



Project Summary

Environmental Assessment of a Commercial Boiler Fired with a Coal/Waste Plastic Mixture

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This report describes emission results obtained from field testing of a stoker-fired commercial boiler firing a coal/waste plastic mixture. Two tests were performed: in one (test 1), the unit fired its typical coal fuel; and in the other (test 2), granulated waste polyethylene terephthalate (PET) beverage bottles were added to the coal to about 16 percent by weight in the mixed fuel. 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 SO₂ and SO₃ emissions; volatile organic sampling train (VOST) testing for volatile organic priority pollutant emissions (test 2 only); HCl train sampling (test 2 only); gas grab sampling for N₂O emissions measurements; and grab sampling of fuel ash bottom and cyclone collector hopper for inorganic composition determination.

NO_x, total unburned hydrocarbon (TUHC), and solid particulate emissions were relatively unchanged for the two tests, averaging 286 and 214 ppm, <2 and 3ppm, and 54 and 69 mg/dscm, respectively, for tests 1 and 2. The emitted particle size distribution was apparently unchanged as well. SO_x emissions decreased with the coal/PET fuel in keeping with its lowered sulfur content. SO₂ and SO₃ levels were 930 and 640 ppm,

and 4.4 and 2.5 ppm (all corrected to 3 percent O₂), respectively, for tests 1 and 2. Average CO emissions at 81 ppm were also decreased in test 2, from 184 ppm in test 1, apparently due to higher excess air levels in test 2. HCl emissions were measured at 336 ppm (at 3 percent O₂) with the coal/PET fuel; however, this level is almost 3 times that which was accounted for by the fuel chlorine level.

Flue gas emissions of most trace elements were comparable for both tests, as were the trace element compositions of corresponding ash streams. However, estimated lead emissions (1,100 μg/dscm) were significantly increased for test 2 when compared to levels for test 1 (30 μg/dscm). This increase apparently reflects the increased lead content of the mixed coal/PET fuel, the increased lead coming inexplicably from the PET additive. The cyclone hopper ash for the coal/PET test had consistently lower leachable trace element and anion content than that for the coal fuel test.

Total flue gas organic emissions were comparable for both tests, in the 1 mg/dscm range. Most (90 percent) of the flue gas organic was nonvolatile (boiling point greater than about 300°C). Of the semivolatile organic priority pollutants, naphthalene was detected in flue gas samples for both tests, emissions increased from about 2 (test 1) to 16 μg/dscm (test 2) with the coal/PET fuel. Phenanthrene, fluoranthene, and phenol were present in test 2 at levels ranging from 2 to 20 μg/dscm; they were not detected in test 1. In addition, several phthalates were measured in the test 2 flue gas at levels of 0.4 to 6 μg/dscm, while none were found in test 1. Phthalates present at such

levels are often ascribed to sample contamination; however, the observed increased emissions of these with the coal/PET in these tests may be real.

Of the volatile organic priority pollutants, several chlorinated C₁ and C₂ hydrocarbons, chlorobenzene, toluene, and ethylbenzene were measured in the test 2 flue gas at levels of 1 to 25 µg/dscm.

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Introduction

Some states, Vermont included, are now requiring deposits on beverage containers as a means of controlling litter and encouraging recycling and reuse. Plastic beverage containers cannot be reused as containers; however, one way to reclaim these is to use them as a fuel supplement in an energy recovery operation. In one such project, the use of waste PET bottles is being evaluated as a fuel supplement in a commercial boiler at a quarry and stonecutting plant in Barre, Vermont. Past efforts have indicated that PET is a clean-burning, high-heating-value fuel with no apparent environmental problems associated with its use as a solid fuel supplement. The tests described in this report were performed to confirm that this is the case by performing a comprehensive evaluation of the emissions and ash discharge compositions from a boiler burning its typical coal fuel and a coal/PET mixture.

