EVALUATION OF PHOSPHATIC CLAY AND OTHER WASTES FOR CONSTRUCTION PRODUCTS: I. TILE

Prepared by New York State College of Ceramics
Alfred University
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Florida Institute of Phosphate Research
Bartow, Florida

December, 1986

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EVALUATION OF PHOSPHATIC CLAY AND OTHER WASTES FOR CONSTRUCTION PRODUCTS: I. TILE

FINAL REPORT

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In March 1981, the Florida Institute of Phosphate Research received a set of small briquettes and tile produced by the U.S. Bureau of Mines' Tuscaloosa Research Center from a 50:50 fly ash-phosphatic clay mixture. The tiles appeared to have excellent structural properties, and the Institute decided to fabricate and install a large number of standard-size clay-fly ash tiles in the walkway of its new headquarters building as an opportunity to advertise the potential uses of phosphatic clays. Numerous tile manufacturers throughout the Southeast were invited to run a firing of 12,000 experimental tiles, but all declined, citing problems with air pollution laws, poor ceramic properties of the mixture, and kiln contamination by colored dust and fluorine. The New York State College of Ceramics at Alfred University, however, was willing to cooperate, and under the direction of Dr. William Crandall, the tiles were manufactured and installed.

During the project, Dr. Crandall identified several characteristics of the tile that would prevent it from ready acceptance by the tile manufacturing industry: (1) the mixture was difficult to extrude with any precision, (2) the "green" tile shrank unevenly and to too great an extent during drying and firing, and (3) the tile would not accept a glaze readily. In order to overcome these problems, Dr. Crandall submitted a two-year research proposal to allow him to investigate each of the three major difficulties he observed.

Three Egyptian scientists, T.R. Boulos, W.I. Abdel-Fattah, and S.M. El-Nozahy ("Ceramic tiles from Egyptian phosphate washing refuse," Sprechsaal, 1981, 114: 194-200), reported on similar research using clay from Egyptian phosphate mines for ceramic tiles after blending with kaolin, feldspar and quartz. These investigators found that phosphate and a low Ca/P ratio in the mix caused the tiles to expand during firing, while the presence of feldspar reduced expansion. They concluded that the tile exhibited satisfactory properties for paving tile that confirm with relevant ASTM standards.

At Alfred University, Dr. Crandall conducted an extensive series of experiments on ceramic tiles formulated with different phosphatic clays from the central Florida phosphate district combined with fly ash, phosphogypsum and grog. He had some success overcoming all three problems observed during his initial experimental firing of 12,000 tiles. A body containing 55% phosphatic clay, 40% fly ash and 5% grog produced a reasonable trade-off in characteristics, improving the working properties for processing a tile in a commercial plant.
Although greater-than-desired amounts of porosity and water absorption were present, a Gerstley borate-type glaze enhanced the market value of the tile and reduced the undesirable effects that porosity would have on the final product.

In the course of this investigation there have been two undergraduate workers and eight graduate workers performing laboratory experiments related to this program. The research has yielded five undergraduate theses, which are available in the Institute's library. In addition, the first year's results of this program were reported to the annual meeting of the American Chemical Society in August 1984.
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1. INTRODUCTION

When minerals are removed from the earth to extract certain chemicals or metals, the extraction process which is used very often creates more unwanted residue (waste) than the desired product. Examples of this may be found in the waste materials generated in the production of copper, steel, aluminum, coal and fertilizer (Crandall, 1974). The waste materials generated in this manner have unpredictable chemical and physical characteristics and therefore are difficult to work into a program which will utilize them effectively. The main constituents of almost all of the waste materials are predominantly oxides which are familiar to the ceramic engineer. Clays, feldspars and quartz are the minerals found in many of the waste materials, but there are many other minerals which also come along with these common ones in unpredictable quantities. When the ceramic engineer tries to work with the wastes made up from these varying compositions, there are always compromises that have to be made in the processing methods and sometimes in the products formed. In addition to this, excessive water is often combined with the solid waste which produces a de-watering problem also.

Phosphate slime, which is a waste material formed while producing fertilizer, is no exception to problems set forth above. The research program described in this final report, deals with phosphatic clay, which is made up of very fine clay and clay-like minerals in a very dilute suspension with water. A number of investigators have dealt with these problems and have produced a number of useful products. Srimi Vason (1971) reported his work and that of the Illinois Institute of Technology Research Institute, and the success that had been obtained in producing a pellitized lightweight aggregate from the phosphatic clay. T. B. Boulos, W. I. Abdel-Futah, and S. M El-Nozahy (1981) have reported on the utilization of Egyptian phosphatic clay with kaolin, feldspar and quartz to produce satisfactory ceramic tile. Also, the Tuscaloosa Research Center of the U.S. Bureau of Mines produced some experimental ceramic tiles from a 50:50 mixture of fly ash and phosphatic clay. Based upon this background information, the Florida Institute of Phosphate Research made a request to produce 12,000 ceramic tiles from a phosphatic clay mixture. The Alfred University Research Foundation and the College of Ceramics at Alfred University fulfilled that request and delivered about 12,000 tiles (8"x4"x1/2").

