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Coolside Waste Management Research

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**Coolside Waste Management Research
Technical Progress Report
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Summary of Activity

The report represents a summary of results from mineralogical studies of the field lysimeter samples. This part of the project is an ongoing task to understand the long term mineralogical reactions that occur in the lysimeters as a function of static loading (compaction) and moisture content. The data is congruent with results obtained from geotechnical characterization of pre-aged and non-aged Coolside samples with and without surcharge. The investigations are expected to aid in the understanding of the processes that control permeability and leaching potential of the materials.

Task 2 Solid Waste Characterization

Subtask 2.2 Chemical and Mineralogical Analysis of Material

Lysimeters #1, #2, and #3, which contain Coolside solid waste, were subjected for the second time to a drilling of bore cores with the main objective being to investigate the variability in mineralogy with increasing depth. The results of the first set of bore cores were described as part of the Technical Progress Report for the period: December 1, 1993 to December 31, 1993. Variations in packing densities and moisture contents for the Coolside waste placed in the field lysimeters are such that Lysimeter #1 was filled with Coolside waste with no compactive effort (loose state). The material was thoroughly blended with water to a target value of 37 % moisture. The Coolside waste material in Lysimeter #2 was compacted at 41 lb/ft³ with 37% moisture, while that placed in Lysimeter #3 was compacted at 66 lb/ft³ with 40% moisture. Based on results from the lab lysimeters, the differences in packing densities in the field lysimeters are expected to impact the mineralogy of the systems upon aging, as increased perk will accelerate the leaching potential and hence, the transport of dissolved ions in the lysimeters downwards.

Sampling Procedures: Drill cores were obtained driving a 1" metal pipe into the lysimeters. Prior

to reaching the desired depth, the Coolside material was discarded. Once the desired depth profile was reached, the Coolside material was saved for chemical analyses. Samples in all lysimeters were taken at 3" depth, 6-8" depth and 16-18" depth.

Analyses: The XRD data indicate that no anhydrite remained in the leached lysimeters (Figures 1, 2 and 3). Similarly, the gypsum diffraction peak intensities, which were recognized in the samples analyzed in December 1993, had completely vanished, indicating that dissolution of the sulfate phase must have occurred in all Coolside lysimeters at least up to a depth of approximately 16-18", independent of differences in packing densities amongst the lysimeters.

Differences are recognized for the relative amounts of ettringite at each sample depth (Figures 1, 2, 3). This is consistent with the data obtained during earlier sampling periods for all field lysimeters. In Lysimeter #1, which had loose compaction, differences in the amounts of ettringite crystals as a function of lysimeter depth are indicated in Figure 1. In Lysimeter #2, which had compacted waste (41 lb/ft³), a similar trend has been noticed; however, the differences in ettringite abundance are much less pronounced when compared to the differences in Lysimeter #1. With increasing degree of compaction of the Coolside waste in Lysimeter #3 (69 lb/ft³), samples obtained at 3" and 18" depths show almost no differences in the amounts of ettringite crystals formed. These results suggest that the degree of compaction must impact the exchange of dissolved ions that are necessary for ettringite formation. This is reflected by differences in the ettringite growth rates and migration of the minerals downwards in the lysimeters. These results are no surprise to this study, as similar results were obtained in earlier laboratory investigations focussing on swell characteristics of the Coolside materials (caused by continued growth of ettringite crystals) with and without surcharge. Field Lysimeter #4 contained fly ash and served as a comparison to lysimeters 1-3. Figure 4 indicates that no mineralogical reactions occurred with increasing depth in field Lysimeter #4.

Portlandite ($\text{Ca}(\text{OH})_2$), which buffers the pH of the pore solutions so that it is at or near the stability of ettringite, was only a minor constituent in the samples obtained earlier (December 1993) and has not been recognized in either of the three field lysimeters during this sampling

period. Nevertheless, ettringite crystals are abundantly present in the upper two feet of the lysimeters. In general, it is assumed that ettringite crystals are only stable within an environment that is characterized by pore fluids at or near the pH equilibrium conditions for ettringite (pH ~12). The pH analyses of leachate for the three lysimeters are buffered near a pH of ~12. It may not be suitable to use the pH values obtained from leachates at the 10 foot depth level, as at greater depths within the lysimeters portlandite probably will not have been consumed in the mineralogical (hydration) reactions and may control the pH of the pore fluids. The results from this study indicate that ettringite may be more resistant to disintegration caused by environmental changes than may be gathered by comparing its thermodynamic stability field.

Calcium carbonate in the lysimeter samples did not increase relative to the earlier tests, suggesting that ettringite decay did not result in a significant recarbonization of the lysimeters. However, scanning electron microscopy (SEM) microphotographs of the ettringite crystals taken from the lysimeters indicate that the crystal morphology is very prism-like (Figure 5). It is, therefore, suggested that partial substitution of carbonate for sulfate must have occurred in the ettringite crystal lattice. Substitution of sulfate by the carbonate group typically results in a thickening of the crystal morphology. A solid-solution between the endmembers ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$) and thaumasite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O}$) in the field lysimeters is suggested by a more blocky morphology of the ettringite crystals which was identified in SEM investigations of the materials (Figure 5).

Anhydrite is relatively more soluble compared to gypsum. Dissolution of anhydrite supersaturates the pore fluids with respect to gypsum.

The solubility of anhydrite (CaSO_4) at 25°C is $K_{\text{sp}} = 4.2 \times 10^{-5}$, while that of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is $K_{\text{sp}} = 2.5 \times 10^{-5}$. The equilibrium constant for the conversion of anhydrite to gypsum is:

$$\begin{aligned}\log K_{\text{sp}(\text{anhy})} &= -4.38 \\ \log K_{\text{sp}(\text{gyp})} &= 4.60\end{aligned}$$

$$\log K = 0.22$$

Hydration of anhydrite rapidly leads to the formation of "primary" gypsum, which is used up in the ettringite formation in the lysimeters. This hydration reaction is not a solid state replacement, but a dissolution-reprecipitation reaction where the dissolving anhydrite crystals act as nucleation surfaces for the gypsum crystals. Secondary gypsum, on the other hand, may precipitate anywhere in the system wherever the concentration of Ca^{2+} and SO_4^{2-} ions is sufficient to exceed the gypsum solubility product. The field lysimeter results support earlier interpretations that gypsum is completely consumed in the formation of ettringite. Additional Ca^{2+} ions for continuous formation of ettringite may be supplied in the dissolution of $\text{Ca}(\text{OH})_2$.

Ettringite and gypsum crystals compete for the available nutrients Ca and SO_4 . In the case of ettringite formation that occurs concurrently with that of gypsum formation, the rate-limiting step in the precipitation reaction is not the availability of sulfate ions, but rather the availability of aluminum ions. In the right pH buffered environment, ettringite growth at the expense of gypsum is favored. Aluminum ions are supplied by the dissolving fly ash spheres. However, the mobility of dissolved aluminum ions in the pH-buffered solutions (pH ~12 due to $\text{Ca}(\text{OH})_2$ buffer) is only small, suggesting that transport of the Al ions in pore solutions may control the location where ettringite needles will form. Transport of nutrient-rich solutions are strongly dependant on the packing densities of the materials. This is, in part, one of the reasons why the different field lysimeters show differences in the amounts of ettringite present.

Ideally, ettringite precipitates on, or in close proximity to, Al-rich surfaces. The dissolution of the glassy Si-Al spheres may be compared to the solubility of crystalline aluminum silicate phases, but probably occurs more briskly than that of the latter. Dissolution of the fly ash surfaces may occur incongruently due to the extremely high pH conditions of the system (Stumm and Morgan (1981). The dominant aluminum hydrolysis species under high pH conditions is $\text{Al}(\text{OH})_4^-$. The dissolution of the glassy spheres and that of some quartz crystals controls the upper limits of dissolved aqueous silica. Under the highly alkaline conditions the solubility of SiO_2 becomes enhanced because of the formation of monomeric and multimeric silicates. Lagerstrom (1959) and Ingri

(1959) indicated that multinuclear species such as $\text{Si}_4\text{O}_2(\text{OH})_6^{2-}$ are present in the solution phase, while under slightly alkaline conditions only $\text{Si}(\text{OH})_4$ species occur. Under local equilibrium, Al-Si-rich gels may precipitate from the solution phase, providing additional nucleation surfaces for ettringite crystals.

Because of the availability and mobility of dissolved silica, ettringite in this system is expected to substitute various amounts of Si in its crystal lattice. However, the XRD analyses in this study are not suitable for determining the degree of Si-substitution. This should be investigated in detail in a separate study, as the degree of Si-substitution may impact on the stability of the ettringite crystals.

