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

ICCI Project Number: 95-1/3.1A-14
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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 tests of fly ash mixed with brick clays at the 20% or higher level; 2) a laboratory-scale study to measure and model the firing reactions of a range of compositions of shale, fireclay, 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 are tested for compliance with market specifications and for leachability of potential pollutants derived from fly ash. The laboratory study combines ISGS databases, ICCI-supported and new 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 converts a disposal problem (fly ash) into valuable products—bricks.

During the second year of this project, we collected and characterized three new fly ashes, their feed coals, a suite of fireclays, and three sets of “in-plant” shale and fireclay samples. The three new fly ashes were from coals with 1) a high Ca content, 2) a high Fe content, and 3) an average Ca:Fe:Al+Si. The high-Al+Si fly ash, used in last year's testing, was our fourth standard and gave us fly ashes that represent the extremes and average of the composition of Illinois coals. Analyses by X-ray diffraction (XRD) showed that iron oxide in fly ash is a mixture of magnetite, hematite, and probably maghemite. Sequential dissolution-ICP-XRD experiments were completed and we obtained the ICP analyses of the water soluble fractions of six fly ashes and the LTAs of three feed coals. XRD characterization was completed on all fly ash samples, fireclays, shales, LTAs of coals, and selected fired mixtures of fly ash, fireclay, and shale. Environmental testing was completed on bricks. Laboratory test results were used to design plant-scale tests. These test data also were used to begin a computer model of the firing reactions of brick clays and fly ashes, and to model ash fusion of coals. We will use a high-Ca, “pond-washed” fly ash for our plant-scale runs, which will be made this fall at Marseilles Brick Company. We continue to construct an up-to-date directory of sources of fly ash in Illinois. A summary paper entitled *Utilization of Fly Ash in Structural and Decorative Ceramic Products* was presented and published at the American Chemical Society Meeting in New Orleans. A slide talk version of this paper was presented at the ISGS Seminar in April and the ISGS Coal Advisory Committee Meeting in May. A paper entitled *Sequential Acid Dissolution of Clay Minerals: Tracking Structural Composition* was presented in June at the annual Clay Minerals Society Meeting in Gatlinburg (TN). Two of the case studies featured in this paper were performed for this project.

EXECUTIVE SUMMARY

This project seeks methods for the efficient utilization of coal combustion wastes, and precisely meets this purpose by examining the use of 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 provides strategies for maximizing the use of fly ash in bricks and related products.

The first task was to obtain one to three sources of approximately 20 tons of fly ash, ship them to Marseilles Brick Company in Marseilles, Illinois, and conduct plant-scale manufacturing runs with mixtures of Marseilles's brick clays and fly ash at the 20% or higher level. A single plant-scale run would be 3,000-10,000 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 were performed on the feed fly ashes, fireclay and shale, and green and fired bricks. This year's leach tests were replaced with more meaningful leach of the bulk fly ash. Chemical analyses of the feed materials were by conventional methods. Methods developed for ICCI were used for mineralogical characterization (¹Kruse et al., 1994; ²Moore, Dreher, and Hughes, 1994). The major goal of the first task was to make realistic tests under manufacturing conditions and detect and solve problems that might occur during scale-up at other sites.

Ceramic materials such as building bricks are among humankind's earliest technologies. However, our understanding of the reactions during the firing of bricks is far from complete. This firing is controlled by the ratio of relatively refractory minerals that maintain the shape of a ceramic body to the easily melted materials that fuse and produce a steel-hard brick. A further consideration is having enough plasticity for good extrusion and enough clay minerals for good green (unfired) strength. The preferred materials for these fired-clay products occur as underclays and roof shales associated with coals. These clays contain variable amounts of three basic mineral groups. They 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 Year 1 test at Colonial Brick seemed to show the opposite. If a manufacturer needs lighter color, greater strength, and/or increased refractoriness, a kaolinitic underclay (fireclay) is normally blended with zones from the shale. The individual minerals within mineralogical groups 1 and 2 are similar enough that the three groups probably can be used

as factors in a simplified model. Furthermore, fly ash is made up of burned equivalents of these three mineral groups, so we are modeling the firing reactions of fly ash and fly ash-brick clay mixtures with the same simplifications. In addition, our preliminary data indicated that the mineralogical and water-soluble composition of the feed coal is the best predictor of fly ash composition and its firing reactions.

In general, fly ash has a composition similar to raw materials used in brick manufacture. However, some fly ashes contain amounts of calcium (from calcite) and iron oxide (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 for by adding water in the cool-down part of the firing cycle. This hydration step was the method by which bricks known as “Chicago Commons” were manufactured. Both the color and lower melting point caused by high levels of iron are best adjusted for by increasing the quartz or kaolinite content of the clay-shale, or by removing magnetic iron oxide from the fly ash.

The goal of the second task was to improve the accuracy of methods that predict the firing characteristics of fired-clay products. Part of the uncertainty about the exact level of fly ash that should have been used at Colonial Brick in Year 1 testing was the result of inadequate methods of prediction of 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 components in the feed material. The approach for task 2 was to use the fireclay and shale at Marseilles Brick Company to represent the range of compositional variation that is typical of clay raw materials in Illinois. A set of Illinois fly ash samples was selected to represent the range of composition of ashes from Illinois coals. In particular, fly ashes with high Al₂O₃ + SiO₂, high CaO, and high Fe_xO_y were chosen. To the extent possible, these fly ashes also were chosen from sites near Marseilles and other brick plants. These samples were fully characterized, and about 600 test bricks were made and tested. Laboratory test bricks were made by mixing three clay bodies (100% fireclay, 50:50 fireclay:shale, and 100% shale) with three percentage levels of each of the four fly ashes. A few tests also were performed with high-Ca fly ash that had been “washed” in a waste pond. About half of the test bricks were fired in a reducing atmosphere and half were fired in an oxidizing atmosphere. The mixtures with 30%⁺ fly ash additions were difficult to extrude, and because of lowered green strength, some of these high-fly ash test bricks broke. Scumming was a problem on shale bricks, but we have not yet determined whether and to what degree additions of fly ash exacerbated scumming problems. To see if Ca²⁺ in fly ash could capture pyritic sulfur during firing, samples of the green and fired test bricks were sent out for sulfur analyses by Marseilles Brick Company. They also performed standard water absorption tests on the test bricks.