The present two-year study funded by the Florida Institute of Phosphate Research has been separated into three study areas. Study Area One: Settling Pond Survey; Study Area Two: Drying and Firing Shrinkage Study; and Study Area Three: Glazing. The objective of this program has been to overcome the problems that developed in the
production of the 12,000 tiles so that the materials and the process would become more acceptable to a commercial manufacturer. The following report describes the research work in the three study areas set forth above and indicates how the process and materials have been made as compatible as possible with present commercial tile-making methods.
2. EXPERIMENTAL PROCEDURE

The experimental procedure is set forth in the three study areas: Study Area One: Settling Pond Survey; Study Area Two: Drying and Firing Shrinkage Study; and Study Area Three: Glazing.

STUDY AREA ONE: SETTLING POND SURVEY

Sample Procurement

On August 21-28, 1983, James E. Thiebaud and William B. Crandall traveled to Bartow, Florida with an Alfred University van for the purpose of meeting with personnel of the Florida Institute of Phosphate Research, surveying the settling ponds in the central Florida phosphate area and procuring sample quantities of phosphatic clay from five different geographical locations. Also, one sample of phosphogypsum was obtained from International Minerals and Chemical's New Wales chemical plant. Each of the samples was placed in a five gallon container, using care to obtain representative materials from each location. A representative from FIPR set up the visit to each location and assisted in the sample procurement. Three five gallon containers were obtained for each location. The phosphatic clay and phosphogypsum were placed in the van and returned to Alfred University where the remainder of the program was conducted.

Sample Characterization

The previous Alfred program on Florida phosphatic clay utilization used samples of clay from the Estech Silver City mine. The characterization of this Estech material was reported in two B.S. theses from Alfred by M. Hanagan and J. Bal. It has been the purpose of the present work to look at each of the new samples obtained and determine the variability among the new samples and between the new samples and the original Silver City clay.

Table 1 indicates the designation of each of the samples.
Not every test was run on each sample, but sufficient data was obtained on each to determine any significant differences that might exist.

Solids Content. Small specimens were removed from the five gallon containers, making sure that they were representative of the entire contents. Several of the samples, i.e., K, L, and M had water standing on top of the contents, so that this water had to be recombined before the specimen was removed for testing. Each specimen was weighed immediately after removal and then it was allowed to stand at temperatures of 25°C, 100°C, 210°C and 550°C. The temperature of 550°C was taken as the last drying temperature because it was just below the point at which the chemically bond water of the clay would be removed. However, gypsum (CaSO₄·2H₂O) loses the 2H₂O at about 165°C.
All of the phosphatic clay specimens had about the same shape of curve for water weight loss, with the exception of Specimen N, (Mobil, Homeland). The strength of the water bonding on this N specimen seemed to be higher than all the rest.

The phosphogypsum specimen P lost water at 25°C and 100°C from the mechanically bonded layers and above 100°C the chemically bonded water was removed. Table 2 shows the weight loss figures for each temperature.

Table 2

Weight Lost in Drying Period

(all weights taken after 30 min. at temperature)

<table>
<thead>
<tr>
<th>Sample</th>
<th>at 25°C</th>
<th>at 100°C</th>
<th>at 210°C</th>
<th>at 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>47.6%</td>
<td>80.9%</td>
<td>81.9%</td>
<td>82.8%</td>
</tr>
<tr>
<td>L</td>
<td>60.5</td>
<td>83.1</td>
<td>84.2</td>
<td>86.2</td>
</tr>
<tr>
<td>M</td>
<td>25.6</td>
<td>50.2</td>
<td>53.1</td>
<td>55.4</td>
</tr>
<tr>
<td>N</td>
<td>19.5</td>
<td>30.8</td>
<td>32.9</td>
<td>38.9</td>
</tr>
<tr>
<td>O</td>
<td>15.4</td>
<td>43.5</td>
<td>44.4</td>
<td>43.1</td>
</tr>
<tr>
<td>P</td>
<td>4.3</td>
<td>12.3</td>
<td>24.9</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Particle Size Distribution. Specimens K, L, M, N, and O were tested for particle size distribution. Table 3 represents the data taken from the particle size distribution plot.
It is necessary to substitute an average specific gravity for all of the particles present to convert the \((\text{m}^2/\text{cc})\) to \((\text{m}^2/\text{g})\). An average specific gravity for this material would be about 2.5 g/cc. The minimum theoretical porosity is the space left between the dry particles, having the distribution shown. It is important to note that the water content found for each of these specimens was far greater than the theoretical porosity, indicating highly adsorbed water layers, far exceeding the pore volume.

The information shown on Table 3 indicates a high degree of similarity in the samples. The fine particle size and the high surface area make it clear why these slimes are difficult to dry and have excessive shrinkage when made up into ceramic shapes.

**X-Ray Analysis.** All of the samples were run on the X-ray analysis system. The mineral content is quite complex, so that only the major minerals were examined in any detail. The major mineral content of the samples is shown in Table 4. Fluorapatite, quartz, montmorillonite, and attapulgite are the major minerals found in all of these samples. The order of these minerals in the table represents relative amounts of each found in that sample. Combining this information with the previous data on particle size, it is easy to see why the phosphatic clay holds so much water and is sticky when dried to a working condition.

