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Project Title: **PRODUCTION OF CEMENTS FROM ILLINOIS COAL ASH**

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Principal Investigator: John C. Wagner, Institute of Gas Technology  
Other Investigators: Javed I. Bhatti, Alex Mishulovich, Construction  
Technology Laboratories, Inc.  
Project Manager: Daniel D. Banerjee, ICCI

ABSTRACT

The objective of this program is to convert Illinois coal combustion residues, such as fly ash, bottom ash, and boiler slag, into novel cementitious materials for use in the construction industry. Currently less than 10% of the 3 million tons of these coal combustion residues generated in Illinois each year are utilized in commercial products. These residues are composed largely of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$ , which are also the major components of cement. The process being developed in this program will use the residues directly in the manufacture of cement products. Since the residues are used as an integral component of the cement and not just as additives to concrete, larger amounts of the residues can be utilized.

The process uses submerged combustion to melt blends of coal combustion residues with lime, clay, and/or sand. The submerged combustion melter utilizes natural gas-oxidant firing directly into a molten bath to provide efficient melting of mineral-like materials. Use of this melter for cement production has many advantages over rotary kilns including very little, if any, grinding of the feed material, very low emissions, and compact size.

During the first year of the program, samples of coal combustion residues were blended and mixed, as needed, with lime, clay, and/or sand to adjust the composition. Six mixtures, three with fly ash and three with bottom ash, were melted in a laboratory-scale furnace. The resultant products were used in mortar cubes and bars which were subjected to ASTM standard tests of cementitious properties. In the hydraulic activity test, mortar cubes were found to have a strength comparable to standard mortar cements. In the compressive strength test, mortar cubes were found to have strengths that exceeded ASTM blended cement performance specifications. In the ASR expansion test, mortar bars were subjected to alkali-silica reaction-induced expansion, which is a problem for siliceous aggregate-based concretes that are exposed to moisture. The mortar bars made with the products inhibited 85 to 97% of this expansion. These results show that residue-based products have an excellent potential as ASR-preventing additions in concretes.

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## EXECUTIVE SUMMARY

### Background

A significant portion of mined Illinois coal is used in utility plants across the State to generate electricity. There are nearly 30 power utilities in the State of Illinois that consume more than 30 million tons of coal every year. The coal is combusted and the residues generated are primarily fly ash, bottom ash, and boiler slag. Over 3 million tons of these coal combustion residues are generated every year. Generally in the U.S., about 25% of the fly ash, 40% of the bottom ash, and 60% of the boiler slag are consumed, mostly in cement, concrete, and structural fills, leaving about 70% of the residues stockpiled in nearby landfills.

In the State of Illinois, the bulk (nearly 90%) of these residues remains unused. As a result, the utilities are faced with an increasing disposal problem because of both the large volume of these residues and the lack of landfill sites. Furthermore, by virtue of their diverse chemical compositions, these residues are susceptible to ground water leaching and possible contamination. The potential pollution scenarios, pressure for environmentally safe disposal, and the "landfill crisis," combined with political opposition to new landfill sites, have exacerbated the waste problems, posing a technical challenge to develop safe alternative disposal routes.

### Approach

The objective of this program is to convert Illinois coal combustion residues, such as fly ash, bottom ash, and boiler slag, into novel cementitious materials for use in the construction industry. These residues are composed largely of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$ , which are also the major components of cement. Success of this program will lead to significantly higher usage of these residues because they will be used to generate cementitious products instead of being added to concrete mixes as aggregates.

To achieve the above objective, a three-phase program is planned. In the first phase, small samples (100-200 g) of coal combustion residues were blended and mixed, as needed, with limestone, clay, and/or sand to adjust the  $\text{CaO}$  composition. Six mixtures were melted in a laboratory-scale furnace at CTL. The resulting products, or novel cementitious materials (NCMs), were then tested for their cementitious properties. These tests included x-ray diffraction, x-ray fluorescence, optical microscopy, grindability index, and pozzolanic activity. After testing, the NCMs were blended at various levels with portland cement and subjected to a series of ASTM and CTL-derived tests including hydraulic activity, compressive strength, and ASR expansion.

With optimal mixing and melting conditions established, the second phase will be used to generate larger quantities of NCMs. The three best raw mix formulations as determined in the first phase will be utilized. A pilot-scale submerged combustion melter assembled at IGT will be used for melting the mixtures. The products generated during this phase

will be subjected to the same tests as in the first phase. The submerged combustion melter utilizes natural gas/oxidant firing directly into a molten bath to provide efficient melting of mineral-like materials. Use of this melter for cementitious materials production has many advantages over rotary kilns as well as other melters including very little, if any, grinding of the feed material, low emissions, and compact size. Economics are improved because grinding, which is very energy-intensive, is responsible for a substantial portion of the cost associated with production of cement using rotary kilns.

Submerged combustion melters have been in commercial operation in Ukraine and Belarus for several years for the production of mineral wool. IGT has licensed the technology from its developer, the Gas Institute of the Academy of Sciences of Ukraine, for exclusive application outside the former Soviet Union. Other applications for the submerged combustion melter include ash vitrification, glass melting, scrap melting, and direct waste processing.

The third phase will be focused on data analysis and interpretation, process economics, and commercialization considerations. The first phase was completed during this first-year program, while the second and third phases were proposed for the second year. CTL, as a subcontractor, performed the bulk of the effort for the first phase. IGT will perform the substantial part of the effort for the second phase. IGT and CTL will share the effort for the third phase.

### Results and Discussion

Initially, two preliminary blends were tested. One blend used fly ash with limestone, while the other used fly ash with cement kiln dust (CKD). Each blend was melted and then quenched, and the resulting product samples were ground to a specific surface area similar to portland cement. Cementitious properties of these product samples were evaluated by accelerated testing of 1-inch cube specimens. The specimens were formed out of cement paste where a certain percentage of the cement paste is displaced by one of the sample products. The specimens were cured for 24 hours at 55°C and 100% relative humidity. The specimens made with the product samples obtained 84 and 89% of the compressive strength of a pure portland cement control cube. For comparison, similar (pozzolanic) materials in standard concrete practice are required to have a compressive strength of at least 75% of that of the control.

Based on these initial results, six experimental mix formulations were designed to cover the entire prospective area of compositions. Mixes 1F, 2F, and 3F used fly ash while Mixes 1B, 2B, and 3B used bottom ash. In Mixes 1F, 2F, 1B, and 2B, the proportions of the three major oxides are equal to eutectic points on the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  ternary phase diagram. The composition of Mixes 3F and 3B is approximately half way between those two eutectic points, in an area of higher melting temperature.

Each of the six mixes was melted in an Inconel 601 crucible in an electric muffle furnace and quenched in water. All products were fully vitrified as confirmed by polarized light

microscopy. The products were ground in a laboratory mill to the fineness characterized by the Blaine specific surface of about 360 m<sup>2</sup>/kg, which is typical for portland cements.

To evaluate the hydraulic reactivity of cementitious materials, a number of chemical methods have been used based mainly on certain calculated or measured chemical properties of the materials. However, in this program reactivity was measure more directly by physical testing of paste and mortar cubes prepared from mixtures of the products with cement. Pastes are mixtures of cement and water. Mortars are mixtures of cement and sand.

The products were subjected to a series of standard tests applied usually to blended cements and their ingredients.

#### Hydraulic Activity By Reaction With Alkali (ASTM C 1073)

For this test, mortar is prepared from a hydraulically active material and sand in a 1:2.75 proportion and mixed with 20% NaOH solution. Hydraulically active materials are those which can react with water to gain strength. Standard 2-in cubes made from the products were tested for compressive strength after 24-hr curing at 55°C (131°F) and 100% humidity. This test method is normally used for evaluation of the hydraulic activity of slags and similar materials from different sources. As a point of reference, it can be noted that these cementless compositions showed compressive strengths comparable to that of standard (ASTM C 91) mortar cements at a 28-day age (900, 2100, and 2900 psi for different types).

#### Compressive Strength of Hydraulic Cement Mortars (ASTM C 109)

For this test, blended cements were prepared containing 75% portland cement clinker and 25% products. Characteristics of such cements should conform to the ASTM C 117 specification. Mortar was prepared from cement and sand in a 1:2.75 proportion and mixed with water (0.484 parts per part of cement). Standard 2-in cubes were cast from the mortar and cured under controlled conditions for up to 28 days. Compressive strength of these cubes exceeded ASTM C 117 performance specifications and obtained 76 to 94% of the strength of a pure portland cement control cube. The results of physical testing indicate that products with higher basicity (lower (S+A)/C ((silica+alumina)/lime) ratio) tend to have higher strength. The bottom ash-based products appear to produce better results but, to confirm it, additional testing is required.

