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Project Summary

Fate of Selected Metals and Emissions from a Sludge/Wastepaper Gasifier

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A study was conducted to analyze a pilot-scale gasification system for sludge and wastepaper and to quantify its gaseous, particulate, and metal emissions. The downdraft, packed-bed, air-blown gasifier processed up to 1800 MJ/hr of fuel. Four different densified mixtures of wastewater sludge and source-separated wastepaper were used as fuel. Eight experimental gasifier runs were conducted to quantify operation characteristics. In addition, particle and metal size distributions and particulate, gaseous, and metal emissions were measured from the combustion of producer gas, a product of the gasification process.

The energy content of the producer gas varied between 4.83 and 7.04 MJ/m^3, with the lowest values associated with the highest fuel ash contents. Measured concentrations of gaseous emissions after combustion of the producer gas varied between 15.1 and 16.5 ppm for CO, 1.39 and 12.7 ppm for total hydrocarbons (THC), 98.6 and 121 ppm for NO_x, and 55.5 and 105 ppm for SO_2. Particle concentrations varied between 35.7 and 193.0 mg/dry standard cubic meter corrected to 12 percent CO_2.

Based on metals balance data, volatile metals like Cd, Pb, and Zn were enriched on particulate matter, and the matrix metals like Cu, Cr, and Fe, were enriched in the char. Based on particle and metal size distribution data, the mass median aerodynamic diameter (MMAD) for particulate matter varied between 0.31 and 0.95 micrometers. It was also found that Cd, Pb, and Zn were enriched on smaller particles, and that Ni, Cr, and Fe were enriched on larger particles.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, 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

The adverse environmental impacts of wastewater sludge on both groundwater and land quality is a growing concern. As a result, incinerators and other thermal devices for neutralization and volume reduction of wastewater sludge will be used to a greater extent in the future. An alternative to conventional sludge incineration is the co-disposal of wastewater sludge and solid waste in a gasifier. The purpose of this report is to analyze the feasibility of using a gasifier for processing various sludge and wastepaper fuels and to quantify its gaseous, particulate, and metal emissions.

The sludge and wastepaper gasification process discussed here involves the gasification of densified mixtures of sludge and source-separated wastepaper in a simple packed-bed, batch-fed reactor using air as the oxidant. The gasification process involves the partial combustion of a carbonaceous fuel with about 20 to 30 percent of the stoichiometric oxygen requirement. The products of gasification are a low-energy combustible gas (producer gas) rich in carbon monoxide, hydrogen and hydrocarbon gases, and a solid residue (char). Producer gas can be used to fuel boilers, heaters, engines, or turbines. Results from eight experimental gasifier runs using various mixtures of sludge and wastepaper were used to

quantify the gasifier performance, the particulate and gaseous emissions, the fate of selected metals, and the distribution of metals emissions with particle size.

Experimental Apparatus and Procedures

The pilot-scale, batch-fed, downdraft gasifier and producer gas burner used in this experimental program were designed and constructed for work previously reported. A schematic of the sludge and wastepaper gasification system is shown in Figure 1. Temperature, pressure, and producer gas analysis data were collected automatically using a dedicated computer and data collection system. Plots were produced showing temperature, flow, and variations in the composition of producer gas throughout the run. A computer program was also developed to calculate mass and energy balances.

Total particulate emissions from the combustion of producer gas were determined using U.S. Environmental Protection Agency (EPA) Method 5. NO_x, CO, O_2, SO_2, THC, and O_2 were determined using California Air Resources Board (CARB) Method 100. Particle size distribution data for the particulate matter in combustion gases were generated for three runs using three impactors for each run—two Anderson Mark III* stack samplers, and one Pilat Mark 3 Source Test Cascade Impactor.

To determine the fate of metals in the gasification process, samples of the fuel, char, fly ash, slag, and particulate matter (Method 5 filter) were analyzed for seven metals. Metals were extracted from each sample using room temperature HCl-HF-H_3BO_3 digestion procedures. Atomic absorption spectroscopy (AAS) was used to determine the concentration of Cd, Pb, Zn, Ni, Cu, Cr, and Fe in each of the gasification process samples for seven gasifier runs. A parallel metals analysis was performed for one run using both AAS and X-ray fluorescence (XRF). In addition, the distribution of metals in a sample preparation for metals analysis was assured by analysis of a National Bureau of Standards (NBS) certified sample of coal fly ash.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Summary and Discussion of Experimental Results

The eight experimental gasifier runs were conducted at nearly identical airflow rates (1.92 to 2.01 m^3/min at 20 °C, and 1 atm) using four different mixtures of sludge and wastepaper. Data on gasifier operations, particulate and gaseous emissions, and the fate of metals are presented in this section.