Initiation of New Study In order to both verify results of the kinetic study thus far, and to gain better control of the experimental variables, a kinetic study was initiated. In this study the sample preparation involved controlled curing conditions. It is expected that changing concentrations of dissolved species and fluctuations in solution pH govern the hydration reactions. The main objective of this new study, therefore, was to precisely control the solution:solid ratio, as it may influence the rates of reactions as well as the type of mineral formation. In the previous study, all samples were placed in a common water bath with a relatively high solution:solid ratio. Upon aging of the sample molds and extraction of individual molds from the water bath, the solution:solid ratios continuously changed as did the equilibrium conditions. To better understand the aging processes that might occur in an emplacement situation with relatively constant free available moisture, the solution:solid ratios of the experiments were kept the same for all samples by preparing individual sample containers (jars). The Coolside material was pre-hydrated with 12 percent (by weight) water. The material (690 g) was then thoroughly mixed with 310 g of water (31% of total weight) and packed into 2.65 cm sections of 2.05 cm diameter pvc pipe. These small cylinders were placed individually into polypropylene jars, and 50 ml of distilled water were added to cover the samples. The jars were then sealed with screw-type plastic lids to prevent evaporation. X-ray diffraction and thermogravimetric analyses will be conducted on these samples every day for two weeks, followed by increasingly longer intervals for one year.

Prior to XRD and TGA analyses, the hydrated Coolside material plus pvc mold are first weighed, followed by extrusion of the solids from the mold and weighing of the pvc alone. These weights, along with the known added moisture, will facilitate the calculation of water:solid ratio for each sample. The pH of the water is then measured, followed by filtration and collection in a 50 ml glass vial, which is subsequently sealed with a foil-lined screw-type lid. The solid (approximately 15 - 16 grams) is then ground in a mortar and pestle, and returned to the polypropylene container.

X-Ray Diffraction (XRD) Approximately 2 grams of material is sampled from the container for x-ray diffraction analysis. As a semi-quantitative standard, 5 wt% TiO_2 is added prior to final preparation. The Coolside material plus standard are then thoroughly ground in an agate mortar and pestle. The diffraction analysis is obtained with a Philips APD 3500 x-ray diffractometer, using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ nm}$), a scan speed of two counts/second, an increment of 0.1° , over a 2θ range from 7 to 40° .

Thermogravimetric Analysis (TGA) Approximately 50 to 100 mg of material is obtained for the TGA analysis. The analyzer is a TA Instruments Hi-Res 2950 TGA interfaced with a P.C., and has been programmed to measure weight loss from 50°C to 900°C . Ettringite, gypsum, and Portlandite dehydrate over this temperature range, and calcite decomposes to calcium oxide and CO_2 .

As of this reporting period, the experimental setup has been completed, as have the initial XRD and TGA analyses. Results from the first 4 months of this kinetic study will be presented in the next reporting period.

Ingri, N. (1959) *Acta Chem. Scand.*, 13, 758

Lagerstrom, G. (1959) *Acta Chem. Scand.*, 13, 722.

Stumm, W. and Morgan, J.J. (1981), *Aquatic Chemistry. An Introduction Emphasizing Chemical*

Equilibrium in Natural Waters, 2nd Ed. John Wiley & Sons, New York.

Figure Captions for Figures 1-4

Abbreviations are as follows: ET = ettringite; Q= quartz; Mu= mullite; Ca= calcium carbonate; H= hematite; Rt= rutile (internal standard).

Figure 1

Samples from three different lysimeter depth profiles from Field Lysimeter #1 are compared with respect to their mineralogical changes. Sample depth corresponds to 3", 6-8" and 18" depths within the lysimeter. X-ray analyses of the samples are plotted as a function of peak intensities. Results indicate that ettringite crystals become more abundant at greater lysimeter depth. There appears to be a small decrease in the amounts of quartz and calcium carbonate with increasing depth. Carbonization is expected to start at the top level of the lysimeter. Lysimeter #1 was loosely packed with Coolside material.

Figure 2

Similar to Figure 1. Lysimeter #2 was compacted at 41 lb/ft³. Results indicate smaller variations in the amounts of ettringite as a function of lysimeter depth when compared to the non-compacted Lysimeter #1. Calcium carbonate in Field Lysimeter #2 shows almost no variations with lysimeter depth.

Figure 3

Field Lysimeter #3 contained Coolside material that was compacted at 69 lb/ft³. The higher compaction appears to have affected the amounts of ettringite crystals that were able to form at greater lysimeter depth. When comparing the peak intensities for ettringite at 3", 6-8", and 16-18" lysimeter depths, it becomes evident that precipitation rates must have been very similar throughout the lysimeter depth profile. Quartz and calcium carbonate show similar trends in Lysimeter #3 compared to the other lysimeter samples.

Figure 4

Field Lysimeter #4 contains fly ash. The x-ray diffraction results of samples from 3", 6-8" and 16-18" depths show no variations in the mineralogy of the materials.

Lysimeter #1

— top 3" --- 6-8" 18"

Figure 1

Lysimeter #2

— top 3" ---- 6-8" 16-18"

Figure 2

Lysimeter #3

— top 3" --- 6-8" 16-18"

Figure 3

Lysimeter #4

Figure 4

FIGURE 5 illustrates ettringite crystals observed in a scanning electron (SEM) microscope. The ettringite crystals infill available porespace in Lysimeter # 2. The sample was derived from 6-8 inches down in the lysimeter. The typical needle-like morphology of ettringite can be recognized for a small number of crystals, while the majority of the crystals have adopted a more prism-like shape. This change in crystal morphology is expected to be caused by partial substitution of the sulfate ions by a carbonate group.

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

The capacity of various FGD wastes to absorb CO_2 has been recently investigated with the results summarized in this report. Waste samples were evaluated in both a hydrated-solid form and mixed with water to form an aqueous slurry. This study represents a continuing effort to identify and evaluate potential commercial applications as such utilization would benefit from both a plentiful low-cost raw material and significant savings in disposal costs. The potential usage investigated here is for the removal of CO_2 from multi-component gas streams, in particular, natural-gas streams. There also appears to be a potential to remove H_2S in a like manner. However, only preliminary results from the study of H_2S absorption by FGD wastes are available at this writing. Assuming favorable findings, a more complete report of these latter results will appear in a subsequent report.

INTRODUCTION.

Over the past decade, numerous FGD units have been or will be added to existing utility boilers in an effort to satisfy federal mandates on SO_2 emissions. Because FGD wastes, particularly dry FGD wastes, have not gained wide acceptance for commercial applications, less than 6% of the ~20 M tons of FGD wastes generated in 1993 (the most recent year for which figures are available) were utilized commercially.¹

As is well established, the lime (or limestone) used to scrub SO_2 in a dry process such as Coolside is not fully sulfated during utilization. That is, a portion of the Ca fed to the unit exits as CaO or $\text{Ca}(\text{OH})_2$. The fraction of available Ca can be quite high ($> 1/3$) depending on scrubber design and operating conditions. When hydrated, such wastes exhibit a strong affinity to absorb CO_2 at ambient temperature. Further, this absorption is both rapid and near complete as will be shown in this study where CO_2 initially at ~2.5 volume% was rapidly reduced to below the detection limit of the measurement device (ppm range) being used.

The work described here represents a preliminary examination of the capacity of dry-FGD wastes to remove CO_2 from multi-component gas streams. Such an absorbent may have numerous commercial uses, e.g., gas purification, removal of CO_2 during H_2 production, etc. However, the current study focuses on the potential to remove CO_2 from natural gas at the well-head. As a rule of thumb, the costs associated with currently available CO_2 -removal technologies (wet scrubbers, molecular sieves, membranes) are prohibitive for gas wells that produce less than about 100,000 SCF/day.² This effectively eliminates commercial CH_4 production from low-porosity, carbonate-containing strata common to many gas-producing deposits. Thus, it is hoped that a low-cost CO_2 absorbent that can be safely disposed or marketed (road base or fertilizer) may have applications in the natural-gas industry.

The CO₂ absorption capacity was evaluated for waste samples generated from four different utility boilers, the Coolside demonstration plant, and the four Coolside pilot-plant runs. With the exception of one of the utility-derived fly ashes that was used as a control (non-FGD waste), all samples examined are dry-FGD waste materials. Absorption capacity was examined for both hydrated-FGD samples as well as aqueous slurries prepared with FGD wastes. Three standard gas blends containing N₂/Ar/CO₂, Ar/CO₂/CH₄, and Ar/CO₂/CH₄/H₂S were used in this evaluation. The leaching behavior as well as changes in the mineralogy of the waste samples exposed to CO₂ were also examined.

EXPERIMENTAL.

Absorption Reactor. A schematic of the absorption reactor as configured to measure CO₂ absorption for the hydrated samples is shown in Figure 1 (shown with 4" X 3/8"-i.d. tube reactors). This is essentially the reactor described in earlier adsorption/cracking studies of liquid hydrocarbons³ with some modification. The more significant modifications include the introduction of standard gases containing CO₂/Ar, CO₂/CH₄/Ar, or H₂S/CO₂/CH₄/Ar via the entry line in which pure Ar was previously metered, plugging of the liquids inlet, use of 4" X 3/8"-i.d. reactors in addition to the 9" X 1/4" reactors (most of the hydrated-sample tests), and placement of the 4" reactors in a vertical alignment to provide a more uniform flow of gases through the hydrated samples.

Essentially the same measurement system was used to measure absorption of CO₂ by the aqueous slurries containing FGD waste except that a pair of 250-mL-capacity gas scrubbers constructed of glass were substituted for the stainless-steel tube reactors. A schematic of the absorption reactor for the slurry tests is shown in Figure 2.

Figure 1. Schematic of the absorption reactor used for the hydrated-waste experiments.

Figure 2. Schematic of the absorption reactor used for the waste-slurry experiments.

