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Utilization of Phosphorus Furnace Slag in Ceramic Wall and Floor Tile



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Utilization of Phosphorus Furnace Slag in Ceramic Wall and Floor Tile

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UTILIZATION OF PHOSPHORUS FURNACE SLAG IN CERAMIC WALL AND FLOOR TILE

by

E. G. Valdez,¹ K. C. Dean,² and L. L. Warner³

ABSTRACT

Laboratory research demonstrated that ceramic wall and floor tile can be produced from electric furnace phosphorus slags composed of calcium silicates. Grinding the slag in a pebble mill, followed by magnetic removal of deleterious magnetite, produced a raw material that could be compounded and formed into wall tile by dry pressing, sintering, and glazing. The effects of process variables such as forming pressure and sintering temperature were investigated. Wall tile bodies produced by this method were comparable to commercial tile. The tiles were readily glazed to a smooth shiny finish and met ASTM Specifications C34-62 for structural clay load-bearing tile. The estimated cost of producing wall tile by this method compared favorably with the retail market value for similar wall tile. Addition of borax or other additives to the ground slag followed by dry pressing and firing likewise produced a commercial grade of floor tile.

INTRODUCTION

Approximately 4 million tons⁴ (3) of phosphate rock is mined annually in the State of Idaho and used to produce phosphoric acid, electric furnace phosphorus, and various types of phosphate fertilizers. More than half of the rock is used in making elemental phosphorus at plants of FMC Corp., Pocatello, and Monsanto Co., Soda Springs. Silica rock added as a flux in producing phosphorus by electric furnace smelting combines with impurities in the phosphate rock to produce about 2 million tons of slag annually. The slag is mainly pseudowollastonite, the alpha form of the naturally occurring mineral wollastonite. At present the slag has no commercial value and it constitutes a disposal problem.

Large tonnages of naturally occurring wollastonite are mined in this country for use by the ceramic industry. The research reported herein

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⁴ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

concerns the possibility of using pseudowollastonite slag as a substitute for naturally occurring wollastonite in producing ceramic wall and floor tile.

ACKNOWLEDGMENT

The authors acknowledge appreciation to William K. Tracy, Manager of Stylon Tile Co., Salt Lake City, Utah, for his professional advice and permission to use the plant facilities for the pilot plant tests.

DESCRIPTION OF SLAG

FMC Corp.'s phosphorus plant at Pocatello, Idaho, supplied the furnace slag which ranged in color from light gray to almost black. A microscopic examination indicated that it was chiefly pseudowollastonite, CaSiO_3 , contaminated with other calcium silicates. Sporadic metallic grains composed of chromium, vanadium, iron, nickel, copper, and phosphorus alloys were also present. A chemical analysis of the slag is presented in table 1.

TABLE 1. - Chemical Analysis of furnace slag
from FMC Corp., Pocatello, Idaho

(Weight-percent)

SiO_2	CaO	Al_2O_3	MgO	K_2O	Na_2O	MnO	FeO	S	F	P
44.8	41.7	6.2	0.75	0.9	0.5	0.3	1.4	0.4	2.8	0.8

COMPOSITION AND PROPERTIES OF CERAMIC WALL AND FLOOR TILE

Wall-tile body compositions may be varied depending upon the physical properties desired in the final product. Typical wall-tile batches contain, in weight-percent, 6 feldspar, 25 flint, 20 ball clay, and 49 kaolin (4). Bodies prepared from wollastonite contain 80 to 85 percent wollastonite, 10 to 20 percent ball clay, and a flux (8). Materials may be pressed dry or may contain up to 12 percent water. The firing cycle must be such as to produce a body that meets the following ASTM C34-62 specifications--shrinkage not to exceed 3 percent of its original size, water absorption not to exceed 16 percent, and a minimum compressive strength of 1,000 psi (1).

Essentially floor tile is prepared in the same manner as wall tile; that is, material preparation, forming, and firing. The compositions of the floor tiles vary depending on the type of product desired, but generally, contain, in weight-percent, 55 feldspar, 10 flint, and 35 clay (8). The finished product must also possess certain physical requirements as set by ASTM Specifications C57-57. Water absorption should not be greater than 4 percent, compressive strength should be at least 2,000 psi (2), and shrinkage must be consistent to produce a uniformly sized tile. Although not a requirement set by ASTM Standards, commercial-grade tiles should possess consistent properties within each batch and from batch to batch.