The boiler tested is a coal-fired firetube unit with an underfeed stoker. The unit is rated at 0.6 kg/s steam at 100 kPa (4,640 lb/hr at 15 psig). Nominal full load coal feed rate is 180 kg/hr (400 lb/hr). The boiler was equipped with a cyclone collector for particulate emissions control.

Summary and Conclusions

Boiler Operation

The test program called for flue gas emission measurements and ash discharge stream sampling with the boiler operating at constant, near-rated capacity with both fuels. Two tests were performed: test 1 with the unit firing its typical coal fuel, and test 2 with a coal/PET mixture containing about 16 percent by weight granulated PET beverage bottles.

Table 1 summarizes the boiler operating conditions and the fuel ultimate analysis

Table 1. Summary of Boiler Operation and Fuel Analyses

	Test 1 (coal fuel)	Test 2 (coal/PET fuel)
<i>Boiler operation (over the SASS sampling period)</i>		
Steam load, kg/s (10 ³ lb/hr)	0.38 (3.0)	0.42 (3.3)
Steam pressure, kPa (psig)	17 (2.5)	21 (3.0)
Feedwater inlet temperature, °C (°F)	12 (54)	13 (55)
Stack temperature, °C (°F)	146 (295)	165 (329)
Firebox temperature, °C (°F)	768 (1,415)	882 (1,620)
Fuel feedrate, kg/hr (lb/hr)	110 (240)	130 (285)
Excess air, percent	47	77
Boiler efficiency, percent	79.3	79.1
<i>Fuel ultimate analysis (percent by weight as fired)</i>		
Carbon	69.5	71.4
Hydrogen	5.2	5.5
Sulfur	1.0	0.6
Nitrogen	1.5	1.4
Oxygen ^a	11.4	11.7
Ash	8.5	6.8
Moisture	2.7	2.4
Chloride	0.2	0.2
Higher heating value, kJ/kg (Btu/lb)	31,212 (13,450)	31,270 (13,479)
PET, weight percent	0	16.4

^aBy difference.

for both tests. As indicated, test 2 was run at about the same coal feedrate as test 1 (110 kg/hr); however, the test 2 fuel mixture contained about 20 kg/hr of added waste PET. Consequently heat input and boiler load were slightly higher for test 2. Boiler efficiency, calculated by the ASME heat loss method, was unchanged at about 79 percent. The boiler underwent some load excursions during test 2. These excursions could have some effect on emissions over and above the change in fuel composition.

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 the unit's stack, downstream of the cyclone collector, except for the continuous flue gas analyzers which were operated both at the stack and at the boiler exit. Emission measurements included:

- Continuous monitoring for O₂, CO₂, NO_x, CO, and TUHC.
- Source assessment sampling system (SASS) for trace elements and semi-volatile and non-volatile organic emissions.
- Volatile organic sampling train (VOST) for volatile organic emissions (test 2 only).
- Combined EPA Method 5/8 for particulate and SO_x.

- HCl train sampling.

- Grab samples for N₂O analysis.

In addition, samples of the fuel, bottom ash, and a cyclone hopper ash were collected for analysis. The analysis protocol included:

- Performing proximate, ultimate, and heating value analyses of fuel samples, and ultimate analyses of bottom and cyclone hopper ash samples.
- Analyzing the fuel, ash, ash aqueous leachates, and SASS train samples for 73 trace elements using spark source mass spectrometry (SSMS), supplemented by atomic absorption spectrometry (AAS).
- Analyzing ash aqueous leachates for selected anions using ion chromatography.
- Analyzing VOST traps for the volatile organic priority pollutants.
- Analyzing ash sample organic extracts for total nonvolatile organic content by gravimetry (GRAV).
- Analyzing the SASS train organic extract samples for total organic content in two boiling point ranges: 100 to 300 °C by total chromatographic organics (TCO) analysis, and >300 °C by 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.
- Performing liquid chromatography (LC) separation of selected sample extracts with subsequent TCO, GRAV, and IR analyses of eluted LC fractions.

