

DETERMINING THE SUITABILITY OF CLAYS FOR THE PRODUCTION OF LIGHTWEIGHT AGGREGATES

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The usual method of evaluating a clay for its suitability for the production of a lightweight aggregate consists of subjecting a large number of samples to differing temperatures for various periods. This method is often laborious and time-consuming. The following article discusses how an understanding of certain physico-chemical processes involved in the bloating of clays will be helpful in predicting the bloating properties of a clay by simple and reliable methods for subsequent pilot plant studies.

LIGHTWEIGHT concrete is finding widespread application in many countries because of several advantages it offers over conventional concrete containing stone aggregate. By the use of lightweight concrete a considerable decrease in self-load is effected resulting in reduction in the sections of structural members. The loads on the foundations are also lessened and economy in foundation costs is achieved. A considerable expenditure on the handling of materials is saved, and construction is speeded up. Furthermore, lightweight concrete possesses a high degree of thermal insulation, sound absorption, and fire resistance. In seismic areas, the lightness of such structures adds to their safety.

Lightweight concrete is obtained either by forming pores or bubbles of air or gas within a cementitious matrix or by incorporating into the concrete an aggregate of low density. Materials which have been used to produce lightweight aggregate are varied, ranging from cereal husks to shales. The compressive strengths of such concretes vary from about 10 lb to 5000-6000 lb/in² and the densities from 10 lb to 110 lb/ft³.

Essentially, lightweight aggregates can be classified under three categories depending on the sources from which they are obtained or manufactured. They are: (i) by-products of industry, (ii) processed aggregates, (iii) natural materials.

The aggregates from by-products of industry include cinders, air-cooled slag ("slaglite" is a trade name of the product obtained from air-cooled slag), coke breeze, grog, saw-dust, rice husk, fibrous wood, and straw. The processed aggregates are obtained from fly-ash, bricks, slags, shales or clays. The well known products, "Waylite", "Celocrete", "Enslite", "Super rock", "Pottasco", "Tuff-lite" are all expanded slags. Several commercially known lightweight aggregates like "Haydite", "Cell-seal", "Gravelite" are manufactured from shales and clays. Natural materials used without any heat treatment or admixtures are pumice, scoria, volcanic cinders, breccia, tuffs and diatomite. The other natural materials are perlite and vermiculite which are used as lightweight aggregates without any admixtures.

Bloated clay aggregates

Lightweight aggregate obtained by bloating of clays is a particularly important member of the lightweight group as it offers several advantages over others. The raw material is usually found at a number of widely distributed spots and often there is a great possibility of producing it at a locality not too far from the place where it is consumed. The aggregate is quite light and has sufficiently high crushing strengths. Furthermore the production costs are dictated by the amount (in weight) of the aggregate produced, while the sale depends on the volume of the material produced. A

reduction in specific weight by even 10 per cent will be of great significance.

In establishing a new enterprise to produce lightweight aggregate from a clay or shale, the following steps are of importance: market analysis, search and testing of raw materials, a pilot plant study, evaluation of the aggregate produced by fabricating into essential end products, and plant design-cost and construction. It is imperative that the aggregate should possess certain important characteristic properties, viz, lightness in weight, strength compatible with weight, particle shape to promote good workability, low water absorption, uniform particle gradation, chemical inertness, and low production cost.

A good deal of work has been done on lightweight aggregate from clays and shales with the primary object of assessing their properties after subjecting them to heat treatment. Since research on the various physico-chemical factors responsible for the phenomenon has been very moderate, the usual procedure followed is to subject all the available material to actual tests and draw out a time-temperature relationship. This seems to be very laborious when large numbers of samples are involved. It seems preferable to have some sort of a preliminary evaluation technique which would sort out promising materials from those having no promise. Such a technique requires a clear understanding of certain basic physico-chemical factors involved in the production of lightweight aggregates. With this end in view, this article discusses some of the more essential factors that play an important role in the production of lightweight aggregates from clays.

Requirements for bloating

A clay will bloat only if it satisfies two conditions. Firstly, enough of the material should fuse to fill in the pore spaces so that the gas formed is trapped. The fused material should necessarily be viscous enough to entrap the gas that is formed as otherwise it may bubble through. Secondly, some mineral or combination of minerals must be present or formed during the heating that will dissociate and liberate a gas at the same time as the mass of clay forms a viscous melt.

