OCDO--93040459

FINAL REPORT

**MANAGEMENT OF SOLID WASTES FROM THE LIMESTONE INJECTION
DRY SCRUBBING (LIDS) CLEAN COAL TECHNOLOGY**

OCDO GRANT AGREEMENT NUMBER: CDO/R-902-8

PREPARED BY:

**THE BABCOCK & WILCOX COMPANY
RESEARCH AND DEVELOPMENT DIVISION
1562 BEESON STREET
ALLIANCE, OHIO 44601**

RECEIVED

AUG 25 1993

PRINCIPAL INVESTIGATORS

**WILLIAM F. MUSIOL, JR.
JEAN M. CZUCZWA**

**DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE**

PREPARED FOR:

**OCDO COAL DEVELOPMENT OFFICE
OHIO DEPARTMENT OF DEVELOPMENT
P. O. BOX 1001
COLUMBUS, OHIO 43266**

MARCH 1993

THIS PROJECT WAS FUNDED IN PART BY:

**THE OHIO COAL DEVELOPMENT OFFICE
DEPARTMENT OF DEVELOPMENT
STATE OF OHIO**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LEGAL NOTICE

This report was prepared by the Babcock & Wilcox Company (B&W) for the Ohio Coal Development Office (OCDO), and neither B&W, OCDO, nor any of their subcontractors, nor any person acting on behalf of either:

- a. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or
- b. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
	EXECUTIVE SUMMARY	1
1.0	INTRODUCTION	2
	1.1 Objectives	2
	1.2 Background	2
2.0	TECHNICAL APPROACH	6
	2.1 Selection of Appropriate LIDS By-product	6
	2.2 Characterization of the LIDS By-product	6
	2.3 Setting Disposal/Utilization Criteria	7
	2.4 Solidification Experiments	7
	2.5 Physical and Chemical Testing of the Solidified Product	8
	2.5.1 Initial Physical Testing	8
	2.6 Evaluation of LIDS By-product as a Portland Cement Raw Material	9
	2.7 Evaluation of LIDS By-product as a Cementitious Low Strength Material (CLSM) for Use as Backfill	10
	2.8 Evaluation of LIDS By-product as a Soil-Cement Component for Use in Soil-Stabilization	10
3.0	RESULTS AND DISCUSSION	11
	3.1 Selection of Appropriate LIDS By-product	11
	3.2 Characterization of the LIDS By-product	12
	3.2.1 Hazardous Characteristics Tests	12
	3.2.2 Chemical and Physical Characteristics Tests	12
	3.3 Setting Disposal/Utilization Criteria	21
	3.4 Solidification Experiments	22
	3.5 Physical and Chemical Testing of the Solidified Product	25
	3.5.1 Initial Physical Testing	25
	3.5.2 Agricultural Liming Agent	26
	3.6 Evaluation of LIDS By-product as a Portland Cement Raw Material	26
	3.7 Evaluation of LIDS By-product as a Cementitious Low Strength Material (CLSM) for Use as Backfill	29
	3.8 Evaluation of LIDS By-Product as a Soil-Cement Component for Use in Soil-Stabilization	31
4.0	RECOMMENDATIONS FOR MOST VIABLE LIDS BY-PRODUCT USES	34
5.0	LIDS PROCESS CHANGES TO OPTIMIZE BY-PRODUCT USES	35
6.0	FINAL BUDGET SUMMATION	36
7.0	REFERENCES	37

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1-1	LIDS Coal Analysis	3
2-1	Hazardous Waste Characteristics Tests	6
2-2	Other Chemical and Physical Tests	7
2-3	Initial Formulation Experiments	8
3-1	Hazardous Waste Testing Results	12
3-2	Results of Chemical Tests	13
3-3	pH of FGD Process By-products	13
3-4	Total Neutralizing Potential (% Calcium Carbonate Equivalent)	14
3-5	20:1 Water Leachate Analyses	15
3-6	Sulfite/Sulfate Leachate Analyses	16
3-7	Ohio Water Quality Standards for Metals	18
3-8	LIDS By-product Particle Size Distribution	19
3-9	Pozzolanic Testing	20
3-10	Disposal/Utilization Criteria	22
3-11	Initial Formulation Experiments	23
3-12	LIDS Waste Observations and Approximate Compressive Strength Measurements	24
3-13	Unconfined Compressive Strength (UCS) of the 15-month Aged LIDS By-product	25
3-14	Calculated Compounds in LIDS By-product	28
3-15	Cement Paste (w/c = 0.5) and Cement Test Results	29
3-16	CLSM Mix Designs	30
3-17	CLSM Compressive Strength	31
3-18	Soil-Cement Compressive Strength	32
4-1	Most Viable Uses for LIDS By-product	34

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	A Schematic of the Limestone Injection Dry Scrubbing (LIDS) Process	3
2	Photograph of LIDS By-product Pellets	27

APPENDICES

Appendix A	A-1
Appendix B	B-1
Appendix C	C-1
Appendix D	D-1
Appendix E	E-1

EXECUTIVE SUMMARY

Conventional coal fly ash has been used for years in cement products, highway construction, structural fill, mine reclamation, and other applications. The current utilization record for coal combustion by-products demonstrates that economic and commercially viable applications exist. The utilization of electric utility coal ash has increased, and in 1986 stood at 21.7% of the total 66.8 million tons of fly ash, bottom ash, and slag produced [1]. As for fly ash itself, a survey by the American Coal Ash Association shows that in 1990 -- the most recent year for which complete figures are available -- 49 million tons of fly ash were produced, but only 12 million tons were used for constructive purposes. The remainder was shipped to landfills, where each ton of ash takes up about one cubic yard of landfill space. LIDS solid waste (referred to in this report as LIDS by-product) contains alkaline sorbent products from the flue gas desulfurization (FGD) process in addition to the coal fly ash residues. Thus, it is unique from conventional coal fly ash, and its most favorable applications would differ accordingly. This report provides the initial information on LIDS by-product characteristics and behavior in cementitious systems. B&W believes that it is important that Clean Coal Technologies be evaluated not only by desulfurization performance, but also by total environmental impact. Therefore, the information from this project is critical to the development of the LIDS technology.

Because LIDS is a developing Clean Coal technology, a database of chemical and physical characteristics of the by-product was first developed.

During the course of this project, it was found that the waste alone did not form high-strength products sufficient for use in construction and engineering applications. Therefore, the project was redirected to evaluate the by-product as a soil-cement and Portland cement raw material, agricultural liming agent, backfill/landfill material component, and mine reclamation/neutralizing agent.

Based on these evaluations, the most viable uses for the LIDS by-product include use in mine reclamation or as a neutralization agent. If soluble sulfites can be minimized by avoiding a dolomitic LIDS reagent, use as an agricultural liming agent has promise.

Interest from an Ohio utility in the LIDS process suggests possible application of results at the demonstration or commercial stages.

1.0 INTRODUCTION

1.1 OBJECTIVES

The objectives of this project were to characterize by-products from a pilot Limestone Injection Dry Scrubbing (LIDS) process and to develop processes directed toward the safe and economic use or disposal of these wastes. The specific technical objectives of this research project were:

1. Develop a database on the chemical and physical characteristics and properties of the LIDS by-products. Determine any hazardous characteristics of the LIDS by-products.
2. Evaluate disposal and waste utilization techniques, including conditioning of the LIDS dry by-product and formation of minimal- and high-strength solidified products that result in stabilized and environmentally benign products. During the course of the project, it was found that the waste alone did not form high-strength products. Therefore, the project was redirected to evaluate the by-product as a soil-cement and Portland cement raw material, agricultural liming agent, backfill/landfill material component, and mine reclamation/neutralizing agent.
3. Document strength and permeability characteristics of the disposal/utilization products prepared from LIDS by-products.
4. Provide brief recommendations on the most viable LIDS by-product disposal and utilization options. Recommend LIDS process changes, if any, to optimize by-product management from the B&W LIDS process.

1.2 BACKGROUND

LIDS Process

Furnace limestone injection with dry scrubbing (LIDS) is a new technology for controlling SO₂ emissions from coal-fired utility boilers. LIDS combines the technologies of limestone furnace injection and dry scrubbing to increase sorbent utilization and reduce reagent costs.

The limestone-based system is shown in Figure 1. Furnace injection provides some initial SO₂ reduction but, more importantly, calcines the limestone, providing fresh calcium oxide (CaO) for the dry scrubbing process. Fly ash, CaO, and spent sorbent pass through the dry scrubber and are removed by the particulate collection system. A portion of the collected material (high in alkalinity) is recycled and slaked (converted to calcium hydroxide) before being reinjected into the dry scrubber module as a slurry. The dry, easily handled by-product is ready for off-site disposal or utilization.

Pilot testing of the LIDS process was completed in the Alliance Research Center (ARC) Small Boiler Simulator (SBS) facility in 1991. The results were very encouraging. Using pulverized limestone, an overall SO₂ removal efficiency greater than 90% (at Ca/S of 2 and an approach to saturation temperature of 20°F) was obtained for LIDS. An analysis of the coal, an Ohio #5, used during the tests in January, 1991, is given in Table 1-1.

FIGURE 1. A Schematic of the Limestone Injection Dry Scrubbing (LIDS) Process

TABLE 1-1 LIDS Coal Analysis		
Sample	C20637	
Basis	As Rec'd.	Dry Basis
Date	12/13/90	
Type	Ohio 5	
Calculated Heating Value (Btu/#) As Rec'd. M&A Free	12831 NA	13549 14788
Measured Heating Value (Btu/#) As Rec'd. M&A Free	12426 NA	13116 14319
H ₂ O	5.26	
C	70.33	74.24
H	4.96	5.24
N	1.42	1.50
S	2.60	2.75
Ash	7.96	8.40
O (by difference)	7.47	7.87
Total	100.00	100.00

FGD By-products

As with many limestone-based flue gas desulfurization (FGD) processes, LIDS produces a by-product containing significant amounts of calcium oxide, calcium hydroxide, calcium sulfite, and calcium sulfate (calcium sulfite is the predominant reaction product for duct injection, spray drying, and LIDS). These constituents may pose disposal problems, such as fugitive dust if transported dry and a high pH leachate (pH greater than 12.5 is considered a corrosive waste). The by-product also liberates heat when unreacted CaO contacts water in a solid waste landfill. This can result in a fire and safety hazard. Increasingly, utilization of FGD product is preferred to landfill disposal.

Treating these by-products to render them more environmentally benign can be fairly simple. High calcium sulfate/sulfite/lime by-products exhibit self-cementing reactions [2] after the addition of water. This self-cementation produces a waste monolith with low permeability; thus, reducing the leaching of salts and heavy metals from the waste. The cementitious properties of FGD by-products have allowed their use in construction applications such as concrete and road sub-base [3].

Two important issues to be considered when utilizing FGD products include the attack on concrete products by sulfates and the leaching of soluble salts from the by-product, thought to occur over long periods, even after solidification. The rate of leaching of soluble salts is likely to be reduced as the permeability of the waste decreases [3]. Initially, less demanding, beneficial uses such as mine reclamation or landfilling are more likely to be implemented.

LIDS By-product

Five (5) applications specific to the LIDS by-product were investigated:

- Construction material
- Raw material (Portland cement and soil cement)
- Agricultural liming agent
- Backfill/landfill material
- Mine reclamation/neutralization

The by-product was tested as a possible construction material using various formulations of by-product and water. This testing included measurement of unconfined compressive strength (UCS) and qualitative measurements of expansion, bulk density, and volume increase. Because the UCS of the initial formulations was low, it was decided to run additional tests to evaluate other possible uses, including substitution of aggregate with LIDS by-product in various construction applications.

The by-product was investigated for use as a raw material for Portland cement and soil-cement. Manufacture of Portland cement requires materials containing calcium, silica, alumina, and iron. Impurities, such as sulfur (as sulfate), sodium, or potassium can have adverse affects on cement performance. Portland clinker raw mixes were prepared with and without the LIDS by-product. Portland clinker was produced from the raw mixes, cements were made from the mixes, and cement performance was determined with and without the by-product.

Soil-cement is a mixture of soil, Portland cement, and water compacted to a high density. Primary uses for soil-cement include base material underlying pavements and runways, embankment stabilization, pond and reservoir liners, backfill, and liner for wastewater treatment lagoons, sludge-drying beds, ash settling ponds, and solid waste landfills. The feasibility of replacing the cement with the LIDS by-product was investigated.

Because the LIDS by-product contains significant amounts of CaO and is highly alkaline, it was investigated for use as a replacement for agricultural limestone. Total neutralizing potential, sulfate/sulfite sulfur (sulfite is toxic to plants), pH, total dissolved solids, trace elements, and pelletizing testing were run on the by-product. The pelletizing testing was conducted to determine if the by-product could be formulated into a more easily handleable form.

The by-product was also tested as a landfill/backfill material. Mixes were prepared with various ratios of LIDS by-product, cement, and water. The engineering properties of compressive strength, modulus of elasticity, and shrinkage potential were evaluated on the mixes after 3, 7, and 28 days.

Mine reclamation on active or abandoned sites is another possible application of the by-product. Acid neutralizing potential, pH, and water leachate analyses were conducted to evaluate this application.

The results of this project support two of OCDO's main goals:

- Promote the use of Ohio coal and electricity sold by utilities in this state that use Ohio coal for power generation, and
- Improve environmental quality, through the use of Ohio coal.

Performing this project on an Ohio coal increases its relevance to OCDO's goals. Interest from an Ohio utility in the LIDS process suggests possible application of results at the demonstration or commercial stages.

2.0 TECHNICAL APPROACH

Five tasks were performed to characterize the LIDS by-product and to develop performance data for the waste disposal and utilization options. These tasks are discussed below:

2.1 Selection of Appropriate LIDS By-product

The LIDS pilot-scale testing was conducted under various conditions. For example, calcite-based and dolomite-based sorbents were used, various Ca/S stoichiometries were tested, and by-product samples were collected from different pieces of equipment, e.g., from the LIDS dry scrubber hopper and the baghouse. Consequently, discussions were held with the B&W LIDS project manager to select the by-product from the testing which was considered most likely to represent the final LIDS process.

2.2 Characterization of the LIDS By-product

The LIDS by-product was analyzed to determine hazardous waste characteristics and chemical characteristics important to solidification and stabilization.

The hazardous waste tests are shown in Table 2-1 (all are U.S. EPA Methods).

TABLE 2-1 Hazardous Waste Characteristics Tests		
Test	EPA Method No.	No. of Samples
Ignitability	1010	1
Corrosivity	1110	1
Reactivity	9040	1
Toxicity Characteristics Leaching Procedure (TCLP)	1311	
- Organics (volatile/semivolatile)		1
- Metals		1

Analyses to determine physical and chemical characteristics which have the potential to affect the solidification and stabilization processes of the by-product were conducted. The liberation of heat when water is added to the by-product, which would indicate unslaked CaO, was observed. These physical and chemical analyses are shown in Table 2.2.

Sampling methods followed the guidelines given in "Test Methods for Evaluating Solid Waste, SW-846, Third Edition, U.S. EPA Office of Solid Waste". Quality assurance/quality control procedures included sample bottle preparation, duplicate analyses for selected tests, laboratory blanks (where appropriate), and performance check samples (for applicable EPA methods). The hazardous waste tests were conducted by Aquatec (N. Burlington, VT) and the pozzolanic reactions test was conducted by Twin Cities Testing (Minneapolis, MN).

<p align="center">TABLE 2-2 Other Chemical and Physical Tests</p>		
Test	Method	No. of Samples
pH, 30% Solution	U.S. EPA 9040	2
Available Lime Index - as CaO	ASTM C25	2
Particle Size Distribution	ASTM D2217	1
Bulk Density - Optimum Moisture Content	ASTM D698	1
Percent Moisture	ASTM D2216	2
Pozzolanic Reactions	ASTM C311	2

2.3 Setting Disposal/Utilization Criteria

Acceptance criteria were established for possible utilization applications for the LIDS by-product. These criteria included, but were not limited to, unconfined compressive strength (UCS), leachability, and permeability. The criteria were based on standards set by the American Society for the Testing of Materials (ASTM), the U.S. Army Corps of Engineers, the Department of Transportation, RCRA limits, and drinking water standards.

Five possible utilization applications for the LIDS by-product were examined:

- Construction material
- Raw material (e.g., cement manufacture)
- Agricultural liming agent
- Landfill/backfill material
- Mine reclamation/acid mine neutralization

2.4 Solidification Experiments

Because of the complexity of cementitious reactions, it was decided that initial studies would try a number of simple formulation mixing conditions using only the LIDS by-product and water. These studies were conducted in 2 phases -- on fresh by-product 2 months old (performed as a separate, B&W-sponsored investigation) and on by-product that had been aged for 15 months. The entire test matrix is shown in Table 2-3.

Fifty (50) gram mixtures of the fresh LIDS by-product and water were mixed and stored in plastic screw-capped bottles and allowed to set. Observations and approximate strength measurements were made at 1, 3, 7, 14, 21, and 28 days.

The mixtures of the aged by-product were produced by mixing the by-product and water in a laboratory mixer and forming standard 2-inch cubes in molds. Strength measurements and qualitative observations were made of these formulations at 1, 5, 7, and 28 days.

