreasing for each pass. To burn COW, the boiler was modified to include a new fuel feed system, enlarged nozzle, an additional combustion air blower, and soot blowers.

The COW and COW+SA mixtures were prepared in-line, prior to being fed to the boiler. Table 1 gives the fuel composition in terms of coal, oil, water and soda ash. Table 2 gives the ultimate analysis of the mixtures. Despite the reduced proportion of coal in the COW+SA, the sulfur and nitrogen contents are nearly equal to those of the COW fuel.

Table 1. Overall Fuel Composition[a]

	COW	COW+SA
Coal	42	38.6
Oil	42	39.2
Water	16	14.5
Soda ash	—	7.7

[a]*Percent by weight.*

Boiler Operation

The test program called for flue gas emission measurements firing each of the two fuels. Table 3 summarizes the boiler operating conditions for the two tests. The addition of soda ash to the COW resulted in several changes in operating conditions. Most evident were that the boiler tubes fouled rapidly, the flame temperature decreased, and the O_2 level at which CO emissions increased markedly rose from 2.5 to 3.2 percent. As a result of the rapid fouling during the COW+SA test, the test had to be terminated after only 3.5 hours; the COW test ran for the full 6 hours required for a complete emissions sampling program. After the tests, 127 kg (281 lb) of ash deposits were removed from the boiler, which had been cleaned prior to the COW test. Based on fuel composition, fuel flowrate, and particulate emission rates, 20 percent of this ash was estimated to be attributed to the COW test and 80 percent to the COW+SA tests. Deposits of this magnitude could preclude using sorbent injection rates needed to obtain significant SO_x reduction.

Emission Measurements and Results

Flue gas emissions measurements were made at the boiler outlet. The sampling and analysis procedures used conformed to a modified EPA Level 1 protocol. Flue gas measurements included:

- Continuous monitoring for NO_x, O_2, CO, CO_2, and SO_2.
- Source assessment sampling system (SASS) for particulate size fractionation, trace elements, and organic emissions.
- Controlled condensation system (CCS) for SO_2 and SO_3.
- EPA Method 5 for particulates.
- Grab sample for onsite analysis of C_1 to C_6 hydrocarbons by gas chromatography (GC).

Particulate mass emissions were measured by Adelphi University personnel using EPA Method 5. These results are also summarized in this report.

The analysis protocol included:

- Analyzing SASS train samples for 73 trace elements using spark source mass spectrometry (SSMS), supplemented by atomic absorption spectrometry (AAS).
- Analyzing SASS train samples for total organic content in two boiling point ranges: 100 to 300°C by total chromatographable organics (TCO) analysis and greater than 300°C by gravimetry (GRAV).
- Analyzing the SASS train sorbent module and particulate extracts for 58 semivolatile organic species including many of the POM compounds.
- Performing infrared (IR) spectrometry analysis of organic sample extracts.
- Performing liquid chromatography (LC) separation of total sample extracts with subsequent GRAV and IR analyses of LC fractions.
- Performing direct insertion probe low resolution mass spectrometry (LRMS) analysis of selected total sample and LC fraction extracts.
- Determining the alpha and beta radiometric activity of the SASS particulate.
- Performing mutagenicity and toxicity health effects bioassays on SASS sorbent module extract samples.

Table 4 summarizes emissions measured in the test program. Emissions are presented as nanograms per Joule heat input (ng/J) and micrograms per dry standard cubic meter of the flue gas (μg/dscm). As a measure of the relative potential significance of the emission levels for further analysis, an occupational exposure guideline concentration for each species is also noted in the table. The occupational exposure guideline noted is either the time-weighted-average Threshold Limit Value (TLV) o

Table 2. Ultimate Fuel Analyses[a, b]

		COW	COW+SA
Carbon		78.02	71.74
Hydrogen		8.60	7.83
Nitrogen		0.76	0.73
Sulfur		1.93	1.90
Oxygen	(by difference)	6.69	4.63
Ash		4.00	13.17
Heating value[c]	kJ/kg	31,413	26,952
	(Btu/lb)	13,491	11,575
Moisture[c]		15.60	15.54

[a]*Percent by weight.*
[b]*Dry basis, except as noted.*
[c]*As received.*

Table 3. Boiler Operating Conditions

	COW	COW+SA
Fuel flow, kg/hr	433.5	429.5
(lb/hr)	(955.9)	(947.1)
Boiler feedwater flow, l/s	18.5	18.8
(gal./min)	(293)	(298)
Excess air, percent[a]	17	14
Temperatures[b], °C (°F)		
Fuel	25	32
	(77)	(90)
Water return	82	80
	(179)	(176)
Water supply	124	119
	(256)	(246)
Ambient air	23	24
	(74)	(75)
Stack	146	181
	(295)	(357)

[a]*Based on stack O_2 measurement (percent, dry) and fuel analysis.*
[b]*Average over test run.*

the 8-hr time-weighted-average exposure limit established by the Occupational Safety and Health Administration (OSHA). Only species emitted at levels exceeding 10 percent of their occupational exposure guidelines in either (or both) tests are noted in Table 4.

