ABSTRACT

This investigation seeks to utilize fly ash in fired-clay products such as building and patio bricks, ceramic blocks, field and sewer tile, and flower pots. This goal is accomplished by 1) one or more plant-scale, 5000-brick tests of fly ash mixed with brick clays at the 20% or higher level; 2) a laboratory-scale study to measure the firing reactions of a range of compositions of clay and fly ash mixtures; 3) a preliminary study to evaluate the potential environmental and economic benefits of brick manufacture with fly ash. Bricks and feed materials were tested for compliance with market specifications and for leachability of pollutants derived from fly ash. The laboratory study combined ISGS databases, ICCI-supported characterization methods, and published information to improve predictions of the firing characteristics of Illinois fly ash and brick clay mixtures. Because identical methods are used to test clay firing and coal ash fusion, and because melting mechanisms are the same, improved coal ash fusion predictions are an additional expected result of this research. If successful, this project should convert a disposal problem (fly ash) into valuable products—bricks.

We completed a manufacturing run at Colonial Brick Co. in April and began laboratory testing of samples from that run: clays, fly ash (from Illinois Power Company), and green and fired bricks, both with and without fly ash. Bricks with 20% fly ash "scummed" during firing, and the fly ash failed to increase oxidation rate or water absorption, which were both expected. Dust from fly ash was an unanticipated problem at the brick plant. We will look for improved methods of handling next year's fly ash deliveries. We obtained chemical and mineralogical analyses of the fireclays and shales at Colonial and Marseilles Brick Companies and ran a series of selective dissolution analyses to more accurately determine the composition of the principal clay minerals in brick clays and the components in fly ash. We began related work of calculating mineralogical analyses from chemical analyses for all clays and fly ashes that we sample. Ilham Demir kindly gave us a copy of the chemical database from their ICCI study of commercial coals; this database has been reformulated to estimate the fly ash composition from each of these coals, which should allow us to select three standard fly ashes for optimization studies. We completed a computer database of the locations and geological affinities of all ceramic clays studied by the Clay Minerals Unit since about 1930 (~25,000 entries). Research for year 2 has begun already, and a revised schedule during year 1 has put us ahead of schedule. A summary report on this project was presented to the Coal Advisory Committee of the ISGS on May 15, 1995 and the ICCI Contractor's Meeting on August 8, 1995.
EXECUTIVE SUMMARY

This project seeks methods for the efficient utilization of coal combustion wastes by using Illinois fly ash in the manufacture of bricks and similar fired-clay products. The project is composed of three parts: 1) one or more plant-level manufacturing runs, and 2) a set of laboratory-scale experiments designed to predict the firing properties of mixtures of a range of compositions of fly ashes with clays and shales that represent the range of compositions typical of mines and power plants in Illinois; 3) a preliminary investigation of the potential environmental and economic benefits of brick manufacture with fly ash. The completion of these three program elements will provide strategies for maximizing the use of fly ash in bricks and related products.

The first task in this project was to obtain approximately 20 tons of fly ash from Illinois Power Co.'s Wood River Plant and ship it to Colonial Brick Company in Cayuga, Indiana, where in-plant tests of mixtures of Colonial's brick clays and Illinois Power's fly ash were planned at the 20% or higher level. A single plant-scale run will probably be 5,000-10,000 bricks with fly ash, with pre- and post-fly ash baseline runs of several thousand bricks. A parallel part of the first task was to characterize the chemical and mineralogical content of the feed materials and to test the fired bricks by conventional procedures. A series of leaching tests also is being conducted on the bricks, with and without fly ash. Procedures employed in previous ICCI studies are being used in the leaching tests of raw materials and bricks (1Dreher, Roy, and Steele, 1993). Chemical analyses of the feed materials will be by conventional methods. Methods developed in current investigations for ICCI will be used for mineralogical characterization (2Kruse et al., 1994; 3Moore, Dreher, and Hughes, 1994).

In general, fly ashes have compositions similar to raw materials used in brick manufacture. However, some fly ashes contain amounts of CaO and CaSO₄ (from calcite) and Fe₂O₃ (from pyrite and marcasite) that would be considered too high by many manufacturers. If special procedures are used, fairly high levels of each of these constituents can be accommodated. If present as CaO or Ca(OH)₂, high levels of calcium can be corrected by adding water in the cool-down part of the firing cycle. This was the method by which bricks known as "Chicago Commons" were manufactured. Both the color and lower melting point caused by high levels of Fe₂O₃ are best adjusted by increasing the quartz and/or kaolinite content of the clay/shale. The fly ash used at Colonial was rich in SiO₂ and Al₂O₃, and it was unusually low in calcium phases and Fe₂O₃. We had unexpected problems with scumming (from calcium salts) and slow burnout, i.e., oxidation of iron and organic carbon. However, additions of fly ash did not provide an expected increase in water absorption.

The major goal of the first task was to make a realistic test under manufacturing conditions and detect and solve problems that might occur during scale-up at other sites. We recently made arrangements for one or more plant-scale tests to be run during the second year of this investigation at Marseilles Brick Company. Marseilles has a laboratory on site and can control more complex plant-scale tests. The raw materials at Marseilles are 'better' representations of the shale and fireclay used in the region. Some of the problems at Colonial may be eliminated by the fact that the Marseilles plant is automated and the production cycle is shortened.