Table 2-3 Initial Formulation Experiments	
% LIDS By-product	% Water
Phase I (By-product - 2 months old)	
80	20
70	30
60	40
50	50
Phase II (By-product - 15 months old)	
80	20
75	25
70	30
65	35
60	40
58	42
55	45

2.5 Physical and Chemical Testing of the Solidified Product

2.5.1 Initial Physical Testing

Physical testing was conducted on the initial formulations consisting of LIDS by-product and water. This testing included measurement of unconfined compressive strength (ASTM D2166) and qualitative measurements of expansion (to determine whether destructive expansive phases are present -- for cubes usually measured in one direction), bulk density, and volume increase (calculated from bulk density or specific volume of solidified by-product compared to original LIDS by-product).

The unconfined compressive strength of all these initial formulations was low. Therefore, the LIDS by-product alone is not suitable as an aggregate for engineering/construction applications. However, it has the potential for use as a substitute or partial substitute for aggregate in other applications. At the suggestion of the OCDO Project Manager, it was decided to run additional tests on the by-product to evaluate other possible applications. Discussions were held with Dravo Lime and Consolidation Coal, both of whom are conducting similar programs on FGD by-product, to elicit ideas for the additional testing. Discussions were then held with the OCDO Project Manager to determine the final test program.

Tests were added to evaluate the by-product as an agricultural liming agent and as a mine reclamation/neutralizing agent. These tests are explained below. Three major tasks were also added: (1) evaluation of LIDS by-product for use as Portland cement raw material for use in cement rotary kilns, (2) cementitious low strength material (CLSM) for use in backfill applications, and (3) soil-stabilization applications. These are described in Sections 2.6, 2.7, and 2.8, respectively.

Agricultural Liming Agent. The LIDS by-product contains alkaline solvent products in addition to the coal fly ash residues. The by-

product contains significant amounts of calcium oxide and is highly alkaline. Therefore, the by-product is attractive for neutralizing acids in soil. Agricultural operations have long used lime to improve soil conditions. The characteristics of the LIDS by-product for this application were assessed.

By-products from four different pilot-scale test conditions were analyzed for total neutralizing potential (%CaCO₃), sulfate and sulfite sulfur, pH, total dissolved solids, and chloride. The neutralizing potential was compared with that of lime to determine if the LIDS by-product could replace lime. Sulfites are of concern because they are toxic to crops. An aqueous solution with a pH greater than 12.5 is considered hazardous. Dissolved solids and chloride can leach into the groundwater.

A 20:1 water leachate analysis was done on one by-product sample to determine what metals and ions, and at what quantities, leached from the by-product.

Because the by-product is so fine, it would be very difficult to handle as is in an agricultural application. If it could be formed into pellets, it would be much easier to handle. Therefore, pelletizing tests were conducted at Dravo Lime on the by-product. Three conditions were used to form pellets:

- LIDS by-product with a water spray.
- LIDS by-product with a 1% lignin/water spray.
- LIDS by-product/1% bentonite with water spray.

Mine Reclamation/Neutralizing Agent. The properties that would enable the LIDS by-product to be used as an agricultural liming agent also make it a possible mine reclamation/neutralizing agent. Treatment of active and/or abandoned mine sites is a possibility.

2.6 Evaluation of LIDS By-product as a Portland Cement Raw Material

Portland cement raw mix is usually composed of three or more mineral raw materials which are carefully compounded based on the chemical analyses of the raw materials. Raw material characteristics such as mineralogy, hardness, free surface energy, and presence of minor chemical elements can cause considerable changes in cement performance.

LIDS by-product from 1/17/91 was sent to Construction Technology Laboratories (CTL, Skokie, IL) for evaluation. CTL planned a program to evaluate the LIDS by-product as a substitute material for potential use in cement rotary kilns. Four Portland clinkers were formed -- three with varying amounts of LIDS by-product with a standard Portland Type I-II raw mix and one with no LIDS by-product. Three of the clinkers -- the two with the highest LIDS by-product levels and the one with no LIDS by-product -- were analyzed to determine clinkering characteristics. Free lime, chemical oxide, and microscopic analyses were performed on the three clinkers. The clinkers were then ground with 5 percent (by weight) gypsum to produce cements. The cements were then tested for compressive strength and time of set. Results were compared with the standard raw cement mix to determine if any change resulted from the presence of the LIDS by-product.

2.7 Evaluation of LIDS By-product as a Cementitious Low Strength Material (CLSM) for Use as Backfill

The 1/17/91 LIDS by-product was also tested at Construction Technologies Laboratories (CTL) as a cementitious low strength material (CLSM) for backfill. CLSM applications include backfilling around utility repairs (penetrations) and buried tanks. Advantages of CLSM include:

- The material is easily placed -- it is almost self-leveling.
- The material is easily removed.
- No compaction or vibration is necessary to place.

Three LIDS by-product to cement ratios (100:0, 97:3, and 95:5) at two water contents were tested to compare strengths versus those commonly specified for CLSM backfill. Compressive strength, modulus of elasticity, and shrinking potential were evaluated for the six mixes. Compressive strength and modulus of elasticity tests were performed on 3" diameter by 6" long cylinders at 3, 7, and 28 days. Compressive strength was determined in accordance with ASTM C39 "Compressive Strength of Cylindrical Concrete Specimens", and the modulus of elasticity was determined in accordance with ASTM C469 "Static Modulus of Elasticity of Concrete in Compression".

2.8 Evaluation of LIDS By-product as a Soil-Cement Component for Use in Soil-Stabilization

Soil-cement is a mixture of soil, Portland cement, and water compacted to a high density. The primary use of soil-cement is as a base material underlying pavement and runways. Other uses of soil-cement include: slope protection for dams and embankments; liner for channels, reservoirs, and ponds; stabilized backfill; and liner for wastewater treatment lagoons, sludge-drying beds, ash settling ponds, and solid waste landfills.

A sample of the LIDS by-product from 1/17/91 was sent to Construction Technologies Laboratories (CTL) for the evaluation. A moisture-density test was conducted in accordance with ASTM D558 "Standard Test Method for Moisture-Density Relations of Soil-Cement Mixture" to determine optimum moisture and maximum density for the soil-cement. Also, cement was formulated with LIDS by-product amounts of approximately 50, 20, 10, and 0 percents. Compressive strength at 7 and 28 days was determined in accordance with ASTM D1633-84 "Standard Test Method for Compressive Strength of Molded Soil-Cement Cylinders." The relative effects of the LIDS by-product on compressive strength of the cement was then evaluated.

3.0 RESULTS AND DISCUSSION

3.1 Selection of Appropriate LIDS By-product

A meeting was held with the 1990-91 B&W OCDO LIDS Project Manager to determine which by-product(s) would most likely represent the final LIDS process and, thus, be the most appropriate for testing. It was determined that the ideal by-product would be characterized as follows:

- The by-product would be from the calcite-based LIDS system, which more efficiently removes sulfur dioxide than the dolomite-based system.
- The by-product would be from a steady-state run with a final Ca/S stoichiometry of approximately 2.0.
- The by-product would be collected from a run with a 20°F approach to saturation temperature.
- The by-product would be collected from the baghouse, which is where material for final disposal collects.
- The by-product would be in good condition after storage and be in sufficient quantity for all testing.

For two by-products, from 1/4/91 and 1/17/91, these conditions were met, with the exception that these by-products were collected from the scrubber hopper. The only difference between the scrubber by-product and the baghouse by-product is an enrichment in fine particles in the baghouse by-product. Therefore, the scrubber by-product was determined to be adequate to evaluate disposal/utilization performance.

The primary LIDS by-product evaluated was that from 1/17/91. This was from a calcite-based system, near steady-state, with a stoichiometry of 1.94. This by-product was used in all the testing. To determine LIDS by-product variability, a second by-product, from 1/4/91, was used for selected analyses and testing. This was from a calcite-based system, at steady-state, with a stoichiometry of 2.42. To further determine LIDS by-product variability, two additional by-products, from 7/20/90 and 1/15/91, were analyzed with respect to characterizing the by-product as an agricultural liming agent. The 7/20/90 by-product was from a dolomite-based system, at steady-state, with a stoichiometry of 2.74. The 1/15/91 by-product was from a calcite-based system, not at steady state, with a stoichiometry of 1.93. The most important difference between these tests is the Ca/S ratio (stoichiometry).

With the exception of a portion of the initial formulation experiments, all the testing for this project was conducted on LIDS by-product that had aged for 15 months in 55-gallon drums. Also, a few initial formulation experiments were conducted on fresh by-product that had aged for two months. Results of tests on fresh material may differ from those reported here for the 15-month aged by-product (the most important change during aging is the re-carbonation of the free lime with formation of the hydroxide as an intermediate step). Also, the LIDS testing was run in a cyclone-fired boiler. For a pulverized coal-fired boiler, the LIDS by-product would probably contain more fly ash, less CaO, and less sulfur.

3.2 Characterization of the LIDS By-product

The LIDS by-product was analyzed to determine hazardous waste, chemical, and physical characteristics important to solidification and stabilization and to add to the LIDS by-product database.

3.2.1 Hazardous Characteristics Tests

The LIDS by-product was analyzed for ignitability, corrosivity by pH, reactive sulfide, and reactive cyanide using U.S. EPA Methods. A toxicity characteristics leaching procedure (TCLP) test (EPA Method 1311) was run on the by-product for organics, volatile organics, and heavy metals. The results are summarized in Table 3-1.

TABLE 3-1 Hazardous Waste Testing Results			
Test	EPA Method No.	LIDS By-product	EPA Hazardous Waste Limit
Ignitability (°F)	1010	>150	
Corrosivity (pH)	1110	12.34	12.5
Reactive Sulfide (mg/kg)	9040	<48	500
Reactive Cyanide (mg/kg)	9040	<35	250
TCLP Metals	1311	All Below Regulatory Limits ¹	
TCLP Semivolatile Organics	1311	All Below Regulatory Limits ¹	
TCLP Volatile Organics	1311	All Below Regulatory Limits ¹	
¹ Results for individual compounds given in Appendix A.			

All five characteristics are below hazardous waste definitions. The results for all organic, volatile organic, and metal analytes were below the detection limits and well below the EPA TCLP limits. The complete analytical reports for the hazardous characteristic and TCLP tests are included in Appendix A.

3.2.2 Chemical and Physical Characteristics Tests

Chemical Testing. The following chemical analyses were conducted on the 1/4/91 and 1/17/91 LIDS by-products: pH @ 30% solution, available lime index (as % CaO), and ash analysis. The results are given in Table 3-2. All results are given on a dry basis (1.45% moisture at 110°C). The CTL report in Appendix E contains similar chemical analyses with similar results.

TABLE 3-2 Results of Chemical Tests			
	Test Method	1/4/91	1/17/91
pH @ 30% solution	EPA 9045	12.7	12.6
ALI (as % CaO)	ASTM C25	28.46	19.70
<u>Ash Analysis</u>	(by ICP)	1/4/91	1/17/91
Silicon as % SiO ₂		7.62	8.86
Aluminum as % Al ₂ O ₃		2.47	3.52
Iron as % Fe ₂ O ₃		2.71	1.87
Titanium as % TiO ₂		0.13	0.18
Calcium as % CaO		52.95	47.01
Magnesium as % MgO		1.19	1.08
Sodium as % Na ₂ O		0.18	0.13
Potassium as % K ₂ O		0.30	0.40
Sulfur as % SO ₃		18.70	21.55
Sulfur as % S		7.48	8.62
Phosphorus as % P ₂ O ₅		0.44	0.48

The pH values measured for both by-products were above 12.5, indicating the by-products are hazardous, as defined by the Resource Conservation and Recovery Act (RCRA), although the by-product is not "aqueous" as required in the rule. The pH of the 1/17/91 by-product, when determined as a hazardous waste parameter by a different laboratory, was 12.34. Subsequent pH measurements (see Table 3-5) indicate pH in the region of 12.5. Therefore, it can be concluded that the LIDS by-product is borderline hazardous as per corrosivity by pH. However, runoff in an actual utilization situation may be less alkaline due to the low permeability of the solidified by-product (to be discussed later). A higher pH would be considered favorable for a mine reclamation/neutralization use, but for a landfill application the runoff would have to be slightly neutralized. The LIDS pH is comparable to that of other FGD process by-products [4] as shown in Table 3-3.

TABLE 3-3 pH of FGD Process By-products		
FGD Process	pH	Available Line Index (ALI)
Duct Injection	12.22	25.5
Fluidized Bed Combustion (FBC)	11.65	26.0
Limestone Injection Multi-Stage Burner (LIMB)	12.31	17.9
Spray Dryer	12.27	9.0
LIDS	12.55	24.1

It should be remarked that pH measurements in the 12.5 region are difficult to perform, especially for high calcium wastes. A special modification to Method 9045 is recommended (but not always performed by

laboratories) for such wastes. The pH meter calibrations are often performed at pH units far below the 12.5 region and the measurements are temperature-dependant (heat liberated after dissolution can lead to higher results) if the sample is not maintained at 25°C.

The percent of sulfur in the by-product (7-8%) is in the middle of the reported range for various FGD by-products (1.04-16.97%) measured in the Dravo project [4]. However, considering the predominance of wet scrubbers in the FGD market (~80%), and the higher % sulfur in wet FGD by-products (on the order of 15%), the LIDS by-product would be considered relatively low in sulfur.

The available lime index (ALI) indicates the amount of unspent sorbent in the form of free lime (% CaO) available for neutralization reactions. The LIDS by-product ALI is also comparable to that of other FGD by-products [4], as shown in Table 3-3.

The ash analysis shows the mineralogy of the by-product and may be used to predict by-product characteristics under varying conditions. Total neutralizing potential was also determined for the LIDS by-product. This is an indication of the effectiveness of a material in neutralizing soil and raising its pH, as compared to calcium carbonate. The results for the LIDS by-product, other FGD by-products [4], and calcium hydroxide are shown in Table 3-4.

TABLE 3-4 Total Neutralizing Potential (% Calcium Carbonate Equivalent)	
FGD By-Product	% CCE
Calcium Hydroxide	136.0
LIDS	73.1
Duct Injection	66.5
Spray Dryer	61.0
FBC	49.4
LIMB	48.6

The variability of the measurements can be explained by the different stoichiometries (Ca/S) used for different LIDS tests. Indeed, in Table 3-2, the largest variability is that for calcium and sulfur. The final, optimized process would be expected to have less variability.

Table 3-4 indicates that the LIDS by-product may be useful as an agricultural liming agent or mine reclamation/neutralizing agent.

ASTM Water Leachate. The ASTM 3987-85 water leachate (20:1, water:LIDS by-product) procedure was performed on one LIDS by-product; a partial procedure was performed on three other by-products. These results are shown in Table 3-5.

TABLE 3-5
20:1 Water Leachate Analyses

Description	LIDS By-product				LIMB By-product
	1/17/91	7/20/90	1/4/91	1/15/91	(EDG-LIM-06) [4]
pH	12.49	12.08	12.56	12.54	10.64
Total Dissolved Solids, %	0.55	0.56	0.71	0.71	0.48
Sulfite Sulfur, ppm S	N.D. ¹	3080	1640	1560	31.3
Sulfate Sulfur, ppm S	580	1030	860	1030	1872
Chloride, ppm Cl	224	390	235	180	54.4
Analyte	(ppm)				
Aluminum	0.10				<0.11
Boron	5.46				3.75
Barium	<0.5				0.24
Beryllium	0.004				<0.002
Calcium	1785				1826
Cadmium	0.004				<0.005
Cobalt	0.003				<0.01
Chromium	0.083				<0.011
Copper	0.002				<0.009
Fluorine	1.6				3.4
Iron	0.020				<0.01
Potassium	3.8				1.5
Lithium	3.8				0.04
Magnesium	0.100				<0.05
Manganese	0.008				<0.053
Molybdenum	<0.5				0.104
Sodium	0.30				1.7
Nickel	0.005				<0.01
Phosphorus	<0.5				<0.108
Lead	0.012				<0.093
Antimony	0.010				<0.06
Silicon	<0.010				0.21
Strontium	<2.0				2.63
Vanadium	<0.05				0.034
Zinc	<0.100				<0.006

¹None detected by iodametric titration.

The complete analysis, including the methods of determination, is included in Appendix B. For comparison, Table 3-5 also shows the results for the leachate analysis for LIMB ash [4]. The LIMB ash was chosen for comparison because both by-products have similar amounts of free lime in the fresh material and thus, similar applications. LIMB ash is considered safe for applications based on comparison to drinking water standards and the maximum criteria for non-toxic fly ash according

to Ohio EPA Policy 4.07 [7]. The two major differences between LIDS and LIMB by-products are the lower LIMB pH and the lower LIMB sulfite levels (discussed below).

The pH has been discussed previously. The total dissolved solids for the raw by-products are well within the allowable limit of the State of Ohio of 15,000 ppm and would be expected to be much lower after treatment for disposal or utilization.

