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**Advanced Coal Technology By-Products: Long-Term Results from Landfill
Test Cells and Their Implications for Reuse or Disposal Applications**

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INTRODUCTION

New air pollution regulations under the 1991 Clean Air Act and other legislation are motivating continued development and implementation of cleaner, more efficient processes for converting coal to electrical power.¹ These clean coal processes produce solid by-products which differ in important respects from conventional pulverized coal combustion ash. Clean coal by-products contain both residual sorbent and captured SO_2 control products, as well as the mineral component of the coal. Since few full-scale clean coal facilities are operational, little data have been available on the field behavior of these wastes or on appropriate methods for their management and disposal or utilization. The Department of Energy/Morgantown Energy Technology Center has contracted Radian Corporation to construct and monitor landfill test cells with a several different advanced coal combustion by-products at three locations around the U.S.; data from these sites provide a unique picture of the long-term field behavior of clean coal combustion by-products.

The test cells included in the study were constructed with circulating fluidized bed combustion ash; bubbling fluidized bed combustion ash; and ash from the Lime Injection/Multiphase Burner (LIMB) combustion. The field testing sites were located in western Colorado, northern Ohio, and central Illinois. Fluidized bed combustion and lime injection residues are characterized by high lime and calcium sulfate contents contributed by reacted and unreacted sorbent materials, and produce an alkaline leachate when wetted.^{2,3} Compared with conventional coal fly ash, the clean coal technology ashes have been noted for potential management difficulties when wetted, including corrosivity, heat generation, cementation, and swelling on hydration.^{4,5} On the other hand, the high lime content and chemical reactivity of clean coal residues offer potential benefits in reuse as a cementitious material.⁶

The goals of the project are to provide field-based data for use in developing disposal facility design guidelines, to provide input for testing and calibrating predictive models used for facility permitting, and to provide data on long-term material behavior in the natural environment. Data gathered during this study will also serve as the basis for an engineering design manual to guide future disposal facility development. The results of three years of data collection suggest a fairly consistent pattern of behavior for the calcium-based dry sorbent systems involved in the project, despite differences in the initial composition of the by-products, differences in the methods of placement, and differences in climate at the test sites.

RESULTS AND DISCUSSION

Methods

In order to make the results of the study more relevant to utility waste managers, the design of the test cell follows as closely as possible current disposal practices at utility waste landfills.⁶ The test cells, shown schematically in Figure 1, are scaled large enough to permit use of full-scale equipment. The cells were constructed in lifts and compacted with a Caterpillar D-6 bulldozer. After construction the test cells were instrumented for data collection, but were left uncovered and exposed to the environment for one year to simulate typical waste management practices.

The monitoring design includes initial characterization of the wastes and the soils at the site for physical properties, bulk chemistry, mineralogy, leaching characteristics, and other selected

properties to define the baseline conditions. Subsequent monitoring includes on site meteorology, in situ moisture and permeability measurements, and laboratory analysis of core samples for detailed chemical and physical properties, similar in scope to the initial characterization. Groundwater, porewater, and runoff sampling and analysis was also included in the test design to evaluate interactions between the test cells and the surrounding environment. Samples from all sources were successfully collected during the course of the field study with the exception of porewater at the Colorado site, where conditions remained too dry for the lysimeters to be sampled.

Conceptual Model of By-Product Hydration and Weathering

A variety of SO_2 control technologies, including all the processes included in this study, are based on reaction of dry, calcium-based sorbent with SO_x in the combustion gases. This basic chemical similarity controls much of the subsequent behavior of the solid by-products, although differences in combustion conditions, primarily related to particle size and combustion temperature, can affect reaction rates and the chemical availability of some constituents as they hydrate and weather on exposure to the environment. The process of cement development and weathering in pozzolanic materials is illustrated schematically in Figure 2. The compacted materials undergo initial set as they hydrate. The leachability of the hydrated ash is reduced because the lower permeability limits access by water, and because the ettringite formed by hydration is much less soluble than the calcium hydroxide, gypsum, and aluminous material from which it forms. Fracturing occurs when initial bonding between grains is disrupted by continued growth of secondary minerals. Secondary porosity develops as movement of water through the material leaches out soluble phases, redistributing their constituent ions to the base of the landfill.

