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Ecotoxicity of Coal Gasifier Solid Wastes

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Small coal gasifiers are being viewed with increasing interest by industry and government in the United States as replacements for dwindling supplies of oil and natural gas. A recent environmental and health assessment of small coal gasifiers (DOBSON et al. 1981) was based on a projection of up to 2500 units in place by the year 2000. As of late 1979, 36 gasifiers were described as operational, installed, or under construction in the United States (USEPA 1979). One of these gasifiers, a Foster-Wheeler/Stoic unit, began operation at the University of Minnesota-Duluth (UMD) campus in late 1978. The gasifier, which is fed low-sulfur western bituminous coal, yields a product gas and by-product tar, both fired in existing boilers to provide campus heating (COAL AGE 1977). There have been only a few studies of the environmental characteristics of the present generation of coal gasifiers (PAGE 1978, THOMAS et al. 1979); the Foster-Wheeler/Stoic design in use at UMD has not yet been assessed. Among the areas of concern for coal gasification are solid wastes (USDOE 1978) which, if discarded in landfills, could potentially contaminate ground and surface water with leachates containing inorganic and organic pollutants. As part of a comprehensive Oak Ridge National Laboratory program (COWSER 1978) to assess the health and environmental effects of the UMD gasifier, we have been testing the two primary solid waste streams (gasifier bottom ash and cyclone separator char). This paper describes the results of initial chemical and toxicological characterization.

METHODS

Solid wastes from three runs (periods of operation) of the UMD coal gasifier were sampled and shipped to Oak Ridge National Laboratory for analysis and testing: bottom ash from May-June 1979, November-December 1979, and February-March 1980 runs, and cyclone char from the February-March 1980 run.

Soluble materials were extracted from the solid wastes, using both the Extraction Procedure (EP) of the U.S. Environmental Protection Agency (USEPA 1980) and a distilled, deionized water protocol. The EP, developed as a tool to enforce the Resource Conservation and Recovery Act (RCRA) of 1976 (PL 94-580), is a 24-h batch aqueous extraction using 0.5 N acetic acid (maximum of 4 mL acid per g sample) to maintain a solution pH of 5. Acetic acid is added in an attempt to simulate leaching conditions that might occur if solid wastes are co-disposed with municipal wastes. The second method is a distilled, deionized water

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leaching technique where there is no adjustment of pH. In each protocol the extracts are passed through a 0.45 µm pore size membrane filter.

All extracts were analyzed for metals. They were prepared according to standard methods (USEPA 1979) and analyzed by flameless graphite furnace atomic absorption spectroscopy (AAS) with the following exceptions: (1) extracts for Hg determination were preserved by addition to a nitric acid/dichromate solution and prepared for cold vapor flameless AAS (FELDMAN 1974); (2) Se was chelated with 5-nitro-o-phenylene diamine and extracted into toluene before analysis (TALMI & ANDREN 1974); and (3) As was determined by an arsine accumulation-helium glow detector procedure (FELDMAN 1979). In the calculation of mean concentrations, all "less-than" values were ignored.

The distilled, deionized water leachates were also screened for effects in a battery of ecological tests which included:

(1) acute toxicity to the zooplanktonic crustacean Daphnia magna, measured as the 48-h LC50 (concentration of the leachate found lethal to 50% of the test organisms in a 48-h exposure). Laboratory-cultured first-instar organisms were tested at 20°C with alternate light-dark periods of 12 h each. Values of the LC50 were determined by computerized probit analysis (BARR et al. 1976);

(2) inhibition of photosynthesis in Microcystis aeruginosa, a blue-green alga, and Selenastrum capricornutum, a green alga, tested at various dilutions of the leachate. Actively growing algal cells were suspended in the test solutions and incubated at 24°C for 4 h. Photosynthesis was measured by th ^{14}C-bicarbonate method during the last 2 h of incubation. Significant inhibition of photosynthesis ($\alpha = 0.05$) was determined using Student's t test to compare leachate-treated algal cultures with control cultures; and

(3) inhibition of root elongation in seedlings of radish, Raphanus sativus (Early Scarlet Globe), and sorghum, Sorghum vulgare (Sugar Drip), with exposures of 48 h and 72 h, respectively, tested at various dilutions of the leachate. Seeds were allowed to germinate in vertical chambers which held them against an absorbant paper saturated with the test solutions. Seedlings were maintained at 25°C. Statistical differences in radicle length ($\alpha = 0.05$) were determined using Student's t test to compare leachate-treated seedlings with control seedlings.

