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A New Synthetic Stone

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Naturally occurring aluminosilicates, such as shales and slates, may be made to react with alkaline earth bases in the presence of water at slightly elevated temperatures, resulting in the formation of a new synthetic stone. X-ray analysis points to the formation of new compounds in the consolidating reaction. By properly incorporating fillers and coloring matters with the reacting materials, commercial products of various and attractive appearance have been obtained. Among these are floor and wall tile, structural building shapes, ornamental tile, vases, and the like. This article describes the procedure, manufacture, and properties of the resulting synthetic stone.

THE technology of clay (or ceramic) materials is based mainly on high-temperature reactions induced by burning. The constitution of the so-called clay substance of clays, shales, slates, etc., has in large measure baffled investigators, owing to its insolubility and to its apparent chemical inertness at low temperatures. However, following Mellor and Holdcroft (*2*), it is now generally agreed that the clay substances of the clay minerals consist of one or more aluminosilicic acids, salts of which have been prepared by Searle (*7*), Pukall (*5*), and others. Records of a number of experiments tending to confirm the existence of aluminosilicic acids, with an extensive bibliography, are given by W. and D. Asch (*1*).

Burnt clay or blast furnace slag and lime are reactive at ordinary temperatures to form pozzuolan cement, but substitution of unburned clay produces either a weak reaction or none at all. Judging from the ease with which silica reacts with lime to form the well-known sand-lime brick body, a somewhat similar reactivity might be expected in case of the aluminosilicates and alkaline earth bases to produce a structural body. In an investigation extending over a period of several years, it has been demonstrated that, under proper and quite simple conditions, such reaction takes place; the reaction products have been subjected to weathering and other tests. Fundamental patents covering this material and the process of making it have been granted (*3, 4, 6*).

Raw Materials

The knobstone shales (lower Mississippian) of western Indiana have been utilized for the most part. Other products containing aluminosilicates have also been successfully used, such as shales and slates from other and widely sepa-

Room of Synthetic Stone

Floor, walls, mantel, ceiling, and lamp base constructed of Rostone

rated sections of the country as well as the residual fly ash resulting from the combustion of powdered coal. Typical analyses of these silicates are as follows:

	Knobstone Shale	Illinois Shale	Vermont Slate
	%	%	%
SiO_2	75.3	62.02	60.3
Al_2O_3	10.62	23.78	14.28
Fe_2O_3	5.25	5.22	5.07
CaO	1.18	1.42	3.93
MgO	1.58	1.60	6.35
K_2O	2.40	0.23	....
Na_2O	0.34	0.38	....
Loss at 110° C.	0.91	1.15	0.19
Loss on ignition	4.23	6.16	6.69

A petrographic analysis of the knobstone shale is given in the following tabulation; this shale has a bedded structure and has evidently been metamorphosed from sedimentary deposits.

%	Primary
60	Clay (of kaolin group)
16	Sericite
12	Calcite
6	Quartz and feldspar sand
3	Glauconite
..	Iron oxides

In addition, the highly micaceous shales of California have been utilized. All of these contain aluminosilicates which are usually held to be feebly reactive at low temperature, and to decompose at temperatures below which they become active. For this investigation principally raw materials containing minerals with the approximate analysis of aluminodisilicates were used, but results were obtained from other members of the aluminosilicic group, on which further work is in progress.

The alkaline earth base mainly employed is lime in the commercial form of calcium hydroxide with the following analysis:

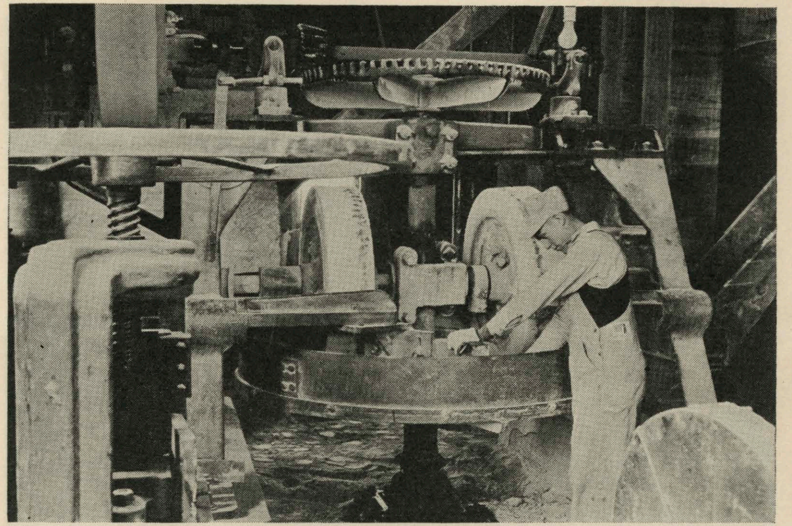
	%		%
CaO	73.48	R_2O_3	0.66
MgO	0.91	CO_2	0.22
SiO_2	1.14	H_2O	23.53