Samples. Some of the study samples examined were obtained from commercial utilities that preferred to remain unidentified. Thus, only cursory descriptions of these samples are given, without identifying the source.

A total of 11 samples were investigated. A very brief description along with the identification label used in this report is given in Table 1. The fly ash utilized as a control (L-FA) is a Class F fly ash from a pulverized-coal-combustion (PCC) utility boiler operating on bituminous coal. The fluidized-bed combustion materials (FU-FA/BA and CC-FA/BA) were derived from circulating or entrained flow units operating on high-sulfur bituminous coal. The coarse material (BA, i.e. bed ash) was drained from the bed while the finer material (FA, i.e. fly ash) represents cyclone and baghouse catch. These samples differ primarily in particle size and the relative proportions of free lime. Two types of dry, post-combustion flue-gas scrubber material were utilized in the study, a spray-dryer ash from a large industrial boiler in the Midwest, and materials from the Coolside duct-injection technology.

Table 1. Waste samples examined.

Sample id	FGD Waste	Free CaO (wt%)	Source
L-FA	N	2.7	Utility-Boiler Fly Ash
FU-FA	Y	19.5	Fluidized bed-cyclone/baghouse
FU-BA	Y	26.8	Fluidized bed-bed ash
SD	Y	5.8	Utility spray dryer
CC-FA	Y	8.6	Fluidized bed-cyclone/baghouse
CC-BA	Y	21.2	Fluidized bed-bed ash
PP1	Y	12.9	Coolside pilot-plant waste
PP2	Y	9.1	Coolside pilot-plant waste
PP3	Y	8.5	Coolside pilot-plant waste
PP4	Y	19.9	Coolside pilot-plant waste
CS	Y	6.5	Coolside Demonstration plant

*FA-Fly Ash; BA-Bed Ash

The Coolside materials include a sample identified as CS that was generated in Ohio Edison's 1990 demonstration of the technology at its Edgewater power plant⁴ (series 3,000 sample) as well as materials derived from the CONSOL's Coolside pilot plant in Library, PA (identified as PP1-PP4).⁵ These are the same samples that have been the focus of extensive study under the Coolside Waste Management Research program.

Run Conditions and Procedures. All absorption measurements were made at ambient temperature. Nominal gas flows of 100 mL/min (ambient temperature) for the hydrated-solids tests and 150 mL/min for the slurry tests were metered through each reactor. The gas streams were comprised solely of N₂ in the bypass line and a standard-gas blend in the absorbent line. The gas blends examined were as follows:

<u>Gas mixture</u>	<u>Concentration-vol%</u>
Ar-CO ₂ -He	7.5--2.5--90.0
Ar-CO ₂ -CH ₄	30.3--49.6--20.1
Ar-CO ₂ -CH ₄ -H ₂ S	25.1--35.0--34.9--5.0

Argon was included in all mixtures as a tracer gas to eliminate measurements problems associated with minor leaks or instrument drift.

Hydrated samples of known water content were obtained by carefully blending measured quantities of distilled water and dry waste inside of a nitrogen-purged glove bag. Between 2 and 5 g of the hydrated samples were then packed to the absorbent reactor between quartz-wool plugs. The bypass reactor was packed with 6 g of Ottawa sand.

For the slurry absorption experiments, ~5 g of dry sample was added to 200 mL of distilled water in a 250-mL gas scrubber. The waste slurry was stirred with a magnetic stir bar

for the duration of the experiment. The bypass scrubber contained distilled water only (200 ml).

For both the hydrated waste and waste slurry experiments, the exit streams from both the bypass and sample reactors were combined prior to analysis. A portion of the combined exit stream was continuously sampled and routed to the inlet of a VG-quadrupole mass spectrometer (QMS). This unit was operated in a selected-ion-monitoring mode in which intensities for m/e 18- H_2O^+ , 20- Ar^{2+} , 28- N_2^+ , 40- Ar^+ , 44- CO_2^+ , and 15- CH_3^+ (for methane) were recorded at approximately 1-second intervals.

For both experimental setups, data collection was initiated with the switching valve in the bypass position, i.e., with the CO_2 stream passing through the bypass reactor. After a minimum of 150 data points were collected (usually 2-4 minutes), the valve was rotated so that the CO_2 stream was switched to the absorbent reactor and the N_2 stream was simultaneously switched to the bypass reactor. After a selected exposure interval, the valve was returned to the initial position to reestablish the QMS baseline.

Following data collection, the QMS data were imported to a spreadsheet where the molecular-ion signal for CO_2 (m/e -44) was ratioed to the Ar-ion signal (m/e -40). The curves described by the CO_2/Ar ratio were then numerically integrated over the interval during which CO_2 was routed to the absorbent reactor to determine the fraction of the CO_2 absorbed. Since both gas-flow rates and sample weights were known, the fraction of CO_2 absorbed could be calculated to an absolute basis then expressed as standard cubic feet (SCF) of CO_2 absorbed per ton of waste assuming ideal gas behavior. For those runs in which H_2S was also routed through the reactor, the QMS signal for H_2S was treated in a manner identical to that described for CO_2 .

Several of the hydrated samples were retained in sealed vials for post-run XRD analysis to investigate changes in mineralogy resulting from CO_2 and H_2S absorption. Likewise, selected

slurry waters were subjected to ICP analysis to determine the concentration of heavy metals/cations extracted by the slurry waters.

RESULTS

A plot of the CO_2/Ar ion-intensity ratios during a test of hydrated waste is shown in Figure 3. In this run, the Ar/CO_2 blend (2.5% CO_2) was initially flowed through the sand-packed bypass reactor, switched to the absorbent bed packed with hydrated FU-FA at 3 min, returned to the bypass reactor at 53 min, then again to the absorbent reactor 3-min later.

The plot in Figure 3 illustrates two points. First, this test demonstrates both the rapid kinetics and the extent to which CO_2 was absorbed in the 9" reactor. Second, it provides an indication of the reproducibility of the QMS response during the two bypass- and the two expose-mode intervals.

A more typical run, also conducted in the 9" reactor with 2.5% CO_2 and FU-fly ash, is shown in Figure 4. This latter plot demonstrates how the QMS signal that is recorded as the CO_2 passes through the bypass reactor (before and after the valve switch) provides a suitable baseline for integration of the ion intensities recorded during passage of CO_2 through the absorbent bed. Thus, by integrating the area under the line defined by the signal recorded before and after exposure then comparing that to the area under the curve obtained during exposure, one can determine the fraction of CO_2 that was absorbed by the waste sample over the exposure interval. Since the flow rate of CO_2 and the weight of the FGD waste are known, this fractional absorption can be converted to an absolute basis and expressed as SCF of CO_2 absorbed/ton of waste.

Hydrated FU-Fly Ash (2.9g dry sample; 24.6% H₂O)

Figure 3. CO₂/Ar ion-ratio response curve as the gas blend is routed through a) bypass reactor, b) absorbent reactor, c) return to bypass reactor, and d) return to absorbent reactor.

1.5g dry FU-FA; 24.4% H₂O

Figure 4. CO₂/Ar-ion ratios during run with FU-fly ash in 9" reactors (1.5 g dry FU-FA; 0.58 g H₂O; 2.5 mL/min CO₂).

Figure 5. Absorption of CO₂ by hydrated wastes as a function of hydration.

Absorption by hydrated solids. Absorption of CO_2 is shown in Figure 5 as a function of the amount of added water. The data in these plots were obtained from runs in which CO_2 was flowed (49.6% CO_2 ; ~100 mL/min total) through 2-5 g of hydrated sample (dry basis) in the 4" X 3/8"-i.d. reactors. When no water was added, none of the wastes examined showed a significant affinity for CO_2 . However, with addition of H_2O , the absorption capacity increased rapidly until the water content was sufficiently high to create a mud-like texture in the waste samples. At these highest moisture levels, absorption capacity showed an abrupt decline, presumably limited by sample permeability. Maximum absorption for these tests ranged from ~1,700 SCF/ton for the FU-fly ash to ~300 SCF/ton for the control fly-ash sample (L-FA). Limited testing in the 9" reactor indicated absorption in excess of 2,000 SCF/ton for the FU-fly ash and a single run conducted with the PP4 sample (discussed later) showed an absorption capacity in excess of 2,500 SCF/ton.

The correlation between absorption capacity and free CaO in the FGD-waste samples is shown in Figure 6. The three fly-ash samples exhibit a near linear relation between CO_2 absorption and free-lime content. This is in contrast to the isolated point on the bottom right of the plot representing the single sample of bed ash (FU-BA). This plot suggests that absorption capacity is dependent on both the free-lime content as well as particle size. It is likely that some of the pores in the larger bed-ash particles have been blocked by chemisorbed SO_2 (forming anhydrite or gypsum). As a consequence, access of CO_2 to the particle interior would be restricted and in turn access to a portion of the free lime. This would account for the lower absorption capacity per unit weight CaO in the bed-ash sample.

The Coolside waste samples were not selected for full testing in this portion of the study. However, a limited number of runs were conducted using the gas blend that contained Ar, CO_2 ,

Figure 6 CO₂ absorption as a function of Calcium oxide content for three fly-ash and one bed-ash waste. The point on the bottom right represents the single bed ash.