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

Table 2 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 emissions levels for further monitoring or evaluation, 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. In this respect, pollutants emitted at levels several orders of magnitude higher than their occupational exposure guidelines might warrant further evaluation, while species emitted at levels significantly lower than their occupational exposure guidelines might be considered of lower priority. Only elements emitted at levels exceeding 10 percent of their occupational exposure guidelines in these tests are noted in Table 2.

Table 2 shows that flue gas concentrations of chromium, sodium, nickel, iron, lead, and cobalt were significantly higher for test 2 than for test 1. The test 2 flue gas levels for all these (except cobalt) were also greater than their respective occupational exposure guidelines. The higher lead emissions for test 2, are thought to be actual increases. The coal/PET fuel had significantly higher lead content (28 ppm) than did the coal itself (3 ppm). The source of the added lead is apparently the waste PET, although no lead source within the PET is known. Unfortunately, the trace element emission levels noted in Table 2 for test 2 are based on an estimated 1 to 3 μm SASS train particulate emission rate and the assumption that the 1 to 3 μm particulate had the same composition as the less-than-1- μm particulate (the 1 to 3 μm SASS particulate sample for test 2 was destroyed in transit from the field to the laboratory). Consequently, the significance

Table 2. Summary of Flue Gas Emissions^a

Component	Concentration				Occupational exposure guideline (mg/m ³) ^b
	Test 1 (coal fuel)		Test 2 (coal/Pet fuel)		
	(ng/J heat input)	(mg/dscm)	(ng/J heat input)	(mg/dscm)	
<i>Major constituents</i>					
NO _x (as NO ₂)	176	270	165	280	6.0
SO ₂	800	1,210	690	1,160	5.0
SO ₃	4.6	7.0	3.4	5.7	1.0
CO	69	105	38	64	55
HCl	— ^c	— ^c	206	347	7.0 ^d
Solid particulate	35	54	41	69	10 ^e
Total semivolatile organics (TCO)	0.049	0.075	0.071	0.12	— ^f
Total nonvolatile organics (GRAV)	0.575	0.875	0.641	1.08	— ^f
<i>Trace elements</i>					
Chromium, Cr	0.0065	0.010	3.03	5.17	0.05
Sodium, Na	0.42	0.65	63	107	2.0 ^d
Nickel, Ni	0.017	0.027	2.23	3.81	0.10
Iron, Fe	2.05	3.18	16.2	27.6	1.0
Lead, Pb	0.020	0.030	0.65	1.10	0.050 ^g
Phosphorous, P	1.39	2.15	0.79	1.35	0.10
Arsenic, As	0.011	0.017	0.029	0.049	0.010
Aluminum, Al	1.38	2.15	1.43	2.45	2.0
Lithium, Li	>0.017	>0.026	>0.081	>0.014	0.025
Calcium, Ca	1.24	1.93	0.28	0.49	2.0
Beryllium, Be	0.00063	0.00097	0.00093	0.0016	0.002
Silicon, Si	>1.52	>2.36	3.00	5.12	10 ^e
Potassium, K	0.59	0.91	0.57	0.97	2.0 ^d
Cobalt, Co	0.0019	0.003	0.024	0.041	0.10
Cadmium, Cd	0.0016	0.0025	0.010	0.018	0.05 ^d
Vanadium, V	0.011	0.018	0.0073	0.012	0.050
Copper, Cu	0.020	0.032	0.021	0.035	0.10 ^g
Platinum, Pt	— ^h	— ^h	0.00031	0.00052	0.002
Silver, Ag	0.0017	0.0026	0.0010	0.0018	0.010
Selenium, Se	0.0068	0.010	0.024	0.041	0.20
Barium, Ba	0.036	0.056	0.012	0.021	0.50

^aFlue gas O₂ and CO₂ averaged 7.0 and 12.0 percent (dry) for test 1 and 5.2 and 12.9 percent for test 2.

^bTime-weighted average TLV unless noted.