The mere fact that a clay will fuse to form a viscous melt would be of no economical value unless it has a fairly low melting point preferably below 1300°C.

The fusion behaviour of a clay is determined by the proportion of SiO₂ to Al₂O₃ and the total fluxing agents. Some limits to these proportions should exist which would form a viscous melt at sufficiently low temperatures and beyond which the material may fuse at a high temperature or may fuse to form a melt not viscous enough to entrap a

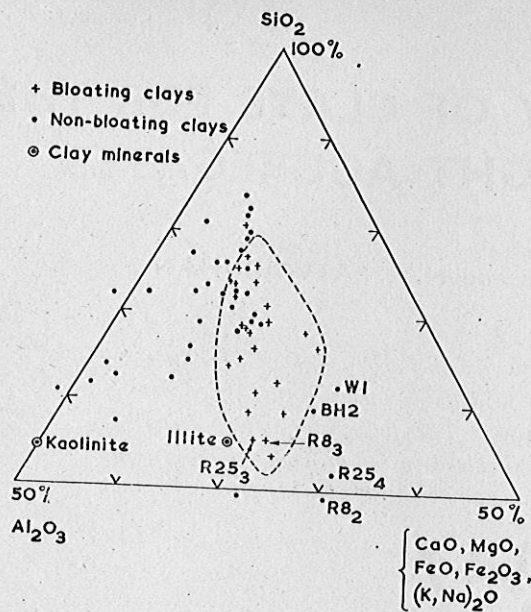


Fig 1 Composition diagram showing bloating and non-bloating clays

gas. Attempts were made to establish these limits by Conley *et al*¹ and by Riley², and the results were plotted on a composition diagram as in Fig 1. The composition diagram contains SiO_2 , Al_2O_3 and total fluxing constituents (CaO , MgO , FeO , Fe_2O_3 , $(Na, K)_2O$) as corners. Minor constituents and volatile material are excluded and the analyses are calculated to 100 per cent. The clays which bloat satisfactorily seem to be concentrated within the line (drawn as dashes) represented in the diagram. The clays representing compositions outside this line are not found to bloat. The points within the area of bloating represent those clays which will form a mass of proper viscosity but need not necessarily represent the condition for producing a gas. This obviously means that points outside this region represent certain compositions which do not produce a melt of proper viscosity though they might contain gas producing constituents. Several such clays are plotted. Some of the non-bloating clays represented on the left of the area of bloating may be deficient in fluxing constituents and may even lack a gas-producing agent. These ideas were confirmed by adding calculated amounts of SiO_2 and Al_2O_3 to the compositions which fell outside the area of bloating. The addition of Al_2O_3 and SiO_2 made them bloat satisfactorily.

Vitrification range

For the manufacture of a well-coated type of aggregate (*i.e.*, aggregate in which the granular particles have a dense non-absorptive skin and vesicular body structure) in addition to the conditions of proper viscosity, a clay should have a wide vitrification range. The actual vitrification range of clay or shale in which a satisfactory bloat could be produced represents the range between the point of incipient fusion and the point at which the viscosity is too low for bloating to take place. The lower limit of this range represents the temperature at which the eutectic composition of constituents starts to liquefy and the upper limit is fixed by the nature and the amount of fluxes. Clays containing Na and K produce highly viscous melts with a wide vitrification range, whereas those containing Mg and Ca produce a melt of low viscosity and shorten the vitrification range. Ferric oxide is believed to be an intermediate flux. Mathews found a relation between the vitrification range of clay and the proportion of $K_2O + Na_2O$ and $CaO + MgO$ fluxes.³ It was observed that, of many clays studied, those which made coated aggregates had a value more than unity for the $K_2O + Na_2O : CaO + MgO$ ratio, and the unsuitable ones

had values less than 1 and had too narrow a vitrification range.