#### ASR Expansion Reduction

In the presence of moisture, concrete can expand due to the alkali-silica reaction (ASR). Low-alkali (<0.6%) cement is specified to be used in concretes for locations with high moisture exposure. In Illinois, ASR is not a serious problem because limestone is the aggregate typically used in concrete. In other areas, particularly western states, siliceous stone is used as the aggregate. There, ASR is a problem.

A further benefit of using coal combustion residue-based cements would be the ability of the cements to inhibit the ASR-induced expansion. The potential of the products to inhibit the ASR in concrete was evaluated using the ASTM C 441 test. In this test, ASR-induced expansion of 10-inch mortar bars containing high-alkali cement and reactive siliceous aggregate is measured. The test results with the coal combustion residue-based products showed ASR expansion reductions of 85% to 97%. These results show these products have an excellent potential as ASR-preventing additions in concretes.

### Fiberization of Melts

Usually, slag-like glasses prepared by water-quenching of melts are harder to grind than portland cement clinker. This leads to non-uniformity of particle sizes in blended cements. The prospective commercial melter is likely to utilize a quenching technique based on dispersing the liquid melt by a jet stream of air or rotating metal cylinder. In either case, the final product would form fiberized mass similar to mineral wool. Since the actual pilot-scale melter is not yet available, mineral wool produced from blast furnace slag was used for a preliminary investigation of some aspects of the future technology. Chemical analysis revealed that the composition of the mineral wool was reasonably close to that of coal combustion residue-based products. Microscopic examination confirmed that the material consisted of completely vitrified fibers 7 to 10  $\mu\text{m}$  in diameter. Experimental study of mineral fibers proceeded in two directions-intergrinding fibers in blended cements and fiber-reinforced composites.

Grindability of fibers in blended cement mixes was studied by preparing a 75:25 mix of portland cement clinker and fibers and grinding it in a jar mill. Fineness was characterized by Blaine specific surface determined at several points during grinding. Photomicrographs taken at 20-min. increments demonstrated the gradual shortening of fibers, along with comminution of the clinker particles.

Adding fiberized material to mortars and concretes is expected to increase their tensile and flexural strength, as well as control drying shrinkage and cracking. Unlike the polymer fibers currently used, this fiberized mineral material would react with cement paste providing for a stronger chemical bond. Accelerated testing showed that mixtures of fiber and coal combustion residue-based products, when activated by 20% NaOH solution, had compressive strengths equivalent to a pure portland cement control sample.

### Conclusions

During this first-year program, it was shown that Illinois coal combustion residues blended with limestone and clay or sand can be successfully used to produce blended cement products. Comprehensive testing of these products using standard cement industry methods has shown strengths meeting or exceeding ASTM performance specifications. The products also have shown an excellent potential to inhibit the expansion induced by the alkali-silica reaction in concretes. Fiberization of the products should lead to reduced grinding cost and increased end-product strength.

## OBJECTIVES

The goal of this program is to generate useful products for the construction industry from coal combustion waste materials. Melted blends of these residues will be tested for their cementitious properties, and submerged combustion melting will be evaluated as a means to produce these blends. This program is a cooperative effort between IGT, with its combustion and melting technology, and CTL, with its experience in the production and testing of cement products.

The specific objectives for the current year are to develop formulations for raw mixes of fly ash, bottom ash, and boiler slag and to prove, at a laboratory scale, that the processed formulations have the proper cementitious properties. The bulk of the experimental effort for this year is being performed by CTL. The following is a brief description, by task, of the work for the current year.

### Task 1. Background Studies and Exploration of Specific Needs

The production of cementitious materials in this study depends heavily on the specific raw materials (i.e., fly ash type, bottom ash, and boiler slag). Because each utility in the State of Illinois burns different coals, and each has a different set of operating conditions, coal residues with a wide range of compositions and properties are generated. Therefore, initial project efforts are devoted to background information collection and discussions concerning the raw materials—coal residues, limestone, clay, sand, etc.. The availability of locally available lime, or, cement kiln dust (CKD) will also be explored.

### Task 2. Material Acquisition and Characterization

Representative samples of fly ash, bottom ash, boiler slag, lime, and CKD, selected in Task 1, will be acquired from an Illinois utility burning Illinois coal, labeled, and stored. The samples will be analyzed for their chemical composition; especially for calcium, silicon, aluminum, and iron contents. Physical characteristics will be determined in order to obtain optimum blending and thermal parameters for product development.

### Task 3. Formulation of Raw Mixes

Appropriate proportions of the fly ash, bottom ash, and boiler slag, combined with limestone and possibly CKD, will be selected on the basis of their calcium, silicon, aluminum, and iron contents to determine the effect of chemistry on the thermal performance and cementitious behavior of the end product. Chemistry of the raw mixes will be confirmed using x-ray fluorescence after careful sample compositing. A number of computer-calculated, optimized raw mix designs will be formulated.

#### Task 4. Bench-Scale Production of Novel Cementitious Materials (NCMs)

The raw mix designs will be blended and ground in a ball mill to a fineness passing No. 200 mesh. The mixtures will be pressed into pellets (200 grams) using a Carver press under a pressure of 10,000 psi. The pellets will be fired in a laboratory muffle furnace at given temperatures for varying times to form melts or sinters. The firing times for each mix will be optimized by evaluating the cementitious properties. The melts will be water quenched to develop vitreous phase in the products. The amount of vitreous content will favorably determine the cementitious character of the products.

#### Task 5. Characterization of the Novel Cementitious Materials (NCMs)

To help determine their cementitious properties, the products, or Novel Cementitious Materials (NCMs), produced in Task 4 will be characterized for their physical and chemical properties using qualitative as well as quantitative tests.

#### Task 6. Development and Evaluation of NCMs-Based Blended Cements

After the characterization and pozzolanicity tests on the NCMs are completed, the most promising NCMs will be selected for bulk production and evaluation as possible candidates for use in blended Portland cements. The NCMs will be blended at 40, 60, and 80% replacement levels. The NCMs can either be ground separately to fineness close to that of the portland cements (350 m<sup>2</sup>/kg) and blended on site, or interground with cement clinker in a ball mill. The blends will then be subjected to a series of tests based on the ASTM C 1157-94 performance specifications.

#### Task 7. Paste Characterization Using CTL Test Protocol

To further evaluate the blended cements prepared from NCMs, the fresh pastes will be subjected to a number of CTL devised tests and compared with controls. These tests may include the blends' temperature variation and flow behavior, initial time of setting, compressive strength, drying shrinkage, and heat of hydration.

### INTRODUCTION AND BACKGROUND

This program is specifically targeted toward ICCI Research Priority 3.1A, "Studies Related to Utilization/Disposal of Residues from Coal Combustion, Including Pulverized Coal Combustion and Fluidized Bed Combustion." The work here is to demonstrate that Illinois coal combustion residues—fly ash, bottom ash, and boiler slag—can be used in the production of cement materials via an efficient melting process utilizing submerged combustion. The objective is to develop novel cementitious materials (NCMs), or mineral addition, from these combustion residues for use as an ingredient of blended cements or for use in ready-mix concretes. Moreover, the combustion residues would make up a significant portion of the resulting cement product.

The proposed process has the potential of converting three waste materials from the combustion of Illinois coal into useful products. In addition, since most cement kilns are coal-fired, and if cement kiln dust (CKD) is also utilized in the process, then another waste product associated with the use of coal can be converted into useful product.

### Cement Chemistry

Ordinary portland cement is produced by pulverizing clinker, the fused product of a kiln consisting essentially of hydraulic calcium compounds, with a small amount of calcium sulfate as an interground addition (ASTM C-150). Blended cements (ASTM C-595 and C-1170) may contain, besides clinker, additional cementitious materials.

Well-known binding materials, such as portland cement and blast furnace slags, consist mostly of calcium silicates and alumina-silicates. Their compositions are limited to relatively small fields in the  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  ternary diagram. However, laboratory studies at CTL have demonstrated cementitious properties of some glasses outside of these fields.<sup>1</sup> This led to the development of supplementary cementitious materials (SCMs) produced by melting and vitrification techniques from various industrial wastes as principal raw sources.<sup>2</sup> This approach may lead to the rational use of wastes and allow a reduction in the carbon dioxide emission usually associated with production of conventional portland cement.

