

**Pilot Demonstration of Technology for the Production of High Value Materials from the
Ultra-Fine (PM_{2.5}) Fraction of Coal Combustion Ash**

Semi-Annual Status Report

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Abstract

Broad range dispersants, including naphthalenesulfonate-formaldehyde condensates (NSF) and polycarboxylate based products, were tested on both wet and dry fly ash samples from the LG&E Energy Corp. plants in the study. Tests included both total adsorption and measurement of sedimentation rate via time density relationships. A wide range of dosages were required, ranging from 0.3 to 10 g/kg. In general the ponded ash required less dispersant. Leaching tests of 5% ash solutions by weight revealed a wide range of soluble salts to be present in the ash, and found a relationship between calcium ion concentration and dispersant dosage requirement. Other parameters measured included SO_4 , Cl, F, NO_3 , PO_4 , Al, Ca, Mg, K, Na and alkalinity. An assessment was made of the available software to digitally model the overall process circuit. No prefabricated digital model was found for hydraulic classification or froth flotation. Work focused on building a model for hydraulic classification in an Excel spread sheet based on Stokes Law. A pilot plant scale hydraulic classifier was fabricated and operated. The performance of the hydraulic classifier was found to be forecastable within reasonable bounds, and work to improve both are ongoing.

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Executive Summary

Progress in This Reporting Period, January 1 to June 30, 2004

A broad range dispersants were tested on fly ash samples recovered from silos, ESP field and ponds for LG&E were evaluated for effectiveness in breaking down aqueous fly ash flocs. The dispersants examined included both naphthalenesulfonate-formaldehyde condensates (NSF) and polycarboxylate based, commercially available, high water reducers (a.k.a. superplasticizers). Testing included the measurement of total adsorption of the NSF based dispersants, as well as tests to determine minimum dosages needed to disperse fly ash flocculates as measured by time density relationships in ash slurries. In general most of the reagents proved effective. Total adsorption of the NSF DisalTM ranged from 0.3 g/kg of ash to 10 g/kg of ash. In general the ponded materials required the least of amount of dispersant. Most of the ashes tested were dispersible with the exception of the ponded materials collected at Brown and the dry silo ash collected at Cane Run. The DisalTM product proved to be the best of the NSF products tested and ADVA 100 of the carboxylates tested for this application. Final reagent selection will be based on trade offs between cost and effectiveness.

Leaching tests were also conducted on all of the ashes tested. The 5% solids solutions showed a wide range of chemistry with pH's varying from 3.9 to 11.4 and conductivity from 39 to 3370 ohms. Conductivity and calcium ion concentration were found to correlate with the amount of NSF dispersant adsorbed on the ash. Other parameters measured included SO₄, Cl, F, NO₃, PO₄, Al, Ca, Mg, K, Na and alkalinity.

An assessment was made of the available software to digitally model the overall process circuit. A leading specialized program titled JKSimMet, along with CadChem, were applicable to much of what would be incorporated into the final process circuit. However, no prefabricated digital model exists for hydraulic classification or for froth flotation. We focused on developing models for hydraulic classification. Developing both an Excel based algorithm and a pilot plant scale hydraulic classifier. Tests of both proved to be successful, and modifications and improvements to both are ongoing.

Progress in Previous Reporting Period, July 1, 2003 to December 31, 2003

Dry fly ash samples were collected from 6 of the 7 largest power plants operated by Louisville Gas and Electric Company (LG&E). Samples were taken from individual ESP hoppers in a continuous flow through stages of particulate collection. A total of 41 samples were taken from 16 operating units. The samples were thoroughly characterized for pertinent physical and chemical composition. The fly ash samples contained 10 to 50% -10µm material, with higher concentrations of finer particles located in the latter stages of particulate collection.

Flotation evaluation was conducted on a continuous flow through a single unit at each power station to assess the viability of using froth flotation to reduce the LOI in the fly ash to very low levels (i.e. 0.5% LOI) in order to enable eventual use as fillers. Ash from all of the units tested

responded favorably with the exception of the ash from Henderson Station, which is attributed to a significant proportion of un-combusted or partially-combusted petroleum coke in the ash at this station.

Bulk samples of dry ash and pond ash were also collected from Mill Creek, Trimble County, E.W. Brown and Coleman power plants and evaluated for carbon removal by froth flotation. Release analyses showed that flotation could effectively reduce carbon to acceptable levels for most of the substrates tested.

Areas of Emphasis in Next Reporting Period, July 1 to December 31, 2005.

The computer model development of the hydraulic classifier will be complete and appropriate samples from the candidate sites will have been tested in the classifier. Also, the polymer filler and superpozzolan testing (Task 2) will be ongoing, and at least preliminary information will be available and reported. The process flow sheet and layout for the PDU of the process will also be completed during this interval.

Results and Discussion

The results and discussion of progress made during this reporting period are summarized in this section, which is organized by Task and Subtask. For clarity, major accomplishments of each Task or Subtask are highlighted with a narrative description of specific activities.

Task 1 – Feedstock Evaluation

The objectives of this task are to obtain the necessary data to finalize equipment selection for the PDU design and the reagent requirements to produce high quality filler and superpozzolan from both dry ESP ash and pond ash.

Subtask 1.1 Sample Procurement

Status: Essentially Completed. The collection of samples by electrostatic field for all of the plants along with their chemical characteristics was presented in the prior report. During the interval for this report the collection of the larger bulk samples was completed. The current status of the bulk samples is presented in Table 1.

Table 1. Quantity of Bulk Samples Collected to Date.

Plant	Type of Sample	Quantity
EW Brown	Dry ESP	6 Barrels
EW Brown	Wet Ponded Ash	2 Buckets
Coleman	Dry ESP	3 Barrels
Coleman	Wet Ponded Ash	4 Barrels
Cane Run	Dry ESP	5 Barrels
Mill Creek	Dry ESP	3 Barrels
Mill Creek	Wet Ponded Ash	3 Barrels
Trimble County	Dry ESP	5 Barrels
Trimble County	Wet Ponded Ash	2 Buckets
Seebree (Henderson)	Dry Fly Ash	3 Barrels

Subtask 1.2 Sample Characterization

Status: Individual Sample Characterization completed and reported, the characterization of the larger samples is on going.