The second task in this project is to attempt to improve the accuracy of methods that predict the firing characteristics of fired-clay raw materials. Part of the uncertainty about the exact type and level of fly ash that should have been used at Colonial in the manufacturing run is the result of inadequate methods for predicting firing behavior. Improving the prediction of
the firing behavior of fly ash-clay mixtures requires a set of working and practical relationships (predictive tools) that takes into account the firing properties of each of the major minerals in the feed material. The preferred materials for these fired-clay products occur as underclays and roof shales associated with coals and contain variable amounts of three basic groups of minerals. These groups are 1) relatively low-melting-point illite, mixed-layered illite/smectite (I/S), and chlorite; 2) refractory kaolinite and mixed-layered kaolinite/expandables (K/E); and 3) somewhat refractory quartz. Common red-firing roof shales generally contain nearly ideal levels of groups 1 and 2, and adequate firing characteristics are obtained by blending clay-rich shale zones with sandier, quartz-rich zones. It is worth noting that some fly ashes probably will act as a sandier additive in combination with normal brick clays, although the fly ash for our manufacturing run at Colonial acted like the shale in terms of the effect of grain size on firing. If a manufacturer needs lighter color, greater strength, and/or increased refractoriness, a kaolinitic underclay (fireclay) is normally blended with the shale. The individual minerals within each of the three mineralogical groups are similar enough that the three groups probably can be used in a simplified optimization model. Furthermore, fly ash is made up of burned equivalents of these three mineral groups, and it should be possible to characterize the firing reactions of fly ash and fly ash-brick clay mixtures with the same or similar simplifications.

The approach for task 2 was to obtain from the ISGS reference collection clays that represent the range of compositional variation that is typical of fired-clay raw materials in Illinois. After review of the database, we chose the shale and fireclay from Marseilles as optimization standards for task 2. A set of Illinois fly ash samples will be selected to represent the range of composition of these materials. These samples will be fully characterized, and firing tests will be conducted to obtain data that describe the firing behavior of fly ashes, brick clays, and their mixtures. A problem with the selection of fly ashes is the lack of accurate information on which coals are burned at which boilers. A related problem is the variation between the mineralogical content of the coal and the resulting fly ash, segregation of inorganic constituents between fly ash and bottom ash, and the degree of fusion of mineral matter during burning. The fly ash sample used for the manufacturing run at Colonial has been chosen as a typical example of a fly ash rich in SiO$_2$ and Al$_2$O$_3$. We are currently testing the samples used by Moore, Dreher, and Hughes (1994) to see if any of them can be used as example fly ashes rich in CaO or Fe$_2$O$_3$. In addition, one or more fly ashes will be needed for the tests at Marseilles.

During the third quarter, we shipped 25 tons of fly ash from Illinois Power's Wood River Station and made a plant-scale brick manufacturing run at Colonial Brick Company. We had problems with dusting during the delivery of the fly ash at Colonial. We will try to anticipate this problem in our future plant-scale tests. The fly ash-containing bricks scummed more than the controls and they 'burned out' (oxidized throughout) more slowly than expected. On the positive side, low permeability caused the test bricks to have lower-than-expected water absorptions. The firing problems do not appear to be insurmountable. We are currently searching for fly ashes that might allow Colonial Brick to make arrangements for permanent use of fly ash in their plant. We completed the characterization of the initial clay samples from Colonial and Marseilles Brick, and we are nearly finished characterizing the shale, fireclay, and fly ash used in the production run at Colonial Brick.

We have constructed a computer database of the occurrence of Illinois brick clays. This database gives the location, type, and geological unit of all the clays evaluated by the Survey's Clay Minerals Unit in the last 60 years. A similar database of fly ash compositions has been calculated from the database of Demir et al. (1994) of the chemical composition of 34 'commercial' coals. This database has been modified to estimate the composition of fly ash that should be produced by burning each of these coals, and it should be possible soon to select the last two 'standard' fly ashes. Where coals from the
same mines are burned and have been sampled for the CCRM sample bank, we also plan to
compare our predictions of fly ash composition with those in the sample bank. Because
brick manufacturers have problems with SO\textsubscript{2} emissions from clays, we will evaluate the
potential of high-CaO fly ash to absorb part of the SO\textsubscript{2} during firing of bricks.

We revised the protocols from the characterization studies for coal combustion wastes and
minerals in coals. All characterization methods were adequate, except for the step-wise
dissolution analysis of fireclays and the fly ash used at Colonial. A 500\textdegree C pre-treatment is
being tested to solve the problem with fireclays, and more grinding and a longer reaction
period will be tested for 3 fly ash samples. We plan to complete these analyses early in the
next quarter. No problems or delays are expected in completing task 2. We also expect to
add one or more properties to the optimization tests. These additions should increase our
understanding of firing with fly ash additions.

Near the end of year 2 of the project, existing information on brick clays and fly ash will be
integrated with the results of this study to suggest solutions to problems that might inhibit
use of fly ash in fired-clay products, to outline manufacturing and market strategies that
might increase the use of fly ash in bricks, and to describe the environmental impact of
using fly ash in these products. Methods to predict the firing characteristics of clays and
fly ash, and of ash fusion of coals will be made available to interested parties. A
preliminary evaluation will be made of potential benefits of the use of fly ash in fired-clay
products. If the initial promise of this project is realized, we expect to be able to recycle
large amounts of fly ash to valuable marketable fired-clay products such as bricks.

