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This issue of "Industrial Minerals Notes" deals with the study of 1) lightweight aggregate from the shale resources of the state, 2) new data on a white-burning kaolin clay from Pike County, Illinois, and 3) light-burning clay resources of LaSalle County, Illinois. The following information is based on field studies and laboratory studies in the Illinois State Geological Survey's Section on Clay Resources and Clay Mineral Technology.

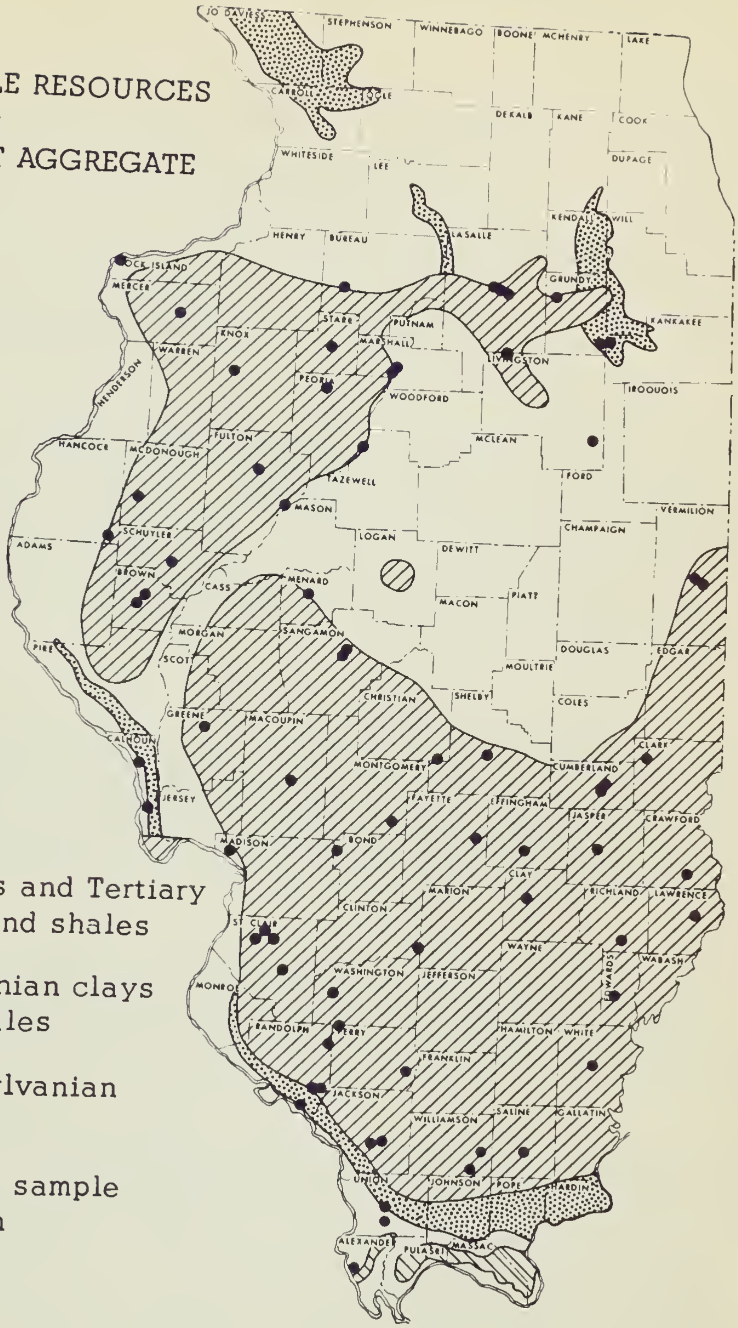
SHALES AS SOURCE MATERIAL FOR SYNTHETIC LIGHTWEIGHT AGGREGATE

W. Arthur White

Interest in synthetic lightweight aggregate from clay materials probably dates back about a century, and patent literature for lightweight aggregate from clay for use in the manufacture of artificial stone appeared at least as early as 1875, but little seems to have been done about this product until Stephen J. Hayde began production of Haydite in Kansas City about 40 years ago. Between World Wars I and II, the industry had expanded with plants in several states, two of which were in Illinois. The largest expansion in the production of lightweight aggregate occurred after World War II, during the late 1940's and early 1950's. During this time, the plants in Illinois increased to five, two with grate type kilns and three with rotary kilns.

