Research and Development

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# **Project Summary**

# Assessment of Fluidized-Bed Combustion Solid Wastes for Land Disposal

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Fluidized-bed combustion (FBC) is an emerging energy technology that holds promise for both high efficiency of energy conversion and minimization of adverse air quality impacts. A major advantage of FBC is that highsulfur coal can be burned without the use of flue-gas desulfurization equipment to meet air quality standards. During combustion in a fluidized bed, sulfur in the coal is oxidized to sulfur oxides (SO<sub>x</sub>) as in conventional boilers, but these SO<sub>x</sub> then react with a sorbent that is injected into the fluidized bed with the coal. During steady state conditions, the sorbent constitutes more than 95% of the bed material. The sorbent, typically lime, limestone, or dolomite, usually forms calcium sulfate compounds, such as anhydrite, when reacting with the SO<sub>x</sub>. The solid residues that are generated in an FBC unit are usually larger in volume and have different properties than the typical bottom ash from a conventional boiler.

The objectives of this investigation were to obtain and analyze representative samples of FBC wastes, assess the characteristics of leachates generated from the wastes under laboratory and field (landfill) conditions, and characterize the attenuation of the leachates by earth materials that are typical of disposal settings. An attempt was made to develop a means of predicting the leachate generation behavior of FBC wastes under landfill conditions on the basis of laboratory test results by estab-

lishing a rigorous statistical relationship between the laboratory and field leaching results. In addition, the compatibility of commonly used landfill liner materials with FBC waste leachates was assessed.

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 a separate report of the same title (see Project Report ordering information at back).

## Introduction

FBC is an emerging energy technology that holds promise for both high efficiency of energy conversion and minimization of adverse air quality impacts. A major advantage of FBC is that high-sulfur coal can be burned without the use of flue-gas desulfurization equipment to meet air quality standards. During combustion in a fluidized bed, sulfur in the coal is oxidized to SO<sub>x</sub> as in conventional boilers, but these SO<sub>x</sub> then react with a sorbent that is injected into the fluidized bed with the coal. The sorbent, typically lime, limestone, or dolomite, usually forms calcium sulfate compounds, such as anhydrite, when reacting with the SO<sub>x</sub>. The solid residues that are generated in an FBC unit are usually larger in volume and have different properties than the typical bottom ash from a conventional boiler.

Although FBC wastes can be used as soil conditioners or disposed of in impoundments or at sea, it is likely that most wastes that will be generated in the future will be landfilled. The objective of this investigation was to assess the suitability of FBC wastes for landfill disposal and to determine several characteristics of the waste important to landfill considerations. The procedures were to obtain and analyze representative samples of FBC wastes, determine the composition of the wastes, assess the characteristics of leachates generated from the wastes under laboratory and field (landfill) conditions, and characterize the chemical interaction of the leachates with earth materials that are typical of disposal settings.

The investigation included both extensive laboratory studies and large field cells to simulate actual landfill conditions. An attempt was made to develop a means of predicting the leachate generation behavior of FBC wastes under landfill conditions on the basis of laboratory test results by establishing a rigorous statistical relationship between the laboratory and field leaching results. In addition, the compatibility of commonly used landfill liner materials with FBC waste leachates was assessed. The laboratory studies were performed at Radian Corporation laboratories in Austin, TX, and the field investigation took place at the former EPA mine drainage control facility, about 9 mi\* south of Morgantown, WV.

## Sources of Samples

Sources of FBC wastes were selected to be as representative of future FBC waste streams as possible while, at the same time, being capable of providing enough sample for laboratory and field experiments. The waste source selected for pressurized FBC (PFBC) was the Exxon Miniplant at Linden, NJ. Two atmospheric FBC (AFBC) sources were selected—the EPRI/B&W unit at Alliance, OH, and the Georgetown University boiler in Washington, DC. Both AFBC units were operating in the recycle mode when wastes were collected.

Several types of geological substrate materials (termed "disposal media") were obtained from the vicinity of the field cells in northern West Virginia and eastern Ohio. They were selected as representative of substrate materials at future disposal sites in the eastern U.S. and included shale, coal mine interburden, sandstone, glacial till, alluvium, and limestone. These samples were used in the laboratory and field studies to investigate the

interaction (contaminant attenuation and mobilization) of the FBC waste leachate with typical substrate materials.

### **Overview of Procedures**

The principal component of the laboratory investigation was a six-step sequential batch equilibration protocol for assessing the characteristics of leachate after both generation from FBC wastes and exposure to samples of the disposal media (Figure 1). The leaching steps of the batch equilibration protocol consisted

of initial leaching of the waste (at a liquidto-solid mass ratio of 10:1) with deionized water, secondary leaching of leached waste with additional deionized water (Step 2) for up to seven repetitions; and secondary exposure, sequentially for up to seven repetitions, of leachate to fresh waste in Step 3.

The leachate was exposed to the disposal media to assess the tendency of contaminants to be attenuated by (or mobilized from) the media. Step 4 of the protocol assessed the initial attenuation of

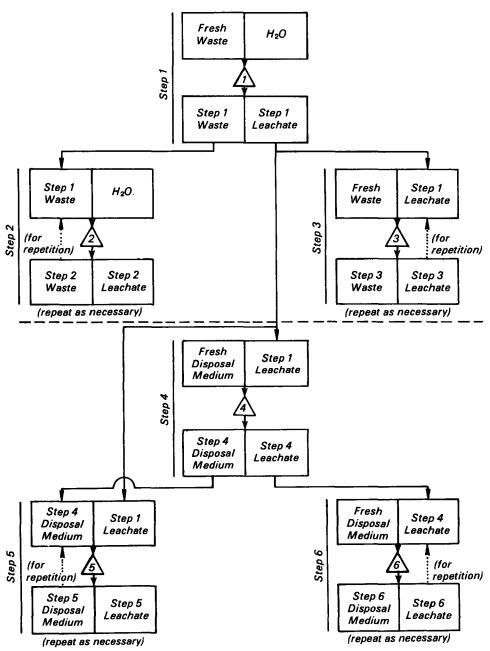


Figure 1. Multistep laboratory leaching protocol.