Slurry Solid Mixtures, Final Technical Report to the Illinois Clean Coal Institute,
Coal Sample Program, Final Technical Report to the Illinois Coal Development
Board, the Illinois Clean Coal Institute, Carterville, IL;
Diffraction Characterization of Flue Gas Desulfurization (FGD) and Fluidized Bed
Combustion (FBC) By-Products, Project funded by the Coal Combustion Residues
Management Program, Carbondale, IL.
OBJECTIVES

The primary goal of this investigation was to test the use of fly ash in fired-clay products, such as bricks. Three tasks were defined to meet this goal:
1. manufacture under normal plant-scale conditions of bricks that contain 20% or more of fly ash;
2. measure the firing characteristics of the known compositional extremes of Illinois fly ashes and brick clays and shales, and, from those measurements, the derivation of practical correlations to predict the firing characteristics of any mixture of clays and fly ashes. And finally, the optimization of mixtures of brick clays with typical fly ashes. (Methods that more accurately predict the firing behavior of brick clays and fly ashes also should improve predictions of ash fusion temperature of coals.)
3. integrate the results of tasks 1 and 2 with preliminary engineering and market assessments to evaluate the feasibility of large-scale utilization of fly ash in fired-clay products;

INTRODUCTION AND BACKGROUND

The large amounts of fly ash that are produced during the burning of Illinois coals represent a continuing disposal problem and a disincentive to increased consumption of those coals. If significant amounts of fly ash could be used in the manufacture of fired-clay products such as brick, this disposal problem would be largely eliminated and a valuable construction product would be created. Furthermore, the clay minerals in coals are fired during burning, and the energy for this firing is "saved" during brick manufacture. Manufacturers of fired-clay products also would reduce mining costs and clay use in direct proportion to the amount of fly ash added to their products. Because this project addresses the needs of industry at both the laboratory- and plant-scale levels, we believe the results can be more easily transferred to the private sector and that the time required for application of those results will be minimized.

Better methods of predicting the firing behavior of bricks and related products are a second important aspect of this investigation. Although general principles guiding the selection of raw materials for fired-clay products have been known for many years (Grim, 1962; Burst and Hughes, 1994), the complexity of the firing reactions suggests the need for improved methods (Hughes, 1993). This need is emphasized by the work at Colonial Brick Company. Because we lack adequate methods of prediction, we were obliged to resort to trial-and-error methods for our plant-scale test. Completion of task 2 of this project will make it possible for us to analyze a ceramic producer's raw materials and locally available fly ashes, and suggest optimum levels of fly ash that could be employed. The large amount of background information at the ISGS and the sophistication of computer programs now available make possible a significant improvement in methods needed to evaluate all the compositions of fly ash, shale, and underclay that might be encountered.

Improved methods of predicting coal ash fusion temperature are a final important outcome that is expected from this study. Laboratory methods for estimation of coal ash fusion temperature are the same as those for ceramic tests. As for ceramic products, the methods used to predict coal ash fusion are based upon chemical analyses and are notoriously inaccurate. For the ceramic and the coal ash fusion tests, we suggest that equations based upon mineralogical composition will yield improved accuracy and precision. A mineralogical basis of prediction also should provide clear indications of how to solve problems that are predicted.

These improvements should make it easier for consumers to use Illinois coals and should benefit our producers accordingly. If successful, the results obtained from this project
should lead to an attractive solution, from an environmental and economic standpoint, for the recycling of fly ash to high-value marketable products. Success also could revitalize the regional ceramics industry, an industry that has been in decline for several years.

The ISGS has a long history of research related to coal and fired-clay products. The utilization of coal combustion wastes was the subject of recent studies by the Principle Investigator (Hughes and DeMaris, 1992). Efforts to find better raw materials and improve the manufacture of fired-clay products have taken place over the last six decades at the Survey. Relevant parts of these efforts are summarized in Hughes and Bargh (1982), Hughes (1983), Hughes, DeMaris, and White (1983), and Hughes (1993). Slonaker (1977) showed that acceptable bricks were produced from feeds of 72% fly ash, 25% bottom ash, and 3% sodium silicate. A general discussion of the properties of fly ash that are important to its use in fired-clay products can be found in Kurgan, Balestrino, and Daley (1984). They report a fairly high alkalinity for fly ash from our region, and this could improve dispersion of the clay body during the forming of bricks. If calcium in these materials is in a form that can react with sulfide during firing, fly ash may reduce SO₂ emission during firing.

The development and use of leaching tests for the measurement of environmental impacts of coal combustion residues has been conducted by one of the Investigators (Dreher, Roy, and Steele, 1993). The PI and another Co-Investigator have recently developed mineralogical characterization methods for the IBCSP samples and coal combustion wastes, respectively (Kruse et al., 1994; Moore, Dreher, and Hughes, 1993). Mineralogical characterization methods for clays and shales are described in Hughes and Warren (1989) and Moore and Reynolds (1989). During the past three years, the PI also has carried out extensive research in ceramic clay products that are closely related to bricks and similar fired-clay products, and he has extensive experience in the clay processing industry. The capabilities of the ISGS in mineral process engineering and technical-economic studies are illustrated in several projects.

EXPERIMENTAL PROCEDURES

Task 2. Plant-scale manufacturing of bricks with fly ash

Subtask 1.1. Brick manufacturing runs. Illinois Power Company provided about 25 tons of dry fly ash from the Wood River Power Plant. Colonial Brick Company conducted a manufacturing run of about 5,000 bricks without fly ash and a similar number with a 20% fly ash added to the normal clay. A single previous run with fly ash by Colonial Brick Company indicated that 20% fly ash additions resulted in bricks that were within standard specifications. A batch of bricks of each of the two compositions was fired side-by-side in the kiln and tested. This subtask was completed during the third quarter of the first year of this investigation. The standard properties of the bricks are being evaluated. Additional manufacturing tests have been arranged at Marseilles Brick Company for the second year of this project.

Subtask 1.2. Standard specification tests. This subtask as carried out by Colonial Brick and to measure the degree of conformance of the manufactured bricks with standard market specifications. Samples with and without fly ash were taken during firing to provide a measure of "clearing" or time required to completely oxidize the core of the bricks. Water absorption tests were carried out on the fired products, and the color was described by comparing bricks with and without fly ash additions.