LABORATORY TEST PROCEDURES FOR WALL TILE

Preparation of Raw Material

As-received slag was not suitable for direct use as a tile-making raw material. Therefore, tests were made to convert the raw slag to a usable material. The initial tests involved grinding to a particle size distribution which would result in a tile with minimum shrinkage, sintering to determine the firing characteristics of the slag, and the use of additives to determine their effects on firing properties.

Effect of Particle Size

Particle size distribution affects plasticity, dry strength, porosity, shrinkage, and firing temperature. To determine the effects of particle size, 2-inch-diameter tile specimens were prepared from slag ground by stages in a pulverizer through minus 28, 48, 65, 150, and 200 mesh. Results presented in table 2 indicate that the minus 65-mesh material produced the most acceptable tile. The minus 65-mesh specimen was white and smooth and met ASTM Standards with respect to color, shrinkage, and water absorption.

TABLE 2. - Effect of particle size on sintered properties

(Firing temperature, 1,100° C)

Particle size, mesh	Shrinkage, ¹ percent	Water absorption, percent	Remarks
-28	+1.32	15.8	Grey with rough surface.
-48	+0.5	16.7	Do.
-65	0	16.1	White, smooth, with few specks.
-100	0	14.2	White, smooth with slightly more specks.
-150	-6.5	0.5	White, vitrified.
-200	-8.4	0	White and warped.

¹Plus sign indicates swelling and minus sign indicates shrinkage.

Table 3 shows the particle size distribution for the minus 65-mesh material.

TABLE 3. - Particle distribution in minus 65-mesh material

<u>Particle size,</u> <u>mesh</u>	<u>Distribution,</u> <u>weight-percent</u>
,-65 +100.....	15.0
-100 +150.....	15.0
-150 +200.....	7.1
-200 +325.....	31.8
-325.....	<u>31.1</u>
	100.0

Effect of Impurities

Preliminary firing tests revealed two distinct defects on the surface of the specimens. One was the formation of brown specks presumably caused by the oxidation of the iron present in the slag. Secondly, fusion or melting believed caused by the presence of fluorine occurred in the center of the body (7, p. 21).

Both problems were resolved. Speckling was eliminated by passing the minus 65-mesh ground slag through a wet Ferrofilter⁵ magnetic separator to decrease the iron content from 1.0 percent to between 0.05 to 0.1 percent. Subsequent tests revealed that iron concentrations greater than 0.1 percent could not be tolerated.

Since fluorine was believed to be the cause of fusion, methods were sought for its removal. The slag was leached with water and strong NaOH solutions and melted at high temperatures in an attempt to remove the fluorine. None of the procedures tried were effective in eliminating the fluorine; therefore, an alternative method for resolving the fusion problem was selected. The slag was blended with small amounts of additives such as feldspar, barium carbonate, and ball clay and kaolin in an attempt to form stable nonfluxing fluorine compounds, or alternatively, to lower the firing temperature of the body to below the fusion temperature. The results of these tests indicated that 5 percent feldspar or 3 percent barium carbonate with 15 percent ball clay or kaolin would effectively prevent fluxing at moderate firing temperatures. Barium carbonate had the additional advantage in that the resulting body had a lower firing temperature and a wider firing range.

Forming of Wall Tile Bodies

Determination of the critical parameters for forming the tile body is as important as preparing a suitable tile-making raw material in that forming pressure is a major contributory factor to the green strength of the unfired body and to the shrinkage and density of the fired tile. Forming pressure was evaluated in this research by empirically testing the green bodies to determine if they could withstand handling procedures to be encountered in commercial production and by measuring the linear shrinkage of each tile after firing.