High-magnesia limes have not produced as successful reactions as the high-calcium limes; although a light burned magnesia has proved satisfactory in combination with knobstone shale.

Technical Operation or Process

The simple sequence of standard operations constituting the production process for the new materials is as follows: The shale or other aluminosilicate is ground to a fineness of 90 per cent through a 325-mesh sieve in the dry state, with a large percentage 15 to 40 microns in size. Shale or other aluminosilicate, reduced to this degree of fineness, is highly reactive, probably because of the increase in surface between the reacting solids. The finely ground mineral is thoroughly incorporated with completely slaked calcium hydroxide by means of an ordinary wet pan with revolving mullers and properly arranged scraper blades. This has been found to give the thorough incorporation which is essential for such a reaction of solid upon solid. During this mixing a specific proportion of water is slowly added to form a damp mass which, for the knobstone shale and lime mix, amounts to 18–22 per cent.

From the wet pan the moist powder is transferred to presses where the material is compressed under a pressure of approximately 2500 pounds per square inch in polished steel molds to the shape of the desired product. The molded shape is then removed from the presses and allowed to stand for 1 or 2 hours to permit any internal moisture differential to adjust itself. If this material, consolidated by pressure, is allowed to stand very long in the open air under room temperature conditions, the reaction starts slowly, and, if there is no loss of essential reacting water, an increasing hardness can be observed after a few hours. After standing for a short period upon removal from the presses, complete reaction between the aluminosilicate and an alkaline earth base is brought about by autoclaving by means of saturated steam at low pressure. The criterion of the completeness of this reaction is the disappearance of the lime, whose absence is judged by obtaining negative results for lime by the ammonium acetate and phenolphthalein tests, as well as the loss



Mixing Constituents in Wet Pan

of the characteristic lines in the x-ray pictures. It is essential in the indurating reaction that the necessary reacting water in the mass, as added during incorporation, be held within narrow limits, which are characteristic for a given shale or slate. If an excess of water is present, the mass crumbles or disintegrates; on the other hand, a deficiency results in a weak, chalky product. In either case a material of no structural value is the result. To complete the reaction in large pressed bodies requires about 2 hours in the autoclave. The material is then allowed to cool for about an hour before removal to the open air.

Analyses and Composition

On first inspection it might be thought that the reactions involved in the formation were similar to those where lime acts upon silica in the making of sand-lime brick. However,

reference to the petrographic analysis of the knobstone shale shows the presence of only a relatively small amount of free silica. X-ray analysis of this product indicates that a new compound has been formed as a result of this reaction. Work in this field is being intensively pursued, but the presumption is that the reaction product is a calcium aluminosilicate of new composition and properties. The x-ray reveals the absence of lime in the final product, when using the proper proportions of lime and shale, but does show that silica, dolomite, and other common ingredients of the original shale remain substantially inert during the process. It is likely that the aluminosilicate reacts in preference to the free silica present, under the conditions of the shorter time and the lower temperature of reaction than is utilized in obtaining a silica-lime product. Analysis shows a microcrystalline mass in which the crystals or particles present are smaller in size than is true of the crystals or particles in present-day Portland cement. Coarsely ground shale, such as is retained on a 48-mesh sieve, shows little reaction and gives an unsound product. The synthetic material exhibits considerable resistance to cold dilute acids and to a boiling solution of sodium carbonate, both of which attack the calcium aluminates.

