Coolside Waste Management Research

(Project No. DE-AC21-91MC28162)

**Annual Report
October 1, 1993 to September, 1994**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Waste Management
Center for Applied Energy Research
University of Kentucky
3572 Iron Works Pike
Lexington, KY 40511

November 28, 1994

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91-MC8162

Report Period: October 1, 1993 to October 31, 1993

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Task 2 - Geotechnical Characterization

Index (Atterberg limits, grain size, and specific gravity) and moisture-density relations (modified and standard) tests were performed on two samples obtained from the Franklin County, Ohio landfill. A summary of index tests and moisture-density relations curves are located in Appendix 1. These samples will be used to evaluate the effect of leachate generated in FGD materials has on clay liners.

Task 3 - Leaching Studies

Monitoring of the Montgomery Co. KY field site continued over the period covered by this report. Rainfall totals recorded at the site were typical for the region with leachate samples being collected during most site visits. Several severe thunderstorms passed through the region over the summer months, the most intense storm depositing over 3.5" of precipitation on October 21, 1993.

Ground/Lysimeter temperatures continued to rise and reached a plateau during the month of September, temperature readings were then observed to slowly decrease as ambient air temperature decreased with the onset of Fall. The surface temperature measurements for Lysimeter#3 were consistently higher than the other 3 Lysimeters, this was attributed to a longer period of exposure to direct sunlight in the mid to late afternoons.

A significant stand of vegetative cover was established atop each lysimeter, consisting predominantly of native grasses. No additional fertilization of the lysimeter surfaces was performed, the grasses being sustained by natural precipitation and nutrients within the soil cap.

Appendix 1

LABORATORY RECORD OF SOIL TEST DATA

SAMPLE NUMBER	LL	PL	PI	SPGR	AASHTO	GI	USC
BROWN TILL	45.0	20.0	25.0	2.66	A-7-6	(22)	CL

MECHANICAL SIEVE ANALYSIS

SIEVE SIZE	WEIGHT RETAINED	TOTAL PERCENT PASSING
3/4 IN	0.00	100.00
1/2 IN	4.70	99.69
3/8 IN	0.00	99.69
NO. 4	0.80	99.64
NO. 10	3.08	99.44

HYDROMETER SIEVE ANALYSIS

SIEVE SIZE	WEIGHT RETAINED	TOTAL PERCENT PASSING
NO. 20	0.28	98.94
NO. 40	0.86	97.40
NO. 60	1.56	94.60
NO. 200	4.86	85.90

HYDROMETER ANALYSIS

TIME (MIN)	TEMP	HYD READING	PERCENT FINER	PARTICLE DIAMETER-M/M
1.00	69.00	50.00	84.19582	0.03803
2.00	69.00	47.00	78.83144	0.02772
5.00	70.00	45.00	75.47159	0.01775
15.00	71.00	40.00	66.67346	0.01064
30.00	71.00	36.00	59.52089	0.00778
60.00	72.00	34.00	56.25256	0.00555
201.00	73.00	30.00	49.40796	0.00311
1407.00	75.00	25.00	41.08316	0.00120

LABORATORY RECORD OF SOIL TEST DATA

SAMPLE NUMBER	LL	PL	PI	SPGR	AASHTO	GI	USC
GRAY TILL	19.0	15.0	4.0	2.52	A-4	(0)	CL

MECHANICAL SIEVE ANALYSIS

SIEVE SIZE	WEIGHT RETAINED	TOTAL PERCENT PASSING
3/4 IN	0.00	100.00
1/2 IN	21.04	98.20
3/8 IN	8.23	97.50
NO. 4	22.34	95.59
NO. 10	37.94	92.34

HYDROMETER SIEVE ANALYSIS

SIEVE SIZE	WEIGHT RETAINED	TOTAL PERCENT PASSING
NO. 20	4.57	84.89
NO. 40	3.74	78.80
NO. 60	3.37	73.31
NO. 200	8.65	59.21

HYDROMETER ANALYSIS

TIME (MIN)	TEMP	HYD READING	PERCENT FINER	PARTICLE DIAMETER-M/M
1.00	69.00	36.00	55.32347	0.04513
2.00	69.00	35.00	53.65137	0.03217
5.00	70.00	29.00	43.82101	0.02114
15.00	71.00	25.00	37.26581	0.01247
30.00	71.00	21.00	30.57729	0.00905
60.00	72.00	19.00	27.52103	0.00644
252.00	73.00	15.00	21.12051	0.00320
1416.00	75.00	13.00	18.35222	0.00135

GRAY TILL

BROWN TILL

BROWN TILL

MODIFIED

10-24-93

OPTIMUM MOISTURE CONTENT (%) = 11.5

WL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 120.6 PCF

GRAY TILL

MODIFIED

10-24-93

OPTIMUM MOISTURE CONTENT (%) = 7.9

HL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 134.6 PCF

GRAY TILL

STANDARD

10-23-93

OPTIMUM MOISTURE CONTENT (%) = 9.0

WL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 127.2 PCF

BROWN TILL

STANDARD

10-23-93

OPTIMUM MOISTURE CONTENT (%) = 19.4

HL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 106.8 PCF

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91-MC8162

Report Period: November 1, 1993 to November 30, 1993

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Summary of Progress for Period

A program for calculating speciation of elements in natural waters was adapted for use in this program. A public domain program, WATEQ4F¹, written in Fortran was selected. This program accesses a single input file and produces a single output file. Thereby, data obtained from the lysimeters can be manipulated to infer chemical species concentrations and the mineral phases present in the column environment. The original program was converted from Fortran to C and tested in DOS using WATEQ4F test case one. The result was modified to run under Windows 3.0/3.1 with menu items and input screens, using Borland C++ v3.1. This program was debugged with all four test cases and is now called WATEQ to differentiate it from the 4F(Fortran) version.

Preliminary data evaluations was conducted. It was assumed that, regardless of lysimeter contents and degree of compaction, pH will be the controlling parameter affecting leachate species and lysimeter mineralization. To test this, WATEQ runs were made on laboratory column and field lysimeter results. While pH trends are usually evident, it is clear that there are differences in the lysimeters and their resulting leachates.

¹ WATEQ4F with Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. USGS Open File Report 91-183. James W. Ball and D. Kirk Nordstrom

Several mineral phases were selected that approach saturation and their behavior over time was evaluated. The minerals were partitioned into groups exhibiting like behavior that account for approximately 90 percent of variability observed. These groups were produced and plotted for field lysimeter 3, level 3 to compare saturation behavior. In addition, the behavior of selected species with concentrations greater than one ppm were evaluated. The results show differences in the lysimeters.

Task 2.2 - Chemical and Mineralogic Analysis

Thermodynamic Data Base

The data obtained from the lysimeters include pH, conductivity and ionic concentrations. This solute data must be manipulated to infer chemical species concentrations and the mineral phases present in the column environment. For this a public domain program WATEQ4F² was selected. This program, written in Fortran, expects a single input file and produces a single output file.

Given the large amount of data collected in lysimeter experiments and the difficulty of extracting relevant data from the voluminous output provided by this program, the following work was performed to simplify the data reduction process:

- The original program was converted from Fortran to C and tested in DOS using WATEQ4F test case one.
- The result was modified to run under Windows 3.0/3.1 with menu items and input screens, using Borland C++ v3.1. This program was debugged with all four test cases.
- Batch data input via Windows clipboard, and output of user-selected data to either

² WATEQ4F with Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. USGS Open File Report 91-183. James W. Ball and D. Kirk Nordstrom

comma-delimited files or Windows clipboard was implemented.

- Options were added to allow saving, reloading or editing input preferences (input species, redox options, input units, and alkalinity options), output preferences (convergence criteria, triggers for species percentage and mineral equilibrium departure for inclusion in output, whether or not to include thermodynamics table and/or weight/molar concentration ratios in the output), and paste preferences (selection of input and individual output items for inclusion in a "cut/paste" process).
- This program is now called WATEQ, to differentiate it from the 4F(Fortran) version.

Preliminary Data Investigation

As an initial premise, it was assumed that, regardless of lysimeter contents and degree of compaction, pH will be the controlling parameter affecting leachate species and lysimeter mineralization. If so, then the approach to saturation of various minerals should vary smoothly with pH, except for errors derived from inherent inaccuracies in test results; any departure from this assumption indicates that there are, indeed, differences in the lysimeters and their leachates. To test this, WATEQ runs were made on laboratory column and field lysimeter results as indicated in Table 6-1. The results are illustrated in Figures 6.1 to 6.5, which show the approach to saturation ($\log[\text{IAP}/kT]=0$)³ for various selected minerals versus pH. While pH trends are usually evident, it is clear that there are differences in the lysimeters and their resulting leachates. This verifies our expectations.

A second preliminary investigation involved selecting mineral phases approaching saturation within five orders of magnitude ($\log[\text{IAP}/kT] > -5$). Plots of saturation behavior over time were produced. Based upon these plots, the minerals were partitioned into groups exhibiting like

³ IAP: Ion Activity Product. $\log[\text{IAP}/kT] < 0$ implies under-saturation; $= 0$ implies equilibrium. It should be noted that supersaturation ($\log[\text{IAP}/kT] > 0$) does not mean that the mineral in question will necessarily be found in solid phase.

behavior. Representative groups are shown for laboratory column 25 (Coolside compressed pellets, wet/dry with average pH about 11.5, rising slightly) in Figures 6.6 through 6.14. They account for approximately 90 percent of variability observed. These groups were produced and plotted for field lysimeter 3, level 3 (Edgewater Coolside, 66#/ft³@37% H₂O with average pH about 12.25, falling slightly) in order to compare saturation behavior (Figures 6.15 through 6.23). While the partitioning remains valid, saturation behavior is different, again indicating differences in the lysimeters and their resulting leachate.