Gasifier Operational Data

During each gasifier run, data were collected on fuel, char, fly ash, process rates, temperatures, pressures, and producer gas composition. From these data, energy balances were calculated.

Fuel Characteristics—Four different densified mixtures of sludge and wastepaper were used as gasifier fuel for these tests. A summary of the fuel composition is presented in Table 1. The bulk density of the fuels varied between 334 and 595 kg/m^3. The higher heating value (HHV) fuels ranged from 17.12 to 19.43 MJ/kg on a dry basis. The fuels with the highest ash contents, the highest bulk density, and the lowest energy contents are all associated with mixtures containing the greatest fraction of sludge.

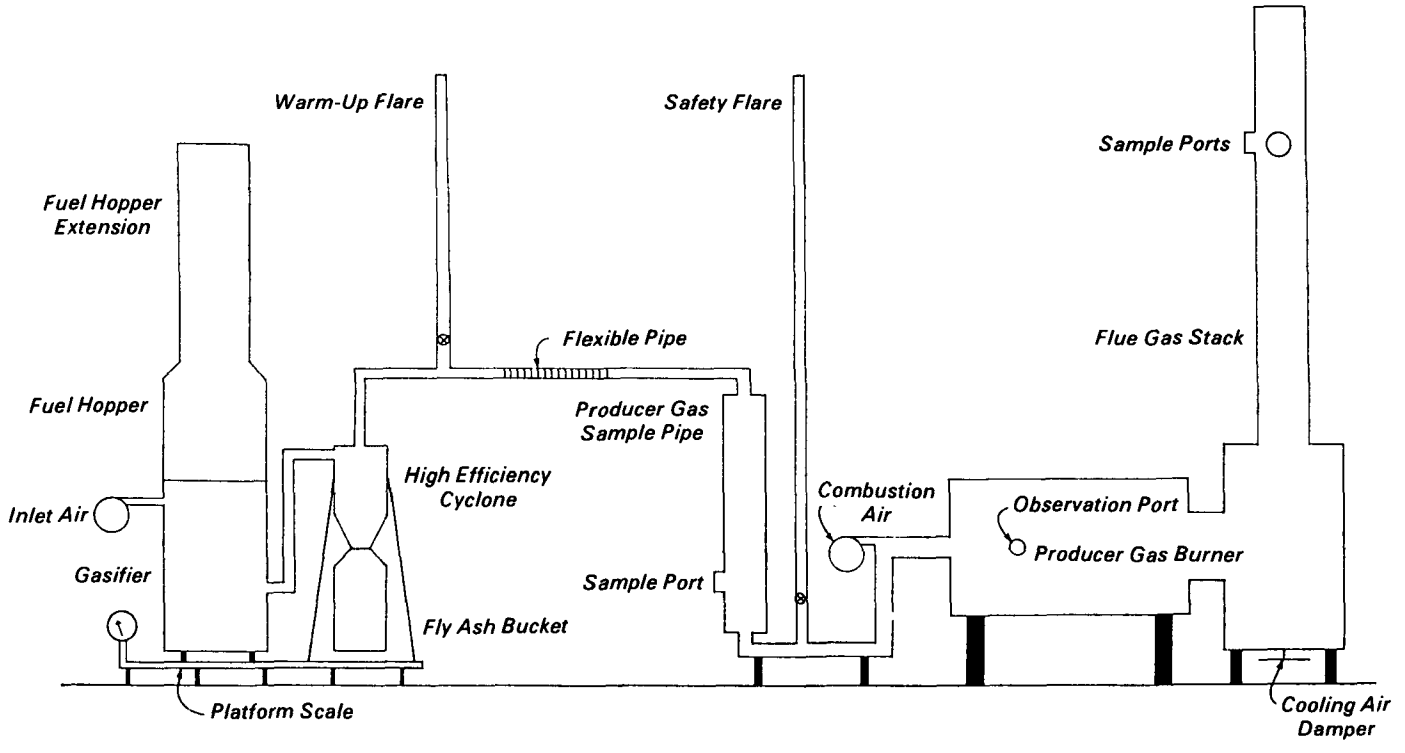

Figure 1. Schematic diagram of the experimental sludge and wastepaper gasification system.