H₂S, and CH₄ along with waste samples from Pilot-Plant Run#4. This particular sample was selected for the final round of tests based on its high free-lime content (~20 wt%) and a substantial level of absorption as measured in the slurry tests to be described in the next section. These latter set of runs were conducted with the 4" tube reactors (as were the runs plotted in Figure 5). CO₂/Ar, H₂S/Ar, and CH₄/Ar ratios are shown from one of these runs (BKR72) in Figure 7. This plot indicates a high level of CO₂ absorption by the PP4 waste (~2,650 SCF/ton) as well as a lesser level of net absorption of H₂S (~125 SCF/ton). CH₄ was not removed from the gas stream to any measurable degree.

Note that some of the H₂S removed from the gas stream during the initial 2-3 minutes of the exposure (Figure 7) is liberated at about 5 min into the exposure as the sorbent becomes

Figure 7. CO_2/Ar , H_2S , CH_4/Ar -ion ratios during exposure to waste from Pilot Plant run#4; 4" reactors; 1.1 g dry PP4; 15.5% H_2O (dry); 35.1 mL/min CO_2 ; 5.0 mL/min H_2S .

saturated. This is presumably due to displacement of H_2S from the sorbent-particle surfaces by CO_2 . However, not all of the absorbed H_2S is fully displaced. We believe that the H_2S that is displaced was likely adsorbed onto the PP4-waste surfaces whereas that portion of absorbed H_2S that was not displaced was likely chemisorbed by the mineral matrix. XRD analysis of the exposed waste samples to verify the formation of CaS are still being evaluated. XRD results obtained to this point will be discussed later in this report. Finally, it is worth reemphasizing the high level of CO_2 absorption measured in this particular test, ~2,650 SCF/ton. This level is

higher than for the other hydrated solids shown in Figure 5 although the level of free CaO in PP4 is only slightly greater than in the FU-fly ash (19.9 vs. 19.5 wt%). The reason for this difference in absorption capacity is not fully understood at this time.

Absorption by waste slurries. For the final phase of the study, the stainless-steel tube reactors were replaced with a pair of glass, 250-mL gas bubbler/scrubbers. As described earlier, ~5 g of solid waste were added to 200 mL of distilled water in the absorbent scrubber and 200 mL of distilled water were added to the bypass scrubber. The gas blend containing CO₂, Ar, and CH₄ (~50:30:20) was bubbled through the water in the bypass reactor during the initial bypass interval then switched to the absorbent slurry for up to one hour before being returned to the bypass mode. The QMS data collected during the slurry tests were processed in the same manner as those collected during the hydration studies.

Results from the slurry tests are shown in Figure 8. Absorption of CO₂ ranged from less than 1,000 SCF/ton for the L-FA control sample to more than 3,500 SCF/ton for the FU-fly ash and PP4 samples.

Although total removal of CO₂ was greater on an absolute basis in the slurry tests, neither the rate or level of maximum absorption was as great as measured for the corresponding samples in the hydrated-solids tests. Slurry runs typically required 10-20 minutes before CO₂ response returned to 95% of baseline in spite of the fact that the flow rate of CO₂ was 50% greater in the slurry tests than in the hydrated-solids tests. Further, even when using the same gas blend and waste sample, the CO₂ level was typically reduced from 49.6% in the feed stream to a minimum of around 12-15% in the exit stream for the slurry tests as compared to as low as 1% or less in the exit stream for the hydrated-waste tests. However, the shape of the adsorption curves

Figure 8. CO₂ absorption by FGD-waste slurries. a) Coolside wastes; b) all others.

obtained from the slurry tests is thought to be more of a reflection of scrubber design rather than absorption kinetics. It is believed that both kinetics and the maximum level of absorption can be markedly improved with a more efficiently designed bubbler/scrubber, e.g. smaller bubbles, longer contact time.

The results for the slurry tests shown in Figure 8 exhibit a strong correlation with the available calcium data in Table 1 when the samples of fly ash are considered separately from the samples of bed-ash as shown in Figure 9. Again, the majority of waste samples exhibit a linear relation between CaO (or Ca(OH)₂) content and CO₂-absorption capacity with the exception of two points that exhibit a markedly lesser capacity. As before, these two outliers represent the two samples of bed ash that were examined (FU- and CC-BA). Again, this plot serves to emphasize the dependency of CO₂ absorption capacity on both available calcium and particle size. That is, the significantly larger particle size of the bed-ash samples as well as potential blockage of particle pores by SO₂ to form gypsum and/or anhydrite (CaSO₄ and/or CaSO₄·2H₂O) likely limits diffusion of CO₂ to the particle interior and, in turn, limits their

Figure 9 CO₂ absorption as a function of the available calcium content of the fly-ash and bed-ash wastes. The points on the bottom right represent the two samples of bed ash.

absorption capacity.

One of the runs conducted in the final test series (BKR77) in which the gas mixture containing H₂S (in addition to CH₄, CO₂, and Ar) was routed through gas scrubbers is shown in Figure 10. This plot illustrates the simultaneous response curves for H₂S, CH₄, and CO₂ as the mixture was routed through an aqueous slurry prepared with a sample of waste from Pilot-Plant Run #4. The results are similar to those shown before for a hydrated sample of PP4 waste (Figure 7). As before, absorption of CO₂ was relatively high (~3,300 SCF/ton), absorption of H₂S was substantially lower (<200 SCF/ton), and absorption of CH₄ was negligible. Again, a portion, but not all of the H₂S absorbed early in the exposure was liberated as the slurry became saturated with CO₂. This is evidenced by a rise in the H₂S/Ar response curve to a level slightly above baseline at about 25 min into the exposure. The absorbed CO₂/H₂S ratio was

Figure 10. CO₂/Ar, CH₄/Ar, and H₂S-ion ratios during exposure to waste from Pilot-Plant run#4; 4" reactors; 1.1 g dry PP4; 15.5% H₂O (dry basis); 35.1 mL/min CO₂; 5.0 mL/min H₂S.

approximately 21 for the slurry tests and about 18 for the hydrated-solids test shown in Figure 7. This compares to an initial CO₂/H₂S ratio of about 7 in the feed gas. These higher absorption versus feed ratios confirm that, although FGD wastes absorb both CO₂ and H₂S, the affinity of FGD wastes appears to be about three times greater for CO₂ than for H₂S.

Post-exposure analysis of hydrated wastes. Selected samples from the hydrated-solids tests were examined by XRD before and after exposure. Plots of the XRD analysis are shown in Figure 11. The top plot (a) in this figure shows the spectrum of a PP4 sample that had been exposed to a gas blend containing CO₂ and H₂S while on bottom (b) is an analogous plot following exposure to H₂S only. The spectrum of the parent PP4 sample is shown in both plots for comparison. The top plot indicates the major minerologic changes were depetion of

Figure 11. XRD spectra of hydrated samples of PP4 following exposure to a) CO_2 and H_2S and b) H_2S only. The parent PP4 appears in both plots (c=calcite; p=portlandite; u=unknown).

portlandite (Ca(OH)_2) and formation of calcite (CaCO_3). There is no indication of an anticipated formation of CaS. In the bottom plot in which the PP4 sample was exposed to H_2S only, again there is an obvious depletion of portlandite with the formation of an as yet unidentified mineral with peaks near 9 and 20 (2-Theta). Again, there is no indication of CaS formation. At this time, we suspect the stoichiometry of the unknown mineral is $\text{Ca(OH)}_{2-x}(\text{HS})_x$, where x is > 0 and < 2 . Additional work is being planned with the objective of identifying this unknown(s).

In addition to the formation of calcite following exposure to gas blends containing CO_2 , there was also minor formation of ettringite, a hydrous calcium sulfo-aluminate phase that can substitute carbonate for sulfate in its structure. However, since the samples remained moisturized following exposure (i.e., they may continue to react), it is possible that these minor changes occurred mostly after the absorption, but prior to the XRD analysis. Regardless, it appears that the absorbed CO_2 reacts primarily with available Ca (CaO or Ca(OH)_2) to form calcium carbonate.

Table 2. Concentration (ppm) of cation/metals in the waters retained from slurry-absorption tests.

	FU-FA	FU-FB		FU-FA	FU-FB
Ag	<.01	<.01	Mg	87	34
Al	<.05	<.05	Mn	0.013	.080
As	<.03	<.03	Mo	0.085	0.075
B	5.7	3.9	Na	3.85	.085
Ba	0.02	0.01	Ni	<.005	0.017
Ca	558	565	P	<.05	<.05
Cd	0.001	0.001	Pb	<.01	<.01
Co	<.005	<.005	Se	<.03	<.03
Cr	<.005	<.005	Si	23	42
Cu	<.005	<.005	Ti	.013	0.013
Fe	0.015	0.013	V	.071	0.038
K	3.50	0.45	Zn	.012	<.002

Values in ppm

Post-exposure analysis of slurry waters. Two of the water samples retained from the slurry tests were subjected to a metal/cations analysis (Table 2). The analyzed waters were from runs in which the gas blend containing CO₂, CH₄, and Ar (but not H₂S) was passed through the gas-scrubber reactors. Elemental release, particularly for the transition elements, is in large part controlled by pH which was >12 for these samples. This likely explains why none of the elements tested were present at levels sufficient to suggest unreasonable disposal problems due to vigorous mixing with the waste samples during the experiments. In fact, not only were the concentrations of toxic elements (shaded elements in Table 2-Hg was not tested) below the allowable levels as specified by TCLP, they are below maximum levels specified for drinking water standards.