Characterization of the raw materials showed that fly ash can be used advantageously in bricks. The advantages of fly ash over brick clays are 1) it saves the energy required to dehydroxylate or fire clay minerals, 2) it contains spherical particles and mullite crystallites that are ideal for “opening” the brick and promoting thorough firing, 3) its

mixture of mineral components gives similar ranges of refractoriness to those for clays, 4) it can be selected to give special colors or other properties that are not possible from clays, and 5) it contains lime (CaO) or portlandite (Ca[OH]₂) that will capture pyritic sulfur from clays and reduce air pollution. A processed fly ash could provide even greater benefits of these types. The disadvantages of using fly ash in bricks are 1) high levels of ash reduce plasticity to the point that extrusion becomes impossible, 2) most dry fly ashes contain excessive amounts of soluble salts such as calcium oxides and sulfates, which cause chalky deposits on the fired bricks that are called "scumming," 3) high-iron fly ashes can reduce melting points below optimum levels, and 4) fly ash sources sometimes require too much freight for them to be cost-competitive at the brick plant.

Coal samples were collected at the same time as the three standard fly ash samples. To analyze these coals, we used new chemical and mineralogical procedures developed for the IBCSP coals (Kruse *et al.*, 1995). The database for this project was expanded to include chemical and mineralogical analyses of IBCSP coals, chemical analyses of the 34 commercial coals analyzed by ³Demir *et al* (1994), and this year's research on fly ashes by ⁴DeBarr *et al* (1996).

The chemical, mineralogical, and sequential acid dissolution experiments needed for constructing a predictive model of the firing reactions of fly ashes, fireclays, and shales were completed. Pyrometric cone equivalent (PCE or melting point) determinations of 56 mixtures of fly ash and clays are being completed late this summer. Both to predict the effect of pond disposal of fly ash and to determine the composition of water soluble salts in fly ashes, a series of water extractions were performed on six fly ashes, the four standards for our tests and two samples used by ⁴DeBarr *et al* (1996) for their current ICCI research on fly ash. Five samples of fly ash mined from a disposal pond were analyzed by X-ray diffraction (XRD). This pond-washed ash will be used in a test at plant production scale. If possible, this fly ash test will be continued on a commercial scale. We also expect this fall to advise other brick plants on the closest and best local sources of fly ash, and if possible, we will schedule preliminary tests of fly ash-brick production at those sites.

The high-Ca fly ash from a waste pond for the plant-scale test may solve three problems: 1) Pond storage may wash out most of the salts that caused scumming in bricks; 2) differential settling in the pond may separate low- and high-density fly ash particles, which may have the effect of separating more and less refractory particles; 3) and perhaps most important of all, wet ash will solve dust problems at brick plants. On the negative side, these ashes may be too wet for normal handling at the brick plants and loss of Ca²⁺ will reduce or eliminate the capacity of these ashes to "scrub" pyritic sulfur from brick clays. As time allows, we intend to sample as many fly ash sources within Illinois as possible; the two fly ashes being tested by ⁴DeBarr *et al* (1996) have been added to our laboratory testing. We also plan to make one or more sets of laboratory test bricks from our four fly ashes after water washing.

Testing was continued on new shale and fireclay samples from mines that supply Marseilles Brick Company. The purpose of these analyses is to make certain that this year's brick clays are chemically unchanged and to investigate the possibility that we could

take advantage of natural variations in Marseilles's clays, *i.e.*, use higher plasticity shale with higher levels of fly ash. Sequential HCl dissolution experiments were completed on a heated fireclay, replicate shale samples, and the four standard fly ashes. These experiments gave results that demonstrated significant differences between the mixed-layered kaolinite/expandables (K/E) and kaolinite constituents of the fireclay and proved that the experimental method gives highly reproducible results. Unfortunately, sequential HCl dissolution of fly ashes fails to give the level of discrimination between components that we had expected. For this reason, we will model firing behavior of the fly ash based upon the mineralogical composition of the feed coal.

In consultation with Marseilles Brick Company, we added to our testing goals some objectives that would broaden the range of products that could be made by the Company. In all cases, these larger objectives seek to increase the extent and amount of fly ash that can be used.

The economic feasibility of using fly ash in bricks is controlled by several factors: 1) availability of a stable source of fly ash, 2) distance that fly ash must be transported to the brick plant, 3) whether cost of disposal saved by the utility is used to ship fly ash, 4) whether the utility is liable for product law suits, and 5) the extent to which the ash is processed to improve its properties. In short, feasibility is driven primarily by cost and secondarily by legalities. Because fly ash sources are relatively near brick plants, our overall judgment is that some level of commercialization is likely. The next few plant-scale tests will probably define this level.

A preprint paper entitled *Utilization of Fly Ash in Structural and Decorative Ceramic Products* was presented at the ash utilization session of the Fuel Division of the American Chemical Society Meeting, held in late March in New Orleans (Hughes *et al.*, 1996). A slide talk version of this paper entitled *Utilization of Fly Ash in Structural and Decorative Ceramic Products (with Additional Comments on New Methods We Developed To Aid This Research)* was presented at the ISGS Scientific Seminar Series in April, and at the ISGS Coal Advisory Committee Meeting in May, the slide talk and last year's ICCI poster were presented. A paper entitled *Sequential Acid Dissolution of Clay Minerals: Tracking Structural Composition* was presented in June at the annual Clay Minerals Society Meeting in Gatlinburg (TN). The basic method and two of the case studies featured in this paper were spin-offs of this ICCI project. Most of our efforts for this fall will be directed at plant-scale firing tests of fly ash-brick clay mixtures and laboratory characterization of samples from plant- and laboratory-scale testing, which in the latter case is research beyond the goals of the project.

¹Kruse, C.W., R.E. Hughes, D.M. Moore, R.D. Harvey, and J. Xu. 1994. Illinois Basin Coal Sample Program, Final Technical Report to the Illinois Coal Development Board, Center for Research on Sulfur in Coal, Carterville, IL;

²Moore, D. M., G. B. Dreher, and R. E. Hughes. 1993. New Procedure for X-ray 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.