---

**Table 3**
Characteristics of Particle Size Distributions

<table>
<thead>
<tr>
<th>Slime</th>
<th>ESA (m²/cc)*</th>
<th>um of 50 PFT⁺</th>
<th>min. Theor. Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.50</td>
<td>8.48</td>
<td>16.57</td>
</tr>
<tr>
<td>L</td>
<td>1.71</td>
<td>9.88</td>
<td>16.85</td>
</tr>
<tr>
<td>M</td>
<td>1.09</td>
<td>8.63</td>
<td>19.08</td>
</tr>
<tr>
<td>N</td>
<td>2.05</td>
<td>8.18</td>
<td>15.25</td>
</tr>
<tr>
<td>O</td>
<td>0.95</td>
<td>14.81</td>
<td>14.76</td>
</tr>
</tbody>
</table>

* Computer value of ESA (Estimated Surface Area)
⁺ Computer value of PFT (Percent Finer Than, in microns)
These minerals are arranged in the general order of amount present in the samples tested.

D.T.A. (Differential Thermal Analysis). Differential thermal analysis information was obtained on each of the slime samples. The endothermic and exothermic peaks were examined and compared to the X-ray data obtained. The D.T.A. information confirmed the presence of each of the mineral types shown by X-ray and did not add sufficient information to warrant its inclusion in this report.

I.R. Analysis (Infrared Analysis). Infrared traces were made on all phosphatic clay samples. These traces were taken from 200-4000 wave numbers. The infrared analysis added more confirmation of the mineralogical content of the samples, and could distinguish small differences in each much like the DTA information. Because no anomalies or contradictions were found, the infrared curves for each sample are not shown in this report.

Summary of Sample Characterization. The information obtained indicates small differences in the particle size distribution and mineral content. The largest difference found was in the solids content of the slime. The slime samples that were taken from waste material entering the ponds had the lowest solids content and the highest solids contents were found in the deposits which had been allowed to dry for the longest period of time. It may not be possible to account for the small variations shown in some of the older samples because of the chance of other overburden material getting into the sample in pasture lands and other farm lands. However, it is believed that these samples are representative of the type of material which would be available if utilization occurs.

<table>
<thead>
<tr>
<th>Mineralological Content*</th>
</tr>
</thead>
<tbody>
<tr>
<td>K  C-F Inc.</td>
</tr>
<tr>
<td>L  Gardinier</td>
</tr>
<tr>
<td>M  IMC</td>
</tr>
<tr>
<td>N  Mobil</td>
</tr>
<tr>
<td>O  Sanlan</td>
</tr>
</tbody>
</table>

* Note:  F = Fluorapatite  
M = Montomorillonite  
Q = Quartz  
A = Attapulgite
The remainder of the study will determine if the minor differences in the character of these slimes, allowed to settle for as much as 30 years, has any effect upon their ability to be used in a commercial ceramic product.

STUDY AREA TWO: DRYING AND FIRING - SHRINKAGE STUDY

It has been the purpose of this program to produce an unglazed red tile suitable for use inside or outside of a building in a severe weather environment. The properties that such a tile must have to be acceptable under these conditions are set forth in a series of ASTM and other tests. These tests cover only the properties of the final product, however, the manufacturer of these products must have the processing variables and economic factors in mind also if a commercial product is to be produced.

The first tiles produced in the feasibility part of this program were made from phosphatic clay and fly ash. Although 12,000 tiles were extruded, dried, fired and shipped on this project, the processing variables were difficult to control because the plastic body was so sticky and the amount of warpage obtained from the excessive shrinkage often caused cracking and unsatisfactory tile. However, the properties of the final tile produced from this mixture were quite acceptable for most applications as seen from the data shown on Table 6, Sample 1, 55% S - 45% Fly Ash. The first composition studied was with the addition of phosphogypsum to fly ash - phosphatic clay, and the second composition studied was with the addition of grog to fly ash - phosphate slime. (Grog is ground fired product - tile which is usually unacceptable for sale). The addition of phosphogypsum and grog was for the purpose of reducing drying and firing shrinkage, hopefully without increasing porosity and absorption.

Phosphatic Clay, Fly Ash, Phosphogypsum Composition

Five phosphatic clays, one fly ash and one phosphogypsum type were placed in the composition study. The weight percent of each constituent in the compositions was within the following range: phosphatic clay 55-65% flyash 10-30% and phosphogypsum 15-35%. All of the phosphatic clay samples were adjusted to 50% water content so that consistent weight data could be maintained and also to obtain a workable plastic state when all three ingredients were mixed together. The economic considerations involved in removing, transporting and using the phosphatic clay in the ceramic plant will undoubtedly dictate that this material be used in the as-received state. However, for the purposes of the study, it was important to use those phosphatic clays having a wetter as well as a drier state, than the 50% water content level. Water could be added to the Mobil and Sanlan materials with little or no loss in economic advantage, however, it would require heat for drying, and thus an economic disadvantage, if the CF or Gardinier materials were used.

