Coolside Waste Management Research

Contract No: DE-AC21-91MC28162
Quarterly Technical Report
Report Period: January 1, 1995 to March 31, 1995

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**Coolside Waste Management Research
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Summary of Progress for the Period

Investigation continued into the similarities and differences between lab column and field lysimeters and the potential thermodynamic considerations underlying those differences. The field and column results generally supported the assumption that initially, hydration of the metal oxides to the hydroxide form will result in an initial high pH, followed at some time by calcite formation reducing the pH to around 8.5. Two of the field lysimeters showed an unexpected initial pH dip. The two lysimeters exhibiting this behavior were the least compacted. The third Coolside material lysimeter, the most compacted, maintained high pH. Comparison of pH and mineral saturation behavior of this field lysimeter with the only compacted laboratory column which gave sufficient data revealed essentially identical behavior. The field and lab column fly ash lysimeter results were also consistent. The thermodynamics indicate a large amount of available carbonate-bicarbonate buffering present during the pH transient, but the model results are suspect. The second difference between column and field lysimeters is an indication of significantly greater periods of time during which ettringite formation is favored in the field lysimeters. Thermodynamic data indicates that soluble aluminum availability controls the formation of ettringite at high pH in the leachate system.

Thermodynamic Investigations of Mechanisms Controlling Leachate Chemistry

Investigation continued into the similarities and differences between lab column and field lysimeters and the potential thermodynamic considerations underlying those differences. The column results generally supported the assumption that initially, hydration of the metal oxides to the hydroxide form will result in an initial high pH, followed at some time by calcite formation reducing the pH to around 8.5. Two of the field lysimeters showed an unexpected pH dip to around 8.5 followed by a rise to around 12, at or above that expected by $\text{Ca}(\text{OH})_2$ equilibrium. The two lysimeters exhibiting this behavior were the least compacted. The third Coolside material lysimeter, the most compacted, maintained high pH. Comparison of pH and mineral saturation behavior of this field lysimeter with the only compacted laboratory column which gave sufficient data revealed essentially identical behavior. Comparison of field and lab column fly ash lysimeters also gave no surprises.

The ionic strength of the solute appears to have a great deal of influence on the pH behavior. A comparison of ionic strength over time for the four field lysimeters shows that the lysimeters with anomalous pH behavior also have the highest initial ionic strength (Figures 1 and 3). Figures 2 and 4 are comparative data for selected column lysimeters. The three Coolside lysimeters approach the same ionic strength and about the same pH over time but the two least compacted exhibit the pH lowering during the high ionic strength period. The two possible reasons for the lack of observed pH dip in the column lysimeters are a) the dip does not occur or b) the dip occurred and corrected before leachate was initially extracted. Both scenarios could be due to the smaller column size. Additional graphic illustration of the relationship of

pH and ionic strength (Figure 5) shows a transition in behavior between ionic strengths of about 0.5 to 1. The three data sets corresponding to the fly ash lysimeter, the most compacted lysimeter and the group representing the two least compacted lysimeters can easily be seen.

Ionic strength has a direct effect on the solubility of mineral species. The saturation index $\log(IAP/KT)$ calculated by WATEQ compares the activity product of the constituent ions (IAP) with that expected at equilibrium at a certain temperature (KT). The activity of a constituent ion is its concentration (arrived at by mass balance considerations iteratively starting with the observed concentration in the solute) multiplied by an activity coefficient. The activity coefficient is 1.0 in dilute solutions. As ionic strength increases, the coefficient initially rises above 1.0, driving the equilibrium condition towards precipitation of the solid phase. As the ionic strength continues to increase above about 0.5, the increased availability of ions in solution accelerates formation of neutral aqueous complexes. The solid phase "sees" less ionic activity and the equilibrium is driven towards dissolution of the solid phase. The effective ionic strength decreases. As an example, the solubility of calcite (CaCO_3) increases by a factor of three as ionic strength increases from 0.5 to 2.0. Another effect of high ionic strength is the reduction in activity of H_2O because of polar bonding with species in solution. That portion of the water is no longer able to act as a solvent.