CO₂ Concentrations in the Field Lysimeters.

The levels of CO₂ measured within hollow tubes inserted to different depths within the field lysimeters are shown in Figure 12. The bottom of the tubes were open to the lysimeter bed while the top was capped with a rubber septum to permit sampling. Lysimeter #'s 1-3 were packed with wastes from the Coolside demonstration-plant runs while Lysimeter #4 was packed with fly ash (non-FGD) generated in a local utility boiler. Gas-phase CO₂ levels were measured at depths of 8, 18, 30, and 42 inches in each lysimeter. Measurements made at 8" reflect CO₂ levels in the top soil covering the lysimeters while the remaining measurements were made at increasing depths within the FGD or fly-ash beds. In the FGD-packed lysimeters, CO₂ levels at 30" and 42" were consistently below about 0.2 ppm, particularly at 42" where CO₂ levels were at or below the detection limit. In addition, with the exception of lysimeter #3, readings taken at 18" were consistently lower than the readings in the corresponding lysimeter taken at 8" in the

Figure 12. Gas-phase CO₂ concentrations measured at varying depths in the field lysimeters. (L1 to L3-Coolside waste; L4-fly ash).

soil 'cap'. These trends indicate selective removal of the atmospheric CO_2 that diffused into the tubes by the FGD wastes. CO_2 readings were on average lower and substantially more scattered for lysimeter #4. However, in spite of the scatter, there is no apparent correlation between CO_2 concentration and depth as some of the more recent measurements indicate CO_2 concentrations ranging up to 0.4 ppm at 42" and 0.6 ppm at 30". These results tend to confirm that the Coolside wastes exhibit a greater affinity for CO_2 than the fly ash.

SUMMARY

The results obtained in this study clearly show that when hydrated, FGD wastes exhibit a strong affinity for CO_2 , ranging as high as 3,600-3,800 SCF/ton in slurry tests with wastes from Pilot Plant Run #4 and FU-fly ash. Further, there are significant differences in the absorption capacity of FGD wastes that were generated under different conditions or in different plants. These differences in absorption capacity are related directly to the available calcium content and inversely to the average particle size of the waste. This is supported by XRD analysis which indicated that the absorbed CO_2 reacts with portlandite (Ca(OH)_2) to form calcite (CaCO_3). Thus, dry wastes from less efficient utility scrubbers should produce higher-capacity CO_2 sorbents.

Preliminary results indicate that the affinity of the FGD wastes is two to three times greater for CO_2 than for H_2S . The mineral(s) formed by absorption of H_2S remains unidentified at this time though it appears that portlandite is involved. However, it does not appear that CaS is being formed to any significant degree, at least in the hydrated-solids tests.

Finally, analysis of the post-exposure slurry waters suggest that process waters that may be used in a liquid scrubber can be safely disposed following contact with FGD wastes.

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**Coolside Waste Management Research
Technical Progress Report
Contract No: DE-AC21-91MC28162
Report Period June 1, 1995 to June 30, 1995**

Summary of Activity

This study comprises results from ongoing geotechnical testing. Additional data obtained during this reporting period support earlier results indicating that swell continues to be a function of prehydration, pre-aging and static loading of the FBC ash. As with earlier results, swell continues to decrease with higher degrees of prehydration, pre-aging, and static loading. The results are concurrent with mineralogical findings that suggest that ettringite, gypsum and calcium-alumino-silicate hydrate phases proceed to form within the aging materials. In specimens with higher degrees of static loading, minerals are forced to grow within available pore space and fractures, which causes less swell. This report also summarizes results from a study of the effects of Coolside leachate on natural clay liners.

Task 2 Materials Characterization

Subtask 2.3 Geotechnical

Continuation of Swell Tests As in the previous experiments, swell was monitored on the hydrated and non-hydrated FBC ash samples. Based on the degree of swell in both types of samples, it is suggested that the primary swell phase is still continuing after ~ three years into the test period (see Figures 1 and 2). Swell of the hydrated ash material has been monitored for 940 days, while swell of the non-hydrated material has been monitored for 828 days. All samples were remolded near 95 % of standard maximum dry density and optimum moisture content. Swell of the samples (all samples were remolded in CBR molds of 6" diameter and 4.58" height) was monitored using (1) approximately 12.5 lb surcharge and no age time; (2) approximately 2.5 lb surcharge and no age time; (3) approximately 12.5 lb surcharge and seven days age time; and (4) approximately 2.5 lb surcharge and seven days age time. In all cases time of aging refers to the amount of time allotted before the samples were submerged in the water bath. To prevent moisture loss in aged samples prior to placement into the water tank, aged specimens were

FBC Ash (Hydrated)

Figure 1. Swell versus Time, Hydrated FBC Ash.

FBC Ash (Non-Hydrated)

■ No Age Time, 2.52 lb. surcharge ◆ No Age Time, 12.62 lb. surcharge
 ▲ 7 Days Age Time, 2.50 lb. surcharge □ 7 Days Age Time, 12.37 lb. surcharge

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

carefully sealed.

Swell data in Figure 1 indicates that the hydrated FBC ash continued to swell with time; however, swell occurs at a slower rate in samples that were (a) aged for seven days, and (b) were subjected to a higher surcharge. Swell data of non-hydrated material in Figure 2 shows the same trends in continuous swell over time as observed in hydrated FBC ash (Figure 1), but the relative amounts of swell are much more pronounced for the non-hydrated samples. As observed for the hydrated materials, swell in the non-hydrated FBC ash occurs at a slower rate in samples that were (a) aged for seven days, and (b) were subjected to a higher surcharge. In summary, swell continues to decrease upon higher degree of prehydration, pre-aging, and static loading.

Task 4 Laboratory Leaching Studies

Subtask 4.1 Natural Clay Liner Tests

This part of the report delineates results from the continuing leaching tests of natural clay liners using three clays and two FGD by-products. The soils selected for study constitute naturally occurring clays that have low enough permeabilities (i.e., less than 10^{-7} cm/sec) to satisfy many state criteria for landfill specifications. The main objectives of the tests are to determine any long-term changes in permeabilities caused by FGD materials leaching through compacted clay liners. Long-term permeability of natural clay liners may be affected by materials such as metals, salts, or hydroxides commonly present in FGD leachates. Permeability tests of compacted clay, FGD, and clay-FGD combinations began in March of 1995. 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.

The flue gas desulfurization materials (FGD) selected for the tests are derived from an electrical

generating station in Pennsylvania and Coolside material from CONSOL's pilot plant, run # 2.

Test Configurations 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. Two tests have 12 inch FBC and Coolside pilot plant #2 specimens. The actual test design and schematic of clay liner leaching tests are illustrated in Figures 12 and 13 of an earlier reporting period from February 1, 1995 to February 28, 1995.

The tests are configured so that each clay will be subjected to leachate from each FGD material. Water is supplied from a reservoir, mounted above the specimens, through 1/4 inch OD nylon tubing connected to the samples. Silica sand was used to fill the annular space in the end cap between the tubing connection and the samples. Three way valves are located in-line between the reservoir and samples. The valves allow the water supply to be cut off 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 measurement tests are being conducted at various intervals to determine changes, if any, of the compacted materials. 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. Permeability data collected to date are presented in Appendix A of this report. No significant changes have been observed in any test configuration to date. Leachate samples collected from permeability tests are available for analysis of dissolved ions, ionic strength, etc., to determine effects of mineral dissolution and precipitation reactions on the leaching behavior of the FGD modified soils. It is expected that test results will help to determine what kind of effects water leaching through the FGD materials into compacted clay soils has on the permeability of the compacted soils.

APPENDIX A

Permeability Test #: 1

Sample Specs: Height (cm) Diameter (cm) x-section area (cm²)
 10.40 7.75 12.1250

Date	Time	Elevation	Volume out	Temp	Elapsed Time	Head Difference	Volume in	Permeability
(mm/dd/yy)	(mm:ss)	(ft) (m) (m ² x 1)	(ft)	(°C)	(sec)	(ft)	(cm ³)	(cm ⁶ /sec)
Start: 03/11/95	15:40	12.10	0.125	12.644				
End: 03/22/95	8:20	8.1	0.075	6.28	15	61	11000	1.79 1.15E-07
Start: 03/27/95	11:45	13.10	0.25	13.654				
End: 03/28/95	8:24	7.10	0.375	7.665	77.5	62	74.300	5.650 7.211E-07
Start: 03/28/95	8:24	7.10	0.375	7.665				
End: 03/29/95	8:6	9.11	0.375	3.948	19	62	65320	5.917 7.64E-07
Start: 03/29/95	8:6	9.11	0.375	3.948				
End: 03/30/95	8:6	1.7	0.125	1.594	11	63	66520	2.354 9.92E-07
Start: 04/03/95	12:46	13.1	0.25	13.104				
End: 04/04/95	8:14	7.8	0.125	7.677	25	64	70080	5.427 7.22E-07
Start: 04/04/95	8:2	7.8	0.125	7.677				
End: 04/05/95	8:14	3.10	0.375	3.865	18.2	65	67120	3.812 7.45E-07
Start: 04/05/95	8:14	3.10	0.375	3.865				
End: 04/06/95	8:13	1.6	0.625	1.552	11		86340	2.913 1.00E-06
Start: 05/01/95	16:35	13.7	0.25	13.604				
End: 05/02/95	15:23	7.5	0.375	7.448	28		82080	6.156 6.94E-07
Start: 05/03/95	10:47	4.8	0.75	4.563				
End: 05/04/95	11:59	1.10	0.0625	1.839	12.2		90720	2.724 9.48E-07
Start: 05/01/95	12:42	13.3	0.75	13.313				
End: 05/02/95	8:30	7.10	0.5	7.875	25	73	71280	5.436 6.97E-07
Start: 06/06/95	12:8	13.4	0.375	10.406				
End: 06/07/95	7:57	7.8	0.875	7.740	28	74	71340	5.667 7.28E-07
Start: 06/08/95	7:58	3.9	0.25	3.771				
End: 06/09/95	8:2	1.4	0.5	1.375	11	74.5	66640	2.396 1.10E-06
Start: 07/05/95	14:5	12.10	0.6875	12.891				
End: 07/06/95	8:5	7.11	0.625	7.969	29	75	64800	4.922 7.02E-07
Start: 07/07/95	7:55	4.0	0.75	4.063				
End: 07/07/95	15:55	3.1	0.125	3.094	5	74	28800	0.969 8.95E-07