<sup>\*1</sup> mi = 1.609 km.

leachate from Step 1 when exposed to a sample of disposal medium. Step 5 evaluated the ability of a disposal medium sample to continue to attenuate fresh leachate from Step 1. In Step 6, the leachate from Step 4 was repeatedly exposed to new samples of disposal medium to evaluate the progressive attenuation of the leachate by exposure to fresh media. Step 5 was repeated up to nine times and Step 6 was repeated five times.

Samples of the FBC waste and disposal media were analyzed in the laboratory for a variety of parameters. Physical properties that were determined included grain size distribution, specific surface area, and particle surface characteristics. The solids composition was investigated by X-ray diffraction to determine the crystalline phases present and by sample digestion and analysis to determine the chemical composition.

The laboratory studies also included two sets of leaching columns, one set containing only disposal media, and another set containing layers of waste and disposal media. In addition, the FBC waste samples were subjected to the Extraction Procedure test for hazardousness (toxicity category) as set forth in regulations developed pursuant to the Resource Conservation and Recovery Act. Another component of the laboratory studies was the assessment of the compatibility of various landfill liner materials with FBC waste leachate.

The main feature of the field investigation was the design, installation, and operation of several large (4 ft\* diameter, 7 ft long) cylindrical field cells. Field cells containing Exxon PFBC and Alliance AFBC waste were constructed and operated below ground surface. These field cells were open at the land surface to natural precipitation and isolated from the subsurface environment. The field cells were intended to simulate actual landfill conditions in the field as closely as practicable. The cells contained layers of waste and disposal media arranged sim-

ilarly to a landfill configuration, with an upper layer of disposal medium to simulate landfill cover material, a layer of waste, and a lower layer of medium to simulate landfill substrate (Figure 2). Leachate sampling points were included at the base of the waste layer (upper sample point) for collection of unattenuated leachate and at the base of the lower layer of disposal medium (lower sample point) for collection of attenuated leachate. Excess leachate was removed from the bottom of the field cells and not allowed to escape into the subsurface environment.

The field studies also included two large-diameter permeameters containing FBC wastes. These permeameters were used to determine the permeability of uncompacted waste initially after emplacement and again after several months of exposure to weathering processes and chemical changes in the wastes.

\*1 ft = 30.48 cm.

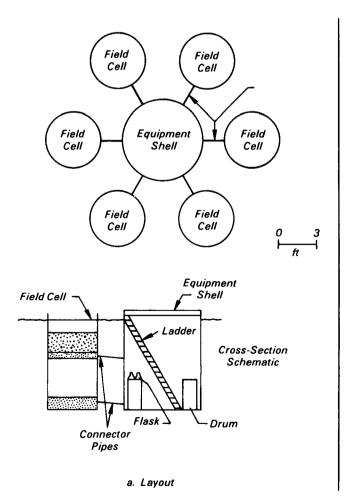
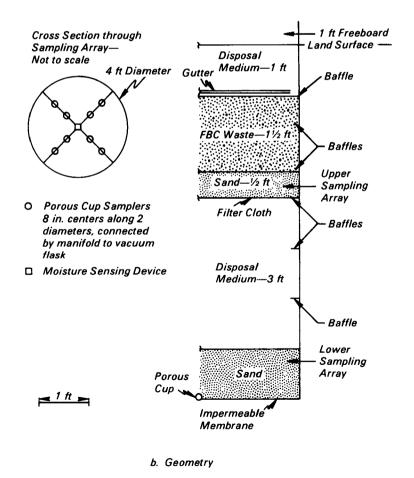


Figure 2. Field cell layout and geometry.



## FBC Waste Composition: Mineralogy and Major Chemistry

The principal crystalline phases found in the unleached Exxon PFBC waste were anhydrite, periclase, and quartz. The most significant components found in the solids analysis were calcium (22%), magnesium (12%), and sulfate (23%). After leaching in Steps 1 and 2 of the batch equilibration protocol, the most prominent minerals were gypsum, brucite, calcite, and quartz. Field cell leaching produced similar crystalline materials and also ettringite. The solids composition of both the laboratory- and field-leached PFBC waste showed a reduction in calcium, sulfate, and magnesium. The leached waste from the laboratory protocol had 12% calcium, 20% sulfate, and 8% magnesium. The field-leached waste contained 14% calcium, 18% sulfate, and 8% magnesium. Both the crystalline and chemical composition data indicated that the minerals were hydrated during leaching.

Both the unleached and leached (Protocol Steps 1 and 2) Alliance AFBC waste contained quartz, calcite, portlandite, and hematite. The unleached and leached waste differed: the former had anhydrite and lime, and the latter had gypsum and ettringite. The leached waste from the field cells had the same crystalline composition as the protocol-leached waste. Unleached Alliance waste had 31-35% calcium and 10-13% sulfate. Laboratory leaching resulted in a reduction of the calcium content to 20-21% and of sulfate to 1.4%. Field cell leaching lowered the calcium to 21-24%, but sulfate remained at 11%. These results again indicate a hydration of minerals during the leaching process.

X-ray diffraction analysis of the unleached Georgetown AFBC waste revealed the presence of portlandite, anhydrite, quartz, calcite, lime, and hematite. Leaching in the laboratory protocol (Steps 1 and 2) resulted in the formation of ettringite and gypsum and the hydration of lime. Before leaching, the Georgetown waste was composed of 38% calcium and 8.5% sulfate. Laboratory protocol leaching reduced the calcium to 15-23%, and the sulfate content was about 7%. Field cells containing Georgetown AFBC waste were not constructed.