Ionic strength also affects alkalinity. WATEQ estimates available carbonate by correcting measured alkalinity for non-carbonate alkalinity; primarily OH^- . It is also known that other species, notably silicate forms, introduce errors in measured alkalinity. The WATEQ model predicts a significant carbonate-bicarbonate buffering

capability during the transition to lower pH (Figure 22). An additional illustration of the inverse relationship between $p\text{CO}_2$ and pH is shown in Figure 23. This is by no means certain. First, the measured alkalinity, and therefore calculated carbonate, may be significantly in error at high ionic strength. Second, inspection of the calcite saturation index reveals that the model also predicts that calcite remains supersaturated during the transition, indicating precipitation except for brief periods initially (Figure 6). It is unlikely that the carbonate is simultaneously extracted by calcite formation and readily available for buffering, although carbonate may be available via equilibrium or non-equilibrium dissolution. Additionally, the comparison of $\log(\text{ionic strength})$ vs pH (Figure 5), which shows a behavioral shift between ionic strengths of 0.5 to 1.0 and $\log(p\text{CO}_2)$ vs pH (Figure 7), which exhibits striking linearity, would most easily be explained by the direct dependence of carbonate on pH in the model calculations. A plot of linear ionic strength vs pH (Figure 8), two assumed independent entities, shows a reasonable (imperfect) linear correlation. In both ionic strength vs pH plots, one can easily distinguish the data points for the fly ash lysimeter, the compacted continuous high pH lysimeter and a single group for the lysimeters which show the pH transient. It must be concluded that the initial high ionic strength plays a major role in the initial lowering of pH, perhaps in a manner similar to the observed high buffering capacity of sea water, which has an ionic strength of approximately 1.0. This capacity may be enhanced by the diversity of ionic constituents available for the formation of neutral aqueous species.

The major species readily available from the constituent waste are Na, Cl, Ca and SO_4 (Figure 9). Cl follows the form of Na closely, and is several thousand ppm

higher initially. Minor species are Al, OH, Mg and Si (Figure 21). Cl does not readily complex with any species except the heavy metals (Pb, Cu, Zn for example).

Examination of the saturation indices for a sample of these shows a general trend for dissolution (Figure 10). Likewise, the saturation indices of common Na mineral forms indicate undersaturation (Figure 11). Some Na-aluminosilicates show regions of supersaturation but, as the equilibrium rates are low, no significant formation of these is expected. It is apparent that the major ions Na and Cl are leached directly into the solute, a major portion of the observed high ionic strength. Major hydroxide forms also show dissolution behavior (Figure 12), except occasionally at higher pH values, so that precipitation of these are not causing a pH dip.

Thermodynamically, Ca and Mg behave similarly, with mineral forms consisting of a solid solution with the substitution of Mg for Ca. The amount of substitution will initially depend upon the Ca/Mg ratio. Equilibrium diagrams show that the expected equilibrium relation between Ca and Mg forms (Figures 13-16) are very comparable to those seen in the laboratory lysimeters (Figures 17 and 18). The fly ash lysimeters have a lower Ca/Mg ratio and remain primarily within a dolomitic regime, while all others show that the equilibrium favors calcite formation, with brief instance of slight possibility of dolomite formation. The conditions under which dolomite forms are not well understood. Attempts to precipitate Dolomite under laboratory conditions have not generally been successful. It is anticipated that any dolomite seen via XRD will be due to either the process addition of dolomitic limestone or a poorly formed solid solution mixture of calcite and brucite.

Different forms of the same mineral have differing thermodynamic

characteristics. Often the least preferred thermodynamic form is the initial solid phase formed, is more soluble and converts slowly to the favored form. Examples of this are silica gel and quartz, aragonite and calcite, and anhydrite and gypsum (Figures 19 and 20). There are ranges of local environmental conditions which lead to more efficient congruent dissolution of the least favored form and simultaneous precipitation of the most favored. The primary SO_4 mineral in arid Coolside waste is anhydrite. This will spontaneously hydrate to gypsum with concomitant swell due to differing densities. Comparison of saturation indices of gypsum and anhydrite illustrate this. Note that the pH range is fairly narrow for the most efficient conversion, with anhydrite in dissolution and gypsum in formation. Excess or insufficient hydration and the resulting pH (as exhibited by the pH differences in the least and most compacted lysimeters) may control the pace of this congruent dissolution/precipitation phenomena. When both are thermodynamically likely to precipitate ($\log(\text{IAP}/K_T)$ above 0) or dissolve ($\log(\text{IAP}/K_T)$ less than 0), equilibrium formation/dissolution will still result in conversion, but at a lower rate.