Subtask 1.3 Evaluation of Dispersion Parameters

Status: Subtask 1.3.1 Evaluation of Flotation Parameters. This task is essentially completed (see previous report).

Subtask 1.3.2 Evaluation of Dispersion Parameters

Status: Subtask 1.3.2 Evaluation of Dispersion Parameters. This task is largely completed with

most of the results presented herein.

Introduction. Both ponded and dry fly ash has a natural tendency to flocculate under aqueous conditions. These flocs must be dispersed otherwise the ash cannot be adequately classified hydraulically. Because fly ash is a glassy material formed from a melt, it does not appear to have strong surface charges, and common dispersants do not work well. We have found that high range water reducers work well in dispersing fly ash (Robl and Groppo, 2003).

The approach taken in this subtask is to first (Part 1) test a wide range of ash types for their total reagent absorption. We used DisalTM for this work. DisalTM is a naphthalenesulfonic formaldehyde condensate (NSF) product of the Handy Chemical Co. which we have used for some time. It is a common, well characterized, high range water reducer. We also examined the causes of some of the adsorption variations that we found among the various ashes and the effect of the use of a chelating agent on the adsorption of the dispersant.

In the second part of the study the actual ability of the dispersant to defloc the ash was directly measured. For this test we developed a procedure based on the settling rate of the ash and tested a number of the ashes, as well as different chemicals.

Table 2 lists the various dispersants that have been tested. Geosperse is a proprietary chemical of unknown composition. Most of the other products are aqueous solutions of naphthalenesulfonic acid, formaldehyde polymer sodium salt or are carboxylate based. Lomar Ca has calcium instead of sodium as the major cation in the aqueous solution. TI-sperse is the solid form of the sodium salt. Glenium is a polycarboxylate based product from Master Builders. ADVA-100 is an aqueous solution of polyoxyalkylene sold by WR Grace.

Table 2: Commercial dispersants and their known compositions.

Dispersant	Composition
Diloflo 987	Napthalenesulfonic acid, formaldehyde polymer sodium salt
Diloflo GS-20	Napthalenesulfonic acid, formaldehyde polymer sodium salt
Diloflo GW	Napthalenesulfonic acid, formaldehyde polymer sodium salt
Disal	Napthalenesulfonic acid, formaldehyde polymer sodium salt
Geosperse	Unknown, trade secret
Lomar Ca	Napthalenesulfonic acid, formaldehyde polymer calcium salt
Lomar LSJ	Napthalenesulfonic acid, formaldehyde polymer sodium salt
Lomar LS Liquid	Napthalenesulfonic acid, formaldehyde polymer sodium salt
MB Glenium 3030	Polycarboxylate
TI-Sperse (solid)	Napthalenesulfonic acid, formaldehyde polymer sodium salt
WR Grace ADVA-100	Polyoxyalkylene sodium salt, tributyl phosphate

Part 1: Total Adsorption Tests

Introduction. Laboratory studies were conducted to evaluate the ability of fly ashes to adsorb DisalTM on a very wide range of fly ash samples. These included Henderson Municipal Power and Light (HMPL of Kentucky) pond ash, fly ash samples from Mill Creek, a pond ash from

Coleman (Sample #15-1) and another pond ash from Ghent (Sample #7). For some of the samples, DisalTM sorption studies were performed on water-washed residues of the ashes or different components of the ashes, including portions that were either enriched or depleted in carbon residues (Table 6).

Table 3. DisalTM sorption results on Kentucky fly ashes and ash pond samples.

Plant	Ash Type, CAER Identification No., and Description	G Disal sorbed per kg ash
Brown	Fly ash 92892 with Na ₂ CO ₃	4.23
Brown	Water washed fly ash 92892	2.19
Brown	Water washed fly ash 92892 with Na ₂ CO ₃	0.97
Brown	Fly ash 92898 with Na ₂ CO ₃	1.29
Brown	Fly ash 92898, 11.0 g of 1% Disal TM used	3.30
Brown	Water washed fly ash 92898	0.52
Brown	Fly ash 92908 with Na ₂ CO ₃	1.82
Brown	Fly ash 040623	3.51
Brown	Water washed fly ash 040623	2.70
Brown	Pond ash 040720	1.57
Cane Run	Fly ash 92913	9.42
Cane Run	Fly ash 92913, Duplicate leaching	9.63
Cane Run	Fly ash 92916	9.53
Cane Run	Fly ash 92922	9.19
Cane Run	Fly ash 92932	9.71
Cane Run	Water washed fly ash 92932	5.54
Cane Run	Fly ash 040623	6.94
Cane Run	Water washed fly ash 040623	6.53
Coleman	Fly ash 92940	3.23
Coleman	Fly ash 93030	6.53
Coleman	Fly ash 93030, 50 grams ash used	9.96
Coleman	Fly ash 93030, 100 grams ash used	9.86
Coleman	Fly ash 93030, 200 grams ash used	9.99
Coleman	Fly ash 92946	4.56
Coleman	Water washed fly ash 92946	2.06
Coleman	Washed carbon residue 92946	2.62
Coleman	Washed carbon residue 92946, Duplicate	2.38
Coleman	Washed carbon-depleted fly ash 92946	2.11
Coleman	Pond core sample, Sample #15-1	1.01
Coleman	Pond core sample, Sample #15-1, Duplicate	1.52
Coleman	Pond core sample, Sample #15-1, 25 grams of ash used	1.91
Coleman	Pond core sample, Sample #15-1, 50 grams of ash used	2.42
Coleman	Pond core sample, Sample #15-1, 100 grams of ash used	2.35

