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


DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/3.1A-13M
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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 only about 30% of the 5 million tons of these coal combustion residues generated in Illinois each year are utilized, mainly as aggregate. These residues are composed largely of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, MgO, and 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. Therefore, a much larger amount of residues can be utilized.

To achieve the above objective, in the first phase (current year) samples of coal combustion residues will be blended and mixed, as needed, with lime or cement kiln dust (CKD) to adjust the CaO composition. Six mixtures will be melted in a laboratory-scale furnace at CTL. The resulting products will then be tested for cementitious properties.

Two preliminary blends have been tested. One blend used fly ash with limestone, while the other used fly ash with 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 compression 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 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.

## 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 in the forms of fly ash, bottom ash, and boiler slag. Over 5 million tons of these coal combustion residues are generated every year. Generally, about 25% of the fly ash, 40% of the bottom ash, and 60% of the boiler slag is consumed, mostly in cement, concrete, and structural fills, leaving about 70% of the residues stockpiled in the nearby landfills.

In the State of Illinois, the bulk of these residues remain 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. Currently only about 30% of the 5 million tons of these coal combustion residues are utilized. These residues are composed largely of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, MgO, and CaO, which are also the major components of cement. Success of this project 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 will be blended and mixed, as needed, with lime or cement kiln dust (CKD) to adjust the CaO composition. Six mixtures will be melted in a laboratory-scale furnace at CTL. The resulting products or novel cementitious materials (NCMs) will then be tested for their cementitious properties. These tests include x-ray diffraction, x-ray fluorescence, optical microscopy, grindability index, and pozzolanic activity. After testing, the NCMs will be blended at various levels with portland cement and subjected to a series of ASTM tests including compressive strength, autoclave expansion, air content, and time of setting. The blends will also be subjected to CTL-devised tests for temperature, abnormal setting/early stiffening, initial time of setting, compressive strength, drying shrinkage, and heat of hydration.

Once optimal mixing and melting conditions are established, the second phase will be used to generate larger quantities (5-10 kg) of NCMs. The three best raw mix formulations as determined in the first phase will be utilized. A bench-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, compact size, and a foamy product that should be easy to grind. Since it is so energy-intensive, grinding represents 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 Byelorus 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 of Ukraine, Russia, and Byelorus. Other applications for the submerged combustion melter include ash vitrification, glass melting, scrap melting, and direct waste processing.

The third phase focuses on data analysis and interpretation, economic and commercialization considerations, and reporting with conclusions and recommendations.

The first phase is scheduled for the first year of the program, while the second and third phases are proposed for the second year. CTL, as a subcontractor, will perform 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 Conclusions

Samples of bottom ash, fly ash, and boiler slag were requested from the Baldwin Power Plant. The Baldwin Power Plant fires Illinois bituminous-type coal and generates a high-quality class F fly ash. Upon receipt of 15 gallons (40-160 lb) of each of these materials, analyses by the x-ray fluorescence method for composition were performed.

Based on the theoretical considerations regarding cementitious properties of vitreous phases in the quaternary system $SiO_2$-$Al_2O_3$-$Fe_2O_3$-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. One mix (75L) was composed of 67% fly ash and 33% limestone, while the other mix (65D) was composed of 56% fly ash and 44% CKD.

Natural high-grade limestone and cement kiln dust (CKD) were considered at this point as the possible additional materials. CKD is a waste product of cement manufacturing and is a low-cost material with a suitable chemical composition. At this point in the program only fly ash has been considered. The boiler slag has a very similar composition to the fly ash. Use of it would just be a duplication of the effort of using fly ash. Use of bottom ash will be considered in the next quarter.

The 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 product samples were practically fully vitrified.

Cementitious properties of the product samples were evaluated by compression testing of 1-inch cube specimens (see table below). 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 sample products were ground to a specific surface of 340 $m^2/kg$ before mixing with the cement paste. The specimens were cured for 24 hours at 55°C and 100% relative humidity.

COMPONENTS IN AND STRENGTH OF TEST SPECIMENS

| Sample Product 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 appeared to be 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.

For the next phase of testing, six raw mix formulations will be prepared covering a larger portion of the target field of compositions. All of these formulations will be evaluated for cementitious properties using ASTM C-1157-94 performance tests and other specialty tests.

# OBJECTIVES

The goal of this program is to utilize residues from coal combustion in a manner such that useful products for the construction industry are generated from these waste materials. The scope of this program is to test melted blends of these residues for their cementitious properties and to evaluate the use of submerged combustion melting to produce these blends. This program is a cooperative effort between IGT, with its combustion and melting technology, and CTL, with its experience in 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 of the tasks for the current year.