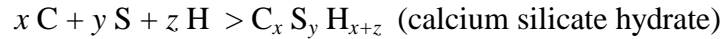
Supplementary cementitious materials for use as ingredients of blended cements or in ready-mix concretes may be subdivided into categories of pozzolanic materials and latent hydraulic cements.<sup>3</sup> ASTM<sup>4</sup> and ACI<sup>5</sup> define pozzolan as “a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties”. Portland-pozzolan cement is blended cement consisting of an intimate and uniform blend of portland cement and fine pozzolan.

Latent hydraulic cements require only certain activating agents to act as cementitious materials. Granulated blast furnace slag, for example, is activated by a basic (high pH) environment provided by hydration of portland cement minerals, thus significantly contributing to the strength of blended cements and concretes. Portland-blast furnace slag cements take advantage of this phenomenon. Concrete itself is a basic material (12.5-13 pH). Below 11.5 pH, it is susceptible to corrosion.

Hydraulic cements form the basis of modern concrete construction, and strength is their most essential property. Blended cements can be fully competitive in this respect with ordinary cements if their supplementary ingredients are of the necessary quality and blended in the proper proportions. The objective of this project was to develop materials exceeding in their cementitious value those currently used in commercial blended cements.



An important advantage of blended cements containing either pozzolans or slags, or both<sup>6</sup> is their ability to improve concrete durability. This stems from their ability to prevent or reduce reaction of alkali and alkaline-earth hydroxides present in cement, with chemically reactive silica in some concrete aggregates. With calcium hydroxide, this reaction known as the alkali-silica reaction (ASR) can be represented by the following simplified equation (in cement chemist's notation):



This reaction results in forming a gel product. In hardened concrete, this gel expands as it absorbs moisture and causes disruptive internal stresses that lead to concrete deterioration.<sup>7</sup>

The essential ingredients of mineral additions, both pozzolans and latent cements, are chemically active siliceous compounds. Since mineral additions are introduced in a finely divided form, they are able to react rapidly with alkalis before concrete setting and reduce the alkali availability for the reactions at later stages thus inhibiting future ASR in concrete structures.

Crystalline compounds in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> system are hydraulically inactive, with the exception of thermodynamically unstable calcium silicates and aluminates comprising most of cement clinker. However, many glasses in this system possess the latent cementitious properties. The quasi-liquid nature of glasses provides them with the necessary degree of thermodynamic instability which results in the enhanced hydraulic activity.<sup>8</sup> Most latent hydraulic materials and some pozzolans owe their chemical reactivity to the predominance of vitreous phase in their composition.

Glass is formed when certain melts are cooled below the melting point in the absence of nucleating agents. Under these conditions, the viscosity of supercooled liquid increases to a point where the mobility of the elements that should constitute the crystalline lattice is sufficiently restricted to hinder their orderly arrangement in the form of nuclei. This results in liquid transformation into an isotropic solid.

Certain compounds, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> are known as glass forming. When rapid quenching creates markedly non-equilibrium conditions for solidification, the corresponding cations tend to connect via oxygen ions and form a three-dimensional network of tetrahedrons or octahedrons.<sup>9</sup>

A preliminary analysis of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system outlines the area of the prospective compositions. Based on previously published studies,<sup>10</sup> there were reasons to expect that glasses in this area could be hydraulically activated by an alkali environment. It was calculated that these compositions can be realized by mixing coal combustion residues with limestone, clay, sand, and/or cement kiln dust in carefully selected proportions.

## Melting Processes for Cementitious Material Production

The basic process for the production of cementitious materials by melting mixtures of blast furnace slag or coal fly ash and limestone was developed by a Belgian cement technologist, Leon Trief.<sup>11-13</sup> The pure Trief binder process consists of four steps—mixing of raw materials, melting of the raw mix, conversion into a granulated slag, and wet crushing. The resultant slag is then mixed with 50% to 60% unprocessed ashes to form commercial grade Trief binder or alkali activated slag cement. The binder becomes hydraulically active (cementitious) when mixed with alkaline compounds such as sodium carbonate, water glass, or even portland cement.

The water glass-activated Trief cement was shown to have greater strength than ordinary portland cement.<sup>11</sup> Production of cement using the Trief process consumes less than 50% of power to run a portland cement plant, while the capital cost for the Trief process is about 33% of that for a portland cement plant.<sup>12</sup>

The melting of the raw mix occurs in two stages. The first stage consists of preheating to 1600°F (900°C) in a suspension preheater or circulating fluid bed. This stage brings about calcination (liberation of CO<sub>2</sub>, mainly from the limestone) of the raw mix. The second stage involves melting in a kiln or vat at 2550° to 2730°F (1400° to 1500°C).

Several high temperature mineral melting technologies were surveyed in order to select one most suitable for manufacturing the vitrified cementitious material. For example, cyclonic, or vortex furnaces are known to provide high efficiency of heat transfer and relatively small physical dimensions.<sup>14-15</sup> However, more detailed analysis led to the conclusion that submerged combustion melting (see Figure 1) offers economical, technical, and environmental advantages over other technologies. The submerged combustion concept has been known in the United States,<sup>16-17</sup> but never reduced to commercial practice. The Gas Institute of the Ukrainian National Academy of Sciences has developed the technology and has applied it to the commercial production of mineral wool in Ukraine and Belarus.<sup>18-19</sup> Submerged combustion melting offers advantages over cupolas, tank furnaces, and electric furnaces with such features as high thermal efficiency, the ability to handle non-homogeneous feed sized up to 3 inches, a small footprint, minimal refractory requirements, ease of start-up and shut-down, low gas-phase emissions, use of inexpensive and clean natural gas fuel, and solids recycle capacity. The Institute of Gas Technology has exclusive license for application of submerged combustion melting outside the former Soviet Union.

In submerged combustion melting (see Figure 1), fuel and oxidant are fired directly into the bath of material being melted. Bubbles are formed from the combustion gases and the CO<sub>2</sub> from calcination of certain mineral materials. The high temperature combustion inside the bubbling melt creates a complex gas-liquid system and a large heat-transfer surface. This significantly increases heat exchange between the products of combustion and the processed material. The intense mixing increases the speed of melting, the rate of chemical reactions of mineral formation, and the homogeneity of the glass melt product.

Carbon in matter such as coal bottom ash is beneficially used to reduce natural gas fuel consumption. Due to the bubbles, the resulting molten product can be made foamy. When the product melt is cooled, its porosity will make it easier to grind than products generated in kilns or other melting furnaces. Grinding costs for feed material are very low because little to no grinding of the raw matter is needed. The melt can also be fiberized to decreasing grinding costs. In the production of mineral wool, the molten product from the melter is discharged into an air fiberizer. This process enables the cooled product to be recovered as fibers with diameters below 10 mm.

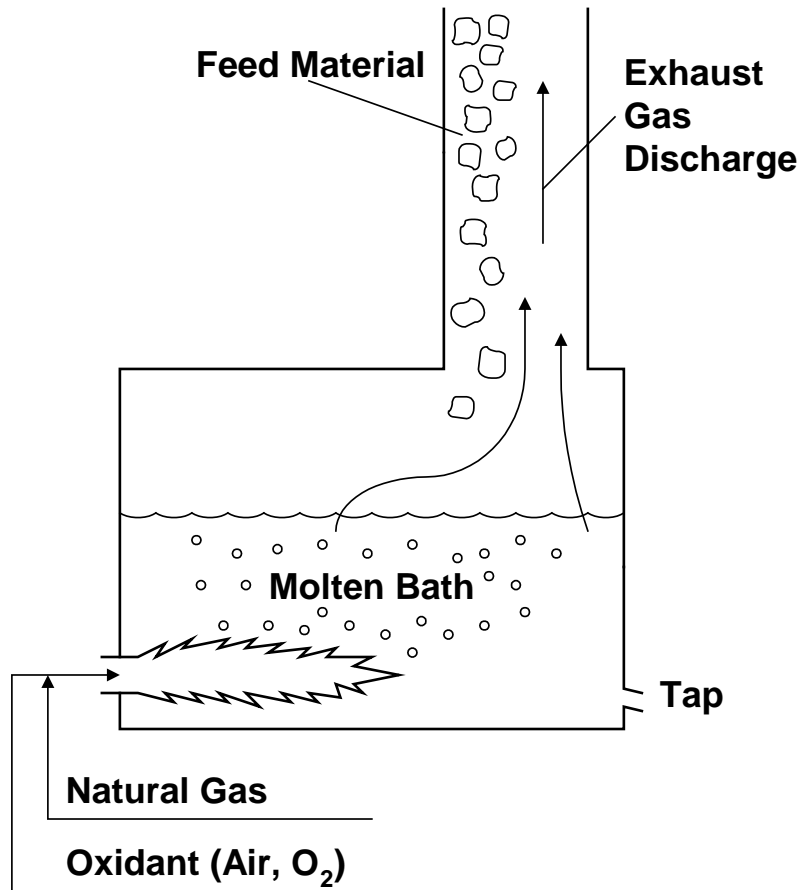


Figure 1. SUBMERGED COMBUSTION MELTING

### EXPERIMENTAL PROCEDURES

Based on typical chemical compositions of fly ash, bottom ash, and boiler slag, which largely consist of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, and CaO, a promising approach is being utilized in which controlled pyroprocessing of fly ash, bottom ash, and boiler slag blends, or any combinations of these, will be carried out to produce a range of cementitious materials for bulk consumption in blended cements. If necessary, locally available lime, or other waste product such as cement kiln dust (CKD) may also be used as a modifier to

raw feed composition. It must be pointed out that our approach will be to develop cementitious products that would potentially be used up to at least 90% by mass in blended cements, not like other pozzolans which are used only up to 25% by mass.