Mineralogical composition

The importance of the mineralogical composition as a factor of a clay for producing lightweight aggregate has been stressed by Everhart.⁴ He tested about 100 clays and found that about 78 clays bloated. The predominant minerals contained in them were kaolinite and illite. In those clays which bloated, the ratio of illite to kaolinite was found to be 2.7, and in those which did not bloat it was 1.6. Accordingly, it would seem that the mineralogical composition of a clay would be an important factor in determining its suitability for the manufacture of lightweight aggregate. Illites are known to fuse between 1830–2370°F and kaolinite between 3000–3230°F. Thus, with increasing amounts of illites, a larger portion of the material would melt in the range 1830–2370°F. In actual practice it would thus be profitable to find out the illite: kaolinite ratio in a mineral containing these two, and separate the illite-rich clays from kaolinite rich clays for further study. D.T.A. provides a valuable technique for such studies. An example is shown in Figs 2 and 3.

In Fig 2 are presented the D.T.A. behaviours of illite and kaolinite. Illites show endothermic peaks at 100–200°C and at about 900°C, and an exothermic peak immediately following the third endothermic peak. The first endothermic peak is due to the loss of interlayer water, the second and third to the accompaniment of loss of water from the lattice and destruction of the illite structure respectively. The exothermic peak is probably associated with the formation of spinel. The intensities of the peaks in case of illite are low compared to those of kaolinite.

Kaolinite exhibits an endothermic peak at 550–600°C accompanying dehydration and an exothermic peak at 980°C associated with the formation of $\gamma-Al_2O_3$.

Fig 3 represents the behaviour of various mixtures of illite and kaolinite.⁶ The substitution of illite for kaolinite in mixtures is indicated quantitatively by peaks representing the reactions. The low temperature endothermic peak area is proportional to the amount of illite. The second endothermic peak area between 500–600°C also can be used to determine the per cent of illite.

The above studies of Everhart are very useful but not exhaustive as they do not take into account the kind of fluxes and their amount that are usually found in clays. The studies are not extended to admixtures of other minerals.

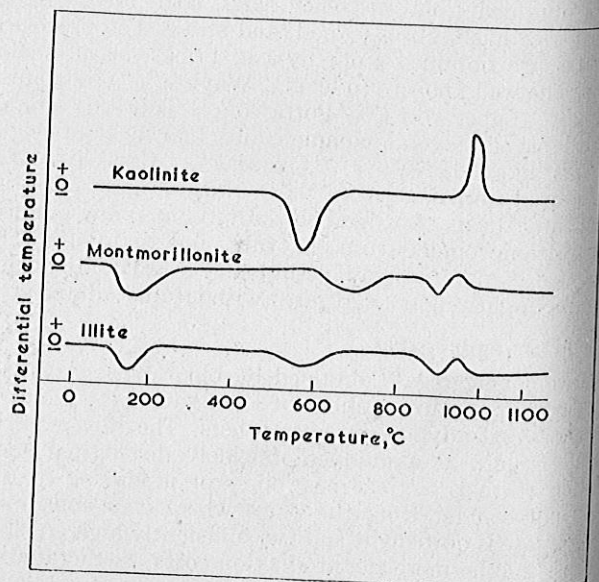


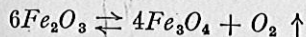
Fig 2 D. T. A. of kaolinite, illite and montmorillonite

Formation of gas during bloating

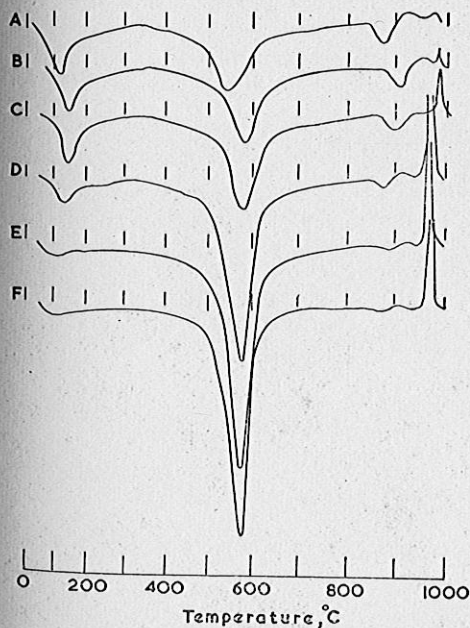
Once it is known that a clay will fuse to form a viscous melt with a sufficiently wide vitrification range, it is important that it should contain a material that evolves a gas at a temperature at which the clay is sufficiently viscous. Either the gas-forming material is present in the clay itself or it may be added externally.