The fly ash was completely dry as-received, and the phosphogypsum was dried at 100°C for all mixtures.
**Processing of Samples Containing Gypsum**  After the compositions had been weighed out, they were mixed, extruded, dried and fired.

**Mixing.** All samples were mixed in the damp plastic state. It was found that if the phosphatic clay was dried to complete dryness, it was impossible to reconstitute it into the same plastic state that it would have had if it was used in a damp stage. Also, after the phosphogypsum was dried at 100°C, it was necessary to crush and grind it to minus 30 mesh size before it could be added to the batch. After these items were performed, the batch was placed in a Read Machinery Co. Sigma blade laboratory mixer. It took 30 minutes in the mixer to produce a smooth uniform condition that would be typical of full-size plant operation.

**Extruding.** A Loomis model 232-2OL hydraulic extruder was used to produce each of the shapes used on this composition. Most of the laboratory testing was conducted on 1/2" diameter rods cut to 6" lengths. Bars 1" x 1/2" were also extruded and cut to 6" lengths. Only a few full-sized floor tiles were extruded in this development study.

**Drying.** Some of the samples were quite sensitive to the drying rate used. It was necessary to control the humidity over the sample during the drying period in much the same way that it is in a full-size plant. The rate of the water leaving the surface by evaporation should be about the same as the rate of water moving from the interior to the surface of the sample in order to avoid drying cracks.

**Firing.** Each of the sample compositions had a slightly different maturing temperature and maturing range, generally called firing temperature and firing range. In order to determine these two conditions, it was necessary to use a gradient furnace where a number of samples could be heated at one time to different final temperatures. Also, this gradient furnace could control the rate of heating over the entire heating range so that any number of heating cycles, involving heating rate changes and holding times could be studied. In the present study it was important to control the heating rate at the critical periods to remove mechanical water (100°C - 200°C), and chemically bond water and organic matter (200°C - 900°C). It is important to fire just to the proper maturing conditions and not overfire, so as to obtain the best final properties of the product.

In some cases it was necessary to do more characterization work on the mixture of raw materials using differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and irreversible thermal expansion (ITE) data to help to control the properties of the final product.

After the optimum firing conditions had been found, then six to twelve samples of each shape were fired in a separate furnace following those optimum conditions.

**Phosphatic Clay, Fly Ash, Grog Compositions**

**Mobil (N)** phosphatic clay and one fly ash were mixed with grog and placed in this composition study. The Mobil phosphatic clay was
selected as the only phosphate material for this study because it had a high solids content and would be a good representative of the group. The phosphatic clay and fly ash have a very small particle size which makes the ceramic body sticky when it is wet and shrink excessively when it dries. The phosphogypsum, being another unwanted material, was thought to have the most advantages to making a ceramic tile if it could be used. However, the large amount of sulfate in the gypsum made processing very difficult and the product was prone to effloresce.

Grog can be made from any fired ceramic product by crushing and grinding to size. When bricks or tile are not produced correctly in a ceramic plant, these unsold tile or brick can usually be crushed and ground to produce a grog. This project produced grog from fired tile made of the S composition, i.e., 55% phosphatic clay and 45% fly ash. The following section describes the procedure used and the results obtained.

Table 5 sets forth the compositions used in the phosphatic clay, fly ash and grog study.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample Type</th>
<th>Phosphatic Clay at 50% Dryness</th>
<th>Fly Ash</th>
<th>Grog</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>B</td>
<td>55%</td>
<td>40%</td>
<td>5%</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>55</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>D</td>
<td>55</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>E</td>
<td>55</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>F</td>
<td>55</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>G</td>
<td>55</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>H</td>
<td>55</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>I</td>
<td>55</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>16</td>
<td>J</td>
<td>55</td>
<td>0</td>
<td>45</td>
</tr>
</tbody>
</table>

Processing of Samples Containing Grog. After the compositions had been weighted out, they were then mixed, extruded, dried and fired in the same manner described in the previous section. The evaluation of samples containing gypsum or grog follows.
**Samples Containing Phosphogypsum** An attempt was made to reduce the undesirable processing variables in this 55% S - 45% Fly Ash composition by adding a large size particle to the batch which would be readily accessible and inexpensive in central Florida. Phosphogypsum seemed to have these desirable features, but it was unknown how the large amount of sulfate would work into the ceramic body. Samples 2 through 7 on Table 6 show the results of that evaluation. Dry and fired shrinkage along with the apparent porosity and water absorption were all reduced when phosphogypsum was added to the phosphatic clay-fly ash mixture (sample 1). It may also be seen from this table that the phosphogypsum, when added to that mixture, also brought down the firing temperature and in some cases expanded the firing range. Although the strength of sample 1 is sufficient for building applications with more than the 113 kg/cm² whole tile limit required, the strength of the tiles with phosphogypsum added were stronger. All of these desirable features would seem to make the addition of phosphogypsum look quite desirable. However, further study showed that the center of the fractured tile with phosphogypsum often had excessive uncombined gypsum material. The firing temperature for these samples was kept below 1100°C so that the sulfate could be retained in the tile and not sent up the stacks where it would become a very difficult clean-up problem for the manufacturer. By keeping the sulfate in the ceramic body, however it caused two other major problems: high thermal expansion of the body and efflorescence after exposure to water. The high thermal expansion of the ceramic body made it almost impossible to place a single-fired glaze over it, and the tendency to effloresce would cause a white deposit to form on the outside surface of the tile after alternate wetting and drying cycles. Because of these problems, a second composition study was made in an attempt to find a better solution to the problem of high shrinkage, warping and cracking in the 55% s - 45% fly ash composition.