Because of the present interest in lightweight aggregate, a resources study of clay materials was made and will be published as an Illinois State Geological Survey Circular when the details are completed. Samples collected from beds of clay materials ranging in age from Ordovician through Pleistocene were taken from clay and shale pits, coal mines, outcrops, and drill cores (fig. 1). The samples were fired in an electric kiln and the apparent specific gravities of their aggregates, which ranged from 0.35 to 1.68, were determined. Shales that produce aggregates with apparent specific gravities of less than 1.0 percent can probably be used in rotary type kilns, whereas those that produce aggregates with apparent

ILLINOIS SHALE RESOURCES
for
LIGHTWEIGHT AGGREGATE



KEY

Cretaceous and Tertiary clays and shales

Pennsylvanian clays and shales

Pre-Pennsylvanian shales

• Clay-shale sample location

specific gravities greater than 1.0 percent would probably have to be bloated in a grate-type kiln in which fuel is added to produce heat and act as a bloating agent.

Bloating Mechanism

The structure and the mineralogical and chemical compositions of clay materials were determined in order to investigate the bloating mechanism. Conditions which must be fulfilled before bloating can take place during the firing of a clay are: 1) enough of the material must fuse to fill the pore spaces so that gases being formed will be trapped; 2) the fused material must be viscous enough so that the gas does not escape by bubbling through it; and 3) some minerals or materials, or combination of minerals and materials, must be present which will dissociate and liberate a gas at the time when the mass of clay has fused to a viscous melt.

The structure in clay materials seems to have an important bearing on their bloating properties. The well laminated shales tended to bloat better than the poorly laminated shales and clays. The presence or absence of lamination in homogeneous clay material is usually a function of the orientation of the clay minerals; in well laminated shales the clay minerals lie parallel to the bedding, whereas in the poorly laminated shales and clays, the clay minerals lie in all directions or have random orientation.

Investigations were made to determine the effect of the orientation of the clay minerals on the bloating properties of clay materials. Cores of well laminated shale from drill holes were placed in the furnace and bloated. Most of the bloating was perpendicular to the bedding of the shale, an indication that most of the bloating was perpendicular to the flat dimensions of the clay minerals. There was very little bloating parallel to the bedding.

Shales were then ground and extruded through a one-inch-square die which oriented the clay minerals parallel to the sides of the die. When the extruded bricks were fired, most of the expansion was perpendicular to the sides of the die or to the flat surfaces of the clay minerals.

Slightly more water was added to the shale, so that the interior of the clay column would flow more rapidly than the exterior, which is in contact with the die. The more rapid movement of the interior of the column caused the clay minerals to orient in such a manner that the clay column, when broken, would break as cones instead of straight across as in the drier material. The clay minerals were oriented parallel to the cone surfaces. When the pieces of the clay column were fired, the bloating was parallel to the flat surfaces of the clay minerals and it appeared that expansion was taking place in all directions.

Mineralogical data indicated that the chief non-clay minerals in the sample studied were quartz, pyrite, siderite, calcite, dolomite, and

minor amounts of other minerals. The clay minerals were kaolinite, illite, chlorite, and mixed-lattice clay minerals. There was little correlation between the mineralogical composition of the shale and its bloating.

The chemical components of the shale control the viscosity and the temperature at which the shale will melt to a viscous mass. The good bloating shales had the following compositions:

SiO_2	48.33-65.01
Al_2O_3	15.48-24.81
Iron	3.42-12.75
Alkaline earths	1.59- 3.70
Alkalies	3.27- 5.74
Organic Carbon	0.49- 1.91

Carbon. - In shales, carbon occurs in two forms, inorganic and organic. The inorganic carbon occurs in minerals such as siderite ($FeCO_3$), calcite or lime ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$). All of them decompose at temperatures below the fusion points of shales and clays. The organic carbon may be adsorbed between the clay minerals, or it may occur as detrital particles in the shale. Cores of shale taken from diamond drill holes were compared as to bloating characteristics. Shale in which the organic carbon is adsorbed on or between the clay particles gave a more uniformly bloated product than shale in which organic carbon occurred as detrital particles.

The strongest aggregates come from shales which have organic contents between about 0.4 and 1.0 percent or less organic matter. Organic contents from 1 to 2 percent give very lightweight aggregates which may have many special uses such as in insulating and acoustical materials, but probably are less desirable for load-bearing materials because of their reduced strength.

Due to the open structure of clays and poorly laminated shale, the organic content would probably have to be higher than for shales in order to produce good aggregate in a rotary kiln. The greater porosity and permeability would allow the oxygen to enter more readily and oxidize the organic matter more rapidly than in a shale.

If the shale contains organic matter in amounts greater than 3 or 4 percent, the organic matter seems to inhibit the bloating. When the organic content was reduced by several hours of preheating, the shale bloated, giving an excellent product.