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

Because each utility in the State of Illinois burns different coals, and each has a different set of operating conditions to work with, the study will heavily depend on the specific materials (i.e., fly ash type, bottom ash, and boiler slag) being generated in Illinois. The initial efforts will therefore be devoted to background information collection and discussions concerning the raw materials. The availability of locally available lime, or, 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, along with their physical characteristics in order to determine 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 and blended with the respective materials.

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 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 $m^2/kg$) 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 will evaluate 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. 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, 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.

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.[1-3] 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%-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.[1] 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.[2]

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 $CO_2$, mainly from the limestone) at the raw mix. The second stage involves melting in a kiln or vat at 2550°-2730°F (1400°-1500°C). Submerged combustion melting[4] is ideally suited for the efficient melting and calcination of mineral solids at temperatures required by the Trief process. In submerged combustion melting (see Figure 1), natural gas and preheated air or oxygen are fired directly into the bath of matter being melted. The bubbles formed from the combustion gases transfer heat to the bath. In addition, the turbulence provided by the bubbles promotes uniformity of composition within the bath. If a preheater/precalciner is not used, then $CO_2$ bubbles from calcination enhance the turbulence. 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 is foamy. When the product is cooled, its porosity will make it easier to grind than products generated by kilns or other melting technologies. Also, very little to no grinding of the raw matter is needed.

Submerged combustion melters are in commercial operation in Ukraine and Byelorus for mineral wool production. IGT has exclusive license of application of submerged combustion melting outside of Ukraine, Byelorus, and Russia.