Laboratory forming tests were conducted by pressing 80-gram samples of a damp mixture composed of 80 to 82 percent minus 65-mesh magnetically cleaned slag, 15 percent ball clay or kaolin, and 3 percent barium carbonate or 5 percent feldspar. Essentially dry pressing was done at 1,500 and 2,500 psi, respectively, in a 3- by 3-inch stainless mold with a laboratory hydraulic press to produce a 1/4-inch thick body. The bodies were then fired at 1,050° C. At 1,500 psi, the resulting bodies had sufficient green strength to withstand commercial handling; after firing, the linear shrinkage was zero, but the bodies crumbled under slight pressure and had a water absorption

⁵Reference to specific company or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

greater than 17 percent. The handling characteristics of green bodies pressed at 2,500 psi were excellent. These bodies after firing were hard, white in color, showed zero shrinkage, and the water absorption was 16.0 percent. Based upon the results, all subsequent forming was done at 2,500 psi.

Effects of Firing Temperature and Time

Firing the greenware is probably the most critical and difficult operation of the tile production cycle. Firing temperature and time determine the physical properties imparted to the product. Generally, a number of individual operations are involved. For example, the firing of the greenware produced from the phosphorus furnace slag encompassed air-drying for 24 hours, preheating for 2 hours to temperature, firing for 4 hours, and cooling to room temperature in 6 hours.

The firing temperature of the specimens varied somewhat depending on whether 5 percent feldspar or 3 percent barium carbonate was used in the mixture. Data presented in table 4 indicate that with feldspar the optimum firing temperature range was between 1,060° and 1,080° C, whereas with barium carbonate, it was between 1,020° and 1,060° C.

TABLE 4. - Effects of firing temperatures

Mix composition	Firing time, 4 hrs		
	Temperature, ° C	Water absorption, percent	Linear shrinkage, percent
Slag plus 15 percent clay and 3 percent barium carbonate.....	960	16.7	0
	1,000	16.7	0
	1,020	16.0	0
	1,060	15.7	0
	1,080	(¹)	-
Slag plus 15 percent clay and 5 percent feldspar.....	1,000	19.2	0
	1,020	16.8	0
	1,050	16.3	0
	1,060	15.5	0
	1,080	15.8	0
	1,100	(¹)	-

¹Overfired.

The effect of firing time was studied by firing specimens for different periods of time starting at 1 hour and increasing the periods by increments of 1 hour to a maximum firing period of 6 hours. Results indicated that 4 hours was the minimum time required to impart the desired physical characteristics.

Physical Testing

Testing of finished products is an essential step in production control. For the tile produced during this research, only the most significant tests were made--compressive strength, fired shrinkage, water absorption, and specific gravity. Compressive strengths for the laboratory-produced tile were measured flatwise on at least five duplicate specimens. Linear shrinkage and expansion were measured by determining the ratio of the linear dimensions of the unfired bodies to the linear dimensions of the fired bodies. Water absorption was determined by measuring the amount of water absorbed by five fired specimens boiled in water for 5 hours. The average absorption of the five specimens was used to designate the absorption for the entire lot of tiles. The apparent specific gravity of the tile, 2.9 grams per cubic centimeter, was determined by the procedure outlined by Singer and Singer (8). Specimens were visually inspected for freedom from cracks, warpage, and other types of surface defects. Table 5 shows a comparison of the ASTM physical property requirements with the range of measurements made on the laboratory-produced wall tile.

TABLE 5. - Physical property measurements

Specimen	Compressive strength, psi	Water absorption, percent	Linear shrinkage, percent
Slag plus 15 percent clay and 3 percent barium carbonate.....	3,550- 9,250	10.9-18.8	0
Slag plus 15 percent clay and 5 percent feldspar.....	5,550-11,625	12.3-19.2	0
ASTM C34-62 Specifications.....	>1,000	<16.0	<3.0

Glazing

Selected tiles were glazed with several kinds of commercial glazes to determine whether commercially acceptable tiles could be produced. For obtaining a good glaze, a white, smooth body surface is desirable. Tile produced by this research met these requirements. The glazes were applied by hand to the tiles with a 1-inch wide brush and immediately fired at temperatures between 800° and 1,000° C for 1 to 5 hours in an electrically heated muffle furnace. Glazing was not particularly a problem, as several of the glazes used were suitable when firing the tiles at 865° C for 4 hours and cooling in the furnace to 200° C, at which point the tiles were removed from the furnace and allowed to cool to room temperature.