Permeability Test #: 2

		Sample Specs.		Height (cm)		Diameter (cm)		x-section area (cm ²)			
				30.15		7.75		47.17297			
Date	Time	Elevation		Volume out		Temp.	Elapsed Time		Head Difference	Volume in	
(MM/DD/YY)	(HH:MM)	(ft)	(in)	(in ³ -1)	(ft)	(F)	(sec)	(ft)	(cm ³)	(cm/sec)	
Start: 03/22/95	8: 40	12	7	0.125	1.2300						
End: 03/24/95	13: 2	8	8	0.125	1.0877	18	60	188520	5.917	17.48	1.87E-07
Start: 03/24/95	8: 20	1	0								
End: 03/31/95	8: 17	2	11	0	2.917	12.6	68	945420	2.752	12.46	1.84E-07
Start: 03/31/95	8: 17	2	11	0	2.917						
End: 04/03/95	8: 13	1	7	0.625	1.635	6.6	68	258960	1.281	5.72	2.11E-07
Start: 04/10/95	8: 5	3	6	0.125	3.510						
End: 04/13/95	8: 10	1	9	0.875	1.823	7.4		259500	1.687	7.53	2.39E-07
Start: 05/02/95	8: 9	11	11	0.25	11.998						
End: 05/04/95	8: 41	6	2	0.625	8.219	17.2		175080	3.719	16.60	2.02E-07
Start: 05/06/95	8: 50	4	5	0.6875	4.474						
End: 05/12/95	8: 3	2	1	0.75	2.146	12.4	69	342780	2.328	10.39	2.03E-07
Start: 06/07/95	8: 1	5	3	0.3125	5.276						
End: 06/08/95	8: 18	3	9	0.3125	3.776	7.3	74.5	173580	1.500	6.70	1.82E-07
Start: 06/09/95	8: 19	3	9	0.3125	3.776						
End: 06/12/95	8: 3	2	3	0.5	2.292	7.4	70	258240	1.484	6.80	1.83E-07
Start: 06/12/95	8: 3	2	3	0.5	2.292						
End: 06/13/95	8: 8	1	11	0	1.917	1.2	71	86700	0.375	1.67	1.95E-07
Start: 07/06/95	8: 8	12	5	0.375	12.448						
End: 07/07/95	7: 58	10	5	0.25	10.498	10.2	75	85860	2.010	8.97	1.94E-07
Start: 07/07/95	7: 58	10	5	0.25	10.498						
End: 07/07/95	15: 58	9	10	0.1875	9.849	3.2	75	28740	0.589	2.63	1.91E-07
Start: 07/11/95	8: 21	5	9	0.1875	5.766						
End: 07/12/95	8: 16	4	11	0.8125	4.984	4.8	75	86100	0.781	3.49	1.60E-07
Start: 07/12/95	8: 16	4	11	0.8125	4.984						
End: 07/14/95	8: 1	3	9	0.5	3.792	7	76	171900	1.193	5.32	1.51E-07
Start: 07/14/95	8: 1	3	9	0.5	3.792						
End: 07/17/95	8: 21	2	7	0.625	2.635	7.5	76	260400	1.156	5.16	1.32E-07
Start: 07/17/95	8: 21	2	7	0.625	2.635						
End: 07/19/95	8: 11	2	4	0.125	2.344	0.5	75	56800	0.292	1.30	1.29E-07
Start: 07/18/95	8: 11	2	4	0.125	2.344						
End: 07/20/95	8: 8	1	10	0	1.833	2	75	172680	0.510	2.28	1.35E-07

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Permeability Test #: 3

		Sample Specs:		Height (cm)	Diameter (cm)		x-section area (cm ²)				
				30.48	7.75	47.172	47.172				
	Date	Time		Elevation		Volume out	Temp	Lapsed Time	Head Difference	Volume in	Permeability
	(mm/dd/yy)	(mm : mm)	(ft) (in)	(in*0-1)	(ft)	(cm ³)	(F)	(sec)	(ft)	(cm ³)	(cm/sec)
Start:	03/22/95	6 : 40	12 5	0.25	12.436						
End:	03/24/95	13 : 3	8 7	0	8.583	17.5	60	108550	254	17.50	1.86E-07
Start:	03/27/95	8 : 22	5 5	0.0625	5.422						
End:	03/31/95	8 : 12	2 5	0.25	2.438	13.5	63	345000	2984	13.32	2.19E-07
Start:	04/03/95	12 : 49	13 6	0.625	13.552						
End:	04/04/95	14 : 19	9 3	0.5	9.292	18.5	63	91800	4260	19.02	3.89E-07
Start:	04/06/95	8 : 17	5 10	0.25	5.854						
End:	04/11/95	8 : 20	1 10	0.125	1.844	18.3		432180	4010	17.90	2.53E-07
Start:	05/02/95	8 : 4	12 4	0.8125	12.401						
End:	05/04/95	12 : 4	8 5	0.9375	8.495	18		187200	3.906	17.44	1.91E-07
Start:	05/08/95	8 : 50	4 6	0.5	4.542						
End:	05/12/95	8 : 3	1 11	0.75	1.979	12.6	69	342780	2.563	11.44	2.29E-07
Start:	06/06/95	16 : 25	5 3	0.375	5.281						
End:	06/09/95	8 : 20	3 0	0.8875	3.057	10	74.5	230100	2.224	9.93	2.25E-07
Start:	06/09/95	8 : 20	3 0	0.6675	3.057						
End:	06/12/95	8 : 6	1 6	0.25	1.521	6.4	70	258360	1.536	6.86	2.56E-07
Start:	07/06/95	8 : 9	12 0	0.5	12.042						
End:	07/07/95	8 : 0	9 10	0.75	9.898	10	75	85560	2.146	9.58	2.16E-07
Start:	07/07/95	8 : 0	9 10	0.75	9.898						
End:	07/07/95	15 : 58	9 2	0.875	9.240	3	75	26660	0.656	2.93	2.26E-07
Start:	07/10/95	8 : 8	5 7	0.75	5.648						
End:	07/11/95	8 : 13	4 7	0.375	4.615	5	75	66820	1.031	4.60	2.20E-07
Start:	07/11/95	8 : 13	4 7	0.375	4.615						
End:	07/12/95	8 : 14	3 8	0.875	3.740	4	75	66460	0.875	3.91	2.30E-07
Start:	07/12/95	8 : 14	3 8	0.875	3.740						
End:	07/14/95	8 : 2	2 5	0	2.417	4	76	172080	1.323	5.90	2.40E-07

Permeability Test #: 4

		Sample Specs:		Height (cm)		Diameter (cm) x section area (cm ^ 2)					
				30.48		1.75 47.17297					
Date	Time	Elevation		Volume out	Temp	Elapsed Time	Head Difference	Volume in	Permeability		
(mm/dd/yyyy)	(mm: ss)	(ft)(in)(in*10^-1)	(ft)	(cm ^ 3)	(F)	(sec)	(ft)	(cm ^ 3)	(cm/sec)		
Start: 05/12/95	8 : 27	13 4	13.385								
End: 05/12/95	11 : 0	8 7	8.651	19.4	71	3597180	4.714	21.04	1.06E - 08		
Start: 05/12/95	11 : 0	8 7	8.651								
End: 05/19/95	16 : 35	8 2	8.209	3.1	71.5	624900	0.448	2.00	8.05E - 09		
Start: 05/19/95	16 : 35	8 2	8.209								
End: 05/25/95	8 : 5	7 10	7.675	1.18	73	487800	0.328	1.46	7.92E - 09		
Start: 07/21/95	8 : 5	5 7	5.661								
End: 07/31/95	8 : 8	5 3	5.307	0.5	75	864180	0.354	1.58	7.07E - 09		