The Daphnia magna, algae, radish, and sorghum test systems have been described in detail by EPLER et al. (1980), EDWARDS & ROSS-TODD (1980), MILLEMANN & PARKHURST (1980), and GIDDINGS (1979). The May-June 1979 bottom ash extract for the seedling tests was adjusted to pH 5 with H_2SO_4 for comparison with other leachates being tested at the pH. It had been observed (unpublished data) that pH 5 would not in itself cause an inhibition of radicle elongation in these tests. All other extracts for ecotoxicity testing were neutralized to pH 7.0 to 7.5 by the addition of H_2SO_4.

RESULTS AND DISCUSSION

Trace element analyses of the UMD coal gasifier solid waste leachates are presented in Table 1. Concentrations of Ba, Cd, Cu, Fe, Ni, Pb, and Zn in EP leachates of UMD coal gasifier solid wastes were greater than in corresponding distilled water leachates of the same materials. In the case of the February-March 1980 gasifier run, from which we tested both the bottom ash and cyclone char, concentrations of As, Ba, Cd, Hg, Pb, and Zn were higher in both leachates of the cyclone char than in the corresponding leachates of the bottom ash; concentrations of Cu and Mo were lower in cyclone char leachates than in corresponding bottom ash leachates. For other elements, a pattern was not apparent.

Replication of chemical analysis of distilled, deionized-water leachates allowed determination of the statistical significance of differences in elemental concentrations between November-December 1979 and February-March 1980 bottom ash leachates, and between bottom ash and cyclone char leachates from the February-March 1980 gasifier run. Based on a Duncan's means separation test, concentrations of As and Mo were significantly ($\alpha = 0.10$) greater in November-December 1979 than February-March 1980 bottom ash leachates, while concentrations of Ba, F, Ni, Se, and Zn were significantly lower. Concentrations of Cu, F, and Hg were significantly greater in bottom ash leachates than in cyclone ash leachates of the February-March 1980 run, while concentrations of As, Ba, Pb, Se, and Zn were significantly lower.

To evaluate the results of the chemical analyses of the leachates, we assembled selected water quality criteria and standards in Table 2. The final column in Table 2 shows the highest leachate concentration for each element, for comparison. Probably the most important standards for regulating solid waste disposal are those promulgated by the USEPA to define toxic "hazardous" wastes in accordance with RCRA; these standards, shown under the column "RCRA" in Table 2, were established

TABLE 1. Concentrations of trace elements in leachates of UMD coal gasifier solid wastes. Values in parentheses represent the standard error of the mean for replicated analyses