Based on CTL's experience of producing synthetic cements, we believe that a number of appropriate feed compositions can be prepared from Illinois coal residues including fly ash, bottom ash, and boiler slag to develop a range of cementitious products through controlled pyrotreatment at appropriate temperature levels. The target product will be vitreous (glassy) materials with enhanced cementitious properties. A minor adjustment for CaO might be necessary. This can be done either by using lime or more economically by adding locally available CKD.

During bench top studies (Phase I, current year), a laboratory scale furnace was used to produce the vitreous melts using different levels of firing temperature to optimize the peak melting conditions. Once the optimum conditions for mix-designing and firing are established, larger-scale production (Phase II, proposed for the following year) will be carried out using a submerged combustion melting furnace.

In submerged combustion melting (see Figure 1), natural gas and preheated air, enriched air, or oxygen are fired into and below the surface of a molten bath of matter. The combustion products bubble through the bath providing very effective heat transfer to the bath. The bubbles also provide increased turbulence in the bath, which promotes uniformity in composition (homogeneity). Any carbon or organic material that is in the matter is utilized, enhancing thermal efficiency. The product generated by the melter can be foamy (porous) and should prove easier to grind than kiln-generated products. In addition, the grinding requirements for the feed material are reduced in that chunk-sized, not pulverized, material can be fed into the submerged combustion melter. Since it is so energy-intensive, grinding represents a substantial portion of the cost of rotary kiln based cement production processes.

Submerged combustion melters of 2.8 to 3.3 ton/hr capacity are in commercial operation in Ukraine and Belarus. These units are used for mineral wool production. IGT has licensed the submerged combustion melting technology from its developer, the Gas Institute of the Academy of Sciences of Ukraine in Kiev, for exclusive application outside the former Soviet Union.

The program is divided into three phases. Phase I includes the preliminary feasibility work. Phase II addresses process considerations, pilot plant production, and full-scale testing and evaluation of the product. Phase III focuses on data analysis and interpretation, economic and commercialization considerations, and recommendations for additional investigation, if needed. Phase I is scheduled for the current year, while Phases II and III are proposed for the following year.

During Phase I six raw mix formulations were melted in a laboratory-scale furnace at CTL. Some suggested raw mix compositions (labeled as 1 to 6) and the corresponding

processing temperatures are shown in Figure 2. The molar ratios of acidic oxides (silica and alumina) over the basic oxide (lime) characterize the compositions as neutral (mixes 1, 3, and 5), and acidic (mixes 2, 4, and 6).

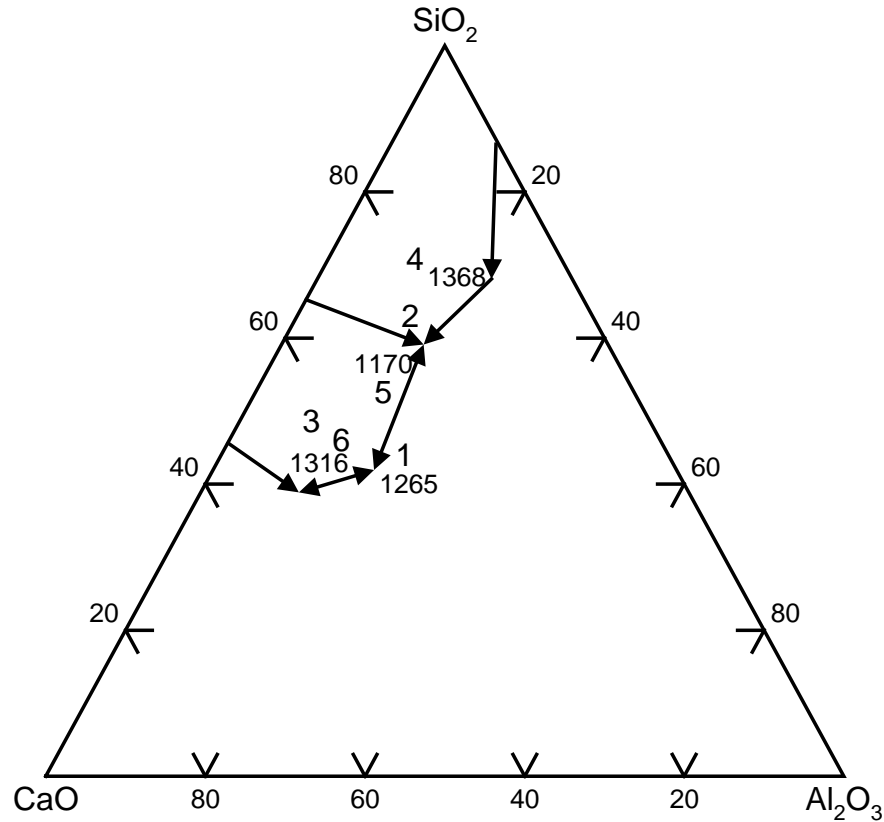


Figure 2. SUGGESTED RAW-MIX FORMULATIONS 1 TO 6 SHOWN ON THE CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> DIAGRAM, SHOWING EUTECTIC TEMPERATURES FOR PRODUCING NOVEL CEMENTITIOUS MATERIALS (Temperatures in °C)

To help determine their cementitious properties, the products (NCMs) were to be characterized for their physical and chemical properties using the following qualitative as well as quantitative tests:

**X-Ray Diffraction:** The x-ray diffraction (XRD) technique will give a quick check on the quality of NCMs by providing information on the major phases present. The technique will also determine the mineralogy, crystallinity, and the vitreous phase distribution in the NCMs. It is the vitreous content of the NCMs that will favorably reflect on their cementitious properties. This information will also help readjust raw mix formulation accordingly.

X-Ray Florescence Analysis: Additional analyses by XRF techniques will be used to determine elemental and oxides analyses. This will also provide quantitative analysis for oxides of interest, loss on ignition, and alkalis as  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  equivalent. Insoluble residue will also be determined using a separate test.

Optical Microscopy: The NCMs will be studied for major phase distribution using a polished section under a reflected optical microscope. Distribution of vitreous phase, crystal formation, size, and distribution will be determined to estimate the effects on their cementitious properties.

Grindability Index: In order to see the effect on the grindability, the NCM specimens will also be tested for a CTL designed grindability index. The data/results will be compared with that of portland cement clinker specimen to see any advantageous effects. A low grindability index suggests a soft product requiring less grinding energy.

Pozzolanic Activity Test: The NCMs will be crushed and ground to suitable fineness, and subjected to a pozzolanic activity test to verify their cementitious properties. This test involves compression strength of pastes and mortar cubes prepared from mixtures of the melts with known amounts of cement and lime. The results are expressed as a percentage of the strength of control samples (without the NCMs) prepared under identical conditions. A pozzolanic index of close to 100 suggests comparable cementitious properties.

The most promising blends were to be selected for bulk production and evaluation as possible candidates for use in Portland blended cements. The blends were then to be subjected to the following series of tests based on the ASTM C-1157-94 performance specifications:

ASTM C-1073 Hydraulic Activity By Reaction With Alkali: For this test, mortar is prepared from a hydraulically active material and sand in a 1:2.75 proportion and mixed with 20% NaOH solution. Hydraulically active materials are those that can react with water to gain strength. Standard 2-in mortar cubes are tested for compressive strength after 24-hr curing at 55°C (131°F) and 100% humidity. This test method is normally used only for evaluation of the hydraulic activity of slags and similar materials from different sources.