Table 6-1

pH	Lysimeter	Description
13.13	column 5, week 4	Coolside 300, static density, saturated
13.05	column 11, week 4	Coolside 1000, static density, saturated
12.86	column 20, week 3	Coolside Pilot 2, static density, saturated
12.66	column 23, week 5	Coolside Pilot 1, static density, saturated
12.41	column 22, week 12	Coolside Pilot 4, static density, wet/dry, 2.5%CO ₂
12.15	field 3-3, 17-Jun-93	Edgewater Coolside, 66#/ft ³ @37%H ₂ O
12.04	column 16, week 9	Coolside Pilot 2, static density, wet/dry
10.75	column 7, week 46	Coolside 300, static density, saturated, 2.5% H ₂ O
10.17	field 2-3, 14-Jun-93	Edgewater Coolside, 49#/ft ³ @40%H ₂ O
9.91	column 8, week 6	Coolside 300, static density, wet/dry, 2.5%CO ₂
9.33	field 1-3, 19-Aug-93	Edgewater Coolside, little/no compaction
9.13	column 3, week 4	Ky. fly ash, static density, wet/dry
8.92	column 2, week 3	Israeli fly ash, static density, wet/dry
8.72	column 1, week 2	Israeli fly ash, static density, saturated
8.00	column 4, week 9	Ky. fly ash, static density, wet/dry, 2.5%CO ₂

The third preliminary investigation looked at the differences in behavior of selected species with concentrations greater than one ppm in the same two lysimeters. These were partitioned by ppm

ranges. Results for column 25 are shown in Figures 6.24 through 6.27. Results for field lysimeter 3, level 3 are shown in Figures 6.28 through 6.31. The results also show differences in the lysimeters.

Future Directions

- Refinement of mineral selection.
- Addition of minerals, such as Ettringite, to the thermodynamic data base.
- Species selection.
- Expansion of results to all lysimeters.
- Exploration of lysimeter differences.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Figure 19

Figure 20

Figure 21

Figure 22

Figure 23

Figure 24

Figure 25

Column 25

Figure 26

Column 25

Figure 27

Figure 28

Figure 29

Figure 30

Figure 31

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91-MC8162

Report Period: December 1, 1993 to December 31, 1993

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Summary of Progress for Period

The mineralogy of the drill cores from the field lysimeter leaching experiments was determined. The drill cores were divided into sub-samples in order to establish a depth profile for ettringite in the lysimeters. Semi-quantitative X-ray diffraction analyses indicated that with increasing depth more ettringite needles had formed in the lysimeters. Ettringite was observed to form on mineral surfaces and within available pore space. Formation of Thaumasite, recognized in the XRD, was probably related to available CO₂ from plant root respiration. Swell tests and sulfate soundness, L.A. abrasion, specific gravity, and absorption tests on FBC samples were performed.

Task 2 - Geotechnical Characterization

Swell Tests

Monitoring of swell continued on the hydrated and non hydrated FBC ash samples. Both types are still in the primary swell phase after one year of monitoring.. All samples were remolded near 95% of standard maximum dry density and optimum moisture content. The samples were remolded in CBR molds (6" diameter, 4.584" height) and swell was monitored under the following conditions:

approximately 12.5 lb. surcharge, no age time

approximately 2.5 lb. surcharge, no age time

approximately 12.5 lb. surcharge, 7 days age time

approximately 2.5 lb. surcharge, 7 days age time

Time of aging represents the amount of time before the samples were placed in water. Aged specimens were sealed at room temperature to prevent moisture loss before placement into the water tank.

Monitoring of swell continued on two samples of FBC pellets. The pellets were loosely placed in CBR molds. Surcharge weights (approximately 2.5 and 12.5 pounds) were placed on the samples prior to saturating in water. Swell is decreasing in the sample with the 2.5 lb. surcharge and continuing to increase for the sample with the 12.5 lb. surcharge.

FBC Aggregate Tests

Sulfate soundness, L.A. abrasion, Specific gravity, and absorption tests were performed on two samples supplied by CONSOL Results of tests on FBC aggregate are presented in Table 1.

Table 1. Pellet Durability			
	Absorption, %	Wear, %	Loss, %
FBC/FA 1 3/8 - No. 4 Uncrushed	17.9 oven dried 6.4 air dried	18.4	17.2
FBC/MS 1 3/8 - No. 4 Uncrushed		18.3	44.7
FBC/MS 1 3/8 - No. 4 Crushed			55.9
FBC/MS 1 No. 4 - No. 8			38.7
Specification		40.0	12.4

Work Planned for Next Month

Unconfined compressive strength and moisture-density relations tests will be performed on FBC soil mixtures to evaluate the potential for FBC as a soil subgrade stabilizer.

Task 2.2 - Chemical and Mineralogic Analysis

Mineralogical Transformations in the Field Lysimeter Samples

The mineralogy of the drill cores from the field lysimeter leaching experiments was determined. The drill cores were provided by the Kentucky Transportation Center. To establish a depth profile for ettringite in the lysimeters, the drill cores were divided into sub-samples. Semi-quantitative X-ray diffraction analyses of the reacted Coolside waste indicated that with increasing depth more ettringite needles had formed in the lysimeters. The results were consistent for the lysimeters with the lowest and highest packing densities. Ettringite was observed in the SEM study to form both on mineral surfaces and within available pore space. Thaumasite was also recognized during the XRD analyses to be present in the top zone of the lysimeters. Its presence is probably related to available CO_2 concentrations from plant root respiration in the upper lysimeter zones.

Core Sampling

The drill cores, all of which are characterized by a 2" diameter, were taken from field lysimeters 1, 2 and 3. The top of the individual cores corresponds to the interface between soil and compacted Coolside material. The depth profiles for the drill cores from lysimeters 1, 2, and 3 are illustrated in Figure 1. The drill core from field lysimeter 1 (L-1 in Figure 1) was divided into 5 sub-samples. The first sub-sample is derived from a core slab that corresponds to a depth between 2'0" - 2'2" from the top of lysimeter 1. The second sub-sample is derived from a core slab that corresponds to a depth between 2'0" - 2'5". The third sub-sample was derived from a slab between 2'5" - 3'0"; the fourth sub-sample is derived from a slab between 3'0" - 3'5"; and the deepest sub-sample is derived from a slab between 3'5" - 4'0" depth. In contrast to field lysimeter 1, field lysimeter 2 has been probed at two different locations and the two drill cores are termed L-2A and L-2B (see Figure 1). The interface between top soil and compacted Coolside material occurs at a depth of 2'0". Both drill cores from field lysimeter 2 reached a maximum depth of 3'6". One drill core was obtained from field lysimeter 3 (L-3 in Figure 1) which also starts at a depth of 2'0", but only reached a maximum depth of 3'0". The drill cores L-2A, L-2B and L-3 were divided into sub-samples which were taken every 2" along the cores (Figure 1).

X-Ray Diffraction Analyses of the Core Samples

Mineralogical analyses of finely ground sub-core samples were obtained using a diffractometer with Cu K α radiation. Mineral phases were identified by reference to the JCPDS powder diffraction files. The main objective was to identify how much ettringite had formed in the lysimeters upon reaction of the Coolside waste with seasonal rain water and to establish a depth profile for the amounts of ettringite present in the field lysimeters. The amounts of ettringite present were evaluated relative to that of quartz in each sub-sample. Results of the semi-quantitative X-ray diffraction analyses of the reacted Coolside waste are illustrated in Figures 2 - 5, indicating that with increasing depth more ettringite needles had formed in the three field lysimeters. The results are consistent for the lysimeters with the lowest and highest packing densities.

Ettringite was observed in the SEM study to form both on mineral surfaces and within available pore space. SEM investigations of core samples from field lysimeter 3, corresponding to 2'0" depth and 3'0" depth, are illustrated in Figure 6. The SEM study indicates that at a greater depth more pores were infilled by ettringite crystals. The ettringite crystals that form a dense layer appear more prism-like while those that nucleate and grow on mineral surfaces are characterized by a needle-like morphology. The results suggest that the ettringite morphology may be controlled by the confining pressure.

Thaumasite was also recognized during the XRD analyses (see Figures 2 -5) and occurs mainly in the top zone of the lysimeters. Its presence is probably related to available CO₂ concentrations from plant root respiration in the upper lysimeter zones.

DRILL-CORES

Experimental Field Lysimeters

Montgomery County, KY

Figure 1

37

Ettringite in Field Lysimeter-1

Depth Profile

■ % Ettringite in L-1 relative to Quartz

Figure 2 b

Lysimeter 1 3'6" - 4'0"

Figure 2c

Ettringite in Lysimeter-2A Depth Profile

Figure 3 a 41

Figure 3 b 12

Lysimeter 2A 2'0"

Lysimeter 2A 2'4"

Figure 3 c 43

Lysimeter 2A 3'6"

Ettringite in Field Lysimeter L-2B

Depth Profile

■ % Ettringite in L-2B rel. to Quartz

Lysimeter 2B 2'0"

Figure 4 b 46

Lysimeter 2B 2'8"

Figure 4c 47

Lysimeter 2B 3'6"

Figure 4 d 48

Ettringite in Field Lysimeter L-3

Depth Profile

Figure 5 b 50

Lysimeter 3 2'0"

Figure 5 c

Infilling of Available Pore Space in Lysimeter 3

Sample A taken at a Depth of 2'0"

Sample B taken at a Depth of 3'0"

Figure 6

COOLSIDE WASTE MANAGEMENT RESEARCH
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period: January 1, 1994 to January 31, 1994

Statement of Project Objectives

Produce sufficient information on the physical and chemical nature of Coolside waste to design and construct physically stable and environmentally safe landfills.

Summary of Progress for Period

Work was initiated to determine if dry-FBC material could be used as a soil stabilizing material. Samples were run at a variety of mixes and the strength of the soil was found to be substantially improved. The addition of only 8% FBC material was found to more than double the load bearing capacity of the soil.

Ettringite has been added to the WATEQ thermodynamics data base. As all data has been collected for the laboratory column lysimeters, WATEQ runs were made for all columns. Data extracted for each column leachate collection include concentrations of 43 aqueous species, 71 mineral species which appear to approach saturation levels, and various other indicators such as ionic strength, CO_2 partial pressure and species activities. This data, in combination with the leachate analytical data, are being examined to infer chemistry controlling leachate behavior.

Coolside waste is composed of metal oxide furnace products with the addition of gypsum/anhydrite (CaSO_4), portlandite ($\text{Ca}(\text{OH})_2$), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and Na from sulfur control regimes. Other elements commonly found in coal and coal combustion products are present in trace amounts. Leaching of the waste introduces H_2O and CO_2 .