Practical Use of Rostone[1]

The high mechanical strength that can be developed in this new material enables it to be used alone or as a matrix to bind together other materials, so that in many instances materials that are now waste, or even expensive to get rid of, can be used successfully. For example, the large piles of waste slate which accompany many quarries function well in these reactions. Likewise, for fillers or aggregates there are eminently suitable, not only the coarser particles of the slate, which in this larger subdivision do not react very energetically, but other wastes such as the irregularly shaped material which is dumped in large amounts from the quarrying of building stones. This latter assertion pertains to such waste material, whether from the marble quarries of Vermont or Tennessee, the granite quarries of the New England states, Georgia, Missouri, Colorado, or the limestone beds of Indiana. In the case of any of the foregoing, the mass takes coloring matter without difficulty, either mineral or organic. In some cases the filler may also be the coloring matter, as would be true of some of the slates. In other cases the filler and coloring matter are separate materials. For these fillers there have been technically employed many substances, most of them hitherto waste materials. The filler serves the same purpose as the aggregate in cement, and, to obtain the best consolidation of the synthetic stone, the sizing of the aggregate must be chosen with care in order to fill the

[1] The name "Rostone" has been applied to the new synthetic stone resulting from these reactions.

voids, to be exposed to the consolidating action of the Rostone reaction, and to influence the final appearance.

The coloring mineral added to the matrix colors the entire mass, and a large range of beautiful shades may be obtained. Owing to the completeness of the reaction between the base and the aluminosilicate, there remains in the Rostone either no trace or very small trace of free base; consequently these colors are permanent. All of these colored synthesized stones have been subjected during the past 5 years to natural weathering conditions such as prevail in the hard Indiana winters, both on the ground and on the roofs of buildings; in addition, artificial tests have been employed utilizing the ultra-violet ray and water. No change of color tone on the tested samples has been discernible when compared with control samples.

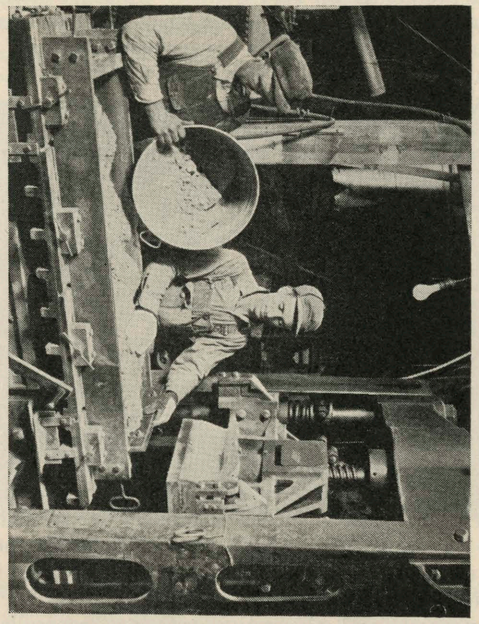
Variegated color effects, as well as solid colors, are obtained by charging into the mold of the press different colored materials. These are then irregularly mixed together to produce beautiful and unusual effects. A colored veneered stone can be produced by charging three-fourths of the mold with a plain material, filling the remainder of the mold with a colored material, and pressing both layers simultaneously, which produces a more economical stone than in the case of a solid color throughout. This procedure is applicable not only to small-size units one-half inch across, but to large sections measuring 2 feet wide, 4 or 5 feet long, and several inches thick, which are to be used for building purposes.

The material can either be used directly as a construction material in the form of brick, tile, and the like, or for certain purposes the surface can be polished or given a special roughening treatment. In this way the effect resulting from the admixture of different size constituents can be enhanced or changed by the mechanical treatment of the surface. These combined effects take Rostone out of the class of ordinary artificial blocks or tile, and enable the fabrication of products with pleasing variety in color and surface, approaching in this regard many of the naturally occurring stone, and indeed surpassing them in many respects.

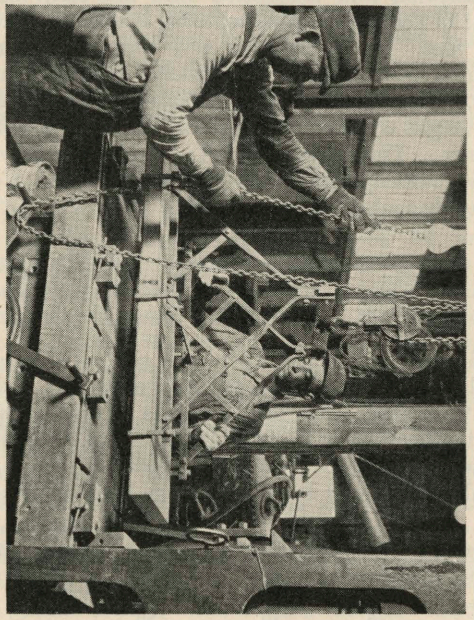
The filler and coloring matter, if desired, can be used up to around 75 per cent of the dry weight of the finished product; in such cases the general properties of the finished product are largely influenced by this filler. For example, using Indiana limestone to 75 per cent, a synthetic colored limestone is produced.