The initial wetting of LIMB ash causes rapid hydration of lime (CaO) to portlandite $\text{Ca}(\text{OH})_2$, typically producing considerable heat. Some lime is also converted to calcite (CaCO_3) by absorption of carbon dioxide from the atmosphere. Additional water promotes conversion of reacted sorbent, present as anhydrite (CaSO_4), to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), although anhydrite may react slowly if it has been "hard burned" at high temperatures⁷; circulating fluidized-bed systems may be particularly prone to this effect because combustion temperatures are typically higher than in bubbling-bed systems and residence times in the combustion zone are greater than for lime injection processes. Gypsum generally forms as relatively large, well defined crystals in the pore spaces of the material and can contribute to early strength development.⁸

Further wetting produces additional reactions. The most important is the formation of the calcium-sulpho-aluminate mineral, ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$] as alkaline pore fluids begin to break down aluminosilicates in the coal ash fraction of the by-products. The rate of ettringite formation is generally limited by the availability of aluminum in the pore solutions, and it typically forms as an encrustation of fine crystals on the surfaces of fly ash or clay particles which are the source of aluminum. These crusts can form interlocking crystalline networks which fill pore spaces and cement the grains together. In many cases, ettringite formation is also associated with expansion of the bulk material.^{9,10} Expansion can disrupt the materials, creating surface fractures and heaving.

Calcium silicate hydrate gel, or CSH, $((\text{CaO})_x(\text{SiO}_2)_y \cdot 11\text{H}_2\text{O})$ may also form as the clean coal by-products hydrate. CSH is responsible for much of the strength of Portland cement products, but does not appear to make a large contribution to strength development in clean

coal by-products.⁸ CSH is difficult to determine analytically, and its role in these materials bears further examination.

Thaumasite [$\text{Ca}_6\text{Si}_2(\text{CO}_3)_2(\text{SO}_4)_2(\text{OH})_{12} - 24\text{H}_2\text{O}$], which is isostructural with ettringite, also forms during the later stages of LIMB ash hydration. Thaumasite forms as silicate and carbonate substitute for aluminum and sulfate in the ettringite structure.¹¹ The mechanism of thaumasite formation is not clearly understood. Several authors have maintained that thaumasite forms as a replacement of ettringite at temperatures below about 15 C, and can exist as a solid solution series with ettringite.¹² Thaumasite is generally associated with swelling and failure of cement and soils.^{12,13} Thaumasite is generally held to have no cementing power¹⁴; whether thaumasite formation has caused additional deterioration of the engineering properties of the materials in the test cells is unclear at this time.

The field monitoring program has gathered data to determine how well this conceptual model explains the actual behavior of clean coal by-products in a field setting, and how this behavior relates to readily measured engineering, geotechnical and geochemical properties.

Field Results

Three years of field monitoring of four landfill test cells containing LIMB and FBC ash found that the cells behaved in a generally similar fashion; differences in behavior are linked to differences in material composition, climate at the test sites, and the initial placement conditions of the ash. All test cells had adequate load bearing strength for landfill stability under normal design conditions, but most have exhibited continuing dimensional instability. Long-term permeabilities were generally higher, and strengths were lower than anticipated from early results.

Mineralogy. The mineralogical reactions outlined in the conceptual model are reflected in the results of semiquantitative x-ray diffraction analysis, shown in Figure 3. Both test cells at the Ohio site have developed large amounts of ettringite and thaumasite, which together account for the majority of the total material after three years. Mineralization at the Colorado site has been limited by the low initial lime and sulfate contents of the ash and by lack of moisture at the test site. Thaumasite has not been detected at this site, although the decline in calcite concentration in the ash suggests that carbonate is being incorporated into some other phase. The Illinois site has much higher gypsum and portlandite concentrations than the other sites, where portlandite was not detected in large quantities after placement in the test cells. It is expected that ettringite formation will continue in the Illinois test cell. Ettringite formation may be slowed since the combustion temperature of the Illinois BFBC ash was much lower than for the LIMB ash, and much less of the mineral matter from the coal is present in a readily available, glassy form.

Physical Properties. The basic physical properties useful in monitoring the extent of hydration and cementation are moisture content, permeability, and compressive strength. The results of physical properties measurements on core samples are shown in Figure 4. Moisture contents of all the test cells continued to increase during the monitoring period, reflecting the gradual saturation of pore spaces and the growth of hydrated minerals in the ash. Moisture content at the Colorado site increased, despite the dry climate and the excess of evaporation over precipitation. The very high moisture content of the Ohio test cells demonstrates the high chemical water demand of these materials.