Table 1. Fuel Composition

Element	Range
Carbon, %	*44.36 - 47.54*
Hydrogen, %	*5.60 - 5.80*
Oxygen, %	*39.70 - 44.67*
Nitrogen, %	*0.12 - 0.63*
Sulfur, %	*0.04 - 0.29*
Ash[a], %	*3.1 - 9.5*
Cadmium, ppm	*2.05 - 5.32*
Lead, ppm	*37.2 - 106.*
Zinc, ppm	*207. - 507.*
Nickel, ppm	*21.0 - 88.5*
Copper, ppm	*109. - 280.*
Chromium, ppm	*118. - 355.*
Iron, ppm	*2500. - 7210.*

[a]*Not an element, obtained from ultimate analysis.*

Char and Fly Ash Characteristics—Char and fly ash collected from each gasifier run were analyzed physically and chemically. The energy content of the char varied between 14.74 and 20.46 MJ/kg (HHV), and the carbon content of the char varied from 39.36 to 58.37 percent. The energy content of the fly ash varied between 18.42 and 21.99 MJ/kg and the carbon content of the fly ash ranged from 52.65 to 61.87 percent.

Slag Formation—Slag is formed in the gasifier when the fuel ash reaches its melting point, flows together, and cools. Excessive slag formation in downdraft gasifiers can block the flow of fuel and char through the gasifier and thus cannot be permitted. Based on experimental gasifier runs, it was found that densified mixtures of sludge and wastepaper with a fuel ash content less than or equal to 6.9 percent can be gasified without significant slag formation.

Process Temperatures—Process temperatures throughout the gasification system varied widely. A knowledge of process temperatures at five different locations in the gasification system was important in understanding the gasification process.

The reduction zone temperature represents the temperature at which most of the producer gas is made. The reduction zone temperature varied betwee 950 and 1000°C. The partial combustion zone temperature represents the temperature at which exothermic combustion reactions occur. Slag formation is initiated in this region. Though not measured in this study, partial combustion zone temperatures are 50 to 100°C higher than those in the reduction zone.

The lower reduction temperature represents the temperature at which the producer gas and char leave the reactor bed. The lower reduction zone temperatures varied between 780 and 830°C.

The cyclone and stack gas temperatures represent those at which fly ash and particulate matter are collected, respectively. The cyclone temperature varied between 550 and 610°C, whereas the stack gas temperature varied between 380 and 420°C.

Producer Gas Composition—Producer gas is the desired product of the gasification process. Carbon monoxide, hydrogen, and total hydrocarbons make up the combustible fraction of producer gas. Results of gas analyses for producer gas are summarized in Table 2. Though the air input rate was relatively constant for all runs reported, a wide variation occurred in the energy content of the producer gas. The lowest producer gas energy contents were generally associated with fuels having high ash contents.

Energy Balances—Energy balances and gasifier efficiencies were calculated using the data described above. The cold gas efficiency of the gasification system (i.e., the efficiency of converting fuel to producer gas at 25°C) varied between 52 and 85 percent. However, because of experimental errors, efficiencies above 75 percent should be considered suspect. If the sensible energy of the producer gas can be used in a boiler, then the conversion efficiency is the sum of the cold gas efficiency and the sensible heat (about 12 percent).

Particulate and Gaseous Emissions

Particulate matter emissions from the combustion of producer gas were measured over a series of six runs. Both gaseous emissions and particle size distributions from the combustion of the producer gas were measured over a series of three runs. Particulate matter emissions samples, particle size distribution samples, and gaseous emissions samples were taken from the sample ports shown in Figure 1.

Based on data from EPA Method 5 tests, concentrations of particulate matter (corrected to 12 percent CO_2) ranged between 36 and 193 mg/DSCM (dry standard cubic meter). The stack velocity was 6.19 to 7.25 m/sec, and the isokinetic ratio varied from 88.6 to 97.4 percent. Based on these measurements, the producer gas burner system met federal standards for particle emissions from incinerators (189 mg/DSCM) for all runs except Run 36.