Chloride levels in the LIDS by-product ranged from 180 to 390 ppm, while the chloride in the LIMB by-product was 54 ppm. Although a study of the fate of chloride in the LIDS process has not been made, one can speculate that the level of chloride in either by-product was related to the level of chloride in the coals combusted (which can vary from 100-8000 ppm chloride for eastern bituminous coals [10]) and the relative capture efficiencies of the two processes. The levels of chlorides in the coal burned for both projects was not determined. Chloride capture efficiencies for three dry scrubbers in Japan ranged from approximately 35% to 95% [10]. Limestone levels of chloride are lower (<50 ppm) and, therefore, may be less important an influence than the coal levels. Because the operating temperatures of the collection devices for LIMB and LIDS are similar (20° approach to saturation typical of both processes), temperature effects are not suggested. If the chloride levels are indicative of the coal and capture efficiency, these levels would differ from the values reported here as one test's by-product from different installations. Indeed, in other tests, the levels in LIMB by-product may be higher than for LIDS. To more directly compare LIDS and LIMB processes effects on by-product chloride levels, use of the same or similar coals would be desirable.

Soluble chloride would contribute to the burden of dissolved solids and may have a deleterious effect on concrete stability.

Sulfite (SO_3) is an important parameter affecting agricultural and soil applications. Calcium sulfite has a detrimental affect on plant growth by increasing oxygen demand; thus, lowering nitrogen availability to the plants. Sulfate (SO_4), in the form of calcium sulfate, has several benefits. It has been shown to reduce subsoil acidity (resulting in deeper rooting and increased water and nutrient use), decrease aluminum toxicity, improve soil structure, and reduce erosion [5]. However, calcium sulfate can be harmful in construction applications. Its hydration results in heat generation and expansion, which would cause detrimental effects to any concrete-like product. The LIDS sulfite/sulfate results are shown with typical values for other FGD by-products [4] in Table 3.6.

TABLE 3-6		
Sulfite/Sulfate Leachate Analyses		
FGD By-product	SO_3 (mg/L)	SO_4 (mg/L)
Duct Injection	31.2	243
Spray Dryer	35.4	152
FBC	<1.0	1699
LIMB	<1.0-31.3	1924
LIDS	ND-3080	583-1030

A portion of the LIDS by-products analyzed are higher in sulfite than the other FGD by-products. The unusually high sulfite concentration for the LIDS by-product is not unusual for dry scrubbing processes, but is much higher than the other spray dryer process in Table 3-6. The probable cause of the high leachable sulfite is the presence of magnesium. Calcium sulfite is a very insoluble salt, but magnesium sulfite is readily soluble. The source of magnesium was most likely the intermittent processing of dolomite ($\text{CaMg}[\text{CO}_3]_2$) LIDS reagent (i.e., the sample with highest sulfite concentration, 7/20/90, was produced from a dolomite reagent). Sulfite is a concern for agricultural application due to plant toxicity. The sulfite can be converted to sulfate by further oxidation of the by-product (e.g., such as is done for gypsum production). Magnesium can be avoided by using all calcite LIDS reagent.

Comparison of LIDS ASTM Water Leachate with Water Pollution Regulations. The Battelle Draft Final Report on "Technical Support for the Ohio Clean Coal Technology Program - Volume I" to Ohio Coal Development Office [8] summarized the regulatory status of clean coal by-products in the State of Ohio as follows:

"Clean coal combustion by-products are considered solid waste under the jurisdiction of the Ohio EPA, Division of Solid and Hazardous Waste, with exemptions awarded on a case-by-case basis. Nonhazardous solid waste is regulated primarily under Section 3734 and Chapters 27 and 37 of Section 3745 of the Ohio Revised Code with other pertinent sections referenced for air and water pollution control associated with land disposal of solid waste. Ohio's hazardous waste rules, Chapters 50 to 58, and 65 to 69 of Section 3745 of the Ohio Revised Code, exempt coal combustion by-products from regulation.

Ohio has a general exemption for nontoxic fly ash, which is not regulated as a solid waste; however, disposal of this by-product is subject to Ohio water pollution and air pollution regulations under the jurisdiction of the Ohio EPA, Division of Water Pollution Control. Utility fly ash is considered to be nontoxic and, therefore, is exempt from regulation as a hazardous or solid waste if its leachate does not exceed 30 times the levels specified in the Ohio Drinking Water Standards (Ohio Revised Code 3745-81-11(B)).

Ohio EPA can waive certain disposal requirements provided the site hydrogeology and by-product leachate characteristics justify the decision. While conventional combustion technology fly ash and bottom ash were grandfathered as exempt waste under the solid waste rules, clean coal technology by-products were not recognized as the same by the Ohio EPA and were grouped with municipal sanitary waste requiring disposal in a licensed landfill. The operator of a clean coal technology facility can petition for an exemption from this requirement. Such a variance has been issued in the past for low-volume demonstration projects in the form of Director's findings and orders which include site-specific disposal requirements. On-site disposal at the Tidd Plant was granted by the Ohio EPA Director upon approval of a ground-water monitoring plan for the site, whereas the LIMB project disposes of by-product at an approved off-site landfill.

House Bill (H.B.) 592 amended Ohio's solid waste law and calls for control of solid waste activities through a planning process initiated at the state level but administered at the county level (Ohio Revised Code 3734). A waste generated from the combustion of coal that is not combined with garbage, or a solid waste facility that disposes of waste generated exclusively by the owner of the solid waste facility (i.e., a utility's on-site disposal facility), is largely exempt from H.B. 592. The Ohio EPA Division of Groundwater is interested in seeing siting criteria established for by-products that do not fall within the category of solid waste."

The Ohio water quality standards for metals are shown in Table 3-7. The metals in the LIDS 20:1 water leachate are well under the hazardous waste guidelines of 30 times the Ohio Drinking Water Standards level and also the Federal criteria. Metal concentrations of the leachate were low due to the low metals concentration in the by-product and due to the low solubility of metals in alkaline solutions.

Arsenic, selenium, and mercury were not measured in the ASTM 20:1 (water) leachate, but were measured in the 20:1 TCLP acetic acid leachate. Since acid generally tends to solubilize metals, the TCLP leachate should be considered a worst case for the water leachate. For the TCLP sample, the concentration (detection limits) for arsenic, selenium, and mercury are given in Table 3-7. Although arsenic, selenium, and mercury are not detected in the TCLP leachate, the limit of detection is too high to say that the leachate is below Ohio water quality standards. The leachate is, however, below the Federal guidelines. Obviously, these results do not completely address the three metals leachabilities. It is recommended that future studies of LIDS by-product reevaluate the question of mercury, arsenic, and selenium in the water leachate.

TABLE 3-7 Ohio Water Quality Standards for Metals				
Parameter	Ohio Drinking Water Standards mg/L	Federal/State 30 x Standard mg/L	RCRA (TCLP) Criteria mg/L	LIDS Water Leachate mg/L
Arsenic	0.05	1.5	5.0	<1*
Barium	1.00	30.0	100.0	<0.5
Cadmium	0.01	0.3	1.0	0.004
Chromium	0.05	1.5	5.0	0.083
Lead	0.05	1.5	5.0	0.012
Mercury	0.002	0.06	0.2	<0.04*
Selenium	0.01	0.3	1.0	<0.1*
*Not measured in the ASTM water leachate; value given is for the TCLP acetic acid leachate.				

Physical Characterization. Physical characterizations were conducted on the 1/17/91 by-product and included percent moisture, particle size distribution (PSD), a Proctor compaction test, and pozzolanic reaction testing. Percent moisture and pozzolanic reaction testing were also conducted on the 1/4/91 by-product.

The percent moisture of the 1/4/91 and 1/17/91 by-products were 1.42% and 1.45%, respectively. The by-products were very dry and free flowing. Dust could be a problem if used in this form. Therefore, as part of the investigation into using the by-product as an agricultural liming agent, pelletizing testing was done on the by-product. This will be discussed later in the report. The PSD of the 1/17/91 by-product is shown in Table 3-8.

TABLE 3-8		
LIDS By-product Particle Size Distribution		
Size (Microns)	% Less	% Difference
300.00		
212.13		
150.00		
106.07		
75.00	100.00	1.52
53.03	98.48	7.43
37.50	91.04	13.34
26.52	77.71	16.86
18.75	60.84	14.39
13.26	46.46	10.67
9.38	35.79	12.29
6.63	23.50	8.93
4.69	14.57	5.39
3.31	9.18	3.35
2.34	5.82	2.14
1.66	3.68	1.58
1.17	2.10	1.14
0.83	0.96	0.66
0.59	0.30	0.30
0.41	0.00	0.00
CS (Cal Surf Area) = 0.82 M ² /CM ³		
MMD (D43) = 17.82 Microns		
SMD (D32) = 7.30 Microns		

The by-product is very fine -100% minus 75 microns (200 mesh). This by-product was collected from the scrubber hopper. Baghouse by-product can be expected to be of a finer size. One possible use for the LIDS by-product could be as a substitute or partial substitute for sand or cement in concrete. The PSD of concrete mixes is important because it affects the quantity of water required to form workable mixes. Concrete contains a wide range of particle sizes, so that space between larger aggregate is filled by the smaller particles. In the case of a mixture containing the LIDS by-product, more of the mix would be fine particles. These particles have a high surface area and would absorb water in addition to the water required to make the mixture workable. This additional water would cause excessive void formation and result in low compressive strength [6]. Therefore, testing was performed on the by-product as a component of soil cement (Section 3.5.2) and Portland cement (Section 3.5.3) to determine the effect of the by-product on cement strength.

A Proctor compaction test was conducted on the 1/17/91 by-product. This test determined the moisture at which the LIDS by-product can be compacted to its maximum density. This is an important consideration in landfill and backfill applications. Results from this test show that at a moisture content of 41.35%, the by-product has a dry density of 67.81 pounds per cubic foot (pcf). After 6 days of curing, a water permeability test was then run on the by-product at conditions very near to this maximum density. The water flow rate was linear with respect to time, and the velocity of the water through the by-product, was 1.72×10^{-5} cm/sec. This is a low flow rate, but too high for the by-product to be used alone in place of a clay landfill liner, for example. A permeability of no more than 10^{-7} cm/sec is required for liners. Further testing of the LIDS by-product as a component in liner mixtures is recommended, particularly tests with longer curing times. The complete reports on the Proctor and permeability testing are included in Appendix C.

Pozzolanic reaction testing was conducted on both by-products to determine whether the by-products qualify as a pozzolan for use as a mineral admixture in Portland cement. The tests were performed in accordance with ASTM C618-91, which sets the specifications of pozzolans, and ASTM C311, which involves the actual testing of the pozzolans. A pozzolan is defined as a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value, but will, in finely divided form in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. There are two main classes of fly ash pozzolans (for the purpose of this testing, the LIDS by-product is considered a fly ash). Class F fly ash has pozzolanic properties -- it will react with calcium hydroxide to form compounds possessing cementitious properties. Class C fly ash is more desirable -- in addition to having pozzolanic properties, it also has some cementitious properties. The results of the pozzolanic tests are shown in Table 3-9.

TABLE 3-9
Pozzolanic Testing

	ASTM:C618-91			
	LIDS By-product		Specifications	
	1/4/91	1/17/91	Class F	Class C
Physical Test				
Fineness, % Retained on 325 mesh	21.1	17.9	Max 34	Max 34
Specific Gravity (s.g.)	2.67	2.68	NA	NA
Pozzolanic Activity Index with Portland Cement, Ratio to Control @ 28 Days (%)	46.9	67.5	Min 75	Min 75
Water Requirements, % of Control	96.8	96.8	Max 105	Max 105
Soundness, Autoclave Expansion (%)	0.12	----	Max 0.8	Max 0.8
Uniformity Requirement				
- s.g. (var. from avg.)	0.2	0.2	Max 5	Max 5
- % ret. on 325M (var. from avg.)	8.2	8.2	Max 5	Max 5

The fineness of both by-products was acceptable for both Class F and Class C fly ash. The specific gravities of both by-products were determined. This parameter is not a factor in the classification of the by-products. The pozzolanic activity indices for the by-products were determined by comparing the compressive strength of "control" cubes (Portland cement, sand, and water), designated by B, and the compressive strength of "test" cubes (Portland cement, sand, LIDS by-product, and water), designated by A. The activity index was calculated by $(A/B) \times 100$. The results do not meet the specification for Class F or Class C fly ash for either LIDS by-product. Adding LIDS by-product to the Portland cement mix reduced the strength of the aged mix.

The water requirements (the water necessary for the flow of the test mixture to be within 5% of the control mixture) were acceptable for both by-products for both classes of fly ash. The soundness, which involved autoclaving a mixture of 20% LIDS by-product and 80% Portland cement to measure expansion, was within specification for the 1/4/91 by-product. Only one by-product was tested. The uniformity of both by-products was acceptable for specific gravity, but not for the fineness.

Based on the results of this series of tests, the LIDS by-product is not an acceptable admixture for inclusion in Portland cement. However, other engineering/construction applications are discussed in subsequent sections.

The complete report for the pozzolanic reaction testing is included in Appendix D.

3.3 Setting Disposal/Utilization Criteria

Initial acceptance criteria were established for possible utilization applications for the LIDS by-product. The criteria were based on standards set by the American Society for the Testing of Materials (ASTM), the U.S. Army Corps of Engineers, the Department of Transportation, RCRA limits, and drinking water standards. The criteria for the applications are shown in Table 3-10. Most criteria apply to more than one use of the by-product. The exact values which should be used for these criteria have not been set by regulatory entities or engineering societies. Thus, the table does not contain numerical criteria. Presumably, as activities progress, acceptance criteria will be developed.

TABLE 3-10
Disposal/Utilization Criteria

Criterion	Application
Unconfined Compressive Strength	EC, LB
Permeability	EC, LB
Expansion	EC, LB, RM
Bulk Density	EC, LB, RM
Volume Increase	EC, LB, RM
Particle Size Distribution	ALL
Percent Moisture	ALL
Compaction	EC, LB
Pozzolanic Reactions	EC, RM
Ash Analysis	ALL
Pelletization	AL, MN
Modulus of Elasticity	EC, LB
Shrinkage Potential	EC, LB
Leachate pH, Salts, Metals	EC, LB, AL, MN
Leachate Trace Elements	EC, LB, AL, MN
Total Neutralizing Potential	AL, MN
SO ₃ /SO ₄	ALL
Available Lime Index	AL, MN
Hazardous Characteristics (Leachate & TCLP for organics, volatile organics, heavy metals)	ALL
EC = Engineering/Construction RM = Raw Material LB = Landfill/Backfill AL = Agricultural Liming Agent MN = Mine Neutralization ALL = All Applications	

3.4 Solidification Experiments

Because of the complexity of cementitious reactions, it was decided that initial studies would try a number of simple formulation mixing conditions using only the LIDS by-product and water. These studies were conducted in two phases -- on fresh by-product 2 months old and on by-product that had been aged for 15 months. The entire test matrix is shown in Table 3-11. The tests on the 2-month old by-product were conducted before the start of the present study but are reported here for the sake of completeness.

Table 3-11 Initial Formulation Experiments	
% LIDS By-product	% Water
Phase I (By-product - 2 months old)	
80	20
70	30
60	40
50	50
Phase II (By-product - 15 months old)	
80	20
75	25
70	30
65	35
60	40
58	42
55	45

Fifty (50) gram mixtures of the fresh LIDS by-product and water were mixed and stored in plastic screw-capped bottles and allowed to set. Observations and approximate strength measurements, by pocket penetrometer, were made at 1, 3, 7, 14, 21, and 28 days. The mixtures were most workable at 40% water. Below 40%, the mixtures were powdery and lumpy. Above 40%, excess water remained in the bottles. Heat was evolved with the addition of water (reaction with CaO). Some of this water evaporated as heat was evolved during the initial curing. There was no evidence of expansion during curing of any of the mixes for 28 days. A pocket penetrometer was used to make rough compressive strength measurements. The 30% and 40% water mixtures had the highest strengths -- greater than 62.5 psi (the maximum limit of the penetrometer). Although no quantitative measure is available, when compared with the mixtures prepared from the 15-month aged material, the 2-month LIDS mixtures were of very high strength. General comments on the curing of these mixtures are given in Table 3-12.

The mixtures of the aged by-product were produced by mixing the by-product and water in a laboratory mixer and forming standard 2-inch cubes in molds. The cubes were stored in a 95% plus relative humidity environment in the molds. Strength measurements and qualitative observations were made of these formulations at 1, 5, 7, and 28 days. During the mixing and curing of these cubes, there was no heat generation and negligible volume increase. A very slight increase of 2-3% was seen on the 40% and 45% water mixtures, most likely due to CaO and CaSO₄ hydration reactions. The unconfined compressive strengths (UCS) were measured using a Geotest S5830 Multi-loader unconfined compression tester. Results after 7 and 28 days are shown in Table 3-13.