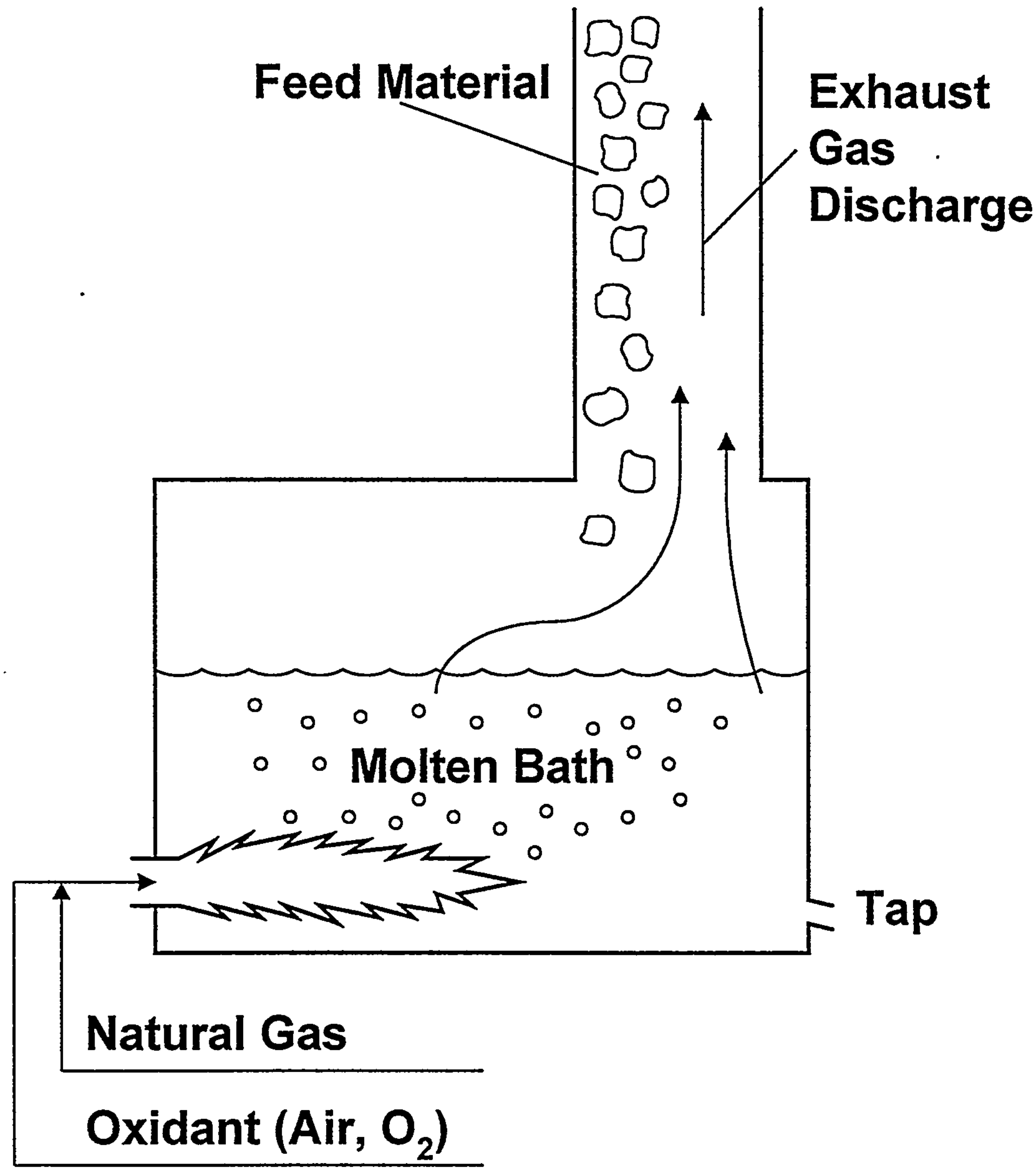


Figure 1. SUBMERGED COMBUSTION MELTING

# EXPERIMENTAL PROCEDURES

## Research Approach

Based on typical chemical compositions of the fly ash, bottom ash, and boiler slag, which largely consist of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, 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 the fly ash, bottom ash, and boiler slag from the Illinois coal residues 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 will be 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) within the bath. Any carbon or organic material that is in the matter is utilized, enhancing thermal efficiency. The product generated by the melter is foamy (porous) and should prove easier to grind than kiln-generated products. In addition, the grinding requirements for the feed material are also 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 producing cement in rotary kilns.

Submerged combustion melters of 2.8 to 3.3 ton/hr capacity are in commercial operation in Ukraine and Byelorus. 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 of Ukraine, Russia, and Byelorus.

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 will be 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 basic one (lime) characterize the compositions as neutral (mixes 1, 3, and 5), and acidic (mixes 2, 4, and 6).

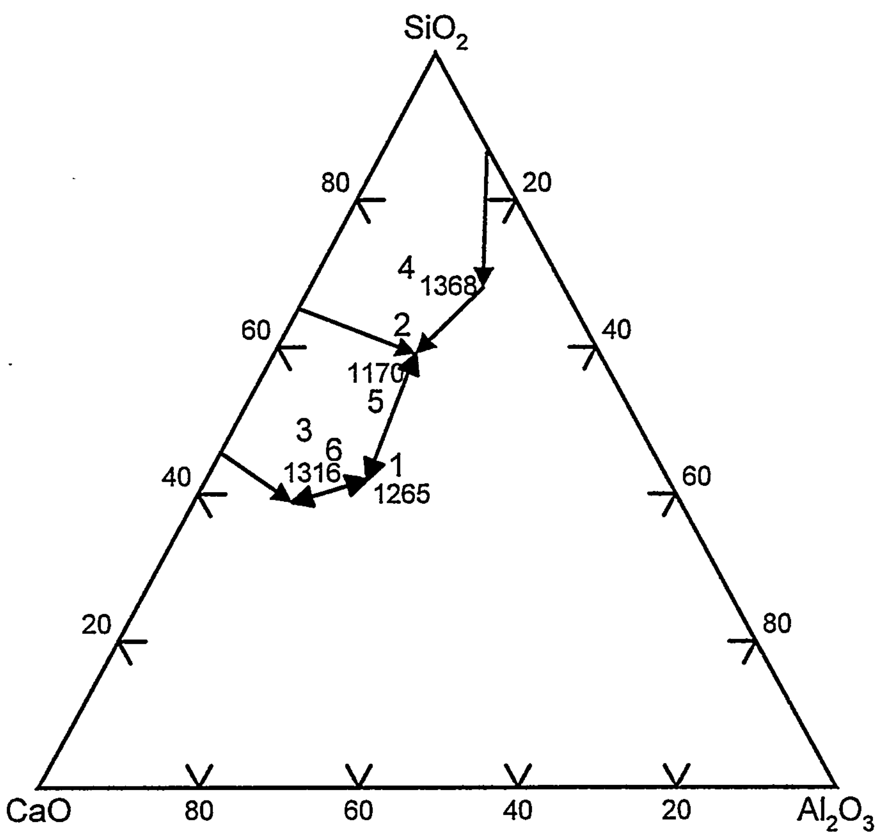


Figure 2. RAW-MIX FORMULATIONS 1 TO 6 SHOWN ON $CaO$-$Al_2O_3$-$SiO_2$ DIAGRAM, SHOWING EUTECTIC TEMPERATURES FOR PRODUCING NOVEL CEMENTITIOUS MATERIALS

To help determine their cementitious properties, the melted formulations will 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 $Na_2O$+$K_2O$ 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. Low grindability index suggests 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 will be selected for bulk production and evaluation as possible candidates for use in Portland blended cements. The blends will then be subjected to the following series of tests based on the ASTM C-1157-94 performance specifications:

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-151 Autoclave Expansion: Pastes of normal consistency will be prepared from these cements and made as 1x1x11.25" prisms for testing for autoclave expansion as specified in the C151 practice The change in length, if any, after the test duration will be measured by a comparator and compared to control paste specimens to assess the fly ash addition in cement making.