Subtask 1.3. Characterization. In this subtask we are characterizing chemically and mineralogically each feed material and the resulting bricks. The characterization includes
the quantitative determination of major, minor, and trace elemental constituents, and major
and minor mineralogical components. The segregation of elements between different
mineral phases in the feed materials is being estimated by using a step-wise dissolution
procedure in conjunction with X-ray diffraction analysis (Moore, Dreher, and Hughes,
1993).

Subtask 1.4. Leaching tests. Leach testing procedures developed by Dreher et al. (1988,
1989) are being used to determine the extent to which environmentally toxic constituents
might leach from bricks to the environment. Batch extraction and wet-dry leaching
experiments (second year of the project), in which the substrate is exposed to deionized
water for a given time period, are conducted on crushed and whole bricks. Except for the
analyses conducted in Subtask 1.3, each solid will be analyzed chemically and
mineralogically prior to extraction and leaching experiments.

In extracting whole bricks, five faces are protected from leaching by application of an
epoxy coating. One long face of each brick was left uncoated to simulate exposure of one
face to weathering.

Batch extraction experiments are being conducted at solution-to-solid ratios of 4:1 for
periods of 3, 10, 30, 90, and 180 days for each of the solids. The 3-, 10-, and 30-day
extractions are completed. Each batch extraction container is agitated periodically during
the extraction period to assure adequate contact between solution and solid. At the end of
each extraction period, the solution and solid phases are separated for chemical analysis.
The solids from the 180-day extraction will be analyzed mineralogically.

Subtask 1.5. Integration. Upon completion of the manufacturing run and characterization
described in subtasks 1.1 - 1.3, an evaluation will be made of the feasibility of manufacture
of fired-clay products with fly ash additions. This evaluation will be used to modify plant-
scale tests during year 2 and to focus detailed experiments planned for the research effort in
Task 2.

Task 2. Predicting the Firing of Fly Ash and Brick Clay Mixtures

Subtask 2.1. Background. This subtask seeks to assemble background information on the
composition of Illinois fly ashes and on clays and shales used in the manufacture of fired-
clay products. For fly ashes, data are needed on the range of chemical and mineralogical
composition that is possible and on the plant location where these fly ashes are generated.
For clays and shales, information that describes where typical deposits occur and the
relative content at each locality of the three basic raw materials used in fired-clay products
in Illinois must be collected. These basic raw materials are 1) clays and shales with a red-
firing or "shale-type" composition; 2) clays with refractory or "fireclay-type" compositions;
and 3) sandier red-firing shales that are often blended with shaley and refractory clays.
Subtask 2.2. Selecting samples. Based on the results of the background search, three fly
ashes and two or three clays or shales are being selected to represent the range of
composition encountered in Illinois. Fresh 50-pound samples of all five or six materials
will be collected and stored at field moisture content.
Subtask 2.3. Characterizing samples. In this subtask, selected samples will be
characterized chemically and mineralogically. The characterization includes the quantitative
determination of major, minor, and selected trace elements and the mineralogical
composition of the samples. The step-wise dissolution procedure in conjunction with X-
ray diffraction analysis also is being conducted in order to estimate the segregation of
elements among various mineralogical phases (Moore, Dreher, and Hughes, 1993).
Subtask 2.4. Firing tests. Determinations of the melting temperature or pyrometric cone
equivalent (PCE), water absorption, and color will be made for each of the six samples and
for 30 mixtures and replicates that measure all possible combinations of the materials. Six replicate and eight standard PCE samples will be included to "calibrate" the method and measure errors.

Subtask 2.5. Predicting firing. Using results from subtask 2.4, factorial and regression computer software will be used to obtain equations that measure the effect on fired properties of additions of each of the basic components from the raw materials. The results of these computer calculation will include an estimate of error, and this estimate will be used to confirm that a sufficient number of samples was tested or that more experiments must be run.

Subtask 2.6. Programming. The equations generated in subtask 2.5 will be incorporated within one or more computer programs. These programs will be made available to interested parties.

Task 3. Integration and Evaluation

Subtask 3.1. Integration and evaluation. This subtask brings all the results together, evaluates them from an engineering- and market-oriented point of view, and estimates the overall feasibility of using significant amounts of fly ash in fired-clay products. This subtask will provide only a preliminary evaluation of the technical, economic, and environmental feasibility of recycling Illinois fly ash in bricks.

RESULTS AND DISCUSSION

Preliminary background studies

Part of the first and second quarters of this project were required to complete the NEPA forms for the plant test at Colonial Brick Company. This task was further complicated by changes to a new set of forms about halfway through the process. Although we were able to comply, this process is a burden on plant tests, and it would become a major impediment as the number of field sites increased.

Early in the first quarter, we collected shale and fireclay samples from Colonial and Marseilles Brick Companies. These were tested by standard X-ray fluorescence (XRF) and X-ray diffraction (XRD) procedures. The results of these tests, and those of later tests are given in Tables 1, 2a, and 2b. The shales used are typical red-firing Pennsylvanian shales, which are common as the roof shale of most coals. At Colonial's pit, a ~30-ft.-thick roof shale overlies a 6-12 in carbonaceous or coaly zone, which overlies ~6 ft of fireclay. The coaly zone may be equivalent to the Colchester (No. 2) Coal. Marseilles Brick Company mines shale and fireclay from different pits, and they plan to open a new fireclay pit in the near future.