Table 3-12 LIDS Waste Observations and Approximate Compressive Strength Measurements

% Water Added	Number of Days After Mix						
	0	1	3	7	14	21	28
20%	lumpy, powdery, heat evolved	soft, powdery	soft, powdery	soft, powdery no strength	soft, powdery no strength	soft, powdery no strength	soft, powdery no strength
30%	lumpy, wet heat evolved	some hardening	some hardening	lumpy, hard strength = 31-56 psi	lumpy, hard strength = > 62.5 psi	lumpy, hard strength = > 62.5 psi	hard, no evidence of expansion, strength = > 62.5 psi
40%	loose paste, cooler than 20% water sample	hard	hard	hard strength = > 62.5 psi	hard strength = > 62.5 psi	hard strength = > 62.5 psi	hard, no evidence of expansion, strength = > 62.5 psi
50%	watery paste	small amount of water on top, some hardening	no free water some hardening	no free water some hardening strength = 6 psi	still soft no strength	still soft no strength strength = 14 psi	still soft strength = 7 psi

TABLE 3-13 Unconfined Compressive Strengths (UCS) of the 15-Month Aged LIDS By-product			
		Unconfined Compressive Strength, psi	
% LIDS By-product	% Water	7 Days	28 Days
80	20	Fell apart when removed from mold	
75	25	Fell apart when removed from mold	
70	30	122	160
65	35	266	330
0	40	194	215
58	42	130	170
55	45	100	120

The maximum UCS occurred at a 35% moisture content -- fairly close to the Proctor test moisture of 41.35% for the maximum LIDS by-product density.

The UCS of all these initial formulations was low. Thus, the LIDS by-product alone is not suitable for most engineering and/or construction applications. For example, a weak concrete would have an UCS of 1,000-2,000 psi after 28 days, and Portland cement has a strength of 5180 psi after 60 days. At the suggestion of the OCDO Project Manager, it was decided to run additional tests on the by-product to evaluate other possible applications. Discussions were held with Dravo Lime and Consolidation Coal, both of whom are conducting similar programs on FGD by-product, to elicit ideas for additional testing. Discussions were then held with the OCDO project manager to determine the final test program.

As a result of these discussions, tests were added to evaluate the by-product as a soil-cement and Portland cement raw material, agricultural liming agent, backfill/landfill material, and mine reclamation/neutralizing agent.

3.5 Physical and Chemical Testing of the Solidified Product

3.5.1 Initial Physical Testing

As mentioned in Section 3.4, Solidification Experiments, unconfined compressive strength measurements (ASTM D2166) were conducted on various formulations consisting of LIDS by-product and water. The UCS of all these formulations was low (maximum of 330 psi after 28 days as compared to a UCS for Portland cement of 5180 psi after 60 days). Rather than perform leachate and other test on the very weak products produced from the LIDS by-product, other applications were evaluated. The applications, which included tests of the by-product as a cement kiln raw material and soil-cement, are described below.

3.5.2 Agricultural Liming Agent

The LIDS waste will have to be converted to another form to be used as an agricultural liming agent. Its current form of a very fine, dry powder would be very difficult to handle. Therefore, pelletizing testing was conducted on the LIDS waste at Dravo Lime to determine whether pelletizing the waste was possible. The purpose of this testing was not to optimize the process.

Three sets of conditions were used in the testing:

- LIDS waste with a water spray on the disc.
- LIDS waste with a 1% lignin water spray on the disc.
- LIDS waste mixed with 1% bentonite with a water spray on the disc.

The pelletizing disc was 15 inches in diameter, and the pressure of the spray was 35 psi. Disc speed was varied between 30 and 40 RPM, and disc slope was varied between 45 and 55 degrees.

Pelletizing the waste with a water spray was easily done. Three pellet sizes were formed. The pellets are shown in Figure 2. However, after drying, the pellets were very brittle and broke easily. These could be difficult to transport without degradation.

Pelletizing with the lignin spray was very difficult. The waste tended to "glob" together instead of pelletizing. Perhaps a lower lignin concentration would reduce this problem. Hot water also had to be used to fully solubilize the lignin. These pellets were also very brittle after drying.

Pelletizing the waste/bentonite mixture was easily done. However, only very small pellets were formed. These pellets were not brittle after drying and appeared to be the most satisfactory of the three types produced. The waste appears to be very useable in this form. Additional testing is recommended to optimize this process.

3.6 Evaluation of LIDS By-product as a Portland Cement Raw Material

Construction Technology Laboratories (CTL) planned a program to evaluate the LIDS by-product as a substitute material for potential use in cement rotary kilns. This by-product was modified by addition of alkalies, then used as a substitute raw material in Type I cement raw mixes, and these were clinkered and evaluated. The computer program, CTLRAWMIX, was used to design four raw mixes for cement manufacturing. One mix was a base case, and the other three mixes incorporated three levels of LIDS by-product. After the clinkers were evaluated, they were ground with Terra Alba gypsum to make cement. Cement pastes were mixed and tested for time of set, and 1" cubes were tested for compressive strengths at 1, 3, 7, and 28 days.

Qualitative X-ray diffraction (XRD) analysis of the 1/17/91 sample of LIDS by-product indicates the following phases were present (listed in order of descending intensity of the most intense peak of each phase): portlandite ($\text{Ca}(\text{OH})_2$), anhydrite (CaSO_4), calcite (CaCO_3), lime (CaO), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Chemical analysis (expressed as oxides) of the LIDS by-product indicates that it contains about 23% sulfur trioxide, 48% calcium oxide, 6% silica and about 3% each of alumina and ferric oxide. The loss-on-ignition is 14.3%. The complete chemical

FIGURE 2. Photograph of LIDS By-product Pellets

analyses along with thermogravimetric results are given in Appendix E. Thermogravimetric and chemical analyses were combined and interpreted to provide semi-quantitative amounts of the major compounds present, and the results are in reasonable agreement with the XRD results, as shown in Table 3-14.

TABLE 3-14 Calculated Compounds in LIDS By-product		
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	11%
Portlandite	$\text{Ca}(\text{OH})_2$	21%
Calcite	CaCO_3	15%
Anhydrite	CaSO_4	29%
Lime	CaO	7%

The high calcium content and the presence of silica, alumina, and iron oxides make this a suitable alternate cement raw material. The other minor oxides should not cause operational problems with a cement kiln except for the high sulfur content. LIDS by-product will not be acceptable at most cement plants because of the sulfur content; however, this may be advantageous at a plant which is using a low sulfur fuel with high alkali material. Some cement plants on the Great Lakes in Canada burn natural gas and have high alkali raw feed. A molar balance of sulfur and alkalies is recommended for good kiln operation. The CTL evaluation was based on use of LIDS by-product at this type of plant which usually produces a Type I cement or its equivalent. Sulfur would combine with alkalies in such a kiln, and most of the alkali sulfates would be incorporated in the clinker. In this evaluation program, alkali was added to the LIDS by-product before mixing with the other raw materials to minimize the loss of sulfur and alkalies during the laboratory clinkering process. The calculated oxide basis analysis of the modified LIDS by-product is shown in Table 3 in the full report in Appendix E.

Four clinkers were made and cement was made from each for paste tests, but only the base case and the clinkers with the two highest by-product addition levels were submitted for chemical and microscopic tests. These clinkers were submitted for chemical analysis by XRF, free lime analysis, and polished section evaluation by light microscopy. The three clinkers all had free lime values below 0.8%. These free lime values indicate the raw materials were sufficiently fine and the time of clinkering long enough. Evaluation of three of the clinkers by microscopy is contained in "Reports of Clinker Polished Section Analyses," in the full report in Appendix E. Clinker microscopy indicated that all three clinkers were of roughly similar quality, but some trends with increasing amounts of LIDS by-product were observed. On an ignited clinker basis, 0, 3.32, 4.80, and 6.28% of LIDS by-product was incorporated in the raw mixes in order to have about 1% alkali and 1.5% SO_3 in the clinker with the highest by-product addition. These addition levels cover the range of most commercial clinkers produced in North America. The quality of all three clinkers was acceptable.

Cement paste tests indicated the setting time decreased with added by-product, and this is expected due to the increasing level of alkalis. Compressive strengths (f'c) at 1 and 3 days increases with the higher levels of by-product, but at 7 days cements made with LIDS by-product have comparable strengths although all three are substantially above the base case with no added by-product. Compressive strength development is known to be accelerated at early ages for cements with higher alkali levels. These results are shown in Table 3-15.

TABLE 3-15				
Cement Paste (w/c = 0.5) and Cement Test Results				
Cement ID	BNW1	BNW2	BNW3	BNW4
LIDS By-products (modified) in Clinker (ignited basis)	0%	3.32%	4.80%	6.28%
Blaine Surface Area (cm ² /g)	3,810	3,770	3,880	3,870
Time of Set	6 hrs. 10 mins.	5 hrs. 14 mins.	5 hrs. 5 mins.	4 hrs. 50 mins.
Average Compressive Strengths of 1" Cubes (p.s.i)				
One Day	1,300	1,650	1,950	2,000
Three Days	2,700	3,250	3,700	3,750
Seven Days	5,400	6,200	6,450	6,050
Twenty-Eight Days	10,900	10,700	9,830	9,430

The high sulfur content and the low alkali level make LIDS by-product a possible alternative material for selected cement manufacturing situations. The quality of the clinker was reasonably good at all levels of usage. Changes in the cement setting times and the compressive strengths were consistent with the known effects of increasing alkali levels in cement. Results obtained in this study for this sample of LIDS by-product indicate its use may be beneficial when used at cement plants using high alkali materials and burning low sulfur fuel. It is expected that certain cement kilns could advantageously utilize material similar to this LIDS by-product sample.

3.7 Evaluation of LIDS By-product as a Cementitious Low Strength Material (CLSM) for Use as Backfill

A testing program at CTL was initiated to evaluate the use of the LIDS by-product as a cement replacement in a flowable fill or soil-cement material. The by-product was heated in platinum dishes in an electrically heated furnace at 560°C for 25 minutes. This process was repeated several times until several pounds had been processed. These conditions were selected in order to convert most, but not all, of the calcium hydroxide in the sample to calcium oxide (lime). Processed samples were checked by X-ray diffraction analysis to verify that this objective was met. (Other possible reactions include the dehydration of calcium sulfate, and the formation of calcium oxide from calcium sulfite.)

Cementitious by-products can be used as a cementitious low strength material (CLSM) for backfill. A CLSM material consists of a cementitious product such as fly ash, cement, or a mixture of cement and fly ash. Non-cohesive soils including silts, sands, or finer coarse aggregates may be used. Water is added to produce a flowable material. Applications using CLSM include backfilling around utility repairs (penetrations) and buried tanks. Advantages in using a CLSM include:

- Material is easily placed as a self-levelling material.
- Material is readily removed due to low design strengths.
- No compaction or vibration is necessary as opposed to other cement stabilized materials such as soil-cement.
- CSLM engineering properties can be modified by changing the water content and/or cement to by-product ratio.
- CSLM is a relatively low-cost stabilized material.

The mix design for a CLSM backfill material is commonly based on achieving a targeted compressive strength. For rapid penetration repair openings to traffic, a compressive strength of 10 to 20 psi at 24 hours is targeted. After 24 hours, the backfill material would be covered with a wearing surface course such as concrete or asphaltic concrete. A 28-day compressive strength of less than 100 psi is designed to allow for possible future removal of CLSM. Suggested cement - fly ash - fine soil CSLM proportions range as follows:

- Cement - 50 to 100 lb/yd³
- Fly ash - 200 to 300 lb/yd³
- Fine aggregate 2600 to 2800 lb/yd³
- Water 50 to 70 gallons/yd³

The LIDS by-product was evaluated for use as a CLSM. A silty soil was used as a fine soil filler. Water-to-cementitious ratios (water to cement plus high lime material) were set at 2.3 and 2.5. Four by-product to cement ratios by weight of 100:0, 80:20, 60:40, and 0:100 were evaluated at both water-to-cementitious ratios. Water and soil content were constant for all six mixes to investigate the effects of changing the water to cementitious ratios on compressive strength. Mix designs for the eight mixes are listed in Table 3-16.

TABLE 3-16
CLSM Mix Designs

Water/ Cementitious	By-product/ Cement Ratio	By-product/ lb/yd ³	Cement, lb/yd ³	Aggregate, lb/yd ³	Water, gal/yd ³
2.3	100:0	250	0	2700	69
	80:20	200	50	2700	69
	60:40	150	100	2700	69
	0:100	0	250	2700	69
2.5	100:0	230	0	2700	69
	80:20	184	46	2700	69
	60:40	138	92	2700	69
	0:100	0	230	2700	69

Compressive strength and modulus of elasticity of 3 x 6 in. moist-cured cylinders were determined at 7, 14, and 28 days in general accordance with ASTM C39, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens", and ASTM C469, "Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression." Two cylinders were tested at each age for each mix. Average compressive strengths are summarized in Table 3-17.

TABLE 3-17
CLSM Compressive Strength

Water/ Cementitious	By-product/ Cement Ratio	By-product, lb/yd ³	Cement, lb/yd ³	7 day f'c, psi	14 day f'c, psi	28 day f'c, psi
2.3	100:0	250	0	NA	NA	NA
	80:20	200	50	18	41	75
	60:40	150	100	48	83	136
	0:100	0	250	238	362	386
2.5	100:0	230	0	NA	NA	NA
	80:20	184	46	16	40	72
	60:40	138	92	35	72	120
	0:100	0	230	183	255	289

NOTE: NA = not available, too soft to test

As listed in Table 3-17, the 100 percent by-product mixes do not gain any measurable strength at ages up through 28 days. Compressive strength at 28 days ranged from 75 psi (80:20 by-product to cement ratio) to 386 psi (100 percent cement) for a water-to-cementitious ratio of 2.3. At the higher water-to-cementitious ratio of 2.5, compressive strength at 28 days ranged from 72 psi (80:20 by-product to cement ratio) to 289 psi (100 percent cement). For each test age, as the water-to-cementitious material ratio increased, the compressive strength decreased.

Increases in 28 day compressive strength are relatively linear with cement content and pass approximately through zero compressive strength at zero cement content. Contributions of by-product to compressive strength would be reflected in significant strengths at zero cement content. The use of high lime content by-product does not appear to contribute any significant increases in compressive strength. Thus, the LIDS by-product, although adequate as filler, would not qualify to replace Portland cement in CLSM.

3.8 Evaluation of LIDS By-Product as a Soil-Cement Component for Use in Soil-Stabilization

Cementitious by-products may also be used as a partial replacement in a soil-cement material. Soil-cement is a mixture of soil and measured amounts of Portland cement and water compacted to a high density. It is produced by blending, compacting, and curing the mixture of soil, Portland cement, and water to form a hardened material with specific engineering properties. The primary use of stabilized materials is a base course underlaying bituminous and concrete pavements and runways. Under concrete pavements, stabilized layers are used as a

base course to prevent pumping of fine-grained subgrade soils in wet environments and heavy truck traffic conditions. Stabilized layers provide a working platform for construction equipment during concrete placement and can provide increased structural capacity to the pavement. When used with a flexible pavement, a hot-mix bituminous concrete wearing surface is placed directly on the stabilized base.

The LIDS by-product was evaluated for use as a cement replacement in a soil-cement mix. The silty soil was the same as that used in the CLSM tests. The soil-cement testing program consisted of the following tests:

- Moisture-density compaction in accordance with ASTM D 558, "Standard Test Method for Moisture-Density Relations of Soil-Cement Mixture."
- Compressive strength at 7, 14, and 28 days in accordance with ASTM D 1633, "Standard Test Method for Compressive Strength of Molded Soil-Cement Cylinders."

Moisture density tests were made to determine optimum moisture content and maximum dry density. For a given cement content, the higher the dry density, the higher the compressive strength. Dry density typically increases and then decreases for increasing moisture content. The optimum moisture content is that at which dry density is maximum. A moisture-density relationship using the silty soil was established for a cement content of 10 percent (by oven-dry weight of soil). Maximum dry density of 129.0 lb/ft³ occurred at a moisture content of 9.0 percent (by dry weight).

Specimens were fabricated at optimum moisture content at cement replacement ratios by weight of 0, 10, 20, and 50 percent. Cementitious content was set at 10 percent of dry soil weight. Two specimens for each age and replacement content were molded at the optimum 9.0 percent moisture content. Specimens 4 in. in diameter and 4.6 in. high were molded with the same compaction equipment as that used in the moisture-density tests and moist-cured (100 percent R.H.) at 72°F until time of test. Specimens were capped and soaked in water for four hours before broken. Results of compressive strength tests are summarized in Table 3-18.

TABLE 3-18 Soil-Cement Compressive Strength			
By-Product/ Cement Ratio	7 day f'c, psi	14 day f'c, psi	28 day f'c, psi
50:50	595	665	825
20:80	1350	1590	1890
10:90	1505	1740	2025
0:100	1745	1955	2190

As listed in Table 3-18, compressive strength at 28 days ranged from 825 psi (50:50 by-product to cement ratio) to 2190 psi (100 percent cement). For each test age, as the cement replacement increased, the compressive strength decreased.

Increases in 28 day compressive strength are relatively linear with cement content (see Figure 2 in full report in Appendix E). Contributions of by-product to compressive strength would be reflected in significant strengths at zero cement content. The use of high lime content by-product does not appear to contribute any significant increases in compressive strength. Thus, the LIDS by-product, although adequate as filler, would not qualify to replace Portland cement as a soil-cement component.

