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COOLSIDE WASTE MANAGEMENT RESEARCH**Annual Technical Progress Report
for Period October 1992 through September 1993**

by

University of Kentucky**Center for Applied Energy Research**

and

Kentucky Transportation Center**October 1993****Prepared for****The U. S. Department of Energy****Under Contract No.****DE-AC21-91-MC8162****DISCLAIMER**

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SUMMARY

Sample Collection and Chemical Characterization of Coolside Materials

The composition (major, minor and trace elements) of approximately 400 Coolside waste samples from the Edgewater Coolside demonstration and CONSOL pilot plant tests are summarized and tabulated in this report. The composition changes in the waste samples collected during the Edgewater Coolside demonstration can be correlated with the processing variables and operation conditions.

Analyses of all samples collected from the Coolside desulfurization process, including the Edgewater demonstration runs and the CONSOL pilot test runs, are summarized and tabulated in this chapter. An attempt to interpret these results is also made. A master list of samples collected from the Coolside Edgewater plant demonstration runs and the CONSOL pilot plant test runs was prepared. An operating log from the Edgewater Coolside Process Demonstration Topical Report was summarized for the Coolside demonstration runs.

The analysis of the Coolside solid waste materials had been completed and tabulated. Samples were characterized for their major, minor and trace elements concentrations by several analytical methods. The concentrations of major and minor elements of 264 individual barrels obtained from the Coolside Edgewater Plant demonstration runs were determined. Large variations in most of the elements were observed which indicate that the composition of Coolside waste dependent on the operating condition. However, the wastes were quite homogeneous within the same barrel. The concentration ranges between two layers of samples were all within one standard deviation of the average value.

From the operating logs, mechanical problems were found to affect the elemental concentrations of the Coolside materials. The concentration of Na varied with the NaOH feed rate. Na dropped when the pump quit but increased again when the pump was back in service. A similar trend for Ca and Fe was observed. As the feed rate of hydrated lime dropped, the concentration

of Ca in the sample decreased. Also, when the solids recycle line plugged, the content of the fly ash components, i.e., concentrations of Fe and Al in the Coolside samples, dropped. Mechanical problems also affected the SO₂ capture. As the concentrations of promoter and hydrated lime increased in the duct, an increase in the SO₂ capture was reflected in the sulfur content of the samples. Analysis for carbon, hydrogen and nitrogen concentrations indicated a wide range of carbon content in these materials.

A wide range of concentration values was observed for most of the minor and trace elements. The elemental concentrations of hydrated limes showed there were no significant amount of trace elements present in the hydrated lime except some fluorine and strontium. Positive correlations were observed between the concentrations of Ca and F, and Ca and Sr. There also was a strong positive correlation between both Na and Ca with halogens (Br and F), which is related to capture of the corresponding hydrogen halides.

Characterization of Mineralogical Reactions That Cause Swelling of FGD Waste

A study was conducted that focused on the formation mechanism of ettringite crystals in FGD - waste materials since they were observed to form in Coolside, FBC, and AFBC derived wastes. The degree of swelling in FGD-derived waste can be correlated to the amounts of ettringite crystals present. Reactions controlling the formation, composition and disintegration of ettringite are critical in determining the overall stability and strength of cements and concretes derived from dry-flue gas desulfurization wastes. Since these wastes consist of fly ash, along with, CaSO₃, and CaSO₄ and unreacted Ca(OH)₂, the sulfites and sulfates react with the Ca(OH)₂ along with the glassy aluminosilicates in the fly ash to form calcium sulfo-aluminate minerals. Ettringite, the most important of these, is the main contributor to the compressive strength development of the FGD waste mixtures. However, excessive ettringite formation causes swelling which often leads to destructive crack formation. It has been shown that the quantity of ettringite formed and compressive strength of the FGD waste mixtures reach a maximum until ettringite begins to disintegrate. Because the formation mechanisms of ettringite are not entirely understood, swelling in FGD derived products is difficult to predict. This study focused on the

formation and disintegration mechanism of ettringite in FGD waste mixtures with varying contents of aluminum (hydr)oxides, and calcium (hydr)oxides of the starting materials. Transformations were followed using X-ray diffraction and SEM observations.

Geotechnical Properties

Geotechnical properties such as strength, permeability, consolidation, and swell of FGD materials must be known to design and construct environmentally safe landfills. These parameters must also be known to utilize FGD materials in highway construction.

Geotechnical properties (unconfined compressive strength, permeability, swelling characteristics, and field compaction) of Coolside and FBC by products have been examined. Unconfined compressive strength tests performed on Coolside material, obtained during a demonstration run at the Edgewater power station in Lorain, Ohio, clearly indicate strength increases with curing time for laboratory specimens sealed to prevent moisture loss, and aged at various times up to one year at room temperature.

Aging of Coolside demonstration materials does not significantly affect the coefficient of permeability. Increasing compactive energy reduces the amount of air voids thereby decreasing the permeability of these materials.

Compacted Coolside (demonstration and pilot plant), and FBC material obtained from a power plant in Pennsylvania will swell when exposed to water. Total amount of swell appears to be related to the amount of sulfur in the by products which contributes to the formation of minerals such as ettringite and gypsum in void spaces. Swell occurs in two phases; primary and secondary. Coefficients of primary and secondary swell have been calculated. Swell of FGD material can be reduced by a combination of sealing and aging compacted specimens before exposing them to water and by the addition of surcharge weight to the specimens while in water.

Coolside materials obtained from the demonstration process were successfully compacted in field

lysimeters to desired moisture and density conditions. Three compaction scenarios: 1) no compaction, material condition with water, 2) static compaction equivalent to the force exerted by a bulldozer, and 3) ninety five percent of standard compaction at optimum moisture content, were used to simulate different environments which Coolside or other FGD materials may be placed in a landfill. Compaction parameters obtained from laboratory tests were applied to field conditions.

Laboratory Leaching Studies

Results from leaching of two laboratory columns packed with Coolside waste at a static density of 49 lb/ft³ at 41% moisture content are provided. These columns were leached at a rate of 70 ml/week and analyzed for metals, alkalinity and conductivity. One column was open to ambient atmosphere while the other was exposed to an atmosphere containing 2.5% CO₂ to simulate the high concentration of CO₂ in the soil. The pH values for these two columns appear to overlap over the entire period of the test starting at 12.7-12.8 and rising over the first several weeks to approximately 13.1 after which they steadily dropped 12.2 over the remaining 15 weeks. The total alkalinity profiles, expressed as calcium carbonate equivalent values, are quite similar for the first 7 weeks but diverge slightly after that time with higher values being observed for the CO₂ sparged column. Initial values climbed from an already very high value of 15,000 mg CaCO₃/Liter to a high of 27,000 mg CaCO₃/Liter after 3 weeks. Between the 5th and 16th weeks the values declined from 7500 to 3000 mg CaCO₃/Liter. The conductivity of these samples reached its maximum in the earliest measurements remaining there through the 3rd week when it dropped quite dramatically to a lower plateau. After 6-8 weeks the level of conductance was about 40% of the maximum value reached in the early stages.

Chloride and sulfate were the main anions present while concentrations of nitrate and bromide were extremely small. The chloride concentrations in the initial leachate was between 28,000 and 33,000 ppm dropping 19 ppm after 20 days on stream. The chloride concentration from the CO₂ purged column exceeded the non-purged column up to 11 days on stream when they merged at approximately 140 ppm. The initial release of sulfate ion from the column behaved very

similarly to the chloride elution pattern. The sulfate ion concentration began at the 6000 ppm and dropped to approximately 100 ppm.

Sodium was the dominate cation present. Like chloride, it initially a very high concentration between 10,000-15,000 ppm dropping to less than 3000 ppm in 10 weeks. At 20 weeks the level for the non-purged column had 340 ppm. Potassium started at 1700 ppm and increased to 3000 ppm after 3 weeks. At this point the potassium concentration in the non-purged column leachate diminished while the CO₂-purged column leachate increased for the next two weeks to a high of 3700 ppm after which it diminished. The concentrations after approximately 15 weeks became nearly the same at approximately 700-800 ppm. Calcium concentration started at 450 ppm dropping to less than 100 after the 2nd week. Higher CO₂ partial pressures appeared not to affect the Ca concentration.

Results on molybdenum, arsenic, vanadium and selenium are also reported because of their high sensitivity to CO₂ partial pressure. Molybdenum concentration in the CO₂-purged column reached a high at 2 weeks at 34 ppm versus a corresponding 2 week level for the non-purged column of 24 ppm. After 15 weeks the two merged. Arsenic in the non-purged column lined out at less than 1 ppm after 10 weeks whereas in the CO₂-purged column leachate the level approached the 1 ppm level only after 19 weeks. At 10 weeks the As level in the CO₂-purged column leachate was 8 ppm. A maximum selenium concentration was found at 6 ppm after 4 weeks for the CO₂-purged column. However, after 10 weeks it had dropped to less than 1 ppm. The vanadium maxima was observed from the CO₂-purged column between 7-14 weeks of from 1.5-3 ppm.

Field Leaching Studies

Loading of the four lysimeter cells at the Hope Creek Environmental Field Research Station that was completed in November 1992. Specifications on the loaded cells, position of the sampling points and thermocouples in the cells, and both target and actually achieved levels for density and moisture are compiled. The protocol for loading the cells is presented and data on

temperature change in the cells after filling and the moisture accumulation are presented. Exotherms were recorded in each of the three cells loaded with Coolside waste whereas an immediate drop in temperature was observed in the cell filled with fly ash. Interestingly, these exotherms were not readily apparent during the mixing operation such as observed in the past in handling AFBC waste. Targets for both moisture and density in each of the cells were met within 1%.

Moisture level of the top clay layers were all reasonably the same after being exposed to rainfall after the tarpaulin covers were removed. In each case, they climbed to an equilibrium level and remained stable until mid-January when a mild drought began. The percolation rate in the fly ash filled cell is entirely different from the Coolside filled cells. In this cell moisture accumulation is from the bottom up while for the Coolside cells the inverse is happening. Data processing and accumulation is continuing.

Thermodynamic Data Base

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

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

are differences in the lysimeters and their resulting leachates.

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

Chapter 1

Sample Collection and the Chemical Characterization of Coolside Materials - Task 2

Highlights

The composition (major, minor and trace elements) of approximately 400 Coolside waste samples from the Edgewater Coolside demonstration and CONSOL pilot plant tests are summarized and tabulated in this report. The composition changes in the waste samples collected during the Edgewater Coolside demonstration can be correlated with the processing variables and operation conditions.

Summary of Progress for Period

Analyses of all samples collected from the Coolside desulfurization process, including the Edgewater demonstration runs and the CONSOL pilot test runs, are summarized and tabulated in this chapter. An attempt to interpret these results is also made. A master list of samples collected from the Coolside Edgewater plant demonstration runs and the CONSOL pilot plant test runs was prepared. An operating log from the Edgewater Coolside Process Demonstration Topical Report was summarized for the Coolside demonstration runs.

The analysis of the Coolside solid waste materials had been completed and tabulated. Samples were characterized for their major, minor and trace elements concentrations by several analytical methods. The concentrations of major and minor elements of 264 individual barrels obtained from the Coolside Edgewater Plant demonstration runs were determined. Large variations in most of the elements were observed which indicate that the composition of Coolside waste dependent on the operating condition. However, the wastes were quite homogeneous within the same barrel. The concentration ranges between two layers of samples were all within one standard deviation of the average value.

From the operating logs, mechanical problems were found to affect the elemental concentrations of the Coolside materials. The concentration of Na varied with the NaOH feed rate. Na dropped when the pump quit but increased again when the pump was back in service. A similar trend for Ca and Fe was observed. As the feed rate of hydrated lime dropped, the concentration of Ca in the sample decreased. Also, when the solids recycle line plugged, the content of the fly ash components, i.e., concentrations of Fe and Al in the Coolside samples, dropped. Mechanical problems also affected the SO₂ capture. As the concentrations of promoter and hydrated lime increased in the duct, an increase in the SO₂ capture was reflected in the sulfur content of the samples. Analysis for carbon, hydrogen and nitrogen concentrations indicated a wide range of carbon content in these materials.

A wide range of concentration values was observed for most of the minor and trace elements. The elemental concentrations of hydrated limes showed there were no significant amount of trace elements present in the hydrated lime except some fluorine and strontium. Positive correlations were observed between the concentrations of Ca and F, and Ca and Sr. There also was a strong positive correlation between both Na and Ca with halogens (Br and F), which is related to capture of the corresponding hydrogen halides.

Phase I - Task 2 -Solid Waste Characterization

Subtask 2.1: Sample Collection

In order to avoid any confusion and duplication of analysis, we prepared a master list of all samples collected from the Coolside Edgewater plant demonstration runs and the CONSOL pilot plant test runs (Appendices 1-A and 1-B). This list described the Coolside operation conditions (Ca/S ratio, Na/Ca ratio, and mode of process), sampling dates, sample numbering system, and sources of hydrated lime, coal and fly ash used for each sample. We also summarized the operating log from the Edgewater Coolside Process Demonstration Topical Report¹ for the Coolside demonstration runs (Appendix 1-C). This log provided a detailed description of the equipment operations and operating problems encountered during the runs, which helped us to interpret some of the results obtained from the Coolside waste samples.

Subtask 2.2 - Chemical and Mineralogic Analysis of the Materials

The analysis of the Coolside solid waste materials was completed and tabulated. The Coolside samples were characterized for their major, minor and trace elements concentrations by several analytical methods, which included proton-induced gamma-ray and X-ray emission analysis (PIGE/PIXE), X-ray fluorescence, direct current plasma/inductively coupled plasma atomic emission, and cold vapor atomic absorption techniques. Sulfur, carbon, hydrogen and nitrogen were determined by the ASTM methods. Selected samples were analyzed for mineralogical composition by X-ray diffraction and scanning electron microscope. The sampling protocols for each analytical technique used have been described in previous technical reports.

The concentrations of major and minor elements of individual barrel obtained from the Coolside Edgewater Plant demonstration runs are given in Table 1-1. A total of 264 samples from the Demonstration Runs 1, 2 and 3 were analyzed by PIGE and PIXE. The typical PIGE/PIXE detection limit for the individual elements in the Coolside waste samples is given in Table 1-2. For trace elements, the detection limits are in tens of ppm. Since a critical absorber (10 μm thick Cr foil) and a 356 μm thick Mylar film were used to reduce iron X-rays signal and bremsstrahlung, respectively, the detection limits for some elements (e.g., iron, potassium, and calcium) are in hundreds of ppm range. The overall average concentrations of major, minor and trace elements in these samples from each run and all runs are given in Table 1-3. The concentrations of major and minor elements in individual barrel samples are listed in Table 1-1. The data from different runs are compared by showing the histograms of individual element from each run (Figure 1-1). From Figure 1-1, we observe large variations among the sample in most of the elemental concentrations. For this reason, it is important to investigate the composition of a large number of samples in order to obtain a reasonable estimate of the elemental composition of the composite waste in the field and laboratory lysimeters.

The evaluation of PIGE/PIXE sample preparation procedures is given in Table 1-4. The duplication test results showed the sample and graphite mixture was very uniform in a given mixing process. The standard deviations were less than 5% for most of the elements with Barrel No. 434 Coolside waste samples. The homogeneity of samples within the sample barrel (Barrel

No. 42) is given in Tables 1-5a and 1-5b. We found the Coolside wastes were quite homogeneous within the same barrel. We observed there was not much difference between Layer No. 1 (42-1x) and Layer No. 2 (42-2x) samples (Table 1-5a). The concentration ranges between two layers of samples were all within one sigma of the average value. For this reason, we only analyzed one sample from each barrel. Although this did not necessarily represent the average elemental concentrations of each barrel, a total of 264 barrels of Coolside solid waste material was analyzed.

In previous reports, we had indicated that the elemental concentrations of the Coolside materials varied with time. This was based on the assumption that the representative barrel numbers corresponded to the time of operations. An effort was made to correlate the operation conditions and the elemental concentrations to see if the wide ranges in concentration values were due to statistical error, or due to the variations in feedstock, or the difference in the capture efficiencies of the elements had a role. We summarized the operation conditions and the daily operating logs from the Edgewater Coolside Process Demonstration Topical Report¹ (Appendices 1-A and 1-C). This information provided a detailed description of the equipment operations and operating problems encountered during the demonstration runs which helped us to explain the variations observed in the Coolside materials.

The concentration of the major elements (e.g. Na, Ca, Fe, and S) of 264 Coolside waste samples from Runs 1 to 3 are plotted against the barrel number (Nos. 28 to 434) in Figures 1-2 to 1-5. The mechanical problems encountered during the Coolside operations are also labelled along the time axis (barrel number). From the operating logs, we found that some mechanical problems, occurred during the demonstration run, such as keeping up the pump pressure for deliveries of sodium hydroxide, hydrated lime, and recycled solid. Sometimes the recycled solids delivery pipes were plugged due to chunks of fused ash clinker materials. These mechanical problems did affect the elemental concentrations of the Coolside materials. The concentration of Na in the Coolside materials clearly varied with the pump pressure of the NaOH pump (Figure 1-2). When the NaOH pump lost its pressure, there was a clear drop in sodium concentration (at the end of Run 1 and during Run 2). When the NaOH pump was back

in service, the concentration of Na increased (at the beginning of Run 3). The concentrations of Ca and Fe also varied greatly with the barrel number (Figures 1-3 and 1-4). As the pump pressure of hydrated lime dropped, the concentration of Ca in the sample also decreased. When the recycled solid pipes were plugged, the ash content (i.e., concentrations of Fe and Al) in the Coolside samples dropped.

These mechanical problems also affected the SO₂ capture. The concentration of S varied greatly with time. The concentration of sulfur in the Coolside samples was 1.87 ± 0.35 %, and ranged from 1.10 % to 2.72 %. The variations in Na, Ca and S concentrations showed a similar trend during Run 1 (Barrel Nos. 28- 176). When the amount of promoter and hydrated lime increased, the SO₂ capture also increased. This was reflected in the sulfur content of these samples. In the sulfur plot (Figure 5), a zig-zag pattern of S concentration in the samples were observed for Run 3. Although the NaOH pump pressure was kept fairly constant during this period of time, there were some mechanical problems encountered in trying keep up the hydrated lime and recycled solid feeding pumps. A similar trend was also observed in the Ca plot (Figure 1-3). However an inverse trend was observed for Ca and Fe in the samples from Run 3.

We analyzed a total of 25 samples from the Coolside demonstration runs for carbon, hydrogen and nitrogen concentrations by the ASTM methods. A wide range of carbon content in these materials was observed. The Coolside samples has an average carbon content of 8.54 ± 1.43 %, and range of 6.12 % to 11.98 %. The differences in carbon content were also observed by looking at the color of samples. The colors of the samples were range from light grey to greyish black. One possible explanations for this variation is variably incomplete coal combustion due to operating change in the boiler. Another possible explanation might simply be the dilution effect. We had observed a similar effect for Fe or Al with Ca earlier. If more hydrated lime was injected into the duct work, the concentration of carbon in the waste would decrease. We can rule out the possible difference in samples which were collected from different ESP units, and only ESP # 2 was in service during the runs.

Therefore we can conclude that, the concentrations of major elements in the Coolside

samples varied with time. It is clear that these variations with the exception of sulfur mainly were due to the mechanical problems (i.e., feed rate variations), and were not due to the chemistry of Coolside process.

The results of the PIXE/PIGE analysis of 264 Coolside waste samples from Runs 1, 2 and 3 (Barrels Nos. 28 to 434) are given in Table 1-3. A wide range of concentration values were observed for most of the minor and trace elements. Due to lack of information on the original feedstock (e.g., coal, and sodium hydroxide solution), it is very difficult to do a mass balance of elements in the feedstock and the waste materials. To overcome this problem, we did interelemental correlations, and tried to interpret the results and hypothesize the possible chemistry of the Coolside process. Before attempting to interpret these data, we obtained some information on the feedstock materials for the Coolside Process from the Edgewater Coolside Process Demonstration Topical Report¹. It provided information regarding the concentrations of major elements only in the feed coal, hydrated lime, ESP hopper ash, recycled solids, and turning vane deposit samples. This information was not very useful in term of interpreting the trace element data obtained from the Coolside waste samples. Table 1-6 gives the major elemental concentrations of feed coal, hydrated lime, ESP hopper ash, recycled solids, and turning vane deposit samples. By comparing these data with the average concentrations of the Coolside waste (Table 1-1), we found the Coolside waste, ESP hopper ash, and recycled solids all had a very similar composition. The concentrations of Na, Ca, Fe, and Al are almost the same. The concentrations of Na and Ca these recycled solids and Coolside samples were much higher than the feed coal.

Table 1-7 gives the elemental concentrations of hydrated limes used in the Edgewater Coolside demonstration runs and the CONSOL pilot test runs. Black River hydrated lime was used during the Edgewater Coolside demonstration runs sampled for this project and in the CONSOL pilot test runs 1, 2 and 4. Mississippi hydrated lime was used during the Advanced Coolside Process (pilot test run 3). Clearly, there were no significant amount of trace elements present in the hydrated lime except for some fluorine and strontium. We observed positive correlations between the concentrations of Ca and F, and Ca and Sr in the Coolside waste

(Figure 1-6).