- ³Demir, I., R.D. Harvey, R.R. Ruch, H.H. Damberger, C. Chaven, J.D. Steele, and W.T. Frankie. 1994. Characterization of Available (Marketed) Coals from Illinois Mines: Ill State Geological Survey Open File Series No. 1994-2, 16 p.
- ⁴DeBarr, J.A., D.M. Rapp, M. Rostam-Abadi, J.M. Lytle, and M.J. Rood. 1996. Valuable products from fly ash, Final Technical Report to the Illinois Coal Development Board, Center for Research on Sulfur in Coal, Carterville, IL;
- ⁵Hughes, R.E., G.B. Dreher, M. Rostam-Abadi, D. M. Moore, and P. J. DeMaris. 1995, Utilization of Fly Ash in Structural and Decorative Ceramic Products: Preprints of the Annual Meeting of the American Chemical Society, New Orleans, March 24-28, 1996,

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OBJECTIVES

The primary goal of the proposed investigation is to test the use of fly ash in fired-clay products such as bricks. This goal is achieved by three tasks, which have as their objectives:

1. the manufacture of bricks with 20% or more of fly ash;
2. the measurement of 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. the integration of results of goals 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 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 used in 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 the proposed 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 year 1 work at Colonial Brick Company. Because we lacked adequate methods of prediction, we had to resort to trial-and-error methods for our first 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 optimal levels of fly ash that could be employed. Recently this goal has been expanded to ways to help brick producers customize their products. Current testing asks how fly ash might increase the product range. 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. 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 will give an attractive solution, from an environmental and economic standpoint, to recycle fly ash to high-value marketable products.

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 Principal 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).

Background studies on using fly ash in brick manufacture are less numerous, but often focus on a local problem. Two approaches are possible. Using present-day technology in existing brick plants, additions of fly ash must be at levels that will give acceptable extrusion. Alternatively, a process could be developed that used dry-press methods and could use higher levels of fly ash (Talmy et al., 1995). 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 this region, and this could improve dispersion of the clay body during forming of bricks. If calcium in these materials is in a form that can react with pyritic sulfur during firing, fly ash may reduce SO₂ pollution, an unexpected benefit.

Although the process of forming, extruding, and drying and firing bricks is an ancient technology that seems simple, our understanding of the reactions during the firing of bricks is far from complete. This firing is controlled by the ratio of relatively refractory (high-melting-point) minerals that maintain the shape of a ceramic body to the amount of easily melted minerals that fuse and produce a steel-hard brick. A further consideration is having enough clay minerals for good extrusion, enough clay minerals for good green (unfired) strength, and enough nonclay minerals to minimize shrinkage. The preferred materials for these fired-clay products occur as underclays and roof shales associated with coals. These clays contain variable amounts of three basic mineral groups. They 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 test at Colonial Brick seemed to show the opposite). Furthermore, Marseilles Brick adds silica sand (quartz) to fireclay-rich bricks to lower the melting point and open the body during

firing. Fly ash is an ideal replacement for these quartz additions. If a manufacturer needs lighter color, greater strength, and/or increased refractoriness, a kaolinitic underclay (fireclay) is normally blended with zones from the shale. The individual minerals within mineralogical groups 1 and 2 are similar enough that the three groups probably can be used as factors in a simplified model. Furthermore, fly ash is made up of burned equivalents of these three mineral groups, so we are modeling the firing reactions of fly ash and fly ash-brick clay mixtures with the same simplifications.

In general, fly ash has a composition similar to raw materials used in brick manufacture. However, some fly ashes contain amounts of calcium (from calcite) and iron oxide (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 for by adding water in the cool-down part of the firing cycle. This hydration step was the method by which bricks known as "Chicago Commons" were manufactured. Both the color and lower melting point caused by high levels of iron are best adjusted for by increasing the quartz and/or kaolinite content of the clay/shale, or by removing magnetic Fe_xO_y from the fly ash.

Part of the uncertainty about the exact level of fly ash that should have been used at Colonial Brick in year-1 testing was the result of inadequate methods of prediction of 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 components in the feed material. The approach for task 2 was to use the fireclay and shale at Marseilles Brick Company to represent the range of compositional variation that is typical of clay raw materials in Illinois. A set of Illinois fly ash samples was selected to represent the range of composition of ashes from Illinois coals. In particular, fly ashes with high Al₂O₃ + SiO₂, high CaO, and high Fe_xO_y were chosen. To the extent possible, these fly ashes also were chosen from sites near Marseilles and other brick plants.

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 Coinvestigator 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 performed 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 1. Plant-scale Manufacturing Runs. Four fly ashes were characterized to seek a optimal raw material for the bricks manufactured at Marseilles Brick Company. Marseilles Brick Company has agreed to form and fire bricks with various levels of fly ash additions. A number of laboratory tests will be conducted on the feed fly ash, clay and shale, and on the manufactured bricks. These tests are described in the subtasks below.

Subtask 1.1. Brick manufacturing runs. About 20 tons of dry fly ash from one or more sources will be shipped to Marseilles Brick Company. The Company will plan manufacturing runs that will make about 5,000-10,000 bricks without fly ash and a similar number with 15-30% fly ash-shale mixture. A single previous run with fly ash indicated that 20% fly ash additions resulted in bricks that were within specifications. A load of bricks of each of the two compositions will be fired side-by-side in the kiln and tested. If the bricks remain well within standard specifications, a higher level of fly ash may be tested. If unexpected problems occur at 20% fly ash, a slightly lower level will be tested with the same experimental approach. For the production of fireclay brick, SO₂ emissions are a problem. One of the fly ashes will be chosen to see the extent to which the Ca²⁺ in fly ash can capture sulfur from pyrite-marcasite in the fireclay. If this fly ash provides significant sulfur capture, Marseilles Brick may be able to eliminate additions of lime that are currently required. This subtask will be completed during the second quarter of the investigation. Upon completion of each production run, the standard properties of the bricks will be evaluated.

Subtask 1.2. Standard specification tests. This subtask will be carried out by Marseilles Brick and will measure the degree of conformance of the manufactured bricks with standard market specifications. Samples with and without fly ash will be taken during firing to provide a measure of "clearing" or time required to completely oxidize the core of the bricks. Water absorption tests will be carried out on the fired products, and color will be described by comparing bricks with and without fly ash additions. Marseilles Brick also will analyze green and fired bricks to determine whether fly ash captures Sphyratic.

Subtask 1.3. Characterization. This subtask provides for the complete chemical and mineralogical characterization of the feed materials and bricks. This characterization will include determination of major and minor elements, quantitative analysis of mineral content by X-ray diffraction (XRD; Kruse, Illinois Basin Coal Sample Program, 1994), and measurement of segregation of elements in phases by methods that combine step dissolution and XRD (Moore, New Procedures for X-Ray Diffraction Characterization of Flue Gas Desulfurization (FGD) and Fluidized Bed Combustion (FBC) By-Products, 1994). The step dissolution-XRD technique will only be used on the feed materials. Because water soluble salts in the fly ashes are extremely reactive and cause scumming, a new characterization step was added, which extracts these salts and analyzes them by ICP.