The following typical formula has been used to produce products of technical significance:

	Parts by weight
Shale	16.7
Calcium hydroxide	10.0
Water	5.3
Limestone aggregate	68.0



Loading a hand mold



Removing slabs from molds

HAND-MOLDING LARGE OUTSIDE WALL SECTIONS

Properties

The product of the reaction between Knobstone shale and calcium hydroxide shows a fine waxy texture. As normally produced it will exhibit a compressive strength of 10,000 pounds per square inch; compressive strengths up to 22,000 pounds have been attained.

Rostone with the typical formula given above and using the limestone aggregate, will have the following properties:

Compressive strength, lb. per sq. in.	6000
Flexure (modules of rupture), lb. per sq. in.	1500
Absorption (5-hour immersion at 70–75° F.; dried at 200° F.), %	9
Dorry hardness coefficient	8
Toughness, cm. (in.)	7–8 (2.8–3.1)
Comparative toughness tests, cm. (in.):	
Limestone and dolomite	3–9 (1.2–3.5)
Sandstone	4–11 (1.6–4.3)
Marble	2–6 (0.8–2.4)
Quartzite	8–21 (3.1–8.3)

The compressive strengths are the yield points of 2-inch cubes which are figured to one square inch. The flexure tests were made on pieces approximately 0.75 × 4 × 8 inches, supported on 7-inch centers and loaded in the middle. The Dorry hardness tests were made on specimens 25 mm. (1 inch) in diameter. The toughness determinations were made on standard cores, 25 mm. in diameter and 25 mm. high, drilled from larger specimens, and the figure represents the height of blow at failure of core.

Absorption and absorption rate are controllable. The weight of the consolidated material is about 130 pounds per cubic foot. In an abrasion test the wear in inches was measured under standard conditions, operating the machine for 50,000 revolutions at approximately 30 r. p. m., and with a total weight of 25 pounds pressing a leather wheel upon the specimen. This leather wheel ran at a slightly different relative velocity from that of the specimen. Comparison with other materials is:

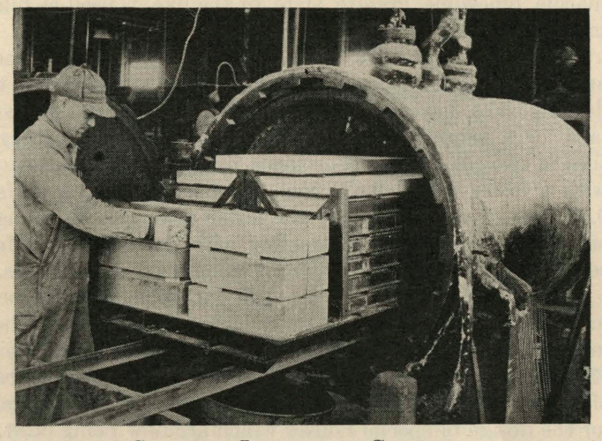
	Inch
Synthetic material (Rostone)	0.115
Slate	0.190
Limestone	0.100
Marble	0.088

A fire test was made where one side of a specimen 0.82 inch thick × 3 × 4.5 inches was exposed to heat, and temperatures were read. The cool side was in contact with air at room temperature of 75° F. At the end of 3 hours the specimen was examined. It did not show any cracks, popping, or spalling, the only apparent change being in color:

	Temperature			Temperature	
Time	Cool side	Heated Side	Time	Cool side	Heated side
Min.	° *F.*	° *F.*	*Min.*	° *F.*	° *F.*
0	75	75	60	370	1030
20	122	480	80	510	1245
40	230	780	180	...	1640

The resistance to weathering compares favorably with other building materials. Extensive outdoor and laboratory

tests conducted during the past 3 years in Indiana and Illinois have proved Rostone to be very satisfactory for outside structural purposes, withstanding freezing and thawing successfully. No efflorescence is exhibited after prolonged exposure to severe conditions.