**Samples Containing Grog** Every tile manufacturer has reject tiles which cannot be sold and are usually treated as waste material. When compared to less expensive incoming raw materials such as clay or shale, these tiles are not usually turned into grog because of the expense of crushing and grinding equipment and the additional operations. A tile plant would normally have a full range of particles to deal with as raw materials entering the plant so that the problem found here with the excessive amount of fines in the phosphatic clay and fly ash would not be usual. However, with the ready availability of the large amounts of phosphatic clay and fly ash in central Florida, and thus its very low cost, the addition of crushing and grinding equipment to a tile plant for the purpose of making grog might be acceptable.

Therefore, the technical evaluation of a grog mixture was undertaken. Because the former study had shown that there were only minor differences in the phosphate slimes and that the higher solids content slimes were generally easier to work with, the Mobil phosphatic clay was selected for inclusion in this composition study. Sample 1 tiles were crushed and ground to a smooth particle size distribution from 150 µm down. This grog was added to phosphatic clay, substituting for the fly ash as shown in Table 6. The purpose of this composition study was to determine how much grog was needed to reduce the excessive
After the same tests were run on all of these samples, it was found that a proper trade-off of properties seemed to occur after 5% of grog had been substituted for the fly ash, i.e., sample B. For example, there was a broad area of low porosity with a corresponding high bulk density for sample B as shown in Figure 1. Overfiring occurred between 1100°C and 1150°C where it may be seen that the porosity increased and the bulk density decreased. This broad firing range in temperature from about 900°C to 1070°C indicates that there is a good possibility that a manufacturer would have very few rejected tiles because of under or overfiring. It would be better to have a lower porosity than 20% as shown here, but this is one of the trade-offs that must be made in order to reduce shrinkage.

The bulk property data were taken from the gradient furnace firings which were made on all sets of compositions. Some of the compositions like D, E, and F showed very narrow firing ranges with the corresponding change in the bulk density. In these cases, there was only a 50°C temperature span which would either cause over or under firing.

After the proper firing range was determined, the rest of the samples in that composition batch were fired according to that schedule. Tiles 4" x 4" x 1/2" and 1/2" diameter x 6" long rods were produced in sufficient quantities to obtain data on these properties: dry shrinkage, fired shrinkage, whole tile fracture, modulus of rupture dry and fired, bulk density, apparent porosity, water absorption, heat rate (schedule), maturing temperature, firing range and in special cases, C/B ratio, x-ray data on fired pieces, scanning electron microscope data (EDS), and freeze and thaw data. Almost all of the property data is shown in Table 6.

General Evaluation. The properties listed above are those considered to be the most important when evaluating a new ceramic body to be used for a building product. The property data obtained and recorded on Table 6 and elsewhere in this report divide into two categories: data important for the ceramic plant working to process these materials and data which is important in the marketing and sale of the product. For example, the market, or customer, would not be interested in the shrinkage, bulk properties and firing and maturing range of the product, but would be concerned about the product's shape and size conformity, strength, and ability to withstand the elements in their local environment such as freezing and cracking and discoloration (efflorescence).

Processing Evaluation. One of the main objectives of the project was to find a way to reduce shrinkage and warpage and thus the loss of efficiency in processing. Samples 2 through 7 were the best compositions incorporating gypsum and the shrinkage was reduced over sample number 1. The rest of the processing variables for samples 2 through 7 were also quite good. The bulk properties including bulk density, apparent porosity and water absorption were acceptable. The firing rate had to be quite slow for all of the samples studied because of the amount of water and organic matter in the phosphatic clay. The maturing temperature of samples 2 through 7 were reduced because of the
BATCH B

Figure 1

Bulk Properties of Florida Phosphatic Clay
Table 6

Property Data on Best Ceramic Tile Bodies

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<tr>
<th>Sample</th>
<th>Comp. Phos. Sil %</th>
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<th>Gypsum %</th>
<th>Grog %</th>
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<th>Bulk Den. g/cc</th>
<th>App. Por. %</th>
<th>Water Absorp. %</th>
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Sample 1 was used in feasibility study
fluxing effect of the gypsum. The firing range of these samples was also acceptable, although sample 4 might experience some losses in a commercial operation. By keeping the firing temperature under 1110°C, the bulk of the sulfate was kept inside the sample so that the stack gases would not require major sulfate removal. However, the excessive amount of sulfate remaining in the sample eventually rendered these compositions unsuitable for commercial use.