The manufacturing process at the two brick plants is similar. At Colonial, red bricks are made from shale with small amounts of cinders from their coal-sawdust mixtures that are used to fire the kilns. Normally, higher quality or stronger bricks require fireclay additions and must then be fired at a higher temperature. The clays are blended in a crusher, pulverized, and water and dispersant are added in a pugmill to produce a plastic clay that can be extruded. An ideal brick clay has enough clay minerals for good plasticity but is coarse-grained enough so that the core of the brick is completely oxidized in the shortest possible time during firing. The 'head' of the extruder can be chosen to provide solid or 'drilled' bricks. The extruded clay can be coated with various materials for color or texture, and is then automatically cut into standard lengths. At Colonial, the green bricks are stacked manually onto cars for drying, and the bricks pass through a drier for several days. At Marseilles, an automatic setter picks up the green bricks and places them on kiln
cars. These cars enter a continuous tunnel drier and kiln, emerging several days later as finished products.

Table 1. Mineralogical analyses of Colonial Brick and Marseilles Brick clays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay No</th>
<th>%I/S</th>
<th>%K/E</th>
<th>%K</th>
<th>%C</th>
<th>%Q</th>
<th>%R</th>
<th>%Pf</th>
<th>%Cc</th>
<th>%Py/Ma</th>
<th>Other</th>
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<td>3521A</td>
<td>10</td>
<td>25</td>
<td>8.9</td>
<td>11</td>
<td>39</td>
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<td>34</td>
<td>0.0</td>
<td>1.3</td>
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<td>6.0</td>
<td>0.0</td>
<td>1.5</td>
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<tr>
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<td>33</td>
<td>0.0</td>
<td>1.3</td>
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<td>16</td>
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<td>apatite?</td>
</tr>
<tr>
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<td>2.5</td>
<td>9.0</td>
<td>0.0</td>
<td>33</td>
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<td></td>
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<td>84</td>
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<td>3.0</td>
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Key: Samples 1, 2 = Colonial Brick 3/94 and 4/95; samples a and b = Marseilles Brick 10/94 and 6/95; I/S = mixed-layered illite/muscovite; I = illite; K/E = mixed-layered kaolinite/expandables; K = kaolinite; C = chlorite; Q = quartz; KF = K-feldspar; Pf = plagioclase feldspar; Py-Ma = pyrite-marcasite; M = mullite; H = hematite; R = repeat; shale-br = unfired brick; fired br = fired brick; (3521D, E, F, G = bricks with 20% fly ash; 3521H, I, J, K = bricks without fly ash); gr clstn = green claystone with calcite; red clstn = purple and green claystone.

Once the bricks are dried at Colonial, they are moved by front-end loaders into beehive kilns, fired, placed on pallets, and stored for shipment. At Marseilles, the bricks emerging from the kilns are automatically set on pallets and moved to storage by front-end loader. There are some differences in the proportions of different types of bricks made at each company. However, the basic materials and methods are the same.

An ideal ceramic material has two components: 1) enough refractory framework grains such as kaolinite and quartz to keep the clay body from bending during firing; 2) enough minerals such as illite, mixed-layered illite/smectite, chlorite, K-feldspar, and plagioclase, which melt and form a steel-hard brick at reasonably low temperatures. Many roof shales are upward coarsening, and this grain-size variation makes possible careful blending for plasticity and firing rate. Fireclays, unlike shales, also contain mixed-layered...
kaolinite/expandables (K/E). This K/E may give special properties because it is composed of a 2:1 clay mineral layer that melts at relatively low temperatures and a 1:1 layer that is refractory. For this reason, the K/E content will be tested as a separate regression factor. Quartz also can have special properties during firing (Chavez and Johns, 1995). We expect that quartz acts as a framework grain, but at high enough temperature, quartz melts and acts as a bonding agent. For these reasons, we expect to carry out the regression with several groupings of factors.

Table 2a. Chemical analyses (in %) of Colonial Brick and Marseilles Brick clays, and bricks from the manufacturing run at Colonial

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay No.</th>
<th>Chem No</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>shale-1</td>
<td>3521A</td>
<td>R20365</td>
<td>61.33</td>
<td>17.7</td>
<td>6.32</td>
<td>0.57</td>
<td>1.9</td>
<td>3.09</td>
<td>1.08</td>
<td>0.98</td>
<td>6.44</td>
</tr>
<tr>
<td>shale br-2</td>
<td>3521C</td>
<td>R20367</td>
<td>60.81</td>
<td>17.66</td>
<td>6.47</td>
<td>0.6</td>
<td>1.91</td>
<td>3.07</td>
<td>1.07</td>
<td>0.97</td>
<td>6.82</td>
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<td>shale-3</td>
<td>3538A</td>
<td>C34430</td>
<td>59.96</td>
<td>18.86</td>
<td>6.5</td>
<td>0.39</td>
<td>2.07</td>
<td>3.36</td>
<td>1.04</td>
<td>0.98</td>
<td>6.34</td>
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<tr>
<td>fireclay-1</td>
<td>3521B</td>
<td>R20366</td>
<td>57.47</td>
<td>21.37</td>
<td>4.71</td>
<td>1.57</td>
<td>1.47</td>
<td>2.68</td>
<td>0.35</td>
<td>1.1</td>
<td>7.98</td>
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<tr>
<td>fireclay-2</td>
<td>3538C</td>
<td>C34431</td>
<td>58.27</td>
<td>21.49</td>
<td>5.06</td>
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<td>1.38</td>
<td>2.35</td>
<td>0.47</td>
<td>1.11</td>
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<tr>
<td>fireclay-a</td>
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<td>R20368</td>
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<td>26.18</td>
<td>1.99</td>
<td>0.31</td>
<td>0.5</td>
<td>0.96</td>
<td>0.94</td>
<td>1.27</td>
<td>8.93</td>
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<tr>
<td>shale-b</td>
<td>3528B</td>
<td>R20369</td>
<td>66.38</td>
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<td>4.96</td>
<td>0.32</td>
<td>1.95</td>
<td>3.22</td>
<td>1.3</td>
<td>1.03</td>
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<td>3521F</td>
<td>C34426</td>
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<td>18.18</td>
<td>6.12</td>
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<td>5.89</td>
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<td>C34427</td>
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<td>C34429</td>
<td>66.37</td>
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<td>6.42</td>
<td>0.64</td>
<td>1.94</td>
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<td>1.09</td>
<td>1.04</td>
<td>0.21</td>
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<td>2.22</td>
<td>1.11</td>
<td>1.35</td>
<td>3.18</td>
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</table>