The permeability was measured both on core samples and using an in situ permeameter; only core results are shown. The permeability of the FBC test cells at the Colorado and Illinois sites is two to three orders of magnitude higher than predicted from initial laboratory tests and increases slightly with time. The initial mean core permeability at the Ohio wetted test cell approached the target value of 10^{-7} cm/sec, but over time the permeability has increased steadily to approximately 4×10^{-4} cm/sec. Gradual hydration of the unwetted cell initially decreased the mean permeability, but later the trend reversed and after three years the permeability of the two Ohio test cells was virtually identical. The permeability of the Illinois test cell has remained essentially constant over the first few measurement intervals, and is similar to the permeability of the Colorado FBC ash.

In situ permeability measurements were initially much higher than core results, but, over time, core permeabilities increased to match the field results. The in situ measurements represent the total permeability more accurately. Since a larger volume of material is tested with the in situ permeameter, fracture permeability as well as diffuse flow is measured with this technique.

The average compressive strength of the LIMB material in the wetted cell at Ohio was initially near 1500 psi; after fractures developed the strength dropped to less than 500 psi by the end of the first year of monitoring. The unwetted cell increased in strength over the first year as it hydrated and cemented, but, as with the permeability, the gains were short-lived. After three years the strength of both LIMB cells was well below 300 psi. The FBC materials in the Colorado and Illinois test cells do not show such large changes in average strength. The Colorado CFBC ash has maintained an average strength of approximately 500 psi, although the range of individual measurements has increased significantly over the course of the three years of monitoring as fracture zones have developed. The Illinois BFBC material has the lowest average strength of all of the test cells, even though no large-scale fracturing has been noted at that site.

Because many samples broke during sampling and could not be tested the reported results for both strength and permeability include some bias towards stronger, unfractured materials which are not disrupted by the coring process. The field permeability measurements provide a check on that measurement system which is not available for the unconfined compressive strength measurements. Because of this bias, the reported strengths probably represent maximum strengths, rather than true averages.

Chemistry and Geochemistry. Analysis of deionized water leachates of the initial ash and of cores taken from the landfills show average concentrations of several major elements decline following hydration. This indicates that the hydration reactions increase the chemical stability of the clean coal ashes. Figure 5 shows results from the unwetted Ohio test cell, which is typical of the other sites. The leachate pH drops from over 12 to about 10.5 following hydration. A few elements, including potassium and sodium, increased in solubility following hydration. These elements are apparently released from the mineral portion of the coal ash as it is broken down by alkaline pore fluids; while calcium, aluminum, and silicon present in the mineral fraction is incorporated into ettringite and thaumasite, the soluble elements such as potassium and sodium accumulate in the pore fluids.

The initial characterization of the LIMB and FBC residues found that the concentrations of regulated metals in RCRA EP leachates were within the range of compositions of conventional

coal ash leachates, except for an elevated pH. Although the pH of the deionized water leachates from clean coal by-products are higher than for conventional coal ash, they are still below the regulatory limit for corrosivity. The high pH may be important in reducing the solubility of some regulated metals which form insoluble hydroxides.

Figure 6 compares the concentrations of seven regulated trace metals in deionized water leachates of core samples and in porewater samples collected from lysimeters in the unwetted Ohio test cell. Results from the other sites have a similar distribution. Some trace elements, including arsenic, molybdenum, and strontium are mobilized at higher concentrations in lysimeter samples than in the initial leachates during some sampling events. Other elements, including barium, boron, cadmium, silver, and zinc are present at much lower concentrations in porewater solutions than in the initial leachate. These differences in behavior represent both differences in the pH sensitivity of the various trace metals, and the extent to which different elements can substitute into the structures of the hydration products and be sequestered from the solution phase. In particular, the element boron, whose distribution resembles that of barium in Figure 6, may substitute into the structure of ettringite as an oxyanion.¹⁵ Concentrations of chromium, lead, and selenium in porewaters vary widely and do not have a consistent pattern.

The high permeability of clean coal ashes has allowed a substantial fraction of the precipitation at the sites to infiltrate the test cells. At the more humid Ohio and Illinois sites this has resulted in the transport of soluble materials out of the surface portion of the test cells. Figure 7 shows the distribution of several major elements with depth in porewater samples collected from the Ohio unwetted cell in the first year of monitoring (left graph), and in the third year (right graph). The upper four feet of the test cell have been depleted of soluble elements, including potassium, sodium, chloride, and sulfate. These species have increased in concentration greatly in porewater at the base of the test cell, although pore fluids in the base soils are not impacted to date. The highly concentrated pore fluid at the base of the test cell is typical of the initial leachate which will be generated by the landfill. Despite the apparent reduction in solubility shown by the laboratory leaching tests following hydration, the field behavior of the materials acts to concentrate soluble materials in the initial leachate volume.