Subtask 1.4. Leaching tests. This subtask will employ leach testing procedures (Dreher et al. 1993) to determine the extent to which environmentally toxic constituents in the fly ash might migrate from bricks to the environment. Batch extraction and wet-dry leaching experiments, in which a substrate is exposed to deionized water for a given time period, will be conducted using the raw fly ash, clay mix used in the brick making process, and crushed and whole bricks prepared with up to five fly ash-clay mixtures. Each solid will be analyzed chemically and mineralogically prior to extraction and leaching experiments. Depending on the number of different mixtures used and the number of bricks made, leaching tests will be modified to better estimate the potential for weathering to mobilize pollutants.

Subtask 1.5. Integration. Upon completion of the manufacturing run and characterization described in subtasks 1.1 and 1.2, 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 possible plant-scale tests 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. The general goal of task 2 is to generate methods that will make it possible to predict with greater accuracy the firing characteristics of mixtures of fly ash and brick clays and shales that represent the range of composition expected in Illinois. This task also is composed of a series of subtasks. It is anticipated that analytical subtasks for tasks 1 and 2 will be carried out at the same time.

Subtask 2.1. Background. This subtask seeks to collect the background information on the composition of Illinois fly ashes and on clays and shales used in fired-clay products manufacture. 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. Preliminary screening will be performed using the coal chemistry database of Demir et al (1994). At the beginning of year 2, we decided to collect samples of feed coal and ash from disposal ponds as an addition to this task. Generally, we also will collect gypsum and other coal combustion residues. For clays and shales, information was collected together 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– 1) clays and shales with a red-firing or "shale-type" composition (Hughes et al., 1987; Hughes et al., 1992); 2) clays with refractory or "fireclay-type" compositions (ibid., 1987 and 1992); and 3) sandier red-firing shales that are usually blended with shaley and refractory clays. Most of the information on clays and shales was compiled during the first year of the project. Because information on fly ash is harder to obtain, significant amounts of data on fly ash were entered in year 2, and this continues to be the largest impediment to fly ash utilization.

Subtask 2.2. Selecting samples. Based on the results of the background search, four fly ashes were selected, and with Marseilles's fireclay and shale, represented the range of composition encountered in Illinois. Fresh, 50-pound samples of all six materials were collected and stored at field moisture content. We collected three different fireclay and

shale samples during the year.

Subtask 2.3. Characterizing samples. This subtask provides for the complete chemical and mineralogical characterization of the selected samples. This characterization will include determination of major and minor elements, quantitative analysis of mineral content by XRD, and measurement of segregation of elements in minerals by methods that combine stepwise dissolution and XRD.

Subtask 2.4. Firing tests. About 600 test bricks were made and tested. Laboratory test bricks were made by mixing three clay bodies (100% fireclay, 50:50 fireclay:shale, and 100% shale) with three percentage levels of each of the four fly ashes and of selected mixtures of clay bodies with water-washed fly ash. About half of the test bricks were fired in a reducing atmosphere, and half were fired in an oxidizing atmosphere. The mixtures with 30%⁺ fly ash additions were difficult to extrude in the laboratory, and because of lowered green strength, some of the test bricks with abundant fly ash broke. To see if Ca²⁺ in fly ash could capture pyritic sulfur during firing, samples of the green and fired test bricks were sent out for sulfur analyses by Marseilles Brick Company. They also performed standard water absorption tests on the test bricks. Determinations of the melting temperature or pyrometric cone equivalent (PCE) were made for each of the clay bodies and for 47 mixtures, an increase over the originally proposed 30 determinations. Essentially these determinations represent all possible combinations of the feed materials. Six replicate PCE analyses were included to measure errors and "calibrate" the method. The color and integrity of each PCE sample will be described. Water absorption tests were obtained from fired bricks made in the laboratory.

Subtask 2.5. Predicting firing. The results from 2.4 will be subjected to factorial and regression analysis to obtain equations that measure the effect of additions of each of the six materials on firing behavior. The results of these computer runs also include an estimate of error, and this estimate can be used to confirm that sufficient samples were 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, Evaluation, and Technology Transfer. Task 3 involves integrating results from tasks one and two, suggesting solutions to problems encountered in plant and laboratory investigations, and informing industry on the potential for use of fly ash in the manufacture of fired-clay products. The main part of task 3 will be completed near the end of the second year of the project. However, periodic reviews of progress will include preliminary evaluations, both to correct problems in ongoing work and to inform others of progress.

Subtask 3.1. Integration and evaluation. This subtask will bring all the results together, make a preliminary evaluation of the results from an engineering- and

market-oriented point of view, and estimate the overall feasibility of using significant amounts of fly ash in fired-clay products.

Subtask 3.2. Quarterly, interim final, and final reports. The results from all phases of this project will be brought together in a final report. This report will include a description of any computer programs that are generated.

Subtask 3.3. Technology transfer. The investigators will communicate the results of this study to interested parties in the public and private sector. This transfer of information will include, but not be limited to, presentations, publications, and visits or telephone calls with industrial representatives.

RESULTS AND DISCUSSION

Selection of fly ash samples. We collected and characterized three new fly ashes this year. Taken together, the four fly ashes chosen for this work represent ashes high in Ca, Fe, and Al+Si, with an ash with average Ca:Fe:Al+Si (Table 1). We also collected the coal that was being burned to produce this year's fly ashes. Last year's fly ash for the production-scale run at Colonial Brick Company was used as a high-Al+Si standard fly ash for laboratory testing. We sampled ash from waste ponds to determine if this source of fly ash would solve any of three problems: 1) Pond storage may wash out most of the salts that caused scumming of the bricks at Colonial Brick Company; 2) differential settling in the pond may separate low- and high-density fly ash particles, which may have the effect of separating more and less refractory particles; 3) Perhaps most important of all, ash with 10-20% moisture could solve the dust problems during unloading and handling at brick plants. On the negative side, these ashes may be too wet for normal handling at the brick plants and reduction of Ca^{2+} will reduce the capacity of these ashes to "scrub" pyritic sulfur from brick clays.

As time allows, we intend to sample as many fly ash sources within Illinois as possible. This sampling will be performed as a no-cost addition to this project and during field trips for other ISGS projects. The two fly ashes being tested by DeBarr and Rapp have been added to our laboratory testing for this reason. For further laboratory testing in the near future, we also hope to resample the high-Al+Si fly ash and its feed coal.