Samples 8 through 10 also had less shrinkage than sample 1, but somewhat more than samples 2 through 7. Samples 11 through 16 had even less shrinkage, but the bulk properties indicate the reason why. Even at the maturing temperature, samples 11 through 16 could not sinter enough to close up the pore structure in the body. As the grog content exceeded 15% by weight of the body composition, these pre-fired particles would not allow the pores to sinter and close up, leaving an open porous microstructure. The increased grog content in samples 11 through 16 also reduced the firing range to a totally unacceptable level. Therefore, the choice of the most acceptable composition was made from the group containing 5 to 15% grog. Trade-offs had to be made at this point because there was not one single best composition. The upper limit of acceptance on water absorption is usually 7% with best values around 2% and below. Samples 9 and 10 had lower water absorption values than sample 8, but the firing ranges for samples 9 and 10 were quite small and unacceptable. Therefore, sample 8 was selected as the trade-off choice to make all of the final tests.

Marketing Evaluation. The C/B ratio is the ratio of cold (C) to boil (B) type of water absorption data and is used as an indication of the sample’s ability to withstand freezing and thawing. The C/B ratio test is used in place of the freezing and thawing test because of the degree of difficulty associated with the ASTM freezing and thawing evaluation. Samples having C/B ratios of 0.20-0.25 and below are considered to have no problems with freezing and thawing and could be given an SW rating, i.e., severe weather, meaning that the product could be used outside in northern environments. The C/B ratio for each of the samples tested was over the 0.20-0.25 safe limit making these samples questionable to receive the SW rating. Therefore, two other types of tests were conducted on samples 1 and 2 full sized tile. Sample 1 tiles, which were produced at the time of the 12,000 tile shipment and the feasibility study, were installed in a 4' x 4' outside setting on a concrete slab beneath the dripping eaves of the pilot plant where they were produced. These sample 1 tiles were put in place in the fall of 1981 and have passed through the winter at Alfred, NY since that time, i.e., winters of 1981-82, 1982-83, 1984-85, and 1985-86. These tiles have been examined after each winter exposure which has involved many freezing and thawing experiences. No chipping, cracking, or other failures have appeared on these tiles even though their C/B ratio was 0.61. This evidence would seem to indicate that not only is the sample 1 composition free from freezing and thawing failure, but also that there might be some hope that a similar tile with a similar C/B ratio might be free from failure under the same conditions. There was not time to give sample 2 the extended actual weather test in the Alfred, NY environment, so the decision was made to give this sample tile the ASTM
freezing and thawing evaluation. Sample tiles produced from composition 2 have been given 35 cycles of freezing and thawing according to the ASTM conditions to this date with no visible evidence of chipping, cracking or other types of failure. There has not been time to give the full days of testing as prescribed by ASTM because of the termination date of this contract and the extended period of time required for full execution of the test. However, from the evidence presented it does appear that both tile compositions 1 and 2 would be able to receive the SW rating as indicated by the ASTM test. It should also be noted that both unglazed tile and glazed tile with number 106 glaze were entered into this test and both have passed 35 cycles out of the required 50 cycles.

Strength was measured in two moduli of rupture (MOR), dry MOR and fired MOR tests, and one on whole tiles. The dry strength MOR values are really for processing information and are an indication of how durable the tiles are in the operation up to the final firing. All tiles tested are strong enough to survive the process. The fired MOR and whole tile strengths are used more for marketing the tile as an indication of their survival rate at the installation site before and after their placement. Sample 1 has a higher fired MOR value than sample 2 and would survive the placement and use as floor tile a little better. However, both compositions had a whole tile fracture strength well above 113 kg (250 lbs) required for the whole specification and thus more than meet the strength requirement.

An efflorescence test is another market requirement that must be met. If a white patina coats the tile during the firing of the piece, it is generally called a scum. This scum may be caused by some volatile substance either in the firing atmosphere or in the tile; scum should not be confused with this efflorescence. Tiles that come through the firing operation without discoloration may develop a whitish patina on their surface after prolonged exposure to the weather, i.e., wet and dry conditions. A certain amount of this patina may be caused by the mortar between the tile, but efflorescence is caused by the leaching of calcium sulfate from the body of the tile and depositing it upon the surface after drying, leaving a white film. Efflorescence was found on the tile containing large quantities of gypsum; however, only one test out of a series of six tests showed any evidence of efflorescence in either sample 1 or 2. Therefore, efflorescence was not considered to be a major problem in either the sample 1 or 2 compositions. However, to be very sure that efflorescence would not occur in even random cases, a 1% barium carbonate addition was made to sample 2 (called B2) and duplicate tests were run on efflorescence, strength, C/B ratio and freezing and thawing. The B2 samples duplicated the values of the regular Sample 2's for strength and freezing and thawing and showed no evidence of efflorescence, indicating that if efflorescence did occur in tiles of Sample 2 composition, the barium carbonate treatment would correct it.
STUDY AREA THREE - GLAZING

Samples Containing Phosphogypsum

Several attempts were made to develop a glaze that would be accepted directly on the tile body having phosphogypsum in it. All these attempts failed because of the high coefficient of thermal expansion and the film which was left on the surface of the tiles after firing. William F. Crowley, a candidate for a B. S. degree in Ceramic Engineering at the New York State College of Ceramics, worked on this project and produced a thesis for graduation titled "The Application of a Durable Ceramic Glaze to Phosphate Waste Bodies." Crowley's work was supervised by Professor Crandall and was directed toward the solution of this problem. Although some good coatings were obtained, the general conclusion was that the two aforementioned problems made the direct glazing of a waste phosphate body containing gypsum impractical.