A clay-like deposit was reported during sample augering in the field lysimeters. Inspection of kaolinite saturation indices indicate that clay mineral formation is possible early in the lysimeter sample period (Figures 24, 25).

While in the proper pH range, ettringite formation will be controlled by the availability of calcium, sulfate and aluminum. The second major difference in laboratory/field lysimeter behavior is the increased amount of time the thermodynamics indicate favorability for ettringite formation in the field lysimeters, as opposed to the laboratory columns (Figures 19, 20, 24, 25). Indications of the availability of the

ettringite precursor forms, gypsum, calcite and diaspore, are shown in Figures 26 and 27. Gypsum and calcite have been discussed. Diaspore (AlOOH) is the basic oxide of Al_2O_3 formed by hydration. Further hydration in high pH solutions yield $\text{Al}(\text{OH})_4^-$, the major ionic carrier of available aluminum. In the lysimeter system, there is an abundance of calcium, sulfate and OH^- , so it is possible that ettringite formation is actually controlled by the availability of soluble aluminum, with ettringite formation likely at high pH under conditions of diaspore dissolution (Figures 19,20,24-27).

Many other mineral forms addressed by WATEQ show regions of supersaturation but do not control leachate chemistry and are unlikely to be formed in any but the most minor amounts. A sample of these (Figure 28) illustrate the typical thermodynamic behaviors of these minerals. Albite is a sodium feldspar. Its saturation index has an inverse relation with pH. Diopside is a Ca-Mg pyroxene which follows pH. These are the most common behaviors seen. The mineral forms which must be suspected of having control of the leachate chemistry are those whose saturation indices remain not far from zero and do not show wild variability. This may sometimes be deceiving, as illustrated by prehnite, $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$. The saturation index shows these classic signs, but it has little to do with leachate chemistry and is unlikely to be found. Its saturation index remains positive and shows little pH effect because of a very low equilibrium rate, which makes it appear constantly supersaturated.

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

Figure 26

Figure 27

Figure 28

**Coolside Waste Management Research
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period February 1, 1995 to February 28 1995**

Summary of Activity

This report presents a summary of results from on going geotechnical testing. The long term swell data is found to be a function of prehydration, pre-aging and static loading with these factors decreasing swell. This data is congruent with considerations of the timing of mineralogic transformations, the most important of which are the formation of gypsum and ettringite. A total of 27 samples were collected during the month during five separate field excursions. Also initiated was the study of effect of Coolside leachates on the permeability of natural liners.

Task 2 Materials Characterization

Subtask 2.3 Geotechnical

Swell Tests Monitoring of swell continued on the hydrated and non-hydrated FBC ash samples. Both types are still in the primary swell phase. Swell of the hydrated ash has been monitored for more than two years, while swell of the non-hydrated material has been monitored for 654 days. 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.

There are three variables which are being investigated in the swell study: prehydration, surcharge and aging. Of these, prehydration appears to have by far the strongest impact. For example, the largest swell recorded in the hydrated samples was ~13% (Figure 1) for a non-aged low surcharge sample, while the equivalent non-rehydrated sample swelled ~38% (Figure 2). The second strongest factor is age time. For the hydrated samples, the non-aged samples expanded by factors of 50-100% more than the aged samples. Surcharge did have a noticeable impact on the non-aged samples; however, it did not have a strong impact on the aged samples. The maximum difference between the samples is almost by a full order of magnitude, ~4% for the aged rehydrated, high surcharge samples to almost 40% for the non-rehydrated, non-aged and low surcharged samples.

Mineralogic Reactions These observations are congruent with research relevant to hydration and mineralogic transformations which take place in the samples. Two phases of hydration and mineralogic transformation are recognized. The first reaction is the formation of ettringite,

This reaction is thought to occur rapidly. Schwiete and Niel investigated the growth of ettringite crystals from solution and reported that ettringite formed as early as 30 seconds after hydration, and needle-like crystals could be identified after only 4 minutes of hydration.¹ Mikhail and Abo-El-Enein suggested, based on XRD analyses of early ettringite, that after 1 day of hydration, the intensities of ettringite peaks increased, while those of the reactants tricalcium aluminate and CaSO_4 decreased.² However, at higher reaction temperatures (60°C), characteristic peaks for ettringite appear as early as 15 minutes after hydration. Muhammad, et al. found that a highly defective, but clearly identifiable ettringite formed within 3 minutes of hydration, and a

Figure 1. Swell versus Time, Hydrated FBC Ash.