The elements of major importance are Ca, S, C, Si, and Al. In addition, Mg is important in fly ash leachate. The aqueous species of major importance are OH^- , silicic acid

(H_4SiO_4) and its derivatives, SO_4^{2-} , the major element hydroxides and their derivatives, carbonic acid (H_2CO_3) and derivatives, and major element carbonates and their derivatives. At this time, the chemistry driving the leachate pH and composition appears to be:

- ◆ Hydrolysis of metal oxides and the resulting high pH. For example, $\text{Ca}(\text{OH})_2$ in equilibrium with pure water at 25°C has pH about 12.45.
- ◆ Sulfated dissolution. The analysis of the water indicates the solution to be at or slightly less than saturation with respect to gypsum.
- ◆ Carbonate precipitation and lowering of pH. For example, CaCO_3 in equilibrium with pure water (no excess CO_2) has pH about 10. This will continue until equilibrium with the available CO_2 is achieved. CaCO_3 in equilibrium with water at equilibrium with atmospheric CO_2 ($p\text{CO}_2 \sim 3.5$) has pH ~ 8.4 .

The preliminary investigation previously reported identified 108 WATEQ mineral forms which approached within 5 orders of magnitude of saturation. This list has been refined to about 40 during the current reporting period. The minerals predominately include oxide, hydroxide, sulfate, silicate and carbonate mineral forms of the major elements Ca, Mg and Al, and those of minor elements Zn, Cu, Ni, Ba, Mn and Cd.

Phase II, Task 1, Subtask 1.2 Subgrade Stabilization

Standard moisture-density relations tests were performed on FBC-soil mixtures to determine changes in maximum dry density and optimum moisture content as the percent of FBC increases. Tests were performed at 0, 4, 8, 12, and 100 percent FBC. Moisture-density relations curves are located in Figure 4. The maximum dry density decreased from 106.8 lbs/ft³ at zero percent FBC to 76.7 lbs/ft³ at one hundred percent FBC and optimum water content increased from 19.4 to 27.8 percent as seen in Figures 1 and 2 and Appendix A. The soil used was one with marginal engineering properties (A-7-6, CL, AASHTO and Unified classification, respectively) obtained from Ohio.

Figure 1. Percent FBC versus Dry Density

Figure 2. Percent FBC versus Moisture Content.

Unconfined compressive strength tests were performed to determine if the addition of FBC would result in an increase in this parameter. Samples were remolded, sealed, and aged at room temperature for seven to fourteen days before testing. Strength increased from 21.1 lbs/in² (0% FBC) to 330.0 lbs/in² (100% FBC aged 14 days) as seen in Figure 3.

Phase I, Task 6 - Data Evaluation

Thermodynamic Data Base

The WATEQ program attempts to infer theoretically, given pH and ionic concentrations of water-borne ions, the active chemical species and approach to saturation of possible mineral entities through which the water has passed. During the current reporting period, a preliminary selection has been made of species and minerals which may drive leachate chemistry, are driven by the chemistry and may be present in significant amounts, or are the predominant carriers of minor ions of interest. In addition, ettringite was added to the thermodynamic database for WATEQ.

WATEQ measures mineral approach to equilibrium by comparing the products of the activities of the constituent ions (Ion Activity Product or IAP) with the equilibrium solubility product, specifically, $\log(IAP/K)$ where K , the equilibrium solubility product, is corrected for temperature. A value greater than zero indicates supersaturation. Individual ion activities are the product of the ion concentration and an activity coefficient which attempts to correct for the ionic strength of the solute. The concentrations are determined by an iterative mass and charge balance over the possible species present given the analytical input data of concentrations and pH.

There are enough sources of error inherent in these calculations that measures of approach to equilibrium must not be viewed as absolute indicators of the presence or absence of a particular mineral, or that any equilibrium has been reached. One source of error is the equilibrium solubility product, K , for each mineral. The range of

Figure 3. Percent FBC versus Unconfined Compressive Strength.

solubilities depends on the degree of crystallinity, particle size effects, order-disorder phenonema, defect structures, range of solid solutions, interlayering and meta-stability. For instance, the calcite (CaCO_3) group consists of calcite plus the substitution in varying amounts of Mg, Mn, Zn, Fe, and Cd in the matrix for Ca, depending on availability. Thus, formation of calcite may also include magnesite (MgCO_3), rhodocrosite (MnCO_3), smithsonite (ZnCO_3), siderite (FeCO_3) and otavite (CdCO_3) as part of the solid solution. These individually do not have equal solubilities. At primary saturation, or thermodynamic equilibrium, the aqueous phase will be undersaturated with respect to the solid components. Conversely, a high degree of supersaturation of the most soluble components will exist at stoichiometric saturation. Other examples exhibiting this behavior include quartz, gibbsite, kaolinite, sepiolite, oxides and hydroxides, feldspars and micas. Additionally, the solid phase initially formed may be meta-stable with respect to the thermodynamically preferred state. For example, calcite is thermodynamically preferred over aragonite, but aragonite may form initially as a very fine solid phase with a disordered lattice and slowly convert to the more stable, relatively inactive, less soluble calcite form. Silica (SiO_2) forms, anhydrite/gypsum and hydroxides also exhibit this behavior. Another source of error is the determination of the ion activity coefficient over large ranges of ionic strength. In very dilute solutions, the activity coefficient is 1, so that the ion activity is equal to the molar concentration. As ionic strength increases, the coefficient first increases. This increase in ion activity drives the equilibrium toward formation of the neutral species, resulting in a "salting out" of the solid phase. As the ionic strength increases toward and past one, the activity coefficient may drop below one due to greater ionic association in the solute, driving the equilibrium reaction toward dissolution of the solid phase. For ionic strengths above about 0.5, the activity coefficients become increasingly uncertain.

The ionic strengths encountered in the Coolside column leachate range from ~0.01 to ~2.5. Representative variation of column leachate ionic strength over time is illustrated in Figure 4. For comparison, the effective ionic strength of a free flowing stream is ~0.01, groundwater ~0.1, seawater ~1. Despite these uncertainties in solubility

Figure 4. Representative ionic strengths vs time

Figure 5. Representative Coolside equilibrium. $\log[(\text{Ca activity})/(\text{Mg activity})]$ vs $\log(p\text{CO}_2)$

constants and ion activity products, the equilibrium calculations performed are useful as an aid in interpreting observed fact.

Selection of Primary Ionic Species

The major components of coal combustion waste are normally oxides of Mg, Na, Fe, Ti, Si, Ca, K, P, and Al. In addition there are a significant amounts of Cl and SO₃. There are trace amounts of other metals such as Zn, Cu, Ni, Co, Cr, Ba, V, As, B, V, Mn, Sr, Zr and Cd. The Coolside sulfur control regime results in the addition of anhydrite (CaSO₄) / gypsum (CaSO₄*2H₂O), portlandite (Ca(OH)₂), dolomite (CaMg(CO₃)₂) and, in some cases, Na. Co, Cr, Mo, Ti, Zr, V and Se are given little or no treatment in WATEQ, so will not be considered further. Upon leaching, it would be expected that hydrolysis would result in the release of the metal ion and OH⁻ into solution, resulting in a highly alkaline solute. Free trivalent ions, such as those of Al, Fe and Mn, are not important, as they tend to form under conditions of low ionic strengths and high acidity. With the exception of Al⁺³, they tend to form insoluble hydroxides. Therefore, Al(OH)₃⁰ and Al(OH)₄⁻ are expected, as are divalent Ca, Mg, Zn, Cu and Ba, monovalent Na and K ions, and OH⁻. The leaching water is generally in equilibrium with a CO₂ source. This source may be the atmosphere or soil. The partial pressure of CO₂ (pCO₂) in water in equilibrium with the atmosphere is approximately 10^{-3.5}. The pCO₂ in soil may be much higher due to organic respiration. It is expected that leaching will introduce significant amounts of CO₂ into the solute. The steps in CO₂ hydration are

Step 2 is rapid at room temperature, while steps 1 and 3 are slow. At higher pH, however, excess hydroxide increases the relative importance of step 3. At the pH's of the leachates, the carbonate ion, CO₃²⁻, will be expected to be the dominate form of carbonate present. Quartz (SiO₂) is slowly acted upon by alkali at room temperature, with long equilibrium time. This reaction rate increases rapidly above pH 9 due to

Figure 6. Fly Ash equilibrium. $\log[(\text{Ca activity})/(\text{Mg activity})]$ vs $\log(p\text{CO}_2)$

Figure 7. Calcium species concentration, Pilot 1 column

ionization of silicic acid (H_4SiO_4 or $\text{Si}(\text{OH})_4$) and formation of monomeric or multimeric domains, so that $\text{Si}(\text{OH})_4^0$ and $\text{SiO}(\text{OH})_3^-$ are expected. SO_4^{2-} and HSO_4^- are expected to be available from the dissolution of anhydrite/gypsum.

Based on these considerations, the following solute species have currently been selected for analysis:

CO_2 total, $\text{Al}(\text{OH})_4^-$, Ca, Cl, CO_3^{2-} , HCO_3^- , Na, OH^- , PO_4^{2-} , SiO_2^0 , SO_4^{2-} , Zn, Al, H, K, Mn, $\text{Al}(\text{OH})_3^0$, CaCO_3^0 , CaHCO_3^+ , CaOH^+ , CaSO_4^0 , CaHSO_4^- , HCO_3^- , MgCO_3^0 , MgHCO_3^+ , MgOH^+ , MgSO_4^0 , NaCO_3^- , NaHPO_4^0 , NaSO_4^- , PbCl^+ , PbCO_3^0 , PbHCO_3^+ , $\text{Pb}(\text{OH})_4^{2-}$, HPO_4^- , SiO_2^0 , $\text{Si}(\text{OH})_4^0$, $\text{SiO}_2(\text{OH})_2^{2-}$, SO_4^{2-} , ZnCl^+ , ZnCO_3^0 , ZnHCO_3^+ , ZnOH^+ , $\text{Zn}(\text{OH})_4^{2-}$, ZnOHCl^0 , ZnSO_4^0 and MnCO_3^0 .

In addition, the following items have also been selected:

pH, $-\log(\text{pCO}_2)$, Effective Ionic Strength, $a_{\text{H}_2\text{O}}$ (activity of water), $-\log(\text{Ca activity})$ and $-\log(\text{Mg activity})$. It is expected that this list will change as analysis and interpretation continues.