WALL TILE PRODUCTION

The successful production of wall tile on a laboratory scale prompted a further investigation to determine if standard tiles, 4 by 4 inches, could be produced in a commercial plant. One hundred and fifty pounds of slag were ground to minus 65 mesh in a pebble mill, magnetically treated to remove most of the iron, dried, rescreened through 65 mesh to break up the lumps, and used to prepare wall tile mixtures that consisted, in weight-percent, of 82 slag,

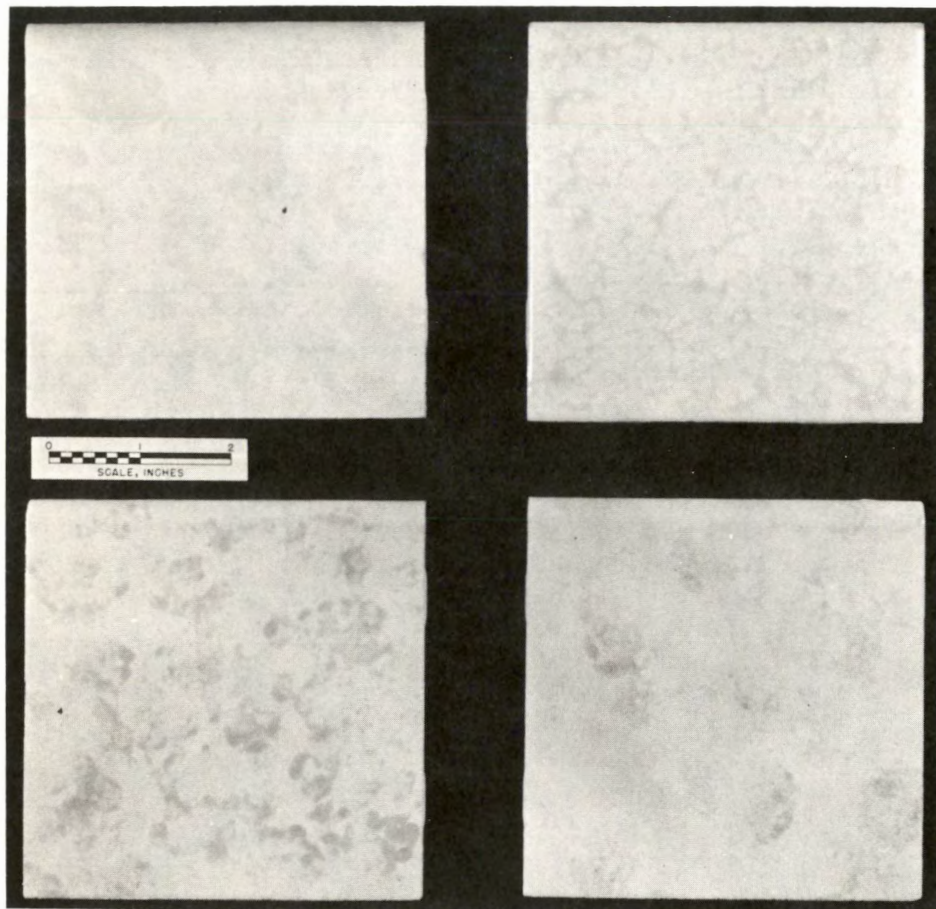


FIGURE 1. - Wall tile.

15 ball clay, and 3 barium carbonate. To facilitate forming and to produce a wall tile body with sufficient green strength, 4 percent water was added to the mixture before delivery was made to Stylon Tile Co., a Salt Lake City manufacturer, for processing.

The tiles were dry pressed at 2,500 psi and fired in three stages with a heat-up time of 2 hours, a 4-hour soaking period at a peak temperature of 982° C, and a cool-down period of 3 hours in the furnace. Although the soaking temperature normally

used by the company was about 40° C lower than desired, the resultant tiles met ASTM specifications and had excellent physical properties.

Glazing was done batchwise in an electrically heated muffle furnace by firing at 865° C for 4 hours and cooling in the furnace to about 200° C before removing the tile. Samples of the finished products are given in figure 1.

ECONOMICS OF WALL TILE PRODUCTION AND MARKETING

Based on the flowsheet shown in figure 2, a cost estimate was prepared for a hypothetical commercial tile production plant in Los Angeles or Denver, as shown in table 6. The estimated cost of about \$0.43 per square foot compares favorably with the normal retail market value of \$0.60 to \$1.00 per square foot for similar tile.