A summary of gaseous emissions is presented in Table 3 and the particle size distribution results are discussed later.

Fate of Metals

The fate of metals in the gasification process is presented and discussed using enrichment factors that are useful parameters for comparing the metal compositions of char, fly ash, and particle emissions with that of fuel. Enrichment factors correct for increases in metal concentration resulting from carbon losses by normalizing the sample and the fuel with an ash matrix constituent. Enrichment factors presented in Figure 2 were normalized with respect to iron according to the following formula:

$$EF = \frac{[M]/[Fe]\ \text{sample}}{[M]/[Fe]\ \text{fuel}}$$

where [M] = concentration of metal in ppm

[Fe] = concentration of iron in ppm

The metals in the samples have been normalized against Fe because it is a reasonably good tracer for the ash matrix of the fuel. It is not volatilized to any significant extent at the thermal conditions experienced in these tests. Any metal that behaves just like Fe will yield an EF equal to 1 in the char, fly ash, and particulate matter.

If $EF < 1$ for the char, then metal has been lost from the matrix, most likely by volatilizaton. If $EF > 1$ for the char, then Fe has been lost from the matrix and the initial assumption of an association of the metals in a common matrix is not a good one. $EF > 1$ implies particles containing a preponderance of Fe are selectively being removed from the char by the producer gas stream.

For the fly ash and particulate matter, if $EF > 1$, then condensation or absorption of volatile metals on the particles has occurred. If $EF < 1$, then metals are leaving the particles. Because the fly ash and particulate matter are in gas streams that are cooling, volatilization is unlikely. If $EF < 1$ for fly ash and particulate matter, it is more likely that the model is faulty and that particles leaving the bed do not have some common ash matrix, but have been classified aerodynamically into a fraction that has a lower metal to Fe ratio than the average ash matrix.

The expectation that Cd, Pb, and Zn might be volatilized is confirmed by

Table 2. *Composition and Energy Content of Producer Gas*

Item	Run 36	Run 37	Run 38	Run 40	Run 41	Run 42	Run 44	Run 44 GC
Dry gas composition (by volume), %								
CO	20.56	19.89	17.93	20.89	19.68	19.83	20.04	19.88
H_2	15.44	15.36	14.52	15.50	15.85	16.14	16.59	15.79
CH_4*	5.38	3.68	2.21	4.26	3.49	2.79	3.09	2.69
C_2H_4*	2.31	1.58	0.95	1.83	1.50	1.19	1.33	0.82
CO_2	13.83	13.78	13.16	13.50+	13.50+	13.50	14.29	10.79
N_2†	42.48	45.71	51.23	44.02	45.98	46.55	44.66	50.03§
Gas moisture content (by wet volume), %	15.47	16.10	16.22	14.31+	14.12	14.42	13.69	13.69
Gas energy content, MJ/m^3 (dry gas, LHV, 25°C, 1 atm)	7.04	5.99	4.83	6.45	5.90	5.55	5.73	5.28

*Measured as total hydrocarbons (THC); CH_4 is assumed to be 70% of THC, and C_2H_4 is assumed to be 30% of the THC.
+Assumed typical value; experimental data not available.
†N_2 includes nitrogen, argon, and trace amounts of nitrogen oxides. N_2 is determined by difference, N_2 = 100% - ($CO + H_2 + THC + CO_2 + O_2$).
§Includes 0.84% O_2.

Table 3. *Gaseous Emission Results*

Gas	Gasifier Run Number 36	37	38
NO_x, ppm	98.6	99.2	121
SO_2, ppm	55.5	62.6	105
THC, ppm	12.7	4.20	1.39
CO, ppm	16.5	16.8	15.1
CO_2, %	4.33	3.19	3.95
O_2, %	16.0	17.3	16.9

consideration of the EF values shown in Figure 2. These metals are removed from the char (EF < 1). Both the fly ash and the particulate matter show evidence of condensation (EF > 1).