ASTM C-185 Air Content: Air contents of the mortar specimens prepared from the cements will be determined in accordance with the ASTM C-185 method. Mortars will be prepared from each cement in accordance with Practice C305 to give a flow of 87.5%, and placed in a 400-ml. measure. The air content will be determined from the differences in the actual and theoretical weights of mortars on a unit-volume basis, and compared with the control.

ASTM C-191 Time of Setting: Cement pastes with appropriate consistencies will be tested for initial and final setting times using Vicat Needle as specified in the procedure. The data will be compared with that of the control to note any variations.

To further evaluate the blends, a number of CTL devised tests will be utilized. Pastes from each blend will be prepared using a 0.5 water-to-cement (w/c) ratio at a controlled shear rate using Waring Blender. The pastes will 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 will be determined using the modified Vicat test method. Compressive strength of 1-inch paste cubes will be measure at 3, 7, 28 days curing. Drying shrinkage of paste strips will be determined to identify any measurable effect of fly ash on clinker/cement formulation. Separate tests to determine heat of hydration of the pastes will 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 |
|---|---|---|---|
| $SiO_2$ | 48.94 | 52.56 | 53.92 |
| $Al_2O_3$ | 18.33 | 19.52 | 20.44 |
| $Fe_2O_3$ | 20.76 | 15.37 | 15.75 |
| CaO | 6.43 | 5.06 | 6.32 |
| MgO | 1.03 | 1.10 | 1.09 |
| $SO_3$ | 0.07 | 0.78 | 0.06 |
| $Na_2O$ | 0.72 | 1.04 | 0.63 |
| $K_2O$ | 2.00 | 2.38 | 1.97 |
| LOI | 0.22 | 1.29 | 0.00 |

Based on theoretical considerations regarding cementitious properties of vitreous phases in the quaternary system $SiO_2$-$Al_2O_3$-$Fe_2O_3$-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. CKD is a waste product of cement manufacturing and is a low-cost material with a suitable chemical composition. At this point in the program only fly ash has been considered. The boiler slag has a very similar composition to the fly ash. Use of it would just be a duplication of the effort of using fly ash. Use of bottom ash will be considered in the next quarter.

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 product samples were practically fully vitrified. The actual chemical compositions of the product samples are given in Table 3.

Table 3. CHEMICAL COMPOSITION OF PRODUCT SAMPLES BY WEIGHT PERCENTAGE

| Sample ID | 65D | 75L |
|---|---|---|
| $SiO_2$ | 40.79 | 40.47 |
| $Al_2O_3$ | 15.06 | 15.31 |
| $Fe_2O_3$ | 11.54 | 11.63 |
| CaO | 23.44 | 24.68 |
| MgO | 1.34 | 1.16 |
| $SO_3$ | 0.16 | 0.30 |
| $Na_2O$ | 1.27 | 0.90 |
| $K_2O$ | 4.26 | 1.83 |

Cementitious properties of the product samples 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 sample products. The sample products were ground to a specific surface of 340 $m^2/kg$ 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 appeared to be 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

For the next phase of testing, three raw mix formulations (see Table 5) will be prepared with bottom ash and covering a larger portion of the target field of compositions:

Table 5. RAW MIX FORMULATIONS BY WEIGHT PERCENTAGE FOR NEXT PHASE OF TESTING

| Sample ID | Bottom ash | Limestone | Clay | Sand |
|---|---|---|---|---|
| Mix 1 | 54 | 33 | 13 | -- |
| Mix 2 | 58 | 19 | -- | 23 |
| Mix 3 | 68 | 24 | -- | 8 |

An additional three raw mix formulations will be prepared using fly ash instead of bottom ash. All of these formulations will be produced during Task 4 and evaluated for cementitious properties using ASTM C-1157-94 performance tests and other specialty tests in Tasks 5-7.

## CONCLUSIONS AND RECOMMENDATIONS

By the end of the first quarter, it was shown that Illinois coal fly ash blended with limestone or CKD can be successfully melted to produce a cementitious product.

Comprehensive testing of blends with fly ash and with bottom ash using standard cement industry methods over the next three quarters will quantify the cementitious properties of these blends and determine optimal formulations for later pilot-scale production.

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