Key: Samples with clay numbers 3521 and 3538 are from Colonial Brick Co.; those with 3528 are from Marseilles Brick Co.; grn brick-1 = unfired brick with 20% fly ash; grn brick-2 = unfired brick without fly ash; brick-1 = fired brick with 20% fly ash; brick-2 and 2R = fired brick samples without fly ash; fly ash-1 and 2R are duplicate samples.

Table 2b. Chemical analyses of Colonial Brick and Marseilles Brick clays, and bricks from the manufacturing run at Colonial (in %, except † are in ppm)

<table>
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<tr>
<th>Sample</th>
<th>Clay No.</th>
<th>Chem No.</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>SO₃</th>
<th>Sr†</th>
<th>Ba†</th>
<th>Zr†</th>
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<td>3521C</td>
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Key: As in Table 2a.
Location of optimization standards

We completed entries to a large database of Illinois ceramic clays during the second quarter. This database lists the locations and material types for the approximately 25,000 samples that have been collected at the ISGS since 1930. The database can be searched and provides easy reference for new companies who want to locate in Illinois.

The location and selection of fly ash standards has proved difficult. Ilham Demir kindly offered a copy of their database of chemical analyses of the 34 coals that were being mined in 1992 (Demir et al., 1994). The inorganic chemistry in this database was modified in an Excel® spreadsheet to estimate the chemical composition of fly ash obtained from each of the coals. We also entered the chemical composition of 8 fly ashes that were part of the characterization study by Moore, Dreher, and Hughes (1994). The estimates of fly ash composition from each data set are shown in figures 1, 2, and 3. Analysis of the plots shows that SiO$_2$:Al$_2$O$_3$ is nearly constant and has a spread from 1.9 to 3.6 and a mean of about 2.5 in the Demir et al. data set and a spread of 2.3 to 3.9 and a mean of about 2.5 in the Moore, Dreher, and Hughes values. The other types of significant variation are caused by differences in CaO, Fe$_2$O$_3$, and K$_2$O + Na$_2$O. For purposes of selecting standards for optimization studies, the fly ash used in production runs this year (Table 2a and 2b) can be used as a SiO$_2$- and Al$_2$O$_3$-rich end member and samples 2 and 8 from the Moore, Dreher, and Hughes set can be used for high CaO and high Fe$_2$O$_3$, respectively.

Plant-scale manufacturing run

During the third quarter of this project, we completed the plant-scale manufacturing run at Colonial Brick Company. Based on recommendations from Illinois Power Company, fly ash was obtained from their Wood River Plant. The dust associated with unloading fly ash at Colonial Brick was an unexpected problem. We tried to minimize this problem by pumping the fly ash under a large tarp that had its edges staked to the ground. However, this method did little to reduce dusting, and for year 2 testing, we will need a solution that provides better dust control at Marseilles Brick Company. If fly ash is used on a more permanent basis, various ways to dampen this material at the power plant may be required.

The results of the production run were somewhat unexpected. We expected the fly ash to increase gas movement into and out of the bricks, and the reverse occurred. Essentially, the fly ash decreased the permeability of the bricks to oxidation, although we expected the fly ash to "open up" the bricks during firing. The bricks with fly ash also had noticeably more "scumming," which also was unexpected. This scumming causes a white to cream dusting on the outside of the bricks and is mostly due to migration of calcium sulfates to the surface during drying, firing, or both. We will attempt to confirm this assumption with chemical analyses. The problem can be corrected by adding barium carbonate, or it may be possible to simply select a fly ash with a lower calcium sulfate content. The positive side of the effect of fly ash on gas permeability was the lack of an expected increase in water adsorption. In general, the bricks from the manufacturing run were within specifications; however, the scumming reduces their marketability.

Finding a permanent fly ash source for Colonial Brick Company is made difficult by the same problems that are discussed above in the section on trying to locate standard fly ash compositions, i.e., the lack of accurate chemical and mineralogical analyses of the coals and fly ashes from each boiler in the region. We plan one or more proposals to the CCRM and ICCI to remedy these problems in the coming year.
Figure 1. Triangular plot of CaO:SiO$_2$+Al$_2$O$_3$:Fe$_2$O$_3$. Symbols: $\square$ = dataset of Demir et al. (1994); $O$ = dataset of Moore, Dreher, and Hughes (1994); ■ = Colonial Brick Company's shale and fireclay; ● = Marseilles Brick Company's shale and fireclay; x = fly ash used for tests at Colonial Brick.

Chemical and X-ray diffraction analyses

The characterization of brick clays available at Colonial Brick and Marseilles Brick Companies was completed in the fourth quarter (see Tables 1, 2a, and 2b). The mineralogical contents of these clays will be used to estimate their chemical composition, and these estimates will be compared to actual analyses. During the fourth quarter, we selected and analyzed two standard 'optimization' clays from Marseilles Brick Company. The shale and fireclay samples from Marseilles are ideal standards for brick clays. The XRD and XRF analyses of the fly ash, shale, fireclay, and green and fired bricks, with and without fly ash, also were completed during the fourth quarter (Tables 1, 2a, and 2b).