The situation is less clear for the non-volatile metals. Cr and Cu behave similarly and all EF's are slightly less than unity. The behavior of Cr and Cu reflects experimental inaccuracies probably related to sampling. Material balances for non-volatile metals can account for 80 percent of the metal, whereas over 100 percent of the iron was found. This discrepancy probably accounts for the low EF's. It appears that these elements are matrix elements that behave much like Fe. The results for Ni are unclear because of poor material balances. Based on fly ash and char results, Ni appears to be a matrix element, but some enrichment of the particulate matter also occurs (EF ~ 5).

Material balances were good, and consistent, for all metals except Ni and ranged from 80 to 110 percent. Total losses of the various metals in the particulate stream are interesting. Average percent values are: Cd - 60; Pb - 40, Zn - 20, Cu - 2, Cr - 2, Fe - 2. Ni losses were between Zn and Cu but a range of values cannot be assigned for this metal.

X-Ray Fluorescence Analysis

To compare XRF with AAS analyses, both procedures were used to determine

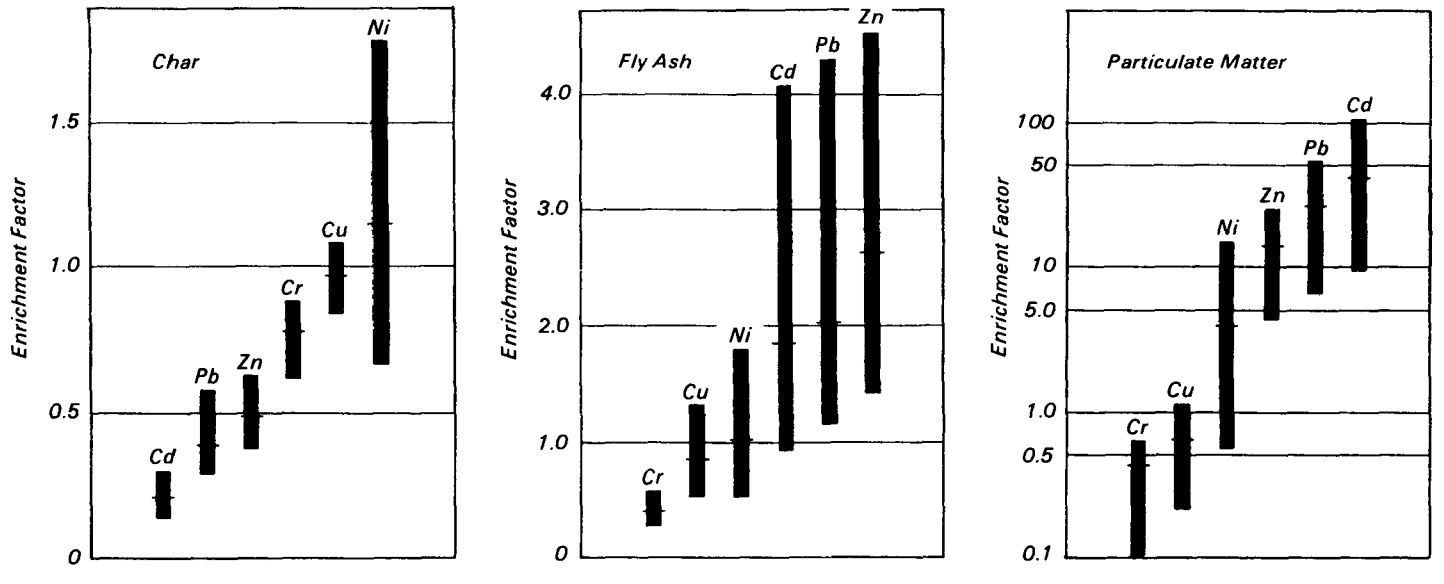

Figure 2. *Enrichment factors for char, fly ash, and particulate matter. Bar represents all values; horizontal line is mean value.*

metal concentrations in gasifier samples during one run and in an NBS-certified sample of coal fly ash. Though only seven elements were analyzed by AAS, 17 metal concentrations were available with XRF from only one sample. However, in comparing the XRF and AAS results, it appears that the latter produced much more accurate results. The lack of XRF accuracy is probably due to difficulties in sample mounting. For example, only 2 mg of sample can be attached to the XRF slide; it is therefore difficult to get a representative sample. In addition, it was impossible to confirm that the sample thickness on the XRF slide was uniform. Because the XRF analysis detects metal mass per square centimeter, it is critical that the sample layer be of a uniform and known thickness. Based on these results, XRF is an excellent method to determine which metals are present, but it should not be used to quantify concentrations of metals.