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

fully developed ettringite in as little as 80 minutes.³ Our own research, as yet unreported, verified that ettringite forms rapidly; however, significant formation was found to still occur for a period of several days.

Ettringite can form either in the material voids or upon mineral surfaces. Its ability to cause expansion is a function of where it forms, with nucleation on mineral surfaces causing expansion.

The second reaction is the formation of gypsum from anhydrite,

This transformation is accompanied by a substantial increase in the molar volume. Gypsum has a molar volume of 74.2 cm³/mole, anhydrite has a molar volume of 52.3 cm³/mole. Thus this reaction results in substantial molar volume increase (+ΔV) of 42%.

The interpretation of the swell data in the light of these two equations is straightforward. The prehydration and aging of samples before they were molded allowed ettringite to form and also allowed the hydration of anhydrite to proceed. Thus these samples had the lowest expansion, due only to the completion of the hydration of anhydrite to gypsum. The non-prehydrated, non-aged samples had the highest swell because ettringite and gypsum formation took place primarily in the molds for these samples. Surcharge has the effect of forcing ettringite formation to take place interstitially. Surcharge only affected samples where ettringite formation took place in the molds, i.e. the non-aged non-prehydrated specimens. Surcharge had no effect on the rehydrated aged samples (Figure 1) because the ettringite had been fully formed before the samples were molded.

Unconfined Compressive Strength Unconfined compressive strength tests were performed on remolded Coolside specimens. The specimens were aged for approximately 730 days in sealed containers. No excess moisture was present during the aging process. 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. Unconfined compressive strengths of specimens sealed and aged at room temperature begin to increase after about 14 days age time as seen in Figures 3, 4, and 5 with data obtained previously.

The data demonstrates two unusual features relative to the geotechnical characteristics of the Coolside materials. The first is the importance of precompaction on the strength development. The lowest degree of compaction (Figure 3) achieved strengths of only ~750 psi which can be compared to highest degree of compaction (Figure 5) where strengths of ~2500 psi have been achieved. The second feature is the length of time which the compressive strengths of the materials are observed. Significant strength gains are observed for samples in the second and third year of observation.

Permeability Permeability 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. The permeability of the materials declined most rapidly during the first 60 days of the test program achieving values approaching 10^{-6} cm/sec for the 90% and 95% compacted samples (Figure 6, 7) and exceeding 10^{-6} in the samples compacted to 100% of optimum moisture (Figure 8). Percolation values which are slower than 10^{-6} can be considered practically impermeable for most purposes.

Unconfined compressive strength tests were performed on some specimens after permeability tests were completed. The tests were performed to determine the unconfined compressive strength of the Coolside material in a saturated condition. The aged Coolside material has high compressive strengths, even if saturated, after aging (Figure 9,10,11). The strength data was found to show a strong inverse relationship

UNCONFINED COMPRESSIVE STRENGTH

90% Compaction

Figure 3. Unconfined Compressive Strength versus Time, 90% Compaction.

UNCONFINED COMPRESSIVE STRENGTH

95% Compaction

Figure 4. Unconfined Compressive Strength versus Time, 95% Compaction.

UNCONFINED COMPRESSIVE STRENGTH

100% Compaction

Figure 5. Unconfined Compressive Strength versus Time, 100% Compaction.

PERMEABILITY

90% Compaction

Figure 6. Permeability versus Time, 90% Compaction.

Figure 7. Permeability versus Time, 95% Compaction.

Figure 8. Permeability versus Time, 100% Compaction

UNCONFINED STRENGTH AFTER PERMEABILITY

90% Compaction

Figure 9. Unconfined Compressive Strength, after Permeability Test, 90% Compaction.

Figure 10. Unconfined Compressive Strength, after Permeability Test, 95% Compaction.

UNCONFINED STRENGTH AFTER PERMEABILITY

100% Compaction

Figure 11. Unconfined Compressive Strength versus Time, after Permeability Test, 100% compaction.

with permeability, with decreasing permeability correlating with increasing strength. Presumably this is a function of cementitious and hydration reaction products filling and blocking pores.