Coleman	Pond core sample, Sample #15-1, 200 grams of ash used	2.32
Coleman	Pond core sample, Sample #15-1, 500 grams of ash used	4.70
Coleman	Pond core sample, Sample #15-1, Washed carbon residue	1.76
Coleman	Pond core sample, Sample #15-1, Washed carbon-depleted	0.29
Ghent	Fly ash 92866 with Na ₂ CO ₃	8.22
Ghent	Fly ash 92866	8.40
Ghent	Water washed fly ash	2.69
Ghent	Fly ash 92877 with Na ₂ CO ₃	3.37
Ghent	Pond core sample, Hole 3 Depth 4	1.67
Ghent	Pond core sample, Hole 4 Depth 3	0.91
Ghent	Pond core sample, Hole 4 Depth 3, Duplicate	1.00
Ghent	Pond core sample, Core #7, 100 g ash used, 103.9 g of 1% Disal TM used	1.83
Ghent	Pond core sample, Core #7, 100 g ash used, 113.4 g of 1% Disal TM used	0.79
Green	Fly ash 93084 with Na ₂ CO ₃	7.38
Green	Fly ash 93084	9.50
Green	Water washed fly ash 93084	7.70
Green River	Fly ash 93062	8.43
Green River	Fly ash 93060	8.57
Green River	Water washed fly ash 93060	2.35
Green River	Washed carbon residue 93060, 11.4 g of 1% Disal TM added	3.21
Green River	Washed carbon-depleted fly ash 93060	2.22
HMPL	Fly ash 93087	9.19
HMPL	Water washed fly ash 93087	5.56
HMPL	Fly ash 93088	9.28
HMPL	Water washed fly ash 93088	5.19
HMPL	Fly ash 93089	8.15
HMPL	Water washed fly ash 93089	4.61
HMPL	Fly ash 93090	7.34
HMPL	Water washed fly ash 93090	3.82
Mill Creek	Fly ash collected on Nov. 17, 2000, 100 g ash used	9.85
Mill Creek	Water washed fly ash from Nov. 17, 2000, 100 g ash	6.69
Mill Creek	Water washed fly ash from Nov. 17, 2000, 100 g ash – Duplicate	6.68
Mill Creek	Fly ash 92830	8.53
Mill Creek	Water washed fly ash 92830	3.12
Mill Creek	Fly ash 92837	8.97
Mill Creek	Fly ash 92842	4.79
Mill Creek	Water washed fly ash 92842	1.13
Mill Creek	Washed carbon residue 92842	2.68
Mill Creek	Washed carbon-depleted fly ash 92842	1.86
Mill Creek	Fly ash 92849 with Na ₂ CO ₃	8.98
Mill Creek	Fly ash 92850	8.29
Mill Creek	"Standard" 2003 Fly ash, 100 g ash used, 109.7 g of 1%	10.78

	Disal TM	
Mill Creek	Pond sample, 2003, 100 g ash used, 106.3 g of 1% Disal TM	8.43
Trimble	Fly ash 92858 with Na ₂ CO ₃	7.85
Trimble	Water washed fly ash 92858	3.15
Trimble	Washed carbon residue 92858, only 4.4 g available for use, 887.5 g water used, 10.1 g of 1% Disal TM added	2.27
Trimble	Washed carbon-depleted fly ash 92858	3.13
Trimble	Washed carbon-depleted fly ash 92858, Duplicate	3.30

Test Procedures. For most of the sorption tests, 10 grams of ash or another solid sample were mixed with approximately 900 grams of distilled and deionized (D&D) water. In some cases, as shown in Table 3, up to 500 grams of the ash were added to 900 grams of D&D water. Furthermore, the Trimble carbon residue (92858; Table 3) only had 4.4 grams available for a sorption test.

Because DisalTM sorption is most effective under neutral to alkaline conditions, up to 130 grams of a 0.02 molar (M) sodium carbonate solution were usually added to any pH < 5 ash-water mixtures to raise the pH above 7 before DisalTM addition. The DisalTM was added to the mixtures in the form of a 1% (10,000 parts per million) stock solution containing D&D water. In most cases, the mass of 1% DisalTM added to the samples was approximately the same as the mass of ash or other solids in the mixtures. However, as shown in Table 6, a few of the samples contained proportionally higher concentrations of 1% DisalTM.

After the addition of DisalTM, the mixtures were tumbled for at least two hours on an end-over-end stirrer. The samples were then filtered at 0.45 microns. The pH values of the filtrates were measured. The dissolved DisalTM concentrations in the filtered samples were determined with a Perkin-Elmer Lambda 12 ultraviolet-visible spectrometer using a wavelength of 295.0 nanometers (nm). By knowing the total amount of DisalTM added to an ash-water mixture and the amount remaining dissolved in the filtered sample through spectrometer measurements, the grams of DisalTM adsorbed per kilogram of ash (g DisalTM/kg ash) could be calculated. Because significant concentrations of dissolved DisalTM are often required to disperse and suspend fly ash particles, and adsorbed DisalTM may not as effectively contribute to dispersion, the most easily dispersed ashes should have relatively low DisalTM sorption values.