Selection of Primary Mineral Species

In the previously reported preliminary investigation, WATEQ minerals which approached to within 5 orders of magnitude of saturation were found. The 108 minerals meeting this criteria have been further investigated to select those which may drive leachate chemistry, are driven by the chemistry and may be present in significant amounts, or are the predominant carriers of minor ions of interest. Given the nature of Coolside waste, the characteristics of the oxides are of immediate importance. Of greatest interest are those present in large amounts, i. e., those of Ca, Al, Fe, K, and Na. It is expected that hydrolysis of these oxides will result in free aqueous hydroxides and metal ions, with a resulting high pH. On introduction of atmospheric CO_2 , metal carbonate precipitation will act to lower pH to some equilibrium value over some unknown period. The pH range seen in Coolside leaching roughly corresponds to that of portlandite ($\text{Ca}(\text{OH})_2$) in equilibrium with pure water (about 12.45) down to calcite

(CaCO_3) in equilibrium with water that is in equilibrium with atmospheric CO_2 (pH about 8.4 at $\log(\text{pCO}_2)=-3.5$) (Figure 7). The dissolution of silica and gypsum/anhydrite add the possibility of silicate and sulfate mineral formation.

Silica The forms of SiO_2 possible are quartz, cristabolite, chalcedony and silica gel. The higher forms, such as tridymite, would naturally convert to the lower forms over time. XRD data show the presence of quartz. Cristabolite is formed under high temperature up to melting and persists in metastable form on cooling, with eventual conversion to quartz. Its highly symmetric, open structure is thermodynamically slightly favored over tridymite and quartz. Chalcedony is a fibrous silica, often occurring in small residues as crusts or cavity filling. It is readily soluble in alkaline solutions. Silica gel is a form favored on formation at STP, most soluble, and ages into poorly crystallized cristabolite. Quartz is most easily recognized by XRD, is the expected initial form, and is least soluble. Inspection of leachate column approach to saturation of the silica members show that quartz most nearly approaches equilibrium, but usually remains below (e.g., Figure 13, other representative approaches to saturation are shown in Figures 8 to 14). If any other form predominated, then quartz would be supersaturated. Its dissolution is expected to supply SiO_2 to the solute. Silica formation, if any, would be expected to be of the silica gel dimorph. Quartz has been chose as the silica member of interest.

Na The initial sodium mineral forms selected, based on approach to equilibrium, were halite (NaCl), nahcolite (NaHCO_3), trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4). They all show significant degrees of supersaturation. All of these are extremely water soluble, however, and are not expected to be formed. Na may be involved in minor silicate mineral formation mentioned later. It is expected that Na from oxide dissolution and sodium addition due to sulfur control regimes will be found as free ions in the solute and will be involved in a very minor way in mineral formation. Its major effect on leachate chemistry is in contributing to the ionic strength of the

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Coolside 300 Static Saturated -CO₂

Figure 14.

leachate.

Cl No major cation interacts significantly with the chloride ion. Minor cations (Pb, Zn, Fe and Mn) may form minor amounts of hydroxy-chloride minerals as mentioned later. Its major effect is also in contributing to the ionic strength of the leachate.

Al Free Al will be available from the dissolution of alumina (Al_2O_3). It is the only trivalent ion which forms a soluble hydroxide. Initially formed is dimorphous boehmite/diaspore (AlOOH or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), the basic oxide of alumina. Diaspore is favored over boehmite by $\sim 0.1 \text{ kcal/mole}$. They hydrate slowly to gibbsite ($\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) at room temperature. Gibbsite is also artificially formed by passing CO_2 into alkali aluminate solution, which describes Coolside leachate conditions. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), which WATEQ indicates approaches or passes saturation at lower pH levels, also dissolves to or forms from gibbsite and silicic acid. Diaspore, gibbsite and kaolinite have been chosen as minerals of interest. Other aluminosilicates are mentioned below. These minerals, for the most part, are not expected to form from solution or control the solution chemistry; however their inclusion does reflect the solute availability of the component ions which in some cases is of interest.

Micas Micas have never been shown to control water chemistry. Reversibility has not been shown, so there is no reason to believe that they attain equilibrium solubilities. K-mica ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) shows a sometimes extreme supersaturation at lower leachate pH and appears to be driven by the leachate chemistry.

Feldspars WATEQ indicates that the feldspars anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), albite ($\text{NaAlSi}_3\text{O}_8$) and adularia (KAlSi_3O_8), become supersaturated. These minerals form a substitutional solid solution. The degree of saturation is adularia > albite > anorthite. They appear also to be driven by leachate chemistry. As adularia appears to be one of the few possible mineral forms containing K, and albite, likewise, contains Na, these two will be retained. Authogenic feldspars are known to form in nature, but are not

considered to be an important species here.

Pyroxenes Clinoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$ or MgSiO_3), analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) (hydrated Jadeite) and diopside ($\text{CaMgSi}_2\text{O}_6$) exhibit supersaturation. Diopside, at times, appears to be driven by pH mediated silica availability, and independent of or opposite pH at other times. Its often very high degree of supersaturation argues against its importance in leachate chemistry, but its role, if any, remains to be determined. Clinoenstatite will be retained, as it is the major magnesium silicate. Analcime rarely approaches saturation, appears to be driven by leachate chemistry and would only be present in minor amounts, if any, so will not be retained.

SO_4 Sulfate availability is controlled by the equilibrium dissolution of anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Anhydrite crystals are not common. Anhydrite converts slowly to gypsum with a corresponding increase in volume giving long-term swell. It is also slightly more soluble than gypsum. WATEQ indicates that both are uniformly at, or slightly under, saturation, with anhydrite slightly less saturated, as expected. Gypsum will be retained as a mineral which controls leachate chemistry. Another source of sulfate is the dissolution of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). It is extremely soluble and is expected to contribute to the very high initial sulfate concentration in the leachate, but is not expected to be present or to control chemistry except initially. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) is commonly found in $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4\text{-H}_2\text{O}$ systems on mineral surfaces and in pore spaces. It is partly decomposed by water to an alkali. WATEQ indicates that, in most cases, ettringite is only initially supersaturated and drops well below saturation very quickly (e.g., Figure 13). It will be retained because of its implication in swell. Other sulfate minerals are mentioned below.

Ca and Mg, Carbonates and Hydroxides The interactions between these drive much of the leachate chemistry: Ca because of its abundance, Mg because of its interchangeability with Ca, and carbonates and hydroxides because of their implication

in pH control. Possible major mineral forms which WATEQ indicates are often or always supersaturated are calcite (CaCO_3), aragonite (CaCO_3), brucite ($\text{Mg}(\text{OH})_2$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), magnesite (MgCO_3), dimorphic MgCO_3 , and huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$). Periclase (MgO) hydrates to brucite, which may further alter to magnesite and hydromagnesite. A precipitate of the hydrate nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), whose slight solubility is enhanced by the presence of CO_2 , NaCl , and Na_2SO_4 , may also be formed at STP. To determine which forms are likely at leachate conditions, an equilibrium diagram which uses $\log[(\text{activity Ca})/(\text{activity Mg})]$ vs $\log(\text{pCO}_2)$ to predict equilibrium conditions was plotted over the leachate collection periods. It was found that calcite is favored, with brief movements into brucite, aragonite or dolomitic regimes. For fly ashes, with a lower Ca/Mg ratio, most of the collection period remains in the dolomitic regime. Representative equilibrium diagrams are given in Figures 5 and 6. Calcite has been selected over aragonite, as calcite is the preferred dimorphic form. The conditions under which dolomite is precipitated in nature are not well understood, and attempts to precipitate dolomite from oversaturation have failed. Dolomite is an ordered crystal which prevents its formation from solutions undergoing rapid crystallization. It is possible, however, that dolomite might be formed under conditions of oversaturation and high ionic strength found in Coolside leachate over a long period of time. Dolomite was most likely present in the original source of lime for the Coolside tests and is of interest. An additional magnesium carbonate of possible interest is artinite ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), which exhibits supersaturation but appears to be driven by leachate chemistry. It will also be retained.

Ca and Mg Silicates Forsterite (Mg_2SiO_4), sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) are indicated to be supersaturated. Talc tends to form in high ionic strength brines at low temperature, but sepiolite tends to precipitate preferentially. Sepiolite should continue to be considered, as its precipitation also lowers pH. Two other calcium-aluminum silicates, prehnite ($\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$) and laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$), show supersaturation but their significance, if any, is currently

unknown. Prehnite does not seem to be driven by leachate pH, while laumontite does. They will continue to be considered.

Minor Species Carriers Mineral carriers of minor ions have little effect on leachate chemistry but will be followed to predict which might be dominant at points in the leachate cycle because the ions are of general interest. It is doubtful that many of these could be confirmed by XRD, as the amounts would be very small. In general, the oxide, hydroxide, carbonate and silicate forms are indicated at appropriate times in the collection cycle.

Ba Barite (BaSO_4) is relatively insoluble and becomes more so in a salt solution. WATEQ indicates that it is often supersaturated. Witherite (BaCO_3) is indicated to be supersaturated, but less often.

PO₄ Ca-hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is the major phosphate carrier. WATEQ indicates a fairly significant degree of supersaturation. The fluor-apatite would be preferred in the presence of fluorine. It forms a solid solution with $\text{Ca} > \text{Pb} > \text{Na} > \text{K}$.

Pb Litharge/massicot (PbO , dimorphs) probably form minor amounts of $\text{Pb}(\text{OH})_2$. Other Pb minerals possibly formed include cerrusite (PbCO_3), anglesite (PbSO_4), larnakite ($\text{Pb}_2(\text{SO}_4)\text{O}$), and laurionite ($\text{Pb}(\text{OH})\text{Cl}$), one of the very few Cl minerals. WATEQ indicates supersaturation for each of these at various times. Pb compounds, however, are not known for solubility.

Cu Tenorite (CuO), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) (crystals rare, but slightly water- CO_2 soluble), atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) (another of the few Cl minerals; alters to malachite; formed by oxidation of other Cu minerals, especially in arid saline environments), and tsumebite ($\text{CuPb}_2(\text{PO}_4)(\text{SO}_4)(\text{OH})$) (unlikely to be found) have supersaturation indicated by WATEQ.

Cd Monteponite (CdO), $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})\text{Cl}$, CdSiO_3 and otavite (CdCO_3) exhibit varying degrees of supersaturation. Otavite is supersaturated only in the fly ash system. In the Coolside leaching, the higher Ca/Mg ratio leads to preferential calcite formation.