ASTM C-109 Compressive Strength: This method will measure the compressive strength of 2" mortar cubes made from the NCMs-blended cements. The specimens will be cured in lime solution and tested at 3, 7,

28 days. The results will be compared to control cement samples without ash addition to evaluate strength development.

ASTM C-441 ASR Expansion: In the presence of moisture, concrete can expand due to the alkali-silica reaction (ASR). Low-alkali (<0.6%) cement is specified to be used in concretes for locations with high moisture exposure. ASR is a problem in certain areas, particularly western states, where siliceous stone is used as the aggregate in the concrete. In this test, ASR-induced expansion of 10-inch mortar bars containing high-alkali cement and reactive siliceous aggregate is measured.

To further evaluate the blends, a number of CTL devised tests may be utilized. Pastes from each blend can be prepared using a 0.5 water-to-cement (w/c) ratio at a controlled shear rate using a Waring Blender. The pastes can be tested for temperature variation and flow behavior using mini-cone slump tests over the first 45 minutes to identify abnormal setting or early stiffening. Initial time of setting of the pastes can be determined using the modified Vicat test method. Compressive strength of 1-inch paste cubes can be measured at 3, 7, 28 days curing. Drying shrinkage of paste strips can be determined to identify any measurable effect of fly ash on clinker/cement formulation. Separate tests to determine heat of hydration of the pastes can be carried out using conduction calorimetry.

## RESULTS AND DISCUSSION

### Task 1. Background Studies and Exploration of Specific Needs

IGT and CTL met to discuss the specific materials to be investigated during this program. Coal fly ash is well known for its pozzolanic properties and already has a market for direct use in concrete. Bottom ash and boiler slag are most usefully utilized as aggregates. Therefore, it was decided that it would be fruitful to investigate the use of bottom ash and boiler slag, as well as fly ash. To convert these materials into a composition more like cement raw mix, a lime source is needed. Limestone is a locally available source. Another source of lime is cement kiln dust (CKD), a waste product from cement manufacture. Being a waste product, CKD has a low cost, and its use would benefit the cement industry as far as disposal is concerned. With the suggestion of ICCI, the Baldwin Power Plant in Baldwin, IL, which fires Illinois bituminous-type coal, was chosen to supply the fly ash, bottom ash, and boiler slag. The Baldwin plant generates a high-quality class F fly ash.

### Task 2. Material Acquisition and Characterization

Samples of bottom ash, fly ash, and boiler slag were requested from the Baldwin Power Plant. Upon receipt of 15 gallons (40-160 lb) of each of these materials, analyses by the x-ray fluorescence method for composition were performed (see Table 1).

Table 1. COMPOSITION OF SOURCE MATERIALS  
BY WEIGHT PERCENTAGE

Compound	Bottom ash	Fly ash	Boiler slag
SiO <sub>2</sub>	48.94	52.56	53.92
Al <sub>2</sub> O <sub>3</sub>	18.33	19.52	20.44
Fe <sub>2</sub> O <sub>3</sub>	20.76	15.37	15.75
CaO	6.43	5.06	6.32
MgO	1.03	1.10	1.09
SO <sub>3</sub>	0.07	0.78	0.06
Na <sub>2</sub> O	0.72	1.04	0.63
K <sub>2</sub> O	2.00	2.38	1.97
LOI (Loss on ignition)	0.22	1.29	0.00

Based on theoretical considerations regarding cementitious properties of vitreous phases in the quaternary system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-CaO, a prospective field of compositions was outlined. Two blends (raw mix formulations) of approximately identical chemical composition were designed for preliminary testing. These mixes were based on using fly ash with one additional material (see Table 2).

Table 2. RAW MIX FORMULATIONS BY WEIGHT PERCENTAGE

Sample ID	Fly ash	Limestone	CKD
75L	67.0	33.0	--
65D	56.0	--	44.0

Natural high-grade limestone and cement kiln dust (CKD) were considered at this point as possible additional materials. At this point in the program only fly ash was considered. The boiler slag has a very similar composition to the fly ash. Use of it was expected to be just be a duplication of the effort of using fly ash. Use of bottom ash was be considered later in the program.

Mixes were prepared by blending and grinding to a fineness of 140 mesh (105 μm). Each ready mix was placed in Inconel 601 crucibles, melted at 1200°C, and quenched in water. The resulting products were practically fully vitrified. The actual chemical compositions of the product samples as determined by X-ray fluorescence (XRF) are given in Table 3.



Table 3. CHEMICAL COMPOSITION OF PRODUCT SAMPLES  
BY WEIGHT PERCENTAGE

Sample ID	65D	75L
SiO <sub>2</sub>	40.79	40.47
Al <sub>2</sub> O <sub>3</sub>	15.06	15.31
Fe <sub>2</sub> O <sub>3</sub>	11.54	11.63
CaO	23.44	24.68
MgO	1.34	1.16
SO <sub>3</sub>	0.16	0.30
Na <sub>2</sub> O	1.27	0.90
K <sub>2</sub> O	4.26	1.83

Cementitious properties of these glassy products were evaluated by compression testing of 1-inch cube specimens (see Table 4). The specimens were formed out of cement paste where a certain percentage of the cement paste is displaced by one of the glasses. The glasses were ground to a specific surface area of about 360 m<sup>2</sup>/kg before mixing with the cement paste. The specimens were cured for 24 hours at 55°C and 100% relative humidity.

Table 4. COMPONENTS IN AND STRENGTH OF TEST SPECIMENS

Sample ID	Cement Paste, g	Sample Product, g	Water, g	Compressive Strength, psi	Compressive Strength, % of control
Control	200	--	80	7270	100
65D	150	50	80	6500	89
75L	150	50	80	6100	84

The results were satisfactory for the initial phase of the investigation. For comparison, similar (pozzolanic) materials in standard concrete practice are required to have a compressive strength of at least 75% of that of the control. Note that though this test is not a standard method used by the cement industry, it is a quick test that establishes whether a composition is worth investigating further. All the test specimens would likely strengthen further after the longer curing periods used in the standard methods.

### Task 3. Formulation of Raw Mixes

Proper chemical composition of the products is essential for the technical and economic feasibility of the process. Fundamental studies of hydration of silicate glasses quoted earlier outlined the area of the most active compositions and to a large extent clarified the hydration mechanism. In this project, composition of the prospective products was subject to some additional conditions. It was defined based on the following criteria:

- adequate cementitious characteristics: strength and ASR-reduction potential;
- efficiency of waste management: sufficiently high content of waste material in the raw mix;
- energy-efficient technology: low melting temperature and low power requirements for raw mix preparation and for product grinding.

The original area of compositions was selected by analysis of the phase equilibriums in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (see Figure 3). It appeared feasible to select the compositions that would melt at temperatures under 1250°C (2280°F). Based on theoretical considerations, it was suggested that glasses in this area could be hydraulically active. On the other hand, if the material was to be used as an ASR-preventing mineral addition, it should contain an adequate amount of active silica. This places the target composition field away from the largely basic area of portland cement clinkers and closer to the area of fly ashes. It has been calculated that these compositions can be realized by mixing coal ash with reasonable amounts of additional ingredients (in carefully selected proportions).

Experimental mix formulations were designed (see Table 5) to cover the entire prospective area of compositions. In Mixes 1 (1B and 1F) and 2 (2B and 2F), the proportions of three major oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO) are equal to those at eutectic points on the ternary phase diagram (see Figure 3) at 1265°C and 1170°C. Mix 3 (3B and 3F) composition is approximately half way between 1 and 2, in an area of higher melting temperature. The molar ratios of acidic oxides (silica and alumina) over the basic oxide (lime) are 1.4, 2.8, and 2.0, respectively.

### Task 4. Bench-Scale Production of Novel Cementitious Materials (NCMs)

Each of the mixes described in Table 5 was melted in an Inconel 601 crucible in an electric muffle furnace and quenched in water. The resultant products (NCMs) were ground in a laboratory mill to the fineness characterized by the Blaine specific surface area of about 360 m<sup>2</sup>/kg, which is typical for portland cements.