Gasifier run:		May-June 1979		November-December 1979		February-March 1980			
Solid waste:		Bottom ash		Bottom ash		Bottom ash		Cyclone char	
Extraction protocol:		EP[a]	DW[b]	EP	DW	EP	DW	EP	DW
Leachate pH[c]:		5.1	9.5	5.1	10.8	5.1	11.6	4.9	8.7
Constituent									
Arsenic	(ng/mL)	2.6	2.0	0.9	0.4 (0.03)	1.4	0.1 (0.00)	31	39 (1.1)
Barium	(μg/mL)	0.4	<0.2	0.6	0.1 (0.004)	2.0	1.4 (0.23)	12.8	5.5 (0.03)
Cadmium	(ng/mL)	0.14	0.01	0.08	<0.02	0.47	0.02	33	0.1 (0.02)
Chromium	(ng/mL)	0.4	4.7	1.2	0.2 (0.01)	0.8	0.2 (0.01)	0.8	0.2 (0.02)
Copper	(ng/mL)	2.3	1.9	2.6	0.9 (0.35)	11	1.4 (0.07)	5.2	0.8 (0.08)
Fluoride	(μg/mL)	0.3	0.2	1.1	0.2 (0.02)	0.7	11.7 (0.21)	11	6.4 (0.00)
Iron	(ng/mL)	11.0	6.8	190	8.1 (0.95)	26	9.9 (0.45)	1000	9.7 (1.46)
Mercury	(ng/mL)	0.04	0.01	0.01	0.01 (0.003)	0.01	0.03 (0.007)	0.02	0.10 (0.046)
Molybdenum	(ng/mL)	3.2	<3.0	1.2	5.0 (0.04)	2.4	1.7 (0.03)	<2.0	1.4 (0.20)
Nickel	(ng/mL)	81	21	34	1.3 (0.23)	28	3.9 (0.08)	69	3.7 (0.90)
Lead	(ng/mL)	2.3	0.4	0.8	<0.1	2.2	0.4 (0.09)	380	12.3 (1.05)
Selenium	(ng/mL)	1.5	0.8	<5.0	1.4 (0.07)	1.8	2.7 (0.60)	1.4	50 (1.9)
Silver	(ng/mL)	0.08	0.06	0.02	0.05	<0.02	0.05 (0.017)	<0.02	0.06
Zinc	(ng/mL)	8.2	0.6	43	0.3 (0.09)	57	0.5 (0.28)	8300	7.2 (0.62)

[a]Extraction Procedure.
[b]Distilled, deionized water.
[c]Final pH of leachate, before adjustment for toxicity tests.

TABLE 2. Selected water quality criteria and standards

Constituent		Criteria and Standards					
		RCRA[a]	DWS	Irrigation[b]	Livestock[c]	Aquatic biota[d]	Highest leachate concentration[e]
Arsenic	(ng/mL)	5000	50[f]	100	200		39
Barium	(μg/mL)	100	1[f]				12.8[g]
Cadmium	(ng/mL)	1000	10[f]	10	50	0.4-12	33
Chromium	(ng/mL)	5000	50[f]	100	1000	100	4.7
Copper	(ng/mL)		1000[h]	200	500		11
Fluoride	(μg/mL)		1.4-2.4[f]	1			11.7[g]
Iron	(ng/mL)		300[h]	5000		1000	1000
Mercury	(ng/mL)	200	2[f]		10	0.05	0.10
Molybdenum	(ng/mL)			10			5.0
Nickel	ng/mL)			200			81
Lead	(ng/mL)	5000	50[f]	5000	100		380
Selenium	(ng/mL)	1000	10[f]	20	50		50
Silver	(ng/mL)	5000	50[f]				0.08
Zinc	(ng/mL)		5000[h]	2000	25000		8300

[a]From USEPA (1980).
[b]For continuous irrigation on all soils, from NAS/NAE (1973).
[c]From NAS/NAE (1973).
[d]From USEPA (1976).
[e]From Table 1.
[f]National Interim Primary Drinking Water Standards, from 40 CFR 141.
[g]Exceeds criterion or standard after assumed dilution.
[h]Secondary Drinking Water Standards, from 40 CFR 143.

(USEPA 1980) as 100 times the National Interim Primary Drinking Water Standards (NIPDWS). Other criteria and standards in Table 2 are for drinking water (DWS), irrigation (irrigation), livestock watering (livestock), and the protection of freshwater life (aquatic biota).