In consultation with Marseilles Brick Company, we added to our testing goals some objectives that would broaden the range of products that could be made by the Company. In all cases, these larger objectives seek to increase the extent and amount of fly ash that can be used. An example of these additions are to test fly ash as a color additive. High-FexOy fly ashes fire to different colors than clays and shales. This also is a single, although typical example of the difference in firing effects between iron bound in clay minerals and that bound in iron oxide minerals.

Laboratory analyses of raw materials. Testing was completed on new fly ash samples, and on shale and fireclay samples from mines that supply Marseilles Brick Company

(Tables 1 and 2; Figs. 1, 2, 3, 4). The purpose of these analyses is to make certain that this year's brick clays are chemically unchanged and to investigate the possibility that we could take advantage of natural variations in Marseilles's clays, i.e., use higher plasticity shale with high levels of fly ash.

Coal samples were collected at the same time as the three standard fly ash samples (Tables 1 and 2). To analyze these coals, we used new chemical and mineralogical procedures developed for the IBCSP coals (Kruse *et al.*, 1995). The database for this project was expanded to include chemical and mineralogical analyses of IBCSP coals, chemical analyses of the 34 commercial coals analyzed by ³Demir *et al.* (1994), and this year's research on fly ashes by (⁴DeBarr *et al.*, 1996).

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Figure 1a. X-ray diffraction (XRD) traces of shale (bottom), fireclay (middle), and Al+Si-rich fly ash (top). Key: M = mullite; Q = quartz; glass hump = diffraction effect from amorphous glass; I = illite; K/E = mixed-layered kaolinite/expandables, K = kaolinite; C = chlorite; Pf = plagioclase feldspar; Kf = K-feldspar.

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Figure 1b. X-ray diffraction (XRD) traces of high-Al+Si fly ash (bottom), high-Ca fly ash (middle), and Fe-rich fly ash (top). Key: M = mullite; Q = quartz; glass hump = diffraction peak of amorphous glass; I = illite; K/E = mixed-layered kaolinite/expandables, K = kaolinite; C = chlorite; Pf = plagioclase feldspar; Kf = K-feldspar.

Table 1a. Chemical composition (wt. %) of fly ash, fireclay, shale, and brick samples.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	LOI
Shale*	64.05	16.67	6.24	0.44	1.95	3.15	1.05	1.01	4.47
Fireclay*	57.78	26.05	2.41	0.66	0.67	1.67	0.05	1.3	8.72
Shale*	61.95	17.6	6.88	0.41	2.11	3.42	0.84	0.99	4.91
shale-1	61.33	17.7	6.52	0.57	1.9	3.09	1.08	0.98	6.44
shale br-2	60.81	17.66	6.47	0.6	1.91	3.07	1.07	0.97	6.82
shale-3	59.96	18.86	6.5	0.39	2.07	3.36	1.04	0.98	6.34
fireclay-1	57.47	21.37	4.71	1.67	1.47	2.68	0.35	1.1	7.98
fireclay-2	58.27	21.49	5.06	0.78	1.38	2.35	0.47	1.11	8.15
fireclay-a	59.22	26.18	1.99	0.31	0.5	0.96	0.04	1.27	8.93
shale-b	66.38	16.81	4.96	0.32	1.95	3.22	1.3	1.03	3.52
grn brick-1	61.09	18.18	6.12	0.88	1.78	2.83	1.04	1.01	6.27
grn brick-2	62.81	17.02	5.89	0.56	1.75	2.74	1.02	0.98	6.52
brick-1	64.71	19.71	6.68	0.86	1.95	3.08	1.08	1.07	0.13
brick-2	66.44	18.61	6.39	0.65	1.96	3.05	1.07	1.04	0.19
brick-2R	66.37	18.51	6.42	0.64	1.94	3.04	1.09	1.04	0.21
ave fly ash*	51.07	18.7	17.13	3.97	0.97	2.2	1.35	0.95	2.31

Ca+fly ash*	54.49	15.22	18.76	3.88	0.77	1.72	1.27	0.87	1.62
Fe+fly ash*	29.64	12.13	47.09	4.15	0.56	1.26	0.22	0.71	2.71
fly ash-1	54.5	25.5	6.39	2.55	1.29	2.22	1.13	1.34	3.42
fly ash-2R*	54.73	25.42	6.38	2.54	1.3	2.22	1.11	1.35	3.18

Key: Samples with * = 1995-1996 Project year; samples 1, 2 = Colonial Brick 3/94 and 4/95; samples a and b = Marseilles Brick 10/94 and 6/95; fly ash 1 and 2R = high-Al+Si.

The chemical, mineralogical, and sequential acid dissolution experiments needed for constructing a predictive model of the firing reactions of fly ashes, fireclays, and shales were completed (Fig 3 and 4). This method seems a promising approach, and we have pursued its development well beyond this project. In particular, we have obtained precise compositional information on the clay minerals that make up the clays and shales, and on the water and acid soluble fractions of fly ash and fired mixtures. The data indicate which salts cause scumming, where chemical components are located within minerals, and unexpectedly, the experiments have shown that it is possible in two steps to analyze the kaolinitic layer separate from the expandable layer in K/E. The data will be further analyzed to see if we can further refine our preliminary estimates of the proportions of hematite:magnetite:magnetite in fly ashes and to determine whether these proportions vary with different feed coals or boiler types.

Testing was continued on new shale and fireclay samples from mines that supply Marseilles Brick Company. The purpose of these analyses is to make certain that this year's brick clays are chemically unchanged and to investigate the possibility that we could take advantage of natural variations in Marseilles's clays, *i.e.*, shales with higher plasticity would allow higher levels of fly ash to be used. Sequential HCl dissolution experiments were completed on a heated fireclay, replicate shale samples (Fig. 3 and 4), and the four standard fly ashes. These experiments gave results that demonstrated significant differences between the mixed-layered kaolinite/expandables (K/E) and kaolinite constituents of the fireclay and proved that the experimental method gives highly reproducible results. Unfortunately, sequential HCl dissolution of fly ashes fails to give the level of discrimination between components that we had expected. For this reason, we will model firing behavior of the fly ash based upon the mineralogical composition of the feed coal and using a "normative" recalculation of bulk chemical analyses of the fly ash.