Much work has been done on the factors that cause the production of gas in the clay. Notwithstanding the fact that bloating properties of clays were well known some fifty years ago, there is still much misconception about the exact chemical phenomena occurring during bloating.

Jackson was probably the first to investigate the causes leading to the production of gases during bloating.⁷ Oxygen liberated from the dissociation of Fe_2O_3 was thought to be responsible for bloating and for the belief that the resulting ferrous oxide probably formed a silicate with other components of the clay. No experimental proof was reported to substantiate the idea. Hostetter and Roberts studied the decomposition of Fe_2O_3 and found that it dissociated at 1000°C in air to form O_2 .⁸ Ruer and Nakamoto gave the decomposition temperature of hematite as 1150°C.⁹ The dissociation was found to proceed well when it was dissolved in a glass. These studies show that in a clay containing Fe_2O_3 , oxygen evolved during the decomposition of the oxide is mainly responsible for bloating. The decomposition proceeds as follows:



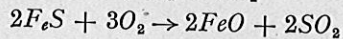
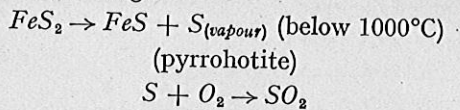
Orton and Staley rejected the theory of O_2 evolution as the source for bloating, as many clays containing iron oxide did not bloat in the range 1100°–1700°C.¹⁰ It was concluded that iron sulphide was the chief source of bloating. Iron sulphide was not considered to be dissociated during firing but dissolved in the low temperature basic melt. As temperature rose, more silica dissolved making the melt more acid thus causing the sulphur to escape out of the solution as SO_2 . This gas was responsible for bloating. Hempel and Schuber found that SO_2 was liberated by the dissociation of pyrite which occurs over a wide range, *viz.*, from 410°C to 1400°C, and thus bloating could take place even at high temperature.¹¹



A = 95% illite; 5% kaolinite
 B = 90% illite; 10% kaolinite
 C = 75% illite; 25% kaolinite
 D = 50% illite; 50% kaolinite
 E = 25% illite; 75% kaolinite
 F = 10% illite; 90% kaolinite

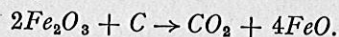
Fig 3 D. T. A. of prepared mixtures of illite and kaolinite

According to Allen and Lambard the dissociation of pyrite takes place in two stages¹²:

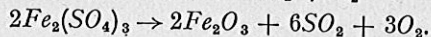
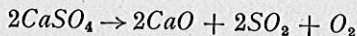
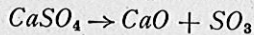


FeO which is not stable in presence of SiO_2 will form a silicate of iron. By heating kaolinite with various impurities, Jackson came to the conclusion that part of the sulphur forms complex compounds such as ferrous thiosulphate and ferro-sulpho-silicate at low temperatures.¹³ The bloating of clay is due mainly to sulphur that is retained at high temperatures in the complex compounds with iron and silica.

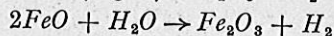
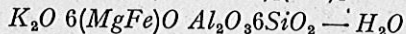
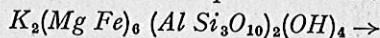
Austin, Nunes and Sullivan studied such factors as the effect of heating rate, the rate of air flow, and the atmosphere on the bloating properties of clays.¹⁴ It was found that the chief gases evolved at the bloating temperatures were CO_2 , SO_2 , and H_2O . Elemental carbon retained in the clay was thought to be responsible for the evolution of CO_2 by reduction of Fe_2O_3 .



Some CO might also form by the reduction process: $Fe_2O_3 + 3C \rightarrow FeO + 3CO$. The residual calcium and magnesium sulphates or other intermediate compounds formed during firing might decompose to form SO_2 or SO_3 .



Water was supposed to evolve from some minerals other than clay. It is probable that the mineral responsible for the evolution of H_2O , was a compound such as hornblende or biotite. Biotite decomposes as follows:



Riley (*loc cit*) observed that some pure illites bloated evolving gas at 2100°F. This shows that it might be due to the presence of either a minor constituent present in undetectable amounts or that illite itself bloats without any extraneous gas-producing materials in it. Whether illite breaks down just as biotite at high temperatures is not clear.