The alkalies and alkaline earths probably should not be much more than 10 percent. When they occur in greater amounts, they are too fluxing, causing too short a firing range and producing a liquid phase which does not have high enough viscosity to retain the gases. In the shale samples, calcium varied more than sodium, potassium, and magnesium. In a few samples the calcium was too high to form good lightweight aggregates.

Iron in shales occurs in both the ferrous and ferric states. It occurs as pyrite (FeS_2), siderite ($FeCO_3$), and limonite ($Fe_2O_3NH_2O$), and in clay mineral and other silicate mineral lattices. The iron in the clay minerals may occur in the ferrous and/or ferric states. In most of the other silicate minerals, it usually occurs in the ferrous state.

During the heating process the ferrous iron oxidizes in the clay mineral and silicate mineral lattice by splitting off the oxygen from the hydroxyl groups. The ferrous iron in pyrite and siderite must be oxidized by oxygen entering from the atmosphere of the kiln in which the shale is being fired.

After the shale has begun to fuse, no more air can enter the shale. Therefore, any remaining organic matter or sulfur in the shale must receive oxygen from some source in order to oxidize. At bloating temperatures the iron will readily give up part of its oxygen to form spinels - hercynite (Al_2FeO_4) and/or magnetite (Fe_3O_4) - or will enter the glass phase. The released oxygen will react with the organic matter and sulfur to give off CO_2, H_2O, and SO_2 or SO_2 gases, which form small bubbles in the fused mass, causing the bloating.

If there is too much organic matter in the shale, either the distillation of the organic matter keeps the interior temperature of the shale too low for a glass phase to form, or it reduces the iron before the bloating temperature has been reached.

Effect of Weathering

When shale weathers, the alternate wetting and drying causes expansion that allows oxygen to enter the shale in rainwater and/or air. The organic matter acts as a catalyst in the presence of oxygen and pyrite. The sulfur oxidizes to SO_3, which reacts with water to give H_2SO_4. The sulfuric acid in turn reacts with iron to give melanterite, and with calcite to give gypsum. The iron may be leached as iron sulfate. If there is enough calcite present to react with the sulfuric acid, the iron will remain as limonite. During the weathering process, the organic matter will be oxidized slowly to water and CO_2. If weathering continues long enough, the organic matter may be reduced to the point where it is not present in sufficient quantities to give a good bloat. This appeared to be the case in one shale pit in which the top part of the shale had been weathered for a long time whereas the bottom had been exposed only recently. The top part bloated poorly whereas the bottom part bloated into a good lightweight aggregate.

When a lightweight aggregate shale is sought for use in a rotary kiln, the deposit should not be abandoned without further investigation if the shale in the outcrop does not bloat or is a poor bloater, because the unweathered shale may contain enough organic matter to make it a good bloater. The best method for obtaining unweathered samples for testing in a large area is by drilling.

NEW DATA ON A WHITE-BURNING KAOLIN CLAY FROM PIKE COUNTY

A white-burning kaolinite clay of Pennsylvanian age was sampled in the NW$\frac{1}{4}$ SW$\frac{1}{4}$ NW$\frac{1}{4}$ sec. 10, T. 4 S., R. 5 W., in the south valley wall of Hadley Creek on north road cut near east end of east-west jog of north-south road, where 8 feet of light gray clay is exposed.

The clay, which burns a grayish white, has the following chemical composition:

SiO_2	53.11	Na_2O	0.28
TiO_2	1.98	K_2O	0.29
Al_2O_3	32.39	P_2O_5	trace
Fe_2O_3	0.36	S	0.00
FeO	0.09	H_2O	0.84
MgO	0.30	Ignition	11.49
CaO	0.13	Total	100.42

The clay contains about 20 percent quartz, 75 percent kaolinite, 3 percent mica and 2 percent anatose. Pyrometric Cone equivalent is above cone -32. The clay has good workability and moderate shrinkage. It could be used for refractories, china, pottery, face brick and wall tile.

The clay probably underlies a few thousand acres. Maximum overburden would probably be about 140 feet but much of the clay would underlie overburden of 40 to 60 feet.

CLAY RESOURCES OF LASALLE COUNTY

LaSalle County is probably one of the oldest clay producing areas in the state and today is a major one. Established companies in the area and from outside recently have shown considerable interest in sites for new clay pits. A detailed study of the light-burning clay resources of the area by Walter E. Parham this past year indicates that several thousand acres of clay close enough to the surface to be stripped could be found by prospecting.

The clays could be used for light-burning structural clay products, stoneware, refractories, tile, sewer pipe, and pottery. The results of this study will be published as an Illinois State Geological Survey circular when the details are completed.