TABLE 6. - Capital and annual operating costs of a small commercial plant for producing wall tile from phosphorus slag

Capital cost:	
Feed preparation.....	\$330,800
Tile production.....	490,900
Facilities, 10 percent.....	82,200
Utilities, 12 percent.....	99,100
Total fixed capital.....	1,003,000
Working capital.....	138,000
Total.....	<u>1,141,000</u>
Direct cost:	
Materials:	
Slag, 2,500 tons, \$10.99 ¹ per ton shipment to Denver or Los Angeles.....	27,500
Kaolin, 500 tons at \$36.00 per ton.....	18,000
Feldspar, 125 tons at \$23.50 per ton.....	2,900
Bright glaze, 50,000 pounds at \$1.50.....	75,000
Total materials.....	<u>123,400</u>
Utilities:	
Electricity, 640 Mkw-hr, \$10 per Mkw-hr.....	6,400
Natural gas, 14,300 Mcf, \$0.40 per Mcf.....	5,700
Total utilities.....	<u>12,100</u>
Direct labor:	
Labor, \$4.00 per man hr.....	116,400
Supervision, \$0.150.....	17,500
	<u>133,900</u>
Plant maintenance:	
Labor.....	20,100
Supervision, \$0.200.....	4,000
Materials.....	20,100
	<u>44,200</u>
Payroll overhead, \$0.250.....	39,500
Operating supplies, \$0.200.....	8,900
	<u>48,400</u>
Total direct cost.....	<u>362,000</u>
Indirect cost:	
Administration and overhead overall, \$0.400.....	74,800
Fixed cost:	
Taxes and insurance, \$0.20.....	19,900
Depreciation, 12.5 years.....	80,300
	<u>100,200</u>
Total annual operating cost.....	537,000
Annual tile production.....	11,350,000
Production cost per square foot tile.....	0.426
Rate of return, per square foot--	
At 20 percent.....	0.561
At 25 percent.....	.601
At 30 percent.....	.643
At 35 percent.....	.686
Anticipated market value per square foot.....	\$0.60 to \$1.00

¹Includes only loading and freight costs.