Table 1-8 gives the Pearson's correlation coefficients of element pairs whose concentrations clearly varied with time during the Edgewater Coolside demonstration runs. The Pearson's correlation coefficient is a measure of the closeness of relationship (linear) between two variables. It is defined as

$$\text{Pearson's Correlation: } r = \Sigma XY / (NS_x S_y)$$

where X and Y are the values of variables X and Y

N is the number of samples

S_x and S_y are the standard deviations of X and Y

Table 1-8 shows some examples of elemental pairs which were significantly correlated at 99% confidence interval (p-value < 0.01). A positive correlation coefficient means that as concentration of one element increases, the concentration of the other element also increases. Positive relationships were observed for elemental pairs like Na-S, Na-Br, Na-F, Ca-S, Ca-F, Ca-Sr, and Al-Fe. Negative correlations were observed for elemental pairs Ca-Fe, Fe-S, and Fe-Sr. We mentioned earlier the dilution effect of used and unused lime (i.e., Ca) clearly affected the content of the fly ash component (i.e., Fe, Al) in the Coolside samples. Another way to examine the relationships between different elements is to use scatter plots. Figures 1-6 to 1-8 are the scatter plots of some elemental pairs. We can clearly observed the "source" contribution effect of elemental pairs (e.g., Al-Fe and Ca-Sr) in Figure 1-6.

We observed strong positive correlations between both Na and Ca with halogens (Br and F) (Figure 1-7). We believe that chlorine is also strongly correlated with Na and Ca in the Coolside solid waste samples. At the present time, our PIGE/PIXE system is not designed to determine chlorine directly. An improvement on the system design will enable us to determine elements from Na to Cl directly by PIXE analysis. We obtained the chlorine information from the leaching data acquired from the field lysimeters and laboratory column experiments. The

data showed high levels of chloride and bromide were leached out from the Coolside waste samples. It is reasonable to conclude that the Coolside waste samples also contained high levels of Cl, though we did not analyze for its concentrations in the solid samples. When we compare the elemental concentrations of Coolside solid waste (Table 1-4) with the average Kentucky, Ohio, and West Virginia fly ashes (Table 1-9), high levels of As, Br, F, Ca, Na, Zn and Pb (possibly S, Cl) were observed in the Coolside samples. In a normal coal combustion process without any scrubbing system, the extremely volatile elements like F, Cl, Br and Hg are usually present in the gas phase. The concentrations of these elements are extremely low in the average fly ash samples. When the halogens are released from the coal, they are likely to form acids, e.g. HF, HCl, and HBr. During the Coolside desulfurization process, alkaline reactants, i.e., NaOH and $\text{Ca}(\text{OH})_2$, are added into the flue gas stream. Acid-base reactions occurred during the Coolside process in which HF, HCl, HBr and possibly H_2SO_4 reacted with bases and formed salts. We conclude that the Coolside process not only captures SO_2 in the flue gas stream, it also captures the volatile elements like halogens (i.e. F, Cl and Br).

There are higher levels of As, Zn and Pb found in the Coolside solid waste compared to some reported values for Kentucky, West Virginia, and Ohio fly ashes. We do not know the source of these elements and do not have an explanation for the high levels of these elements without gathering more information on the feed coal. Table 1-10 gives the averages and ranges of elemental concentrations in Appalachian coal and U.S. bituminous coal. The concentrations of trace elements in coal are greatly depended on the source of coal. We are trying to obtain more information on the types and sources of coals used during the Edgewater demonstration runs.

One of the ways to understand the chemistry of the Coolside materials is to calculate the enrichment factors of the elements with respect to the parent materials (feedstock). Since we do not have any trace element information on the parent coal, we chose to compare the Coolside materials with respect to the crustal abundance. The enrichment of element X relative to average crustal material is given as:

$$EF_{crustal} = \frac{[X]_{ash} / [Al]_{ash}}{[X]_{crustal} / [Al]_{crustal}}$$

where EF = Enrichment factor

[X] = Concentration of element X in ash or crustal material

The enrichment factors of elements in the Coolside materials with respect to the crustal abundance are given in Table 1-11. These also are compared to the enrichment factors of elements in the average Kentucky, West Virginia, and Ohio fly ashes. From Table 1-11, we observed both Coolside waste and Appalachian fly ash samples have large enrichment factor for As and Se, whereas Mn was depleted compared to the crustal abundance in both samples. The Coolside materials also had much higher enrichment factors for Br, Zn, and Pb.

The results of the Coolside samples obtained from the CONSOL pilot test runs are given in Table 1-12. The elemental concentrations of the parent fly ash materials (Avon Lake fly ash) used in the test runs, and the control fly ash (Trans Ash) and Ottawa sand used in field lysimeters are given in Table 1-13. Some of the LIMB waste samples results are given in Table 1-14.

Reference

- 1) McCoy, D. C., Scandrol, R. O., Statnick, R. M., Stouffer, M. R., Winschel, R. A., Withum, J. A., Wu, M. M. and Yoon, H., "The Edgewater Coolside Process Demonstration", a topical report, (CONSOL, Inc., Pittsburgh, PA 15129), February 1992, Appendix C.

Appendix 1-A

Master List of Coolside Solid Waste Samples

I. Edgewater Demonstration Runs:

A. Coolside Operations

Location: Ohio Edison's Edgewater Power Plant, Lorain, OH
105 Mwe Unit 4, Boiler 13 utility boiler, No. 2 ESP

Date:

Run 1: Feb 8-10, 1990, 26 tons (170 drums @ 300 lbs each)

Run 2: Feb 13, 1990, 18 tons

Run 3: Feb 14-16, 1990, 21 tons

Operations: Recycle Mode using recycle sorbent along with hydrated lime G (Black River Hydrated Lime, Carntown, KY (Dravo Lime Co.)) with sodium additive at 25°F approach to adiabatic saturation. The average SO₂ removal is about ~ 26%

Feedstock:

Average sulfur content in coal: 1.47 ± 0.12 % (compliance Ohio coal)

Ca/S mol ratio = ~2.0 (fresh hydrated lime provided 0.7 to 0.8 fresh Ca/S molar ratio
and
the recycle sorbent provided an available Ca/S of 0.5 to 0.7 in the form of unreacted Ca(OH)₂)

Na/Ca mol ratio = 0.2

B. Sample Information

Storage Location: South Broadway Warehouse

Sampling Date: 7-9-91, 7-10-91

Total number: 345 vials @ ~200 g each

Run 1 Drums # 1-170, 1001-1069, 2000-2023

Run 2 Drums # 171-293

Run 3 Drums # 294-433, 4000-4011

Composite A Drums # 42, 52, 45, 80, 122

Composite B Drums # 344, 377, 434, 397, 401

1000-series Drums # 1040, 1030, 1042

300-series Drums # 339, 387, 362

Appendix 1-A (cont.)

II. Pilot Test Runs:

Fly Ash:

Cleveland Electric Illuminating Company (CEI) Avon Lake Plant Unit No. 9

Feed coal: medium-sulfur Ohio coal

Operations: (see Appendix B)

Sample Information: (see Appendix B)

Test 1: Jan 7-9, 92, Standard once-through with Na additive

Test 2: Jan 10-15, 92, Recycle mode with Na additive

Test 3: Jan 15-22, 92 (?), Advanced Coolside mode without Na additive

Test 4: Jan 23, 92, Once-through without Na additive

III. FBC Waste:

A. FBC Waste (from a coal-fired combustor, P. H. Glatfelter Co.)

FBC waste, as received

FBC waste, hydrated

B. FBC waste (from an oil refinery, Ashland Oil)

IV. Control Ash

Commercial available fly ash used in Field Lysimeter No. 4 (from EKPC Spurlock station)

Appendix 1-B

Brief Summary of Pilot Plant Production of Coolside Waste Samples (a)

I. Operation Conditions:

Pilot Plant Site: CONSOL's 0.1 MWe Coolside pilot plant

Date of Operations: Test 1: Jan 7-9, 92
Test 2: Jan 10-15, 92
Test 3: Jan 15-22, 92
Test 4: Jan 23, 92

Test 1: Standard once-through with Na additive

Ca/S mol ratio = 2.08 Na/Ca mol ratio = 0.19
lb recycle/lb lime = 0
SO₂ Removal = 78 % Sorbent Utilization = 34 %

Test 2: Recycle mode with Na additive

(Baghouse solids were recycled on a semi-continuous basis, the baghouse ash was collected and returned periodically to the recycle feeder in batches.)

Ca/S mol ratio = 1.25 Na/Ca mol ratio = 0.21
lb recycle/lb lime = 2.9
SO₂ Removal = 72 % Sorbent Utilization = 52 %

Test 3: Advanced Coolside mode without Na additive

(Fly ash was mixed with the spent sorbent first before injected into the duct work.)

Average fresh Ca/S ratio: 1.2 No sodium additive
SO₂ Removal = 73-97 % Sorbent Utilization = 49-61 %

Test 4: Once-through without Na additive

Ca/S mol ratio = 2.42 Na/Ca mol ratio = 0
lb recycle/lb lime = 0
SO₂ Removal = 60 % Sorbent Utilization = 25 %

Appendix 1-B (cont.)

II. Materials and Process:

Hydrated Lime: Black River hydrated lime, Carntown, KY (Dravo Lime Co.)
- used in Pilot Test Runs 1, 2, 4 and Coolside Edgewater Demonstration Run

Mississippi hydrated lime, St. Genevieve, MO (Mississippi Lime Co.)
- used in Pilot Test Run 3 (Adv. Coolside mode)

Fly Ash: Cleveland Electric Illuminating Company (CEI) Avon Lake Plant Unit #9
(feed coal: medium-sulfur Ohio coal)

Flue Gas: Flue gas composition consists of CO₂, H₂O, SO₂, and fly ash.
The inlet flue gas conditions can be matched to the flue gas conditions downstream of the air preheater in a coal-fired boiler (burning a medium sulfur Ohio coal).

Process:

Flue gas composition and condition was controlled to simulate that which would be produced by burning a medium sulfur Ohio coal. Hydrated lime is injected into the flue gas at the top of humidifier. The amount of water spray controls the humidifier exit gas temperature for the desired approach to saturation. A water-soluble additive such as NaOH can be fed as aqueous solution into the humidification water stream.

- 1) SO₂ Content: 2000 ppmv (dry basis)
Fly ash / S ratio = 4.0 lb/lb
- 2) Temperature: 300°F at the inlet of flue gas
25°F approach to adiabatic saturation

(a) Based on the "OCDO Coolside Waste Management Project Milestone Report for Phase 3 Pilot Plant Production of Coolside Waste Samples," (Stouffer, M. R., Wu, M. M., and Rosenhoover, W. A., CONSOL, Inc., June 9, 1992).

Appendix 1-C

Operating Log Summary

- 2/8 Two recycle solids injector lines developed plugs which were cleared
- 2/9 Recycle solids flow was lost through 5 of the 9 feed lines from the distribution bottle. Clinker material in the recycled ash solids plugged the 2" diameter feed line block valves.
- Had problems maintaining ESP energization during the day.
- 2/10 At 12:40 hrs, the sodium additive feed was lost due to low pump discharge pressure. At 16:49 hrs, the sodium additive pump tripped off.
- 2/11 Attempts to add packing to the sodium additive pump failed to stop shaft leakage. (pump failure)
- The recycle solid feed was lost for a while at 16:30 hrs due to clinker material jamming the feed valve at the pneumatic conveying line inlet.
- 2/12 The recycle feed system was down from 00:55 hrs to 01:21 hrs, jamming in the rotary feed valve. The recycle solids feed lines continually plugged at the distribution bottle.
Sodium pump was placed back in service at 20:36 hrs.
- 2/13 Coolside Operating condition: $\text{Ca/S} = 0.75$ $\text{Na/Ca} = 0.185$, 20°F approach, and 4,000-8,000 lb/hr recycle solids.
- 2/14 Maintained operating conditions
- 2/15 At 02:00 hrs, the hydrated lime feed was lost due to the plugging of a feeder vent line. Between 11:00 - 11:37 hrs, the hydrated lime feed was off again.
- At 14:49 hrs, the sodium additive feed pump was readjusted due to low pressure.
- 2/16 Conducted a 5-hour test at the same operation as above, except 17°F approach
- Conducted a 4-hour test at 19°F approach, with recycle solid only no sodium additive and no fresh hydrated lime.

TABLE 1-1

CONCENTRATIONS OF MAJOR AND MINOR ELEMENTS IN COOLSIDE SOLID WASTE SAMPLES

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
28	0.91	12.80	1.49	8.24	0.43	7.33	2.21	7.56	0.18	0.18
32	0.85	13.59	1.65	7.36	0.49	8.20	1.61	8.11	0.13	0.18
36	0.89	12.75	1.47	8.13	0.42	7.74	1.64			
37	0.86	11.98	1.39	8.16	0.42	7.22	1.79			
39	0.90	13.12	1.50	8.29	0.44	7.73	1.76			
40	0.82	12.21	1.54	7.89	0.44	7.65	1.66			
41	0.80	11.51	1.42	7.70	0.42	7.34	1.76			
42-11*	0.79	11.80	1.38	8.02	0.44	8.27	1.53			
42-12*	0.78	12.48	1.37	7.61	0.42	7.68	1.47			
42-13*	0.76	11.65	1.37	7.68	0.44	8.16	1.50			
42-14*	0.84	12.95	1.47	7.82	0.46	8.94	1.53			
42-15*	0.79	13.04	1.44	8.11	0.45	8.32	1.52			
42-16*	0.88	12.11	1.41	8.10	0.46	8.15	1.50			
42-21*	1.09	13.15	1.54	9.79	0.46	8.20	1.53			
42-22*	0.91	12.94	1.46	8.67	0.46	8.06	1.53			
42-23*	0.90	11.97	1.52	8.63	0.46	8.60	1.59			
42-24*	0.90	16.02	1.56	9.05	0.50	8.84	1.55			
42-25*	0.91	13.09	1.52	8.33	0.46	8.67	1.60			
42-26*	0.90	16.45	1.42	8.33	0.42	7.89	1.60			
42-1*	0.77	11.22	1.28	7.16	0.39	7.14	1.65	7.87	0.15	0.27
42-1b*	0.81	12.26	1.46	8.08	0.45	8.66	1.59			
42-2a*	0.81	12.46	1.48	8.19	0.46	8.79	1.59			
42-2b*	0.82	11.67	1.43	8.16	0.47	8.72	1.59			
42-2c*	0.44	6.37	1.56	7.93	0.43	8.01	1.59			
42-4*	0.89	12.48	1.26	7.80	0.42	7.05	1.59			
42-5*	0.85	12.21	1.48	7.91	0.42	8.05	1.59			
43	0.88	12.35	1.40	7.99	0.43	6.74	1.67			
44	0.85	11.88	1.36	7.67	0.39	7.76	1.74	7.89	0.21	0.86
45	0.84	12.17	1.33	7.04	0.38	7.18	1.77			
46	0.78	11.10	1.48	8.58	0.45	7.19	1.67			
47	0.82	11.84	1.27	7.24	0.39	7.63	1.68			
48	0.85	11.51	1.31	7.82	0.42	7.86	1.72			
49	0.15	19.89	1.46	8.07	0.43	7.70	1.60	7.52	0.22	0.63
50	0.76	11.39	1.40	8.39	0.41	6.50	1.76			
52	0.83	11.19	1.41	8.06	0.40	7.14	1.80			
53	0.77	10.40	1.30	8.55	0.40	6.89	1.86			
54	0.86	11.17	1.32	8.58	0.39	6.82	1.95			
56	0.95	11.07	1.52	10.16	0.42	6.83	1.88			
58	0.93	10.88	1.50	10.14	0.41	7.10	2.08			
60	1.07	10.61	1.30	11.67	0.38	6.05	2.01			
62	1.26	12.23	1.34	11.46	0.36	5.71	2.28			
64	1.28	12.65	1.46	12.27	0.39	6.31	2.44	6.20	0.16	0.27
66	1.33	12.53	1.62	13.20	0.41	6.49	2.34			

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
68	1.28	12.02	1.46	12.68	0.40	6.40	2.05			
70	1.26	11.95	1.45	12.59	0.40	6.32	2.35			
72	1.30	11.86	1.31	12.37	0.38	6.31	2.40			
74	1.27	12.02	1.45	12.51	0.39	6.12	2.43			
76	1.22	11.45	1.35	11.78	0.38	6.17	2.34			
78	1.17	11.23	1.52	12.37	0.39	6.11	2.48			
80	1.32	14.21	1.48	11.93	0.42	6.30	2.35			
82	1.22	13.72	1.64	11.97	0.46	7.06	2.08			
84	1.23	13.28	1.66	11.45	0.43	6.74	1.96			
86	1.18	12.85	1.55	12.10	0.44	6.35	2.16			
88	1.15	12.48	1.59	11.19	0.41	6.38	1.87			
90	1.08	12.08	1.53	10.97	0.42	6.46	1.87			
92	1.17	12.31	1.48	10.93	0.42	6.20	1.85	6.90	0.23	1.22
94	1.15	12.96	1.66	11.82	0.45	6.71	1.98			
96	1.09	11.94	1.44	10.43	0.44	6.23	1.80			
98	1.08	12.44	1.44	10.24	0.44	6.17	1.96	6.12	0.18	0.28
100	1.09	12.36	1.49	10.87	0.45	6.37	1.88			
102	1.01	11.27	1.37	10.04	0.40	6.01	1.89			
104	1.06	11.18	1.38	10.83	0.42	6.23	1.95			
106	1.10	11.06	1.43	11.28	0.41	6.29	1.87			
108	1.07	10.44	1.46	11.83	0.42	6.37	1.84			
110	1.09	10.17	1.40	11.93	0.40	6.11	2.00			
112	1.13	11.00	1.35	11.18	0.38	6.05	2.02			
114	1.08	10.25	1.34	11.45	0.38	6.12	2.00			
116	0.64	1.93	0.76	7.38	0.28	4.18	1.98			
118	1.14	11.71	1.43	11.68	0.42	6.84	1.87			
120	1.09	10.76	1.33	11.30	0.38	6.15	1.92			
122	1.15	11.32	1.39	11.06	0.37	6.30	2.00			
124	1.12	11.07	1.41	11.08	0.38	6.17	1.95			
126	1.15	10.25	1.37	11.51	0.36	5.92	2.15			
127	1.28	10.53	1.35	10.90	0.40	5.71	2.60			
128	1.28	11.07	1.43	12.23	0.38	6.37	2.16			
130	1.19	10.47	1.41	12.07	0.38	6.13	2.15			
132	1.14	10.12	1.41	11.76	0.37	6.04	2.16			
134	1.29	10.95	1.60	12.69	0.39	6.36	2.18			
136	1.20	10.14	1.50	12.27	0.36	5.69	2.22			
138	1.12	10.00	1.34	12.11	0.35	5.71	2.14			
140	1.07	10.17	1.48	11.54	0.34	6.07	1.91			
142	1.18	10.36	1.47	13.80	0.40	6.58	2.05			
144	1.19	10.43	1.33	11.97	0.36	6.05	2.15			
146	1.09	10.53	1.24	12.17	0.37	6.09	2.04			
148	1.04	9.90	1.36	12.34	0.38	6.06	2.04	11.58	0.25	0.79
150	1.17	10.66	1.39	12.73	0.38	6.15	2.10	11.98	0.28	0.78
152	0.97	11.45	1.48	10.68	0.41	6.85	1.75			
154	0.94	11.50	1.54	10.50	0.44	7.11	1.68			
156	1.04	10.38	1.40	10.72	0.40	6.49	1.75			