CTL found simple mixtures of the by-product and water to show heat release and rapid strength growth, but little strength growth in the three applications (raw material, CLSM, and soil-cement component). For the by-product applications, CTL suggested three possible reasons for the minimal strength gain observed:

- high water-to-solids ratio;
- lack of reactive silica in the soil; or
- a strength gain that requires more than 28 days to develop.

4.0 RECOMMENDATIONS FOR MOST VIABLE LIDS BY-PRODUCT USES

The most viable uses for LIDS by-product are given in Table 4-1. Special qualifiers for the proposed uses are in the discussion below.

TABLE 4-1	
Most Viable Uses for LIDS By-product	
<i>Uses with Greatest Promise:</i>	
Mine Reclamation/Neutralization Agent	
<i>Uses with Moderate Promise:</i>	
Agricultural Liming Agent	
<i>Uses with Minor Promise:</i>	
Cement Kiln Raw Material	
Soil-Cement Component for Use in Soil Stabilization	
Cementitious Low Strength Material (CLSM) for Use as Backfill	

Use as a replacement of Portland cement is not viable, especially when the affect of aging on strength development performance is considered. This adds uncertainty to the by-product performance.

For use in mine reclamation/neutralization, agricultural lime, and the three CTL applications, fresh LIDS by-product would be preferred to aged product. Use in a cement kiln seems viable only for kilns with low sulfur inputs. Re-release of SO₂ from the waste is a concern when heating in a kiln.

If the solubility of the sulfite can be minimized by use of calcite LIDS reagent, use as an agricultural liming agent would have greater promise.

One use not studied here, sewage sludge sterilization, has promise. The high heat release from the fresh by-product would be an advantage. The fate of sulfites in such a process should be addressed, especially when the product is used for soil amendment.

5.0 LIDS PROCESS CHANGES TO OPTIMIZE BY-PRODUCT USES

Optimization of residue processing can ensure a consistent by-product quality [9]. Users of a by-product will tend to prefer even a detrimental constituent of consistent concentration rather than a product with wide swings in concentration, even if some of it outperforms the consistent by-product.

Because the final, full-scale process details are still uncertain, it is difficult to give many recommendations regarding process changes. However, for applications involving neutralization, sewage sludge sterilization [7], agricultural lime replacement, or soil cementitious low strength material, as fresh a by-product as possible is desirable (quick transportation to the end-use). This maximizes the free lime content.

Process changes which would tend toward sulfate rather than sulfite products (e.g., oxidation) would produce a better material for agricultural use. Larger sized product (very unlikely to be practical) would ease soil application without the need for pelletizing and would suppress dusting in many applications.

Process changes which would tend toward sulfite production may be advantageous for cement applications. Process changes, such as ammonia use with LIDS (A+ LIDS), would affect end uses; for example, as an agricultural product. Residual ammonia may pose a disposal problem if the odor from released ammonia is offensive. Methods to recapture and reuse the unreacted ammonia are under development as a part of A+LIDS.

6.0 FINAL BUDGET SUMMATION

Co-Sponsors	Cost Share
OCDO	\$74,491
B&W	\$38,000

7.0 REFERENCES

1. Jablonski, G. J., and Tyson, S. S., "Overview of Coal Combustion By-Product Utilization," Proceedings of the Fifth Pittsburgh Coal Conference, 1988, pg. 15-22.
2. Ross, G. C., Anthony, E. J., Kissel, R. K. and Dorian, C. C., "Field Demonstration of Fluidized Bed Combustion Residue Management," Proceedings of the Tenth International Conference on Fluidized Bed Combustion, San Francisco, California, April 1989.
3. Stabilization/Solidification of CERCLA and RCRA Hazardous Wastes: Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities, U.S. EPA 162516-891022, 1989.
4. Ohio State University, "Land Application Uses for Dry FGD Products, Second Technical Progress Report," December 1991 to Dravo Lime.
5. Baligar, V. C., Ritchey, K. D., and Clark, R. B., "Evaluate and Optimize Agricultural Utilization of Coal-Fired Power Plant By-products," U.S. Department of Agriculture project, April 1992.
6. Bland, A. E., and Kissel, R. K., "Laboratory Evaluation of CFBC Waste Disposal and Utilization Options".
7. Beeghly, J. H., Grathwol, K., and Deuth, J., "LIMB Ash Mixed with Sewage Sludge to Produce a Soil Amendment," Proceedings of the 9th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, October 1992.
8. Battelle, Draft Final Report on "Technical Support for the Ohio Clean Coal Technology Program - Volume I", June 5, 1989, to Ohio Coal Development Office.
9. Clarke, L. E., Applications for Coal-Use Residues, IEA Coal Research, London, 1992.
10. Sloss, L. L., Halogen Emissions from Coal Combustion, IEA Coal Research, London, 1992.

APPENDIX A

aquatec INC.
An InChcape Company

CORPORATE OFFICES
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

LABORATORY LOCATIONS
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

75 GREEN MOUNTAIN DRIVE
SOUTH BURLINGTON, VT 05403

150 HERMAN MELVILLE BOULEVARD
NEW BEDFORD, MA 02740

ANALYTICAL REPORT

Babcock & Wilcox Company
R&D Division, Att: A/P
1562 Beeson Street
Alliance, OH 44601

Attention : Bill Musoil

Date : 02/27/92
ETR Number : 30117
Project No.: 92000
No. Samples: 5
Arrived : 01/20/92
P.O. Number: 5370A311-028

Page 1

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020, Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater. All results are in mg/l unless otherwise noted.

Lab No./ Method No.	Sample Description/ Parameter	Result
152898	LIDS: 01/17/92 (Ash)	
1010	Ignitability (F)	>150
QSIA	Corrosivity by pH	12.34
IN703	Reactive Sulfide	<48 e
IN703	Reactive Cyanide	<35 e
152899	LIDS: (TCLPZHE)	
8240	Benzene	<0.10
8240	Carbon Tetrachloride	<0.10
8240	Chlorobenzene	<0.10
8240	Chloroform	<0.10
8240	1,2-Dichloroethane	<0.10
8240	1,1-Dichloroethylene	<0.10
8240	Methyl Ethyl Ketone	<0.10
8240	Tetrachloroethylene	<0.10
8240	Trichloroethylene	<0.10
8240	Vinyl Chloride	<0.10
152899MS	LIDS: [MS] (TCLPZHE)	
8240	Benzene	101%
8240	Carbon Tetrachloride	100%

Comments/Notes

e = mg/Kg as received

Corrosivity by pH performed on a slurry of 1 part sample to 2 parts DI water.

Results reported for Lab No's. 152899MS and 152900MS are matrix spike percent recoveries. Results shown for the corresponding samples have not been corrected for these spike recoveries.

< Cont. Next Page >

aquatec INC.
An Incheape Company

CORPORATE OFFICES
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

LABORATORY LOCATIONS
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

75 GREEN MOUNTAIN DRIVE
SOUTH BURLINGTON, VT 05403

150 HERMAN MELVILLE BOULEVARD
NEW BEDFORD, MA 02740

ANALYTICAL REPORT

Babcock & Wilcox Company
R&D Division, Att: A/P
1562 Beeson Street
Alliance, OH 44601

Attention : Bill Musoil

Date : 02/27/92
ETR Number : 30117
Project No.: 92000
No. Samples: 5
Arrived : 01/20/92
P.O. Number: 5370A311-028

Page 2

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020, Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater. All results are in mg/l unless otherwise noted.

Lab No./ Method No.	Sample Description/ Parameter	Result
152899MS	LIDS: [MS] (TCLPZHE)	
8240	Chlorobenzene	99%
8240	Chloroform	101%
8240	1,2-Dichloroethane	99%
8240	1,1-Dichloroethylene	111%
8240	Methyl Ethyl Ketone	115%
8240	Tetrachloroethylene	100%
8240	Trichloroethylene	178%
8240	Vinyl Chloride	102%
152900	LIDS: (TCLPExt)	
8270	m+p-Cresol	<0.050
8270	o-Cresol	<0.050
8270	1,4-Dichlorobenzene	<0.050
8270	2,4-Dinitrotoluene	<0.050
8270	Hexachloro-1,3-butadiene	<0.050
8270	Hexachlorobenzene	<0.050
8270	Hexachloroethane	<0.050
8270	Nitrobenzene	<0.050
8270	Pentachlorophenol	<0.25
8270	Pyridine	<0.050
8270	2,4,5-Trichlorophenol	<0.25
8270	2,4,6-Trichlorophenol	<0.050
6010	Arsenic, Total	<1
6010	Barium, Total	<10
6010	Cadmium, Total	<0.1
6010	Chromium, Total	<1
6010	Lead, Total	<1
7470	Mercury, Total	<0.04
7740	Selenium, Total	<0.1

< Cont. Next Page >

aquatec INC.
An InChcape Company

CORPORATE OFFICES
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

LABORATORY LOCATIONS
55 SOUTH PARK DRIVE
COLCHESTER, VT 05446

75 GREEN MOUNTAIN DRIVE
SOUTH BURLINGTON, VT 05403

150 HERMAN MELVILLE BOULEVARD
NEW BEDFORD, MA 02740

ANALYTICAL REPORT

Babcock & Wilcox Company
R&D Division, Att: A/P
1562 Beeson Street
Alliance, OH 44601

Attention : Bill Musoil

Date : 02/27/92
ETR Number : 30117
Project No.: 92000
No. Samples: 5
Arrived : 01/20/92
P.O. Number: 5370A311-028

Page 3

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020, Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater. All results are in mg/l unless otherwise noted.

Lab No./ Method No.	Sample Description/ Parameter	Result
152900	LIDS: (TCLPEExt)	
6010	Silver, Total	<1
152900MS	LIDS: [MS] (TCLPEExt)	
8270	m+p-Cresol	83%
8270	o-Cresol	87%
8270	1,4-Dichlorobenzene	64%
8270	2,4-Dinitrotoluene	69%
8270	Hexachloro-1,3-butadiene	53%
8270	Hexachlorobenzene	79%
8270	Hexachloroethane	50%
8270	Nitrobenzene	74%
8270	Pentachlorophenol	113%
8270	Pyridine	35%
8270	2,4,5-Trichlorophenol	114%
8270	2,4,6-Trichlorophenol	92%
6010	Arsenic, Total	104%
6010	Barium, Total	98%
6010	Cadmium, Total	83%
6010	Chromium, Total	100%
6010	Lead, Total	77%
7470	Mercury, Total	72%
7740	Selenium, Total	113%
6010	Silver, Total	72%

< Last Page >

Submitted By :

Aquatec Inc.

A Member of the Inchcape Environmental Group

55 South Park Drive, Colchester, Vermont 05446

TEL. 802/655-1203 FAX 802/655-1248

ANALYTICAL REPORT

Babcock & Wilcox Company

Date: 27 February 1992

Project No: 92000

ETR No: 30117

Sample(s) Received On: 20 January 1992

Page 1 of 1

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020, Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater. All results are in mg/l unless otherwise noted.

Parameter	ZBLKD8							
Benzene	<0.10							
Carbon Tetrachloride	<0.10							
Chlorobenzene	<0.10							
Chloroform	<0.10							
1,2-Dichloroethane	<0.10							
1,1-Dichloroethylene	<0.10							
Methyl Ethyl Ketone	0.13							
Tetrachloroethylene	<0.10							
Trichloroethylene	<0.10							
Vinyl Chloride	<0.10							

Lab No.

Sample Description

ZBLKD8 - TCLP extraction blank for the method 8240 analysis of the TCLP extracts of Aquatec Lab No's. 152899 and 152899MS.

Submitted By:

Aquatec Inc.

A Member of the Inchcape Environmental Group

55 South Park Drive, Colchester, Vermont 05446
TEL 802/655-1203 FAX 802/655-1248

ANALYTICAL REPORT

Babcock & Wilcox Company

Date: February 18, 1992

Project No: 92000

ETR No: 30117

Sample(s) Received On: 20 January 1992

Page 1 of 1

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020, Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater. All results are in mg/l unless otherwise noted.

Parameter	PKLK							
Arsenic	<1.0							
Barium	<10.0							
Cadmium	<0.1							
Chromium	<1.0							
Lead	<1.0							
Mercury	<0.04							
Selenium	<0.1							
Silver	<1.0							

Lab No.

Sample Description

PBLK - Prep blank for sample numbers 152900 and 152900MS. Results reported in mg/l.

Submitted By:

R. Mason McKee

Aquatec Inc.

QC Summary
ETR 30117

<u>Parameter</u>	<u>EPA Standard</u>	<u>Found (UG/L)</u>	<u>True (UG/L)</u>	<u>% Recovery</u>
Arsenic	IVQCS	3953.00	4000.0	98.8
		3756.70	4000.0	93.9
		3717.15	4000.0	92.9
		3979.35	4000.0	99.5
Barium	IVQCS	495.02	500.0	99.0
		509.58	500.0	101.9
		499.02	500.0	98.8
		490.98	500.0	98.2
Cadmium	IVQCS	486.49	500.0	97.3
		486.75	500.0	97.4
		486.99	500.0	99.4
		475.70	500.0	95.1
Chromium	IVQCS	493.17	500.0	98.6
		482.01	500.0	96.4
		489.99	500.0	98.0
		509.52	500.0	101.9
Lead	IVQCS	1043.33	1000.0	104.3
		999.92	1000.0	100.0
		1013.14	1000.0	101.3
		1018.51	1000.0	101.9
	IVQCS	999.29	1000.0	99.9
		950.01	1000.0	95.0
		997.47	1000.0	99.7
		1007.18	1000.0	100.7
Mercury	Standard	1.75	1.8	97.2
		1.81	1.8	100.6
Selenium	IVQCS	27.58	25.0	110.3
		25.36	25.0	101.4
Silver	IVQCS	494.14	500.0	98.8
		506.29	500.0	101.3
		532.61	500.0	106.5
		497.49	500.0	99.5

A Member of the Inchcape Environmental Group

55 South Park Drive, Colchester, Vermont 05446
TEL. 802.655-1203 FAX 802.655-1248

ANALYTICAL REPORT

Babcock & Wilcox Company

Date: 27 February 1992

Project No: 92000

ETR No: 30117

Sample(s) Received On: 20 January 1992

Page 1 of 1

Standard analyses were performed in accordance with Methods for Analysis of Water and Wastes, EPA-600/4/79-020,
Test Methods for Evaluating Solid Waste, SW-846, or Standard Methods for the Examination of Water and Wastewater.
All results are in mg/l unless otherwise noted.

Parameter	EBLKA2							
m+p-Cresol	<0.050							
o-Cresol	<0.050							
1,4-Dichlorobenzene	<0.050							
2,4-Dinitrotoluene	<0.050							
Hexachloro-								
1,3-butadiene	<0.050							
Hexachlorobenzene	<0.050							
Hexachloroethane	<0.050							
Nitrobenzene	<0.050							
Pentachlorophenol	<0.25							
Pyridine	<0.050							
2,4,5-Trichlorophenol	<0.25							
2,4,6-Trichlorophenol	<0.050							

Lab No.

Sample Description

EBLKA2 - TCLP extraction blank for the method 8270 analysis of the TCLP extracts of
Aquatec Lab No's. 152900 and 152900MS.

Submitted By:

Aquatec Inc.

Company

SEMI-VOLATILE

**** ADVISORY LIMITS ONLY**

7185

APPENDIX B

ACG-93-42540-600
September 8, 1992

Sample No.	<u>M-50003</u>
Description	ARC LIDS Ash, 1/17/92
	<u>As Received Analysis</u>

Solids, % @ 105°C	98.42
----------------------	-------

Total Neutralizing Potential as CaCO ₃ equivalent, % CaCO ₃	56.62
--	-------

Slaking Rate

Temperature Rise @ 30 sec, °C	0.8
Temperature Rise, Total, °C	1.7
Total Slaking Time, min	7.0

Leachate* Analysis

Chloride, ppm Cl (Gravimetric)	224
-----------------------------------	-----

Fluoride, ppm F (ISE)	1.6
--------------------------	-----

Sodium, ppm Na (GFAAS)	0.30
---------------------------	------

Potassium, ppm K (Flame Photometry)	3.8
--	-----

Lithium, ppm Li (Flame Photometry)	3.8
---------------------------------------	-----

Aluminum, ppm Al (GFAAS)	0.10
-----------------------------	------

Boron, ppm B	5.46
--------------	------

Note: Leachate analysis for metals by ICP unless indicated otherwise. ppm = mg/L

* ASTM 3987, 20:1 water leach. Results reported as ppm of the element in the leachate obtained from 70g of sample as received leached in 1400 mL of deionized water.