Particle and Metal Size Distribution

The "metal size distribution" represents the fraction of the total metal mass found in particulate matter of a given size range. The MMAD of a metal represents the particle diameter at which 50 percent of the total metal mass is found on particles with a diameter less than the MMAD. A summary of the MMAD's for particulate matter in the flue gas is presented in Table 4. The MMAD for particles in the flue gas varied between 0.31 and 0.95 micrometers based on impactor studies.

Metal enrichment on small particles can be determined by comparing the MMAD's of particulate matter and metals. Because the MMAD for Cd and Pb is less than or equal to that for particulate matter, metal enrichment on small particles is indicated. Small particle enrichment of Zn is shown on all runs except PT1 and AN6. Based on these analyses, the enrichment of Cd, Pb, and Zn on smaller particles is consistent with the relatively high vapor pressure of these metals. By contrast, it can be concluded that Ni, Cr, and Fe are concentrated in the larger particles (see Table 4). Based on the data presented, Cu seems to behave like a volatile metal, which is not consistent with vapor pressure data.

Conclusions

1. Four different mixtures of sludge and wastepaper with fuel ash contents varying between 3.1 and 9.5 percent were gasified. The fuel mixture with the highest ash content that did not cause significant slag formation is considered to be the maximum feasible fuel ash content. For these tests, the maximum feasible fuel ash content was 6.9 percent.
2. The producer gas generated during eight gasifier runs had an energy content that varied between 4.83 and 7.04 MJ/m^3 (dry, LHV, 25°C). The lowest producer gas energy contents were associated with high fuel ash contents.
3. The cold gas efficiency of the gasifier varied between 52.35 and 84.58 percent. Because of experimental errors, however, efficiencies above 75 percent should be considered suspect.
4. The measured concentrations of gaseous emissions after the producer gas was burned varied between 15.1 and 16.8 ppm for CO, 1.39 and 12.7 ppm for THC, 98.6 and 121 ppm for NO_x, and 55.5 and 105 ppm for SO_2. Particle concentration values varied between 35.7 and 193.0 mg/DSCM corrected to 12 percent CO_2.
5. Based on the enrichment factor data, volatile metals like Cd, Pb, and Zn are enriched on particulate matter, and the matrix metals like Cu, Cr, and Fe are enriched in the char. Ni cannot be classified either as a volatile or a matrix metal.
6. Based on the data from one run, the AAS results are more accurate than the XRF results.
7. Based on particle and metal size distribution data, (a) the MMAD for particulate matter varied between 0.31 and 0.95 micrometers; (b) Cd, Pb, and Zn were enriched on smaller particles; and (c) Ni, Cr, and Fe were enriched on larger particles.

The full report was submitted in fulfillment of agreement CR 809747-01-0 by the University of California under the sponsorship of the U.S. Environmental Protection Agency.

Table 4. Mass Median Aerodynamic Diameter

Gasifier Run Number	Impactor Run Number	Particulate Matter	Distribution Element (diameter in micrometers)						
			Cd	Pb	Zn	Ni	Cu	Cr	Fe
	PT1	NA	<0.33	<0.33	0.95	2.5	2.6	2.8	2.2
40	AN1	NA	NA	NA	NA	NA	NA	NA	NA
	AN2	NA	<0.33	<0.32	<0.32	4.5	0.43	4.6	1.8
	PT2	0.95	<0.33	0.62	<0.33	3.9	0.48	9.0	6.0
41	AN3	0.31	NA	NA	NA	NA	NA	NA	NA
	AN4	0.31	<0.31	<0.31	<0.31	4.6	<0.31	3.6	1.3
	PT3	0.92	NA	NA	NA	NA	NA	NA	NA
42	AN5	<0.32	<0.32	<0.32	<0.32	5.5	<0.32	5.0	2
	AN6	<0.33	<0.32	0.38	0.8	6.5	<0.33	4.5	2.0

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The complete report, entitled "Fate of Selected Metals and Emissions from a Sludge/Wastepaper Gasifier," (Order No. PB 86-131 026/AS; Cost: $16.95, subject to change) will be available only from:
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