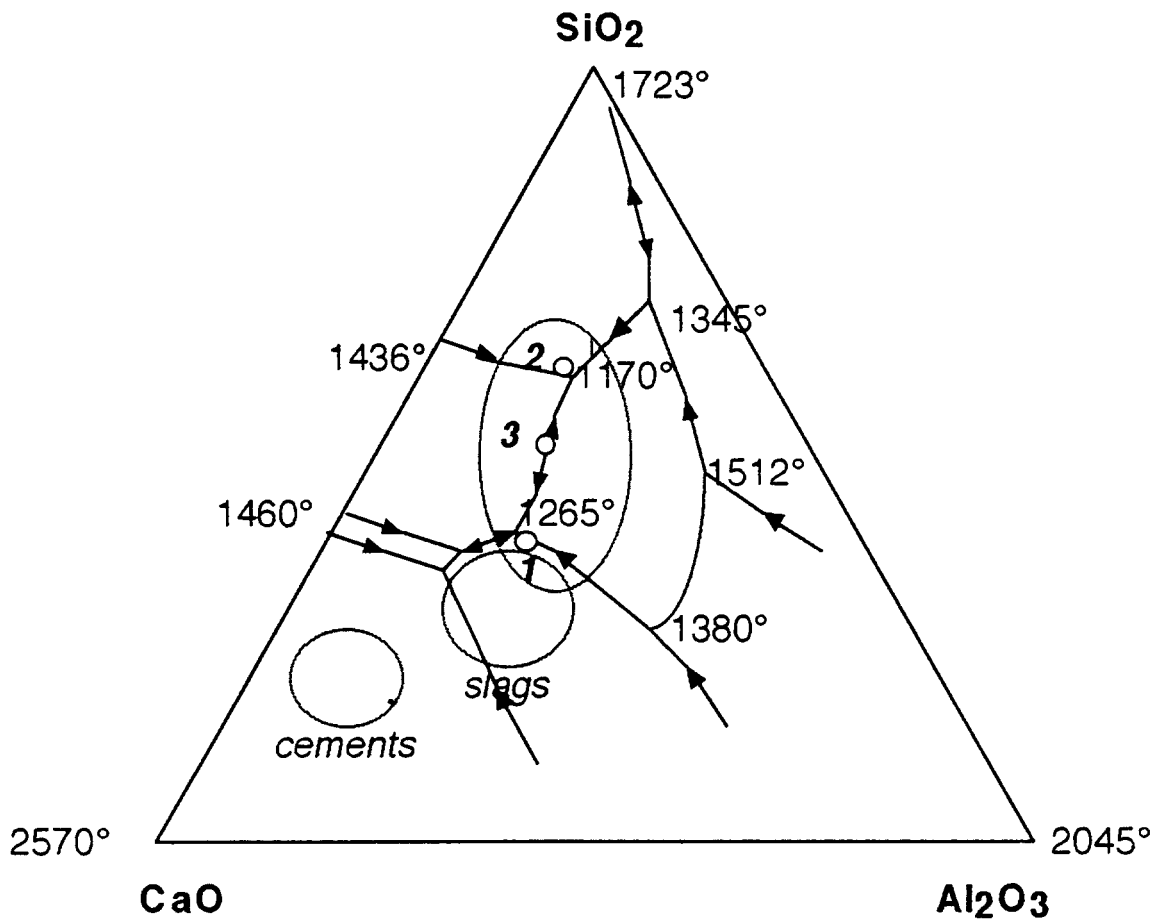


Figure 3. RAW-MIX FORMULATIONS 1 TO 3 SHOWN ON CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> DIAGRAM, SHOWING COMPARISON WITH TYPICAL SLAG AND CEMENT COMPOSITIONS  
(Temperatures in °C)

Table 5. RAW MIX COMPOSITIONS BY WEIGHT PERCENTAGE

Mix	Bottom ash	Fly ash	Limestone	Clay	Sand
1B	54	--	33	13	--
2B	58	--	19	--	23
3B	68	--	24	--	8
1F	--	52	34	14	--
2F	--	57	20	--	23
3F	--	67	26	--	7

### Task 5. Characterization of the Novel Cementitious Materials (NCMs)

The products generated in Task 4 were examined by polarized light microscopy. All products were confirmed as fully vitrified. To evaluate the hydraulic reactivity of cementitious materials, a number of chemical methods have been used based mainly on certain calculated or measured chemical properties of the materials.<sup>20</sup> Based upon the Task 2 results, however, a decision was made to proceed with more direct determination of reactivity by physical testing of paste and mortar cubes prepared from mixtures of the products with cement.

### Task 6. Development and Evaluation of NCMs-Based Blended Cements

In Task 2, an accelerated compressive strength testing method was used. One-inch paste cubes were prepared from the blends of cement with the manufactured material in the proportion of 75:25 and cured for 24 hours at 55°C (131°F) and 100% humidity. The test results were expressed as a percentage of the strength of control samples cured under the same conditions.

Products generated in Task 4 were used in pastes and mortars which were subjected to a series of standard tests applied usually to blended cements and their ingredients. Pastes are mixtures of cement and water. Mortars are mixtures of cement and sand.

#### Hydraulic Activity By Reaction With Alkali (ASTM C 1073)

For this test, mortar is prepared from a hydraulically active material and sand in a 1:2.75 proportion and mixed with 20% NaOH solution. Hydraulically active materials are those that can react with water to gain strength. Standard 2-in cubes made from the products were tested for compressive strength after 24-hr curing at 55°C (131°F) and 100% humidity. Compressive testing results are given in Table 6.

Table 6. HYDRAULIC ACTIVITY WITH ALKALI

Mix	1F	1B	2F	2B	3F	3B
Compressive strength, psi	2820	2320	1200	1170	1760	1825

This test method is normally used only for evaluation of the hydraulic activity of slags and similar materials from different sources. As a point of reference it can be noted that these cementless compositions showed compressive strength comparable to standard (ASTM C 91) mortar cements at a 28-day age (900, 2100, and 2900 psi for different types).

Compressive Strength of Hydraulic Cement Mortars (ASTM C 109)

For this test, blended cements were prepared containing 75% portland cement clinker and 25% glasses. Characteristics of such cements should conform to the ASTM C 117 “Standard Performance Specification for Blended Hydraulic Cement”. Mortar was prepared from cement and sand in the 1:2.75 proportion and mixed with water (0.484 parts per part of cement). Standard 2-in cubes were cast from the mortar and cured under controlled conditions for up to 28 days. The results are given in Table 7, along with the requirements of C 117 performance specification. In addition, Figures 4 and 5 demonstrate the test results separately for the products based on fly ash and bottom ash.

The results of physical testing indicate that glasses with higher basicity (lower (S+A)/C ((silica+alumina)/lime) ratio) tend to have higher strength. The bottom ash-based products appear to produce better results but, to confirm it, additional testing is required.

Table 7. COMPRESSIVE STRENGTH OF STANDARD  
(C 109) MORTAR CUBES IN psi

Age, days	Mix 1F	Mix 1B	Mix 2F	Mix 2B	Mix 3F	Mix 3B	Control Sample	Required Strength
1	860	880	810	780	760	810	1230	--
3	2130	2240	2040	2050	1940	2010	3090	1740
7	2910	3090	2910	2740	2690	2790	4230	2900
28	4990	5220	4220	4680	4440	4420	5550	4060

ASR Expansion Reduction

In the current quarter, ASR expansion tests were completed. In the presence of moisture, concrete can expand due to the alkali-silica reaction (ASR). Low-alkali (<0.6%) cement is specified to be used in concretes for locations with high moisture exposure. In Illinois, ASR is not a serious problem because limestone is the aggregate typically used in concrete. In other areas, particularly western states, siliceous stone is used as the aggregate. There, ASR is a problem.

A further possible benefit of using coal combustion residue-based cements would be the ability to inhibit ASR-induced expansion. The potential of the products to inhibit the ASR in concrete was evaluated using the ASTM C 441 test. In this test, ASR-induced expansion of 10-inch mortar bars containing high-alkali cement and reactive siliceous aggregate is measured. Table 8 summarizes the ASR expansion test results.