Zn Zincite (ZnO), $\text{Zn}(\text{OH})_2$, $\text{Zn}_2(\text{OH})_3\text{Cl}$, $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$ and ZnSiO_3 are indicated.

Mn Pyrochroite ($\text{Mn}(\text{OH})_2$) and rhodochrisite (MnCO_3) exhibit varying degrees of supersaturation. The oxide form, pyrolusite, remains well undersaturated.

Ni Bunsenite (NiO), $\text{Ni}(\text{OH})_2$ and Ni_2SiO_4 are indicated.

Fe There is no analytical information on relative amounts of divalent and trivalent Fe. Goethite (FeOOH), the trivalent analogue to diaspore (AlOOH), does not show saturation. Also, no divalent Fe mineral approaches saturation, so it is probable that hematite/maghemite (Fe_2O_3) and magnetite (FeFe_2O_4) are nearly insoluble.

Future Activities

Refinement of mineral selection will continue. Further investigation is necessary to explain the disparate behavior of different columns. Results must be expanded to include field lysimeters. Thaumassite and mullite will be added to the thermodynamics data base.

An asphalt mix design will be developed using natural aggregates blended with synthetic aggregate produced from FBC.

Appendix A

Moisture Density Curves for FBC-Modified Soils

12-13-93

STANDARD

100 % FBC

OPTIMUM MOISTURE CONTENT (%) = 27.8

OPTIMUM DRY DENSITY = 76.7 PCF

DEC = 3

HP =

WL =

Figure A1. Moisture Density Curve for 100% FBC Material

4% FBC

STANDARD

12-16-93

OPTIMUM MOISTURE CONTENT (%) = 23.9

HL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 92.3 PCF

Figure A2. Moisture Density Curve for 4% FBC Material in Soil

76

8% FBC

STANDARD

12-16-93

OPTIMUM MOISTURE CONTENT (%) = 24.4

NL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 91.0 PCF

Figure A3. Moisture Density Curve for 8% FBC Material in Soil

12% FBC

STANDARD

12-16-93

OPTIMUM MOISTURE CONTENT (%) = 25.1

WL =

WP =

DEG = 3

OPTIMUM DRY DENSITY = 90.6 PCF

Figure A4. Moisture Density Curve for 12% FBC Material in Soil

100% SOIL

STANDARD

10-23-93

OPTIMUM MOISTURE CONTENT (%) = 19.4

HL =

HP =

DEG = 3

OPTIMUM DRY DENSITY = 106.8 PCF

79

**Coolside Waste Management Research
Technical Progress Report**

Contract No: DE-AC21-91MC28162

Report Period: February 1, 1994 to February 28, 1994

Summary of Progress for the Period

Unusually wet and cold weather resulted in the field lysimeters having to be sampled on a bi-weekly basis through the reporting period. A review meeting was held on February 11, in Library, at CONSOL R&D, Inc.

Monitoring for expansion continued. The tests have been conducted for over a year and the materials are still in a primary swell phase. To date the greatest swell has been observed in the unhydrated unaged material with 2.5 lbs. of surcharge. The aged unhydrated and the hydrated materials show much less swell. The details of the monitoring are discussed herein.

Phase I, Task 2, Swell Tests

Monitoring of swell continued on the hydrated (Figure 1) and non hydrated (Figure 2 and 3) FBC ash samples. Both types are still in the primary swell phase after one year of monitoring. All samples were remolded near 95% of standard maximum dry density and optimum moisture content. The samples were remolded in CBR molds (6" diameter, 4.584" height), and swell was monitored under the following conditions:

- approximately 12.5 lb. surcharge, no age time
- approximately 2.5 lb. surcharge, no age time
- approximately 12.5 lb. surcharge, 7 days age time
- approximately 2.5 lb. surcharge, 7 days age time

Time of aging represents the amount of time before the samples were placed in water. Aged specimens were sealed at room temperature to prevent moisture loss before placement into the

FBC Ash (hydrated)

CBR Samples

Figure 1. Swell versus Time, Hydrated FBC Ash.

FBC ASH (Non-Hydrated)

CBR Samples 7 day Age Time

Figure 2. Swell versus Time, Non hydrated FBC Ash.

FBC ASH (Non-Hydrated)

CBR Samples, No Age Time

Figure 3. Swell versus Time, Non-hydrated FBC Ash.

water tank.

Monitoring of swell also continued on two samples of FBC pellets (Figure 4). The pellets were loosely placed in CBR molds. Surcharge weights (approximately 2.5 and 12.5 pounds) were placed on the samples prior to saturating in water. Swell is decreasing in the sample with the 2.5 lb. surcharge and continuing to increase for the sample with the 12.5 lb., surcharge.

Work Planned for Next Period

An asphalt mix design will be developed using synthetic FBC aggregate. CBR and swell tests will be performed on FBC soil mixtures. A compilation of the field data to be reported next month is also planned.

FBC Pellets

Figure 4. Swell versus Time, FBC Aggregate

**Coolside Waste Management Research
Technical Progress Report**

Contract No: DE-AC21-91MC28162

Report Period: March 1, 1994 to March 31, 1994

Summary of Progress for the Period

Both the coarse and fine aggregate which are to be used in the road demonstration of the FBC pellets were examined. The proposed materials met the specifications as outlined by the Ohio DOT.

The field lysimeters continued their trend of increasing moisture through the late winter. Many of the elements in the lysimeter leachates show a consistent decline in concentration. For example, Cl has declined in all the leachates, from levels of tens of thousands of ppm to only a few hundred over a 12 month period. This and other soluble elements, such as sodium, have a release pattern which is constant with simple "washing out" of these elements with time. Other elements such as calcium do not show as simple a pattern. This element is increasing in some leachates and decreasing in others. In addition, an annual pattern of concentration variation is found. This chemistry suggests mineralogical transformations may be exerting a control over the solution chemistry of these materials.

Phase II, Task 1, Subtask 1.3

Gradation Tests

Gradation tests were performed on a coarse aggregate (AASHTO No. 8) sample and a fine aggregate (natural sand) sample obtained from a paving contractor in Belmont County, Ohio. The tests were performed to determine if the aggregate met Ohio DOT specification number 404 for aggregates in bituminous concrete surface. The aggregates will be blended with synthetic aggregate, supplied by Consol Inc., produced from FBC ash to make a bituminous concrete surface demonstration project in Belmont County, Ohio. Results of gradation tests show the aggregate meets grain size specifications as seen in Figures 1 and 2.

Figure 1. Grain Size of Natural Sand and Specification Limits.

Phase I, Task 3, Subtask 3.2 Lysimeter Monitoring

Bed temperatures for each of the lysimeters are plotted in Figure 3. The bed temperatures decreased rapidly over the winter months, to reach a minimum of 5°C. The temperature minimums attained were identical to those measured over the 92/93 winter months.

The plots of lysimeter moisture levels are shown in Figure 4. Whilst leachate flow rates were significantly higher than for the same period the previous year, overall moisture levels continued to increase within the beds. This indicates that the material within the lysimeters has increased its moisture retention capacity, most likely as a result of a mineralogical transformation creating a material capable of a higher level of hydration. The pH of the leachates do not show a clear trend among the cells as the pH in Lysimeter 1 continues to increase, while 3 and 2 remain relatively stable.

Figure 5 shows the change in leachate pH over time for each of the lysimeters. The graphs show the data measured for port #3 in each lysimeter (i.e. the left side port on the lowest level). Data from ports 2 and 4 showed similar trends. The measured pH values from cells 1 and 2 have risen by more than 2 units over the previous 3 months, whilst the values measured in cells 3 and 4 have stayed constant. At this time no explanation is offered for the sudden increase in pH; however, core samples were recently taken from cell 1 and it is hoped that x-ray analysis may provide sufficient data to elucidate the mineralogic transformations which have taken place.

Figure 6 plots alkalinity against time for each of the cells. With the exception of cell 2, alkalinity has continued to decrease with time as the soluble hydroxides have been leached from the beds. The measured alkalinity values for cell 2 have shown a significant increase over the previous 2 months and may be a result of increased leachate flow through the bed causing the solubilization of material previously isolated from the leachate stream.

68

Figure 3

06

Figure 4

Figure 5

The plots of conductivity against time for each of the cells (Figure 7) all show a decrease in conductivity, consistent with the removal of soluble species from the bed.

Concentrations of potassium, sodium and calcium are plotted against time in Figures 8, 9 and 10. Sodium and potassium levels have both decreased, with the plots of each metal showing virtually identical trends for each lysimeter, albeit at different concentrations. The calcium plots for cells 1 and 2 also reveal a decrease in concentration over time; however cell 3 shows an increase in leachate calcium concentration with time, possibly indicating the onset of a mineralogic transformation within cell 3 as alkalinity levels have decreased with the removal of stabilizing hydroxide ions from the system.

Chloride and sulphate levels (Figures 11 and 12) have also consistently decreased over the monitoring period. The overall trends of both anions match those of both sodium and potassium very well and also suggest some relationship to calcium levels, albeit to a lesser extent.

The concentration plots of molybdenum and arsenic are shown in Figures 13 and 14. Both plots show an increase in leachate concentration over the late summer months, decreasing again with the onset of winter. High levels of soil CO₂ have been observed to result in the mobilization of metals in previous studies. In order to verify this hypothesis, gas monitoring wells have been placed in each lysimeter at depths of 8", 18" and 30" and will be sampled at two week intervals in order to monitor both the build up of CO₂ levels within the soil over the summer months and any vertical migration which may occur down into the Coolside material.

Work Planned for Next Period

An asphalt mix design will be developed using natural aggregates blended with a synthetic aggregate produced from FBC ash. Monitoring of the Montgomery County field site has continued over the period covered by this report. Leachate flow has been observed to be significantly higher than that for the same period in 92/93. As a result, site visits have been conducted two times a week in order to prevent leachate loss from the overflow of the collecting vessels.

Ed

Figure 6

Figure 7

Figure 8

96

Figure 9

47

Figure 10

Figure 11

bb

Figure 12

Figure 13

101

Figure 14

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period: April 1, 1994 to April 30, 1994

Statement of Project Objectives

Produce sufficient information on the mineralogical and chemical changes of FBC-waste pellets to aid in the design and manufacture of physically stable pellets that can be used toward road applications.