Charging Indurating Cylinder

The fact that the material can be molded into precise shapes and even into large sizes enables the architect to fit together the individual pieces by exact engineering procedures. In this connection it should be noted that the change of shape and size of the initially pressed material when going through the consolidating reaction is insignificant. This enables a predetermined and exact size to be insured.

Practical Application

In the last few years in and around Lafayette, Ind., in numerous instances Rostone has been used for interior flooring and wall tiling. Owing to its flexibility as to color and texture, unusual effects have been obtained. Also in the past few years exposure tests have been run out of doors, giving full exposure to the elements in winter and summer. At the present time houses are being constructed, using Rostone as the exterior wall medium and also for the interior. An example is shown as a model house at A Century of Progress in Chicago. Other practical applications have been bricks, flooring slabs, inside wall tile, decorative intaglio tile, outside wall sections, hollow wall sections, vases, and other ornaments.

The bricks that have been made show good physical and weather-resisting properties and will be described more in detail in a special article. The flooring slabs are fabricated in regular designs for laying in geometric figures, or they have been made in random sizes and shapes for irregular laying. In most cases these slabs are 0.625 to 0.75 inch thick. As the material is adaptable for the incorporation of various coloring materials in the mix, these flooring slabs are made to exhibit an unusual variety of color. Also, as the Rostone matrix can receive a wide variety of filling material, these flooring slabs show a considerable range in texture, depending upon whether, for example, pulverized marble, limestone, granite, slate, or the like, is used as filling material.

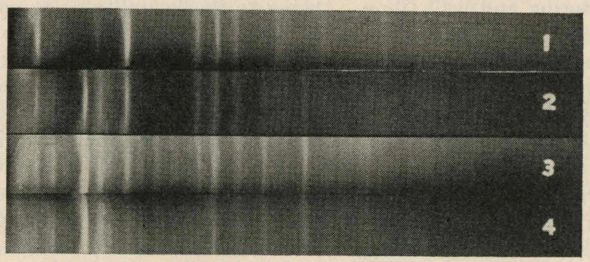
Inside wall tiles have been made of Rostone, and these are susceptible to the same artistic effects as are secured in the flooring slabs, having a soft patina finish, a natural dull surface, or a semidull polish. Handsome decorative intaglio tiles in two colors have been made by fabrication of Rostone with a lower 0.5 to 0.625 inch of one color and a surface 0.25 inch of another color; the lower color can be brought out in pleasing effect, contrasting with the original surface coloration. Such operations have been used in wall tiles.

During the last year and a half large blocks have been manufactured from Rostone for outside wall sections. These measure, when laid on the wall, 17 × 48 × 2 inches and weigh 130 pounds. Special dimensions of these wall sections can, of course, be varied, but they are chosen to fit in economically for the design of special houses which are now being built.

Various vases, boxes, and other ornaments have been fabricated from Rostone. These are unusually handsome, owing to the variation in color, texture, and surface appearance which can be secured with this synthetic stone.

Economic Value

The raw materials utilized, such as shales and slates, are found throughout the country in large undeveloped beds and in quarry wastes and dumps; consequently they can be obtained at a nominal cost. Limestone suitable for use both



X-Ray Photographs

1. Calcium hydroxide
2. Knobstone shale, 100 parts; calcium hydroxide, 100 parts; indurated 2 hours with 75 pounds steam pressure
3. Knobstone shale, 100 parts; calcium hydroxide, 60 parts; indurated one hour with 40 pounds steam pressure
4. Knobstone shale, 100 parts; calcium hydroxide, 60 parts; indurated 2 hours with 75 pounds steam pressure

as a filler and as a source of lime, is also found extensively throughout the country. The availability of the raw materials will permit low transportation cost for finished material. This, coupled with the relatively simple and consequently low cost of the chemical processing and fabrication, produces a relatively economical structural material.

Acknowledgment

Paul W. Jones and Floyd P. Wymer have made important contributions to this entire subject. W. Harold Tomlinson made the petrographic analysis of the knobstone shale. Data on the properties of Rostone were supplied by the laboratories of the R. W. Hunt Company.

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