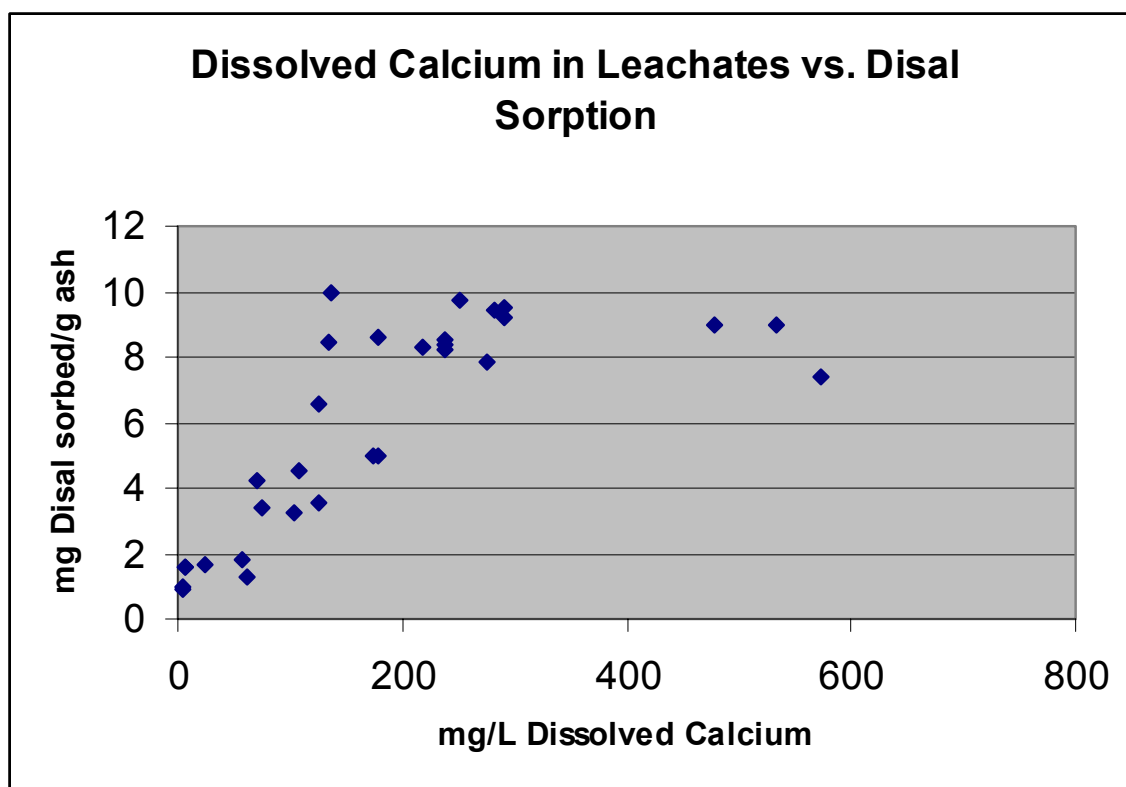
Discussion of Results. The adsorption results for the test samples range from 0.29 g DisalTM/kg ash (carbon-depleted Coleman ash pond sample) to 10.78 g/kg ash (Mill Creek 2003 "Standard" fly ash). Based on visual inspections of the data in Table 3, the pond core samples and some of the fly ashes from the Brown, Coleman, and Ghent plants have the lowest sorption values. The data also indicates that the storage of ashes in disposal ponds at the Brown, Coleman and Ghent facilities may significantly reduce their capacity to adsorb DisalTM. Washing the ashes with D&D water may also reduce the ability of the ash to adsorb DisalTM. Obviously, water washing and weathering in ponds would tend to remove even some moderately water-soluble compounds, such as calcium sulfates.

The chemistry of the ash batch leachates (See Subtask 1.4.3 below) was also compared with the

DisalTM sorption values (Table 3). In most cases, strong relationships were not observed between the ions or combinations of ions in the aqueous leachates and the DisalTM sorption values. However, a significant correlation (squared Pearson correlation coefficient [R^2] = 0.73) was found between the amounts of adsorbed DisalTM in the ashes and the conductivities of their leachates. Again, the conductivities of the leachates would be related to their total dissolved solids (TDS) concentrations, which would include dissolved calcium and other major ions. An R^2 of 0.73 also exists between the sorption values and the dissolved calcium concentrations (Ca^{2+}) in the leachates (Figure 1).

Ashes that generate high concentrations of water-soluble calcium tend to adsorb more DisalTM. This is most likely due to the calcium ion binding with the sulfate ion on the DisalTM. The reduction of the overall charge of the DisalTM would diminish the dispersive effectiveness of the DisalTM and require higher concentrations. The exact mechanism for effect is not known at this time.

Figure 1: Relationship between water-soluble calcium (mg/L) and DisalTM sorption (mg/g ash) in aqueous suspensions of Kentucky coal ashes. The three points on the right side of Figure 1 probably represent gypsum saturation.