Task 3 Field Lysimetry

Subtask 3.2 Field Lysimeter Monitoring

The field lysimeters were sampled on the 2nd, 9th, 15th, 20th and 23rd of February. A total of 27 samples were taken, primarily from the leachate transport tubes located at the 10 foot depth. Temperatures in the bottom of the lysimeters were at their annual low of 6 to 8° C, while recorded surface soil temperatures were in the 1 to 3° C range.

Task 4 Laboratory Leaching Studies

Subtask 4.1 Clay Liner Testing

Natural clay liner tests have been initiated with three clays and two FGD by-products. The soils being used are naturally occurring clays which meet most states' criteria for a landfill liner; that is, they have permeabilities less than 10^{-7} cm/sec when compacted. The FGD by-products are a FBC material from an electrical generating station in Pennsylvania and Coolside material from CONSOL's pilot plant, run #2. The tests are being performed by compacting the soils and FGD by-products in 3-inch diameter by 12-inch length PVC cylinders near 95% of standard maximum density and optimum moisture content. Soil #1 is a residual clay collected in Fayette County, Kentucky. Soil #2 is a glacial till collected at the Franklin County Landfill just south of Columbus, Ohio. Soil #3 is a residual clay collected from a landfill in Kentucky. Three tests consist of water moving through the compacted 12 inch soil specimens. Six tests have water leaching through six inches of compacted FBC and Coolside material and six inches of compacted clay. The tests are configured so that each clay will be subjected to leachate from each FGD material (Figure 12). Permeabilities of the clays in these six tests will be determined at the end of the leaching period (approximately 1.5 years) and will be compared to values obtained before leaching. Hopefully, this will indicate any effects that water leaching through the FGD materials into compacted clay soils has on

Figure 12. Schematic of Clay Liner Leaching Tests

Figure 13. Schematic of water tubing in Clay Liner Leachate Tests.

the permeability of the compacted soils. Two tests have 12 inch FBC and Coolside pilot plant #2 specimens.

Water is supplied from a reservoir, mounted above the specimens, through 1/4 inch OD nylon tubing connected to the samples. Silica sand is used to fill the annular space in the end cap between the tubing connection and the sample. Three way valves are located in-line between the reservoir and samples. The valves allow the water supply to be cutoff and the water remaining in the nylon tubing to be vented to atmospheric pressure. Falling head permeability tests can be performed by measuring the water elevation change with time. Permeability tests will be performed at various intervals to determine changes, if any, of the compacted materials. Details of the leachate testing setup are shown in Figures 12 and 13.

References

1. Schwiete H.E. and E. Niel, 1965, *Journal of the American Ceramic Society*, V48, p. 12-14.
2. Mikhail, R. Sh., S.A. Abo-El-Enein, S. Hanafi and R. Good, 1981, *Cement and Concrete Research*, V11, p. 665.
3. Muhammad, M.N., P. Barnes, C.H. Feniman and D. Hauserman, et. al., 1993, A Time-Resolved Synchrotron Energy Dispersive Study of the Dynamic Aspects of the Synthesis of Ettringite During Minepacking, *Cement and Concrete Research*, V23, p. 267-272.

COOLSIDE WASTE MANAGEMENT RESEARCH
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period: March 1, 1995 to March 31, 1995

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.

Preliminary data from the laboratory lysimeters packed with Coolside-waste materials were obtained during the past reporting period. Details of the construction, packing, and test matrices for the majority of these columns were described in the November 1994 monthly report.¹ In addition to the eighteen columns described in that report, four additional columns have been constructed and added to the study since that time. These four columns (LC #33-36) were included in an effort to examine the effect of prehydration on leachate chemistry in accordance with suggestions made at the January 1995 Coolside contractor's meeting in Morgantown WV.