TABLE 1-1 -- PAGE 16

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
158	0.91	11.74	1.46	10.06	0.43	7.14	1.70			
160	0.84	10.30	1.37	9.45	0.40	6.41	1.82			
162	1.13	11.93	1.56	11.04	0.43	7.10	1.92			
164	0.98	11.12	1.48	10.19	0.42	6.82	1.77			
166	1.06	10.23	1.51	11.33	0.40	6.40	2.01			
168	1.07	11.02	1.45	11.38	0.41	6.77	1.99			
176	0.82	12.60	1.46	8.10	0.41	7.04	1.13			
180	0.73	11.25	1.34	6.94	0.39	6.40	1.11			
186-1*	0.79	12.38	1.50	8.20	0.44	6.85	1.10	8.10	0.17	0.54
186-2*	0.75	11.70	1.45	8.49	0.45	6.67	1.10	9.03	0.17	0.70
188-1*	1.15	9.83	1.36	11.95	0.36	5.69	2.21			
188-2*	0.76	11.72	1.67	7.85	0.40	6.43	2.21			
190-1*	1.11	10.06	1.30	10.88	0.33	5.41	2.24			
190-2*	0.70	11.11	1.51	7.55	0.41	6.41	2.24	8.68	0.20	0.68
190-3*	1.14	10.12	1.35	11.90	0.37	5.94	2.24			
190-4*	1.20	10.84	1.76	13.73	0.40	6.59	2.24			
196	0.82	12.19	1.86	9.55	0.45	7.86	1.18	8.66	0.17	0.77
200	0.86	12.37	1.90	10.67	0.48	8.08	1.21	9.66	0.23	0.63
210	0.84	11.72	1.71	10.47	0.46	7.46	1.19			
212	0.85	11.50	1.69	10.99	0.46	7.44	1.21			
224	0.91	12.13	1.77	10.51	0.47	7.39	1.41			
228	0.91	11.58	1.80	10.55	0.47	7.60	1.41			
240	0.89	11.05	1.64	10.63	0.45	7.56	1.33			
246	0.89	11.05	1.87	11.47	0.49	7.97	1.33			
262	0.98	12.57	1.45	9.79	0.44	7.27	1.33			
274	0.84	12.52	1.47	8.71	0.46	7.33	1.24			
276	0.93	12.71	1.56	9.17	0.44	7.16	1.47			
280	0.96	12.07	1.51	10.08	0.45	7.02	1.62			
294	1.19	10.51	1.26	9.62	0.38	5.35	1.71			
295	1.23	10.89	1.26	9.81	0.40	5.57	1.73			
296	1.11	10.66	1.34	9.41	0.38	5.44	1.72	9.45	0.23	0.76
297	1.18	10.78	1.34	9.46	0.39	5.28	1.76	7.60	0.15	0.66
298	1.21	10.60	1.27	9.29	0.38	5.17	1.79			
299	1.14	10.80	1.30	9.15	0.37	5.29	1.77	8.52	0.25	0.41
300	1.12	9.78	1.23	8.75	0.36	5.06	1.68			
301	1.21	10.58	1.38	9.91	0.40	5.51	1.76			
302	1.14	9.60	1.25	8.67	0.36	5.15	1.72			
303	1.17	9.47	1.22	8.85	0.37	5.08	1.80	9.73	0.16	0.48
304	1.18	9.81	1.23	7.86	0.38	5.38	1.57			
305	1.22	9.30	1.40	9.10	0.39	6.22	1.74			
306	1.20	8.76	1.32	8.21	0.37	6.23	1.68			
307	1.28	10.22	1.44	8.42	0.40	6.39	1.63			
308	1.16	9.03	1.22	7.21	0.35	5.88	1.60			
309	1.26	9.23	1.26	7.48	0.36	6.09	1.48			
310	1.17	9.82	1.32	7.23	0.36	6.09	1.57			
311	1.30	10.09	1.28	7.35	0.39	6.42	1.61			

TABLE 1-1 -- PAGE 17

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
312	1.27	10.36	1.22	6.78	0.36	6.46	1.54			
313	1.27	9.76	1.36	7.00	0.37	6.42	1.55			
314	1.25	9.61	1.26	6.83	0.38	6.68	1.59			
315	1.14	9.41	1.32	6.93	0.36	6.38	1.58			
316	1.25	10.36	1.35	7.15	0.38	6.71	1.57			
317	1.23	10.08	1.26	6.44	0.37	6.75	1.51			
318	1.22	9.93	1.30	6.56	0.37	6.11	1.49			
319-1*	1.32	10.11	1.21	6.15	0.35	6.23	1.49			
319-2*	1.26	10.54	1.24	6.43	0.37	6.96	1.49			
320	1.27	10.38	1.30	7.45	0.37	6.53	1.54			
321	1.26	10.50	1.36	6.63	0.39	7.09	1.28			
322	1.17	9.73	1.25	5.81	0.35	6.62	1.47			
323	1.38	10.75	1.31	7.08	0.38	6.28	1.46			
324	1.30	11.02	1.29	6.26	0.36	7.18	1.50			
325	1.27	10.72	1.33	6.26	0.38	7.31	1.54			
326-1*	1.21	9.91	1.28	6.08	0.37	6.72	1.42			
326-2*	1.30	11.76	1.41	6.14	0.41	6.83	1.42			
327	1.34	10.70	1.34	6.50	0.38	6.96	1.46			
328	1.34	11.42	1.33	6.45	0.38	6.73	1.53	8.67	0.20	0.63
329	1.28	10.32	1.33	6.43	0.38	6.62	1.53			
330	1.36	10.08	1.31	6.50	0.38	6.73	1.45			
331	1.30	10.10	1.25	6.34	0.37	6.42	1.55			
332	1.28	9.88	1.30	6.70	0.36	6.53	1.46			
333	1.28	10.11	1.30	7.13	0.36	6.39	1.54			
334	1.26	10.04	1.31	7.85	0.36	5.98	1.57			
335	1.31	10.50	1.32	8.28	0.37	6.38	1.67			
336-1*	1.40	11.61	1.38	8.44	0.41	5.74	1.63			
336-2*	1.33	10.24	1.26	7.83	0.34	5.87	1.63			
337	1.27	9.45	1.29	8.30	0.34	5.86	1.72			
338	1.32	9.23	1.29	8.51	0.34	5.80	1.68			
339	1.36	9.47	1.19	8.40	0.33	5.64	1.70			
340	1.26	10.45	1.22	8.63	0.34	5.50	1.76			
341	1.37	9.93	1.34	9.11	0.35	5.64	1.76			
342	1.42	10.08	1.31	9.27	0.35	5.81	1.84			
343	1.26	8.93	1.24	8.64	0.34	5.35	1.79			
344	1.19	8.81	1.18	8.53	0.33	5.40	1.80			
345-1*	1.09	8.29	1.17	8.36	0.33	5.44	1.77			
345-2*	1.19	8.64	1.11	7.92	0.31	5.12	1.80			
346-1a*	1.04	9.22	1.20	8.57	0.34	5.93	1.73			
346-1b	1.04	8.60	1.17	8.20	0.36	5.24	1.73			
346-2*	1.13	9.33	1.19	7.94	0.31	4.87	1.73			
347	1.15	8.92	1.17	8.20	0.32	5.59	1.75			
348	1.00	7.72	1.08	7.44	0.30	5.12	1.72			
349	1.09	8.35	1.10	8.01	0.32	5.66	1.70			
350-1*	1.02	8.86	1.17	8.42	0.33	5.82	1.70			
350-2a*	1.11	8.52	1.24	8.41	0.32	5.71	1.70			

TABLE 1-1 -- PAGE 18

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
350-2b	1.15	9.13	1.19	8.20	0.33	5.91	1.70			
350-2c	1.13	8.86	1.13	7.47	0.33	6.43	1.70			
351	1.12	7.83	1.23	8.46	0.33	5.62	1.69			
352	1.19	9.71	1.23	8.79	0.35	6.17	1.75			
353	1.18	9.89	1.21	8.65	0.34	6.23	1.72			
354	1.21	9.21	1.22	9.12	0.35	6.05	1.69			
355	1.17	9.32	1.25	8.81	0.33	5.97	1.74			
356	1.17	9.24	1.25	8.94	0.34	5.70	1.76			
357	1.23	9.24	1.19	9.12	0.34	5.61	1.82			
358	1.24	8.92	1.18	9.10	0.33	5.73	1.82			
359	1.20	10.02	1.17	9.18	0.34	5.61	1.85			
360	1.22	10.57	1.20	8.91	0.32	5.47	1.87			
361	1.16	9.43	1.19	9.14	0.33	5.26	1.85			
362	1.17	8.64	1.20	9.31	0.33	5.38	1.89			
363	1.17	8.27	1.20	9.15	0.33	5.22	1.90			
364	1.17	8.81	1.20	9.28	0.33	5.44	1.89			
365	1.17	9.45	1.22	9.23	0.33	5.30	1.94			
366	1.16	8.74	1.19	9.06	0.33	5.23	1.88			
367	1.16	8.63	1.20	8.95	0.32	5.02	1.94			
368	1.17	8.52	1.19	9.52	0.34	5.47	1.94			
369	1.11	8.11	1.09	8.74	0.31	5.01	1.84			
370	1.18	8.42	1.32	9.76	0.34	5.38	1.91			
371	1.22	8.34	1.27	9.77	0.34	5.34	1.95			
372	1.26	10.73	1.21	9.74	0.34	5.38	2.05			
373	1.20	9.48	1.22	10.70	0.32	5.53	2.11			
374	1.17	9.31	1.29	10.45	0.31	5.26	2.18			
375	1.21	8.67	1.30	10.87	0.33	5.57	2.08			
376	1.05	8.80	1.20	10.41	0.31	5.31	2.13			
377	1.18	8.79	1.32	10.67	0.31	5.28	2.13			
378	1.29	10.08	1.32	11.58	0.34	5.69	2.23			
379	1.30	9.42	1.46	11.73	0.34	5.64	2.18			
380	1.28	10.74	1.37	11.41	0.33	5.54	2.20			
381	1.20	9.14	1.35	10.57	0.32	5.44	2.14			
382	1.14	8.75	1.24	10.77	0.33	5.76	2.06			
383	1.22	9.91	1.34	10.91	0.33	6.01	2.11			
384	1.17	9.27	1.19	10.24	0.32	5.66	2.09			
385	1.25	9.08	1.36	10.37	0.33	5.78	2.64			
386	1.24	10.19	1.29	10.40	0.33	6.00	2.06			
387	1.20	9.57	1.22	9.92	0.32	6.08	2.05			
388	1.18	8.44	1.20	9.48	0.31	5.65	2.01			
389	1.15	9.39	1.26	9.54	0.33	6.23	1.93			
390	1.18	10.38	1.38	10.02	0.33	6.36	1.88			
391	1.17	9.89	1.27	9.30	0.33	6.48	1.85			
392	1.18	13.24	1.32	9.68	0.33	6.33	2.07			
393	1.18	9.16	1.20	9.21	0.31	6.24	1.81			
394	1.24	8.98					1.91			

TABLE 1-1 -- PAGE 19

BRL#	Na, %	Al, %	K, %	Ca, %	Ti, %	Fe, %	S, %	C, %	H, %	N, %
395	1.20	8.99	1.34	10.09	0.34	6.44	1.81			
396	1.14	9.37	1.40	10.07	0.35	6.47	2.00			
397	1.12	9.31	1.18	9.17	0.31	5.97	2.01			
399	1.06	9.64	1.16	8.93	0.35	5.65	1.98			
400	1.12	9.60	1.31	9.94	0.38	6.07	1.96			
401	1.15	9.37	1.25	9.81	0.33	6.05	2.01			
402	1.06	9.39	1.32	10.25	0.39	5.96	2.06			
403	1.12	9.41	1.23	9.84	0.36	5.47	2.06			
404	1.13	9.93	1.29	10.08	0.37	5.65	2.06			
405	1.12	9.99	1.30	10.18	0.38	5.80	2.08			
406	1.17	10.38	1.29	9.68	0.36	5.55	2.11	10.32	0.21	0.69
407	1.06	8.55	1.21	9.26	0.34	5.51	2.13			
408	1.06	8.55	1.32	9.84	0.36	5.59	2.22			
410	1.11	9.49	1.20	9.45	0.33	5.53	2.09	7.43	0.22	0.62
411	1.11	9.61	1.24	9.15	0.34	5.55	2.10			
413	1.31	11.51	1.41	10.51	0.36	5.76	2.21			
414	1.22	10.76	1.24	9.91	0.34	5.46	2.31			
415	1.36	11.74	1.45	11.27	0.37	5.58	2.30			
418	1.16	8.85	1.11	9.88	0.30	5.31	2.51			
423-a	1.19	8.36	1.36	10.51	0.31	5.12	2.71	9.64	0.30	0.89
423-b	1.14	7.86	1.19	10.34	0.30	5.09	2.71			
423-c	1.15	8.69	1.15	10.31	0.31	5.10	2.71			
424	1.22	10.32	1.38	10.40	0.36	5.31	2.58			
428	1.24	10.21	1.28	9.63	0.35	5.26	2.67	8.17	0.16	0.37
429	1.22	9.96	1.31	9.73	0.36	5.17	2.66	8.12	0.13	0.36
430	1.22	10.30	1.39	9.96	0.37	5.37	2.77			
431	1.28	10.55	1.29	10.52	0.39	5.59	2.60			
432	1.52	12.35	1.47	10.14	0.42	6.00	2.68			
433	1.46	11.82	1.40	9.15	0.38	5.61	2.72			
434-1a	1.20	9.09	1.24	8.91	0.34	5.93	2.74			
434-1b	1.24	9.43	1.24	8.95	0.34	3.14	2.74			
434-1c	1.25	9.26	1.26	8.70	0.33	5.68	2.74			
434-2a	1.20	8.59	1.16	8.28	0.32	5.62	2.74			
434-2b	1.25	9.56	1.17	8.69	0.33	5.43	2.74			
434-2c	1.23	10.01	1.17	8.69	0.33	5.43	2.74			
434-3	1.43	11.47	1.44	9.10	0.38	5.47	2.74	8.13	0.13	0.39
434-4	1.39	11.20	1.25	8.60	0.36	5.43	2.74			

* First numeral suffix (e.g., XXX-1 and XXX-2) refers to separate samples taken from the same barrel. Second numeral suffix (e.g., XXX-X1 and XXX-X2) refers to separate samples taken from the same layer of the same barrel. Letter suffix (e.g., XXX-a and XXX-b) refers to replicate analyses of the same sample.

TABLE 1-2

**TYPICAL DETECTION LIMIT OF PIGE AND PIXE ANALYSIS
OF COOLSIDE WASTE SAMPLES**

Element	Detection Limit (ppm)
Li (a)	14
F (a)	6
Na, % (a)	0.003
Al, % (a)	0.076
K	864
Ca	202
Sc	29
Ti	52
V	65
Cr	12
Mn	16
Fe	105
Co	544
Ni	28
Cu	11
Zn	10
Ga	9
Ge	10
As	13
Se	7
Br	13
Rb	12
Sr	7
Y	13
Zr	24
Nb	18
Mo	12
Ba	310
Pb	63

(a) Obtained by PIGE analysis. $LOD = 3 * \sqrt{BKG} * F_o / N_o$, where BKG is the background over 1 FWHM about the peak's centroid, N_o is the area under the γ -ray peak, F_o is the concentration of element in the sample.

TABLE 1-3

SUMMARY OF PIGE & PIXE ANALYSIS OF COOLSIDE SOLID WASTE MATERIALS
(Concentration in ppm, except as indicated otherwise)

ID	F	Li	Na, %	Al, %	K, %	Ca, %	Ti, %	V	Cr	Mn	Fe, %	Ni	Cu	Zn	Ga
All Runs															
AVG	450	86	1.11	10.56	1.35	9.39	0.38	186	138	116	6.29	73	79	281	36
STD	95	27	0.18	1.65	0.15	1.69	0.05	14	19	20	0.91	10	8	35	6
RSD	21	31	17	16	11	18	12	7	14	17	14	14	10	13	16
N	264	263	264	264	263	263	263	263	155	263	263	263	263	263	263
MIN	93	8	0.15	1.93	0.76	5.81	0.28	151	87	81	3.14	41	53	190	19
MAX	682	201	1.52	19.89	1.90	13.80	0.50	215	183	217	8.94	167	105	424	50
MED	451	83	1.16	10.38	1.33	9.21	0.38	188	133	113	6.15	73	79	283	36
Run 1															
AVG	433	90	1.00	11.67	1.43	10.11	0.41	185	142	119	6.89	70	78	268	34
STD	106	34	0.20	1.84	0.11	1.86	0.03	16	17	13	0.91	8	6	41	6
RSD	24.46	37.68	20.00	15.73	8.00	18.37	8.34	8.49	12.05	10.73	13.16	11.38	7.76	15.48	16.53
N	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96
MIN	93	16	0.15	1.93	0.76	7.04	0.28	151	87	81	4.18	41	53	190	19
MAX	651	201	1.33	19.89	1.66	13.80	0.50	215	179	204	8.94	85	92	360	46
MED	474	91	1.05	11.69	1.44	10.59	0.41	188	139	117	6.72	70	79	270	34

ID	F	Li	Na, %	Al, %	K, %	Ca, %	Ti, %	V	Cr	Mn	Fe, %	Ni	Cu	Zn	Ga
All Runs															
Run 2															
AVG	471	74	0.91	11.55	1.59	10.00	0.43	190	152	158	6.98	75	86	317	36
STD	66	36	0.14	0.85	0.19	1.66	0.04	15	21	29	0.74	13	9	28	4
RSD	14.00	49.02	15.83	7.32	11.99	16.57	9.78	7.92	14.08	18.26	10.61	17.69	10.73	8.78	11.74
N	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21
MIN	246	8	0.70	9.83	1.30	6.94	0.33	158	112	103	5.41	57	67	268	30
MAX	558	142	1.20	12.71	1.90	13.73	0.49	208	183	217	8.08	98	105	403	45
MED	476	79	0.89	11.70	1.56	10.47	0.45	193	148	163	7.16	69	86	311	36
Run 3															
AVG	458	86	1.21	9.69	1.27	8.83	0.35	186	120	108	5.79	76	79	284	38
STD	90	19	0.09	0.94	0.08	1.34	0.03	12	10	12	0.57	11	8	27	5
RSD	19.69	22.35	7.33	9.71	6.30	15.14	7.53	6.54	7.95	11.20	9.78	14.04	10.41	9.41	14.31
N	147	146	147	147	146	146	146	146	38	146	146	146	146	146	146
MIN	286	41	1.00	7.72	1.08	5.81	0.30	155	107	83	3.14	57	61	220	27
MAX	682	134	1.52	13.24	1.47	11.73	0.42	214	150	160	7.31	167	98	424	50
MED	436	83	1.20	9.60	1.26	9.08	0.34	186	119	106	5.66	76	79	283	38

Note: Concentration in ppm, except as indicated otherwise.

TABLE 1-3

SUMMARY OF PIGE & PIXE ANALYSIS OF COOLSIDE SOLID WASTE MATERIALS
(Concentration in ppm, except as indicated otherwise)

ID	Ge	As	Se	Br	Rb	Sr	Y	Zr	Mo	Ba	Pb	S, %	C, %	H, %	N, %
All Runs															
AVG	47	219	12	113	97	318	62	175	29	428	112	1.880	8.54	0.20	0.59
STD	8	31	4	51	10	32	8	29	6	190	32	0.360	1.43	0.04	0.25
RSD	16	14	31	45	10	10	13	17	21	44	28	19.173	16.72	22.65	42.99
N	263	263	263	263	263	263	263	263	154	222	263	264	25	25	25
MIN	24	135	2	48	59	121	37	110	14	86	53	1.097	6.12	0.13	0.18
MAX	69	317	22	812	125	400	87	321	49	949	196	2.774	11.98	0.30	1.22
MED	48	222	12	115	97	318	61	176	29	392	106	1.830	8.17	0.20	0.63
Run 1															
AVG	45	211	11	95	100	306	63	195	29	578	129	1.885	8.17	0.20	0.55
STD	11	41	4	78	10	26	7	24	6	172	28	0.275	2.02	0.05	0.36
RSD	23.93	19.50	33.92	82.19	9.77	8.57	11.65	12.16	20.95	29.81	21.74	14.61	24.74	23.74	65.90
N	96	96	96	96	96	96	96	96	96	76	96	96	10	10	10
MIN	24	135	2	48	59	203	37	113	14	246	66	1.125	6.12	0.13	0.18
MAX	69	317	19	812	125	362	86	321	49	949	196	2.604	11.98	0.28	1.22
MED	46	193	11	96	100	306	63	193	29	588	132	1.872	7.72	0.20	0.46

ID	Ge	As	Se	Br	Rb	Sr	Y	Zr	Mo	Ba	Pb	S, %	C, %	H, %	N, %
All Runs															
Run 2															
AVG	49	247	12	106	107	319	68	200	31	561	153	1.553	8.83	0.19	0.66
STD	6	19	4	22	11	23	11	24	7	205	18	0.457	0.57	0.03	0.09
RSD	11.82	7.54	30.33	20.38	10.54	7.15	16.65	11.97	21.75	36.57	11.92	29.41	6.49	14.27	12.89
N	21	21	21	21	21	21	21	21	21	13	21	21	5	5	5
MIN	39	208	5	72	84	275	47	163	14	251	118	1.097	8.10	0.17	0.54
MAX	62	282	20	161	121	352	87	243	41	861	187	2.240	9.66	0.23	0.77
MED	50	250	12	108	108	322	69	204	33	500	154	1.332	8.68	0.17	0.68
Run 3															
AVG	49	221	13	126	95	326	60	158	28	330	95	1.924	8.77	0.20	0.59
STD	5	19	3	15	9	34	7	22	5	124	23	0.373	0.98	0.05	0.18
RSD	9.84	8.78	26.81	11.97	9.58	10.33	12.04	13.81	19.47	37.70	23.65	19.37	11.13	25.95	30.16
N	146	146	146	146	146	146	146	146	37	133	146	147	10	10	10
MIN	36	162	4	96	72	121	42	110	19	86	53	1.278	7.43	0.13	0.36
MAX	61	277	22	174	121	400	76	239	42	680	156	2.774	10.32	0.30	0.89
MED	48	223	13	123	94	327	60	153	28	312	90	1.818	8.60	0.21	0.63

Note: Concentration in ppm, except as indicated otherwise.