# Physical Properties of FBC Waste

Scanning electron micrographs were obtained for each of the three wastes,

both unleached and leached. The unleached Exxon PFBC waste consisted of irregularly shaped particles covered with fine material. A few spherical particles were also present. The leached PFBC waste also consisted mostly of irregular particles, but it also contained lath-shaped crystals (probably precipitated calcite or a hydration product of calcium sulfate, possibly gypsum).

The unleached Alliance AFBC waste also consisted mostly of irregular particles and a few spheres. The leached waste consisted of generally smaller particles than the unleached waste, including laths similar to those in the PFBC waste. Unleached Georgetown AFBC waste contained two different groups of particle sizes, one from the bed draw and one from the fly ash component of the waste. The leached waste contained little of the original fine fraction, but had small needles adhering to the coarser grains.

Mixed (composite) samples of Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes were dry-sieved to determine the particle size distribution of the as-received wastes. The mean grain sizes of these wastes were 195  $\mu$ m for the Exxon waste, 270  $\mu$ m for the Alliance waste, and 230  $\mu$ m for the Georgetown waste. The grain size distributions for the Exxon and Alliance waste were quite similar, although the Exxon waste was consistently finer grained. The Georgetown waste had a different grain size distribution than the other two wastes: there was a higher percentage of material below 100  $\mu$ m.

The specific gravities of the Exxon PFBC, Alliance AFBC, and Georgetown AFBC wastes (after sample grinding) were 2.49, 2.65, and 2.42, respectively. The apparent bulk densities (after sample grinding) were 1.10, 1.29, and 1.21 g/cm³, respectively. The specific surface area for the ground Exxon PFBC waste was 0.9 m²/g.

The field permeabilities of Alliance AFBC and Georgetown AFBC waste were determined by constructing large (4 ft diameter and 4 ft long) cylindrical permeameters at the field site. Permeameters were constructed above ground, separate from the field cells. The waste was emplaced in the cells without compaction. The permeability of the waste was determined initially, at an interim point in the program, and at the conclusion of the field studies. The Alliance AFBC permeameter was operated about 19 months, and the Georgetown AFBC permeameter was in place for about 13 months. Data are given for the initial permeability and the permeability after comparable periods of operation.

The initial permeabilities of the two wastes were quite similar: 1.1 × 10<sup>-3</sup> cm/sec for the Alliance AFBC waste and 1.7 × 10<sup>-3</sup> cm/sec for the Georgetown AFBC waste. These initial permeabilities are within the range typical of a sandy loam soil. After 15.5 months of operation, the permeability of the Alliance AFBC waste decreased to 1.1 × 10<sup>-4</sup> cm/sec. The permeability of the Georgetown waste decreased to 1.7 × 10<sup>-5</sup> cm/sec after 13 months of operation. These permeabilities are comparable to a silty clay soil

# Composition of FBC Waste Leachate

The leaching properties of the FBC wastes were evaluated in the laboratory sequential batch equilibration protocol (Steps 1-3), in laboratory leaching columns, and in the large field cells. The Exxon PFBC and Alliance AFBC waste were investigated in all three sets of studies: the Georgetown AFBC waste was evaluated in the batch equilibration protocol. All three wastes were also subjected to the Extraction Procedure (EP) toxicity test set forth in regulations developed pursuant to the Resource Conservation and Recovery Act (RCRA) of 1976. The concentrations reported below are mean values from analysis of aliquots from several repetitions of the protocol steps and sample replicates. The interpretation included here is based on overall averages and trends observed from about 65,000 individual analytical determinations.

## Exxon PFBC Waste Leachate

Leaching of Exxon PFBC waste for 7 days (Step 1) produced leachates that had calcium and sulfate in the highest concentrations. The pH of the leachate was about 12. The calcium concentration was about 1670 mg/L, and the sulfate concentration was about 1600 mg/L. Also present in relatively high concentrations were potassium (250 mg/L), sodium (17 mg/L), and boron (11 mg/L). Other significant species were chloride (4 mg/L), strontium (2.8 mg/L), molybdenum (2.5 mg/L), magnesium (1.4 mg/L), and silicon (1.3 mg/L). Other species were present in concentrations less than 1 mg/L. Comparison of the mass of each of the major species leached to the mass in the bulk solids of the PFBC waste showed that chloride was as much as 26% leached, boron was 20% removed, strontium about 13%, calcium about 7%, sodium about 5%, and sulfate about 6%.

Repeated leaching of the Exxon PFBC waste in Step 2 of the protocol resulted in constant or decreasing concentrations of all species except silicon and aluminum, which showed an increase. Repetition of Step 3, where the same leachate was exposed to fresh waste, resulted in increasing concentrations. Only aluminum, iron, and silicon showed decreases. Magnesium remained constant.

Two small, 3-in.\* diameter leaching columns containing layers of Exxon PFBC waste and disposal media were used to evaluate the characteristics of leachate generated under laboratory column conditions. These columns contained an upper layer of shale (to simulate natural cover material) and a lower layer of PFBC waste. Leachate was collected from the bottom of the columns, so the composition of the leachate reflected the combined effect of exposure to the layers of shale and PFBC waste.

The leachates from these columns again had calcium and sulfate as the species of highest concentration: as high as 1000 mg/L for calcium and 3000 mg/L for sulfate. The pH was again very high (11-12). Potassium and chloride ranged as high as 3500 mg/L and 410 mg/L, respectively. The total dissolved solids (TDS) reached 8500 mg/L. Boron was as high as 25 mg/L, lithium reached 4 mg/L, and molybdenum was as high as 2.8 mg/L. Aluminum and barium reached 1.7 and 1.2 mg/L, respectively.