A different approach was also attempted which might help to create a more acceptable surface for a glaze on a waste phosphate body. Bruce D. MacLeod, a candidate for a B. S. degree in Ceramic Engineering at the New York State College of Ceramics, worked on the use of a terra sigillata seal to "block" the migration of sulfate compounds to the surface of the body. MacLeod's thesis on this subject was supervised by Professor Crandall and made a part of his graduation requirements. The terra sigillata seal made a much better surface on which to place a single-firing glaze. A number of acceptable glaze-body combinations were produced by this method. However, the high coefficient of thermal expansion still remained as a difficult problem so the best glaze "fit" could not be obtained.

After these two attempts failed, there was a small effort placed upon trying to reduce the effect of the water soluble calcium sulfate in the unglazed body so that efflorescence would not occur. Kristin Triepel, a candidate for a B. S. degree in Ceramic Engineering at the New York State College of Ceramics, worked on this project. Triepel's work was supervised by Professor Crandall and used barium carbonate and other mixed alkali silicates in an attempt to combine these compounds with the sulfate, replacing the calcium and thus producing a water insoluble product in the fired tile. The barium carbonate was the most effective in reducing the amount of efflorescence in the final tile, but the quantity of sulfate was so great that even this treatment was not completely acceptable.

Therefore, after these attempts failed to eliminate the problems associated with the phosphogypsum additions to the tile, this body composition was discontinued and a better body composition was sought.

Sample Containing Grog

The use of grog in the body to reduce the high shrinkage of the bodies containing all fine particles was found to be much more satisfactory as determined in Study Area Two. The bodies with grog were found to have a much more reasonable coefficient of thermal expansion
and had no sulfate layer on the surface so that glazes were much more acceptable.

Glazes for tile bodies generally incorporate a glassy frit in their compositions. A frit is a glass which has been formulated from 5 to 12 starting raw materials melted into a smooth glassy substance at high temperature and poured into water to cause it to fragment. This fragmented material is then ground into a powdered form, usually passing a 200 mesh size. The thermal coefficient of expansion and the fusion temperature are two of the important features of these frits. Also it is important to know whether the frit has lead in its composition or it is lead free. Many applications today call for lead-free frits. Other compounds are added to the frit, usually when the glaze is being prepared in a ball milling operation. These additions are usually added to the ball mill with the frit and are called mill additions. Very often the manufacturer of the frits supply the composition of the frits, suggested mill additions, and also technical advice or to what frit to use with certain ceramic applications. There are four or five good frit manufacturers in the U.S.A. and they are generally called upon by the tile manufacturers to assist in the technical formulation of glazes and proper fits to the body. In some cases in the larger ceramic manufacturing plants, the technical staff is competent enough to do all of the glaze formulation and even the production of frits. However, the red quarry tile industry is served by a number of small manufacturing plants that do not have full technical capabilities and they need quite a bit of assistance in setting up their first tile operation. These plants, even the larger ones, are quite reluctant to deviate very much from these formulations once a successful combination of starting materials is found to work well.

These things were kept in mind as the glazing portion of this project got underway. Frit from the Ferro Corp. was selected for the first study and after about 24 combinations of frits and mill additions were attempted on the grog-type body, it was found that Ferro #3404 frit was the most satisfactory. Table 7. sets forth the compositions of glazes studied in two different series. The first series covers the compositions utilizing frits and the second a whole new concept in glazing.

Although the #3403 Ferro frit seemed to be compatible with this body type, it was felt that there might be some improvement in the technical quality of the glaze and also a cost reduction if a less expensive substitute could be found for this frit. In the first series of glaze composition studies it was found that even when #3403 frit was used, the addition of Gerstley borate was a great improvement in obtaining better compatibility with this grog body.
| Compound         | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number | Glaze Number |
|------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Sample #         | 25           | 26           | 27           | 28           | 29           | 30           | 31           | 32           | 33           | 34           | 35           | 36           | 37           | 38           | 39           | 40           |             |             |             |             |
| Bertonite        | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            |             |             |             |             |
| Superpax         | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            | 2            |             |             |             |             |
| NY Tole          | 15           | 15           | 15           | 15           | 15           | 15           | 15           | 15           | 13           | 13           | 13           | 13           | 13           | 13           | 13           | 13           |             |             |             |             |
| Gerstley Borate  | 8            | 8            | 8            | 8            | 8            | 5            | 5            | 0            | 0            | 0            | 0            | 8            | 8            | 8            | 8            | 8            |             |             |             |             |
| Frit #3105       | -            | -            | -            | -            | 73           | 78           | 70           | 70           | -            | -            | -            | -            | -            | -            | -            | -            |             |             |             |             |
| Frit #3403       | 73           | 36           | 55           | -            | -            | -            | -            | -            | 65           | 65           | 65           | 65           | 65           | 65           | 65           | -            |             |             |             |             |
| Frit #3417       | -            | 73           | 37           | 18           | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            |             |             |             |             |
| Color Dk. Yellow | -            | -            | -            | -            | -            | -            | 6            | -            | 10           | -            | -            | -            | -            | -            | -            | -            |             |             |             |             |
| Color Lt. Yellow | -            | -            | -            | -            | -            | -            | 6            | -            | 10           | -            | -            | -            | -            | -            | -            | -            |             |             |             |             |
| Color Golden Brown | -          | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            | -            | -            | -            | -            |             |             |             |             |
| Color Golden Amber | -          | -            | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            | -            | -            | -            |             |             |             |             |
| Color Fr. Green  | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            | -            | -            | -            |             |             |             |             |
| Color De. Blue   | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            | -            | -            |             |             |             |             |
| Color Vic. Green | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            | -            |             |             |             |             |
| Color Turq. Blue | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | -            | 10           | -            | -            |             |             |             |             |