TABLE 1-4

Elemental Concentrations of Barrel # 434 Coolside Waste Sample (a)

Element (ppm)	Homogeneity of Mixing (n=3)			Homogeneity of Mixing (n=3)			Average of #434 (n=8)			Coolside Wastes (n=263)		
	434-1x avg	SD	RSD	434-2x avg	SD	RSD	AVG	SD	RSD	AVG	SD	RSD
F	477	45	9.5	476	18	3.7	476	26	5.5	450	95	21
Li	76	3	4.5	72	6	8.3	85	22	25.8	86	27	31
Na, %	1.23	0.03	2.3	1.23	0.02	1.9	1.27	0.09	7.0	1.11	0.18	17
Al, %	9.26	0.17	1.8	9.39	0.73	7.8	9.83	1.02	10.4	10.56	1.65	16
K, %	1.25	0.01	1.2	1.17	0.00	0.3	1.24	0.09	7.1	1.35	0.15	11
Ca, %	8.85	0.13	1.5	8.55	0.23	2.7	8.74	0.25	2.9	9.39	1.69	18
Ti, %	0.34	0.00	1.2	0.32	0.00	1.1	0.34	0.02	5.6	0.38	0.05	12
V	190	8	4.4	198	16	8.1	190	14	7.5	186	14	7
Mn	99	4	3.7	105	5	4.8	101	5	5.0	116	20	17
Fe, %	4.92	1.54	31.3	5.49	0.11	2.0	5.26	0.87	16.6	6.29	0.91	14
Ni	83	6	7.7	78	3	3.4	79	6	7.2	73	10	14
Cu	79	6	7.2	76	3	4.0	77	6	7.4	79	8	10
Zn	309	16	5.3	294	1	0.4	294	17	5.9	281	35	13
Ga	41	4	9.3	43	1	2.7	40	4	10.2	36	6	16
Ge	58	3	5.0	56	5	9.5	56	4	7.5	47	8	16
As	229	6	2.5	228	10	4.3	226	8	3.5	219	31	14
Se	13	2	12.8	14	1	3.8	12	2	18.3	12	4	31
Br	161	13	8.0	148	2	1.2	158	11	6.9	113	51	45
Rb	91	7	7.5	95	9	9.0	94	6	6.8	97	10	10
Sr	391	8	2.0	371	2	0.7	375	14	3.9	318	32	10
Y	64	6	9.2	58	2	3.0	59	8	12.8	62	8	13
Zr	142	4	2.9	148	5	3.5	154	18	11.4	175	29	17
Nb	33	3	10.0	23	4	18.1	24	10	42.0	22	8	39
Ba	288	89	30.8	320	25	7.8	334	96	28.9	428	190	44
Pb	84	14	16.1	78	10	12.7	90	22	24.3	112	32	28
Th	7	1	15.7	8	2	24.7	9	4	44.2	12	7	59

(a) Elemental concentrations of Barrel No. 434 Coolside waste samples. Concentration in ppm except as indicated otherwise.

TABLE 1-5A

THE RESULTS OF EVALUATING THE HOMOGENEITY OF COOLSIDE WASTE SAMPLES (a)

Element (ppm)	Repeat Irradiations, No. 42 (b) (n=3)			Barrel No. 42-Layer No.1 42-1x, (n=6)			Barrel No.42-Layer No.2 42-2x, (n=6)		
	Avg	SD	RSD	Avg	SD	RSD	AVG	SD	RSD
F	314	11	3	316	12	3.82	351	18	5.05
Li	72	23	31	88	9	10.48	93	28	30.53
Na, %	0.82	0.00	0.1	0.81	0.04	5.47	0.94	0.08	8.19
Al, %	12.13	0.41	3	12.34	0.59	4.75	13.94	1.84	13.17
K, %	1.46	0.03	2	1.41	0.04	2.96	1.50	0.05	3.42
Ca, %	8.15	0.06	0.7	7.89	0.22	2.76	8.80	0.55	6.30
Ti, %	0.46	0.01	1	0.44	0.01	3.32	0.46	0.02	5.12
V	172	9	5	172	12	7.15	189	4	2.36
Cr	169	1	0.5	169	7	4.23	167	7	4.19
Mn	135	2	2	124	6	4.46	126	8	6.18
Fe, %	8.72	0.06	0.7	8.25	0.41	4.91	8.38	0.38	4.53
Ni	60	6	11	66	7	10.64	64	4	6.67
Cu	81	2	3	79	4	5.37	82	5	6.21
Zn	209	2	1	222	9	4.07	234	10	4.29
Ga	29	1	3	32	2	7.61	32	5	14.99
Ge	31	3	9	33	2	7.31	37	3	8.05
As	179	4	2	185	5	2.65	192	8	4.04
Se	9	4	48	10	1	13.44	9	5	57.27
Br	55	6	11	57	5	8.08	64	5	8.00
Rb	103	6	6	106	8	7.66	109	9	7.82
Sr	289	9	3	295	15	5.03	305	12	4.09
Y	62	10	17	64	1	1.57	63	5	8.45
Zr	221	7	3	206	20	9.48	211	17	8.31
Mo	26	2	6	29	4	14.88	30	5	18.14
Ba	702	59	8	487	77	15.75	502	111	22.11
Pb	110	13	12	109	17	15.37	115	11	9.73

(a) Elemental concentrations of Barrel No. 42 Coolside waste samples concentration in ppm except as indicated otherwise.

(b) Samples 42 1b, 42-2a, 42-2b.

TABLE 1-5B

THE RESULTS OF EVALUATING THE HOMOGENEITY OF COOLSIDE WASTE SAMPLES (a)

Element (ppm)	Barrel No. 42 Samples (n=17)			Average Coolside Wastes (n=263)		
	AVG	SD	RSD	AVG	SD	RSD
F	319	43	14	450	95	21
Li	80	29	36	86	27	31
Na, %	0.83	0.12	15	1.11	0.18	17
Al, %	12.44	1.99	16	10.56	1.65	16
K, %	1.44	0.09	6	1.35	0.15	11
Ca, %	8.18	0.57	7	9.39	1.69	18
Ti, %	0.45	0.02	5	0.38	0.05	12
V	177	12	7	186	14	7
Cr	166	8	5	138	19	14
Mn	126	7	6	116	20	17
Fe, %	8.22	0.53	6	6.29	0.91	14
Ni	66	8	13	73	10	14
Cu	81	4	5	79	8	10
Zn	224	11	5	281	35	13
Ga	31	4	12	36	6	16
Ge	34	3	10	47	8	16
As	186	8	4	219	31	14
Se	9	3	36	12	4	31
Br	59	6	10	113	51	45
Rb	106	7	7	97	10	10
Sr	293	16	6	318	32	10
Y	63	5	8	62	8	13
Zr	207	17	8	175	29	17
Mo	29	4	15	29	6	21
Ba	558	131	24	428	190	44
Pb	110	15	14	112	32	28

(a) Elemental concentrations of Barrel No. 42 Coolside waste samples, concentration in ppm except as indicated otherwise.

TABLE 1-6

CONCENTRATIONS OF MAJOR AND MINOR ELEMENTS (IN WEIGHT %) IN FEED COAL, HYDRATED LIME, ESP HOPPER ASH, RECYCLED SOLIDS AND DEPOSIT SAMPLES DURING EDGEWATER COOLSIDE PROCESS DEMONSTRATION RUNS (a)

Operation Date	Ohio Compliance Coal Feed Stock (n=8)		Turning Vane Deposit (n=1)	Hydrated Lime (n=1)	ESP Hopper Ash (n=12)		Recycled Solids (n=14)	
	AVG	SD	AVG	AVG	AVG	SD	AVG	SD
Feb. 8-16, 90								
Moisture	4.16	0.19	0.40	0.70	0.61	0.17	0.38	0.11
Ash	10.38	0.002	96.53	77.50	90.21	1.28	89.39	1.73
C	74.35	0.37	1.44	-	5.85	1.27	6.87	2.52
H	4.92	0.02	0.88	-	0.51	0.10	0.48	0.12
N	1.39	0.03	0.08	-	0.06	0.03	0.08	0.03
S	1.47	0.12	16.52	-	2.60	0.39	2.23	0.46
Si	2.29	0.07	4.84	1.87	16.84	0.81	16.61	1.08
Al	1.20	0.03	2.76	0.62	9.07	0.45	8.78	0.53
Ti	0.06	0.001	0.16	0.04	0.46	0.01	0.45	0.02
Fe	1.11	0.14	2.39	0.25	6.89	0.50	9.02	1.39
Ca	0.10	0.01	20.16	70.89	10.52	1.30	9.80	2.04
Mg	0.05	0.002	0.60	2.23	0.61	0.02	0.60	0.03
Na	0.03	0.01	4.54	0.03	1.36	0.37	1.10	0.35
K	0.19	0.01	0.53	0.10	1.45	0.08	1.40	0.08

- (a) Based on the daily operation logs of the Coolside process demonstration runs. These logs provide a detailed description of the equipment operations and operating problems encountered. McCoy, D. C., Scandrol, R. O., Statnick, R. M., Stouffer, M. R., Winschel, R. A., Withum, J. A., Wu, M. M. and Yoon, H., "The Edgewater Coolside Process Demonstration", a topical report, (CONSOL, Inc., Pittsburgh, PA 15129), February 92, Appendix C.

TABLE 1-7

**ELEMENTAL CONCENTRATIONS OF HYDRATED LIMES USED IN
EDGEWATER COOLSIDE DEMONSTRATION RUNS AND PILOT TEST RUNS**

Element	Black River Hydrated Lime		Mississippi Hydrated Lime	
	AVG (b)	SD (b)	AVG (b)	SD (b)
F	100	1	90	1
Si, % (a)	0.61	0.05	0.37	0.05
Mg, % (a)	1.27	0.01	0.36	0.01
Na, %	0.01	0.00	0.01	0.00
Al, %	0.24	0.01	0.18	0.00
K, %	<DL	-	<DL	-
Ca, %	57.10	1.65	59.01	2.15
Mn	27	4	24	4
Fe, %	0.08	0.01	0.06	0.00
Cu	3	2	3	2
Zn	14	6	31	7
Ga	2	1	2	1
Sr	519	19	381	24

(a) Based on XRF data from UK/CAER

(b) n=2

TABLE 1-8

**CORRELATION COEFFICIENTS (R) FOR PAIRS OF ELEMENTS
WHOSE CONCENTRATIONS IN COOLSIDE WASTES VARIED WITH TIME**

Element Pair	Correlation Coefficient	p-Value	n
Na-S	0.392	< .0005	263
Na-Br	0.365	< .0005	263
Na-F	0.515	< .0005	263
Ca-S	0.516	< .0005	263
Ca-F	0.477	< .0005	263
Ca-Sr	0.347	< .0005	263
Ca-Fe	-0.191	0.0018	263
Fe-S	-0.537	< .0005	263
Fe-Sr	-0.207	0.0007	263
Al-Fe	0.650	< .0005	263
As-Zn	0.822	< .0005	263
As-Se	0.326	< .0005	263
As-Pb	0.273	< .0005	263
Se-Zn	0.374	< .0005	263

TABLE 1-9

**ELEMENTAL CONCENTRATIONS (PPM) OF KENTUCKY, OHIO,
AND WEST VIRGINIA FLY ASH SAMPLES (a)**

Element	KY	OH	WV	AVG	STD
Al*	13.15	13.12	8.88	11.72	2.01
As	79	62	27	56.00	21.65
Ba	769	772	618	719.67	71.90
Br	4	2.4	6.6	4.33	1.73
Ca*	5.47	0.60	1.753	2.61	2.08
Cr	162	177	105	148.00	31.02
Cu	107	153	113	124.33	20.42
F	0.8	3.1	1.7	1.87	0.95
Fe*	3.81	4.86	7.99	5.55	1.78
Ga	110	40	15	55.00	40.21
K*	2.23	2.25	1.26	1.91	0.46
Mn	117	103	90	103.33	11.03
Mo	12	18	14	14.67	2.49
Na*	0.13	0.18	0.32	0.21	0.08
Ni	21	15	24	20.00	3.74
Pb	19	15	8	14.00	4.55
Rb	279	256	127	220.67	66.89
Se	16	16.3	5.4	12.57	5.07
Sr	220	650	1484	784.67	524.74
Th	50	60	27	45.67	13.82
Ti*	0.76	0.79	0.44	0.66	0.16
V	257	238	152	215.67	45.68
Zn	41	21	16	26.00	10.80

*Concentration in weight %

(a) Based on Furr, A. K., et al, *Environ. Sci. Technol.*, 1977, 11, 1194-1201.

TABLE 1-10

**MAJOR, MINOR AND TRACE ELEMENT CONCENTRATIONS (PPM):
CRUSTAL ABUNDANCE, KENTUCKY, OHIO, AND WEST VIRGINIA COAL**

Element (ppm)	Crustal Abundance (a)	KY,OH, and WV Coal Average (b)	Range of U.S. Bituminous Coal (c)
S, %	0.026	2.3	
F	625	80	< 13 - 1900
Li	20	28	1.1 - 370
Na, %	2.36	0.032	0.04 (b)
Al, %	8.23	1.600	2.0 (b)
K, %	2.09	0.230	0.24 (b)
Ca, %	4.15	0.120	0.07 (b)
Sc	22	5	0.6 - 27
Ti, %	0.57	0.090	0.15 (b)
V	135	20	2 - 120
Cr	100	20	2 - 84
Mn	950	600	1 - 1400
Fe, %	5.63	1.900	0.44 (b)
Ni	75	15	1.4 - 130
Cu	55	24	3 - 160
Zn	70	20	1 - 1600
Ga	15	7	0.7 - 35
Ge	1.5	6	<0.07 - 36
As	1.8	27	<1 - 170
Se	0.05	4.7	<0.6 - 20
Br	2.5	12	<0.6 - 160
Rb	90	22	-
Sr	375	100	4 - 920
Y	33	10	<1 - 41
Zr	165	50	1 - 170
Nb	20	5	-
Mo	1.5	3	<0.1 - 16
Ba	425	100	4 - 570
Pb	12.5	15	<1 - 62
Th	9.6	5	<3 - 26

(a) Taylor, S. R, *Geochimica et Cosmochimica Acta*, 28, 1064. 1273-1285.

(b) U.S. National Geochemistry Committee, "Trace-Element Geochemistry of Coal Resource Development Related to Environmental Quality and Health", National Academy Press, Washington, DC, 1980, p.21.

(c) Swaine, D. J., "Modern Methods in Bituminous Coal Analysis: Trace Elements" in *Crit. Rev. Anal. Chem.*, 15(4), 315-346.

TABLE 1-11

ENRICHMENT FACTORS OF ELEMENTS IN AVERAGE KENTUCKY, OHIO, WEST VIRGINIA FLY ASH AND COOLSIDE WASTE SAMPLES WITH RESPECT TO CRUSTAL ABUNDANCE (a)

Element	<u>Avg. Fly Ash</u> (b) EF $\pm$ σ	<u>Coolside Avg.</u> (c) EF $\pm$ σ
As	22 $\pm$ 11	95 $\pm$ 13
Ba	1.19 $\pm$ 0.15	0.79 $\pm$ 0.35
Br	1.22 $\pm$ 0.60	35 $\pm$ 16
Ca	0.44 $\pm$ 0.43	1.76 $\pm$ 0.32
Cr	1.04 $\pm$ 0.27	1.08 $\pm$ 0.15
Cu	1.59 $\pm$ 0.32	1.12 $\pm$ 0.11
F	-	0.56 $\pm$ 0.12
Fe	0.69 $\pm$ 0.27	0.87 $\pm$ 0.13
Ga	2.58 $\pm$ 2.31	1.89 $\pm$ 0.29
Ge	-	25 $\pm$ 4
K	0.64 $\pm$ 0.19	0.50 $\pm$ 0.06
Li	-	3.37 $\pm$ 1.06
Mn	0.08 $\pm$ 0.01	0.10 $\pm$ 0.02
Mo	6.87 $\pm$ 1.43	15 $\pm$ 3
Na	0.06 $\pm$ 0.03	0.37 $\pm$ 0.06
Nb	-	0.85 $\pm$ 0.33
Ni	0.19 $\pm$ 0.04	0.76 $\pm$ 0.11
Pb	0.79 $\pm$ 0.31	7.00 $\pm$ 1.97
Rb	1.72 $\pm$ 0.64	0.84 $\pm$ 0.09
Se	177 $\pm$ 87	188 $\pm$ 58
Sr	1.47 $\pm$ 1.20	0.66 $\pm$ 0.07
Th	3.34 $\pm$ 1.24	1.00 $\pm$ 0.59
Ti	0.81 $\pm$ 0.23	0.52 $\pm$ 0.06
V	1.12 $\pm$ 0.29	1.08 $\pm$ 0.08
Y	-	1.46 $\pm$ 0.19
Zn	0.26 $\pm$ 0.13	3.13 $\pm$ 0.39
Zr	-	0.83 $\pm$ 0.14

(a) Taylor, S. R, *Geochimica et Cosmochimica Acta*, 28, 1064. 1273-1285.

(b) Average concentration of KY, OH, W.Va fly ash, based on Furr, A. K., et al, *Environ. Sci. Technol.*, 1977, 11, 1194-1201.

(c) Average concentration of Coolside waste samples from all three runs (n=263).

TABLE 1-12

**ELEMENTAL CONCENTRATIONS (PPM) OF PILOT TEST RUNS (a)
SAMPLES BY PIGE/PIXE ANALYSIS**

Element	Test 1 (n=5) AVG $\pm$ 1 σ	Test 2 (n=5) AVG $\pm$ 1 σ	Test 3 (n=5) AVG $\pm$ 1 σ	Test 4 (n=5) AVG $\pm$ 1 σ
C, % (b)	1.66	1.51	1.36	1.32
H, % (b)	1.21	0.92	0.95	1.36
S, % (b)	7.72	8.21	9.52	5.90
N, % (b)	0.48	0.53	0.48	0.55
F	102 $\pm$ 10	120 $\pm$ 12	59 $\pm$ 4	116 $\pm$ 8
Li	50 $\pm$ 9	57 $\pm$ 7	44 $\pm$ 5	27 $\pm$ 3
Na, %	2.08 $\pm$ 0.03	2.03 $\pm$ 0.04	0.18 $\pm$ 0.01	0.18 $\pm$ 0.01
Al, %	5.50 $\pm$ 0.30	6.30 $\pm$ 1.40	5.40 $\pm$ 0.40	4.70 $\pm$ 0.40
K, %	0.78 $\pm$ 0.08	0.72 $\pm$ 0.02	0.80 $\pm$ 0.03	0.78 $\pm$ 0.02
Ca, %	24.1 $\pm$ 0.7	17.2 $\pm$ 0.5	21.1 $\pm$ 0.1	27.00 $\pm$ 0.10
Sc	868 $\pm$ 85	635 $\pm$ 23	685 $\pm$ 157	728 $\pm$ 57
Ti, %	0.12 $\pm$ 0.09	0.16 $\pm$ 0.03	0.15 $\pm$ 0.03	0.11 $\pm$ 0.03
V	150 $\pm$ 2	157 $\pm$ 1	13 $\pm$ 2	149 $\pm$ 2
Mn	78 $\pm$ 2	88 $\pm$ 9	80 $\pm$ 1	69 $\pm$ 5
Fe, %	3.72 $\pm$ 0.05	4.48 $\pm$ 0.02	4.22 $\pm$ 0.02	3.34 $\pm$ 0.01
Ni	39 $\pm$ 3	25 $\pm$ 3	24 $\pm$ 3	31 $\pm$ 4
Cu	31 $\pm$ 8	35 $\pm$ 7	27 $\pm$ 4	21 $\pm$ 3
Zn	60 $\pm$ 1	73 $\pm$ 1	76 $\pm$ 2	54 $\pm$ 3
Ga	18 $\pm$ 1	22 $\pm$ 5	21 $\pm$ 1	12 $\pm$ 2
Ge	13 $\pm$ 1	20 $\pm$ 2	14 $\pm$ 1	10 $\pm$ 1
As	43 $\pm$ 9	54 $\pm$ 4	50 $\pm$ 5	36 $\pm$ 4
Se	<DL	<DL	<DL	<DL
Br	10 $\pm$ 2	12 $\pm$ 1	<DL	1 $\pm$ 2
Rb	39 $\pm$ 3	51 $\pm$ 4	41 $\pm$ 7	39 $\pm$ 2
Sr	389 $\pm$ 3	461 $\pm$ 4	417 $\pm$ 25	399 $\pm$ 4
Y	11 $\pm$ 4	14 $\pm$ 4	18 $\pm$ 1	15 $\pm$ 8
Zr	91 $\pm$ 9	99 $\pm$ 12	95 $\pm$ 5	63 $\pm$ 5
Mo	14 $\pm$ 1	<DL	14 $\pm$ 1	11 $\pm$ 4
Ba	<DL	<DL	<DL	<DL
Pb	11 $\pm$ 1	8 $\pm$ 2	14 $\pm$ 2	18 $\pm$ 1

- (a) Test 1 = once-through mode with Na Test 2 = recycle mode with Na
 Test 3 = adv. Coolside mode without Na Test 4 = once-through without Na
- (b) Concentrations of C, H, N and S are based on 1 determination.