The leaching behavior of Exxon PFBC waste under field (landfill) conditions was evaluated by collecting and analyzing leachates from the upper sample point of the field cells. This leachate reflected the combined effects of exposure of infiltrating precipitation to an upper layer of disposal medium (to simulate landfill cover material) and an 18-in. layer of PFBC waste. Two of the six PFBC field cells had shale in the upper layer, and the remaining four cells had glacial till, alluvium, limestone, and sandstone. The cells were operated for about 27 months, including a 6-month period during which they were covered and not operated. A total of 30 leachate samplings occurred during this period.

In general, many of the species in the upper sample point leachates had high concentration in the initial samples, but the concentrations showed considerable fluctuation. After the first month of

sampling, the concentrations oscillated much less, and smoother trends were observed. The concentration ranges in leachates from the more stable period of operation, when concentrations were more stable, were highest for sulfate and TDS (generally 1000 to 10,000 mg/L), calcium and potassium (100 to 1,000 mg/L), and chloride, silicon, sodium, magnesium, and potassium (10 to 100 mg/L). The pH of the field cell leachates was generally much lower (7-8) than in the laboratory protocol or laboratory leach column leachates. There was little cell-tocell variation in the concentration ranges of the various species, indicating that the upper layer of disposal medium ("natural cover material") did not have a dominating influence on the composition of the leachate.

The Extraction Procedure (EP) set forth to determine the hazardousness of waste (toxicity category) under the provisions of RCRA was performed on the Exxon PFBC waste. The EP extractant was analyzed for the eight metallic ions specified by the regulations (Ag, As, B, Cd, Cr, Hg, Pb, and Se). None of these elements had a concentration higher than the limits specified in the RCRA regulation, so the PFBC waste would likely be classed as nonhazardous in the toxicity category.

#### Alliance AFBC Waste Leachate

Leaching of Alliance AFBC waste in the batch equilibration protocol (Step 1) vielded leachates with a mean calcium concentration of 1340 mg/L and a mean sulfate concentration of 1110 mg/L. The pH was also very high (12.3 to 12.5). Other species having somewhat elevated concentrations were chloride (51 mg/L), potassium (44 mg/L), and sodium (13 mg/L). Step 1 leaching resulted in removal of 63% of the chloride, 25% of the strontium, and 13% of the molybdenum from the Alliance AFBC solids. Calcium and sulfate, which had the highest leachate concentrations, were 4.5% and 8.5% removed by leaching, respectively.

With continued leaching in repetitions of Step 2 of the protocol, the leachate concentrations of the major species, calcium and sulfate, generally decreased, although sulfate decreased only slightly. For the other species examined, 14 increased in concentration and 7 decreased. The pH remained constant. Repetitions of Step 3, where the same leachate sample was repeatedly exposed to fresh waste samples, resulted in increasing concentrations for almost all parameters, except pH and magnesium, which remained con-

stant. Aluminum, beryllium, and silicon showed a decrease followed by an increase.

A laboratory leaching column containing Alliance AFBC waste was constructed and operated. It had an upper layer of sandstone (to simulate landfill cover material) and a lower layer of waste. Calcium and sulfate were again the predominant species in the leachate samples, with concentrations up to 1300 and 2000 mg/L, respectively. Chloride (levels up to 1200 mg/L) and potassium (levels up to 950 mg/L) also had elevated concentrations. The pH was again very high (12).

Five field cells containing Alliance AFBC waste were constructed and operated. Two of the cells contained alluvium in the upper layer, and the other three cells contained shale, interburden, and limestone. The cells were operated for 21 months, from March 1980 to November 1981. During the period of operation, 24 samples were collected from the upper sample point and analyzed.

Leachates from the upper sample points for all the cells had highest concentrations (1000 to 10,000 mg/L) for sulfate and TDS. Next highest were calcium and potassium, with concentrations generally of 100 to 1000 mg/L. Also significant, with concentrations of 10 to 100 mg/L, were silicon, sodium, and strontium. Chloride ranged from 10 to 100 mg/L in some cells and from 100 to 1000 mg/L in others. The pH values were at or near neutral.

The RCRA Extraction Procedure was performed on the Alliance AFBC waste, and the extracts were analyzed for the eight metallic ions specified by the RCRA regulations. The results of these analyses showed that the waste is likely to be classified as nonhazardous in the RCRA toxicity category.

## Georgetown AFBC Waste Leachate

Steps 1 and 2 of the laboratory protocol were used to determine the leaching characteristics of the Georgetown AFBC waste. The species with the highest concentration in the Step 1 leachate were calcium and sulfate, with mean values of 1500 and 1400 mg/L, respectively. Other species with lower but still substantial concentrations were chloride (24 mg/L), potassium (18 mg/L), and strontium (13 mg/L). The mean pH value was 12.5. Comparison of the mass leached to the mass originally present in the solids for each species showed that chloride and

<sup>\*1</sup> in. = 2.54 cm.

strontium were leached the most, with 63% and 52% removed, respectively. Sulfate and calcium, the highest concentration species, were leached 17% and 5%. About 13% of the lithium was leached from the Georgetown AFBC waste.

Successive repetitions of Step 2 on the Georgetown AFBC waste resulted in decreasing leachate concentration trends for most species. No species showed a consistent increase in concentration with increased leaching, although barium showed an initial increase followed by a decrease. Fluoride remained constant during the Step 2 repetitions.

Extraction and analysis of the Georgetown AFBC waste by RCRA procedures showed that the waste is nonhazardous in the toxicity category.

# Attenuation of FBC Waste Leachate

The attenuation of leachates from each of the three FBC wastes was evaluated

separately for each of the six types of disposal media. Attenuation was studied in the laboratory and field for the Exxon PFBC and Alliance AFBC waste and in the laboratory for the Georgetown AFBC waste. In general, attenuation was evaluated by reference to a derived parameter termed "fractional attenuation" (A). For the laboratory protocol results, fractional attenuation is defined as:

$$A_{L} = \frac{C_{i} - C_{f}}{C_{i}}$$

where:  $A_L$  = laboratory fractional attenuation,

C<sub>i</sub> = initial leachate concentration (before exposure to the disposal media, protocol Step 1), and

C<sub>f</sub> = final leachate concentration (after exposure to the disposal media, protocol Step 4).