Hi-Fe	1120	4.6	26.7	2	92.5	778	7580	91	73.9	28.5	7.8	22.3
No	Sn	Sr	Ta	Tb	Th	Tl	U	V	W	Yb	Zn	Zr
sh1	<5	102	1.3	1.1	12.5	2	1.9	66	<.7	4	84	277
fc1	<5	211	1.8	2.9	20.8	1	8.5	108	2.3	6.2	<10	297
sh2	<5	102	1.5	1.4	15.2	2	3.5	69	1.9	4.8	101	247
Hi-ALSi	10	750	1.7	3.4	24.2	2	9.3	83	3.2	6.8	230	317
Ave	9	323	1.3	1.3	16.8	3	17	199	4.4	5	590	161
Hi-Ca	10	222	1	1.8	11.9	5	18.8	376	2.2	3	493	155
Hi-Fe	12	214	1	5	12.7	3	10.8	166	2.3	12.1	1280	151

Key: Sh1, fc1, and sh2 = shale 1, fireclay 1, and shale 2; HiALSi, Ave, Hi-Ca, Hi-Fe = fly ash samples with high Al+Si content, average major-element composition, high calcium content, and high iron content.

Scanning electron micrographs (SEM) were made of the four standard fly ashes (Fig. 5). These micrographs show a large number of spherical particles with lesser numbers of irregularly shaped particles and large porous particles that are apparently unburned carbon particles. The latter contain a large number of pore-filling spherical particles. In Fe-rich fly ashes, the surface texture of iron-rich spherical particles displays large numbers of <1 μ m crystallites. These crystallites fit well with the observation from XRD that the iron oxides in these fly ashes are mostly crystalline phases, while a large percentage of the silicates seem to occur as amorphous, smooth spherical particles. The sharp images obtained for these samples suggests that the water-wash step gives us a better SEM picture of the mineral matter.

Table 2. Mineralogical percentages for standard reference samples of fireclay, shale, coal-LTAs (top), and fly ash (bottom).

Type	ClayNo	%I/S	%I	%K/E	%K	%C	%Q	%Kf	%P f	%C c	%P y	%M a
sh	3583A	10	19	12	2.7	4.4	42	0.3	9.1	0.0		
fc	3583B	22	2.5	38	7.6	0.0	26	0.0	0.0	1.3	2.4	0.5
sh	3583C	12	20	11	3.2	5.1	41	1.0	6.5	0.0		
sh	3622A	13	17	8.5	4.2	4.5	45	0.6	7.5	0.0		
fc	3622B	23	0.9	31	8.2	3.6	29	0.0	0.0	2.1	2.0	0.0
lta	3580B	28	3.0	7.3	6.7	0.0	30	0.0	1.1	0.0	20	3.7
lta	3581B	22	5.2	7.7	8.3	0.0	29	0.0	1.5	0.4	25	1.0
lta	3582B	12	4.3	5.3	7.8	0.0	15	0.0	0.9	0.0	45	9.3
	Fly ash			%gla ss		%M u	% Q			%C c	%H	%M g
fl	3538H			61		19	12			0.6	2.6	5.6
fl	3580A			66		5.9	6.3			1.3	1.9	19
fl	3581A			54		9.1	10			1.0	3.5	22
fl	3582A			14		13	5.7			0.8	11	56
fl*	3582C			31		0.0	3.9			0.2	10	54

fl*	3587A			58		14	7.1			1.5	3.3	16
fl*	3587B			61		6.4	8.9			1.4	3.1	19
fl*	3587C			67		8.7	6.5			1.0	2.3	15
fl*	3587D			64		0.0	10			1.7	4.2	20
fl*	3587E			69		6.6	6.4			1.3	2.2	14

Key: Type: sh, fc, lta, fl, fl* = shale, fireclay, LTA of coals, fly ash, and fly ash from pond, respectively; I/S = mixed-layered illite/smectite; I = illite; K/E = mixed-layered kaolinite/expandables; K = kaolinite; C = chlorite; Q = quartz; Kf = K-feldspar; Pf = plagioclase feldspar; Py = pyrite; Ma = marcasite; Mu = mullite; H = hematite; Mg = magnetite-maghemite.

Table 3. Laboratory test bricks, Wt. % fly ash (% FA) and 24 hr H₂O mixed with shale (Sh), 50:50 shale:fireclay (Sh:Fc), and fireclay (Fc) clay body.

Type	%FA-Sh	%H ₂ O-Sh	%FA-Sh:Fc	%H ₂ O-Sh:Fc	%FA-Fc	%H ₂ O-Fc
None	0	6.9	0	5.7	0	6.9
Al+Si	7.6	8.1	6.9	5.8	8	5.7
Al+Si	17	10.8	16.7	5.3	15.1	5.2
Al+Si	33.1	12.5	32	7.5	32	5.8
Ca	6.5	8.2	6	4.8	6.3	4.9
Ca	17.2	11.1	15.4	5.3	14.5	4.1
Ca	32.4	11.2	32	6.2	32.3	3.1

Ave.	7.7	6	8	6.2	7.7	7.5
Ave.	16.7	6.9	17.2	6.2	14.4	7
Ave.	31.6	7.8	31.8	6.7	31.8	6.2
Fe	9.6	10.9	8.3	5.4	9.3	5
Fe	15.6	10.2	15.3	5.6	15.1	4.5
Fe	32	12.5	32	6.6	31.6	4.7

Table 4. Concentrations of ions extracted by demineralized water from four standard fly ash samples (in mg/l).

Clay No	Chem No	Al	B	Ba	Ca	K	Li	Mg	Mo	Na	Si	Sr	V
3538H	C34927	1.5	5.1	0.32	150	5	0.28	0.04	0.33	27	2.1	1.3	0.11
3580A	C34928	1.5	14.3	0.05	204	11	0.13	4.12	0.07	45	1.7	0.67	0
3581A	C34929	4.3	17.2	0.36	252	11	0.15	4.24	0.54	71	0.43	0.73	0.03
3582A	C34930	3.6	9.9	0.17	245	26	0.22	0.06	0.55	15	0.55	0.49	0.02

Key: 3538 = high-Al+Si fly ash; 3580 = average fly ash; 3581 = high-Ca fly ash; 3582 = high-Fe fly ash.

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Figure 2a. Plot of water adsorption versus fly ash content of laboratory test bricks made of four standard fly ashes mixed with shale. (● = high-Al+Si fly ash, s = high-Ca fly ash, n = average composition fly ash, and ○ = high-Fe fly ash.)