TABLE 1-13

**ELEMENTAL CONCENTRATIONS (PPM) OF AVON LAKE FLY ASH,
TRANS ASH AND OTTAWA SAND**

ID	Trans Ash (n=2)		Avon Lake Ash (n=2)		Sand (n=1)
	AVG	SD	AVG	SD	
C, %	1.90	0.06	0.72	0.04	-
H, %	0.07	0.04	0.10	0.02	-
S, %	0.13	0.01	0.36	0.02	-
N, %	0.40	0.12	0.42	0.06	-
F	68	3	155	8	-
Li	188	14	151	15	-
Na, %	0.225	0.002	0.46	0.01	0.00
Al, %	17.40	0.05	12.86	0.03	0.05
K, %	2.17	0.03	1.95	0.08	0.00
Ca, %	0.85	0.006	2.81	0.09	0.01
Ti, %	0.88	0.01	0.65	0.04	0.00
V	241	4	218	49	1
Cr	176	4	247	6	14
Mn	136	6	211	20	7
Fe, %	7.99	0.28	12.46	0.91	0.05
Ni	76	2	160	139	8
Cu	172	1	95	3	1
Zn	149	1	150	6	6
Ga	58	2	47	3	1
Ge	39	3	52	2	1
As	108	4	141	11	1
Se	3	1	14	3	
Rb	142	2	121	15	
Sr	632	8	814	54	
Y	98	10	56	4	
Zr	376	4	344	4	29
Nb	38	7	22	11	
Mo	25	3	23	8	
Ba	1805	86	1401	152	
Pb	93	11	46	1	
Th	29	6	17	5	

Note: Avon Lake Fly Ash is the parent materials used in the pilot test runs.
Trans-Ash is the control ash used in the field lysimeter experiments.

TABLE 1-14

ELEMENTAL CONCENTRATIONS OF FBC WASTES BY PIGE/PIXE ANALYSIS

Element	AFBC Waste (from Ashland Oil)		FBC Waste (from P. H. Glatfelter)		FBC-Hydrated (b)	
	AVG	SD	AVG	SD	AVG	SD
C, % (a)	2.91	-	5.15	-	5.07	-
H, % (a)	0.63	-	1.25	-	0.34	-
N, % (a)	0.71	-	0.32	-	0.66	-
S, % (a)	0.02	-	5.06	-	4.08	-
F	1046	42	281	2	315	2
Li	<DL	-	32	4	39	7
Na, %	0.05	0.001	0.16	0.02	0.18	0.02
Al, %	1.22	0.12	2.88	0.10	3.48	0.29
K, %	0.54	0.05	0.59	0.04	0.88	0.03
Ca, %	26.00	2.13	29.41	0.83	23.62	7.18
Ti, %	<DL	-	0.05	0.02	0.08	0.04
V	105	57	135	24	133	20
Cr	12	3	41	16	55	20
Mn	91	7	126	27	130	22
Fe, %	0.28	0.05	2.53	0.58	2.99	0.85
Ni	14	3	4	2	10	4
Cu	12	3	32	6	24	5
Zn	174	46	26	12	59	4
Ga	3	2	9	7	8	3
Ge	4	1	9	1	20	5
As	10	2	21	4	16	9
Se	3	1	9	2	7	2
Br	11	3	30	3	32	2
Rb	6	2	28	10	45	14
Sr	348	26	713	101	738	31
Y	3	1	20	2	18	2
Zr	20	6	101	19	91	12
Ba	<DL	-	3486	343	3838	378
Pb	6	3	15	3	37	23

(a) Concentrations of C, H, N, and S are based on 1 analysis.

(b) FBC waste from the P. H. Glatfelter Co. hydrated by CONSOL.

Figure 1-1. Elemental Concentrations of Coolside Solid Materials.

Figure 1-2. Na Concentration vs. Barrel Number.

Figure 1-3. Ca Concentration vs. Barrel Number.

Figure 1-4. Fe Concentration vs. Barrel Number.

Figure 1-5. S Concentration vs. Barrel Number.

Figure 1-6. Correlations of Coolside Waste Elemental Concentrations.

Figure 1-7. Correlations of Coolside Waste Elemental Concentrations.

Figure 1-8. Correlations of Coolside Waste Elemental Concentrations.

CHAPTER 2

Characterization of Mineralogical Reactions That Cause Swelling of FGD Waste Mixtures

Introduction

A study was conducted that was focused on the formation mechanism of ettringite crystals in FGD - waste materials. Ettringite crystals form in Coolside, FBC, and AFBC derived wastes. The degree of swelling in FGD-derived waste can be correlated to the amounts of ettringite crystals present. It was observed that ettringite forms on mineral surfaces and inside pore space. Under a confining pressure ettringite formed only within the available pore space. At higher packing densities in the FGD materials, less ettringite was observed to form.

The objective of this project was to produce information on the mineralogy and mineralogical transformations of dry FGD by-products and the formation mechanism of the mineral ettringite in these materials. From this information, the objective was to develop methods to predict the swelling characteristics of FGD-derived materials.

Reactions controlling the formation, composition and disintegration of ettringite are critical in determining the overall stability and strength of cements and concretes derived from dry-flue gas desulfurization wastes. These wastes typically consist primarily of fly ash, along with, CaSO_3 , and CaSO_4 and unreacted Ca(OH)_2 . The sulfites and sulfates in these materials react with the portlandite (Ca(OH)_2) along with the glassy aluminosilicate portion of the fly ash to form calcium sulfo-aluminate minerals. Ettringite, the most important of these, is the main contributor to the compressive strength development of the FGD waste mixtures. Excessive ettringite formation causes first lateral and horizontal swelling of the concrete which often leads to destructive crack formation. It has been shown that the quantity of ettringite formed and compressive strength of the FGD waste mixtures reach a maximum until ettringite begins to disintegrate. Because the formation mechanisms of ettringite are not entirely understood, swelling in FGD derived products is difficult to predict.

This study focused on the formation and disintegration mechanism of ettringite in FGD waste mixtures with varying contents of aluminum (hydr)oxides, and calcium (hydr)oxides of the starting materials. Mineralogical transformations were documented in X-ray diffraction and scanning electron microscope (SEM) observations of the materials.

Experimental Approach

The cause of swelling in FGD waste mixtures was monitored by performing X-ray diffraction analyses on samples of Coolside, FBC (received from Wormser Development Company), and AFBC (received from Ashland Oil Company) materials both before and after swelling was observed as monitored by the Kentucky Transportation Center.

Dry flue gas desulfurization wastes typically swell at a given time. This swelling indicates that mineralogical reactions may have occurred, thereby causing the expansion of the FGD derived materials. The utilization of FGD waste materials in engineering applications can only be successful if the amount and, ultimately the rate of the swelling can be accurately predicted. Research into the swelling characteristics of by-products from coal fired power plants was documented in previous technical progress reports (see January 93 report and February 93 report). In this study X-ray diffraction work was performed on precisely the same materials that were earlier analyzed for: (1) total amount of swelling and; (2) rate of swelling.

Sample Materials:

Coolside:

Coolside Run #2 (ash as received)

Coolside Run #2 / 12.57 lb surcharge / 99 Days

Coolside Run #2 / 2.5 lb surcharge / 100 Days

Pilot Plant 1 in Laboratory Column 19

Pilot Plant 2 in Laboratory Column 20

Pilot Plant 3 in Laboratory Column 21

Coolside 1000 in Laboratory Column 9 / High Density: 69 lb/ft³ / 36 % Moisture

Coolside 1000 in Laboratory Column 10 / Medium Density: 65 lb/ft³ / 45 % Moisture

Coolside 1000 in Laboratory Column 11 / Low Density: 49 lb/ft³ / 41 % Moisture

FBC:

FBC (ash as received)

FBC Non-hydrated #1; #2; #3; #4

FBC Hydrated

FBC Pellets

AFBC

AFBC (ash as received)

AFBC ash (7 %) mixed with soil: Field experimental site #2

AFBC ash (7 %) mixed with soil: Field experimental site #18

Experimental Methods

X-ray diffraction (XRD) patterns of the samples were obtained from randomly-oriented powder mounts using CuK α radiation. Diffraction patterns were recorded from 6 to 60 2 θ with step interval of 2° 2 θ and a counting time of 6 seconds per step. Scanning electron microscopic (SEM) examination of the FGD derived mixtures, using a Hitachi S-2700 (magnification up to $\times 10^4$), allowed a comparison of the morphological features.

XRD - Analyses

Table 2-1 lists the mineral phases observed in the FGD waste materials.

Ettringite

Leaching of a mixture of fly ash and calcium-based scrubber waste results in the formation of an ettringite structure phase. Scrubber ash adds sulfate and calcium to a high-pH, high-Na, high-Al solution which results from fly ash - water reactions. This combination is apparently ideal for ettringite formation.

Table 2-1 Mineralogical Composition in FGD Waste Mixtures

	P	C	A	Q	G	M	Cl	E	MO
Coolside #2	x	x	x	x	x			< X	
Coolside #2 12.57 lb surcharge/ 99 days		x	x	x			x		X
Coolside #2 2.5 lb surcharge / 100 days		x	x	x			x		X
Pilot Plant 1 (Column Lysimeter 19)		x	x	x	x	x			X
Pilot Plant 2 (Column Lysimeter 20)		x	x	x	x	x			X
Pilot Plant 3 (Column Lysimeter 21)		x	x	x	x	x			X
Coolside 1000 (Column Lysimeter 9)		x	x	x	x	x			X
Coolside 1000 (Column Lysimeter 10)		x	x	x	x	x			X
Coolside 1000 (Column Lysimeter 11)		x	x	x	x	x			X
FBD ash as received	x		x	x	x	x		< X	
FBC Non-hydrated #1	x	x	x			x		X	
FBC Non-hydrated #2	x	x	x			x		X	
FBC Non-hydrated #3	x	x	x			x		X	
FBC Non-hydrated #4	x	x	x			x		X	
FBC Pellets	x	x	x			x		< X	
AFBC Ash as received	x	x	x	x					x
AFBC Ash + Soil in Field Site #2		x	x	x	x	x		x	X
AFBC Ash + Soil in Field Site #18		x	x	x	x	x		x	X

P = portlandite; C = Calcium Carbonate; A = anhydrite; Q = quartz; G = gypsum; M = mullite; Cl = clay;
E = ettringite; MO = magnesium oxide
x = occurrence <x = very minor occurrence

Ettringite is a calcium aluminum hydroxy-hydrate mineral. It is both an individual mineral with the formula $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ and the group name for a series of chemically analogous isostructural compounds. The ettringite structure is shown in Figure 2-1.

Previous studies indicate that ettringite formation could be enhanced through the addition of the proper amounts of aluminum and/or sulfate. For example, sulfate is thought of as the limiting factor in ash derived from low ash sulfur coals.

Coolside Material

XRD analyses of Coolside # 2 (ash as received) indicates that no ettringite occurs in the raw mixture (Figure 2-2a). Portlandite ($\text{Ca}(\text{OH})_2$), calcium carbonate (CaCO_3), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), and quartz (SiO_2) are the main ingredients observed. After 100 days and 2.5 lb surcharge, massive amounts of ettringite formed in the sample (Figure 2-2c). At 12.57 lb surcharge after 99 days, ettringite formed in the Coolside #2, but the amount was less than in the sample that was exposed to lower surcharge (Figure 2-2b) for approximately the same amount of time. The sample that had more ettringite also showed greater swell characteristics. In both aged samples, ettringite crystals appear to have formed on mineral surfaces as well as in the available pore space. In case of the higher surcharge, more ettringite formed in interstitial parts. These findings may indicate that the formation mechanism of ettringite (formation either occurs on mineral surfaces or in pore space) could be controlled by the amount of pressure exerted on the FGD waste sample.

Coolside #2 sample was further sub-divided into four samples (by KTC) which were tested for their swell characteristics as a function of time. Investigations included: (i) varying surcharge and, (ii) aged or non-aged samples (Table 2-2). The swell characteristics of the Coolside #2 material are illustrated in Figure 2-3 a-d.

TABLE 2-2

<u>Coolside #2 **</u>		
#2-1 1.09 kg surcharge		
<u>NO AGE TIME</u>		CaO + Ca(OH) ₂ present
#2-2 5.60 kg surcharge		

#2-3 1.19 kg surcharge		
<u>7 DAYS AGE TIME</u>		Ca(OH) ₂ present
#2-4 5.70 kg surcharge		

** Mineralogical Composition of Coolside #2 is given in Table 2-1.

In this study, XRD-analyses were prepared for the four Coolside #2 samples before surcharge was applied. The aged samples were observed to have much more portlandite (Ca(OH)₂ present, while the non-aged samples have some lime (CaO) present.

The four Coolside #2 samples are still swelling. As soon as the swelling stops, samples will be X-rayed and investigated using SEM applications to determine how much and where ettringite crystals formed.

Figure 2-4 compares three XRD pattern for the Coolside 1000 samples packed with high density (69 lb/f³), medium density (65

lb/f³), and low density (49 lb/f³) in column lysimeters 9, 10 and 11, respectively. The results clearly demonstrate that the Coolside 1000 sample with the highest packed density has the smallest amount of ettringite present.

Pilot Plant samples # 1, #2, and #3 located in laboratory column lysimeters 19, 20, and 21, respectively, were separated from the columns, dried, and prepared for XRD-analyses (Figure 2-5). Representative samples were taken from the top, middle and bottom of the columns for comparative purposes. The semi-quantitative XRD analyses of the samples indicate that the largest amount of ettringite crystals formed in Pilot Plant sample #3 (Figure 2-5c), which was characterized by the lowest packed density (49 lb/f³) of the three samples under investigation.

Figure 2-6 compares the XRD patterns for the Pilot Plant sample #2 that were taken from the top, middle, and bottom from column lysimeter 20. The results indicate that ettringite crystals appear to be highly concentrated in the middle zone of the column lysimeter, while the top and bottom samples have less ettringite crystals. Samples taken from the top and bottom of the lysimeter have approximately the same amounts of ettringite present. It is not clear at this time what caused the enrichment in ettringite crystals in the middle zone of the column lysimeter, however, it is speculated at this time that leaching from top, and availability of water may have caused this enrichment pattern.

The results observed for the Coolside 1000 sample and Pilot Plant sample from column lysimeters indicate that FGD waste samples exposed to high packing density, or exposed to higher surcharge, always result in less ettringite formation than those with low packing densities.

FBC Samples

XRD analyses of the FBC residue (as received) indicate the presence of portlandite, anhydrite, gypsum, quartz, and a negligible amount of ettringite (Figure 2-7).

Figure 2-8 compares the XRD pattern for the non-hydrated FBC ash with that of the hydrated FBC ash. The non-hydrated sample contains large amounts of calcium oxide (CaO), while in the hydrated sample portlandite (Ca(OH)_2) dominates. During hydration, the majority of anhydrite was converted to gypsum (Figure 2-8). The hydration process furthermore resulted in the formation of ettringite crystals (Figure 2-8b), which continued to grow upon hydration of the FBC ash (Figure 2-8 c-d). The ettringite crystals are shown in the SEM image of Figure 2-9.

Pellets were produced from the FBC ash (by CONSOL). XRD analyses of the pellets are shown in Figure 2-10, indicating that the pellets are very similar in their mineral composition compared to the hydrated FBC ash. The amount of ettringite crystals present in the pellets was very minor.

Small amounts of hemi-hydrate ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) were present in the pellets which was determined in XRD analyses of powder samples prepared from the "raw" pellets (Figure 2-11). After the pellets were submerged in water (with a standing water pressure of 50 -70 pounds), large amounts of hemi-hydrate crystals formed particularly at the surfaces of the pellets (Figure 2-11). The hemi-hydrate crystals occur as white, needle shaped crystals which are often large enough to be recognized on the pellet surfaces. The hemi-hydrate crystals were separated from the pellet surface and the XRD pattern of these crystals is indicated in Figure 2-11c.

SEM observation of the hemi-hydrate (bassanite) showed that almost all crystals are characterized by abundant crack formation

at the crystal surfaces (Figure 2-12). Portlandite was also observed on the crystal surfaces (Figure 2-13).

The growth of hemi-hydrate crystals must have affected the strength of the pellets. This is based on SEM observations of a polished surface prepared from a hydrated pellet after dissecting the pellet in half. SEM observations indicate the presence of numerous cracks throughout the pellet interior (Figure 2-14 and 2-15) which are most likely responsible for the low strength of the pellets. The number of cracks and size of cracks increased immensely after the samples were submitted to the soundness test.

After these results were discussed with Dr. Milton Wu from CONSOL, who prepared pellets at lower curing temperatures to avoid the formation of hemi-hydrate crystals. CONSOL reported that pellets formed at lower curing temperatures after addition of ~ 10 weight percent silica dust passed the soundness test. XRD observations of this type of pellets indicate the absence of hemi-hydrate crystals. Furthermore, SEM investigations of the same samples showed much less crack development in the samples.

AFBC Material

Results of ettringite formation in soil mixtures obtained from field experiments using AFBC ash are compared in this report to ettringite in Coolside samples and FBC samples to help investigating the formation mechanism of the ettringite crystals. The AFBC ash was supplied by Ashland Oil. The ash sample was mixed with soil (7 wt % AFBC ash) and placed above untreated subgrade in experimental sections (tested by the Kentucky Transportation Center for road base purposes). The mineral phases in the ash were identified and are summarized in Table 2-1. Ettringite was not present in the ash (Figure 2-16). After approximately six years, core samples were taken from the field experimental site #2 and site #18. XRD analyses of the soil-ash

mixture are shown in Figure 2-17, indicating that ettringite crystals had formed at site #2 (Figure 2-17a) and site #18 (Figure 2-17b). The soil-ash mixture was then observed in the SEM (Figure 2-18, 2-19) to identify the spatial relationship between ettringite crystals and mineral phases present in the soil. Ettringite crystals appear to form both on mineral surfaces and inside available pore space. These results are very similar to those observed for ettringite formation in Coolside column lysimeters described earlier.

The addition of water to AFBC ash resulted in the formation of large white crystals which were identified as calcium carbonate and typically resulted in the formation of a thin calcium carbonate crust on top of the ash - water mixture. Although the results of the XRD analyses of this crusty material indicated the presence of only calcite (CaCO_3), SEM observations suggest that based on the crystal morphology aragonite (CaCO_3 polymorph of calcite) crystallized first and was transformed into the calcite structure. The formation of a calcium carbonate-enriched crust was also observed when water was added to FBC residue.

Ettringite:

Ettringite is a **calcium - aluminosulfate - hydroxide - hydrate** mineral

Ettringite is both an *individual mineral* $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}]$, and the *group name* for a series of chemically analogous isostructural compounds.

The ettringite structure is shown below:

Figure 2-1

Ettringite structure after Moore and Taylor (Nature, 218, p. 1085, 1968) or (Acta Cryst. B26, p. 386-393, 1970).

The trigonal - hexagonal unit cell of the mineral ettringite consists of columns of composition $(\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24 \text{H}_2\text{O})^{6+}$ which are aligned along the crystallographic c-axis (Figure). These columns are accompanied by channels of composition $\{(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}\}^{-6}$. In this structure the Al^{3+} ions are octahedrally surrounded by $(\text{OH})^-$ ions. Sulfate ions occur in a tetrahedral orientation.

Coolside #2. (a) XRD pattern of Coolside #2 (as received). No ettringite crystals recognized in XRD pattern. (b) Coolside #2 aged for 99 days in water with 12.57 lb/F surcharge. XRD pattern indicates the presence of ettringite crystals. (c) Coolside #2 sample aged 100 days in water with 2.5 lb/F surcharge. More ettringite crystals formed compared to the sample exposed to higher surcharge for approximately same amount of time.

Figure 2-2

Figure 2-3(a) Coolside #2: Swell Characteristics (determined by KTC)

Figure 2-3 (b) Coolside #2: Swell Characteristics (determined by KTC)

Figure 2-3 (c) Coolside #2: Swell Characteristics (determined by KTC)

Figure 2-3 (d) Coolside #2: Swell Characteristics (determined by KTC)

Figure 2-4 Comparison of XRD patterns obtained from Coolside 1000 samples from (a) column lysimeter 9, (b) column lysimeter 10 and, (c) column lysimeter 11. The largest amount of ettringite formed in lysimeter 11 which was packed with the lowest density.

Figure 2-5 Comparison of XRD patterns of (a) Pilot Plant #1 from column lysimeter 19; (b) Pilot Plant #2 from column lysimeter 20 and; (c) Pilot Plant #3 from column lysimeter 21. All XRD patterns show two major ettringite peaks. The largest amount of ettringite was observed in column lysimeter 21 which was characterized by the lowest packing density.

Figure 2-6 Comparison of XRD pattern of Pilot Plant #2 samples from column lysimeter 20 (a) Top Zone, (b) Middle Zone and, (c) Bottom Zone. Ettringite crystals appear to be enriched in all zones however, the middle zone has the highest ettringite concentration.

Figure 2-7 XRD Pattern

FBC RESIDUE

FBC Residue (as received)

FBC Ash Non-Hydrated

FBC Ash Hydrated

Figure 2-8 XRD Pattern of (a) non-hydrated FBC ash. No ettringite crystals are observed (b) hydrated FBC ash with ettringite crystals present.

FBC Hydrated, 161 Days in H₂O

Figure 2-8

Figure 2-9

SEM microphotograph illustrating FBC ash after addition of water. Needle shaped ettringite crystals grow on mineral surfaces. The FBC ash was not compacted and ettringite crystals were able to grow without tension from neighboring mineral phases. Ettringite crystals appear to grow in a randomly oriented fashion, forming a complex network of intergrowing crystals. The largest ettringite needles in this FBC sample are approximately 15 microns long.