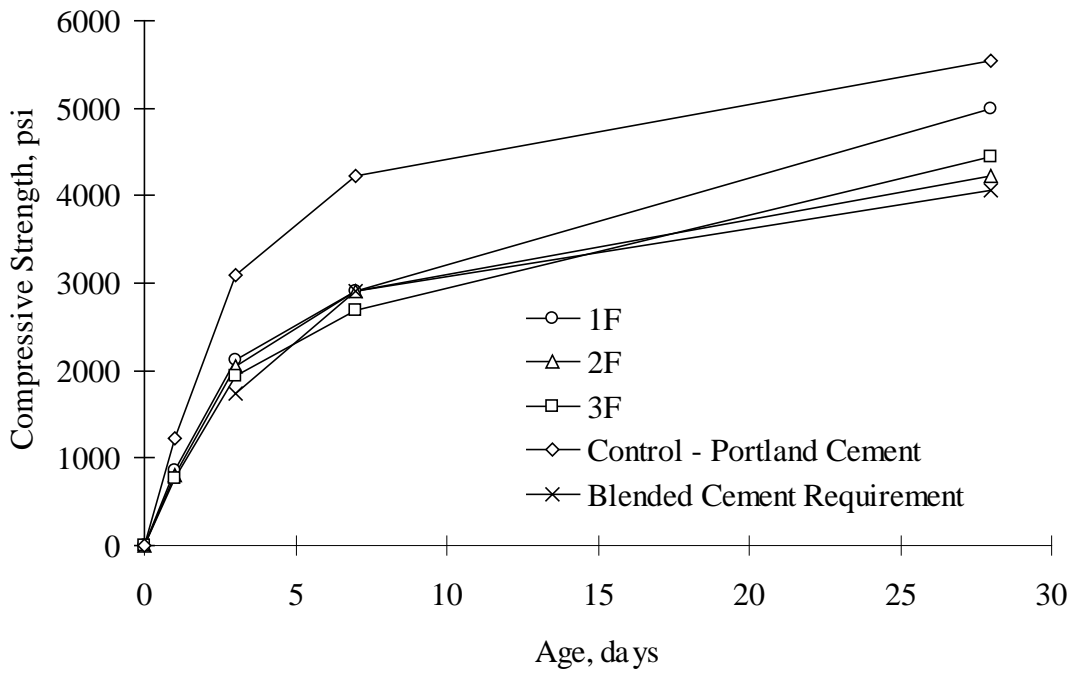


Figure 4. STRENGTH OF BLENDED CEMENTS WITH FLY ASH-BASED INGREDIENTS

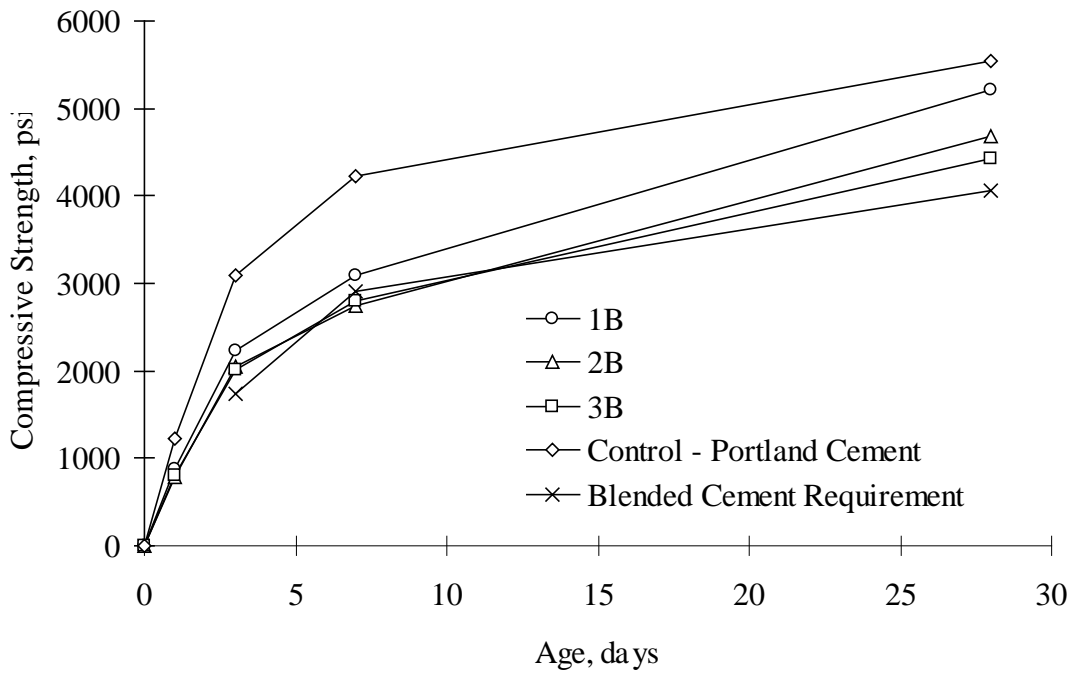


Figure 5. STRENGTH OF BLENDED CEMENTS WITH BOTTOM ASH-BASED INGREDIENTS

Table 8. REDUCTION OF ASR EXPANSION BY ADDING  
COMBUSTION RESIDUE-BASED PRODUCTS

Mix	1F	1B	2F	2B	3F	3B
Reduction, %	85	87	93	97	87	86

The best results were produced with the more acidic glass compositions (2B and 2F), although the least acidic samples (1B and 1F) were better than most commercial pozzolans. These results show that coal combustion residue-based products have an excellent potential as ASR-preventing additions in concretes.

#### Task 7. Paste Characterization Using CTL Test Protocol

The prospective commercial submerged combustion melter is likely to utilize a quenching technique based on dispersing the liquid melt by a jet stream of air or rotating metal cylinder. In either case, the final product would form a fiberized mass similar to mineral wool. While an actual commercial or demonstration melter is not available, mineral wool produced from blast furnace slag can be used for a preliminary investigation of some aspects of the future technology.

In this task of the project, a surrogate commercial mineral wool, produced by a conventional process, was used. Chemical analysis revealed that its composition was reasonably close to that of the prospective melts although it did not necessarily meet the optimum requirements described in the previous sections. Microscopic examination confirmed that the material consisted of completely vitrified fibers 7 to 10  $\mu\text{m}$  in diameter.

Experimental study of mineral fibers proceeded in two directions-intergrinding fibers in blended cements and fibers in fiber-reinforced composites.

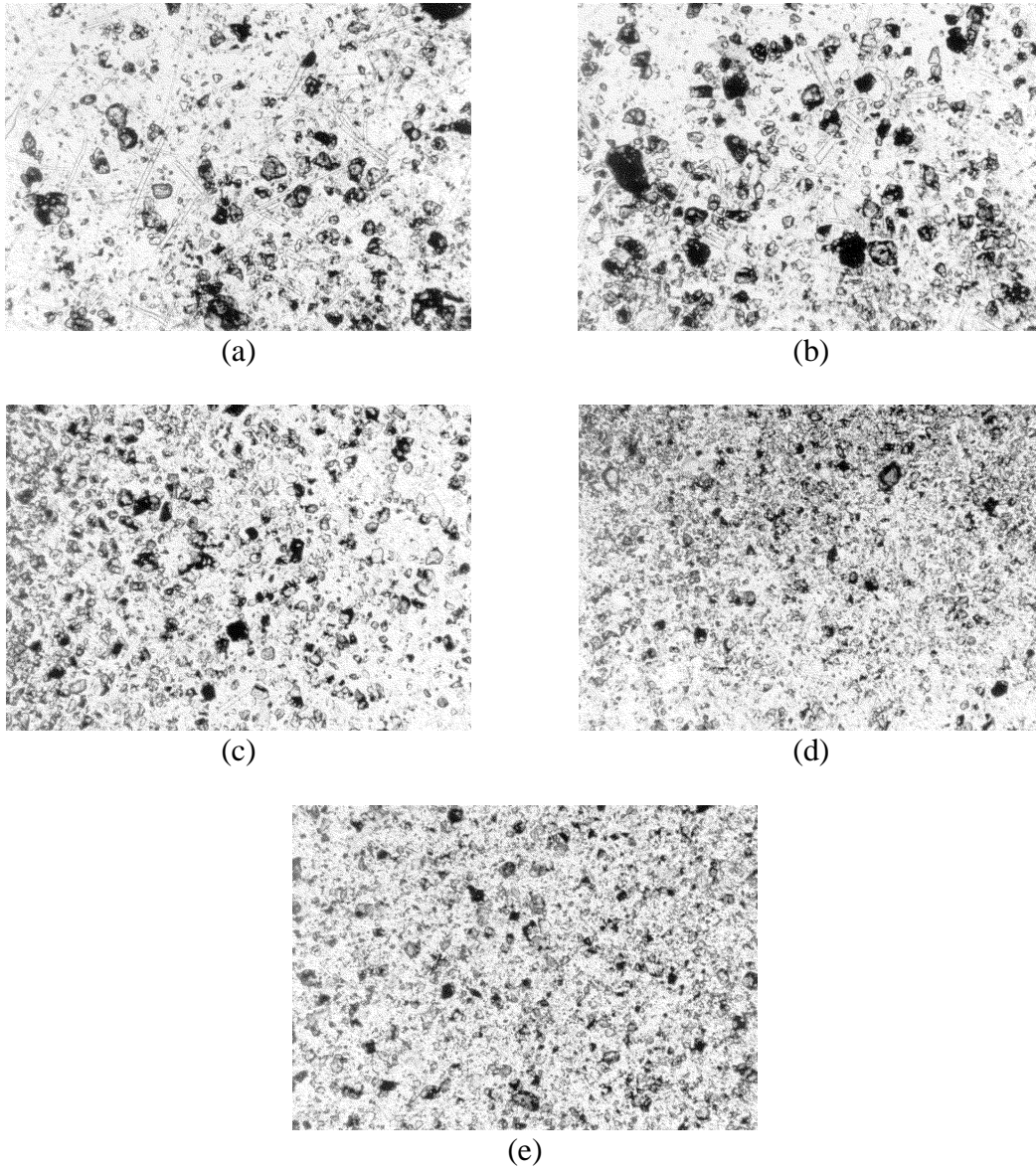
#### Intergrinding Fibers in Blended Cements

Usually, slag-like glasses prepared by water-quenching the melts are much harder to grind than portland cement clinker. This leads to non-uniformity of particle sizes in blended cements. It could be expected that fibers will be advantageous in this respect. Grindability of fibers in blended cement mixes was studied by preparing a 75:25 mix of clinker and fibers and grinding it in a jar mill. Fineness as characterized by Blaine specific surface was determined at several points during grinding (see Table 9).