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Figure 2b. Plot of water adsorption versus fly ash content of laboratory test bricks made of four standard fly ashes mixed with fireclay. (● = high-Al+Si fly ash, s = high-Ca fly ash, n = average composition fly ash, and ○ = high-Fe fly ash.)

Laboratory test bricks. The standard fly ash compositions represent optimal choices of materials that are close to Marseilles and relatively rich in 1) $\text{SiO}_2 + \text{Al}_2\text{O}_3$, 2) Fe_2O_3 , and 3) CaO , and 4) equal amounts of the three components (an average case; Tables 1 and 2). Characterization of these fly ashes was completed, and approximately 600 laboratory test bars of 30 compositions of fly ash with fireclay, shale, and 50:50 fireclay:shale were mixed, extruded, and fired at Marseilles Brick Company (Table 3). About half of the test bricks were fired in a reducing atmosphere. Most of the other half were fired in an oxidizing atmosphere. Because Marseilles's current shale and fireclay raw materials may cause firing problems with fly ashes, individual strata from the Company's fireclay and shale quarries were analyzed by XRD.

The mixtures with 30%⁺ fly ash additions were difficult to extrude, and because of lowered green strength, some of these high-fly ash test bricks broke. However, these problems were not encountered in last year's testing at Colonial Brick Company, and much higher levels of fly ash use may be possible on a commercial extruder. Scumming was a problem on shale bricks, but we have not yet determined whether and to what degree additions of fly ash exacerbated scumming problems. To see if Ca^{2+} in fly ash could capture pyritic sulfur during firing, samples of the green and fired test bricks were sent out for sulfur analyses by Marseilles Brick Company. They also performed standard water absorption tests on the test bricks (Figs. 2a and 2b).

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Figure 3. Plot of the XRD peak intensity ratio of the chlorite 001 to the illite 001 peaks from solid samples. This plot shows the dissolution of chlorite in 2N HCl with time. [See figure 4 for a plot of the dissolved species from chlorite.]

Pyrometric cone equivalent (PCE or melting point) determinations were made on 56 mixtures of fly ash and clays. During consolidation of the year 1 and 2 final reports, XRD determinations will be made on selected PCE samples. When time allows for a trip to a site in Kentucky, Lab® color determinations will be obtained for ground PCE samples. These results will be condensed in the ISGS Open File Series report that will be the final product of this project.

Both to predict the effect of pond disposal of fly ash and to determine the composition of water soluble salts in fly ashes, a series of water extractions were performed on the four standards for our tests (Table 4). The ICP chemical analysis of the water soluble fractions of our four fly ashes are shown in Table 4. The table shows that several trace ions are easily soluble from these ashes. Furthermore, the scumming that was observed in last year's production run and the ions leached during environmental evaluation can easily be explained by the large amount of soluble calcium in these ashes.

Five samples of fly ash mined from a disposal pond were analyzed by XRD (Table 2). This pond-washed ash will be used in a test at plant-production scale. If possible, this fly ash test or another fly ash source will be continued on a commercial scale. The high-Ca fly ash from a waste pond for the plant-scale test may solve three problems: 1) Pond storage may wash out most of the salts that caused scumming in bricks; 2) differential settling in the pond may separate low- and high-density fly ash particles, which may have the effect of separating more and less refractory particles; 3) and perhaps most important of all, wet ash will solve dust problems at brick plants. On the negative side, these ashes may be too wet for normal handling at the brick plants and loss of Ca^{2+} will reduce or eliminate the capacity of these ashes to "scrub" pyritic sulfur from brick clays. As time allows, we intend to sample as many fly ash sources within Illinois as possible. To simulate washing fly ash in a waste pond, we also made laboratory test bricks from our four water-washed fly ashes.

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Figure 4. Plot of data from sequential dissolution of two Marseilles shale samples (3583A & C). Plots are of the ionic concentration at sample time divided by ionic concentration at end of experiment. [Sample times are 6.55, 30.6, 164, and 281 hr.]

Sequential-dissolution analyses. Several sequential-dissolution experiments were completed. Figure 3 shows the decrease in intensity for the chlorite peaks in similar samples of Marseilles's shale. Figure 4 shows the concurrent dissolution of Al, Fe, Mg, and Si from chlorite in these shales. From these data, we can calculate the percent chlorite and the chemical formula of the chlorite in these samples. All XRD analyses of fly ash and LTA samples of coals are made after water washing (Table 2). We characterized a new, water-washed sample of last year's high-Al+Si fly ash, too.

Although they are incomplete, the sequential dissolution experiments on fly ash samples have revealed some interesting results. The experiments are discouraging in that all components appear to be relatively insoluble in 2N HCl. However, the X-ray diffraction (XRD) traces show the dramatic difference in composition between the ashes (Fig. 1). Our high-Al+Si fly ash is distinguished by the highest content of amorphous silicate glass, mullite, and quartz, which makes sense in view of the high aluminosilicate content of this coal [Note that the Al_2O_3 content of this fly ash is similar to that of Marseilles Brick's fireclay (Table 1)]. On the other end of the scale, the high-Fe fly ash contains so much Fe_xO_y as hematite, maghemite, and magnetite, that mullite and amorphous glass are

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Figure 5a. Scanning electron micrograph (SEM) of Al+Si-rich fly ash showing predominantly spherical particles (left) and on the right, a residual carbon particle with its pores filled with fine-grained spherical particles. Scale = 10 μm .

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Figure 5a. SEM of Fe-rich fly ash showing large spherical particle of aluminosilicate glass (left) and on the right, a large spherical particle of iron oxide; presumably, the grainy surface on this particle reflects the abundance of crystalline magnetite, hematite, and probably maghemite in these fly ashes. Scale = 10 μm .

reduced to near their detection limits by XRD. Unfortunately, high calcium content of fly ash sample 3581 is not readily apparent from XRD (Table 2). This is partly due to the fact that soluble calcium phases have been removed by water washing and probably due too to the formation of calcium-rich glasses, which are amorphous to XRD.

Figures 6a and 6b show plots of the compositions of fly ashes, brick clays, and calculated fly ashes from Demir *et al* (1994). The comparison shows that most fly ashes contain more CaO and Fe_2O_3 than do brick clays. The plots also show that the high-Al+Si fly ash standard is more similar in composition to clays than to other fly ashes.