The triangular plots of the calculated ash content from Demir et al. (1994), the compositions of fly ash samples from Moore, Dreher, and Hughes (1994), the chemical analyses of clays from Colonial and Marseilles Brick Companies, and the fly ash used at Colonial were superimposed on figures 1, 2, and 3. These figures show that most fly ashes contain more iron and calcium than brick clays. Because they are fused, the fly ash sources also may differ in the degree to which chemical constituents are segregated in 'phases.' However, to represent the range of available materials, we will select locally
available fly ash compositions that are relatively rich in 1) SiO₂, Al₂O₃, 2) Fe₂O₃, and 3) CaO. These constituents represent most of the ash content of Illinois coals, and the ratio of these oxides to Na₂O and K₂O is relatively constant. Where there is overlap, we also plan to obtain, from CCRM, chemical analyses of fly ashes produced from the coals represented in the Demir et al. database. These analyses will be compared with spreadsheet predictions, and adjustments will be made if they seem necessary. A final goal in this area for the next quarter is to construct regression equations between the chemical and mineralogical contents of the IBCSP coals and use those equations to estimate the mineralogical content of the 34 commercial coals.

Figure 2. Triangular plot of Fe₂O₃:Al₂O₃:SiO₂. Symbols: □ = dataset of Demir et al. (1994); ◯ = dataset of Moore, Dreher, and Hughes (1994); ■ = Colonial Brick Company's shale and fireclay; ● = Marseilles Brick Company's shale and fireclay; x = fly ash used for tests at Colonial Brick.

An unanticipated benefit from using fly ash may be its ability to capture sulfur from the clays during firing. Problems with SO₂ emissions are common in brick production, and the testing of high-CaO fly ashes has been added to the project for that reason. In particular, Marseilles brick adds limestone to their fireclay brick to control SO₂ emissions.
Figure 3. Triangular plot of CaO:Fe₂O₃:Na₂O+K₂O. Symbols: □ = dataset of Demir et al. (1994); ○ = dataset of Moore, Dreher, and Hughes (1994); ■ = Colonial Brick Company's shale and fireclay; ● = Marseilles Brick Company's shale and fireclay; x = fly ash used for tests at Colonial Brick.

The problem with predicting the firing behavior of mixtures of materials was discussed above. We believe that the solution to these problems is an approach to characterization that accurately measures the major and minor 'phases' that make up a material. For unfired materials, XRD analyses are a good start. However, some of the clay minerals are difficult to accurately determine, and we have chosen step-dissolution chemical and XRD analyses to improve the determinations (Cicel and Komadel, 1994; Moore, Dreher, and Hughes, 1994). Figures 4, 5, and 6 show the dissolution of shale samples used at Colonial Brick Company. Chlorite is the most difficult clay mineral to determine by XRD, and it is the most soluble in HCl. Therefore, XRD analyses of the solid fraction of the samples shows a decline in chlorite with greater time of reaction (Fig. 4). Similarly, the ICP chemistry of the supernates records the increase in chlorite-containing elements with the passage of time (Figs. 5 and 6). The ICP plots can be analyzed to calculate a structural formula of the chlorite in the sample. These calculations will be completed early in the second year, and they will be used to make the optimization equations more accurate.
Figure 4. Plot of the XRD peak intensity ratio of the chlorite 001 to the illite 001 from solid samples; this plot shows the dissolution of chlorite in 2N HCl with time. (See figures 5 and 6 for plots of the dissolved species from chlorite.)

A problem with step dissolution analysis is that, as minerals are less soluble, it becomes more difficult to dissolve one mineral at a time. For fireclay and fly ash samples, this can be a major analytical problem. The fly ash sample for the Colonial production runs gave pretty good results, although burning the minerals partly fuses easily melting and refractory clay minerals. It also appears that we will have to grind the samples longer, leave them in acid longer, increase the strength of the acid, or use some combination of these methods to remove all the amorphous material from fly ash samples. For fireclays, only 3-6% of the sample dissolved. A current test employs a 500°C pre-treatment, which should increase the solubility of K/E. Because fireclays contain relatively fewer phases, a less-accurate step dissolution analysis may be adequate.

Research—year 2

For startup of year 2 work, we plan to begin testing in Marseilles's laboratory. A laboratory has been located to perform firing tests for the optimization. If we are able to obtain information on standard fly ash samples in the next month, these tests can be completed in another month. Philip DeMaris will join us on October 1. We hope to begin testing at Marseilles shortly after his arrival. Depending on the current step dissolution experiments, a new set of experiments will probably be run to improve chemical
characterization of the three standard fly ashes. Most of the necessary computer tools for the optimization work are in place and operating.

![Graph](image)

**Sum of ions in solution (g)**

Figure 5. Plot of the ratio of Al ions in solution to the sum of the total ions in solution, which shows the increase in Al as the least soluble part of the chlorite structure (tetrahedral sheet) goes into solution. The concentration at the end of the experiment measures the total content of Al in chlorite.

Recent studies of the firing behavior of bricks and related materials suggest that we may need to expand the number of tests that are used to quantify the quality of fired-clay products. This expansion could add water adsorption, shrinkage, rate of burnout, and hardness-strength to the planned pyrometric cone equivalent (PCE) tests for year 2. Many of these determinations can be obtained from the PCE samples and most only moderately increase analytical costs.