^cHCl sampled for test 2 only.

^dCeiling limit.

^eFor nuisance particulate.

^fNo occupational exposure guideline applicable.

^g8-hour time-weighted-average OSHA exposure limit.

^hLess than the method detection limit.

of the increased lead emission levels cited deserves further study.

Several possibilities exist to explain the higher concentration of chromium, sodium, nickel, iron, lead, and cobalt. These are conjectures, however, so additional sampling and analysis may be merited.

Emission levels of the other elements noted in Table 2 were quite comparable between the two tests. In fact, the trace element content of all SASS train samples (except the impinger solution and lead in

the fine particulate noted above), the bottom ash, and the cyclone hopper ash were quite comparable for both tests.

The data in Table 2 show that boiler emissions of NO_x, solid particulate, and total semi- and non-volatile organics were relatively unchanged with the addition of the PET to the boiler fuel. Emissions of SO₂, and SO₃ were decreased, in keeping with the lower sulfur content of the coal/PET fuel (the apparently small difference noted in Table 2 is amplified considerably when corrected in each instance

to a common flue gas O₂ level; e.g., 3 percent). On a mass loading basis, total sulfur emissions were relatively unchanged due to the constant coal firing rate. CO emissions were decreased with the coal/PET fuel as well due probably to the higher level of excess air used with the mixed fuel.

The HCl emission level noted in Table 2 for test 2 corresponds to almost 3 times the amount which would be expected from the chlorine content of the fuel. The above discussion regarding the possible introduction of inorganic chloride into the SASS train suggests that perhaps extraneous chloride was introduced into the HCl train as well. This train measures total vapor phase (at stack temperature) inorganic chloride, not strictly HCl.

Further analysis of the SASS train organic sorbent module extract via LC fractionation and IR spectroscopy of both the total extract and the eluted LC fractions suggests that the organic emissions for both tests were roughly 25 to 35 percent aliphatic hydrocarbons, 40 percent less polar oxygenated hydrocarbons, and 25 to 35 percent more polar oxygenates.

Table 3 summarizes the organic priority pollutant emission results. Emission levels of the semivolatile compounds detected were significantly increased with the coal/PET fuel, despite the fact that total semivolatile organic emissions were relatively unchanged. The phthalates noted in the table could be sample contaminants. Phthalates are common contaminants in SASS train samples at levels comparable to those noted in Table 3. However, that levels detected in the test 2 samples were generally significantly higher than those in the test 1 samples, and that phthalates are expected to be found in PET, suggest that these compounds may actually have been present in the test 2 flue gas.

Table 3 also notes that several chlorinated C₁ and C₂ aliphatic hydrocarbons, chlorobenzene, toluene, and ethylbenzene were emitted during test 2 at levels of from <1 to about 24 µg/dscm. The levels of the aromatic hydrocarbons noted (toluene and ethylbenzene) are in the range typically encountered in VOST tests of combustion sources. The source of the chlorinated compounds is not clear, although these compounds do arise whenever chlorine, even inorganic chloride, is introduced into a combustion process. It is interesting that these compounds were detected in the test 2 flue gas, the same test with apparent chloride introduction into the SASS train, and unaccountably high (perhaps again due to extraneous flue

Table 3. Summary of Organic Priority Pollutant Emissions

Compound	Emission concentration (µg/dscm)	
	Test 1 (coal fuel)	Test 2 (coal/PET fuel)
<i>Volatile organic priority pollutants:</i>		
	— ^a	
Chloromethane		1.0
Chloroform		4.5
1,2-Dichloroethane		2.0
Trichloroethylene		24
Tetrachloroethylene		2.5
Toluene		14
Chlorobenzene		7.5
Ethylbenzene		0.7
<i>Semivolatile organic priority pollutants:</i>		
Naphthalene	2.2	16
Phenanthrene	>0.4	3.0
Fluoranthene	>0.4	2.2
Phenol	>0.4	20
Bis(2-ethylhexyl)phthalate	4.4	4.2
Diethyl phthalate	>0.4	6.0
Di-n-butyl phthalate	>0.4	0.4

^aVolatiles sampled for test 2 only.

gas chloride) chloride emissions measured with the HCl train.