A systematic investigation was carried out by Riley (*loc cit*) on some potential gas-producing agents like pyrite, calcite, dolomite, hematite, siderite, and magnesite. Known quantities of these were added to non-bloating mixtures containing calculated amounts of kaolinite, silicic acid and microcline. D.T.A. of a few of these samples given in Fig 4 show their decomposition behaviours.

Dolomite was found to cause an excellent bloating. This was not explicable on the dissociation point of view as it decomposes in stages below the temperature required for bloating. $MgCO_3$ decomposes at 750°C and calcite at 890°C. The evolution of CO_2 may continue upto temperatures not higher than 950°C.¹⁵ This indicates that some dolomite might form a compound with a material present within the clay and then evolve CO_2 at higher temperatures. It is probable that some K_2CO_3 might be formed or it may be due to the formation $3K_2Al_2Si_2O_8 \cdot 2CaCO_3$. This compound is stable at temperatures high enough to provide a source of CO_2 .

Calcite was found to produce a poor bloat. Excess of calcite brings about a quick fusion and the melt formed may be of low viscosity. Everhart (*loc cit*) found that out of 78 clays that bloated, 64 contained calcite. The bloating property is not explicable from the decomposition of $CaCO_3$ which occurs at lower temperatures. It is probable that in

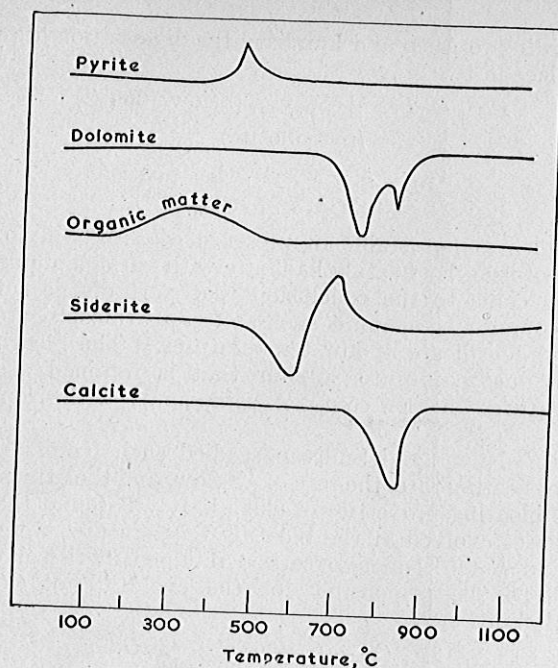


Fig 4 D. T. A. of some gas-producing constituents

the samples studied the amounts of calcite involved was low and the gas evolution would have taken place consequent to the decomposition of some intermediate compound formed during heating, as in case of dolomite.

Conley and Riley (*loc cit*) made certain computations to calculate the theoretical minimum of the gas-producing materials needed to produce 100 cm³ of gas at 1260°C to bloat 10 g of the sample. The results are given below :

Constituent	Weight, per cent	Gas formed
FeS	0.700	S or SO ₂
FeSO ₄	1.208	SO ₃
FeCl ₂	1.000	Cl ₂
NaCl	0.930	Cl ₂
CaSO ₄	1.082	SO ₃
Na ₂ CO ₃	0.843	CO ₂
CaCO ₃	0.796	CO ₂
Ca, Mg(CO ₃) ₂	0.855	CO ₂
Fe ₂ O ₃	7.632	O ₂

Some of the basic ideas outlined above have been applied to study the bloating properties of some Indian clays. The clays containing montmorillonite clay mineral and sufficient amounts of Fe₂O₃ and CaCO₃ generally bloat at lower

temperatures, *i.e.* 1000°–1100°C with a shorter vitrification range, whereas those containing kaolinite and illite (with or without CaCO₃) bloated at higher temperatures, *i.e.* 1100°–1250°C with a wider vitrification range. Illite and kaolinite clays produced a better type of coated aggregate. Further studies are under way to find a correlation between the mineralogical analysis, chemical analysis, and bloating properties of various clays.

Acknowledgment

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