Jock Laird, plant manager at Marseilles, has identified other firing problems that could impact the use of fly ash in brick manufacture. Without adding to our planned work, we may include optimization analyses that address some of these problems. They also could be addressed after year 2 testing is complete, and some of these problems may 'fall out' of the data analysis for our planned work.
CONCLUSIONS AND RECOMMENDATIONS

Additions of fly ash at the 20% level increased scumming and 'burn-out' problems during plant-scale tests at Colonial Brick Company. Therefore, we will put more emphasis in the next quarter on identifying the composition of fly ashes available near brick plants. These problems are not expected to cause insurmountable difficulties, but they need to be addressed in the near future. In particular, we will look for fly ashes high in CaO, SiO₂, and Al₂O₃. With that information and an analysis of the fly ash that we used in the Colonial Brick tests, we may be able to test another fly ash at Colonial. When we know the composition of fly ashes at each source, we also can select the three that will act as 'standards' in our optimization study, and choose one or more fly ashes for year 2 testing at Marseilles Brick Company. With clays and fly ashes in hand, the task 2 firing experiments can be completed (although we may perform preliminary tests in the laboratory at Marseilles). Some additional optimization studies will be performed to address firing problems raised by the plant manager at Marseilles.

Characterization of the clays used at Colonial and Marseilles Brick Companies was completed in the third and fourth quarters. A large computer database of the ceramic clays of Illinois also was completed, and the database of Demir et al. (1994) was processed to
estimate the fly ash composition that would be derived from burning each of those coals. This information will be used to locate representative fly ashes for task 2 and for materials to test at Marseilles in year 2. By extrapolating the correlations between mineral and chemical content from Hughes et al. (1994), it may be possible to extrapolate a mineralogical composition for the 34 coals used by Demir et al. An estimate of mineralogical composition would simplify the selection of fly ashes.

Characterization by XRD, XRF, INAA, and step dissolution analyses have been completed on the fly ash, shales, fireclays, green bricks, and fired bricks that were part of year 1 research. Environmental leaching studies are slightly behind schedule and will be completed in year 2. The combination of chemical and mineralogical approaches that were used should provide increased accuracy for the optimization studies. To date, the step dissolution analysis has worked particularly well on chlorite-containing shales and fireclays, and it gave reasonably good results for the fly ash sample. A new set of experiments with new protocols will be performed early in year 2 to improve step dissolution of fireclays and fly ashes.

Determinations of water absorption, shrinkage, rate of burnout, and hardness may be added to the planned pyrometric cone equivalent (PCE) tests for year 2. By speeding up the work on task 2 and completing task 1 during our first year, we are at or ahead of schedule for all parts of the project, except the aqueous extraction tests. Only the 3- and 6-month samples are unfinished at the end of the contract year 1. Furthermore, completion of background characterization for task 2 optimization studies will provide more funds in year 2 for optimization tests. No technical, budgeting, or management problems are expected at this point.

REFERENCES


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PROJECT MANAGEMENT REPORT
June 1, 1995 through August 31, 1995

Project Title: **BRICK MANUFACTURE WITH FLY ASH FROM ILLINOIS COALS**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/3.1A-10M
Principal Investigator: Randall E. Hughes, ISGS
Other Investigators: Gary Dreher, ISGS; Tanda Fiocchi, Ill. Power Co.; Joyce Frost, ISGS;
Duane Moore, ISGS; Massoud Rostam-Abadi, ISGS; Daniel Swartz, Colonial Brick Co.
Project Manager: Dr. Daniel B. Banerjee, ICCI

COMMENTS

No significant variances in project management have occurred. Actual expenditures finally have matched projected, primarily because bills for analytical services were processed during the last quarter.

Kristi K. Redding left the ISGS on May 31, 1995. On October 1, 1995, we plan to appoint Philip J. DeMaris to replace Ms. Redding on this project. Mr. DeMaris is an Associate Staff Scientist and brings extensive experience in coal research, including our joint effort on utilization of coal combustion residues.

We had difficulty in project scheduling in the second quarter that resulted from delays in obtaining fly ash from Illinois Power’s Wood River Plant. Those delays were worked around during the fourth quarter. The analytical chemistry for aqueous extraction tests after 90 and 180 days will be completed in year 2 of the research. We also have had problems locating representative and geographically close sources of fly ash. We believe that this information is available, and we need only obtain it from CCRM and perhaps other agencies. The poor level of knowledge about mineralogical and chemical transformations that take place on burning coal suggests to us that a proposal for characterization will be critical to many projects aimed at fly ash utilization. We plan such a proposal in the next round of RFPs. Otherwise, all personnel are in place, and the project is proceeding as planned.
EXPENDITURES - EXHIBIT B
Projected and Estimated Expenditures by Quarter

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<th>Types of Cost</th>
<th>Direct Labor</th>
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<th>Materials &amp; Supplies</th>
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*Cumulative by Quarter
COSTS BY QUARTER
BRICK MANUFACTURE WITH FLY ASH FROM ILLINOIS COALS

Months and Quarters

- ○ = Projected Expenditures
- △ = Actual Expenditures

Total Illinois Clean Coal Institute Award $58,401
SCHEDULE OF PROJECT MILESTONES

Milestones:

Task 1. Plant Scale Manufacture of Bricks With and Without Fly Ash
A  1.1. Manufacturing runs at brick plant
B  1.2. Testing brick for standard specifications
C  1.3. Characterization of raw materials
D  1.4. Leaching tests (drained Yr1 and wet/dry Yr2)
E  1.5. Integration of results

Task 2. Predicting Firing Characteristics of Fly Ash-Clay Mixtures
F  2.1. Background assessment
G  2.2. Sample selection
H  2.3. Characterization
I  2.4. Firing tests
J  2.5. Predicting firing behavior
K  2.6. Programming results

Task 3. Integration, Evaluation, and Technology Transfer
L  3.1. Integration and evaluation
M  3.2. Quarterly, interim final, and final reports
N  3.3. Technology transfer

Begin 9/1/94  End 8/31/96