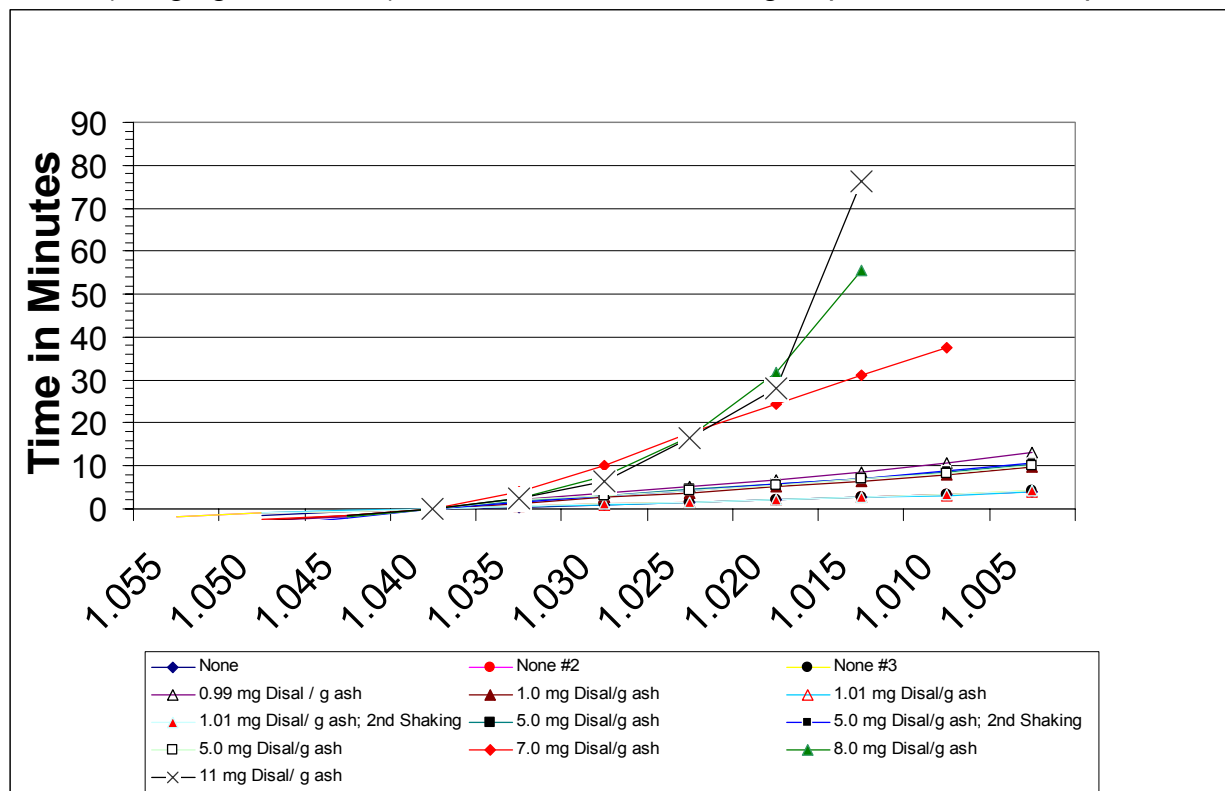
Part 2: Ash Settling Tests

Procedures. Based on the results of the sorption studies, a smaller number of fly ashes, water-washed fly ashes and pond ashes (Table 4) were selected for a series of additional dispersion tests. These ashes represent wide range of Disal™ adsorption.

The ability of Disal™ and other products to disperse ash particles in water was estimated by monitoring the specific gravities of ash-water suspensions over time. Because the residence time of an ash in the CAER pilot system is approximately 30 minutes, ash dispersion should be maintained for at least that amount of time.

The laboratory settling tests consisted of placing 100 grams of an ash into a one-liter glass cylinder. Because the pilot scale tests utilize Lexington, Kentucky municipal tap water, the laboratory settling studies included tests with the tap water as well as D&D water. Disal™ or other commercial dispersants were then added to the aqueous mixtures either directly or as a 1% aqueous solution. The total mass of liquids in each mixture was approximately 900 grams. After the dispersants were added, the mixtures were agitated. A variety of agitation methods were tested. However, back-and-forth hand shaking was found to provide the most consistent

Figure 2. Plot of Time-Density data for a sample from Mill Creek. The three highest curves (7 mg/kg and above) meet the minimum settling requirements for the procedure.



results. After the samples were shaken by hand, a stopwatch was immediately started and a hydrometer, calibrated to the appropriate range, was placed into the suspension. As the ash settled in the suspension, specific gravity declined. For consistency, "zero time" was defined as

when the specific gravity of the suspension reached 1.040. As the specific gravity of each suspension reached 1.035, 1.030, 1.025, 1.020, 1.015, and 1.010, the times were recorded. Dispersant dosages were adjusted until the specific gravity of the suspensions was maintained at 1.010 or greater for 30 minutes. A plot of typical test results is presented in Figure 2.

Discussion. Table 4 lists the minimal dosage (g of dispersant per kg of ash) of DisalTM, ADVA-100, or Glenium (Table 1) that is required to maintain the specific gravity of the ash-water suspensions at 1.010 or greater for 30 minutes. The presence of calcium in the city tap water may explain why just as much or more DisalTM is required for a thirty minute ash suspension when compared with D&D water. The results also indicate that adequate dispersion should be possible with the Mill Creek pond ash without using any, or at most very little, dispersant. The Ghent #7 pond ash also required low levels of dispersant. In contrast, the Brown pond ash and the Cane Run ashes did not respond to the dispersants at all. The "Standard" dry Mill Creek fly ashes required relatively high dosages of dispersant. Sieving the Brown pond ash and using only the finest fraction (-100 mesh) did not lower the required dosages of the dispersants. Washing the ashes with D&D water to remove most of the salts also often failed to lower the dosages. It is likely that long-term weathering changed the sorption chemistry of the Mill Creek and Ghent pond ashes in ways that were not duplicated by the Brown pond ash or laboratory ash washing.

Table 4: Minimal dispersant dosage (g of dispersant per kg of ash) required to maintain the specific gravity of an ash-water suspension (100 g ash in approximately 900 g liquid) at 1.010 or higher for 30 minutes.

Sample	Disal + D&D Water	Disal + Tap Water	ADVA-100 + Tap Water	Glenium + Tap Water
E.W. Brown (0406-23)	nd	3.7	1.7	6.1
Water Washed E.W. Brown (0406-23)	nd	0.9	1.0	2.5
E.W. Brown Pond Ash (040720)	nd	>>100	nd	nd
-100 Mesh E.W. Brown Pond Ash (040720)	nd	>>100	>>100	>>100
Cane Run (0406-30)	nd	>>100	>100	>>100
Water Washed Cane Run (0406-30)	Nd	>100	>100	>>100
Ghent #7 Pond Ash	0	0.5	0.5	0.8
Mill Creek, Unit 1, Nov. 2000	7	11	2.8	3.4
Water Washed Mill Creek, Unit 1, Nov. 2000	5	5	2.6	100
Mill Creek 2003 "Standard" Ash	7	7	2.6	3.4
Water Washed Mill Creek "Standard" Ash	5	12	3.3	9.7
Mill Creek Pond Ash	0	0	0	0

Comparison of Different Dispersants with Mill Creek Fly Ash As comparisons, settling studies with other dispersants were performed on the Mill Creek 2003 "Standard" ash in Lexington city tap water. The results are shown in Table 5. ADVA-100 required the lowest dosage to achieve the required 30-minute suspension with the Mill Creek ash.

Table 5: Minimum dosage of various dispersants to maintain a specific gravity of 1.010 or more for 30 minutes for an aqueous (tap water) suspension of Mill Creek 2003 "Standard" fly ash (100 g ash in approximately 900 g liquid).