Table 7
Glaze Compositions

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Comments: XL'n XL'n XL'n XL'n good best XL'n XL'n crazed good poor poor good good poor poor poor
Gerstley borate has a composition of approximately:

- 28% $\text{B}_2\text{O}_3$
- 21% $\text{CaO}$
- 5% $\text{Na}_2\text{O}$
- 18% $\text{SiO}_2$ (shale)
- 28% LOI (loss on ignition)

The lime and borate bring down the coefficient of thermal expansion and tend to reduce the surface tension. Therefore, it was thought that perhaps this Gerstley borate could be substituted for the frit and build new glaze compositions around it. The second series of glazes starting with number 101 have these compositions. The first compositions in this second series of glazes tended to overcrystallize and crawl on the surface. Superpax was added to most of the compositions to add some crystallization to make the tile glaze more resistant to abrasion. The flint ($\text{SiO}_2$) also had about the same effect. A proper trade-off of these and other factors seemed to be obtained in composition #106, so this glaze was used to complete the rest of the glaze-tile study.

The #106 glaze was placed on each of the grog tile bodies and found to be quite acceptable for each of the required firing temperatures. As a result, the glazes could be put on the dry "green" body by spraying and they dried and fired all at once. (Single-firing was considered essential if the cost of the product was to be reduced to an acceptable level.) This #106 glaze was then placed in the final study along with body composition number 8, as shown in Tables 5 and 6. This body-glaze composition was then made in sufficient quantity to obtain full data for the rest of the glaze-body evaluation, including all of the tests for the body given in the previous section plus surface abrasion tests as set by ASTM or PEI (Porcelain Enamel Institute).

Evaluation of Glazed Samples. The addition of Gerstley borate to the frit-type glaze improved the adherence glaze numbers 25 through 40. A number of these glazes (i.e., 25, 34, 35 and 36) had smooth surfaces and only a few pin holes in the glaze. These glazes also matured during the same firing period required for the body so that they could be made into a single firing operation. An improvement was sought over these fritted glazes to reduce the surface imperfections and to find a less expensive glaze composition. Glaze compositions based upon Gerstley borate without frit were tested and found to produce an acceptable glaze which would do all of the things the fritted glaze would do and also reduce surface imperfections and cost. The most acceptable glaze in this series was number 106 and was used for the full evaluation tests.

Evaluation of sample 8 body with #106 glaze (8/106) included all of the tests which were made on the sample 2 body plus an abrasion test.
The ASTM (PEI) abrasion test was run on a commercial glazed tile produced by Mid-State and the sample produced in our laboratory. Two runs of 450 cycles each (15 minutes) were made on each tile. The commercial tile lost 0.12% of weight while the 8/106 glazed sample did not show any weight loss. There was a very slight loss in gloss in the 8/106, but a considerable loss in gloss on the commercial glaze. However, the 8/106 sample had very fine hairline cracks in the glaze tested area after testing indicating a slight imperfection in the body/glaze combination. This body-glaze combination would require some minor adjustments in composition if it were to be put in commercial use, but it would seem very close to commercial quality from all the tests conducted.
3. CONCLUSIONS

An extensive series of experiments concerning ceramic tile body and glaze compositions and test evaluations have been conducted on a number of ceramic tiles formulated with different phosphatic clays from the central Florida phosphate district, combined with fly ash, phosphogypsum or grog. The purpose of this investigation was to determine if any improvement could be made in the body composition which would decrease the shrinkage, warpage and cracking found in the sample produced for the feasibility study which contained only phosphatic clay and fly ash. A second purpose was to determine if a glaze could be found for this improved body composition which could be produced in a single firing of glaze and body combination. Some success was obtained in both objectives. A body containing 55% phosphatic clay, 40% fly ash and 5% grog produced a reasonable balance or trade-off in properties, improving the working properties for processing a tile in a commercial plant. Although a greater-than-desired amount of porosity and water absorption was present in this fired body, the marketing properties of the glazed body with a Gerstley borate-type glaze enhanced the market value of the tile and reduced the undesirable effects that porosity would have on the final product.
4. REFERENCES