ACG-93-42540-600
September 8, 1992

Leachate Analysis

Sample No.	<u>M-50003</u>
Description	ARC LIDS Ash, 1/17/92
Barium , ppm Ba	<0.5
Beryllium, ppm Be (GFAAS)	0.004
Calcium, ppm Ca	1,785
Cadmium, ppm Cd (GFAAS)	0.004
Cobalt, ppm Co (GFAAS)	0.003
Copper, ppm Cu (GFAAS)	0.002
Chromium, ppm Cr (GFAAS)	0.083
Iron, ppm Fe (GFAAS)	0.020
Magnesium, ppm Mg (GFAAS)	0.100
Manganese, ppm Mn (GFAAS)	0.008
Molybdenum, ppm Mo	<0.5
Nickel, ppm Ni (GFAAS)	0.005
Phosphorus, ppm P	<0.5
Lead, ppm Pb (GFAAS)	0.012
Antimony, ppm Sb (GFAAS)	0.010

ACG-93-42540-600
September 8, 1992

Leachate Analysis

Sample No.	<u>M-50003</u>
Description	ARC LIDS Ash, 1/17/92
Silicon, ppm Si (GFAAS)	<0.010
Strontium, ppm Sr	<2
Vanadium, ppm V (GFAAS)	<0.05
Zinc, ppm Zn (GFAAS)	<0.100
Sulfate Sulfur, ppm S	583*
Sulfite Sulfur, ppm S**	N.D.
pH @ 21°C	12.49
Total Dissolved Solids, %	0.55

* Average of replicate analysis: 579 and 587 ppm S in acid preserved leachate.

** EDTA - NH₄OH preserved before filtering. N.D. = None Determined by Iodometric Titration.

ACG-93-42540-600
January 7, 1993

Sample No.	<u>M-50462</u>	<u>M-50463</u>	<u>M-50464</u>
Description	LIDS, Ash, 7/20/90	LIDS, Ash 1/4/91	LIDS, Ash 1/15/91

As Received Analysis

Total Neutralizing Potential, as % CaCO ₃	74.16	73.67	87.90
% Solids, Dried @ 105°C	96.96	97.89	99.71

Leachate Analysis*
(ASTM 3987)

pH @ 21°C	12.08	12.56	12.54
Total Dissolved Solids	0.56	0.71	0.71
Sulfite Sulfur, % SO ₃	0.77	0.41	0.39
Sulfate Sulfur, % SO ₃	2.60	2.15	2.58
Chloride, ppm Cl	390	235	180

* Samples are leached as received (not dried at 105°C).

APPENDIX C

MOISTURE-DENSITY RELATIONSHIP

Client
Client Project
Project No.
Boring No.
Depth (ft.)
Sample No.

B&W
LIDS ASH
92112
NA
NA
LIDS ASH

Tested By
Checked By

JWP
JCM

DATE
DATE

01-29-92
2-3-92

Test Type
Wt. of Mold (gm.)
Mold Volume (cm³)

STANDARD
4240
944

Description:

GRAY ASH

WET DENSITY

Wt. Mold & WS(gm.)	5490	5575	5690	5725	5718
Wt. Mold(gm.)	4240	4240	4240	4240	4240
Wt. WS(gm.)	1250	1335	1450	1485	1478
Mold Volume(cm ³)	944	944	944	944	944
Wet Density(gm./cm ³)	1.32	1.41	1.54	1.57	1.57
Wet Density(pcf)	82.63	88.25	95.85	98.16	97.70

WATER CONTENT

Tare Number	781	210	730	677	728
Wt. Tare & WS(gm.)	228.96	213.88	294.28	252.07	334.19
Wt. Tare & DS(gm.)	193.85	179.82	233.51	196.15	253.53
Wt. Water(gm.)	35.11	34.06	60.77	55.92	80.66
Wt. Tare(gm.)	85.22	85.89	86.55	74.71	86.64
Wt. DS(gm.)	108.63	93.93	146.96	121.44	166.89
Moisture Content(%)	32.32	36.26	41.35	46.05	48.33
Dry Density(pcf)	62.44	64.76	67.81	67.21	65.86

DRY
DENSITY
(pcf)

Specific Gravity
2.70
ASSUMED

Zero Air Voids

Moisture Content (%)	Dry Unit Weight (pcf)
45.00	76.06
49.00	72.53
53.00	69.30

WATER CONTENT, %

PERMEABILITY TEST

Client	B&W	Tested By JCM	Date 2-4-92
Client Project	LIDS ASH	Checked By	Date
Project No.	92112	Specific Gravity	2.70
Boring No.	NA		ASSUMED
Depth(ft.)	NA		
Sample No.	LIDS ASH		

SOIL DESCRIPTION GRAY ASH
(REMOLDED)

BEFORE TEST

AFTER TEST

MOISTURE CONTENT

Tare Number	730	785
Wt. Tare & WS(gm.)	378.01	504.10
Wt. Tare & DS(gm.)	286.18	350.80
Wt. Water(gm.)	91.83	153.30
Wt. Tare(gm.)	86.60	85.91
Wt. DS(gm.)	199.58	264.89
Moisture Content(%)	46.01	57.87

UNIT WEIGHT

Wt. Tube & WS.(gms.)	890.40	NA
Wt. Of Tube(gms.)	269.80	NA
Wt. Of WS.(gms.)	620.60	671.02
Length 1 (in.)	3.983	4.031
Length 2 (in.)	3.983	3.991
Length 3 (in.)	3.983	4.020
Top Diameter (in.)	2.891	2.928
Middle Diameter (in.)	2.891	2.957
Bottom Diameter (in.)	2.891	2.900
Average Length (in)	3.98	4.01
Average Area (in.)	6.56	6.73
Sample Volume(cc.)	428.45	443.01
Unit Wet Wt.(gms/cc)	1.45	1.51
Unit Wet Wt.(pcf.)	90.39	94.52
Unit Dry Wt.(pcf.)	61.90	59.87
Unit Dry Wt.(gms/cc)	0.99	0.96
Void Ratio,e	1.72	1.81
Porosity, n	0.63	0.64
Pore Volume, cm^3	271.03	285.59

PERMEABILITY TEST

Client B&W
 Client Project LIDS ASH
 Project No. 92112
 Boring No. NA
 Depth(ft.) NA
 Sample No. LIDS ASH

Tested By JCM Date 2-4-92
 Checked By Date
 Specific Gravity 2.70
 ASSUMED

Pressures		Final Sample Dimensions	
Top Cap (psi)	25.0	Sample Length (in.)	4.01
Bottom Cap (psi)	30.0	Sample Diameter (in.)	2.93
Cell (psi)	35.0	Sample Area (in.^2)	6.73
Total Head (cm)	351.5		

TIME 1	0.0	hrs.	PERMEABILITY	1.71e-005	CM/SEC
TOTAL FLOW 1	0.0	cm^3	AVG. TEST TEMP	19.6	CELSIUS
TIME 2	4.3	hrs.	PERMEABILITY	1.72e-005	CM/SEC
TOTAL FLOW 2	395.5	cm^3	CORRECTED TO	20.0	CELSIUS

DATE	TIME	ELAPSED TIME	BURETTE READINGS		TOTAL FLOW	FLOW PERMEABILITY		
			INITIAL cm^3	FINAL cm^3		0 FLOW 1 STOP	cm^3/sec	
mon-dy-yr	hr	min	hrs		cm^3			
2-4-92	9	47	0.00	1.5	1.5	0.0	0	NA
2-4-92	10	7	0.33	28.4	28.4	26.9	0	1.50e-005
2-4-92	10	35	0.80	66.5	66.5	65.0	0	1.52e-005
2-4-92	11	0	1.22	102.7	0.0	101.2	0	1.61e-005
2-4-92	11	50	2.05	61.6	61.6	162.8	0	1.37e-005
2-4-92	12	20	2.55	102.7	102.7	203.9	1	1.52e-005
2-6-92	7	40	2.55	18.1	18.1	203.9	0	NA
2-6-92	8	0	2.88	54.8	54.8	240.5	0	2.04e-005
2-6-92	8	15	3.13	81.6	81.6	267.4	0	1.99e-005
2-6-92	8	25	3.30	101.2	0.0	287.0	0	2.18e-005
2-6-92	8	44	3.62	29.8	29.8	316.8	0	1.75e-005
2-6-92	8	55	3.80	51.3	51.3	338.3	0	2.18e-005
2-6-92	9	10	4.05	79.7	79.7	366.7	0	2.10e-005
2-6-92	9	25	4.30	108.5	107.6	395.5	0	2.14e-005

CLIENT: B&W
 CLIENT PROJECT: LIDS ASH
 PROJECT NO.: 92112
 SOIL DESCRIPTION: GRAY ASH (REMOLDED)

BORING NO.: NA
 DEPTH: NA
 SAMPLE NO.: LIDS ASH

PERMEABILITY TEST
 PERMEABILITY = 1.72×10^{-5} CM/SEC

APPENDIX D

twin city testing
corporation

662 CROMWELL AVENUE
ST. PAUL, MN 55114
PHONE 612/645-3601

TO: Mr. Bill Musiol
B & W Alliance Research Center
1562 Beeson Street
Alliance, OH 44601

DATE: May 1, 1992

PROJECT NO: 4122 92-3190

COPY TO: 1-B & W Alliance
Attn: B S Twyman

PROJECT: MATERIAL CHECK

TEST OF FLY ASH

INTRODUCTION

This report presents the results of laboratory testing performed on a fly ash samples submitted to our laboratory on March 2, 1992 by Mr. Bill Musiol of Babcock & Wilcox Co. The scope of our work was limited to performing physical tests in accordance with ASTM:C618-91.

Our work was requested by Mr. Bill Musiol and authorized under Babcock & Wilcox P.O. # 5370A315826US of March 2, 1992.

SAMPLE IDENTIFICATION:

Sample Description -	Fly Ash	Fly Ash
Sample Location -	Not Given	Not Given
Date Sampled -	1-4-92	1-7-92
Sample Size -	20 lbs.	20 lbs.
Date Submitted -	3-2-92	3-2-92

TEST PROCEDURES:

Laboratory testing was performed on March 17, 1992 and subsequent dates in accordance with ASTM:C311, "Sampling and Testing Fly Ash or Natural Pozzolons for use as a Mineral Admixture in Portland Cement Concrete."

PROJECT NUMBER: 4122 92-3190

DATE: May 1, 1992

PAGE: 2

TEST OF FLY ASH

PHYSICAL TEST RESULTS:

**ASTM:C618-91
SPECIFICATIONS**

			<u>Class F</u>	<u>Class C</u>
Fineness				
Retained on #325 Sieve, %	21.1	17.9	Max 34	Max 34
Specific Gravity	2.67	2.68		
Pozzolanic Activity Index				
With Portland Cement (%)				
Ratio to Control @ 28 Days	*	*	Min 75	Min 75
Water Requirements, % of Control	96.8	96.8	Max 105	Max 105
Soundness				
Autoclave Expansion (%)	*		Max 0.8	Max 0.8
Uniformity Requirement				
Specific Gravity (Var. from Ave.)	0.2	0.2	Max 5	Max 5
% Ret. on #325 (Var. from Ave.)	8.2	8.2	Max 5	Max 5

REMARKS:

Northwestern States Type I Portland Cement was used in all tests when applicable.

* This testing is underway and the results will be reported when available.

If you have any questions about this report, please contact me at (612) 659-7399.

TWIN CITY TESTING CORPORATION

John Stieben

Materials Engineer

Construction Services

APPENDIX E

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Client: **Babcock & Wilcox**
Project: **LIDS Ash Evaluation**
P.O. Number: **05054 WFMRB**
Submitter: **Mr. William F. Musiol**

CTL Project No.: **050453/405085**
CTL Proj. Mgr.: **P. B. West**
Approved: **W. A. Klemm**
Date: **March 26, 1993**

Evaluation of LIDS Ash
As a Substitute Material for Making Cement

Sample and Program Description

On November 9, 1992, a five gallon sample of material marked LIDS Ash was received from William F. Musiol of Babcock & Wilcox and was assigned CTL number 907361. This material is a waste product from a pilot plant simulation of a coal fired boiler with a new type of air pollution control device and consists predominately of calcium and sulfur compounds with lesser amounts of silica, alumina, magnesia and iron oxides and traces of other oxides. A sample of the LIDS ash was submitted for oxide analysis by X-ray fluorescence spectrometry and X-ray diffraction analysis.

Construction Technology Laboratories planned a program to evaluate the LIDS ash as a substitute material for potential use in cement rotary kilns. This ash was modified by addition of alkalies, then used as a substitute raw material in Type I cement raw mixes, and these were clinkered and evaluated. The computer program, CTLRAWMIX, was used to design four raw mixes for cement manufacturing. One mix was a base case, and the other three mixes incorporated three levels of LIDS ash. After the clinkers were evaluated, they were ground with Terra Alba gypsum to make cement. Cement pastes were mixed and tested for time of set, and 1" cubes were tested for compressive strengths at 1, 3, 7, and 28 days.

Findings

Qualitative X-ray diffraction analysis of sample 907361 of LIDS ash indicates the following phases were present (listed in order of descending intensity of the most intense peak of each phase): portlandite ($\text{Ca}(\text{OH})_2$), anhydrite (CaSO_4), calcite (CaCO_3), lime

(CaO), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Chemical analysis (expressed as oxides) of sample 907361 of LIDS ash indicates that it contains about 23% sulfur trioxide, 48% calcium oxide, 6% silica and about 3% each of alumina and ferric oxide. The loss-on-ignition is 14.3%. The complete chemical analyses along with thermogravimetric results are shown in Table 1. Thermogravimetric and chemical analyses were combined and interpreted to provide semi-quantitative amounts of the major compounds present and the results, which are in reasonable agreement with the XRD results, are shown in Table 2.

The high calcium content and the presence of silica, alumina and iron oxides make this a suitable alternate cement raw material. The other minor oxides should not cause operational problems with a cement kiln except for the high sulfur content. LIDS ash will not be acceptable at most cement plants because of the sulfur content, however, this may be advantageous at a plant which is using a low sulfur fuel with high alkali material. Some cement plants on the Great Lakes in Canada burn natural gas and have high alkali raw feed. A molar balance of sulfur and alkalis is recommended for good kiln operation. The CTL evaluation was based on use of LIDS ash at this type of plant which usually produces a Type I cement or its equivalent. Sulfur would combine with alkalis in such a kiln and most of the alkali sulfates would be incorporated in the clinker. In this evaluation program alkali was added to the LIDS ash before mixing with the other raw materials to minimize the loss of sulfur and alkalis during the laboratory clinkering process. The calculated oxide basis analysis of the modified LIDS ash is shown in Table 3. Analyses of this ash and the other raw materials appear in Table 4. Raw mix designs are in Tables 5A to 5D.

Four clinkers were made and cement was made from each for paste tests, but only the base case and the clinkers with the two highest ash addition levels were submitted for chemical and microscopic tests. These clinkers were submitted for chemical analysis by XRF, free lime analysis, and polished section evaluation by light microscopy. Chemical analyses are in Tables 6A, 6B, and 6C. The three clinkers all had free lime values below 0.8%. Clinker microscopy indicated that all three clinkers were of roughly similar quality, but some trends with increasing amounts of LIDS ash were observed. On an ignited clinker basis, 0, 3.32, 4.80, and 6.28% of LIDS ash was incorporated in the raw mixes in order to have about 1% alkali and 1.5% SO_3 in the clinker with the highest ash addition. These addition levels cover the range of most commercial clinkers produced in North America.

Cement paste tests indicated the setting time decreased with added ash and this is expected due to the increasing level of alkalies. Compressive strengths at 1 and 3 days increases with the higher levels of ash but at 7 days cements made with LIDS ash have comparable strengths although all three are substantially above the control. Compressive strength development is known to be accelerated at early ages for cements with higher alkali levels. These results are shown in Table 7.

The high sulfur content and the low alkali level make LIDS ash a possible alternative material for selected cement manufacturing situations. The quality of the clinker was reasonably good at all levels of usage. Changes in the cement setting times and the compressive strengths were consistent with the known effects of increasing alkali levels in cement. It is expected that certain cement kilns could advantageously utilize material similar to this LIDS ash sample.

Raw Mix Design and Clinkering

LIDS ash (CTL sample #907361) was submitted for oxide analysis by X-ray fluorescence spectrometry and a customized thermogravimetric analysis. Results for both are shown in Table 1. Sodium hydroxide and potassium hydroxide was added in solution to the LIDS ash in amounts calculated to combine with the sulfate during clinkering and the slurry was then dried at 110°C. The added alkali, the loss on ignition and analysis from Table 1 were combined to give the calculated analysis shown in Table 3. This calculated oxide analysis was used in the calculation of the cement raw mixes. A raw mix design for a Type I cement was calculated using the program CTLRAWMIX, a linear regression computer program. The mix was calculated to have a lime saturation factor (LSF) of 93%, a silica modulus of 2.85, and an iron modulus of 2.20 for all four clinkers. Raw materials were a high quality limestone, clay, sand, iron ore, magnesium carbonate, and for three of the mixes, the alkali modified LIDS ash. Analyses of the raw materials are shown in Table 4. The four clinkers (and cements) were designated BNW1, BNW2, BNW3, and BNW4 from the lowest to highest ash addition level. In order to obtain the four raw mix designs, the program was constrained to use 0, 3.32, 4.80, and 6.28% LIDS ash (identified as LIDSASH+NK in the program output), while the LSF, silica, and iron moduli were kept constant. The resulting calculated potential compound contents were about 56% C₃S, 22%

C₂S, 10% C₃A, and 7% C₄AF as is shown in Tables 5A, 5B, 5C, and 5D, along with the mix design and calculated oxide analyses.