Product	g product/kg ash
ADVA-100	2.6
MB Glenium 3030	3.4
Tl-Sperse (solid)	5.3
Disal + 5 g EDTA/kg ash	6.2
Ca-Lomar	6.8
Diloflo 987	6.9
Disal	7
Lomar LSJ	7.0
Diloflo GW	7.3
Diloflo GS-20	9
Lomar LS	10
Geosperse	46

Chelating Tests. EDTA (ethylenediaminetetraacetate) is a strong chelating agent that complexes divalent ions including Ca and Mg. The addition of EDTA was tested to determine if it would result in the reduction of DisalTM needed to pass the specific gravity test. Baker Na₂EDTA•2H₂O was initially dissolved in tap water and ash mixtures before the addition of DisalTM. All other procedures were the same as those used to generate the data in Table 5. As shown in Table 6, the addition of sodium EDTA only slightly decreased the required DisalTM dosages for the Ghent #7 and Mill Creek ashes.

Table 6: Comparison of DisalTM dosages with and without the use of Na₂EDTA•2H₂O to maintain a specific gravity of 1.010 and greater for 30 minutes in tap water-fly ash (100 g ash in approximately 900 g liquid) suspensions.

Ash	Required DisalTM dosage without EDTA (g Disal/kg ash)	Required DisalTM dosage with EDTA (g Disal/kg ash)	Dosage of EDTA (g Na₂EDTA•2H₂O /kg ash)
Mill Creek, Unit 1, Nov. 2000	11	8.8	10.5
Water Washed Mill Creek, Unit 1, Nov. 2000	5	4.1	5.5

Mill Creek 2003 "Standard" Ash	7	6.2	5
Washed Mill Creek 2003 "Standard" Ash	12	10	10.3
Mill Creek Pond Ash	0	-----	-----
Ghent #7 Pond Ash	0.5	0.3	10.2

Conclusions. Disal™ as well as the other naphthalenesulfonic formaldehyde additives were effective in dispersing the fly ash. The carboxylate based ADVA 100 was the best dispersant overall, and Glenium 3030 proved to require higher dosages than the ADVA in this application. The Disal™ adsorption data and the aqueous leaching studies of the fly ashes suggest that water-soluble calcium, probably from the dissolution of calcium sulfates and carbonates, increased the dosage of the Disal™ needed to effectively disperse the ash particles in water. Washing the ashes or using a low salt disposal pond ash reduced the required dispersant dosages. The use of Na₂EDTA•2H₂O only slightly lowered the required Disal™ dosage, perhaps by chelating some of the calcium. Overall pricing along with dispersant efficacy will both be required to make the final reagent selection. With the exception of the Brown material ponded ash had very low dispersant requirements. Because of its availability and chemistry, ponded ash appears to be an excellent candidate to produce filler products.

Subtask 1.4 Testing of Processing Parameters

This Subtask is divided further into three Subtasks

Subtask 1.4.1 Testing of Dispersion Parameters.

No activity.

Subtask 1.4.2 Testing of Dewatering

Two limited tests were conducted. This task will be further addressed in the next report.

Subtask 1.4.3 Environmental Testing

Introduction. Testing the environmental safety acceptability of the filler or superpozzolan made from the ash is an important aspect of the project. The final products will be subjected to extensive leaching tests for a wide range of trace elements. Leaching tests were conducted to determine the most readily soluble materials in all of the candidate fly ashes. This was done to obtain more environmentally relevant information regarding final feedstock selection. Also, this information was used as part of the dispersant evolution.

Procedures and Results. Aqueous batch leaching tests were performed on 26 ashes (Table 7). As part of quality control/quality assurance procedures, duplicate leaching tests were run on Samples #5, 12, 14, 17, and 23 as shown in Tables 3-5. The purpose of the leaching tests was to

determine whether any of the ashes contain significant concentrations of water-soluble species, the identity of those species, and whether they could possibly interfere with dispersion agents.

In this study, the batch leaching tests consisted of placing 48 grams of an ash into a borosilicate glass jar with approximately 900 grams of distilled and deionized (D&D) water (>17 Mohm.cm). The samples were agitated for at least 35 minutes on an end-over-end tumbler. Afterwards, pH measurements were taken on the leachates after they were filtered at 0.45 microns. The pH measurements were determined with a ThermoOrion model 410+ Meter using pH 4.00 +/- 0.01, 7.00 +/- 0.01 and 10.00 +/- 0.02 Fisher Scientific, Inc. buffers.

The filtered leachates were also analyzed for conductivity, major anions (chloride, fluoride, nitrate, phosphate and sulfate), and major cations (aluminum, calcium, magnesium, potassium, and sodium) (Tables 3-5). Alkalinities were determined on most leachates, which used EPA titration method 310.1 (US EPA, 1993). A YSI Inc. Model 32 meter provided the conductivity measurements, which are related to the total dissolved solids concentrations of the samples. Chloride, fluoride, bromide, sulfate and phosphate concentrations were measured on a Dionex LC-20 ion chromatograph using EPA Method 300.0 (US EPA, 1993). The cations were analyzed with a Spectrometrics Inc. Inductively Coupled Argon Plasma-Atomic Absorption Spectrometer (ICP-AA) using EPA Method 200.7 (US EPA, 1994).

Table 7: Leaching data on Kentucky ashes: conductivity, alkalinity, and pH results. Samples 5D, 12D, 14D, 17D, and 23D are duplicate leaching tests of samples 5, 12, 14, 17, and 23, respectively.