Figure 2-10 XRD Pattern of

Figure 2-11 Comparison of XRD pattern of (a) FBC pellets before hydration, (b) FBC pellets after hydration for 14 days (50-60 pounds water pressure). Minor amounts of hemi-hydrate (bassanite) formed inside hydrated FBC pellets. (c) XRD pattern of hemi-hydrate crystals that were concentrated at hydrated FBC pellet surfaces.

Figure 2-12

SEM microphotograph of hemi-hydrate (bassanite) crystals. The hemi-hydrate crystals grow on the surfaces of the FBC-pellets after the pellets were submerged for 14 days in water (with 50-60 pounds of water pressure). Crystals of various sizes are observed. Most hemi-hydrate crystals are characterized by abundant cracks which occur on the mineral surface.

Figure 2-13

SEM microphotograph of a single hemi-hydrate (bassanite) crystal. The crystal surface shows multiple fractures and cracks. At some areas along the hemi-hydrate crystal surface portlandite ($\text{Ca}(\text{OH})_2$) crystals occur in small agglomerations.

Figure 2-14

SEM microphotograph of FBC pellet interior. The sample consists of a multitude of micron-sized mineral agglomerations of portlandite and anhydrite. The agglomerations are typically surrounded by a thin precipitation layer consisting of calcium carbonate (in the SEM photo represented by a white rim around granular mineral agglomerations). At 70 times magnification large cracks are recognized throughout the pellet interior.

Figure 2-15

450 times magnification of FBC pellet interior. The SEM image illustrates the presence of small cracks that typically surround mineral agglomerations.

Figure 2-16

AFBC Ash (as received)

NO SMOOTHING

AFBC Site #2

AFBC Site #18

Figure 2-17 XRD pattern of AFBC ash - soil mixtures. AFBC ash (7 wt% mixed in soil) at experimental road station at Kentucky Route 11. (a) XRD pattern of sample taken at site #2. (b) XRD pattern of sample taken at site #18

Figure 2-18

SEM microphotograph of soil - AFBCash mixture from field experimental site #2. Needle like ettringite crystals occur intergrown with the clay minerals and sand. The box in the left side photo includes the ettringite crystals which are enlarged at the right side photo. Ettringite crystals appear to grow inside pores and on mineral surfaces.

Figure 2-19

SEM microphotograph of ettringite crystals that grow on mineral surfaces in soil - AFBC ash mixtures from experimental field site #2.

Figure 2-20

**White Crystal Agglomerations
Separated from Soil - Ash Mixture**

SITE 2-1 WHITE CRYSTAL

NO SMOOTHING

Chapter 3

GEOTECHNICAL PROPERTIES

UNCONFINED COMPRESSIVE STRENGTH

Unconfined compressive strengths performed on compacted specimens of by-products obtained from the Coolside SO₂ removal process are substantially greater than strengths of compacted specimens of many different types of natural soils (1). For

Figure 3-1. Unconfined Compressive Strength, 90% Compaction

Figure 3-2. Unconfined Compressive Strength, 95% Compaction

example, unconfined compressive strengths of specimens of Coolside by-products compacted to 95 percent of maximum dry density (ASTM D 698) and optimum moisture content approach values of 1500 psi. Unconfined compressive strengths of many clayey soils typically range from 10 to 60 psi. (ASTM D 2166) Several unconfined compressive strength tests have been performed on remolded Coolside by-product, specimens. The material was obtained from a successful demonstration of Coolside SO₂ removal technology at the Ohio Edison Edgewater Station in Lorain, Ohio. The

Figure 3-3. Unconfined Compressive Strength, 100% Compaction

The samples were sealed in airtight containers and aged for various times, up to one year, at room temperature after remolding. To examine how compaction affects the Coolside material nine series of tests are being conducted on specimens remolded at

or near 90, 95, and 100 percent of maximum dry density and optimum moisture content as determined from low-energy, standard, and modified compaction (KTC procedure, ASTM D 698, and ASTM D 1557, respectively) Unconfined compressive strength has increased with aging time for all series of tests. Very little or no strength gain occurs for 14 days. Strength increases quickly from about 14 to about 365 days, except for specimens compacted to ninety-five percent of low energy and modified compaction which did not increase in strength after ninety days, as seen in Figures 3-1 through 3-3. Unconfined compressive strength values range from about 13 psi (90% low energy compaction, 1 day age) to 2,611 psi (100% modified compaction aged one year).

PERMEABILITY

Figure 3-4. Permeability, 90% Compaction

Figure 3-5. Permeability, 95% Compaction

Permeability tests (U.S. Army Corps of Engineers EM 1102-2-1906) have been performed on specimens remolded to densities and moisture contents similar to those tested for unconfined compressive strength. The tests were performed in air pressurized chambers using a back pressure saturation technique and falling head method. Equations for calculating the coefficient of permeability, k , have been described by Daniel (1). Permeability data is plotted as a function of aging time in Figures 3-4 through 3-6. Analyses of the

Figure 3-6. Permeability, 100% Compaction

Figure 3-7. Permeability as a Function of Void Ratio

Figure 3-8. Saturated Unconfined Compressive Strength, 90% Compaction

permeability data to date -- one year age time -- indicates sealing and aging Coolside specimens at room temperature does not significantly affect the coefficient of permeability except for specimens remolded near 90, 95, and 100 percent of modified compaction which are decreasing with time. However, the coefficient of permeability decreases as the void ratio (volume of voids divided by the volume of solids) decreases and the dry density increases as seen in Figure 3-7. The degree of permeability ranges from about 1.3×10^{-5} cm/sec to 7.5×10^{-7} cm/sec. The degree of permeability of the compacted specimens may be described as low to very low. A coefficient of permeability of 10^{-7} cm/sec is considered practically impermeable and is the minimum value allowed for landfill liners in many states.

Unconfined compressive strength tests were performed on specimens after testing for

Figure 3-9. Saturated Unconfined Compressive Strength, 95% Compaction

Figure 3-10. Saturated Unconfined Compressive Strength, 100% Compaction

permeability. These tests were performed to determine any strength loss (as compared to unsaturated tests) of the Coolside materials in a saturated condition. Saturating the Coolside material after aging does not significantly affect the strength as seen in Figures 3-8 through 3-9. This is not an indicator of strength of the materials aged in an environment where excess water other than that used to compact the samples is present.

SWELL CHARACTERISTICS

TABLE 3-1. INDEX PROPERTIES

Sample Number	Liquid Limit (%)	Plasticity Index (%)	Grain-size Percent Finer Than:		Classification	
			No. 10 (%)	No. 200 (%)	UNIFIED	AASHTO
COOLSIDE*	NP	NP	100	95	ML	A-4(0)
FBC ASH	NP	NP	100	51	SM	A-4(0)
SILTY CLAY	36	11	90	70	CL	A-6(8)
PLASTIC CLAY	71	37	99	93	CH	A-7-5(44)
AFBC (7%)-SOIL MIXTURE	49	14	91	49	SM	A-7-5(5)

* Specimens CS-2, 388, 397, 1040, and 1050

be used to stabilize and improve the bearing strengths of clayey subgrades of highway pavements. However, to qualify as materials for uses in the highway industry, swelling must be predictable. If swelling is severe, then the physical and geochemical mechanisms that cause swelling must be understood and means to control the swelling must be devised. The physical swelling characteristics of by-products from two SO₂ removal technologies are being examined. Additionally, swelling characteristics of an AFBC (Atmospheric Fluidized Bed Combustion) spent lime-soil mixture and two typical soils -- clays that have been used to construct many subgrades in Kentucky -- were included for comparative purposes.

Sources of Materials and Index Properties

Coolside by-products were obtained from the Ohio Edison Edgewater Station at Lorain, Ohio and the CONSOL Coolside pilot plant in Pennsylvania. Three series (numbers 1, 2, and 3) of Coolside by-product samples were collected from the ESP

By-products produced from flue gas desulfurization (FGD) technology for removal of SO₂ in coal-fired power plants have potential applications in the highway construction industry. Compacted by-products could be used, for example, to construct base courses of highway pavements. Moreover, by-products containing high percentages of CaO or Ca(OH)₂ can

hopper of the Edgewater Station in February of 1990 during the Coolside process demonstration program. Samples identified herein as CS-388 and CS-397 are composite materials from Edgewater sample series number 3. CS-1040 and CS-1050 are two samples from Edgewater sample series number 1. Samples identified as CS-2 were obtained from the CONSOL Coolside pilot plant operating in the recycling mode. These samples were produced at conditions that simulate operation of the Coolside process installed on a unit burning medium-sulfur (2.5 percent) Ohio coal. Sulfur content of CS-2 was about 8 percent. Edgewater Coolside samples contained about 2 percent of sulfur. Detailed analyses are given elsewhere(1). Samples of a FBC ash were obtained from a silo of a coal-fired circulating fluidized bed combustor in a coal-fired co-generating plant in Pennsylvania on February 18, 1992. The FBC by-product was hydrated by CONSOL before testing. The AFBC spent lime (non-hydrated) was obtained from an oil refinery in 1987 and is a by-product of an AFBC process used in cracking crude oil. The AFBC spent lime contained about 10 percent of calcium sulfate. Two typical, residual clayey soils were obtained from Kentucky. Index properties of the samples are compared in Table 3-1.

Swell Testing Procedures

Swelling characteristics were determined by submerging specimens in water in confined CBR molds and consolidometers. Diameter and height of CBR-size specimens were 6.0 and 4.58 inches, respectively. Consolidometer specimens measured 2.5 inches in diameter and 1.0 inch in height. All specimens were compacted to about 95 percent of standard dry density and optimum moisture content, as obtained from ASTM D 698-87, following a procedure proposed by Hopkins et al (3). Field specifications of many agencies require those compaction criteria. Laboratory bearing ratio tests were performed on some of the larger specimens as a means of evaluating strength properties after swell. Immediately after inundation of the specimens, dial deflection measurements were obtained as a function of time.

Test Results and Analysis

Swelling of FGD by-products due to the absorption of water (and chemical reactions) may affect the structural integrity of the disposed material at a disposal site and the potential uses of the by-product in structural applications (e. g., road construction). For example, swelling of a compacted by-product, used as a base course, may do little structural damage to the highway pavement if it occurs very rapidly and ceases before placement of the pavement, although the magnitude of swelling may be very large. Although the time rate of swelling may be very slow, taking many years to complete, little damage may occur if the magnitude of swelling is small.

A typical swelling - time curve of a compacted specimen of the Coolside material (CS-2) is shown in Figure 3-11. Swelling may be divided into two parts: primary and

Figure 3-11. Vertical Swell of Coolside Specimen 2

secondary swelling. Usually, primary swelling represents a large portion of the total swelling. Secondary swelling is linear when the vertical swelling is plotted as a function of the logarithm of time. Hence, coefficients of primary swelling and secondary swelling may be computed using principles proposed by Terzaghi (4) and used to forecast the time rate of swelling for a given field problem. The magnitude of primary swelling (of thin layers) may be estimated by the vertical strain observed from a laboratory test.

Magnitudes of primary swelling are shown in Figure 3-12. Numbers (0, 7, or 14) shown at the bottom of each bar refer to the aging time (in days) of each specimen in sealed containers before submerging in water. Numbers at the top of each bar represent a small surcharge pressure (0, 0.1, or 0.5 psi) applied to each specimen. A pressure of 0.5 psi is about equivalent to

Figure 3-12. Comparison of Primary Swelling Magnitudes

Figure 3-13. Primary Swelling Coefficients

the pressure exerted by a 6-inch layer of pavement. When the aging time and the applied surcharge pressure were zero, the magnitude of primary swelling of specimens CS-388, 397, 1040, and 1050 ranged from 8 to 16 percent. The amount of primary swelling decreased as the surcharge pressure was increased. For example, when the surcharge pressure of CS-388 and 1040 was increased from zero to 0.5 psi, the amount of swelling decreased from about 15 percent to 2 percent. Swelling of CS-2 was reduced from 29 percent to 15 percent when the surcharge was increased from 0.1 to 0.5 psi. A similar trend was observed for the other specimens. Additionally, the amount of swelling decreased when the specimens were allowed to age prior to

soaking. For instance, the amount of swelling of CS-388 decreased from about 16 percent at no aging time to about 5 percent at a 7-day aging period. Primary swelling of the two soils were about 5 and 12 percent, respectively. Primary swelling of the AFBC spent-lime soil mixture was 25 percent. Primary swelling of the Coolside specimens that had been aged for seven days prior to soaking and surcharged at 0.5 psi was less than five percent, or equal to or less than, values of primary swell observed for the two typical soils. Even though a surcharge pressure of 0.1 psi was used, the primary swelling of CS-2 (no aging) was much larger than the primary swelling of the other Coolside specimens that were not surcharged or aged. The higher sulfur content of CS-2 may have played an important role in producing a swelling magnitude that was greater than those observed for the other Coolside samples.

Coefficients of primary swelling are compared in Figure 3-13. This coefficient is calculated by the equation shown in Figure 3-12. Specimen aging generally had a significant effect on the observed values. For example, coefficients of primary

swelling of specimens CS-388, 397, 1040, and 1050 at zero aging time ranged from 5.6 to 15.8 in² per day. Coefficients of the same Coolside samples that had been aged ranged from only 0.017 to 1.52 in²/day. Primary coefficients of those specimens increased when the surcharge pressure was increased from zero to 0.5 psi. Coefficients of primary swelling of the AFBC spent lime-soil mixture, the silty clay, and plastic clay were 0.07, 0.053, and 4.35 in²/day, respectively. Changing the aging period or increasing the surcharge pressure did not appear to cause significant changes in the coefficient of primary swell of CS-2. Values ranged from 0.05 to 0.08 in²/day.

Figure 3-14. Secondary Swelling Coefficients

Generally, coefficients of secondary swelling of CS-2 specimens (Figure 3-14) were slightly larger than the secondary coefficients of CS-388, 397, 1040, and 1050. The equation shown in Figure 3-14 was used to calculate the secondary coefficients. Coefficients of secondary swelling of all Coolside specimens ranged from zero to 0.1. Secondary coefficients of CS-2, CS-388, and CS-397 that had not been aged appeared to be slightly larger than coefficients of specimens that had been aged for seven or 14 days. However, secondary coefficients of specimens surcharged 0.5 psi were generally slightly smaller than those of specimens that were not surcharged. CBR strengths of Coolside by-products after swelling ranged from 133 to 430 - exceptionally high values.

Figure 3-15. Swelling of FBC Ash

Magnitudes of swelling of compacted specimens of the FBC ash are shown in Figure 3-15. Although primary swelling is still in progress, even after 107 to 179 days, the magnitude of swelling of aged specimens is much less than specimens that were not aged. Moreover, where surcharge pressures were applied, the magnitude of swelling is less than the magnitude of swelling of specimens that had no surcharge loading. Swelling trends of the FBC by-product are similar to those observed for the Coolside specimens.

Case Study

FGD by-products have the potential to be used to stabilize clayey subgrades of highway pavements. For example, a by-product obtained from an AFBC process of an oil refinery was mixed with a clayey subgrade of a highway route in Kentucky (3). Combined length of the two highway subgrade sections was about 2.5 miles. The pavement section consisted of 8.5 inches of asphaltic concrete, 5 inches of crushed limestone aggregate, and a 12-inch compacted mixture of the AFBC spent lime (7 percent) and clayey soil (93 percent). The AFBC - soil subgrades were allowed to cure for seven days. Approximately two months after placement of the asphaltic base courses and a rainy period, noticeable "humps", running perpendicular to centerline, formed on the pavement surface.

Figure 3-16. Field and Predicted Time Rates of Swelling

Numerous points were immediately established on the surface of the sections and optical surveys were performed periodically. Placement of the asphaltic surface course was delayed for several months. Magnitudes of pavement heaving as large as 3.5 inches were measured during a 5-month period. Additional laboratory swelling tests were performed. Based on laboratory coefficients of primary and secondary swell, the magnitude and time rate of swelling were estimated. Time required to complete 95 percent of primary swell was estimated to be about 1.1 years after completion of the subgrades (Figure 3-16).

About 10 months after observed differential heaving, the pavement was milled to remove "humps" and the surface course was placed. Survey points were re-established. These points have been monitored for about 5 years. Observed swelling at one location is compared to the estimated swelling in Figure 3-16. Five years after placement of the surface course, only about 0.2 inch of swelling has occurred. Based on the projected linear relationship of swelling and the logarithm of time, an additional 0.2 inch will occur over the next 22 years. In situ CBR tests performed on top of the AFBC spent lime on numerous occasions over a 6-year period show that the bearing strength decreased only slightly after construction. However, CBR strengths during this period generally exceed 10 and range as high as 40. Pavement rutting, 5 years after placement of the surface pavement, is nominal and generally does not exceed about 0.13 inch.

Had the 12-inch layer been constructed of Coolside material of a nature similar to CS- 2, the magnitude of swelling, based on the results in Figure 3-12 could, potentially, range from 3.5 inches (no surcharge pressure) to about 0.6 inch (with some surcharge pressure). Considering that a six-inch layer of pavement provides a surcharge loading of about 0.5 psi, the magnitude of swell is estimated to be about 1.9 inch. However, based on the coefficient of primary swelling ($0.05 \text{ in}^2/\text{day}$), a time of about 2.1 years would be required to complete 95 percent of primary swelling. Moreover, based on a coefficient of secondary swelling (Figure 3-14), approximately 0.8 inch of secondary swelling would occur between the approximate end of primary swelling and 27.4 years after construction. Total estimated swell would be about 2.7 inches. This amount of swelling would probably adversely affect the structural integrity of the pavement. However, field trials and more study would be required to determine the exact swelling behavior of the Coolside by-product.

Assuming that a 12-inch layer of plastic clay was used as the subgrade, the magnitude of primary swelling is estimated to be about 1.4 inches. Time required to complete 95 percent of primary swelling is estimated to be about 1.6 years. Estimated secondary swelling that would occur between the end of primary swelling and 27.4 years is 0.1 inch. Total swelling is 1.7 inches. If the silty clay is used to construct the 12-inch subgrade layer, then estimated primary swelling is about 0.5 and about 1.3 years would be required for this amount of swelling to occur. Secondary swelling is estimated to be 0.05 inch. Total swelling is less than 0.6 inch. Hence, swelling of the two typical clayey soils ranges from 0.6 to 1.7 while estimated swelling of the CS-2 is 2.7 inches.

Although by-products produced from FGD technology, such as the Coolside and FBC by-product, have potential applications in the highway industry, the physical and geochemical processes that lead to swelling of these materials need to be fully understood. Means of controlling the swelling of these materials need to be devised. The physical swelling characteristics of materials from the Coolside technology and an FBC by-product were briefly examined above. Results of swelling tests performed

on compacted specimens indicated that primary swelling decreased as the surcharge pressure was increased. Aging the materials prior to inundating the materials also appeared to reduce the amount of primary swelling. Coolside by-products that contained less sulfur or were aged swelled less.

Lysimeter Filling

Large amounts of FGD materials are currently being disposed of in landfills. This practice will continue until suitable recycling uses can be developed. Compacting ash and FGD materials conserves landfill space while increasing disposal costs. Laboratory and field compaction characteristics of the Coolside by-product and techniques that were used in placement of the materials in field lysimeters under controlled conditions are described below. In placing the materials, different compactive efforts were used in an attempt to simulate different compactive states of the Coolside by-product as it might exist in a landfill. Leachate from the lysimeters will be collected over a period of three years. Chemical analysis of the leachate will be performed to assess the potential impact on the environment and to observe relations between leachate characteristics and different compactive states of the Coolside by-product. Coolside by-products were obtained from the Ohio Edison Edgewater Station at Lorain, Ohio during a demonstration program in February of 1990. Sulfur content of the Coolside materials was approximately 2%.

Figure 3-17. Dry Density as a Function of Compactive Energy

Laboratory Compaction

Different laboratory compactive energies were used to examine the effects of increased compactive effort on dry density and moisture content of the Coolside by-products. Laboratory moisture-density tests were performed at modified, standard, and low energy compaction. Compactive energies of these tests were 56,246, 12,374, and 4,050 ft-lbs/ft³, respectively. A low energy compaction procedure was devised to examine engineering properties of lightly compacted materials (5). The test is similar to standard methods, except a lighter (1.8 lbs.) rammer is used. Dry density increased as the compactive effort was increased. Values ranged from 36 lbs/ft³ (loose state) to 78.1 lbs/ft³ (modified compaction) as shown in Figure 3-17. When the

compactive energy was increased above the low energy compactive energy, the dry density increased from 65.5 lbs/ft³ to 78.1 lbs/ft³. The maximum dry densities obtained from standard (ASTM D698) and modified compaction (ASTM D1557) were only 6.4 % and 19.2 %, respectively, greater than the maximum dry density obtained from the low energy test, although the compactive energies were 3.1 and 13.9 times larger than the low energy compactive effort. Consequently, efforts to compact the Coolside material to a dry density greater than maximum dry density obtained from standard or low energy compaction would probably be uneconomical. However, the economics would depend on such variables as land cost, equipment cost, and haul distances. Moreover, the economics of environmental impacts would play a major role in formulating a field compaction scheme. Optimum moisture content decreased as compactive energy increased as shown in Figure 3-18.