The raw materials were all reduced to approximately 30 mesh or finer and then the proportions weighed. The mixes were then ground in a ceramic ball mill until greater than 99% passed through a No. 200 mesh sieve. Pressed pellets 2.25 inches in diameter and about 150g each were made from each mix and then put into platinum dishes and clinkered in an electric furnace. The clinkering was done in a simulated kiln atmosphere of 77.6% N₂, 1.6% O₂, 18.4% CO₂, and 2.4% H₂O. Temperature was carefully controlled to give the following profile: temperature increasing 20°C per minute from 950°C to 1430°C and the temperature held at 1430°C for 30 minutes. The clinkered pellets were then promptly removed from the furnace and air cooled.

Small samples of clinker were taken for microscopical analysis of polished sections, Franke free lime analysis, and oxide analyses by XRF. The oxide analyses and the free lime results appear in Tables 6A, 6B, and 6C. Free lime values indicate the raw materials were sufficiently fine and the time of clinkering long enough. Oxide analyses agree reasonably well with the calculated oxide values after normalization of the former. Evaluation of three of the clinkers by microscopy is contained in "Reports of Clinker Polished Section Analyses," and they appear in this report after the tables. The quality of all three clinkers is acceptable. Trends that were observed with the increasing ash addition levels in the microscopy reports include an increasing alite size, an increase in both alite decomposition and cannibalism, increasing porosity, and a change of clinker color from black to brown. Free lime was also observed to increase confirming the trend seen in the Franke free lime analyses. Less than optimum distribution and shape of the belite is probably due to the large pellets and conditions typical of static electric furnace burns. These trends are in large part due to the increasing sulfur and alkali levels and do not indicate large changes in clinker quality with the level of LIDS ash.

Cement Preparation and Paste Tests.

The remaining clinker was ground in several steps. The amount of gypsum added was calculated in order to obtain an increasing amount of SO_3 in the finished cement from 2.90% to 3.40% to parallel the increasing alkali levels. Terra Alba gypsum was added at 5.88%, 5.16%, 5.07%, and 4.89% to BNW1, BNW2, BNW3, and BNW4, respectively. This gypsum was added to the partially ground clinkers and then the clinker and gypsum were interground in a ceramic ball mill until they all had a Blaine fineness of $3800 \pm 50 \text{ cm}^2/\text{g}$.

Cement paste was made in a Hamilton-Beach mixer at a water to cement (w/c) ratio of 0.5 for all four cements using a two minute mix, three minute rest, two minute mix mixing schedule. A modified Vicat test was used to measure time of set, and nine 1" cubes were cast for compressive strength tests. The cubes were cured at 23°C and 100% relative humidity until tested with the cubes in the molds only for the first 23 hours. These data are summarized in Table 7.

As indicated earlier the time of sets decreased with increasing alkali level. Compressive strengths at 1 and 3 days were greater as the alkali level of the cements increased. At 7 days, strengths for all cements with added LIDS ash were similar and significantly greater than the strength of the base case with no added ash. At twenty-eight days the compressive strengths of all four cements is expected to be similar. Results obtained in this study for this sample of LIDS ash indicate its use may be beneficial when used at cement plants using high alkali materials and burning low sulfur fuel.

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Table 1

Client: **Babcock & Wilcox**
Project: **Chemical analysis**
Submitter: **Jean Czuczwa**

CTL Project No.: **405085**
CTL Proj. Mgr.: **Presbury West**
Analyst: **Don Broton** *DS*
Approved: **JoAnne Delles** *JAD*
Date: **12/1/92**

REPORT OF CHEMICAL ANALYSIS

Client's Sample ID: **B&W Lids Ash**
Material type: **Ash**
CTL Sample ID: **907361**

<u>Analyte</u>	<u>Weight %</u>	
	<u>(as rec'd)</u>	<u>(Ignited)</u>
SiO ₂	5.81	6.81
Al ₂ O ₃	3.23	3.78
Fe ₂ O ₃	2.66	3.11
CaO	47.53	55.64
MgO	1.20	1.40
SO ₃	22.57	26.43
Na ₂ O	0.15	0.17
K ₂ O	0.25	0.29
TiO ₂	0.19	0.22
P ₂ O ₅	0.13	0.15
Mn ₂ O ₃	0.03	0.04
SrO	0.01	0.02
LOI	14.30	0.00
Total	98.06	98.06

Alkalies as Na₂O 0.31

TGA analysis

Wt loss @ 45 C	0.13
Wt loss @ 130 C	1.80
Wt loss @ 230 C	0.59
Wt loss @ 600 C	5.10
Wt loss @ 950 C	6.68

Notes:

1. This analysis represents specifically the sample submitted.
2. Results reported on an as received basis.
3. Oxide analysis by X-ray fluorescence spectrometry. Samples fused at 1000C with Li₂B₄O₇.

TABLE 2
Calculated Compounds in LIDS Ash

Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	11%
Portlandite	$\text{Ca}(\text{OH})_2$	21%
Calcite	CaCO_3	15%
Anhydrite	CaSO_4	29%
Lime	CaO	7%

TABLE 3
Calculated Chemical Analysis of LIDS ash with added Alkali

<u>Analyte</u>	<u>Weight %</u> <u>(as rec'd)</u>	<u>(ignited)</u>
SiO_2	4.39	5.31
Al_2O_3	2.43	2.95
Fe_2O_3	2.00	2.42
CaO	35.84	43.35
MgO	0.90	1.09
SO_3	17.02	20.59
Na_2O	3.33	4.03
K_2O	14.87	17.98
TiO_2	0.14	0.17
P_2O_5	0.10	0.12
Mn_2O_3	0.03	0.03
SrO	0.01	0.02
<u>LOI</u>	<u>17.00</u>	<u>0.00</u>
Total	98.06	98.06

Table 4: Raw Materials Analyses

--- CONSTRUCTION TECHNOLOGY LABORATORIES ---

-- CTLRAWMIX PROGRAM - OCT 1990 VERSION --

BABCOCK & WILCOX CO FEB 15 '93

EVAL OF B & W LIDS ASH PROJ# 050453

PRES WEST

RAW MATERIALS (IGNITED)	BUFF	LMSTN	KRAFT	CLAY	IND SAND	IRON ORE	MGO03	LIDSASH+NK
PCT. OF S	.605	53.538	96.677	2.048	.000	5.289		
PCT. OF A	.409	44.053	.823	.942	.000	2.928		
PCT. OF F	.000	.197	.361	92.288	.000	2.410		
PCT. OF C	97.546	.000	.000	1.125	.000	43.181		
PCT. OF M	1.102	.104	.000	.865	98.547	1.084		
PCT. OF SO3	.320	.012	.030	.115	.000	20.506		
PCT. OF N	.000	.046	.000	.288	.000	4.012		
PCT. OF K	.000	.069	.060	.067	.000	17.916		
PCT. OF OTHER	.018	2.212	.402	1.019	1.453	.337		
PCT. OF LOSS	77.809	15.808	.392	-3.846	134.412	20.482		
TOTALS (EXCL. LOSS)	100.000	100.232	96.354	98.760	100.000	97.663		

(AS IS)

PCT. OF S	.340	46.230	96.300	2.130	.000	4.390		
PCT. OF A	.230	38.040	.820	.980	.000	2.430		
PCT. OF F	.000	.170	.360	95.980	.000	2.000		
PCT. OF C	54.860	.000	.000	1.170	.000	35.840		
PCT. OF M	.620	.090	.000	.900	42.040	.900		
PCT. OF SO3	.180	.010	.030	.120	.000	17.020		
PCT. OF N	.000	.040	.000	.300	.000	3.330		
PCT. OF K	.000	.060	.060	.070	.000	14.870		
PCT. OF OTHER	.010	1.910	.400	1.060	.620	.280		
PCT. OF LOSS	43.760	13.650	.390	-4.000	57.340	17.000		
TOTALS	100.000	100.200	98.360	98.710	100.000	98.060		

(TARGETS)

Y5= 1.3500004
Y6= .0000000
M1=93.0000000
M2= 2.8500004
M3= 2.2000008

Table 5A: Raw Mix for BNW1

RAW MATERIAL PROPORTIONS

	IGNITED BASIS	AS IS BASIS
BUFF LMSTN	67.951	77.224
KRAFT CLAY	11.428	8.459
IND SAND	16.664	10.693
IRON ORE	2.607	1.602
MGO03	1.350	2.023
LIDSASH+NK	.000	.000
TOTALS	100.000	100.000
LOSS OF MIX	56.458	36.085

COMPUTED OXIDE COMPOSITION

S 22.69312
A 5.47421
F 2.48828
C 66.31287
M 2.11395
SO3 .22683
N .01281
K .01973
OTHER .37797

TOTAL 99.71979

POTENTIAL COMPOUND CONTENT

C4AF 7.57233
C3A 10.29869
C2S 21.99701
C3S 57.10048

TOTAL 96.96851

LIME SATURATION FACTOR= $C/(K12*S+K13*A+K14*F)$ = 93.00000
K12= 2.80 K13= 1.10 K14= .70

SILICA MODULUS= $S/(A+F)$ = 2.85000

IRON MODULUS= A/F = 2.20000

% LIQUID PHASE AT 1470 DEGREES C= 24.00667

BURNABILITY INDEX= $C3S/(C3A+C4AF)$ = 3.19514

P&W'S BURNABILITY FACTOR=108.56049

(TARGETS)

Y5= 1.3500004
Y6= 3.3199997
M1=93.0000000
M2= 2.8500004
M3= 2.1999998

Table 5B: Raw Mix for BNW2

RAW MATERIAL PROPORTIONS

	IGNITED BASIS	AS IS BASIS
BUFF LMSTN	65.447	75.013
KRAFT CLAY	11.050	8.249
IND SAND	16.353	10.582
IRON ORE	2.481	1.538
MGCO3	1.350	2.040
LIDSASH+NK	3.320	2.578
TOTALS	100.000	100.000
LOSS OF MIX	55.134	35.539

COMPUTED OXIDE COMPOSITION

S 22.34723
A 5.39078
F 2.45035
C 65.30212
M 2.12086
SO3 .89933
N .14547
K .61400
OTHER .37783

TOTAL 99.64798

POTENTIAL COMPOUND CONTENT

C4AF 7.45692
C3A 10.14172
C2S 21.66174
C3S 56.23012

TOTAL 95.49049

LIME SATURATION FACTOR= $C/(K12*S+K13*A+K14*F)$ = 92.99997

K12= 2.80 K13= 1.10 K14= .70

SILICA MODULUS= $S/(A+F)$ = 2.85000

IRON MODULUS= A/F = 2.20000

% LIQUID PHASE AT 1470 DEGREES C= 24.40732

BURNABILITY INDEX= $C3S/(C3A+C4AF)$ = 3.19514

P&W'S BURNABILITY FACTOR=106.35895

(TARGETS)

Y5= 1.3500004
Y6= 4.7999992
M1=93.0000000
M2= 2.8500004
M3= 2.1999998

Table 5C: Raw Mix for BNW3

RAW MATERIAL PROPORTIONS

	IGNITED BASIS	AS IS BASIS
BUFF LMSTN	64.330	74.015
KRAFT CLAY	10.881	8.154
IND SAND	16.214	10.532
IRON ORE	2.425	1.509
MGO03	1.350	2.048
LIDSASH+NK	4.800	3.742
TOTALS	100.000	100.000
LOSS OF MIX	54.543	35.293

COMPUTED OXIDE COMPOSITION

S 22.19304
A 5.35358
F 2.43345
C 64.85158
M 2.12394
SO3 1.19912
N .20461
K .87891
OTHER .37776

TOTAL 99.61601

POTENTIAL COMPOUND CONTENT

C4AF 7.40546
C3A 10.07175
C2S 21.51224
C3S 55.84216

TOTAL 94.83160

LIME SATURATION FACTOR= $C/(K12*S+K13*A+K14*F)$ = 92.99998

K12= 2.80 K13= 1.10 K14= .70

SILICA MODULUS= $S/(A+F)$ = 2.85000

IRON MODULUS= A/F = 2.20000

% LIQUID PHASE AT 1470 DEGREES C= 24.58591

BURNABILITY INDEX= $C3S/(C3A+C4AF)$ = 3.19514

P&W'S BURNABILITY FACTOR=105.37759

(TARGETS)

Y5= 1.3500004

Y6= 6.2799988

M1=93.0000000

M2= 2.8500004

M3= 2.1999998

Table 5D: Raw Mix for BNW4

RAW MATERIAL PROPORTIONS

	IGNITED BASIS	AS IS BASIS
BUFF LMSTN	63.214	73.010
KRAFT CLAY	10.713	8.059
IND SAND	16.075	10.482
IRON ORE	2.369	1.479
MGCO3	1.350	2.056
LIDSASH+NK	6.280	4.915
TOTALS	100.000	100.000
LOSS OF MIX	53.952	35.045

COMPUTED OXIDE COMPOSITION

S 22.03883
A 5.31639
F 2.41654
C 64.40099
M 2.12702
SO3 1.49891
N .26375
K 1.14382
OTHER .37770

TOTAL 99.58395

POTENTIAL COMPOUND CONTENT

C4AF 7.35402
C3A 10.00177
C2S 21.36272
C3S 55.45435

TOTAL 94.17285

LIME SATURATION FACTOR= $C/(K12*S+K13*A+K14*F)$ = 92.99997

K12= 2.80 K13= 1.10 K14= .70

SILICA MODULUS= $S/(A+F)$ = 2.85000

IRON MODULUS= A/F = 2.20000

% LIQUID PHASE AT 1470 DEGREES C= 24.76451

BURNABILITY INDEX= $C3S/(C3A+C4AF)$ = 3.19515

F&W'S BURNABILITY FACTOR=104.39616

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Table 6A

Client: **Babcock & Wilcox**
Project: **P.O. 05054WFMRB**
Submitter: **Jean Czuczwa**

CTL Project No.: **405085**
CTL Proj. Mgr.: **Dr. Presbury West**
Analyst: **Don Broton** *DB*
Approved: **JoAnne Delles** *JAD*
Date: **3/3/93**

REPORT OF CHEMICAL ANALYSIS

Client's Sample ID: **BNW 1**
Material type: **Clinker**
CTL Sample ID: **908248**

<u>Analyte</u>	<u>Weight %</u>
SiO ₂	23.15
Al ₂ O ₃	5.43
Fe ₂ O ₃	2.72
CaO	65.82
MgO	2.20
SO ₃	0.12
Na ₂ O	0.02
K ₂ O	<.01
TiO ₂	0.32
P ₂ O ₅	0.04
Mn ₂ O ₃	0.05
SrO	0.03
LOI	0.17
<u>Total</u>	<u>100.06</u>

Alkalies as Na ₂ O	0.02
Insoluble Residue	
Free CaO	0.23

Calculated Compounds per ASTM C 150-89

C ₃ S	49
C ₂ S	29
C ₃ A	11
C ₄ AF	8
ss(C ₄ AF + C ₂ F)	---

Notes:

1. This analysis represents specifically the sample submitted.
2. Oxide analysis by X-ray fluorescence spectrometry. Samples fused at 1000C with Li₂B₄O₇.
3. Values for TiO₂ and P₂O₅ are added to the Al₂O₃ when the compounds are calculated, in accordance with ASTM C 150.
4. X-Ray Fluorescence oxide analysis meets the precision and accuracy requirements for rapid methods per ASTM C 114-88. Most recent re-qualification date is August 22, 1991.

Construction Technology Laboratories, Inc. • Skokie • Los Angeles • Seattle/Tacoma

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Table 6B

Client: **Babcock & Wilcox**
Project: **P.O. 05054WFMRB**
Submitter: **Jean Czuczwa**

CTL Project No.: **405085**
CTL Proj. Mgr.: **Dr. Presbury West**
Analyst: **Don Broton** *DB*
Approved: **JoAnne Delles** *JAD*
Date: **3/3/93** *J*

REPORT OF CHEMICAL ANALYSIS

Client's Sample ID: **BNW 3**
Material type: **Clinker**
CTL Sample ID: **908249**

<u>Analyte</u>	<u>Weight %</u>
SiO ₂	22.54
Al ₂ O ₃	5.29
Fe ₂ O ₃	2.59
CaO	64.60
MgO	2.20
SO ₃	0.93
Na ₂ O	0.18
K ₂ O	0.64
TiO ₂	0.32
P ₂ O ₅	0.04
Mn ₂ O ₃	0.05
SrO	0.03
<u>LOI</u>	<u>0.26</u>
Total	99.66

Alkalies as Na₂O 0.60
Insoluble Residue
Free CaO 0.67

Calculated Compounds per ASTM C 150-89

C ₃ S	47
C ₂ S	29
C ₃ A	11
C ₄ AF	8
ss(C ₄ AF + C ₂ F)	---

Notes:

1. This analysis represents specifically the sample submitted.
2. Oxide analysis by X-ray fluorescence spectrometry. Samples fused at 1000C with Li₂B₄O₇.
3. Values for TiO₂ and P₂O₅ are added to the Al₂O₃ when the compounds are calculated, in accordance with ASTM C 150.
4. X-Ray Fluorescence oxide analysis meets the precision and accuracy requirements for rapid methods per ASTM C 114-88. Most recent re-qualification date is August 22, 1991.