The RCRA standards were met in all cases by the UMD gasifier solid waste leachates. On the basis of these tests, it would appear that the solids would be considered "nonhazardous" according to the present interpretation of RCRA. However, several other standards and criteria were not met. The USEPA expects that considerable dilution would occur before a leachate would appear in surface or ground waters (EPLER et al. 1980); ten-fold dilution is assumed before availability in groundwater (and therefore availability to plant roots, and via wells, to livestock, irrigated crops, and drinking water), and one-thousand-fold dilution is assumed before availability in surface waters (and therefore to freshwater biota). Bearing this in mind, we applied a 10X dilution factor before comparison of leachate concentrations with irrigation, livestock watering, and drinking water criteria and a 1000X dilution factor before comparison with aquatic biota criteria. Taking into account assumed dilution, only the measured values of 12.8 μg/mL barium (drinking water standard) and 11 μg/mL fluoride (irrigation criterion) in the February-March 1980 cyclone char EP leachate, and 11.7 μg/mL fluoride (irrigation criterion) in the February-March 1980 bottom ash distilled water leachate would equal or exceed a standard or criterion.

Table 3 presents the results of the ecological tests with distilled water leachates. In some cases, a toxic effect was noted only with full-strength (i.e., 100%) or nearly full-strength leachate, but not with diluted leachate; in other cases, there was no toxic effect even with full-strength leachate.

TABLE 3. Results of ecotoxicity tests of distilled, deionized water leachates of UMD coal gasifier solid wastes. Concentration percentages are strengths of leachate

Test system	Gasifier run: Solid waste:	May-June 1979 Bottom ash	November-December 1979 Bottom ash	February-March 1980 Bottom ash	February-March 1980 Cyclone char
Daphnia magna		no mortality at 100%	LC50 = 82%	LC50 > 100% (LC38 = 100%)	no mortality at 100%
Algae:					
Selenastrum capricornutum		48% inhibition at 100% NSE[b] at 10%	a	a	a
Microcystis aeruginosa		50% inhibition at 100% NSE at 10%	NSE at 100%	NSE at 10%	NSE at 10%
Seedlings:					
Radish		19% inhibition at 100% 9% inhibition at 50% NSE at 10%	NSE at 100%	NSE at 100%	NSE at 100%
Sorghum		NSE at 100%	NSE at 100%	NSE at 100%	NSE at 100%

[a]Not tested.
[b]No significant effect (see text).

Only the results of ecotoxicity tests with distilled water leachates are presented here. Earlier work (EPLER et al. 1980, MILLEMANN & PARKHURST 1980, FRANCIS et al. 1980) had demonstrated that EP leachates are not suitable for ecotoxicity testing because of toxicity or stimulation caused by acetate in the extracts. MILLEMANN & PARKHURST (1980) discussed possible underestimation of toxicity using leaching protocols and ecotoxicity tests as applied here. They pointed out that (1) filtration of the leachate could remove toxic constituents, and (2) volatile toxic chemicals could be lost during the extraction. CAMERON & KOCH (1980) demonstrated the effect of pH on the ecological testing of leachates and recommended that leachates be tested at their natural pH in addition to an adjusted pH.

The assumed leachate dilution would dictate that a leachate would have to demonstrate a toxic effect at a concentration of 10% or less for the seedling test, or 0.1% or less for the aquatic biota tests, to be considered "hazardous" by these tests. The ecotoxicity tests performed to date indicate that the UMD gasifier solid wastes would be considered essentially "nonhazardous" along the lines of RCRA (allowing for the use of distilled water leachates rather than EP leachates). In most cases, there was no significant toxicity even at full strength (no dilution); when toxicity was found, it was always at concentrations of the leachate well above what might be assumed to occur in the rooting zones of soils or in surface waters.

Based on inorganic chemical analysis and ecotoxicity tests performed on leachates of bottom ash and cyclone char, the two principal components of solid wastes from the UMD coal gasifier, the materials do not appear to pose a significant threat to ground or surface water quality or to terrestrial and aquatic biota. Evidence to date indicates that the solids would be considered "nonhazardous" according to RCRA. Data are needed on the validity of (1) the simulation of natural processes by laboratory extraction techniques and (2) assumptions of leachate dilution from disposal sites to ground and surface waters.

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