Relevant information for all the laboratory columns packed with Coolside wastes, including those added in the hydration study, is summarized in Table 1. With the exception of columns LC #33-36, additional information is available in a prior report.¹

Table 1. Test matrix for the laboratory columns packed with Coolside waste.

lysim #	SAMPLE	Compaction	Fixed Feed	Rain simulation	Fixed double	% CO ₂	COMMENT	Dry wt (lb)	Prehydration water (% dry basis)	Column height (in)	Dry Density (lb/cu ft)
1	3000 SERIES	loose	X			0	REPEAT	2.138	40.4	24.0	49.0
2	3000 SERIES	loose	X			5.8		2.138	40.4	24.0	49.0
3	3000 SERIES	loose		X		0	REPEAT	2.138	40.4	24.0	49.0
4	3000 SERIES	loose		X		2.5	REPEAT	2.138	40.4	24.0	49.0
5	3000 SERIES	moderate	x			0		2.138	40.4	18.0	65.3
6	3000 SERIES	moderate	x			2.5		2.138	40.4	18.0	65.3
7	1000 SERIES	loose	x			2.5	DUPLICATE	1.473	40.4	16.5	49.1
8	1000 SERIES	loose	x			2.5	DUPLICATE	1.473	40.4	16.5	49.1
9	PP1	loose	x			2.5		2.138	41.1	24.0	49.0
10	PP2	loose	x			0	REPEAT	2.138	40.4	24.0	49.0
11	PP2	loose	x			2.5		2.138	40.4	24.0	49.0
12	PP2	loose	x			5.8		2.138	40.4	24.0	49.0
13	PP3	loose		x		0	REPEAT	2.138	40.6	24.0	49.0
14	PP3	loose		x		2.5		2.138	40.6	24.0	49.0
15	PP3	moderate		x		0		2.138	40.6	18.0	65.3
16	PP4	loose	x			2.5		2.138	40.4	24.0	49.0
25	PP2	loose	x				no prehydration	2.138	0.0	23.5	50.0
26	PP2	loose	x				excess water	2.138	50.0	14.5	81.1
33	PP2	loose			X	0	Hydration study	2.138	0.0	24.0	49.0
34	PP2	loose			X	0	Hydration study	2.138	15.0	24.0	49.0
35	PP2	loose			X	0	Hydration study	2.138	30.0	24.0	49.0
36	PP2	proctor			X	0	Hydration study	2.138	45.0	18.0	65.3

ADDITION OF THE HYDRATION STUDY.

Changes in leachate chemistry that can be attributed to variations in the amount of prehydration water added to the Coolside-waste samples prior to packing in a lysimeter is unknown. Therefore, columns LC #33-#36 were added to the study in an effort to determine if leachate chemistry is measurably affected by this parameter.

The four *hydration-study* columns were packed with waste material from Coolside Pilot-Plant run #2 (PP2). Lysimeter construction and sample hydration and loading were conducted in a manner similar to that previously described.¹ Equal amounts of dry PP2 sample (2.138 lb) were added to each column. Prehydration water was added at 0, 15, 30, and 45 wt% (dry waste basis) to LC #33, #34, #35, and #36, respectively. A loose packing density (49 lb/ft³) was targeted for each of the four columns. However, the physical (mudlike) consistency of the sample in LC #36 containing 45% prehydration water was such that loose compaction was not possible as the density was initially greater than 49 lb/ft³. Therefore, proctor density (65.3 lb/ft³) was chosen for this column instead. Achieving proctor density required only light tamping of the column. On the other hand, Column #33 which contained no prehydration water had to be tamped quite vigorously in order to obtain the targeted, loose-compaction density. It should be noted that even though the packing densities are different and different levels of energy were required to attain the packing densities shown in Table 1, all four columns contain equivalent amounts of dry PP2

sample and will receive the same amount of water each week.

Water addition to the hydration-study columns. Because columns #33-36 were several weeks into the study, the initial addition of water to these columns lagged that of the other columns by exactly six weeks. Furthermore, since this group of columns was added for the purpose of examining of the effects of prehydration on chemistry and flow rates, a decision was made to accelerate this particular phase of the study by doubling the amount of water added each week over that added to the fixed feed columns, i.e., 93.0 vs 46.5 mL/week.

PRELIMINARY RESULTS

Due mostly to the manner in which water has been added to the laboratory columns, little analytical data are available at this time. Unlike the preliminary column-leaching study in which the columns were maintained under saturated conditions from the start, for this study, a predetermined amount of water is being added to each column each week beginning with week #1. What this means is that for most of the columns, breakthrough of the water being added did not occur for several weeks into the study. Even now, 15 weeks into the study (9 weeks for columns #33-36 at double additions), several of the columns have yet to pass a significant amount of leachate water. In addition to the problem of not having leachate samples available for several weeks into the study, the sheer volume of data that has since been generated has generated in a backlog of data awaiting processing and computer entry. This is in spite of

the fact that the analyses are being conducted within a reasonable period (1-2 days) for those columns which are now flowing.