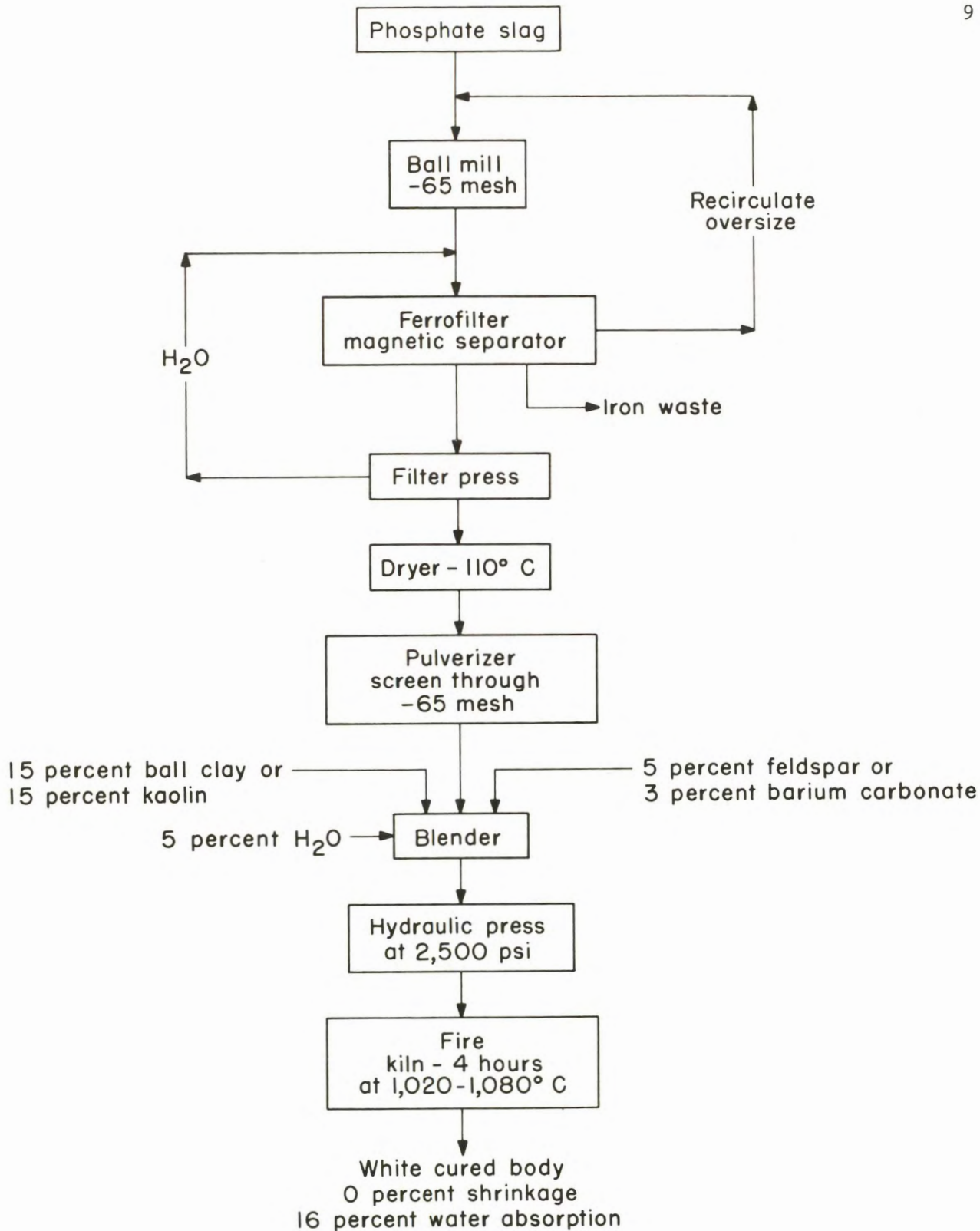


FIGURE 2. - Flow diagram of wall tile process.

FLOOR TILE

Two compositions formed at 1,600 psi were tested to determine the feasibility of making floor tile from finely ground (minus 200-mesh) slag. Two-inch-diameter specimens were prepared by the dry-press method and cured to a smooth finished product in a muffle furnace. Conclusions were that floor tile with zero water absorption, and meeting other specifications, could be produced at conditions outlined in table 7. Samples of the tiles are shown in figure 3.

TABLE 7. - Properties of floor tile

(Forming pressure, 1,600 psi)

Sample No.	Mixture		Firing		Water absorption, percent	Shrinkage, percent	Compressive strength, psi
	Composition	Per-cent	Temp, ° C	Time, hours			
S-71-B (light green)	Slag	87	} 1,100	4.0	0.0	16.8	6,660
	Bentonite	7					
	Calcium hydroxide	3					
	Borax	3					
S-7 (very light green)	{ Slag Borax	{ 95 5	} 1,075	1.75	0.0	12.5	8,340
ASTM C57-57 specifications	-	-	-	-	<4.0	Should be consistent.	>2,000