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For the field cells, fractional attenuation is defined as:

$$A_F = \frac{C_U - C_L}{C_U}$$

where:  $A_F$  = field fractional attenuation.

Cu = concentration in leachate from upper sample point, and

C<sub>L</sub> = concentration in leachate from lower sample point.

The attenuation of FBC waste leachate was found to be quite variable for different wastes, for different disposal media, and for laboratory and field conditions (Table 1). Overall, strong attenuation was observed for more species in the laboratory protocol than in the field cells. More parameters were found to exhibit strong mobilization in the field cells than in the protocol. In the laboratory protocol, about the same number of parameters experienced strong attenuation and strong mobilization.

Table 1. Comparison of the Attenuation of Leachates from Three FBC Wastes Resulting from Exposure to the Disposal Media

Element/		Shale		Interburden		Sands	tone	Glacia	al Till	Allu	vium	Limestone	
Species		Lab <sup>2</sup>	Field <sup>3</sup>	Lab	Field	Lab	Field	Lab	Field	Lab	Field	Lab	Field
Al	EP4	SA		WA	#	*8	SM	WM	SM	WM	SM	SM	SM
	AA 5	N	SM	WA	SM	WA	#	WA	#	WA	SM	WA	SM
	GA 6	_ 7	#°	-	#	-	#	-	#	_	#	_	#
В	EP	SA	WA	SA	#	SA	N	SA	WA	SA	N	SA	Ν
	AA	SM	N	WA	SM	WA	#	SA	#	WA/SA	SM	SA	SM
	GA	-	#	-	#	-	#	_	#	_	#	_	#
Ba	EP	*	WA	WA	#	*	N	*	N	WM	N	WM	WA
	AA	WA	<i>N</i>	WA	WA	SA	#	WA/SA	#	N	WM	WA	WM
	GA.	WA	#	WA	#	WA	#	WA	#	N	#	WA	#
Ca	EP	WA	N	WA	#	WA	N	WA	N	WA	N	WA	N
	AA	WA	WM	WA	SM	WA	#	WA	#	WA	**10	·WA	N
	GA	WA	#	WA	#	WA	#	WA	#	WA	#	WA	#
CI	EP	_	_	SM	#	_	_	_	_	_	_	_	_
	AA	*	_	N	-	*	#	N	#	N	_	Ν	_
	GA	WA	#	WA	#	WA	#	WA	#	WA	#	WA	#
Cr	EP	SA	N/WA	*	#	WA	SM	WM	N	WM	WM	WM	WM
	AA	WA	SM	WA	SM	WA	#	WA	#	WA	WA	SA	WM
	GA	-	#	_	#	_	#	-	#	-	W	-	#
F	EP	WA	_	WM	#	WA	_	WA	_	WA	_	N	_
	AA	*	_	SM	_	WM	#	WM	#	SM	_	SM	_
	GA	EM/SM	#	SM	#	WM	#	SM	#	WM	#	SM	#
Fe	EP	*	N/WA	WA	#	WA	WA	WA	WA	SM	N	WA	WM
	AA	WA	SM	SA	SM	WA/SA	#	*	#	SM	N/WM	\$A	SM
	GA	~	#	_	#	-	#	_	#	_	#	_	#
κ	EP	N	N/WA	_	#	_	М	_	WA	_	WA	_	N
	AA	N	WA	N	WA.	WM	#	WA	#	N	SA	SM	WA
	GA	N	#.	N	#	WM	#	WA	#	WA	#	SM	#

Table 1.	(Conti	nued)												
Element/	5		Shale	Interburden		Sands	stone	Glacia	al Till	Allu	vium	Limestone		
Species		Lab <sup>2</sup>	Field <sup>3</sup>	Lab	Field	Lab	Field	Lab	Field	Lab	Field	Lab	Field	
Li	EP	SA	WA	SA	#	SA	WM	SA	WA	WA	WA/SA	WA	WM	
	AA	WA	SA	WA/SA	SM	WA	#	WA	#	SA	SA	WA	N	
	GA	SA	#	WA	#	SA	#	WA/SA	#	SA	#	WA	#	
Mg	EP	SA	WM/SM	SA	#	SA	SA	SA	SA	SA	SA	SA	SA	
•	AA	_	SM	_	SM	_	#	_	#	_	SM		SM	
	GA	WA	#	WA	#	*	#	WA	#	WA/SA	#	WA	#	
Na	EP	_	**	WM	#	SA	WM	SA	WM	SA	N	WA	SM	
	AA	WM	N	WM	WA	WM	#	WM	#	N	WA	SM	SM	
	GA	WM	#	WM	#	WM	#	WM	#	N	#	SM	#	
Ni	EP	_	_	SA	#	_	_	SM	_	SA	_	SM	_	
	AA	WM	SM	SA	SM	WA	#	SA	#	SA	WM/SM	SA	SM	
	GA	N	#	SA	#	SA	#	WM	#	SA	#	WA	#	
Si	EP	*	N/WA	WA	#	WA	WA	WM	WA	WM	WA	WM	WA	
	AA	SM	WA	SM	SM	SM	#	SM	#	SM	WA	SM	N	
	<i>GA</i>	SM	#	N	#	N	#	SM	#	N	#	N	#	
SO <sub>4</sub>	EP	WA	N/WM	NA	#	WA	WM	WA	N	WA	N	WA	WM	
	AA	WA	WM	WA	SM	WA	#	WA	#	WA	WA	WA.	WM	
	GA	WA	#	NA	#	NA	#	WA	#	WA	#	WA	#	
Sr	EP	WA	N/WM	*	#	N	WM	WA	WA	WA	WA	N	SM	
	AA	WA	WA	WA	WA	N	#	WA	#	N	WA .	Ν	WA	
	GA	WA	#	WA	#	WA/SA	#	WA	#	WA	#	N	#	
TDS	EP	WA	_	WA	#	WA	_	WA	_	WA	_	WA	_	
	AA	WA		WA	_	WA	#	WA	#	WA	_	WA	_	
	<i>GA</i>	WA	#	WA	#	WA	#	WA	#	WA	#	WA	#	
Zn	EP	*	NA/WM	*	#	SA	WM	SA	WM	SA	SM	WA	SM	
	AA	WM	SM	SA	SM	WA	#	SA	#	SA	-	SA	SM	
	GA	_	#	_	#		#	_	#	_	#	_	#	