Summary of Progress for Period

FBC-waste pellets were prepared by CONSOL in a disk pelletizer. The FBC-pellets were then characterized for their soundness and freeze/thaw durability. The task of this study has been to investigate the mineralogy and mineralogical changes of the pellets before and after the physical testing periods. The information gained concerning the mineralogical and chemical changes that are observed in the aged pellets will assist in the development of an optimum mix and curing conditions necessary to produce physically stable pellets.

The sample characterization was based on X-ray diffraction and SEM investigations of the pellets and pellet fragments that formed in weathering tests conducted by CONSOL. Samples discussed in this report include pellets # 6, pellets # 7 and pellets FBC-WT-1P, FBC-WT-1F, FBC-WT-2F, FBC-WT-3F, FBC-WT-4P, and FBC-WT-4F (the last character in the label stands for pellets (P) and fractured (F) pieces. Pellets with significant additions of fly ash (pellets # 7) are characterized by a low soundness number while those with small fly ash additions (pellets # 6) are not. Both types of pellets (# 6 and # 7) formed abundant fractured pieces when subjected to freeze/thaw tests. Pellets from tests # 6 and # 7 were studied after the curing, but prior to the weathering procedures. Pellets that are similar in composition to pellets # 6 and # 7 were collected by CONSOL from natural weathering tests (FBC-WT-1P; FBC-WT-1F; FBC-WT-2F) and laboratory freeze/thaw tests (FBC-WT-3F; FBC-WT-4P; FBC-WT-4F). A list of all pellet samples is presented in Table 1.

Table 1 Pellet Samples Submitted to the XRD and SEM Study

SAMPLES	CURING	NATURAL WEATHERING *	FREEZE/THAW **
Test #6	Pellets		
Test #7	Pellets		
FBC-WT-1P		Pellets	
FBC-WT-1F		Fractured Pieces	
FBC-WT-2F		Fractured Pieces	
FBC-WT-3F			Fractured Pieces
FBC-WT-4P			Pellets
FBC -WT-4F			Fractured Pieces

* Duration of natural weathering tests was several months

** Duration of laboratory freeze/thaw tests was several months

Pellets from tests # 6 and # 7

Based on XRD analyses it was observed that the mineralogical characteristics of pellets # 6 and # 7 are very similar. The main mineral components are anhydrite (CaSO_4), calcium hydroxide (Ca(OH)_2), calcium carbonate (CaCO_3), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}26\text{H}_2\text{O}$). Very minor amounts of gypsum are only indicated in the XRD pattern of pellets # 7. The greater additions of fly ash to pellets # 7 result in larger amounts of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), calcium aluminum silicate ($\text{CaAl}_2\text{SiO}_6$) and calcium silicate (CaSiO_3) in pellets # 7 compared to pellets # 6; however, all of these phases are only minor components in the samples. No free lime was recognized for either pellets # 6 or pellets # 7. Table 2 highlights the results for the XRD analyses for all samples selected for this study. The XRD plots for pellets # 6

and # 7 are illustrated in Figures 1 and 2, respectively.

Table 2 Major Mineral Components from XRD Results for Pellets and Fractured Pieces

Sample ID	Anhydrite (CaSO ₄)	Gypsum (CaSO ₄) ₂ H ₂ O	Portland (Ca(OH) ₂)	Calcite (CaCO ₃)	Ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O)	Thaumasite (Ca ₃ Si ₂ (OH) ₄ (SO ₄)(CO ₃)12H ₂ O)
Test # 6	>A		>P	C	E	
Test # 7	>A	<<G	>P	C	E	
FBC-WT-1P		>G	>P	C	E	?
FBC-WT-1F		> >G	P	>>C	E	T
FBC-WT-2F		>>G	P	>>C	E	T
FBC-WT-3F-L		>>G	>P	>C	E	?
FBC-WT-3F-S		>G	P	>>C	<E	<T
FBC-WT-4P	>A	<G	>P	C	E	
FBC-WT-4F		>>G	P	>C	<E	?

< = small amounts; << = very small amounts; > = large amounts; >> = very large amounts

Character (P) stands for pellets; Character (F) stands for fractured pieces

Character (L) stands for large fractured pieces; Character (S) stands for small fractured pieces

The SEM study of pellets # 6 showed different structural and morphological features in the surface layer compared to the pellet interior. In the pellet # 6 surface, fly ash particles are intergrown with a very fine grained (submicron-sized) matrix. This matrix is partly crystalline, but also resembles the glassy structures that were previously observed in the pellets that had additions of silica fume. The interior of pellet # 6 is very dense. Fly ash particles are engulfed by a matrix consisting predominantly of anhydrite, calcium hydroxide (portlandite), calcium carbonate, and lesser amounts of ettringite. The SEM study revealed that ettringite predominantly starts to nucleate and grow on the surfaces of fly ash particles. This process is illustrated in Figures 3a, b. Fly ash particles provide Al and Si for the formation of ettringite. When the fly ash particles are surrounded by calcium hydroxide crystals (see Figure 3a), the pH conditions of the pore fluids are ~12 and, hence, are ideal for

ettringite to nucleate. After ettringite nucleation, larger ettringite crystals may grow and spread out to form a network of crystals which can contribute to the strength gain of the pellets. This is particularly well demonstrated in pellets # 7, which have higher additions of fly ash than # 6, and, hence, more nucleation surfaces for ettringite to form. In pellets # 7, large amounts of ettringite crystals form clusters and networks (Figures 4a, b).

The surfaces of both pellets # 6 and # 7 are heavily fractured. The cracks are illustrated in Figure 5a. A close up of the pellet surface (# 7) is shown in Figure 5b where large quantities of fly ash particles are recognized in the surface layer. The pellets were dipped in fly ash before the curing procedure to prevent them from sticking and also to densify the surface. Figure 5b also shows very fine ettringite needles around fly ash particles. Many of these fly ash particles are heavily corroded. The corrosion may indicate that Si and Al were utilized to form ettringite. The availability of Al may determine how much ettringite can form within the pellets.

FBC-WT - Pellets and Pellet Fragments

The FBC waste pellets were similar in composition compared to pellets # 6 and # 7. Samples FBC-WT-1P and FBC-WT-1F were collected by CONSOL after the natural weathering tests were completed. Pellets (P) were heavily fractured and collapsed easily under pressure. The fragmented portion (F) consisted of a fine powder. XRD analyses of the pellets FBC-WT-1P and powder FBC-WT-1F are shown in Figures 6 and 7, respectively. Both samples were characterized by abundant gypsum crystals, but no anhydrite. During the weathering process all of the anhydrite must have been hydrated to form gypsum. Calcium hydroxide, calcium carbonate and ettringite were also abundant in the pellets (FBC-WT-1P; see Figure 6). The SEM study shows abundant gypsum crystals (up to 100 μm in size) that had formed in the weathered sample (Figures 8a, b). The XRD analysis of the fragmented portion indicated a very high concentration of calcium carbonate (Figure 7). The calcium carbonate crystals are shown in the SEM photos of Figures 9a, b. Besides ettringite, this sample was further characterized by the presence of thaumasite crystals which are shown in the SEM photos of Figures 10a, b.

Sample FBC-WT-2F was also collected from the weathering tests. The XRD analysis for this sample is shown in Figure 11 and indicated great similarities to sample FBC-WT-1P.

Anhydrite was entirely hydrated to form large gypsum crystals (Figures 12a, b).

Sample FBC-WT-3F was collected by CONSOL from the laboratory freeze/thaw tests. It consisted of fractured pieces which were sieved into two size fractions. Both fractions were analyzed by XRD. The results for the larger pieces are shown in Figure 13, and those of the fine powder are shown in Figure 14. All anhydrite was hydrated to gypsum. The larger pieces had higher amounts of gypsum and calcium hydroxide, while the powder predominantly consisted of calcium carbonate and gypsum, with lesser amounts of calcium hydroxide. Ettringite was observed in both samples. The powdered sample also had traces of thaumasite present.

Samples FBC-WT-4P and FBC-WT-4F were collected from lab freeze/thaw tests and have more added fly ash compared to FBC-WT-3. The XRD analyses of the pellets (FBC-WT-4P; see Figure 15) indicate that they are very similar in composition when compared to pellets # 7. Large amounts of anhydrite were preserved during the freeze/thaw tests and the pellets are very hard even after the freeze/thaw tests. In the fractured pieces (FBC-WT-4F) no anhydrite was preserved. Instead, large amounts of gypsum were recognized in the XRD pattern (Figure 16). The SEM study showed very large gypsum crystals in the fractured pieces (Figures 17a, b).

Conclusions

The results of this combined XRD/SEM study of waste FBC-pellets showed that the majority of the swelling and fracturing process, which occurs when the FBC-pellets are exposed to moisture (natural weathering and freeze/thaw), is not caused by the formation of ettringite crystals, but rather can be contributed to the delayed hydration of anhydrite. The formation of gypsum via hydration of anhydrite results in a volume increase, which may be the main cause for the fracturing of the FBC pellets.

Figure 1 Pellet # 6

Gypsum = G
 Anhydrite = A
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumatinite = T
 Quartz = Q

P-7

Figure 2

Pellet # 7

Gypsum = G
 Anhydrite = A
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumascite = T
 Quartz = Q

108

Figure 3a Nests of ettringite needles form on a fly ash particle in the immediate vicinity of large calcium hydroxide ($\text{Ca}(\text{OH})_2$) crystals.

Figure 3b Fly ash particles are preferentially overgrown by ettringite crystals.

Figure 4a Clusters of fly ash particles act as nucleation surfaces for ettringite crystals. Ettringite occurs in a large size range.

Figure 4b Growth of ettringite crystals. Ettringite crystals fill pores and form networks.

Figure 5a SEM image of surface of pellet # 7. The surface is covered by abundant cracks

Figure 5b Accumulation of fly ash particles in the surface layer of pellet # 7. Very fine ettringite crystals are observed along fly ash grain boundaries. The particles are heavily corroded.

Figure 6 FBC-WT-1P

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumateite = T
 Quartz = Q

FBC-WT-1P

FBC-WT-1F

Figure 7

FBC-WT-1F

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumascite = T
 Quartz = Q

113

Figure 8a Large elongated gypsum crystals occur in a matrix of calcium hydroxide and calcium carbonate.