Table 4 summarizes the results of the nonvolatile (GRAV) organic analyses of the bottom ash and cyclone hopper ash extracts. For test 1, only the cyclone hopper ash contained measurable levels of nonvolatile organics. For test 2, the organic content of the bottom ash increased, although that of the cyclone hopper ash was about half that for test 1. The total ash loading was less in test 2 than test 1. In test 1, total ash was 13.5 percent of fuel fed, whereas ash was only 8.2 percent in test 2. For both tests, cyclone ash was about 3 percent of total ash.

Infrared spectra of bottom ash extracts suggest that only aliphatic hydrocarbons were present. Analyses of cyclone ash extracts via LC fractionation and IR spectroscopy suggest that these contain: 30 to 40 percent aliphatic hydrocarbons, 15 to 20 percent less polar oxygenated hydro-

carbons (e.g., aldehydes and ethers), and 40 to 55 percent more polar oxygenates (e.g., carboxylic acids, alcohols, and ketones).

Table 5 summarizes the concentrations of the priority pollutant trace metals in aqueous leachates of the ash stream samples prepared according to Level 1 guidelines. As a measure of the potential significance of these concentrations for further analyses, the water quality criterion for each element is noted in the table. Again, these are noted only to aid in ranking the potential significance of the leachable element levels noted. Only elements having at least one leachate concentration greater than its water quality criterion are noted. On a mass flow basis, it is noteworthy that the ash mass flow was 40 percent lower for test 2.

The data in Table 5 show that the cyclone ash leachates for both tests contained considerably higher levels of the

Table 4. Ash Stream Total Organic Content

Sample	Total nonvolatile organics by gravimetry (mg/kg ash)	
	Test 1 (coal fuel)	Test 2 (coal/PET fuel)
Bottom ash	>80	220
Cyclone hopper ash	1,100	500

Table 5. Inorganic Priority Pollutants in Ash Leachates at Concentrations Exceeding Their Water Quality Criteria

Element	Bottom ash leachate concentration (µg/l)		Cyclone hopper ash leachate concentration (µg/l)		Water quality criterion (mg/l)
	Test 1 (coal)	Test 2 (coal/PET)	Test 1 (coal)	Test 2 (coal/PET)	
Arsenic	0.030	0.010	4.1	0.20	$2.2 \times 10^{-5}^a$
Beryllium	>0.001	>0.002	0.32	0.070	$3.7 \times 10^{-5}^a$
Nickel	0.01	0.02	4.0	0.80	0.0134
Selenium	0.10	0.10	0.80	0.20	0.010
Chromium	0.02	0.06	3.7	1.0	0.050
Cadmium	>0.001	0.004	0.17	0.10	0.010
Thallium	>0.001	>0.002	0.21	0.09	0.013
Mercury	0.002	>0.001	>0.001	>0.001	1.44×10^{-4}
Lead	>0.004	0.009	0.27	0.10	0.050
Barium	0.06	0.30	2.1	0.05	1.0
Antimony	>0.004	0.20	0.15	0.05	0.146

^aWater quality criterion based on cancer risk; level noted corresponds to increased lifetime risk of 10^{-5} .

inorganic priority pollutants than did the bottom ash leachates. The test 2 bottom ash leachate contained slightly higher levels of most of the elements noted. However, the cyclone ash leachate for test 2 contained significantly lower levels of all the elements noted (with the possible exception of mercury). This suggests that the addition of waste PET to the boiler's fuel may have had the beneficial effect of decreasing leachable toxic trace element discharges in the cyclone hopper ash stream. This effect is augmented by the observed 40 percent reduction in ash output in test 2 relative to fuel flow.