Figure 3-18. Optimum Moisture Content as a Function of Compactive Energy

18. Optimum moisture contents for low energy, standard, and modified compactions were 45.0, 36.5, and 28.5 %, respectively.

Lysimeter Description and Instrumentation

Four concrete lysimeters located at the University of Kentucky's Environmental Field Research Station in Montgomery County, Kentucky are being used to study field behaviors of material generated from the Coolside process and fly-ash (from a Kentucky coal-fired power plant). The four lysimeters surround a central chamber used for leachate collection and instrumentation. Each individual lysimeter is 8 feet by 8 feet by 10 feet deep (Figure 3-19). The tops of the lysimeters are flush with the ground surface. The inner walls, adjacent to the central access chamber, are fitted with knock-outs at various depths to allow installation of leachate transport tubes and access to instrumentation. Pressure cells were mounted in lysimeter 3 (L-3 in Figure 3-19) at depths of 4 and 6 feet from the surface. An additional pressure cell was installed in lysimeter 4 at the mid-point of the fly ash fill. Before filling, a stainless steel tube was placed in the center of each lysimeter to allow access for a nuclear moisture probe. The probe has been used to monitor changes in moisture under natural weathering conditions. Thermocouples were placed at various depths in the lysimeters to measure temperature differences which might occur from hydration or mineralogical phase changes. Settlement (swell) platforms were placed at the soil-Coolside interfaces and the soil-fly ash interface to measure vertical movements of the materials.

Filling Operations

The material was transported to the site in barrels. Enough material was mixed with water to construct one lift. Each lift ranged from 4 to 6 inches in thickness. Usually about five barrels of Coolside was sufficient to make one lift. To avoid weighing each individual barrel, a correlation was established to determine the weight. The distance

Figure 3-19. Schematic of Field Lysimeters

from the top of the barrel to the surface of the Coolside residue was measured for several barrels. The barrels were then weighed on a portable field scale. A correlation was established whereby the weight of the material could be determined by simply measuring the distance from the top of the barrel to the surface of the material. This procedure worked very well in determining the weight of the material because of the uniform particle size and density of the material. The average weight of each barrel was approximately 250 pounds. The amount of water needed to reach the desired moisture

content was then calculated. Each lift consisted of approximately 1,250 pounds of dry Coolside material. The residue was placed on a concrete mixing pad which was built with three side curbs to contain the materials on the pad while mixing. Water from a calibrated tank was then applied to sufficiently moisten the material to control dust. The mixture was blended with a rear thine tiller. Water was continually added until the desired moisture content was reached. A front end loader was used to place the mixture into the lysimeters. The front end of the concrete pad did not contain a side curb so that the front end loader was free to move onto to the pad to load the mixed materials.

One foot of Ottawa sand was placed in the bottom of each lysimeter (Figure 3-19) to improve leachate collection. Three leachate transport tubes were embedded in the sand. Lysimeters were filled with 7 feet of Coolside materials. Lysimeter 4 was filled with 7 feet of fly ash. Leachate collection tubes were also placed at the soil-Coolside interfaces and the fly ash-soil interface and at various depths in the four lysimeters. A native silty clay was loosely placed, to facilitate the downward movement of rainfall, on the residue in the top two feet of each lysimeter. Moisture and density measurements were obtained from drive-tube and sand-cone tests. A nuclear moisture-density gauge was also used. Results obtained from the nuclear gauge were used for comparison and calibration purposes and were not used to determine actual density and moisture conditions. Because of the fine-grained nature of the materials, the drive-tube sampler technique provided the most reliable means of measuring dry density and moisture content of each lift.

Results and Analysis

Dry density and moisture content

Coolside material was placed in lysimeter 1 (L-1 in Figure 3-19) with no compactive effort. The material was mixed to a target moisture content of 37 % before placement. No target density was established because the material was placed loosely. The average dry density and moisture content of the 16 loosely placed lifts were 44.1 lbs/ft³ and 37.5 %, respectively. Average lift thickness was approximately 5.3 inches.

Coolside materials placed in the second lysimeter (L-2) were compacted to target dry

Figure 3-20. Dry Density of Each Lift, Lysimeter 3.

moisture-density curve was similar to those established in standard moisture-density tests. Field compaction was performed with a hand-held plate compactor. The dry density and moisture content obtained for 17 lifts averaged 49.2 lbs/ft³ and 38.9 %, respectively. The average lift thickness was about 4.9 inches.

Figure 3-21. Moisture Content of Each Lift of Lysimeter 3.

gasoline-powered compactors. Vibratory plate and static (jumping jack) compactors were used. Target density was easily obtained with the static compactor; therefore, it was used more frequently. Average values of dry density and moisture content obtained for 23 lifts of compacted Coolside material were 66.2 lbs/ft³ and 37.0%, respectively. Moisture content exceeded optimum moisture content by more than 2% in a few lifts. Liquefaction occurred in these few lifts because of the excess moisture and the silt-sized particles.

A commercial fly ash was placed in the fourth lysimeter (L-4). Fly ash was used as a control material for leachate monitoring. The fly ash was purchased and transported to the field site in seventy pound bags. Approximately 1750 pounds (25 bags) of material was used for each lift. The material was lightly compacted with a hand compactor near 90% of standard maximum dry density 2% below optimum moisture content. Maximum dry density and a moisture content that was about optimum moisture content for the fly ash were 85.8 lbs/ft³ and 22%. Target density and moisture content were 77.2 lbs/ft³ (90% of standard density) and 20% percent

density and moisture content values of 49.6 lbs/ft³ and 41.2 %, respectively. These values were obtained from moisture-density tests designed to simulate the compactive efforts of a D9 bulldozer. This test was performed by applying a static pressure of 17 psi (the stress exerted by the track of a D9 bulldozer) to the Coolside by-product, which was placed in one lift in a standard 4 inch diameter Proctor mold. The material was then compacted at various moisture contents. The pressure was applied until the maximum load was reached. It was then held for 1 minute and released. The

The third lysimeter (L-3) was filled with Coolside material compacted near 95% of standard maximum dry density and optimum moisture content. Target values for density and moisture were 66.5 lbs/ft³ (95 percent of standard compaction) and 37.0 %, respectively. Maximum dry density and optimum moisture content obtained from standard moisture-density tests were 70.0 lbs/ft³ and 36.5 %, respectively. Dry densities and moisture contents obtained for each lift of lysimeter 3 are compared in Figures 3-20 and 3-21, respectively. The material was compacted with a hand-held

moisture. The average density and moisture content values obtained for nineteen lifts were 76.4 lbs/ft³ and 20.5%, respectively. Target and actual values of dry density and moisture content obtained for each Lysimeter are compared in Table 3-2.

Table 3-2. Summary of Dry Density and Moisture Content Measurements.

Lysimeter	Average Dry Density (lbs/ft ³)	Target Dry Density (lbs/ft ³)	Average Moisture Content (%)	Target Moisture Content (%)	Number of Lifts
1	44.1	N/A	37.5	37.0	16
2	49.2	49.6	38.9	41.2	17
3	66.2	66.5	37.0	37.0	23
4	76.4	77.2	20.5	20.0	19

Pressure, Temperature, and Swell Measurements

Pressure at a depth of 6 feet in lysimeter 3 increased slightly as fill was placed. A maximum pressure of 15 psi was reached a few days after filling operations were completed. The pressure eventually returned to near zero. Pressure at 4 feet increased to about 7 psi and returned to near zero. Pressure increase in the lysimeter containing fly ash was less than 2 psi. In the three lysimeters containing Coolside materials, the moisture accumulated near the top of the materials, initially, and gradually moved downward in the materials with increasing time. Moisture from precipitation in lysimeter 4 initially increased at the bottom of the fly ash and gradually increased upward to the top of the material. Lysimeters containing Coolside materials increased in temperature and reached a maximum value of 120 degrees Fahrenheit about two weeks after placement of the Coolside residue. Subsequently, the temperature decreased. Thermocouples installed in the lysimeter containing fly ash showed no increase in temperature. To date no significant swell(or consolidation) has occurred in the Coolside or fly ash materials.

Unconfined compressive strength

Unconfined compressive strength tests were performed on thin-walled tube samples collected from lysimeter 3. The samples were obtained after the material had been compacted to 95% of standard density. The specimens were allowed to age for various times before testing. The strengths of the field specimens are compared in Figure 6 to laboratory strengths of specimens remolded near 95% of standard maximum dry density. Strength tests on lysimeter samples were performed after permeability tests were conducted. Unconfined strength of the lysimeter specimens ranged from 1.2 psi at a 1-day aging time to approximately 188 psi at a 7-day aging time. As seen in Figure 3-22, the unconfined compressive strengths of the field lysimeter samples correlated well with unconfined

compressive strengths of the laboratory specimens.

Permeability

Permeability tests were performed on selected samples obtained from lysimeters 3 and 4. The coefficients of permeability (k) for the lysimeter samples are shown as a function of void ratio (the volume of voids divided by the volume of solids) and

Figure 3-22. Unconfined Compressive Strength of Laboratory and Lysimeter Samples.

Figure 3-23. Permeability Coefficient as a Function of Void Ratio.

compared to permeability coefficients of remolded laboratory samples in Figure 3-23. The coefficient of permeability of the Coolside materials increases as the void ratio increases. The tests were performed in a pressurized cell using a back saturation technique and falling head, rising tailwater method. Equations for calculating the coefficient of permeability have been described by Daniel (5).

Moisture-density test results obtained from laboratory testing procedures can be applied to field applications for Coolside material and fly ash. The material can be compacted to the desired density and moisture content if proper procedures are used. Unconfined compressive strength and permeability coefficients obtained from field lysimeter samples correlated well with laboratory data.

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Chapter 4

Task 4

Laaboratory Leaching Studies

Summary

Results from leaching of two laboratory columns packed with Coolside waste at a static density of 49 lb/ft³ at 41% moisture content are provided. These columns were leached at a rate of 70 ml/week and analyzed for metals, alkalinity and conductivity. One column was open to ambient atmosphere while the other was exposed to an atmosphere containing 2.5% CO₂ to simulate the high concentration of CO₂ in the soil. The pH values for these two columns appear to overlap over the entire period of the test starting at 12.7-12.8 and rising over the first several weeks to approximately 13.1 after which they steadily dropped 12.2 over the remaining 15 weeks. The total alkalinity profiles, expressed as calcium carbonate equivalent values, are quite similar for the first 7 weeks but diverge slightly after that time with higher values being observed for the CO₂ sparged column. Initial values climbed from an already very high value of 15,000 mg CaCO₃/Liter to a high of 27,000 mg CaCO₃/Liter after 3 weeks. Between the 5th and 16th weeks the values declined from 7500 to 3000 mg CaCO₃/Liter. The conductivity of these samples reached its maximum in the earliest measurements remaining there through the 3rd week when it dropped quite dramatically to a lower plateau. After 6-8 weeks the level of conductance was about 40% of the maximum value reached in the early stages.

Chloride and sulfate were the main anions present while concentrations of nitrate and bromide were extremely small. The chloride concentrations in the initial leachate was between 28,000 and 33,000 ppm dropping 19 ppm after 20 days on stream. The

chloride concentration from the CO₂ purged column exceeded the non-purged column up to 11 days on stream when they merged at approximately 140 ppm. The initial release of sulfate ion from the column behaved very similarly to the chloride elution pattern. The sulfate ion concentration began at the 6000 ppm and dropped to approximately 100 ppm.

Sodium was the dominate cation present. Like chloride, it initially a very high concentration between 10,000-15,000 ppm dropping to less than 3000 ppm in 10 weeks. At 20 weeks the level for the non-purged column had 340 ppm. Potassium started at 1700 ppm and increased to 3000 ppm after 3 weeks. At this point the potassium concentration in the non-purged column leachate diminished while the CO₂-purged column leachate increased for the next two weeks to a high of 3700 ppm after which it diminished. The concentrations after approximately 15 weeks became nearly the same at approximately 700-800 ppm. Calcium concentration started at 450 ppm dropping to less than 100 after the 2nd week. Higher CO₂ partial pressures appeared not to affect the Ca concentration.

Results on molybdenum, arsenic, vanadium and selenium are also reported because of their high sensitivity to CO₂ partial pressure. Molybdenum concentration in the CO₂-purged column reached a high at 2 weeks at 34 ppm versus a corresponding 2 week level for the non-purged column of 24 ppm. After 15 weeks the two merged. Arsenic in the non-purged column lined out at less than 1 ppm after 10 weeks whereas in the CO₂-purged column leachate the level approached the 1 ppm level only after 19 weeks. At 10 weeks the As level in the CO₂-purged column leachate was 8 ppm. A maximum selenium concentration was found at 6 ppm after 4 weeks for the CO₂-purged column. However, after 10 weeks it had dropped to less than 1 ppm. The vanadium maxima was observed from the CO₂-purged column between 7-14 weeks of from 1.5-3 ppm.

Introduction

The results from the leaching of laboratory columns which were packed with Coolside plant waste will be reported. These 2 inch diameter columns, suspended on a glass wool mat, were packed to a level of 2 feet and topped with 1 inch of Ottawa sand. The results from the two columns that are discussed in this report were packed at a static density of 49 lb/ft^3 at 41% moisture content. The columns were continuously kept saturated by topping with a 1 inch head of water and were leached at a rate of 70 ml/week to generate adequate sample for weekly analysis of metals, alkalinity and conductivity. Leaching of these columns commenced upon addition of 70 ml of water and terminated when the head level reached the 1 inch starting level.

One column was left open to the ambient atmosphere while the other was exposed to an atmosphere containing 2.5% CO_2 which was piped to the columns in a parallel flow pattern through a common manifold to provide an exchange of the void space over the columns. Since the concentration of CO_2 in the soil is a function of both plant root respiration and microbiologic activity, with root respiration being the major factor, the concentrations in the soil would be greater than would be experienced at ambient carbon dioxide partial pressures. In soil samples the upper limit of CO_2 concentration with normal anaerobic respiration would be about 21% or equal to the amount of oxygen in the normal atmosphere. However, conditions normally encountered would be much less. In at least two previous studies the CO_2 concentrations in ground environments were found to be as high as 11-15% of the composition of the gas phase. In studies where groundwater carbon dioxide concentrations were directly correlated to CO_2 partial pressures, atmospheres containing from 0.3 to 3.8% CO_2 were observed. These values compare to the ambient atmospheric concentration of 0.03%. These factors will definitely affect leachability properties of waste samples.

Leachate Properties

The values of pH, alkalinity and conductivity of the two static-density packed columns have been measured over a 22 week period. The pH profiles for these two columns are shown in Figure 4-1. The pH values for these two columns appear to overlap over the entire period of the test up to this point. The initial values started at 12.7-12.8 rising over the first several weeks to approximately 13.1, after which they steadily dropped to 12.2 over the remaining 15 weeks. This drop would be consistent with both elution of the OH^- ion from the column as well as some possible reaction of dissolved carbon dioxide with the OH^- ion to form HCO_3^- . Although CO_2 concentration may ultimately affect pH values, at these pH levels no distinct differences were observed.

The total alkalinity profiles over a 17 week period were measured using EPA Method 310.1, Titrametric pH 4.5. The calcium carbonate equivalent values, which are shown in Figure 4-2, are quite similar for the first 7 weeks but diverge slightly after that time with higher values being observed for the CO_2 sparged column. Initial values climbed from an already very high value of 15,000 mg CaCO_3 /Liter to a high of 27,000 mg CaCO_3 /Liter after 3 weeks. The next week (4th) the value dropped back to 14,000 mg CaCO_3 /Liter, a level slightly lower than at the start. Between the 5th and 16th weeks the values declined from 7500 to 3000 mg CaCO_3 /Liter. These values represent total alkalinity including OH^- , CO_3^{2-} , and HCO_3^- ions. From the pH values, which were all in excess of 12, the concentrations of OH^- and CO_3^{2-} ions are quite significant.

The conductivity of these samples as shown in Figure 4-3, which reflects the ion abundance in the aqueous phase, was measured over the course of this time period. The conductance was near its maximum in the earliest measurements remaining there through the 3rd week when it dropped quite dramatically to a lower plateau. After 6-8 weeks the level of conductance was about 40% of the

maximum value reached in the early stages. This dramatic drop can be related to the changing ionic composition of the leachates observed during this period. Quite significantly, the rate of decrease in conductance between the CO₂ and non-CO₂ purged columns were quite similar except that the drop occurred one week later for the CO₂ purged column. Even during the later periods from the 5th through the 12th weeks the CO₂ purged column remained offset from the non-CO₂ purged column by 1 week. From that time, the two appear to become superimposed. As yet we have no clear understanding as to why the increased partial pressure of the CO₂ in the atmosphere should increase the conductance of the solution.

Anion Concentrations

An ion chromatograph was used to qualitatively identify the anions present in representative samples of leachate. Chloride and sulfate were the main anions present. Concentrations of others, such as nitrate and bromide, were extremely small. The actual concentrations of chloride and sulfate in the leachates are reported for periods up to 18 days on stream. The chloride concentrations, as shown in Figure 4-4, in the initial leachate for the two columns was between 28,000 and 33,000 ppm. As expected, because of the high solubility of chloride salts, the concentration dropped significantly over the period up to 18 days to a level of 19 ppm after 20 days on stream. During the period from 4 to 10 days the readings for the CO₂ purged column exceeded the non-purged column by up to approximately 14,000 ppm, this occurring after 5 days on stream. These values narrowed until they become superimposed after 11 days on stream having diminished to approximately 140 ppm.

The initial release of sulfate ion from the column behaved very similarly to the chloride elution pattern as shown in Figure 4-5. The sulfate ion concentration began at the 6000 ppm level dropping to approximately 100 ppm for both columns. It then increased

slowly reaching a maxima after 7 days with the concentration for the CO₂ purged column reaching approximately 1500 ppm versus 900 ppm for the non-purged column. During the period 7-10 days these levels then declined reaching an apparent steady state of 1000 ppm for the purged column and less than 100 ppm for the non-purged column.

Cation Concentrations

Sodium concentration, like chloride, had initially a very high concentration between 10,000-15,000 ppm dropping to less than 3000 ppm in 10 weeks as shown in Figure 4-6. The concentration in the leachate from the CO₂ purged column lagged behind comparable measurements in the leachate from the non-purged column by approximately 2 weeks. At 15 weeks the level for the non-purged column had reached 650 ppm with the level being 340 ppm after 20 weeks.

Potassium also had a significant impact on the overall charge density in these solutions starting off at 1700 ppm and increasing to near 3000 ppm after 3 weeks (see Figure 4-7). At this point the potassium concentration in the non-purged column leachate diminished while the CO₂-purged column leachate increased for the next two weeks to a high of 3700 ppm after which it diminished. The concentration of potassium in the CO₂-purged column leachate lagged behind the non-purged column until approximately 15 weeks after which they become nearly the same at approximately 700-800 ppm.

Calcium concentration in the leachate started off at a concentration of approximately 450 ppm at 1 week dropping to less than 100 after the 2nd week as shown in Figure 4-8. Thereafter the concentration leveled out at 7 ppm. The profiles for both columns were superimposable over the entire 20 week period.

Although other cations are being followed, molybdenum, arsenic, vanadium and selenium are of particular interest because of their apparently higher sensitivity to CO₂ concentrations in the leaching solution. Molybdenum, for example, during the first 10 week interval, shows a difference of 5-10 ppm concentration in leachate concentrations between the CO₂-purged and non-CO₂-purged columns (see Figure 4-9). The concentration in the CO₂-purged column reached a high at 2 weeks of 34 ppm versus a corresponding 2 week level for the non-purged column of 24 ppm. After 15 weeks the two merged.

The same happened for arsenic (Figure 4-10), selenium (Figure 4-11), and vanadium (Figure 4-12), except the maxima appeared after 4-9 weeks of leaching. Arsenic concentration in the non-purged column appears to line out at less than 1 ppm after 10 weeks whereas in the CO₂-purged column leachate the level approached the 1 ppm level only after 19 weeks. At 10 weeks when As was at 1 ppm from the non-purged column, the As level in the CO₂-purged column leachate was 8 ppm.

Selenium behaved somewhat similarly. After 10 weeks the leachate concentrations for the two had dropped to less than 1 ppm for both whereas only 1 week earlier the concentration in the CO₂-purged column leachate was 3 ppm. The maximum value in these columns was in excess of 6 ppm at 4 weeks for the CO₂-purged column. The behavior of vanadium was quite similar to selenium. The maximum leachate concentration was observed from the CO₂-purged column between 7-14 weeks where the concentration was between 1.5-3 ppm. The concentration from the CO₂-purged column continued to exceed the non-purged column after 20 weeks being 1.0 and 0.5 ppm, respectively.

Status

Leaching of these two columns and analysis of the data that have

been generated from these columns is continuing. An explanation of the effect of CO₂ on the leaching behavior of these columns and the individual ions is being developed. This sensitivity suggests that the cover placed on the field lysimeters may have a dramatic effect on the leaching behavior of those materials, especially in the vadose zone during the initial period after being exposed to aqueous leaching solution.