Figure 8b Large platy gypsum crystal grows within pellet interior causing many fractures to develop.

Figure 9a Large, well developed calcium carbonate crystals.

Figure 9b Clusters of calcium carbonate crystals form a white, very fine powdered precipitate on top of the FBC pellets.

Figure 10a Thaumassite crystals form nests of interlocking needles. They occur predominantly on surfaces of large fly ash particles in FBC pellets after weathering.

Figure 10b Enlargement of SEM photo 10a. Thaumassite form shorter, thicker needles compared to ettringite.

2F-FFP

Figure 11 FBC-WT-2F

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumasite = T
 Quartz = Q

Figure 12a Large gypsum crystals formed during hydration and recrystallization of anhydrite

Figure 12b Cluster of gypsum crystals

Figure 13 FBC-WT-3F- (large pieces)

FBC-WT-3F-LP

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumascite = T
 Quartz = Q

FBC-WT-3F -FP

Figure 14 FBC-WT-3F- (fine pieces)

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumascite = T
 Quartz = Q

Figure 15 FBC-WT-4P

Gypsum = G
 Anhydrite = A
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumasite = T
 Quartz = Q

FBC-WT-4F.

Figure 16 FBC-WT-4F

Gypsum = G
 Portlandite = P
 Calcium Carbonate = C
 Ettringite = E
 Thaumasite = T
 Quartz = Q

Figure 17a Very large elongated gypsum crystals occur in a matrix of calcium carbonate crystals and fly ash particles. Fly ash particles are overgrown by ettringite needles.

Figure 17b. Enlargement of 17a showing hexagonal calcium hydroxide crystals on top of very large gypsum crystals.

Coolside Waste Management Research

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period May 1, 1994 to May 30, 1994

Summary of Progress for Period

WATEQ analysis has been extended to include some of the current field lysimeter data. Data extracted for each leachate collection include concentrations of 43 aqueous species, 71 mineral species which appear to approach saturation levels, and various other indicators such as ionic strength, CO_2 partial pressure and species activities. This data, in combination with the leachate analytical data, are being examined to infer the chemistry controlling leachate behavior.

Coolside waste is composed of metal oxide furnace products with the addition of gypsum/anhydrite (CaSO_4), portlandite ($\text{Ca}(\text{OH})_2$), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and Na from sulfur control regimes. Other elements commonly found in coal and coal combustion products are present in trace amounts. Leaching of the waste introduces H_2O and CO_2 .

The elements of major importance are Ca, S, C, Si, and Al. In addition, it now appears that Mg is also important in Coolside leachate, as well as in fly ash leachate, since some preliminary results indicate equilibrium conditions to be in the brucite ($\text{Mg}(\text{OH})_2$) regime rather than the calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) areas seen in the column leachate equilibrium diagrams. Preliminary results also indicate that formation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) may continue longer than the column data indicated. The chemistry driving the leachate pH and composition still appears to be:

a) Hydrolysis of metal oxides and the resulting high pH. For example, $\text{Ca}(\text{OH})_2$ in equilibrium with pure water at 25°C has a pH of about 12.45.

b) Carbonate precipitation and lowering of pH. For example, CaCO_3 in equilibrium with pure water (no excess CO_2) has a pH of about 10.

c) Continuing until in equilibrium with CO_2 available. CaCO_3 in equilibrium with water at equilibrium with atmospheric CO_2 ($p\text{CO}_2 \sim 3.5$) has a pH of ~ 8.4 .

Geotechnical characterization of the road base soil stabilization characteristics of the FBC material continued. California Bearing Ratio (CBR) determinations were performed on an Ohio soil. An 8% addition of FBC material produced a 100% increase in compressive strength and reduced natural swell of the soil by half.

Phase I

Task 6 - Data Analysis

Thermodynamic Data Base

The WATEQ program attempts to infer theoretically, given pH and ionic concentrations of water-borne ions, the active chemical species and approach to saturation of possible mineral entities through which the water has passed. During the current reporting period, WATEQ analysis was extended to a portion of the field lysimeter data. Even though data collection and analysis are not complete, sufficient data exists to make preliminary observations.

WATEQ analysis has been extended to leachate data available for field lysimeter 3 (Coolside solid waste at 49 lb./ft.^3 compaction and 37% H_2O) at levels 2 and 4. For each collection, data on the 43 aqueous species, 71 mineral species and other indicators as detailed in a previous report were gathered. Of the 71 mineral species, 28 were selected for comparison with data from a column lysimeter which exhibited like pH behavior (Coolside 300 Static Wet/Dry without additional CO_2).

Inspection of the comparisons (Figures 1-18) reveal the same relative and numeric behavior in each data set for artinite ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), calcite (CaCO_3), brucite ($\text{Mg}(\text{OH})_2$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), forsterite (Mg_2SiO_4), clinoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$ or MgSiO_3), albite ($\text{NaAlSi}_3\text{O}_8$), adularia (KAlSi_3O_8), K-mica ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$), portlandite ($\text{Ca}(\text{OH})_2$), quartz (SiO_2), laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), $\text{Ni}(\text{OH})_2$, gibbsite ($\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), Ca-Hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), otavite (CdCO_3), barite (BaSO_4), (ZnSiO_3), pyrocroite ($\text{Mn}(\text{OH})_2$), diopside ($\text{CaMgSi}_2\text{O}_6$), prehnite ($\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$), diaspore (AlOOH or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Two minerals of interest exhibit different behavior. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) shows supersaturation for a significantly greater portion of the collection period in the field lysimeter sections. This may imply that ettringite formation occurs for a much longer period than previously expected. Sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) becomes supersaturated towards the end of the field lysimeter collection period. This is a minor consideration, but dissolution of any formed sepiolite could accelerate pH decline later. Although saturation levels of brucite, calcite and dolomite remain comparable, inspection of the equilibrium diagrams (Figures 19 and 20) reveal that equilibrium conditions have shifted to favor brucite rather than the calcitic/dolomitic domains favored by the column lysimeters. This is due to both an order of magnitude decrease in available CO_2 and an order of magnitude shift of ion activity from calcium to magnesium.

Future activities

Further investigation is necessary to explain the disparate behavior of different columns and the field lysimeters. Results must be expanded to include the rest of the field lysimeter data.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Coolside 300

Static Saturated +CO₂

◄ Static Wet/Dry +CO₂

▲ Static Saturated -CO₂

► Static Wet/Dry -CO₂

Figure 20

Phase II

Task 1 Road Construction Tests

Subtask 1.2 Evaluation as a Chemical Admix in Road Base

Soil Stabilization

California Bearing Ratio (CBR) tests were performed on an Ohio soil and on the same soil modified with eight percent dry weight FBC. The tests were performed on specimens remolded near ninety five percent of maximum standard dry density and optimum moisture content. The tests were performed following ASTM procedures, except the soak time was extended until specimen swell ceased. The samples were soaked for a total of 19 days. The sample modified with FBC swelled about four percent compared to about eight percent for the natural soil. FBC and other flue gas desulfurization materials tested previously had tendencies to swell large amounts when soaked in water. Surcharge weight for the two samples was approximately 12.7 pounds Unconfined compressive strength tests were performed previously (January 1994 Monthly Report) on the same soil and at 0, 4, 8, 12, and 100% addition of FBC. Addition of eight percent FBC increased the unconfined compressive strength more than one hundred percent. Eight percent addition of FBC increased the CBR at 0.1 inch penetration from 2.07 to 5.20. Similar increases occurred at 0.2, 0.3, 0.4 and 0.5 inches as seen in Table 1. Stress versus penetration curves for the two samples are presented in Figures 21 and 22.

Table 1. Results of CBR Tests

SAMPLE ID	CBR				
	0.1"	0.2"	0.3"	0.4"	0.5"
Soil	2.07	1.64	1.46	1.33	1.28
8% FBC	5.20	5.07	4.88	4.72	4.74

Figure 21. Stress versus Penetration, 100% Soil.

Figure 22. Stress versus Penetration, 8% FBC.

Coolside Waste Management Research

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period June 1, 1994 to June 30 1994

Summary of Activity

Field lysimeter sampling continued through the period. Precipitation was significant during the period which was marked by a rainfall pattern which did not include a single major storm event. The precipitation pattern continued to require twice weekly sampling.

The monitoring of swell continued as we entered the second year for the CBR molded samples of FBC ash and pellets. The materials remained in the primary swell phase during this period.

Task 2 Geotechnical Testing Swell Tests

Monitoring of swell continued on the hydrated and non hydrated FBC ash samples. Both types are still in the primary swell phase after one year of monitoring. All samples were remolded near 95% of standard maximum dry density and optimum moisture content. The samples were remolded in CBR molds (6" diameter, 4.584" height) and swell was monitored under the following conditions:

approximately 12.5 lb. surcharge, no age time

approximately 2.5 lb. surcharge, no age time

approximately 12.5 lb. surcharge, 7 days age time

approximately 2.5 lb. surcharge, 7 days age time

Time of aging represents the amount of time before the samples were placed in water. Aged specimens were sealed at room temperature to prevent moisture loss before placement into the water tank.

Monitoring of swell also continued on two samples of FBC pellets. The pellets were loosely placed in CBR molds. Surcharge weights (approximately 2.5 and 12.5 pounds) were placed on the samples prior to saturating in water. Swell is decreasing in the sample with the 2.5 lb. surcharge and continuing to increase for the sample with the 12.5 lb, surcharge. Swell data is summarized in Figures 1 through 4.

Figure 1. Swell versus Time, Hydrated FBC Ash.

FBC ASH (Non-Hydrated)

CBR Samples 7 day Age Time

Figure 2. Swell versus Time, Non hydrated FBC Ash.

FBC ASH (Non-Hydrated)

CBR Samples, No Age Time

Figure 3. Swell versus Time, Non-hydrated FBC Ash.

FBC Pellets

Figure 4. Swell versus Time, FBC Aggregate

Phase I**Task 3 Leaching Studies****Subtask 3.2 Monitoring of Field Lysimeters (Summary of Sampling for the Quarter)**

The Coolside field lysimeter site was visited on 25 occasions during the time period of April 1 to June 30, 1994. Routine visits were made each Monday and Thursday morning. The only exception was Monday, May 30th, which was canceled due to the dry weather. Rainfall and soil moisture measurement were performed every Thursday. Rainfall exceeded 12 mm (0.5") each week except for the periods May 19 through May 26 and May 27 through June 2. Only 4.5 mm (0.18") of precipitation fell during this two week period. The total rainfall recorded at the site was 271 mm (10.68 inches), with no single event larger than 42 mm. The total sample volume through the four lysimeters was 5951 liters.