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Figure 6a. Triangular plot of $2 X \text{Fe}_2\text{O}_3:2 X \text{Al}_2\text{O}_3:\text{SiO}_2$. Stippled area = data set of Demir *et al.* (1994); Solid symbols are fly ash compositions calculated from Demir *et al.* (1994); Δ = chemical composition of high-Al+Si fly ash; \ddagger = shale used by Marseilles Brick Co.; q = fireclay used by Marseilles Brick Co.

Sequential dissolution of Marseilles's clays produced two other unexpected results. We heated a sample of fireclay to about 400°C to dehydroxylate the kaolinitic layers in the mixed-layered kaolinite/expandables (K/E) and make those layers more soluble. We confirmed the need for this procedure in last year's work. Our results indicated that, as the kaolinitic layers dissolved, the insoluble expandable layers appear on the XRD trace as smectite. We plan follow-up experiments to confirm this result. If true, however, the sequential dissolution-XRD method will provide new data for a large number of interesting fundamental problems. In a second discovery, routine dissolution of a greenish layer within the fireclay from Marseilles also produced smectite, but the source was illite or I/S in this case. These are unlike any results of which we are aware, and they may have far-reaching importance.

The economic feasibility of using fly ash in bricks is controlled by several factors: 1) availability of a stable source of fly ash, 2) suitability of products, 3) energy saved, 4) distance that fly ash must be transported to the brick plant, 5) whether the cost-of-disposal savings is used to ship fly ash, 6) whether the utility is liable for product law suits (general problem for utilization), and 7) the extent to which the ash is processed to improve its properties. In short, feasibility is driven primarily by cost and product quality, and secondarily by legalities. Because fly ash sources are relatively near many brick plants, our overall judgment is that some level of commercialization is likely. The next few plant-scale tests will probably determine the extent of this commercialization.

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Figure 6b. Triangular plot of $3 X \text{CaO}:2 X \text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3+\text{SiO}_2$. Symbols as in figure 6a.

Presentations/Publications

A preprint paper authored by R.E. Hughes, G.B. Dreher, M. Rostam-Abadi, D.M. Moore, and P.J. DeMaris and entitled *Utilization of Fly Ash in Structural and Decorative Ceramic Products* was presented at the ash utilization session of the Fuel Division of the American Chemical Society Meeting (Hughes *et al.*, 1996). A slide talk version of this paper

entitled *Utilization of Fly Ash in Structural and Decorative Ceramic Products (with Additional Comments on New Methods We Developed To Aid This Research)* was presented at the ISGS Scientific Seminar Series in April, and, at the ISGS Coal Advisory Committee Meeting in May, the slide talk and last year's poster from the ICCI Contractor's Meeting were presented (Hughes, *et al.*, 1995). A paper entitled *Sequential Acid Dissolution of Clay Minerals: Tracking Structural Composition* was presented in June at the annual Clay Minerals Society Meeting (Hughes and Moore, 1996). The basic method and two of the case studies featured in this paper were part of this project.

CONCLUSIONS AND RECOMMENDATIONS

Characterization of the raw materials and analysis of over 600 laboratory test bricks showed that fly ash can be used advantageously in bricks. The advantages of fly ash over brick clays are 1) it saves the energy required to dehydroxylate or fire clay minerals, 2) it contains spherical particles and mullite crystallites that are ideal for "opening" the brick and promoting thorough firing, 3) its mixture of mineral components gives similar ranges of refractoriness to those for clays, 4) it can be selected to give special colors or other properties that are not possible from clays, and 5) it contains lime (CaO) or portlandite [Ca(OH)₂] that can capture pyritic sulfur from clays and reduce air pollution. A processed fly ash could provide even greater benefits of these types. The disadvantages of using fly ash in bricks are 1) high levels of ash reduce plasticity to the point that extrusion becomes impossible, 2) most dry fly ashes contain excessive amounts of soluble salts such as calcium oxides and sulfates, which cause chalky deposits on the fired bricks that are called "scumming," 3) high-iron fly ashes can reduce melting points below optimum levels, and 4) fly ash sources sometimes require too much freight for them to be cost-competitive at the brick plant.

Completion of last year's sequential dissolution experiments and a set from this quarter on fly ash samples suggested that it is impossible to extract all the amorphous glass with our current and modified protocols. Furthermore, our preliminary data indicated that the mineralogical and water-soluble composition of the feed coal is the best predictor of fly ash composition and its firing reactions. Sequential dissolution-XRD methods provide new ways to analyze LTAs of coals and brick clays, as well as a large number of industrial minerals and metals.

Testing continued on new shale and fireclay samples from mines that supply Marseilles Brick Company. The purpose of these analyses is to make certain that this year's brick clays are chemically unchanged and to investigate the possibility that we could take advantage of natural variations in Marseilles's clays, *i.e.*, use higher plasticity shale with high levels of fly ash. Mineralogical and chemical analysis of fly ash samples indicates that the range of fly ash compositions from Illinois coals is quite large, and some fly ashes contain about the same amount of Al₂O₃ as fireclays while other fireclays contain more Fe₂O₃ than typical shales. This range could allow brick producers to replace expensive additives and produce an expanded line of products. These advantages will be fully exploited in the next year.

Most of our efforts for the next three months will be directed at plant-scale testing at Marseilles and further analysis and modeling of the data from laboratory-scale firing tests of fly ash-brick clay mixtures. In addition, we plan to continue to sample and analyze coals and combustion byproduct samples. These analyses also will be compared to our fly ash compositions calculated from Demir *et al.* (1994) and the mineralogical analyses from the 1996-1997 ICCI project of Demir *et al.*. During plant-scale tests at Marseilles, we will continue to make laboratory bricks with dry, water washed, and pre-wetted fly ashes, and the fireclay and shale used by Marseilles. Tests of standard fly ashes plus various water additions and aging or drying time will be made to see if these treatments eliminate scumming, improve forming and firing of bricks, or both. These tests will fill in gaps in our knowledge of the firing behavior of fly ash-brick clay mixtures. We also to advise other brick plants on the closest and best local sources of fly ash, and, if possible, we will schedule preliminary tests of fly ash-brick production at those sites.

More research in two or three areas would increase the likelihood that significant amounts of fly ash would be used in brick manufacture. These areas of research include investigating 1) physical and chemical modification of the fly ash at the boiler site, 2) further processing of fly ash into more and less refractory fractions, and 3) expanding the dataset for the modeling of fly ash-brick clay firing reactions. More effort should also be directed at mass balance studies that trace the fate of minerals in coal during combustion and separation into bottom ash, fly ash, scrubber, and emitted fractions.

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