Figure 4.1

Figure 4.2

Figure 4.3

Figure 4.4

Figure 4.5

Figure 4.6

Figure 4.7

Figure 4.8

Figure 4.9

Figure 4.10

Figure 4.11

Figure 4.12

Chapter 5

Task 3

Field Leaching Studies

Loading of the four lysimeter cells at the Hope Creek Environmental Field Research Station of the University of Kentucky Center for Applied Energy Research in Montgomery County, Kentucky, was completed in November, 1992. The design and specifications of the cells are shown in Diagrams 5-1 and 5-2 which highlight the structural features of the cells.

Filling Procedure

All of the cells were filled following essentially the same sequence of steps which varied only in so far as the target specifications of density and moisture. One foot of Ottawa silica sand was placed in the bottom of each cell covering each of the four sets of three collection tubes that actually rested on and was spread over the bottom of each cell. Specific weights of the solid waste were then poured from individual drums onto the diked mixing pad and blended with water, which was taken from the calibrated storage tank. The stored water, which had previously been trucked from Jeffersonville, Kentucky, was then blended with the waste using a tiller until the desired moisture level was achieved. Mixing continued until the desired consistency of the solid was obtained. The mixture was then placed into the lysimeter using a front-end loader and spread to a uniform depth. Samples were taken of fill at each 0.5 foot interval and measured in the laboratory for dry density and moisture content.

A 2" OD stainless steel pipe spanning the entire length of the cell was mounted in the center in a vertical position prior to initiating the filling operation. These tubes were sealed at the bottom to prevent egress of moisture and protruded above the upper level of the top layer of cover soil of the cell by approximately 6 inches. Each was fitted with

Diagram 5-1. Schematic Diagram of Field Lysimeters

Diagram 5-2. Schematic of Instrumented Lysimeter with Material Emplacement

a cap to prevent moisture from entering the pipes. As filling progressed, horizontally placed slotted PVC leachate collection tubes (4 " OD) which were wrapped with porous nylon sheeting which spanned the width of the cell passing through opening in the cell wall which were sealed with silicone sealant to prevent water from leaking. The placement of these sampling lines in all lysimeters were at the bottom in the sand layer close to the interface of the sand-solid waste, at variable elevations which were generally halfway up the bed (see Table 5-1), and at the upper ground cover-waste interface. Each of the leachate sampling tubes are capable of sampling horizontally across the cells. 90° elbows were placed on each of the tubes immediately after passing through the lysimeter wall to divert leachate flow downward to 20-liter plastic collection vessels.

Multiple K-type stainless steel sheathed 1/8" OD thermocouples were installed in each lysimeter and temperatures are read using a portable battery powered meter. The thermocouples are mounted on the 90° leaching-tube elbows perpendicular to the face of the lysimeter wall. Each thermocouple then passes perpendicularly through the lysimeter cell walls along the axis of the leachate collection lines. Each thermocouple is then horizontally redirected through the perforated tube wall at approximately 8 inches inside the inner face of the lysimeter wall. Thermocouples in all the lysimeters are located at the midpoint of the waste layer and in the sand layer at the bottom, which corresponds to positions of the leachate collection tubes (see Table 5-1). In lysimeter #3, two additional thermocouples were added. One was added at the position of the leachate collection tube located at the top clay/waste interface and the second was inserted through the middle leachate collection tube but was directed downwardly to read temperatures 3 ft above the sand/waste interface level or 4 ft. above the bottom of the cell. Both these thermocouples are mounted on the elbow.

Filling Operation

The time required for filling the individual cells varied depending on the amount of tamping necessary to reach target fill density. Generally, about 3-5 layers or about 1.5 to 2.5 ft of fill could be applied in one day. During the early stages of the operation the

procedure progressed at a steady pace. The latter cells were filled during the fall when the weather became seasonably variable which slowed the filling operation. During the filling period the cells that were either in progress or had been completed were covered with plastic tarpaulins to divert any rainfall from entering the cells. Following the complete filling of all the cells, the tarpaulins were removed simultaneously exposing the cells to an identical sequence of rainfall.

Table 5-1. Lysimeter Cell Configurations ^a				
	1	2	3	4
Fill	Coolside	Coolside	Coolside	Fly Ash ^b
Geotechnical Fill Description	Loose ^c	Low Energy	Standard	Loose ^c
Elevation range, ft. from bottom of cell				
Cover Soil	8 - 10	8 - 10	8 - 10	8 - 10
Waste Material	1 - 8	1 - 8	1 - 8	1 - 8
Ottawa Sand	0 - 1	0 - 1	0 - 1	0 - 1
Leachate Sampling Points, ft from bottom				
Top, clay/fill interface	8 ft	8 ft	8 ft ^d	8 ft
Midpoint	3 ^d	4 ^d	6 ^d	6 ^d
Lower			4 ^d	
Bottom, sand layer	0.25 ft ^d	0.25 ft ^d	0.25 ft ^d	0.25 ft ^d
Moisture Target, wt%	37.5	40	37.5	22
Moisture Actual, avg wt%	37.5	38.9	37.7	20.5
Target Dry Density, lbs/ft ³	none	49.0	66.8	none
Avg Dry Density, lbs/ft ³	44.0	49.2	66.2	76.4
a.. Swell platforms installed in each cell 8 feet from bottom. b. Commercially available fly ash which was purchased from TransAsh. c. Cell loaded with little or no compactive effort. d. Location of thermocouple.				

Filling of Cell #1 progressed quite rapidly occurring over an approximately 5 day period in late September. Cell #2, which was filled at low-energy density, took place over a slightly longer period of 7 days. Cell #3 was started immediately after completion of Cell #2 around 13 October but was not completed until about 1 month later because of unfavorable weather conditions during this period. As the filling procedure progressed the temperatures were monitored as the individual thermocouples were buried. Filling of the last cell, Cell #4, began immediately after completion of Cell #3 and was completed over a period of 12 days.

Moisture and Density Targets

In filling the cells, targets for most of the density and moisture levels were established. The actual densities achieved for loading lysimeters #2 and #3 deviated by less than 1% from the target values. In fact, the target and actual density values for cell #2 are 49.0 and 49.2 lbs/ft³, respectively. The achieved values for the Coolside loaded cells are related directionally, as expected, to the amount of compactive energy used in filling the cells, as shown in Table 5-1. The densities ranged from 44.0 lbs/ft³ for the lightly compacted material in lysimeter #1 up to 66.2 lbs/ft³ for the material in lysimeter #3, which was compacted to 95% of standard dry density. The density of the lightly compacted fly ash in lysimeter #4 was significantly higher, i.e., 76.4 lbs/ft³, than the Coolside material in lysimeter #3, which was compacted to 95% of standard dry density. The standard dry density of the fly ash material of 88 lb/ft³ was significantly higher than the 70 lb/ft³ standard dry density of the Coolside waste. The significantly lower density of the Coolside material is probably related to the amount of hydrated lime contained in the material.

The actual moisture levels attained in lysimeters #1 and #3 containing the Coolside material were essentially the same as the target values while the value for cell #2 was 38.9 wt% actual versus 40 wt% target. The 20.5 wt% actual moisture level in lysimeter #4 was considerably lower than for the Coolside material which probably relates to the absence of lime in the sample.

Temperature Monitoring

The recorded bed temperatures for all three of the Coolside containing lysimeters rapidly increased upon hydration and emplacement into the lysimeters with the highest temperature of 48°C being observed in lysimeter 1 two weeks after packing. The magnitude of the exotherms appeared to be inversely proportional to the bed packing densities. Following the initial increase the temperatures decreased slowly over the period from October 1992 to January 1993 followed by a slow increase in line with surrounding soil temperatures.

Temperature monitoring was initiated as the cells were being filled in order to observe any indication of the onset of chemical reactions. Temperatures, which were recorded twice weekly, are plotted for each individual cell in Figures 5-1, 5-3, 5-5 and 5-7. The staggered start of readings for a couple of the cells reflects the time delay related to filling of the individual cells. This delay was particularly observable for lysimeter #3 where initial readings covered a period of over 30 days. Lysimeters #1 - 3, which were all filled with Coolside waste, showed significant exotherms while for lysimeter 4, which contained fly ash, no exotherm was observed.

The temperature plots indicate that the exothermic reaction develops immediately, presumably upon addition of water to the waste. The increase in temperature in the sand layer, which is due to the exotherm of the waste portion of the bed, follows the bed temperature-time profile. The time required to reach the bed maxima in the bottom sand layer is the same for both lysimeters #1 and 2. The temperature maxima observed at the mid height of these two cells ranged from 32 to 48°C.

In lysimeter 4, the initial 16-17°C readings in both the fly ash layer and in the bottom sand layer were also the maximum observed. Temperatures immediately began dropping upon loading the cell reaching the 10°C level within about 30 days. The higher temperatures were at the bottom of the bed indicating the main direction of heat loss was in an upward

direction. Correspondingly, for cells #1 and #2, both of which experienced significant exotherms, about 4 months passed before the temperatures dropped to the 8°C level. Although the magnitudes of the exotherms within the waste portion of lysimeters #1 and #2 cannot be determined from this data, they were both greater than the temperatures observed in lysimeter #4 by from about 15 to 30 C°.

The temperatures increased in lysimeters #1 and #2 as soon as the material was loaded into the cells reaching the maximum in 2 - 3 weeks after making between 4-6 individual readings. The inverted temperature profiles in the lysimeters filled with Coolside waste versus lysimeter #4 which contained the fly ash leaves no doubt that the Coolside waste is the source of the exotherm.

Since filling of lysimeter #3 took place over a much longer period of time, the pattern of temperature increases is more complicated as shown in Figure 5-5. The initial rise in temperature in the sand layer reflects the exotherm related to an initial loading of Coolside ash to a level somewhat below the position of the lower thermocouple. In fact, the first three readings taken on the lower thermocouple over a period of about 10 days indicates the level of waste in the cell had not reached that thermocouple or significant cooling of the material had occurred. Recall that thermocouple was placed 4 ft. above the bottom of the cell. The next reading jumped dramatically from approximately 18°C to 36°C. It appears the exotherm occurs upon mixing the waste with water since in all these cases mixing with water immediately preceded placing the material within the cell.

When the loading reached the lower thermocouple level, the onset of the exotherm maximum was observed on the 4th reading (2 weeks) as for lysimeter #1. Likewise, when the loading reached the middle level for this cell, the temperature increased dramatically from 24°C to 31°C.

The temperatures for the thermocouples in cells #1, #2 and the lower and bottom thermocouples in cell #4 leveled out at ~8°C. The lower middle temperature in lysimeter #4, to which fly ash was added, dropped to 9°C for 3 readings at the end of January

which was 1°C lower than for the corresponding readings for the Coolside containing cells. It appears that the residual heat had dissipated from the cells by mid to late January. The temperature of the top and middle thermocouples in cell #3 had dropped 4°C and 7°C, respectively, indicating response to the cold seasonal temperatures.

From the temperature lows observed in mid-winter, the readings continued to increase for all of the lysimeters as overall soil temperatures in the region increased over the summer months. The two thermocouples in lysimeters 1 and 2 reached 20°C and 22°C during mid-summer. The thermocouple in the waste layer of lysimeter 4 appeared to be slightly higher which may be related to the absence of saturation of this lysimeter. During the summer, the top and middle thermocouples in Lysimeter 3 (Figure 5-5) showed the unusual feature of a higher than background temperature increase, which most likely indicates a continuation of the exothermic reaction that commenced upon the hydration of the materials prior to emplacement. Since lysimeter 3 contains the most densely packed bed, and hence the highest concentration of material, it is possible that insufficient water was added during the packing period to drive the exothermic reactions to completion.

Bed Moisture Measurements

Moisture measurements have been made since about 1 December when the covers were removed from all the cells. These measurements were made following a standard monitoring protocol using a Troxler Neutron Moisture Probe. This instrument, which contains both a neutron source and a neutron detector encased within a probe, is lowered into the centrally placed, vertically orientated stainless steel pipe. The rate of emission of slowed backscattered neutrons at regularly spaced vertical intervals along the pipe is measured which provides an indication of the moisture concentration in the bed. Plots of the actual neutron counts made at 5 different elevations for each of the lysimeters over the year are shown in Figures 5-2, 5-4, 5-6, and 5-8. The readings are absolute values and were not calibrated for either the Coolside or fly ash materials at the specific loading densities in the respective cells. The readings made at 2.5, 4.5 and 6.5

ft. above the base of the cells represent moisture contents in the Coolside material while the readings at 0.5 ft. is a measure of the moisture in the sand layer and the reading at 8.5 ft. is a measure of the moisture level in the clay overlayer. The absolute readings made in the sand layer at 0.5 ft. and in the clay overlayer at 8.5 ft. can be related since these materials were all identical.

The lysimeters containing the coolside material were observed to undergo hydration from the surface downwards. The upper layers hydrated to saturation before allowing moisture to pass through to lower levels with the rate of hydration being greater than the rate of percolation. The lysimeter containing the fly ash control however (Figure 5-8) underwent hydration from the bottom upwards, the rate of percolation being greater than the rate of hydration. The lineout moisture level of the top clay layers were all between 500-575 counts/min. The initial values varied somewhat and were considerably lower. The lower values reflected the difference of wetting of the clay during the loading process as well as the effect of drying during the period after the loading of the individual cells was completed and the tarpaulins were removed.

The weekly rainfall totals measured at the field site are shown in Figure 5-27. Over the monitoring period to date, the observed weather patterns have been typical for the region. The average weekly rainfall over the period November 19, 1992 to September 30, 1993 was 0.87 inches with a maximum of 3.08 inches and a total of 4 weeks with no recorded precipitation. Two periods of heavy snowfall occurred, the most severe over the weekend of March 13/14 which left over 8 inches of snow atop each lysimeter.

Of the Coolside containing lysimeters, lysimeter 3 produced leachate much earlier than lysimeters 1 and 2 (March 1993 to June 1993 for lysimeters 1 and 2). However once each lysimeter underwent complete hydration, the flow of leachate was observed to be similar for each lysimeter regardless of packing density. The majority of leachate samples have been collected from the lower leachate ports; only after heavy rainfall is any leachate collected from the middle ports.

Site Security

In order to prevent unauthorized access to the field site the gate leading to the site was locked using a chain and padlock. Keys to the gate were left with university staff as well as the property owner. The access manhole to the collection chamber was also padlocked to prevent unauthorized entry. Over the weekend of April 23/24 1993, an attempt was made to break into the collection chamber by persons unknown. A section of the padlock mount was cut through with a hacksaw, however the attempt was unsuccessful as the remainder of the locking mechanism was undamaged by the attempt. In order to prevent any further attempts a section of 4" pipe was welded over the padlock to limit access to the lock with cutting equipment. To date since the modification was completed, no further attempt has been made to break into the chamber.

pH

The leachate pH values measured from Lysimeters 1 and 2 are significantly lower than those measured from Lysimeter 3 (Figures 5-9, 5-10, 5-11) and have remained consistent at a pH $\approx$ 9.0 over the observed period compared to a pH of $\approx$ 12.2 measured from Lysimeter 3. This lower pH has had a significant effect of the observed metal release profiles from Lysimeters 1 and 2.

Alkalinity

In addition to the observed differences in leachate pH measured from each Coolside lysimeter, total alkalinity levels are also lower for cells 1 and 2. (~ 200 mg/l cf. 2000 mg/l for Lysimeter 3) (Figures 5-12, 5-13, 5-14)

The alkalinity values measured for L3 have decreased steadily over the monitoring period, i.e., down to 2000 ppm from 8000 ppm at the start of leachate collection, indicating that the buffering system holding the pH at $\approx$ 12.2 is near exhaustion and that the leachate pH should fall rapidly to a lower value in the near future.

Conductivity

For Lysimeters 1 and 2, total conductivity measurements are much higher than for lysimeter 3 indicating a higher ionic content in the leachate samples from these cells. (Figures 5-15, 5-16, 5-17)

Arsenic

The arsenic levels measured in the leachates collected from Lysimeters 1 and 2 are an order of magnitude lower than those measured in Lysimeter 3 (Figures 5-18, 5-19, 5-20) and are indicative of the lower pH values measured for these samples. The solubility of the arsenate anion decreases with pH, and as a result the levels measured in Lysimeter 3 with a pH of 12.2 are significantly higher than those measured from Lysimeter 1 and Lysimeter 2.

Sodium.

The levels of sodium measured in samples of leachate from Lysimeters 1 and 2 are much higher than those observed from Lysimeter 3 (Figures 5-21, 5-22, 5-23). This is consistent with the higher conductivities measured for these samples. The solubility of sodium within this system is obviously increased at lower pH's and may be attributed to the lack of formation of mineralogic species observed in the Coolside materials at high pH values.

Sulfate.

The sulfate levels observed in the leachate from cells 1 and 2 are also significantly higher than those measured in Lysimeter 3 (Figures 5-24, 5-25, 5-26) and are also most likely due to the lack of formation of mineralogic species at the lower pH values existing in Lysimeters 1 and 2.

Figure 5.1

Moisture Profile : Lysimeter 1 Neutron Probe Readings

▽ 0.5 ✕ 2.5 + 4.5 ○ 6.5 ■ 8.5

Figure 5.2

Figure 5.3

Figure 5.4

Lysimeter 3 Temperature Profile Coolside :- Standard Density

Figure 5.5

Moisture Profile : Lysimeter 3 Neutron Probe Readings

Figure 5.6

Lysimeter 4 Temperature Profile Fly Ash :- Low Energy Density

Figure 5.7

Moisture Profile : Lysimeter 4 Neutron Probe Readings

Figure 5.8

Figure 5.9

Figure 5.10

Figure 5.11

Figure 5.12

Figure 5.13

Figure 5.14

Figure 5.15

Figure 5.16

Figure 5.17

Figure 5.18

Figure 5.19

Figure 5.20

Figure 5.21

Figure 5.22

Figure 5.23

Figure 5.24

Figure 5.26

Figure 5.27

Chapter 6

Thermodynamic Data Base

The data obtained from the lysimeters include pH, conductivity and ionic concentrations. This solute data must be manipulated to infer chemical species concentrations and the mineral phases present in the column environment. For this a public domain program WATEQ4F¹ was selected. This program, written in Fortran, expects a single input file and produces a single output file.

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

- The original program was converted from Fortran to C and tested in DOS using WATEQ4F test case one.
- The result was modified to run under Windows 3.0/3.1 with menu items and input screens, using Borland C++ v3.1. This program was debugged with all four test cases.
- Batch data input via Windows clipboard, and output of user-selected data to either comma-delimited files or Windows clipboard was implemented.
- Options were added to allow saving, reloading or editing input preferences (input species, redox options, input units, and alkalinity options), output preferences (convergence criteria, triggers for species percentage and mineral equilibrium departure for inclusion in output, whether or not to include thermodynamics table and/or weight/molar concentration ratios in the output), and paste preferences (selection of input and individual output items for inclusion in a "cut/paste" process).

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

- This program is now called WATEQ, to differentiate it from the 4F(Fortran) version.

Preliminary Data Investigation

As an initial premise, it was assumed that, regardless of lysimeter contents and degree of compaction, pH will be the controlling parameter affecting leachate species and lysimeter mineralization. If so, then the approach to saturation of various minerals should vary smoothly with pH, except for errors derived from inherent inaccuracies in test results; any departure from this assumption indicates that there are, indeed, differences in the lysimeters and their leachates. To test this, WATEQ runs were made on laboratory column and field lysimeter results as indicated in Table 6-1. The results are illustrated in Figures 6.1 to 6.5, which show the approach to saturation ($\log[\text{IAP}/kT]=0$)² for various selected minerals versus pH. While pH trends are usually evident, it is clear that there are differences in the lysimeters and their resulting leachates. This verifies our expectations.

A second preliminary investigation involved selecting mineral phases approaching saturation within five orders of magnitude ($\log[\text{IAP}/kT] > -5$). Plots of saturation behavior over time were produced. Based upon these plots, the minerals were partitioned into groups exhibiting like behavior. Representative groups are shown for laboratory column 25 (Coolside compressed pellets, wet/dry with average pH about 11.5, rising slightly) in Figures 6.6 through 6.14. They account for approximately 90 percent of variability observed. These groups were produced and plotted for field lysimeter 3, level 3 (Edgewater Coolside, 66#/ft³@37% H₂O with average pH about 12.25, falling slightly) in order to compare saturation behavior (Figures 6.15 through 6.23). While the partitioning remains valid, saturation behavior is different, again indicating differences in the lysimeters and their resulting leachate.

The third preliminary investigation looked at the differences in behavior of selected species with

² IAP: Ion Activity Product. $\log[\text{IAP}/kT] < 0$ implies under-saturation; $= 0$ implies equilibrium. It should be noted that supersaturation ($\log[\text{IAP}/kT] > 0$) does not mean that the mineral in question will necessarily be found in solid phase.

concentrations greater than one ppm in the same two lysimeters. These were partitioned by ppm ranges. Results for column 25 are shown in Figures 6.24 through 6.27. Results for field lysimeter 3, level 3 are shown in Figures 6.28 through 6.31. The results also show differences in the lysimeters.

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

Future Directions

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

Figure 6.1

Figure 6.2

Figure 6.3

Figure 6.4

Figure 6.5

Figure 6.6

Figure 6.7

Figure 6.8

Figure 6.9

Figure 6.10

Figure 6.11

Figure 6.12

Figure 6.13

Figure 6.14

Figure 6.15

Figure 6.16

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Figure 6.28

Figure 6.29

Figure 6.30

Figure 6.31

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