Photomicrographs (see Figure 6) taken in 20-min increments demonstrate the gradual shortening of fibers, along with comminution of the clinker particles.

Table 9. FINENESS OF FIBER-CLINKER BLENDED CEMENTS

Grinding time, min	20	40	60	90	120
Specific surface, m <sup>2</sup> /kg	103	172	227	310	369

Figure 6. PHOTOMICROGRAPHS OF FIBER-CLINKER BLENDED CEMENTS  
TAKEN AT 20-min INTERVALS



One-inch paste cubes were prepared from cement produced in the grinding test and cured under controlled conditions according to the C 109 protocol. The compression test results are shown in Table 10 and Figure 7.

In evaluation of these results, it should be kept in mind that the chemical composition of the fibers differed from the suggested optimum composition. Nevertheless, the test results exceeded significantly the C 1157 performance specifications for blended cements.

Table 10. COMPRESSIVE STRENGTH OF FIBER-CLINKER CEMENT PASTE CUBES, PSI

Sample	1 day	3 days	7 days	28 days
Test	600	2250	2900	5500
Control	950	3000	4300	7150

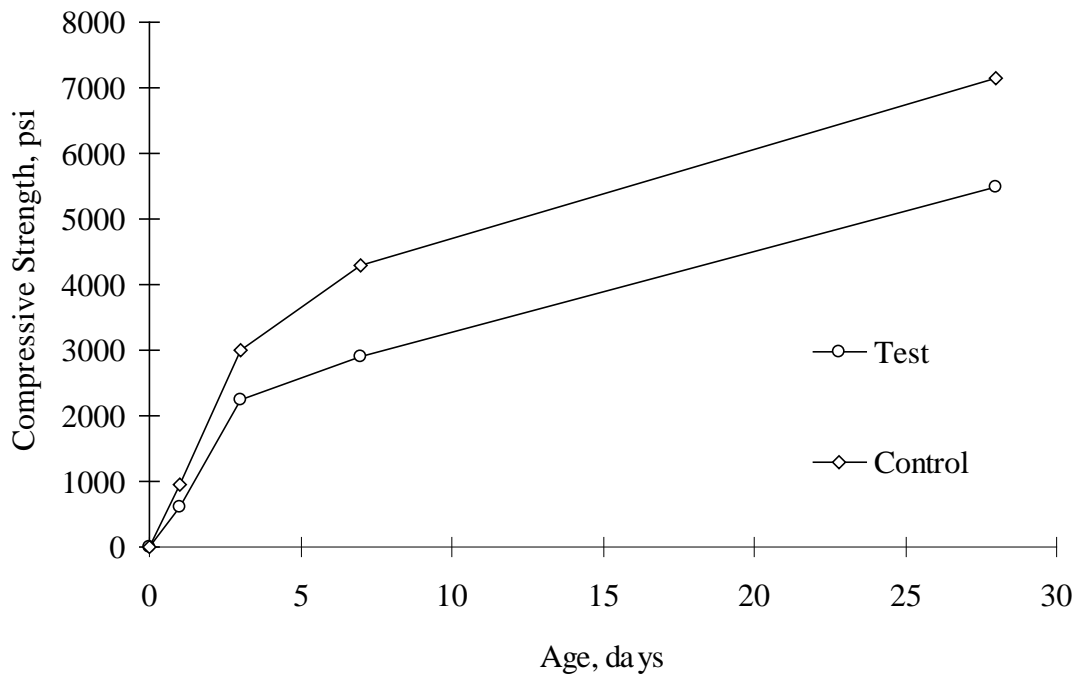


Figure 7. COMPRESSIVE STRENGTH OF FIBER-CLINKER CEMENT PASTE CUBES

### Fibers in Fiber-Reinforced Composites

Although the prime objective of fiberization is rapid quenching of melt and facilitation of subsequent grinding, there are reasons to expect that the fiberized material added to mortars and concretes would increase their tensile and flexural strength, as well as control drying shrinkage and cracking. Unlike polymer fibers in fiber-reinforced concrete, this fiberized mineral material would react with cement paste providing for stronger chemical bonding. Physical testing established that mineral fibers were sufficiently reactive when activated by alkaline solutions or cement paste.

After several trials, two types of mixes were produced. The first series consisted of cements with 4 to 10% fibers (by weight) added and a water/solid ratio close of 0.5. The mixes were based on portland cement and clinkerless compositions with vitrified products 1F and 3B (see above) activated by 20% NaOH solution. These mixes were suitable for casting paste specimens for determination of flexural and compressive strength (prisms and cubes). The specimens were subjected to accelerated curing at 55°C and 100% humidity. Tables 11 and 12 show the best results produced with this type of mixes.

Table 11. COMPOSITION AND PHYSICAL TESTS  
OF CEMENT-BASED SPECIMENS

Sample ID	Fibers g	Water g	Portland cement g	Compr. Strength, psi	Rupture Modulus, psi
Control		200	400	3930	490
Test	32	200	400	4150	550

Table 12. COMPOSITION AND PHYSICAL TESTS  
OF NCM-BASED SPECIMENS

Sample ID	Fibers g	NaOH 20% g	NCM g	Compr. Strength, psi	Rupture Modulus, psi
1F	40	200	360	4050	400
3B	40	200	360	3910	370

Another series of mixes was produced with fiber/cement ratios from 1:1 to 2:1. To produce workable mixes, the water/solid ratios were kept in the range from 1:1 to 4:1 (see Table 13). Specimens from these mixes were made by vacuum filtration.

Table 13. HIGH-FIBER CEMENT-BASED COMPOSITES

Fibers	Water	Cement
g	g	g
25	200	175
45	300	45
50	300	25

Using this approach, it was possible to manufacture composites potentially usable as insulating material or in some special applications. Although no standard strength tests have been done on these composites, the preliminary evaluation seems to indicate that an interesting class of new materials may be produced from the fiberized melts.

The results from this stage of the project demonstrated that vitrified and fiberized products from Illinois coal combustion residues can be used as energy efficient (requiring no pre-grinding) constituents of blended cements and as an ingredient of fiber-reinforced composites.

### CONCLUSIONS AND RECOMMENDATIONS

During this first-year program, it was shown that Illinois coal combustion residues blended with inexpensive waste or raw materials (limestone and clay or sand) can be successfully used to produce NCMs or blended cement products. Formulations were developed to produce vitreous NCMs at low melting temperatures. Comprehensive testing of these products using standard cement industry methods has shown strengths meeting or exceeding ASTM performance specifications. The products also have shown an excellent potential to inhibit the expansion induced by the alkali-silica reaction in concretes. Fiberization of the products should lead to reduced grinding effort and increased end-product strength. The products are suitable for use as an ingredient of both blended cements and ready-mix concretes. The use of the products in blended cements reduces clinker consumption for cement production and, therefore, offers certain economic advantages for prospective consumers.

Future experimental work should concentrate on development of the NCM production process and evaluation of the performance of concrete containing the products. Optimized chemical compositions should be finalized based on a combination of requirements for material strength characteristics, including ASR reduction potential; economically justified proportions of the raw mixes; and economical melting temperatures. Another important question is the optimum fineness of the material. The strength characteristics reported above can be certainly improved by additional grinding. The next project phase requires pilot-scale melting and production using the submerged combustion melter. Future work should also focus on economic analysis and engineering for commercial-scale plants and on commercialization activities.

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