Construction Technology Laboratories, Inc. • Skokie • Los Angeles • Seattle/Tacoma

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Table 6C

Client: **Babcock & Wilcox**
Project: **P.O. 05054WFMRB**
Submitter: **Jean Czuczwa**

CTL Project No.: **405085**
CTL Proj. Mgr.: **Dr. Presbury West**
Analyst: **Don Broton** *DB*
Approved: **JoAnne Delles** *JAD*
Date: **3/3/93**

REPORT OF CHEMICAL ANALYSIS

Client's Sample ID: **BNW 4**
Material type: **Clinker**
CTL Sample ID: **908250**

<u>Analyte</u>	<u>Weight %</u>
SiO ₂	22.44
Al ₂ O ₃	5.33
Fe ₂ O ₃	2.57
CaO	64.32
MgO	2.22
SO ₃	1.35
Na ₂ O	0.22
K ₂ O	0.88
TiO ₂	0.32
P ₂ O ₅	0.04
Mn ₂ O ₃	0.05
SrO	0.03
LOI	0.24
<u>Total</u>	<u>100.00</u>

Alkalies as Na₂O 0.80
Insoluble Residue
Free CaO 0.75

Calculated Compounds per ASTM C 150-89

C ₃ S	46
C ₂ S	30
C ₃ A	11
C ₄ AF	8
ss(C ₄ AF + C ₂ F)	---

Notes:

1. This analysis represents specifically the sample submitted.
2. Oxide analysis by X-ray fluorescence spectrometry. Samples fused at 1000C with Li₂B₄O₇.
3. Values for TiO₂ and P₂O₅ are added to the Al₂O₃ when the compounds are calculated, in accordance with ASTM C 150.
4. X-Ray Fluorescence oxide analysis meets the precision and accuracy requirements for rapid methods per ASTM C 114-88. Most recent re-qualification date is August 22, 1991.

Construction Technology Laboratories, Inc. • Skokie • Los Angeles • Seattle/Tacoma

TABLE 7**Cement Paste (w/c = 0.5) and Cement Test Results**

Cement ID	BNW1	BNW2	BNW3	BNW4	
LIDS ash (modified) in clinker (ignited basis)	0%	3.32%	4.80%	6.28%	
Blaine Surface Area	3810	3770	3880	3870	cm ² /g
Time of Set	6 hrs 10 min.	5 hrs 14 min.	5 hrs 5 min.	4 hrs 50 min.	

Average Compressive Strengths of 1" Cubes

One Day	C.S.	1300	1650	1950	2000	p.s.i.
Three Day	C.S.	2700	3250	3700	3750	p.s.i.
Seven Day	C.S.	5400	6200	6450	6050	p.s.i.
Twenty-eight Day	C.S.	10,900	10,700	9830	9430	p.s.i.

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Client: **Babcock & Wilcox**
Project: **LIDS Ash Evaluation**
P.O. Number: **05054 WFMRB**
Submitter: **Mr. William F. Musiol**

CTL Project No.: **220394/102446**
CTL Proj. Mgr.: **P. A. Okamoto**
Approved: **W. A. Klemm**
Date: **March 26, 1993**

LABORATORY TESTING PROGRAM FOR USE IN SOIL CEMENT AND CSLM

A testing program was initiated to evaluate the use of the LIDS ash (CTL #907361) as a cement replacement in a flowable fill or soil-cement material. The ash was heated in platinum dishes in an electrically heated furnace at 560 °C for 25 minutes. This process was repeated several times until several pounds had been processed. These conditions were selected in order to convert most but not all of the calcium hydroxide in the sample to calcium oxide (lime). Processed samples were checked by X-ray diffraction to verify that this objective was met.

Cementitious Low Strength Material (CLSM)

Cementitious by-products can be used as a cementitious low strength material (CLSM) for backfill. A CSLM material consists of a cementitious product such as fly ash, cement or a mixture of cement and fly ash. Non-cohesive soils including silts, sands, or finer coarse aggregates may be used. Water is added to produce a flowable material. Applications using CLSM include backfilling around utility repairs (penetrations) and buried tanks. Advantages in using a CLSM include:

- Material is easily placed as a self-levelling material.
- Material is readily removed due to low design strengths.
- No compaction or vibration is necessary as opposed to other cement stabilized materials such as soil-cement.

Construction Technology Laboratories, Inc. • Skokie • Los Angeles • Seattle/Tacoma

- CSLM engineering properties can be modified by changing the water content and/or cement to by-product ratio.
- CSLM is a relatively low cost stabilized material.

The mix design for a CLSM backfill material is commonly based on achieving a targeted compressive strength. For rapid penetration repair openings to traffic a compressive strength of 10 to 20 psi at 24 hours is targeted. After 24 hours the backfill material would be covered with a wearing surface course such as concrete or asphaltic concrete. A 28 day compressive strength of less than 100 psi is designed for to allow for possible future removal of CLSM. Suggested cement - fly ash - fine soil CSLM proportions range as follows:

- Cement - 50 to 100 lb/yd³
- Fly ash - 200 to 300 lb/yd³
- Fine aggregate 2600 to 2800 lb/yd³
- Water 50 to 70 gallons/yd³

The high lime content waste material was evaluated for use as a CLSM. A silty soil was used as a fine soil filler. Water to cementitious ratios (water to cement plus high lime material) were set at 2.3 and 2.5. Four by-product to cement ratios by weight of 100:0, 80:20, 60:40, 0:100 were evaluated at both water to cementitious ratios. Water and soil content were constant for all six mixes to investigate the effects of changing the water to cementitious ratios on compressive strength. Mix designs for the eight mixes are listed in **Table X1**.

Compressive strength and modulus of elasticity of 3 x 6 in. moist-cured cylinders were determined at 7, 14, and 28 days in general accordance with ASTM C39 "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" and ASTM C469 "Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression." Two cylinders were tested at each age for each mix. Average compressive strength and elastic modulus are summarized in **Table X2** and **Table X3**, respectively.

As listed in Table X2, the 100 percent by-product mixes do not gain any measurable strength at ages up through 28 days. Compressive strength at 28 days ranged from 75 psi (80:20 by-product to cement ratio) to 386 psi (100 percent cement) for a water to cementitious ratio of 2.3. At the higher water to cementitious ratio of 2.5, compressive strength at 28 days ranged from 72 psi (80:20 by-product to cement ratio) to 289 psi (100 percent cement). For each test age, as the water to cementitious material ratio increased, the compressive strength decreased.

As shown in Figure 1, increases in 28 day compressive strength are relatively linear with cement content and pass approximately through zero compressive strength at zero cement content. Contributions of by-product to compressive strength would be reflected in significant strengths at zero cement content. The use of high lime content by-product does not appear to contribute any significant increases in compressive strength.

SOIL-STABILIZATION

Cementitious by-products may also be used in as a partial replacement in a soil-cement material. Soil-cement is a mixture of soil and measured amounts of portland cement and water compacted to a high density. It is produced by blending, compacting, and curing the mixture of soil, portland cement, and water to form a hardened material with specific engineering properties. The primary use of stabilized materials is a base course underlaying bituminous and concrete pavements and runways. Under concrete pavements, stabilized layers are used as a base course to prevent pumping of fine-grained subgrade soils in wet environments and heavy truck traffic conditions. Stabilized layers provide a working platform for construction equipment during concrete placement and can provide increased structural capacity to the pavement. When used with a flexible pavement, a hot-mix bituminous concrete wearing surface is placed directly on the stabilized base.

The high lime content waste material was evaluated for use as a cement replacement in a soil-cement mix. The silty soil was the same as that used in the CLSM tests. The soil-cement testing program consisted of the following tests:

- Moisture-density compaction in accordance with ASTM D 558 "Standard Test Method for Moisture-Density Relations of Soil-Cement Mixture."

- Compressive strength at 7, 14, and 28 days in accordance with ASTM D 1633 "Standard Test Method for Compressive Strength of Molded Soil-Cement Cylinders."

Moisture density tests were made to determine optimum moisture content and maximum dry density. For a given cement content, the higher the dry density, the higher the compressive strength. Dry density typically increases and then decreases for increasing moisture content. The optimum moisture content is that at which dry density is maximum. A moisture-density relationship using the silty soil was established for a cement content of 10 percent (by oven-dry weight of soil). Maximum dry density of 129.0 lb/ft³ occurred at a moisture content of 9.0 percent (by dry weight).

Specimens were fabricated at optimum moisture content at cement replacement ratios by weight of 0, 10, 20, and 50 percent. Cementitious content was set at 10 percent of dry soil weight. Two specimens for each age and replacement content were molded at the optimum 9.0 percent moisture content. Specimens 4 in. in diameter and 4.6 in. high were molded with the same compaction equipment as that used in the moisture-density tests and moist-cured (100 percent R.H.) at 72 °F until time of test. Specimens were capped and soaked in water for four hours before broken. Results of compressive strength tests are summarized in **Table X4**.

As listed in **Table X4**, compressive strength at 28 days ranged from 825 psi (50:50 by-product to cement ratio) to 2190 psi (100 percent cement). For each test age, as the cement replacement increased, the compressive strength decreased.

As shown in **Figure 2** increases in 28 day compressive strength are relatively linear with cement content. Contributions of by-product to compressive strength would be reflected in significant strengths at zero cement content. The use of high lime content by-product does not appear to contribute any significant increases in compressive strength.

Table X1 - CLSM Mix Designs

Water/ Cementitious	By-Product/ Cement Ratio	By-Product, lb/yd ³	Cement, lb/yd ³	Aggregate, lb/yd ³	Water, gal./yd ³
2.3	100:0	250	0	2700	69
	80:20	200	50	2700	69
	60:40	150	100	2700	69
	0:100	0	250	2700	69
2.5	100:0	230	0	2700	69
	80:20	184	46	2700	69
	60:40	138	92	2700	69
	0:100	0	230	2700	69

Table X2 - CLSM Compressive Strength

Water/ Cementitious	By-Product/ Cement Ratio	By-Product, lb/yd ³	Cement, lb/yd ³	7 day f _c , psi	14 day f _c , psi	28 day f _c , psi
2.3	100:0	250	0	NA	NA	NA
	80:20	200	50	18	41	75
	60:40	150	100	48	83	136
	0:100	0	250	238	362	386
2.5	100:0	230	0	NA	NA	NA
	80:20	184	46	16	40	72
	60:40	138	92	35	72	120
	0:100	0	230	183	255	289

NOTE: NA = not available, too soft to test

Table X3 - CLSM Modulus of Elasticity

Water/ Cementitious	By-Product/ Cement Ratio	By-Product, lb/yd ³	Cement, lb/yd ³	7 day Ec, 1000 psi	14 day Ec, 1000 psi	28 day Ec, 1000 psi
2.3	100:0	250	0	NA	NA	NA
	80:20	200	50	NA	45	159
	60:40	150	100	53	115	145
	0:100	0	250	354	417	377
2.5	100:0	230	0	NA	NA	NA
	80:20	184	46	NA	52	151
	60:40	138	92	64	100	150
	0:100	0	230	293	323	334

NOTE: NA = not available, too soft to test

Table X4 - Soil-Cement Compressive Strength

By-Product/ Cement Ratio	7 day f _c , psi	14 day f _c , psi	28 day f _c , psi
50:50	595	665	825
20:80	1350	1590	1890
10:90	1505	1740	2025
0:100	1745	1955	2190

Figure 1 - Effects of Cement Content on 28 Day Compressive Strength

Figure 2 - Effects of Cement Proportions on 28 Day Compressive Strength

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Client: **Babcock and Wilcox**
Project: **Clinker Evaluation**

Contact: **Jean Czuczwa**
Submitter: **Jean Czuczwa**

CTL Proj. No.: **405085**
CTL Proj. Mgr.: **P. B. West***
Analyst: **L. M. Hills**
Approved: **H. M. Kanare**
Date: **March 18, 1993**

REPORT OF CLINKER POLISHED SECTION ANALYSIS

IDENTIFICATION OF SAMPLES

CTL ID Client ID
908248 BNW 1

FINDINGS

Alite

Size range 15-25 microns Max. size 35 microns
Alite crystals are moderate in size. A small amount of decomposition of edges to belite is observed.
Alite cannibalism (fused crystals) is evident only in localized areas.

Belite

Size range 20-30 microns Max. size 40 microns
Belite crystals are moderate in size and rounded in shape. Some belite crystals demonstrate ragged edges. Belite and alite are not well distributed.

C3A

Crystals up to 25 microns in size are observed

C4AF

Average reflectivity

MgO (periclase)

Trace to small amount observed; idiomorphic in form

Free lime

Trace amount observed

Alkali Aluminate

None observed

Clinker is black in color

Clinker porosity appears moderate to high

* Contact for more information.

CTL

Client: Babcock and Wilcox

NO ETCH

908248 400x MgO (Periclase)

WATER ETCH

908248 400x Free CaO

NITAL ETCH

908248 200x Alite/belite distribution
High porosity

908248 400x Alite crystals

Client: Babcock and Wilcox

NITAL ETCH

908248 600x Alite decomposition
Large C₃A in matrix

908248 400x Belite crystals

908248 600x Ragged and spintering
belite crystals

5420 Old Orchard Road, Skokie, Illinois 60077-1030

Phone: 708/965-7500 Fax: 708/965-6541

Client: **Babcock and Wilcox**
Project: **Clinker Evaluation**

Contact: **Jean Czuczwa**
Submitter: **Jean Czuczwa**

CTL Proj. No.: **405085**
CTL Proj. Mgr.: **P. B. West***
Analyst: **L. M. Hills**
Approved: **H. M. Kanare**
Date: **March 18, 1993**

REPORT OF CLINKER POLISHED SECTION ANALYSIS

IDENTIFICATION OF SAMPLES

CTL ID Client ID
908249 BNW 3

FINDINGS

Alite

Size range 15-30 microns Max. size 45 microns
Alite crystals are moderate in size. A small amount of decomposition of edges to belite is observed.
More alite cannibalism (fused crystals) is observed compared to 908248.

Belite

Size range 20-30 microns Max. size 40 microns
Belite crystals are moderate in size and rounded in shape. Belite crystals demonstrate ragged edges in localized areas. Belite and alite are not well distributed.

C₃A

Crystals up to 25 microns in size are observed

C₄AF

Average reflectivity

MgO (periclase)

Small amount observed; idiomorphic in form

Free lime

Trace amount observed in some clinker pieces, abundant in others.

Alkali Aluminate

Small amount observed

Clinker is black to brown in color.
Clinker porosity appears high.

* Contact for more information.

Client: Babcock and Wilcox

NO ETCH

908249 400x MgO (Periclase)

WATER ETCH

908249 400x Free CaO

NITAL ETCH

908249 200x Alite/belite distribution
High porosity

908249 400x Alite crystals

Client: Babcock and Wilcox

NITAL ETCH

908249 600x Alite decomposition
Alkali aluminate in matrix

908249 400x Belite crystals

908249 600x Ragged and splintering
belite crystals

5420 Old Orchard Road, Skokie, Illinois 60077-1030
Phone: 708/965-7500 Fax: 708/965-6541

Client: **Babcock and Wilcox**
Project: **Clinker Evaluation**

Contact: **Jean Czuczwa**
Submitter: **Jean Czuczwa**

CTL Proj. No.: **405085**
CTL Proj. Mgr.: **P. B. West***
Analyst: **L. M. Hills**
Approved: **H. M. Kanare**
Date: **March 18, 1993**

REPORT OF CLINKER POLISHED SECTION ANALYSIS

IDENTIFICATION OF SAMPLES

CTL ID Client ID
908250 BNW 4

FINDINGS

Alite

Size range 15-30 microns Max. size +55 microns
Alite crystals are moderate in size. Decomposition of edges to belite is evident in localized areas.
More alite cannibalism (fused crystals) is observed compared to 908248 and 908249.

Belite

Size range 10-25 microns Max. size 40 microns
Most belite crystals are moderate in size and rounded in shape; some areas contain poorly formed, ragged, small crystals. Belite and alite are not well distributed.

C₃A

Crystals up to 30 microns in size are observed

C₄AF

Average reflectivity

MgO (periclase)

Small amount observed; idiomorphic in form

Free lime

Trace amount observed in some clinker pieces, abundant in others

Alkali Aluminate

Trace amount observed

Clinker is black to brown in color (more brown than 908248 or 908249).
Clinker porosity appears high.

* Contact for more information.

Client: Babcock and Wilcox

NO ETCH

908250 400x MgO (Periclase)

WATER ETCH

908250 400x Free CaO

NITAL ETCH

908250 200x Alite/belite distribution
High porosity

908250 400x Alite crystals

Client: Babcock and Wilcox

NITAL ETCH

908250 600x Large C₃A in matrix
Ragged belite
Alite cannibalism (fused crystals)
and decomposition

908250 400x Belite crystals

END

**DATE
FILMED**

11 / 12 / 93