No.	Power Plant	Unit	g of ash leached	g of water in leachate	pH	Conductivity (ohms/cm)	Alkalinity (mg/L as CaCO ₃)
1	Brown	1	48.1	892.1	4.14	723	0
2	Brown	2	48.9	903.2	4.69	442	< 7
3	Brown	3	48.0	908.3	3.90	764	0
4	Brown	?	48.1	911.0	10.45	736	-----
5	Brown	Pond	48.1	915.2	9.31	49	-----
5D	Brown	Pond	48.1	902.0	9.38	46	-----
6	Cane Run	4A	48.0	884.0	11.40	1760	396
7	Cane Run	4B	48.0	890.8	11.24	1750	301
8	Cane Run	5	48.0	882.6	10.76	1220	249
9	Cane Run	6	48.0	905.7	11.35	1810	326
10	Cane Run	?	48.0	904.0	10.81	638	-----
11	Coleman	1	48.3	898.3	9.16	492	38
12	Coleman	2	47.9	902.1	10.10	648	118
12D	Coleman	2	48.6	884.3	10.06	664	124
13	Coleman	3	48.0	909.5	9.73	569	110
14	Ghent	1	48.1	894.8	4.22	1566	0
14D	Ghent	1	48.0	904.8	4.24	1563	0
15	Ghent	2	48.0	900.5	6.67	746	< 7
16	Ghent	Pond #3	48.1	899.3	9.36	135	31

17	Ghent	Pond #4	48.1	905.0	9.09	39.1	12
17D	Ghent	Pond #4	48.0	891.8	8.92	37.9	12
18	Green	1	48.3	910.5	3.96	3370	0
19	Green River	4	48.0	901.5	10.17	847	88
20	Green River	3	48.0	871.9	8.72	930	37
21	Mill Creek	2	48.1	905.4	11.00	1375	300
22	Mill Creek	3A	48.2	907.2	8.37	2190	17
23	Mill Creek	3B	48.0	905.6	8.66	702	31
23D	Mill Creek	3B	47.9	878.4	8.62	845	29
24	Mill Creek	4A	48.3	895.0	5.38	2380	< 7
25	Mill Creek	4B	48.2	894.6	11.20	1517	280
26	Trimble	1	48.6	910.3	4.82	1676	< 7

Table 8: Leaching data on Kentucky ashes: Concentrations of major anions. Samples 5D, 12D, 14D, 17D, and 23D are duplicate leaching tests of samples 5, 12, 14, 17, and 23, respectively.

No.	Power Plant	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)
1	Brown	546	<0.04	1.45	<0.20	<0.20
2	Brown	205	0.26	1.18	0.33	<0.20
3	Brown	485	0.06	5.95	0.35	0.25
4	Brown	274	0.26	0.59	0.21	0.36
5	Brown	5.33	0.25	0.10	0.41	0.97
5D	Brown	4.85	0.21	0.10	0.37	0.80
6	Cane Run	413	0.21	0.51	0.21	<0.20
7	Cane Run	451	0.31	0.53	<0.20	<0.20
8	Cane Run	564	0.22	0.79	<0.20	<0.20
9	Cane Run	420	0.13	0.63	<0.20	0.29
10	Cane Run	227	4.83	0.28	-----	-----
11	Coleman	278	0.30	0.67	<0.20	<0.20
12	Coleman	279	0.16	0.75	<0.20	0.40
12D	Coleman	273	0.13	0.70	<0.20	<0.20
13	Coleman	241	0.37	1.12	<0.20	<0.20
14	Ghent	1020	<0.04	7.95	<0.20	<0.20
14D	Ghent	1010	<0.04	7.32	<0.20	<0.20
15	Ghent	336	0.30	0.26	<0.20	<0.20
16	Ghent	32.4	0.80	0.07	<0.20	<0.20
17	Ghent	4.62	0.76	0.06	<0.20	0.88
17D	Ghent	4.62	0.73	0.05	<0.20	1.01
18	Green	3090	0.82	0.63	1.25	0.75
19	Green River	384	0.52	0.41	1.18	<0.20
20	Green River	483	0.37	0.90	<0.20	<0.20

21	Mill Creek	507	0.71	1.43	<0.20	<0.20
22	Mill Creek	1450	3.63	1.92	0.43	<0.20
23	Mill Creek	429	0.30	0.99	<0.20	<0.20
23D	Mill Creek	440	0.31	0.97	<0.20	<0.20
24	Mill Creek	1500	5.33	0.86	0.35	<0.20
25	Mill Creek	383	0.82	0.71	<0.20	<0.20
26	Trimble	1040	8.33	4.55	2.68	<0.20

Table 9: Leaching data on Kentucky ashes: Concentrations of major cations. Samples 5D, 12D, 14D, 17D, and 23D are duplicate leaching tests of samples 5, 12, 14, 17, and 23, respectively. Analyses for Sample #10 (Cane Run) are still in progress.

No.	Power Plant	Aluminum (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)
1	Brown	48.7	71.6	9.27	19.2	7.82
2	Brown	2.68	61.0	6.18	6.20	8.72
3	Brown	51.5	57.4	7.06	20.6	7.01
4	Brown	13.49	126	7.34	11.75	9.13
5	Brown	4.02	7.03	2.53	0.27	1.19
5D	Brown	3.72	7.64	2.8	0.35	1.24
6	Cane Run	20.3	282	0.02	24.1	14.7
7	Cane Run	27.5	292	0.03	24.6	14.9
8	Cane Run	34.3	292	0.17	23.1	12.2
9	Cane Run	19.0	251	0.03	21.6	15.5
10	Cane Run	-----	-----	-----	-----	-----
11	Coleman	6.11	103	3.51	20.2	8.85
12	Coleman	19.6	126	1.78	8.83	5.67
12D	Coleman	20.5	137	1.96	8.95	5.77
13	Coleman	13.8	109	2.81	10.9	7.93
14	Ghent	54.0	237	10.0	26.2	34.9
14D	Ghent	55.4	237	10.3	26.4	35.2
15	Ghent	0.37	75.8	5.92	17.5	56.1
16	Ghent	3.46	23.8	0.15	1.02	1.47
17	Ghent	0.73	5.40	0.61	0.41	0.82
17D	Ghent	0.77	5.09	0.58	0.40	0.82
18	Green	286	573	35.7	26.0	36.3
19	Green River	9.50	134	2.85	43.8	24.7
20	Green River	3.27	178	5.04	22.7	17.6
21	Mill Creek	34.5	237	0.10	15.1	20.1
22	Mill Creek	1.49	478	15.7	32.3	45.2
23	Mill Creek	3.29	178	5.59	1.93	6.95
23D	Mill Creek	3.29	175	5.62	2.05	6.91
24	Mill Creek	2.20	533	22.3	30.2	20.4
25	Mill Creek	18.4	218	0.01	15.3	11.2
26	Trimble	6.54	276	13.0	4.51	18.8