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period: July 1, 1994 to July 31, 1994

Statement of Project Objectives

Investigate chemical mineralogical and physical changes in FBC-waste pellets, to understand the importance of hydration reactions on the long-term stability aspects of the pellets.

Summary of Progress for Period.

The objective of this research program was to observe mineralogical transformations when the FBC-wastes are converted into concretes or aggregates. The main emphasis of the research program, therefore, was to examine mineral formation-, transformation-, and disintegration reactions using XRD and SEM applications and to relate the mineral reactions to long-term stability factors of the FBC-derived materials. The long-term stability of the materials cannot be guaranteed as long as there are questions concerning the mineral transformations that occur when the materials are exposed to moisture. Reactions controlling the formation, composition and disintegration of ettringite and gypsum are critical in determining the overall stability and strength of aggregates derived from the FBC material. These mineral reactions have been examined using X-ray diffraction and scanning electron microscope. The utilization of FBC waste material in engineering applications can only be successful, if the amounts and, ultimately, the rates of formation can be accurately predicted and controlled.

Pellets were produced by CONSOL in a disc pelletizer. Formation of pellets occurs by pendular and funicular bonds. The cavities of air are dispelled and replaced by water due to the mechanical forces generated as a result of the simultaneous rotation and frequent collisions of the pellets within the pelletizer. This state is referred to as capillary bonding or the capillary stage. Capillary bonding provides sufficient green pellet strength which allows the pellets to be handled and transported to the curing oven. Once the pellets are cured, they were characterized in terms of

chemical characteristics.

Sub-Task 2.2 Chemical Characterization

The pellets were characterized in terms of mineralogical composition and mineral transformations based on X-ray diffraction data. Changes are monitored before and after aging of the pellets. The information gained concerning the mineralogical and chemical changes that are observed in the aged pellets are expected to help assist in the development of an optimum mix and curing conditions necessary to produce physically stable pellets.

The main mineral ingredients of the pellets are anhydrite (CaSO_4), portlandite ($\text{Ca}(\text{OH})_2$), quartz, free lime (CaO), minor calcium carbonate (CaCO_3), and minor mullite ($\text{Al}_2\text{Si}_2\text{O}_7$). During curing anhydrite did not hydrate to spontaneously form gypsum. Thermodynamically the transformation of anhydrite to gypsum would be favored under the current curing conditions, however, the type of anhydrite that formed in the FBC unit may cause some retarded reaction mechanisms. This will be referred to as 'delayed' hydration reactions. Delayed hydration of anhydrite may be caused by various reasons, the most probable cause being the degree of crystallinity. Anhydrite crystals produced in different FBC units can exhibit different degrees of crystallinity which is a function of the operating conditions. Anhydrite crystals that react faster in the presence of moisture to form gypsum would be preferred in a pelletization operation. Fast hydration could prevent the detainment associated with hydration-related expansion. Volume gain or expansion at a late stage after the FBC material already hardened will be a detrimental step towards disintegration of the pellets.

In this study a model was developed that suggests the different pathways of hydration reactions that occur in the wetted FBC material during curing. Hydration reactions are responsible for the bulk of the expansive properties of the materials, strength gain and long term durability. Figure 1 highlights the temporal relationships among various hydration reactions. Potential swell can be subdivided into three phases. Phase I relates to the swell caused by hydration of some residual lime and can be controlled in a pre-hydration of the materials. Phase II relates to the swell caused by formation of ettringite crystals. Ettringite has been shown in XRD analyses to form very early

in the hydration of the materials (Figure 2) and its formation continues as long as there are nutrients for ettringite crystals to grow. The formation of ettringite may depend on the availability of sulfur, aluminum and silica as well as on the equilibrium pH. Greater amounts of ettringite may be formed upon addition of fly ash. Phase III relates to the swell caused by the hydration of anhydrite to gypsum. This hydration reaction may be the most difficult to predict since it strongly depends on the character of the anhydrite crystals. The model introduced in Figure 1 suggests that there exists an early time period, referred to as Δt in Figure 1, when hydrated lime and ettringite are formed as the only hydrated phases. The formation of gypsum starts after Δt and contributes to the swell of the materials. With increasing time the simultaneous formation of gypsum and ettringite continues, contributing to increased swell and also strength gain (Figure 1). The hydration model in Figure 1 further indicates that there are different types of gypsum crystals in the aged FBC pellets. Primary gypsum forms due to the hydration of anhydrite crystals and continues until all anhydrite is converted. Secondary gypsum crystals are formed during the disintegration reaction of ettringite crystals after prolonged aging (Figure 4), which will not cause expansion but rather a volume decrease due to the smaller molar volumes of gypsum compared to ettringite. Secondary gypsum formation will not cause harmful cracks and decay of the pellets.

Future work

This research indicated that it is of paramount importance to understand the reaction mechanism of the hydration of anhydrite crystals. Future research efforts should focus on determining experimentally what controls the rates of hydration.

Figure 1
Model Illustrating Hydration Reactions

Hydration of FBC material

ETTRINGITE HYDRATED LIME

SEM

151

XRD

Figure 2

Gypsum Formation 160 Day Curing Submerged in Water

SEM

XRD

Figure 3

Hydration and Aging of FBC Pellets

160 Days Curing
Submerged in Water

153 Disintegration Reaction
of Ettringite and Formation
of Secondary Gypsum

SEM

Disintegration of Ettringite to Gypsum is accompanied by a reduction of the unconfined compressive strength of the material due to a molar volume decrease.

Figure 4

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period: August 1, 1994 to August 31, 1994

Statement of Project Objectives

Investigate chemical and mineralogical variations in laboratory column lysimeters to understand the importance of hydration reactions on the long-term stability of the materials.

Summary of Progress for Period.

The objective of this research program was to observe the changes caused in solid wastes that were packed in the laboratory column lysimeters and flushed with water. The main emphasis of this research period, therefore, was to sample the solids after prolonged exposure to moisture and examine mineral transformations and disintegration reactions. This phase of study focused on the sampling procedures and will be continued using XRD and SEM applications which are expected to relate the mineral reactions to long-term changes of the materials.

Sampling of laboratory column lysimeters.

The laboratory column lysimeters were removed from the stationary wall mountings (Figure 1) and individual drill holes were placed strategically at the top, middle and bottom parts of the lysimeters (Figure 2). The plastic columns were drilled using 1/4 inch holes and the contents of the bore holes were sampled for future XRD, SEM, FTIR, and petrographic investigations. The physical conditions of the samples were reported, including graininess and moisture content. The information gained concerning the mineralogical and chemical changes that are observed in the various laboratory column lysimeters are expected to help assist in developing an improved design for new column lysimeters that will be prepared for the next research period to monitor the influence of CO₂ on the mineralogical transformations of the materials. In all, 60 samples were taken and ground for chemical analyses.

Future Work

The XRD and SEM study of 60 laboratory column lysimeter samples are presently conducted and the results will be reported as part of a comprehensive discussion of mineralogical changes and transformations in the Coolside waste materials. Results will also be compared with data gained on field lysimeters. The effects of CO₂ in the field lysimeters will be compared to the materials aged in the laboratory column lysimeters and will help design new experiments with controlled CO₂ flux.

Figure 1

Figure 2

COOLSIDE WASTE MANAGEMENT RESEARCH

Technical Progress Report

Contract No: DE-AC21-91MC28162

Report Period: September 1, 1994 to September 30, 1994

Statement of Project Objectives

Investigate chemical, mineralogical and physical changes in Coolside waste materials to determine suitability for environmentally safe disposal.

Summary of Progress

The field lysimeters were sampled bi-weekly during the period. All leachate analysis from the field is now current. An updated summary of data is planned for next month. An updated summary of the swell and compressive strength data is presented herein.

Phase II, Task 1, Subtask 1.3

Swell Tests

Monitoring of swell continued on the hydrated and non hydrated FBC ash samples. Both types are still in the primary swell phase after one year of monitoring.. All samples were remolded near 95% of standard maximum dry density and optimum moisture content. The samples were remolded in CBR molds (6" diameter, 4.584" height) and swell was monitored under the following conditions:

approximately 12.5 lb. surcharge, no age time

approximately 2.5 lb. surcharge, no age time

approximately 12.5 lb. surcharge, 7 days age time

approximately 2.5 lb. surcharge, 7 days age time

Time of aging represents the amount of time before the samples were placed in water. Aged specimens were sealed at room temperature to prevent moisture loss before placement into the water tank.

Monitoring of swell also continued on two samples of FBC pellets. The pellets were loosely placed in CBR molds. Surcharge weights (approximately 2.5 and 12.5 pounds) were placed on the samples prior to saturating in water. Swell has stopped in the sample with the 2.5 lb. surcharge and continuing to increase for the sample with the 12.5 lb. surcharge. Swell data is summarized in Figures 1 through 4.

Unconfined Compressive Strength

Unconfined compressive strength tests were performed on remolded Coolside specimens. The specimens were aged for approximately 730 days in sealed containers. Samples tested were remolded near; 1) one hundred percent of standard and modified dry density; 2) ninety five percent of standard, modified, and low energy dry density; and, 3) ninety percent of standard dry density. Results of unconfined strength tests are presented in Figure 5, 6, and 7 with previous data.

FBC Ash (hydrated) CBR Samples

Figure 1. Swell versus Time, Hydrated FBC Ash.

FBC Ash

Non-Hydrated

Figure 2. Swell versus Time, Non-Hydrated FBC Ash.

FBC Pellets

Figure 3. Swell versus Time, FBC Aggregate

UNCONFINED COMPRESSIVE STRENGTH

90% Compaction

Figure 4. Unconfined Compressive Strength versus Time, 90% Compaction.

UNCONFINED COMPRESSIVE STRENGTH

95% Compaction

Figure 5. Unconfined Compressive Strength versus Time, 95% Compaction.

UNCONFINED COMPRESSIVE STRENGTH

100% Compaction

Figure 6. Unconfined Compressive Strength versus Time, 100% Compaction.