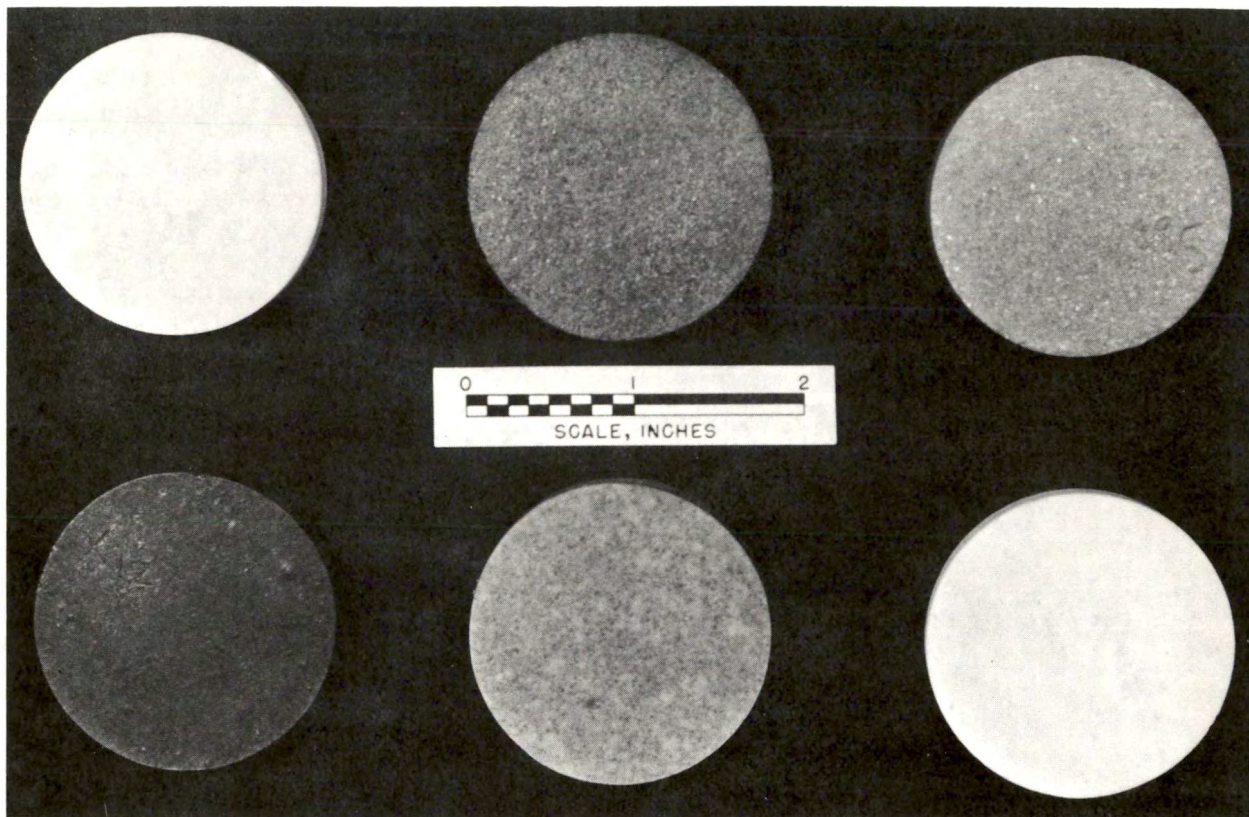


FIGURE 3. - Floor tile.

CONCLUSION

This investigation indicated that phosphorus furnace slag can be used as a raw material for producing wall tile. A production cost of about \$0.43 per square foot was estimated on the basis of laboratory data. The slag, when mixed with the proper additives, can also be used to produce a commercial grade of floor tile.

REFERENCES

1. American Society for Testing and Materials. Standard Specifications for Structural Clay Load-Bearing Wall Tile. C34-62 in 1971 Book of ASTM Standards. Part 12. Mortars; Clay and Concrete Pipe and Tile; Masonary Units; Asbestos-Cement Products. Philadelphia, Pa., 1971, pp. 37-40.
2. _____. Standard Specifications for Structural Clay Floor Tile. C57-57, in 1971 Book of ASTM Standards: Part 12, Mortars; Clay and Concrete Pipe and Tile; Masonary Units; Asbestos Cement Products. Philadelphia, Pa., 1971, pp. 53-55.
3. Carrillo, Fred V., Mary Anne McComb, and Norman S. Petersen. The Mineral Industry of Idaho. BuMines Minerals Yearbook 1968, v. 3, 1970, pp. 233-248.
4. Kirk, R. E., and D. F. Othmer. Encyclopedia of Chemical Technology, v. 3, Interscience Encyclopedia, Inc., New York, 1949, p. 547.
5. Lewis, Richard W. Phosphate Rock. BuMines Minerals Yearbook 1967, v. 1-2, 1968, pp. 949-964.
6. Lowrie, R. C., and I. B. Cutler. A Study of the Utilization of Solid Wastes in Ceramic Products. Tech. Prog. Report, Dept. of Ceramic Eng., Univ. of Utah, Salt Lake City, Utah, October 1967, p. 21.
7. Schramm, E. Problems in Whiteware Glazes. Bull. Am. Ceram. Soc., v. 17, 1938, pp. 436-446.
8. Singer, F., and S. S. Singer. Industrial Ceramics. Chemical Publishing Co., Inc., New York, 1963, p. 1455.