 $<sup>{}^{1}</sup>SA = Strong Attenuation (A \ge 0.9)$ 

# Assessment of FBC Waste Leachate Quality

An overall assessment of the environmental "acceptability" of the FBC wastes for land disposal was performed by comparing: (1) the bulk composition of FBC wastes with that of the disposal media; (2) the quality of FBC waste leachate with similar leachate derived from the disposal media; and (3) the con-

centrations of various parameters found in FBC waste leachate with accepted water quality reference values. The third comparison is presented here.

Opinion concerning "safe" ambient concentrations as well as "safe" concentrations in leachates and other discharges to the environment is quite varied. Several authoritative sources were surveyed to form the basis of comparison for the FBC waste leachates. These sources include

the Primary and Secondary Drinking Water Regulations, the Resource Conservation and Recovery Act Regulations, and the Quality Criteria for Water.

From these sources, the most stringent reference value was selected for purposes of the comparisons. In some instances, the most stringent value may not be directly applicable to likely avenues of FBC waste leachate discharge to the environment. The purpose of drawing a

 $WA = Weak \ Attenuation (0.2 < A \le 0.9)$ 

 $N = No \ Attenuation \ or \ Mobilization \ (-0.2 < A \le 0.2)$ 

WM = Weak Mobilization  $(-0.9 < A \le -0.2)$ 

 $SM = Strong Mobilization (A \le -0.9).$ 

<sup>&</sup>lt;sup>2</sup>Lab Protocol Steps 1 and 4.

<sup>&</sup>lt;sup>3</sup>Field Cell Upper and Lower Sample Point. Last Few Months of Operation.

<sup>\*</sup>EP = Exxon PFBC.

<sup>\*</sup>AA = Alliance AFBC.

<sup>&</sup>lt;sup>6</sup>GA = Georgetown AFBC.

<sup>&#</sup>x27;(-) = Step 1 concentration was at detection limit.

<sup>\*(\*) =</sup> One value of duplicate pairs was negative and one was positive so no mean value is reported,

<sup>9(#) =</sup> No field cell.

<sup>10\*\* =</sup> Different results from duplicate field cells.

comparison in those instances is to emphasize that some of the FBC leachate concentrations do not exceed even the most stringent value. For many of the parameters, the most stringent criterion possibly is too low and could be increased to allow for dilution and dispersion of FBC leachate in the environment.

A comparison of the leaching and attenuation results showed that several parameters exceeded the reference values in almost all phases of the study (both

laboratory and field), including boron, calcium, chromium, sulfate, and TDS (Table 2). The reference value for pH was exceeded in all phases of the laboratory investigation, and potassium, manganese, and nickel generally exceeded the reference value for all phases of the field study. Barium, fluoride, iron, molybdenum, strontium, and titanium were generally below the reference values for all phases of the investigation. Magnesium was below the reference value for the laboratory studies. In the field studies,

only pH was consistently within the reference value (besides the parameters mentioned above for both the laboratory and field studies). There was little or no difference between the laboratory and field results in terms of parameters which were consistently above or below the reference value.

For the field cells, there appeared to be no significant difference between cells containing disposal media only and cells containing both waste and disposal media.

Table 2. Summary of Parameters Which Consistently Exceeded or Were Consistently Below the Most Stringent Reference Value

Laboratory Investigations										Field Investigations											
										Exxon PFBC				Alliance AFBC							
Exxon PFBC Alliance AFBC Georgetov						wn AFBC		Upper		Lower		Upper				Field					
Genera- tion		Attenua- tion		Genera- tion		Attenua- tion			Genera- Attenua tion tion <sup>3</sup>			Sample Point		Sample Point		Sample Point		Sample Point		Control Cells	
E1	B <sup>2</sup>	E	В	E	В	Ε	В	E	В	Ε	В	E	В	E	В	E	В	Ε	В	E	В
В	As	В	Ba	AI	Ba	В	Ba	Са	Al	SO <sub>4</sub>	Ba	E	Ba	Al	Ва	В	Ва	Al	Ba	Ca	Ва
Ca	Ba	Ca	CI	В	Co	Ca	CI	ρН	C/		Cd	Co	F	В	CI	Ca	Co	В	Co	Cr	C/
Cr	Cd	Cr	F	Ca	F	Cd	Co	TDS	Со		Cr	Cr	Fe	Ca	F	C/	F	Ca	F	Mg	F
pΗ	CI	Co	Li	Cd	Fe	Cr	F		Cu			Mg	Mo	Cr	Fe	Cr	Мо	CI	Li	Mn	Fe
SO <sub>4</sub>	Co	Cu	Mg	Cr	Mg	Cu	Fe		F			Mn	Sr	Mg	Li	Li	Sr	Mn	Мо	K	Li
TDS	Cu	Ni	Sr	Cu	Mn	Ni	Mg		Fe			Ni	Ti	Mn	Мо	Κ	Ti	Ni	Κ	SO₄	Мо
Zn	F	K	Ti	K	Мо	κ	Мо		Κ			K	pΗ	Ni	Sr	<i>SO</i> ₄	Zn	Κ	Sr	V	Sr
	Fe	SO₄		Ni	Ti	SO₄	Sr		Mg			SO <sub>4</sub>		K	Ti			SO₄	Ti	Zn	Ti
	K	pΗ		pН	Zn	V	Ti		Mn			V		SO₄	pΗ			TDS	рΗ	TDS	рΗ
	Mg	TDS		SO₄		pΗ	Zn		Мо			TDS		V							
	Mn			TDS		TDS			Sr					TDS							
	Mo			V					Ti												
	Pb								Zn												
	Se																				
	Sr																				
	Ti																				
	V																				