As noted in the table, several trace elements were present at significant levels in the boiler outlet flue gas for either or both tests. 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.

Emissions of SO_2 decreased significantly using the soda ash additive; changes in emission levels of other species were less substantial. The data in Table 4 suggests that the most significant environmental effect of soda ash addition for SO_2 control would be the attendant reduction in SO_2 emissions.

Tables 5 and 6 summarize organic emission results for the COW and COW+SA tests, respectively. The top portion of each table summarizes the total chromatographable organic (TCO) content and the GRAV organic content of the XAD-2 sorbent extract as it eluted into the seven LC fractions. The bottom portion of each table summarizes the organic categoreis identified by LRMS of the LC fractions with inferences from the IR spectroscopy. Organic matter collected in the XAD-2 sorbent accounted for approximately 100 and 60 percent ot total

Table 4. *Emission Summary*

	Emission concentration				
	COW test		*COW+SA test*		*Occupational exposure*
Compound	*(mg/dscm)*	*(ng/J)*	*(mg/dscm)*	*(ng/J)*	*guideline[a] (mg/m³)*
SO_2	2,900	1,060	36	14	5.0
SO_3	20	0.74	—	—	1.0
NO_x	900	332	830	330	6.0
CO	29	11	490	195	55
Particulate					
Method 5	— [b]	—	3,720	1,460	
SASS	1,970	722	3,720	1,460	10[c]
Total volatile organics (C_1 to C_5)	3.8	1.4	4.1	1.6	—[d]
Total semivolatile organics (TCO)	<0.04	<0.01	<0.02	<0.01	—[d]
Total nonvolatile organics (GRAV)	2.9	1.1	9.0	3.5	—[d]
Trace Elements					
Chromium	>1.1	>0.39	0.40	0.16	0.050[e]
Barium	>1 2	>0.44	1.1	0.42	0.50
Phosphorous	>2 0	>0 72	0.85	0.33	0.10
Lead	0.78	0.29	0.93	0.37	0.050
Vanadium	0.92	0.34	0.68	0.27	0.050
Arsenic	0.16	0.059	<0.089	<0.035	0.010[e]
Nickel	>1.1	>0.38	0.65	0.26	0.10
Beryllium	0 012	0.0045	0.0028	0.0011	0.0020
Iron	2.7	1.0	5.3	2.1	1.0
Platinum	0.0016	0.00060	0.011	0.0042	0.0020
Lithium	0.11	0.039	0.033	0.013	0.025
Uranium	0.15	0.055	<0.068	<0.027	0.050[e]
Fluorine	0.14	0.050	0.41	0.16	0.20[e]
Copper	0.13	0.047	0.14	0.055	0.10[e]
Zinc	>1.1	>0.38	0.28	0.11	1.0
Chlorine	0.15	0.055	3.3	>1.3	3.0
Silver	<0 00087	<0.00032	0.0095	0.0038	0.010
Calcium	>1.8	>0.66	>1.1	>0.43	2.0
Mercury	0.00047	0.00017	<0.085	<0.034	0.10
Selenium	0.16	0 058	0.067	0.026	0.20
Potassium	>1.5	>0.56	>1.2	>0.46	2.0[f]
Cobalt	0 029	0.011	<0.0097	<0.0038	0.050
Sodium	>0.79	>0.29	>0.85	>0.34	2.0[f]
Magnesium	>2.0	>0.73	>2.3	>0.92	10
Manganese	>1.1	>0.39	0.41	0.16	5.0[f]
Titanium	>2.0	>0.73	1.7	0.67	10[c]
Thallium	0.020	0.0072	0.0085	0.0033	0.10
Silicon	>1.4	>0.51	>1.0	>0.41	10[c]
Yttrium	0.13	0.046	0.040	0.016	1.0
Bromine	0.049	0.018	0.076	0.030	0.70

[a] *Time-weighted-average TLV, unless noted.*
[b] *Method 5 not performed for the COW test.*
[c] *For nuisance particulate*
[d] *No occupational exposure guideline applicable.*
[e] *8-hr time-weighted-average OSHA exposure limit.*
[f] *Ceiling limit.*