Column flows.

As described in the November, 1994 report,¹ water was added to the laboratory lysimeters in one of three manners. The majority of columns referred to as *fixed-feed* columns received a fixed amount of water weekly, 46.5 mL. Water was added to a second set of columns (#'s 3, 4, 13, 14, and 15) in amounts which matched the rainfall measured at a weather station located near the field lysimeter site. At the end of a twelve month period, the cumulative amount of water added to these *rain simulation* columns should be equal to the amount of water added to the fixed-feed columns. The third set of columns (LC #33-36; *hydration study*) receive exactly twice as much water per week (93.0 mL) as do the fixed feed columns.

Flow rates through the fixed-feed columns. The rates of water flow through the fixed-feed columns are shown in Figure 1. Flow through those columns that were loosely compacted are shown separately (top) from that of the moderately compacted columns (bottom). As can be seen, none of the columns exhibited flow until at least the second week of collection. Two of the loosely compacted columns, #8 and #16 have yet to exhibit significant flow. However, the majority of these loosely-compacted, fixed-feed columns have begun to flow freely thereby providing sufficient sample for the full suite of analyses. Although all three of the moderately-compacted columns have begun to flow, the water passing through these columns tended to lag

Figure 1. Flow rates through columns receiving a fixed amount of water (46.5 mL) each week. Top-flow through loosely compacted columns; Bottom-flow through moderately compacted columns.

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behind that of the loosely compacted columns both in terms of the initial breakthrough and the average rate of flow following breakthrough. Due to the relatively high concentrations of ions in the leachate waters that are present early in the study, the small sample size has generally not been a problem in terms of generating sufficient sample for analysis. However, as ion concentrations decrease with time, we will soon be compelled to combine the leachate from two or more weeks collection to obtain adequate sample if the column flow do not improve.

Flow through the Coolside 3000 series samples is shown in the top of Figure 2. As shown in Table 1, these columns represent both loose and proctor compaction as well as both fixed-feed rates and rain simulation. An analogous plot for LC #7 and #8, packed with Coolside 1000 samples, is shown on the bottom of Figure 2. These latter columns were prepared as duplicates in an effort to examine the reproducibility of the results from the laboratory lysimeters. However, flow through these two columns has, to this time, been radically different. LC #7 exhibited breakthrough at week #11 which was followed in week #12 by a relatively large slug of leachate water. In contrast, LC #8 has exhibited only minimal flows thus far. As additional data becomes available, it will be interesting to follow the trends in ion concentrations for these two columns to determine if such trends follow similar patterns despite obvious differences in the interval of breakthrough and the overall volume of flow.

Rain simulation flow rates. Water flow through the five rain-simulation columns is shown in Figure 3. The first breakthrough for this set occurred for column 3 during the third week of collection followed by column 4 the following week. Both of these columns are packed with

Figure 2. Flow through the lysimeters packed with Coolside 3000 (top) and Coolside 1000 samples (bottom).

Figure 3. Water flow through the rain-simulated columns.

Figure 4. Water flow through the hydration-study columns.

Coolside 3000 samples and both are tracking water feed reasonably well at this time. The remaining three columns, which are packed with FGD wastes from Pilot Plant run #3 (PP3), have exhibited no or minimal flow to date.

Flow rates in the hydration-study columns. Flows through the four columns (LC #33-36) that were added for the hydration study are shown in Figure 4. Even though these columns receive double the amount of water as the fixed-feed columns, breakthrough did not occur until week 7 for LC35 (30% prehydration water) and week 8 for LC34 (15% prehydration water). Columns 33 (0%) and 36 (45%) have yet to flow. Due to the relatively high rate of water feed, a standing head of water can be observed above all four of these columns with the height of this water column increasing steadily from LC 33 to LC 36.

In addition to columns 33-36, columns 25 and 26 were included in the original set of lysimeters in an effort to examine the effects of hydration. These two columns are also packed with wastes from PP2 (as are LC #33-36) but receive only half the amount of feed water each week (46.5 mL) than LC #33-36. The FGD waste loaded to LC #25 was not prehydrated whereas LC #26 was packed after addition of prehydration water to 40% by weight (dry basis). Leachate flow through these two columns is shown in Figure 5. Although small quantities of water were collected during week 2 for both columns, no water flow has been measured since week 5. For LC #26, the water collected is believed to originate from excess prehydration water. The 0.2 mL collected from LC #25 during week 2 likely originated from the sand layer at the bottom of the column which was wetted prior to packing. As with LC #36, there is a significant water covering

Figure 5. Water flow through LC25 (no prehydration) and LC26 (40% prehydration).
over LC #26. LC #25 appears to be simply soaking up the added water at this time.