<sup>&</sup>lt;sup>1</sup>E = Consistently exceeds the most stringent criterion or standard (approximately 50% or more).

## Prediction of Field Leaching Behavior of FBC Wastes Based on Laboratory Results

One of the goals of this investigation was to determine the feasibility of developing a method of reliably predicting the leachate generation (and attenuation) behavior of FBC wastes under landfill disposal conditions. The hope was that the field behavior might be predicted on the basis of simple and relatively inexpensive laboratory tests of the waste. Two empirical but rigorous statistical approaches were taken to predict the chemical behavior of FBC wastes after disposal in landfills. Both approaches involved the development of statistical models from laboratory leaching data to predict field leachate properties. An extensive

tistical analysis of leaching and attenuation data for Exxon PFBC and Alliance AFBC waste was performed in the first approach. A feasibility study for the second approach employed leaching data for the PFBC waste.

The two methods differed in the steps used to develop the statistical models. In the first approach, the "direct" method, a model was developed directly to predict the concentrations of a particular species as a function of volume of leaching solution per mass of waste leached. The concentrations of other species did not come into play. In the second approach, the "indirect" method, a regression model was first developed in which the concentration of a chemical species was predicted in terms of the concentrations of itself and other chemical species at the preceding batch equilibration protocol

leaching step and possibly pH at the preceding or current leaching step. Subsequently, transformations were made through a set of mathematical steps to produce models which predicted concentration as a function of leachate volume per mass of waste leached.

## Direct Method

In the direct method of analysis, leaching behavior was first analyzed. Models were developed from laboratory data to predict field leachate concentrations. When these models were developed, those chemical species whose concentrations were predominantly near or below detection limits were excluded. Subsequently, an analysis was performed to quantify the agreement between observed field concentration and corresponding values predicted from the

 $<sup>^{2}</sup>B$  = Consistently below the most stringent criterion or standard (approximately 10% or less).

<sup>&</sup>lt;sup>3</sup>Based on only two data points.

laboratory models. It was found that, for the 13 species investigeated in leachates from the Exxon PFBC waste, the mean agreement between the observed field values and the laboratory-predicted field values was within a factor of 10 in 11 cases, a factor of 5 in 8 cases, and a factor of 2 in 3 cases. For 19 species investigated in leachates from the Alliance AFBC waste, the mean agreement was within a factor of 10 in 17 cases, a factor of 5 in 16 cases, and a factor of 2 in 10 Thus, laboratory models are capable of predicting field trends within an order of magnitude in most cases. The difference between the laboratorypredicted and field-observed values was statistically significant for most species, however

The prediction of field data involved an extrapolation, since the laboratory volumes of leachate per unit mass of waste leached were much larger than those for the field cells. Further investigation showed, however, that the differences between field-observed and laboratory-predicted values are not attributable wholly or predominantly to the extrapolation. Actual differences between the behavior of the laboratory and field chemical systems are believed to explain a significant part of the discrepancies between observed and predicted values.

It was found that prediction of field fractional attenuation  $(A_F)$  values by models developed from laboratory  $(A_L)$  values was not possible in most cases. The reasons were the scatter in the fractional attenuation data and the dissimilarity in the trends observed in the field and the laboratory.

#### Indirect Method

For the indirect method, more limited investigation was undertaken to assess the overall feasibility of the approach. Only leaching (no attenuation) data were used, and only the Exxon PFBC waste data (not the data from the two AFBC wastes) were used. The analysis was performed using laboratory protocol Steps 1 and 2 data and upper sample point leachate data from the PFBC field cell containing shale in the upper layer.

The principal finding of the modeling by the indirect method was that the species fell into two groups. In the first group, consisting of sulfate, silicon, chromium, barium, sodium, iron, calcium, zinc, and strontium, the species were self-controlled; that is, the concentration (at a given extraction step) of one of these species was related to concentrations (in

the preceding step) of species within the group. Sulfate and silicon were individually self-controlled. Concentrations for the second group (magnesium, boron, fluoride, chloride, and aluminum) were largely controlled by the first group. That pH did not play a crucial role as a predictor variable is not surprising, since pH varied between only 11.0 and 12.0 during the sequence of laboratory extractions for the Exxon PFBC waste.

For predicting field observed values from the laboratory, the indirect method was close for barium and strontium and nearly as close for zinc. Sulfate was predicted within a factor of two, and calcium and chromium were predicted within a factor of three. Except for sulfate, silicon, and sodium, the predicted values were higher than the observed values.

# Compatibility of Landfill Liners with FBC Waste Leachate

If some future FBC wastes are disposed of in secure landfills with liners, the compatibility of commonly used landfill liner materials with FBC waste leachate was investigated. Under certain conditions (e.g., in shallow water table conditions or where ground water is used as a nearby drinking water source) even nonhazardous FBC waste landfills may utilize liners.

The objective of the liner investigation was to determine if the liner integrity is reduced as a result of exposure to FBC waste leachate by using several chemical and physical tests. Six synthetic liner materials and one clay were tested: Neoprene, polyvinyl chloride (PVC), chlorinated polyethylene (CPE), chlorosulfonated-polyethylene (Hypalon), butyl rubber, ethylene propylene diene monomer (EPDM) rubber, and sodium bentonite clay.