Table 5. *Organic Extract Summary — COW XAD-2 EXTRACT*

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Total organics, mg	14	12	10	<2	<2	6	3	45
TCO, mg	—	—	—	—	—	—	—	<1
GRAV, mg	14	12	10	<2	<2	6	3	45
			Assigned Intensity — mg/dscm					
Category	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Aliphatic HC s[a]	100-0.59							0.59
Aldehydes, ketones, acids		100-0.50	100-0.42				100-0.13	1.05
Alchols						100-025		0.25

[a]*Aliphatic background present in all LRMS samples.*

Table 6. *Organic Extract Summary — COW+SA XAD-2 EXTRACT*

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Total organics, mg	<1	6	9	2	<1	2	<1	19
TCO, mg	—	—	—	—	—	—	—	<1
GRAV, mg	<1	6	9	2	<1	2	<1	19
			Assigned Intensity — mg/dscm					
Category	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Aliphatic HC s[a]		100-0.5	100-0.8					1.3
Aldehydes, ketones, esters, acids		100-0.5	100-0.7	100-0.3		100-0.3		1.8

[a]*Aliphatic hydrocarbons background present in all LRMS samples.*

Table 7. *Compounds Detected in GC/MS Analysis and Their Concentrations*[a]

	COW Test				
	10 μm and 3 μm cyclones	Filter and 1μm cyclone	XAD-2 extract	OMC[b]	Total
Fluorathene	<0.05	<0.07	0.05	<0.04	0.05
Penanthrene	<0.05	<0.07	0.1	<0.04	0.1
Other Polynuclears	<0.05	<0.07	<0.05	<0.04	<0.07
	COW+SA Test				
	10 μm and 3 μm cyclones	Filter and 1 μm cyclone	XAD-2 extract	OMC[a]	Total
Phenanthrene	<0.3	<0.3	0.7	<0.2	0.7
Other Polynuclears	<0.3	<0.3	<0.2	<0.2	<0 3

[a]*μg/dscm.*
[b]*Organic module condensate.*

Table 8. *Particulate Radiometric Activity*[a, b]

	Alpha	Beta	Gamma
COW Test			
10 μm and 3 μm	196.7 ± 20.0	79.3 ± 11.3	183 ± 292
1 μm and filter	224.1 ± 47.7	128.8 ± 38.6	553 ± 300
COW+SA Test			
10 μm and 3 μm	93.7 ± 8.5	40.5 ± 14.7	219 ± 293
1 μm and filter	24.8 ± 4.8	16.3 ± 2.9	100 ± 290

[a]*pCi/g sample.*
[b]*The ± values are the 2 sigma Poisson standard deviation of the counting error.*

Table 9. *Radiometric Emissions*[a]

	Emission Rate	
	pCi/s	pCi/g fuel
COW test	817	6.78
COW+SA test	314	2 63

[a]*Alpha plus Beta only.*

Table 10. *Bioassay Results of XAD-2 EXTRACTS*

	Bioassay	
Test	Ames[a]	CHO[b]
COW test	M/H	M
COW+SA test	H	<M

[a]*H = high mutagenicity; M = moderate mutagenicity.*
[b]*M = moderate toxicity. ≤M = absolute toxicity, could not be determined due to limited sample size, but toxicity moderate or less.*

SASS organics for the COW and COW+SA tests, respectively. The inferences from the LRMS and IR data are that the organic samples are primarily composed of aliphatic hydrocarbons with some oxygenated hydrocarbons. The only POMs detected were phenanthrene and fluoranthene in the COW samples and phenanthrene in the COW+SA sample, as shown in Table 7.

Radionuclide emissions were measured by analysis of the alpha and beta activities of the flyash particulate samples. The activities of the particulate and the total emission rates were given in Tables 8 and 9. Compared to controlled emissions from model coal-fired powerplants, these emission rates are 40 to 16 times higher for the COW and COW+SA tests, respectively. However, the particulate samples were taken from the flue gas upon leaving the boiler and before any control device; controlled emissions from such COW sources should be comparable to the model cases.

Bioassays (Ames mutagenicity and CHO cytotoxicity) were performed on the organic sorbent (XAD-2) module extracts from both tests. The results of these tests, summarized in Table 10, suggest that the material trapped in the XAD-2 resin is of moderate to high mutagenicity and moderate (or less) toxicity. These are common bioassay responses for combustion source XAD-2 extracts. Current studies are investigating if such bioassay responses are due to artifact components formed when combustion product gas containing NO_x is passed over XAD-2 resin.

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The complete report consists of two volumes, entitled "Environmental Assessment of a Firetube Boiler Firing Coal/Oil/Water Mixtures:"
"Volume I. Technical Results," (Order No. PB 85-108082; Cost: $13.00)
"Volume II. Data Supplement," (Order No. PB 85-108 090; Cost $17.50)
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