Table 6 summarizes the leachable anion content of the ash stream aqueous leachates. As for the inorganic priority pollutants, the anion levels in cyclone ash leachates are significantly higher than those of bottom ash leachates. However, no consistent trend in composition be-

tween corresponding ash leachates for the two tests is apparent. Interestingly, the chloride and sulfate concentrations in the test 2 ash stream leachates are slightly lower than those from test 1. One might expect that, if a corrosive component were present in the test 2 combustion gas, as implied by the results of the SASS, HCl, and VOST analyses discussed above, evidence of this component would appear in the ash leachates, especially the cyclone ash leachate. An alternative explanation would be that the component was present in the vapor phase at the cyclone temperature, although this seems unlikely.

Bioassay tests were performed on the SASS train organic sorbent module extract and the ash stream samples. The health effects bioassays included the Ames mutagenicity assay and the CHO cytotoxicity assay. The results of these assays are summarized in Table 7. The results sug-

gest that the flue gas was of moderate to high toxicity and mutagenicity for both tests. The cyclone hopper ash had nondetectable toxicity for both tests. However, this sample's mutagenicity apparently decreased from borderline moderate/high in test 1 to borderline low/moderate for test 2. This observation is consistent with the decreased leachable arsenic and beryllium contents noted in Table 5, and confirm that the addition of waste PET to the unit's fuel may have had the beneficial effect of decreasing the potential environmental hazard posed by this discharge.

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) performed for these tests to establish the precision and accuracy of the laboratory analyses generally gave results within the project QA objectives for these measures. However, the precision of the SSMS analyses, as determined by analysis of blind duplicate samples, was of only borderline acceptability and the accuracy of this analysis, as determined by analyzing a blind audit sample, was not generally within a factor of 3 as specified by Level 1 protocol. However, this failure to achieve reasonably good precision and accuracy has little effect on test conclusions. The conclusion that corresponding samples from both tests had comparable trace element compositions (except for lead) should be unaffected. The high lead levels in test 2 samples were quantified using AAS analyses, which met appropriate QA objectives for precision and accuracy. The conclusions that cyclone ash leachates had significantly higher trace element concentrations than bottom ash leachates, and that the test 1 cyclone ash leachate had higher trace element concentrations than that from test 2, were based on observed order of magnitude differences. Furthermore, these differences were often substantiated by AAS analyses which, again, met appropriate QA objectives.

Table 6. Ash Stream Leachable Anion Analysis Results
Concentration (mg/l)

Anions	Test 1 (coal fuel)		Test 2 (coal/PET fuel)	
	Bottom ash leachate	Cyclone hopper ash leachate	Bottom ash leachate	Cyclone hopper ash leachate
Chloride	2.6	300	1.3	180
Fluoride	0.25	0.46	0.10	1.8
Nitrate	>1.0	>10	>1.0	>10
Nitrite	>1.0	>10	>1.0	>10
Phosphate	>1.0	>10	>1.0	>10
Sulfate	300	19,000	220	12,000
Sulfite	20	5,000	20	5,000

Table 7. Bioassay Results

Test	Sample	Bioassay response ^a	
		Ames mutagenicity	CHO clonal toxicity
1 (coal)	XAD-2 extract	H	M
	Bottom ash	ND	ND
	Cyclone hopper ash	M/H	ND
2 (coal/PET)	XAD-2 extract	M	H/M
	Bottom ash	ND	ND
	Cyclone hopper ash	L/M	ND

^aND – Nondetectable mutagenicity/toxicity.

L – Low mutagenicity/toxicity.

M – Moderate mutagenicity/toxicity.

H – High mutagenicity/toxicity.

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The complete report consists of two volumes, entitled "Environmental Assessment of a Commercial Boiler Fired with a Coal/Waste Plastic Mixture:"

"Volume I. Technical Results," (Order No. PB 86-183 811/AS; Cost: \$16.95)

"Volume II. Data Supplement," (Order No. PB 86-183 829/AS; Cost: \$22.95)

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