Leachate from protocol Step 1 leaching of the Exxon PFBC waste was used in the experiment. For the synthetic liners, uniformly sized strips of the liner material were attached to a rack and immersed in a tank containing the leachate. The bentonite clay was suspended in with the leachate, and the mixture was continuously agitated. Degradation of the synthetic liner materials with time was monitored by removing samples of the liner strips monthly and testing them for tensile strength. The leachate was also sampled monthly and analyzed for total organic carbon (TOC) concentration to indicate the release of liner carbon constituents to the leachate. In addition, the liner surfaces were examined by scanning

electron microscope for direct visual evidence of liner degradation.

For the clay liner material, degradation was monitored by monthly sampling and analysis of the clay by X-ray diffraction to detect clay mineral breakdown. Also, the leachate was analyzed for aluminum as a means of detecting the release of clay mineral components to the leachate solution. The investigation of both the synthetic liner and the clay liner continued for 18 months.

For the synthetic liners, Hypalon was the strongest overall. Four of the six (EPDM rubber, butyl rubber, Neoprene, and CPE) had very similar strengths, all lower than Hypalon's. PVC had a strength intermediate between Hypalon and the other four. All liners showed a decrease in strength with increasing time of exposure to the leachate. In terms of percentage of the maximum tensile strength observed. the greatest drop in strength was observed for CPE, with a decrease to 50% of maximum. The least decrease in strength was seen for the Hypalon and EPDM rubber liners (to 70% of maximum).

Under SEM magnification, only two of the six liners showed evidence of significant deterioration resulting from exposure to the Exxon PFBC waste leachate. Most of the liners could not be easily observed because of the formation of a precipitate on their surfaces. The TOC concentration trends showed the greatest gain in carbon content in the leachates containing the Hypalon and CPE liners. EPDM rubber and Neoprene showed the lowest increases in TOC content in these leachates.

In general, the liner showing the least compatibility with the Exxon PFBC waste was CPE, which showed the clearest sign of chemical degradation under SEM observation and by the TOC analysis. Its tensile strength was in the group of four liners having the lowest strength. Hypalon, on the other hand, showed signs of chemical degradation in the SEM and TOC studies, but its strength (which was initially high) remained the highest of all the liners for the duration of the experiment.

X-ray diffraction analysis of the bentonite clay that was suspended in the PFBC waste leachate revealed that one of the first changes to occur was a change in the clay from a sodium- to a calcium-montmorillonite as the calcium in the leachate replaced the sodium ions in the surface positions of the montmorillonite. Although one of the peaks on the XRD

patterns changed slightly as the experiment progressed, which may have been an indication of incipient breakdown of the aluminosilicate structure of the clay, the patterns in general showed no major structural change in the clay. After the first month, a new mineral, ettringite, was identified in the XRD pattern, which indicated a possible change in the basic structure of some of the initial clay material.

Throughout the experiment, the concentration of aluminum in the leachate was at or below the levels found in the leachate prior to interaction with the clay. Thus, the aluminum concentration data did not substantiate breakdown of the aluminosilicate structure of the clay over the 18 months of the test.

In general, the liner materials tested were found to be quite compatible with Exxon PFBC waste leachate insofar as could be determined in this relatively short and simple investigation. If there had been strong incompatibility of the liners with the leachate, then the degradation would have been readily detected in this program. Although no strong incompatibility was observed, some of the polymer liners did show a significant loss of tensile strength during the 18 months of leachate exposure. The formation of a new mineral phase, ettringite, as a possible reaction product of the montmorillonite and the high-calcium leachate, could also lead to eventual breakdown of the effectiveness of the clay or a liner material.

#### Conclusions

Overall, this investigation shows that, with proper consideration of waste- and site-specific factors and with good engineering practice, the disposal of wastes should not be an inhibitive factor in the development and use of the FBC energy conversion technology. The wastes do not contain (or release to leachate) large concentrations of highly toxic species or other species that are hazardous to human health or the environment. There is some potential concern for certain species, such as calcium and sulfate, which will need to be addressed at future disposal sites, but proper design and operation should allay these concerns. It appears feasible to use readily available liner materials when necessary in the design of FBC landfills.

T. W. Grimshaw, R. A. Minear, A. G. Eklund, W. M. Little, H. J. Williamson, T. S. Gibson, D. L. Heinrich, and R. C. South are with Radian Corporation, Austin, TX 78766; J. E. Dunn is with the University of Arkansas, Favetteville, AR 72701. John O. Milliken is the EPA Project Officer (see below). The complete report consists of eight volumes, entitled "Assessment of Fluidized-Bed Combustion Solid Wastes for Land Disposal:" (Set Order No. PB 85-175 859/AS; Cost: \$130.50) "Volume 1. Final Report," (Order No. PB 85-175 867/AS; Cost: \$22.00) "Volume 2. Appendices A thru C." (Order No. PB 85-175 875/AS: Cost: \$16.00) "Volume 3. Appendices D and E." (Order No. PB 85-175 883/AS; Cost; \$28.00) "Volume 4. Appendix F," (Order No. PB 85-175 891/AS; Cost: \$13.00) "Volume 5. Appendix G," (Order No. PB 85-175 909/AS; Cost: \$22.00) "Volume 6. Appendix H," (Order No. PB 85-175 917/AS; Cost: \$13.00) "Volume 7. Appendix I," (Order No. PB 85-175 925/AS; Cost: \$14.50) "Volume 8. Appendix J," (Order No. PB 85-175 933/AS; Cost: \$25.00) The above reports will be available only from: (costs subject to change) National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650 The EPA Project Officer can be contacted at: Air and Energy Engineering Research Laboratory

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