CONCLUSIONS

The results of this field study suggest that calcium-based clean coal by-products perform acceptably in landfill settings, but may require engineering controls to limit leachate production. The strength of the materials in the test cells declined over time in most cases, and was not sufficient for most utilization applications. The handling properties of the lime and sulfate rich by-products did not pose any serious problems during cell construction. Steaming and heat build-up were moderate, and required dry handling in some cases. Water loss to evaporation also affected the in-place moisture content and compaction of the ash. The ash did not set prematurely and handled well in the field.

Following construction the ash expanded and fractured, especially at the Ohio site. Fracturing created additional channels for water to enter the test cell. The landfills in Ohio and Illinois reached saturation in a little over a year, and leachate drainage has occurred from the base of the cells. Leachate is characterized by a pH near 10.5, with potassium, sodium, chloride, and sulfate the dominant ions. Porewater concentrations of some trace metals exceeded federal

primary drinking water limits in some samples, and the chloride, sulfate, pH and total dissolved solids concentrations of the leachate typically exceed federal secondary maximum contaminant levels for drinking water. Leachate migration has been limited.

The high variability in the strength and permeability measurements of the landfill test cell suggest that increased attention to construction and engineering could be beneficial. Decreased permeability of the waste and/or cover soil could prevent the moisture build-up noted in the present test cells. This could be achieved through better control of the initial moisture content of the residues and/or additional effort in compaction of the residues and cover soils. Increased slope on landfills would also limit percolation.

The chemical model of hydration and weathering is generally followed at all the test sites. Thaumasite has not yet been detected at the Colorado and Illinois sites, but it is expected to form there as hydration reactions progress. Core materials examined for this project suggest that thaumasite formation does not occur at the expense of ettringite, and indicate only partial solid solution. The mechanisms for thaumasite formation and their implications for the strength and permeability of the bulk materials will be crucial to determining the proper engineering design for disposal or utilization of the clean coal by-products. If thaumasite formation can be prevented by eliminating transport of dissolved carbonate into the materials, or by maintaining temperatures above 15 C, the engineering design will be different than if thaumasite formation cannot be avoided.

Hydration and weathering reactions may also affect how leachate production and dispersion in groundwater are modelled for permit acquisition. The results of leaching tests conducted for this study indicate problems inherent in basing management decisions regarding clean coal materials on test results using the raw by-products. The hydration reactions which these materials undergo transform them into a different form. The results of standard leaching test on raw materials are misleading in their prediction of the leaching behavior of materials placed in a landfill.

Better engineering practices may provide substantial increases in performance over the results obtained from this study, and reuse of calcium-based clean coal by-products may find wide application. The results presented here indicate potential failure mechanisms for such materials which need to be better defined before wide-spread reuse is possible.

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Figure 1 Conceptual Design of Landfill Test Cell

Figure 2. Conceptual model of hydration and cement development in lime-based dry scrubber by-products.

Figure 3. Semiquantitative X-ray diffraction analyses of core samples from the four test cells. Analytical results for all the first-year quarterly samples at the Ohio and Colorado sites are averaged for clarity. Only selected potentially reactive phases are shown; at the Illinois site portlandite is shown instead of thaumasite.

Figure 4. Average values of moisture content, permeability and unconfined compressive strength for cores from the four test cells. The high moisture content of the Ohio and Illinois test cells reflects both chemically bound water and free moisture. Permeability and compressive strength measurements vary widely around the average values shown

Figure 5. Average concentrations of selected major analytes in deionized water leachates of the initial ash and subsequent core samples from the Ohio unwetted cell. Concentrations of calcium, chloride, and sulfate are significantly lower in leachate from core samples than in the initial ash leachate. Potassium and sodium (not shown) exhibit marked increases in concentration over the initial ash leachate. Similar changes in concentrations occur for samples from the other test cells.

Figure 6. Average concentrations of selected trace metals in Ohio unwetted cell lysimeters and ASTM deionized water leachates of core samples. Cadmium, silver, and zinc (not shown) exhibit a sharp decline from initial leachate concentrations, similar to barium. Molybdenum and strontium (not shown) are found in higher concentrations in porewaters than in the initial leachate, similar to arsenic. Concentration trends are similar for the test cells.

Figure 7. Porewater chemistry of samples from the North Cell. Where more than one sample was analyzed from a given depth for the time period shown the results were averaged, although in some cases the values shown represent a single analysis. Porewater concentrations were constant with depth in the first year; by the third year soluble species are concentrated near the base of the test cell.

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