Permeability Test #: 5

Sample Specs: Height (cm) 30.48 Diameter (cm) 7.75 x-section area (cm²) 47.17297

	Date	Time	Elevation	Volume ou	Temp.	Elapsed Time	Head Difference	Volume in	Permeability
	(mm/dd/yyyy)	(hr : mm)	(ft)(in) (in ³ e-1)	(ft)	(F)	(sec)	(ft)	(cm ³)	(cm/sec)
Start:	05/15/95	8 : 12 13	5 0.625	13.489					
End:	05/25/95	8 : 9 13	3 0.875	13.323	0	73	663460	0.146	0.65 1.19E-09
Start:	05/25/95	8 : 11 13	3 0.875	13.323					
End:	06/09/95	8 : 11 13	0 0.25	13.021	0	74.5	1296480	0.302	1.35 1.67E-09
Start:	06/19/95	8 : 11 13	0 0.25	13.021					
End:	06/13/95	8 : 17 12	10 0.9375	12.911	0	74.5	345960	0.109	0.49 2.31E-09
Start:	06/13/95	8 : 17 12	10 0.9375	12.911					
End:	06/26/95	8 : 50 12	8 0.0625	12.672	0	75	1125180	0.240	1.07 1.58E-09
Start:	06/26/95	8 : 50 12	8 0.0625	12.672					
End:	07/07/95	8 : 0 12	5 0.25	12.438	0	75	947400	0.234	1.05 1.86E-09
Start:	07/07/95	8 : 0 12	5 0.25	12.438					
End:	07/17/95	8 : 27 12	3 0	12.250	0	76	895620	0.189	0.84 1.66E-09
Start:	07/17/95	8 : 27 12	3 0	12.250					
End:	07/31/95	8 : 10 11	11 0.4375	11.953	0	75	1206580	0.297	1.33 1.92E-09

Permeability Test #: 6

Sample Specs: Height (cm) 30.48 Diameter (cm) 7.75 x-section area (cm²) 47.17297

Date	Time	Elevation	Volume out	Temp	Elapsed Time	Head Difference	Volume in	Permeability
(mm/dd/yyyy)	(mm : mm)	(ft) (in) (in*in-1)	(ft) (cm ³)	(F)	(sec)	(ft)	(cm ³)	(cm/sec)
Start: 03/27/95	11 : 45 13 10	0.375 13.865						
End: 03/28/95	8 : 24 9 7	0.25 9.604	21.2	62	74340	4.280	19.02	4.67E-07
Start: 03/29/95	12 : 18 5 9	0.75 5.813						
End: 03/31/95	8 : 8 2 1	0.625 2.135	19.5	63	157800	3.677	16.41	6.00E-07
Start: 04/03/95	12 : 47 13 7	0.125 13.594						
End: 04/04/95	14 : 20 9 10	0.5 9.875	18.5	67	91960	3.719	16.60	3.29E-07
Start: 04/04/95	14 : 20 9 10	0.5 9.875						
End: 04/05/95	8 : 6 8 0	0.875 8.073	9.5	65	63960	1.802	8.04	2.98E-07
Start: 04/07/95	8 : 10 4 10	0.3125 4.859						
End: 04/10/95	14 : 35 1 11	0.0625 1.922	14.5		282300	2.938	13.11	3.11E-07
Start: 05/01/95	16 : 35 13 4	0.875 13.406						
End: 05/03/95	13 : 47 8 3	0.375 8.261	25.1		162720	5.125	22.66	2.60E-07
Start: 05/04/95	8 : 8 5 3	0.625 5.302						
End: 05/06/95	8 : 59 2 1	0.25 2.104	17		348300	3.198	14.27	2.51E-07
Start: 06/05/95	8 : 13 5 5	0.875 5.490						
End: 06/07/95	16 : 50 2 8	0.6875 2.724	15	76.5	203820	2.766	12.34	3.25E-07
Start: 06/07/95	16 : 50 2 8	0.6875 2.724						
End: 06/09/95	8 : 15 1 5	0 1.417	6.3	74.5	141900	1.507	5.64	4.36E-07
Start: 07/06/95	8 : 11 12 4	0 12.333						
End: 07/07/95	8 : 6 10 6	0.625 10.552	9	75	86100	1.781	7.95	1.71E-07
Start: 07/07/95	8 : 6 10 6	0.625 10.552						
End: 07/07/95	15 : 59 10 0	0.125 10.010	3	75	26360	0.542	2.42	1.76E-07
Start: 07/11/95	8 : 19 5 8	0 5.667						
End: 07/12/95	8 : 17 4 9	0.4375 4.786	5	75	86280	0.880	3.93	1.85E-07
Start: 07/12/95	8 : 17 4 9	0.4375 4.786						
End: 07/14/95	8 : 3 3 5	0.1875 3.432	8	76	171960	1.354	6.04	1.83E-07
Start: 07/14/95	6 : 3 3 5	0.1875 3.432						
End: 07/17/95	8 : 22 1 11	0.625 1.969	7.5	76	260340	1.464	6.53	2.02E-07

Permeability Test #: 7

Sample Specs: Height (cm) Diameter (cm) x-section area (cm²)
30.48 7.75 47.17297

	Date (mm/dd/yyyy)	Time (mm : mm)	Elevation (ft) (in) (ln*e-1)	Volume out (cm ³)	Temp (F)	Elapsed Time (sec)	Head Difference (ft)	Volume in (cm ³)	Permeability (cm/sec)
Start:	03/22/95	8 : 40	13 7 0.5	13.625					
End:	03/24/95	13 : 16	12 1 0.375	12.115	6.5	60	189360	1.510	0.74 5.87E-08
Start:	03/24/95	13 : 16	12 1 0.375	12.115					
End:	03/27/95	8 : 25	11 0 0.125	11.010	5.5	60	241740	1.104	4.98 3.74E-08
Start:	03/27/95	8 : 25	11 0 0.125	11.010					
End:	04/17/95	8 : 5	7 11 0.125	7.927	12.2		1813200	3.083	13.76 1.71E-08
Start:	05/17/95	8 : 38	5 7 0.9375	5.661					
End:	05/25/95	8 : 9	5 4 0.0625	5.339	1.2	73	689460	0.323	1.44 8.06E-09
Start:	05/25/95	8 : 9	5 4 0.0625	5.339					
End:	06/09/95	8 : 23	4 9 0.6875	4.807	2	74.5	1296840	0.531	2.37 7.65E-08
Start:	06/09/95	8 : 23	4 9 0.6875	4.807					
End:	06/12/95	8 : 14	4 7 0.125	4.594	0.3	70	258660	0.214	0.95 1.66E-08
Start:	06/12/95	8 : 14	4 7 0.125	4.594					
End:	06/26/95	8 : 47	4 0 0.5	4.042	1.6	75	1211580	0.552	2.46 1.00E-08
Start:	06/26/95	8 : 47	4 0 0.5	4.042					
End:	07/07/95	8 : 1	3 9 0.125	3.760	0.7	75	947640	0.281	1.26 7.20E-09
Start:	07/07/95	8 : 1	3 9 0.125	3.760					
End:	07/11/95	8 : 14	3 8 0	3.667	0.5	75	346380	0.094	0.42 6.90E-09
Start:	07/11/95	8 : 14	3 8 0	3.667					
End:	07/12/95	8 : 15	3 7 0.875	3.656	0	75	86460	0.010	0.05 3.11E-09
Start:	07/12/95	8 : 15	3 7 0.875	3.656					
End:	07/17/95	8 : 23	3 7 0	3.583	0.4	76	432480	0.073	0.38 4.41E-08
Start:	07/17/95	8 : 23	3 7 0	3.583					
End:	07/20/95	8 : 10	3 6 0.3125	3.526	0.3	75	256420	0.057	0.26 5.90E-09
Start:	07/20/95	8 : 10	3 6 0.3125	3.526					
End:	07/31/95	8 : 5	3 4 0.375	3.365	0.5	75	950100	0.161	0.72 4.87E-09

Permeability Test #: 8

Sample Specs:

Height (cm) 30.46 Diameter (cm) 7.75 x-section area (cm²) 47.17297

	Date (mm/dd/yyyy)	Time (mm : mm)	Elevation (ft) (in)	(in*in)	(ft)	Volume out (cm ³)	Temp. (F)	Elapsed Time (sec)	Head Difference (ft)	Volume (cm ³)	Permeability (cm/sec)
Start:	03/22/95	8 : 40	12 8	0.625	12.602						
End:	03/24/95	13 : 17	9 4	0.25	9.354	17.5	60	169420	3.448	15.38	1.57E-07
Start:	04/03/95	16 : 33	13 7	0.875	13.656						
End:	04/07/95	6 : 15	7 11	0.5	7.958	30.2	63	315720	5.698	25.43	1.62E-07
Start:	04/10/95	8 : 8	5 2	0.0625	5.172						
End:	04/13/95	8 : 21	9 1	0.1875	3.099	10.7		259960	2.079	9.25	1.88E-07
Start:	05/02/95	6 : 5	11 4	0.375	11.365						
End:	05/05/95	12 : 14	8 8	0.125	8.677	13.8		274140	2.688	12.00	9.31E-08
Start:	05/09/95	8 : 10	5 6	0.375	5.698						
End:	05/16/95	8 : 10	1 10	0.0625	1.839	20	70	604600	3.859	17.23	1.77E-07
Start:	06/02/95	8 : 27	13 1	0.25	13.104						
End:	06/05/95	8 : 25	9 4	0.1875	9.349	19.5	76	259060	3.755	16.76	1.23E-07
Start:	06/05/95	8 : 25	9 4	0.1875	9.349						
End:	06/08/95	16 : 22	8 0	0.5	8.042	7.4	75	115020	1.307	5.84	1.24E-07
Start:	06/12/95	8 : 12	3 11	0.1875	3.932						
End:	06/13/95	8 : 12	3 4	0.9375	3.411	2.9	71	66400	0.521	2.67	1.56E-07
Start:	06/13/95	8 : 12	3 4	0.9375	3.411						
End:	06/15/95	8 : 6	2 5	0.4375	2.453	4.8	72	172560	0.956	4.26	1.81E-07
Start:	06/15/95	8 : 8	2 5	0.4375	2.453						
End:	06/16/95	16 : 26	1 11	0.0625	1.922	2.7	74	116280	0.531	2.37	1.99E-07
Start:	07/06/95	8 : 13	13 4	0.8125	13.401						
End:	07/07/95	8 : 2	12 4	0.875	12.406	5	75	85740	0.995	4.44	8.51E-08
Start:	07/07/95	8 : 2	12 4	0.875	12.406						
End:	07/07/95	16 : 0	12 1	0.25	12.104	1.5	75	26680	0.302	1.35	8.13E-08
Start:	07/07/95	16 : 0	12 1	0.25	12.104						
End:	07/10/95	8 : 9	9 11	0.3125	9.943	10.5	74	230940	2.161	9.65	8.06E-08
Start:	07/10/95	8 : 9	9 11	0.3125	9.943						
End:	07/11/95	8 : 16	9 2	0.625	9.219	3.5	75	86620	0.724	3.23	8.24E-08
Start:	07/11/95	8 : 16	9 2	0.625	9.219						
End:	07/12/95	8 : 16	6 6	0.5	8.542	3.5	76	96520	0.677	3.02	8.34E-08
Start:	07/18/95	8 : 13	5 4	0.625	5.385						
End:	07/20/95	8 : 11	4 6	0.5	4.542	4.5	75	172680	0.844	3.77	9.34E-08
Start:	07/20/95	8 : 11	4 6	0.5	4.542						
End:	07/26/95	7 : 55	2 8	0	2.667	9.5	75	517440	1.875	8.97	9.74E-08
Start:	07/26/95	7 : 55	2 8	0	2.667						
End:	07/28/95	8 : 3	2 2	0.1875	2.182	3	76	173280	0.484	2.16	1.09E-07

Permeability Test #: 9

Sample Specs:

Sample Specs: Height (cm) 30.46 Diameter (cm) 7.75 x-section area (cm²) 47.17297

	Date	Time	Elevation		Volume out	Temp.	Elapsed Time	Head Difference	Volume in	Permeability
	(mm/dd/yyyy)	(mm : sec)	(ft) (in)	(in ² - 1)	(ft)	(cm ³)	(F)	(sec)	(ft)	(cm ³) (cm/sec)
Start:	03/27/95	11 : 45	13 7	0.75	13.646					
End:	03/28/95	8 : 20	8 11	0.625	8.969	21.2	62	74100	4.677	20.88 5.36E-07
Start:	03/29/95	8 : 8	5 5	0	5.417					
End:	03/30/95	11 : 46	2 7	0.875	2.656	12.6	63	99420	2.760	12.32 6.78E-07
Start:	04/03/95	12 : 48	13 2	0.375	13.196					
End:	04/04/95	14 : 21	8 9	0	8.750	20.5	67	91980	4.448	19.65 4.23E-07
Start:	04/06/95	8 : 21	5 4	0.875	5.406					
End:	04/13/95	8 : 13	1 11	0.375	1.948	15.7	65	604320	3.458	15.44 1.60E-07
Start:	05/01/95	13 : 0	13 4	0.125	13.344					
End:	05/02/95	15 : 22	8 7	0.4375	8.620	22.5		94920	4.724	21.09 4.36E-07
Start:	05/04/95	8 : 40	4 1	0.675	4.156					
End:	05/05/95	12 : 13	2 3	0.5	2.292	8.8		99160	1.865	8.32 5.68E-07
Start:	06/08/95	8 : 5	9 7	0.875	9.658					
End:	06/08/95	16 : 21	8 3	0.625	8.302	6.2	75	20760	1.354	6.04 4.80E-07
Start:	06/07/95	16 : 45	5 3	0.9375	5.328					
End:	06/09/95	8 : 7	2 2	0.4375	2.203	14	74.5	141720	3.125	13.95 5.90E-07
Start:	07/05/95	14 : 5	12 9	0.5	12.792					
End:	07/06/95	8 : 6	8 9	0.5625	8.797	18.4	75	64860	3.995	17.63 5.46E-07
Start:	07/07/95	7 : 56	5 6	0.25	5.521					
End:	07/07/95	15 : 56	4 8	0.125	4.677	4	75	28800	0.844	3.77 5.45E-07

Permeability Test #: 10

Sample Specs: Height (cm) Diameter (cm) x-section area (cm²)
30.48 7.75 47.17297

	Date (mm/dd/yyyy)	Time (hh:mm)	Elevation (ft) (in)	(in ⁴ ft ⁻¹)	(ft)	Volume out (cm ³)	Temp. (°F)	Elapsed Time (sec)	Head Difference (ft)	Volume in (cm ³)	Permeability (cm/sec)
Start:	03/22/95	8:40:13	10	0.25	13.854						
End:	03/24/95	13:19:12	6	0.1875	12.516	5.0	60	189540	1.339	5.97	5.07E-08
Start:	03/24/95	13:19:12	6	0.1875	12.516						
End:	03/27/95	8:27:11	0	0.75	11.063	7.4	60	241680	1.453	6.49	4.83E-08
Start:	03/27/95	8:27:11	0	0.75	11.063						
End:	03/31/95	8:25:08	10	0.6875	8.891	9.4	63	345480	2.172	9.69	5.99E-08
Start:	04/10/95	8:10:04	8	0.875	4.740						
End:	04/18/95	8:00:01	9	0.4375	1.786	13.4	68	777000	2.953	13.16	1.19E-07
Start:	05/02/95	8:07:13	9	0.5	13.792						
End:	05/12/95	11:13:08	3	0.8125	6.316	25.4	71	675160	5.474	24.43	5.47E-08
Start:	05/19/95	8:12:05	6	0.25	5.521						
End:	05/25/95	8:07:03	4	0.375	3.365	10.4	73	518100	2.156	9.62	9.04E-08
Start:	05/25/95	8:07:03	4	0.375	3.365						
End:	05/30/95	7:57:01	10	0.5	1.875	7.2	72	431400	1.490	6.65	1.28E-07
Start:	06/05/95	8:28:12	0	0.9375	12.078						
End:	06/09/95	8:10:09	10	0.9375	9.911	10	74.5	344640	2.167	10.7	5.40E-08
Start:	06/09/95	8:10:09	10	0.9375	9.911						
End:	06/12/95	8:16:08	5	0.375	6.446	5.4	70	259560	1.464	6.53	5.82E-08
Start:	06/12/95	8:16:08	5	0.375	6.446						
End:	06/13/95	8:14:08	0	0	8.000	1.2	71	86280	0.448	2.00	5.97E-08
Start:	06/20/95	9:05:05	3	0.4375	5.286						
End:	06/26/95	8:45:03	3	0.125	3.260	9.5	75	517200	2.026	9.04	8.84E-08
Start:	06/26/95	8:45:03	3	0.125	3.260						
End:	06/29/95	8:47:02	4	0.875	2.406	3.2	75	259320	0.854	3.81	1.11E-07
Start:	06/29/95	8:47:02	4	0.875	2.406						
End:	07/03/95	11:05:01	4	0.375	1.365	4.8	74	353880	1.042	4.65	1.52E-07
Start:	07/06/95	16:25:13	6	0.625	13.552						
End:	07/07/95	16:01:12	11	0.3125	12.943	3.2	75	84960	0.609	2.72	5.12E-08
Start:	07/07/95	16:01:12	11	0.3125	12.943						
End:	07/10/95	8:11:11	4	0.4375	11.370	7.5	74	231000	1.573	7.02	5.31E-08
Start:	07/10/95	8:11:11	4	0.4375	11.370						
End:	07/11/95	8:17:10	9	0.875	10.823	3	75	86760	0.547	2.44	5.38E-08
Start:	07/11/95	8:17:10	9	0.875	10.823						
End:	07/12/95	8:20:10	3	0.3125	10.276	2.8	75	86580	0.547	2.44	5.67E-08
Start:	07/12/95	8:20:10	3	0.3125	10.276						
End:	07/14/95	8:06:09	2	0.25	9.188	5	76	171980	1.089	4.86	6.18E-08
Start:	07/14/95	8:06:09	2	0.25	9.188						
End:	07/17/95	8:25:07	9	0.25	7.771	6.8	76	260340	1.417	6.32	6.09E-08
Start:	07/24/95	8:05:05	0	0.9375	5.078						
End:	07/28/95	8:05:03	8	0.5	3.708	7.5	75	345600	1.370	6.11	8.61E-08
Start:	07/28/95	8:05:03	8	0.5	3.708						
End:	07/31/95	8:02:02	9	0.6875	2.807	4.4	75	259020	0.901	4.02	1.02E-07