ANALYSES OF LEACHATE WATERS

pH. Thus far, pH values have typically ranged from about 11.6 to 12.8 for all columns packed with Coolside wastes with the exception of those columns (LC 13-15) packed with materials from Pilot Plant #3. These latter have ranged from about 9.5 to 11.5. However, due to the low flow rates through these latter columns to date, it is uncertain if the pH values will remain relatively low or increase as larger volumes of water pass through these columns. pH values are shown in Figure 6 for columns packed with FGD wastes from Coolside 3000 (LC1-6), PP run #2 (LC10-12), and PP run #3 (LC13-15) wastes.

Figure 6. pH values for leachate waters from columns packed with Coolside 3000 (top), PP run #2 (middle), and PP run #3 (bottom) wastes.

Selected results for columns packed with Coolside 3000 and Pilot Plant 2 wastes.

Similar to the results from the preliminary laboratory-leaching studies, sodium and potassium are the major cations and chloride and sulphate are the major anions being removed from the Coolside wastes at this early stage of the study. Calcium concentrations are relatively low at this time (<200 ppm) but appear to be increasing as the concentrations of Na and K decline. These ions are plotted on the following pages for columns 1-6 (Coolside 3000) and for columns 10-12 (PP #2) for which the most complete sets of analytical data are currently available.

Sodium is the most prevalent cation for both sample sets ranging up to 3% of the leachate water for the PP2 columns versus about 2% for the Coolside 3000 samples. The concentration of the second and third most prevalent cations, K and Ca, are about twice as high in the leachate from the Coolside 3000 columns than from the PP2 columns. Sulfate ($\text{SO}_4^{=}$) is by far the dominant anion in the leachate from the PP2 columns. This anion ranges up to about 48,000 ppm which is about four times as high as in the leachate from the Coolside 3000 columns. Chloride is the most prevalent anion in the leachate waters from the Coolside 3000 columns ranging from about 10,000 to 38,000 ppm. This is in contrast to an approximate range of 400 to 1,400 ppm Cl^- measured in the leachate from the PP2 columns.

Alkalinity and conductivity data are plotted for the same two sets of columns in Figure 11 and Figure 12, respectively. The alkalinity of the leachate from the PP2 columns is substantially

Figure 7. Concentrations of the major cations (Na-top, K-center, Ca-bottom) in the leachate from columns 1-6 (Coolside 3000).

Figure 8. Concentrations of the major cations (Na-top, K-center, Ca-bottom) in the leachate from columns 10-12 (Pilot Plant run #2).

Figure 9. Concentrations of the major anions (Cl-top, SO_4 -bottom) in the leachate from columns 1-6 (Coolside 3000).

Figure 10. Concentrations of the major anions (Cl-top, SO₄-bottom) in the leachate from columns 10-12 (Pilot Plant run #2).

Figure 11. Alkalinity of the leachate from columns packed with Coolside 3000 (top) and Pilot Plant #2 (bottom) wastes.

Figure 12. Conductivity of the leachate waters from columns packed with Coolside 3000 (top) and Pilot Plant #2 (bottom) wastes.

greater than for the waters from the Coolside 3000 samples. Both alkalinity and conductivity for both data sets appears to be dropping rapidly as one would expect as highly soluble anions and cations are rapidly depleted.

SUMMARY

In addition to the data presented in this report, additional analyses are being conducted including analysis of 23 additional cations and dissolved solids (on selected samples). Suffice it to state that none of the additional data collected thus far demonstrates a reason for alarm. These data will be summarized in a later report. It is still too early in the study to attempt to understand the full impact of compaction, method of water feed, or the addition of gaseous CO₂ to selected columns.

The most significant finding presented in this report is that the majority of the 22 laboratory lysimeters packed with Coolside waste have begun to flow. Thus, at least one significant hurdle in this particular phase of the Coolside study appears to be no longer a reason for concern.

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