Discussion. The chemical properties of the batch leachates are extremely diverse (Tables 7-9). The pH values of the samples range from 3.90 (Brown Unit 3) to 11.40 (Cane Run Unit 4A). As expected, the aluminum concentrations of the leachates roughly correspond to the amphoteric nature of the metal. That is, aluminum solubility tends to be relatively high under acidic (around pH 4) and alkaline (around pH 11) conditions, but low near neutral pH values. Except for the Brown and Ghent ash pond samples (#5, 5D, 16, 17, and 17D), which have been well-leached by groundwater and infiltrating rainwater, the leachates are dominated by the presence of at least 200 milligrams/liter (mg/L) of sulfate and often more than 100 mg/L of calcium. The chemistry of the high sulfate and high calcium leachates is consistent with the presence of gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$) and/or anhydrite (CaSO_4) in the ashes. The ash pond samples probably contain calcium carbonate (CaCO_3) and other less water-soluble calcium compounds.

Subtask 1.5 Process Simulation.

Introduction. The development of the process circuit will require the integration of a number of unit processes. Their integration will be greatly facilitated by the ability to conduct computer simulation of the overall process in advance of actual construction. Also, process simulation is of value in optimizing the operation of the final circuitry.

A reconnaissance of the available commercial software was conducted. We found that probably the leading software for simulation of mineral processing circuitry is that of the Julius Kruttschnitt Mineral Resources Center. Their software, JKSimMet V5.1 offers the ability to digitally model and integrate a variety of unit processes including spiral concentrators, hydrocyclones, screen decks, and various mills. Good piping circuitry and ancillaries are also present. CadChem, a chemical engineering software modeling program, has similar features and abilities at a lower cost.

What we failed to find was any software that modeled hydraulic classifiers or froth flotation. The latter is under development in the JKSimMet program. These operations are of key importance to the process. Because of the lack of availability, we began developing our own model during the research period. Because we think that the standard release analysis that we use for froth flotation will generate adequate data for process modeling, we focused on hydraulic classification. The development of the model required the construction of a small pilot classifier to generate data. We went through several modifications of the classifier some of which are ongoing. The work on the hydraulic classifier itself and ash test results will be completed and reported in the next period.

Modeling of Hydraulic Classification. The model of the hydraulic classification was developed using an Excel spread sheet. This base for the model can be integrated into the commercial software. Important assumptions included that the ash particles are all of constant density and that they followed Stokes Law:

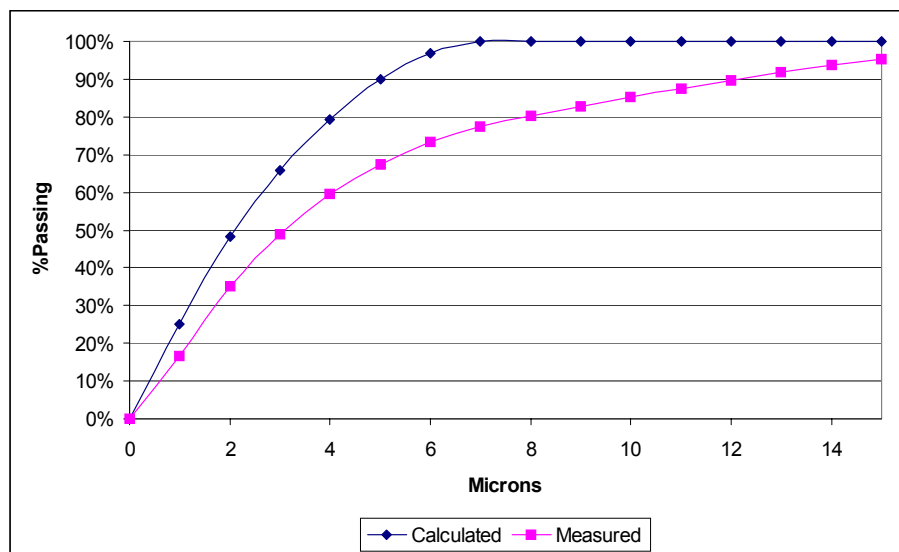
$$V_p = G (\rho_s - \rho) D^2 / 18\mu$$

where:

- V_p = rising or settling velocity of discrete particle
- G = gravity constant
- ρ_s = density of particle
- ρ = density of carrier fluid
- D = diameter of discrete particle
- μ = viscosity of carrier fluid

We also assumed laminar flow conditions and that when the particles left the zone of sorting, i.e. dropped below the “mud line,” they were removed from the system as underflow. No shape factor or other corrections were employed.

Figure 3. Comparison of cumulative size distribution between model and actual hydraulic classification data.



The particle size of the ash feedstock, product and underflow from the actual classifier was determined with a Quantichrome laser analyzer. The feed rate, density and particle size distribution were input into the model, and the product size distribution and mass were calculated and compared with the actual data.

Conclusions. The development of a digital model of the hydraulic classifier has been, in our judgment, relatively successful. In general, the model produces reasonably accurate yields, but somewhat overestimates the recovery of fine particles ($<1 \mu\text{m}$) and underestimates the recovery of coarser particles ($>10 \mu\text{m}$). Additional work is under way to enhance the usefulness of the program, which will be presented in the next report.

Task 2 - Filler and Superpozzolan Testing

No activity.

Task 3 - Finalization of Flowsheet Design

No activity.

Task 4 - Construction of PDU Facility.

A small pilot scale hydraulic classifier was fabricated during the reporting period which will most likely be incorporated into the final PDU facility.

Task 5 - Operation of PDU

No activity.

References.

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