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OF LEVIGATING CERAMICS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School
of the Ohio State University

By

Arthur Joseph Metzger, B. Cer. E.

The Ohio State University
1967

Approved by

[Signature]
Adviser
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To

Sally and Bob

and to their children

Gregory, Christopher, Anne Marie and ?
ACKNOWLEDGMENTS

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Finally, the most important, I find words are inadequate to express my indebtedness to my wife, Loraine, who not only suffered through the trials and tribulations of producing this dissertation but in the end saved the day by typing it.
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"Low Density Foamed Ceramics", U.S.Navy Report N 383s - 31915 (1952)


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I. INTRODUCTION

During the course of a research program initiated to design a low density ceramic composite suitable for use as a missile radome it quickly became apparent that there was a large gap in the fundamental knowledge of low density ceramics. This lack of knowledge encompassed not only properties of the finished products but also methods of producing many types of low-density materials.

An examination of the literature reveals that the many methods of manufacture and their variants have resulted in over 400 patents. A close examination of these patents as well as the articles published in the technical press shows that most of the apparently different methods can be reduced to one of six basic types. These are:

1. The incorporation in the body of a combustible substance, which is destroyed during firing, leaving behind voids. This process is the most widely used of all. It may safely be said that at least 90% of all commercial lightweight ceramic products, either refractory or structural, rely on the burning out of a combustible for the development of the desired bulk density. This process has been the subject of more papers than any other process but most of these have been of a general or popular nature and do not convey any information of note. The British Refractories Association has done a great deal of work upon this process, using the dry-press method of forming.

2. The inclusion in the batch of a material which sublimes at low or high temperatures. This process which was at one time used for the
production of light-weight refractories has never been publicized. Knowledge concerning it is to be found in the patent literature\(^5\).

3. The use, as one of the batch ingredients, of a material which is itself porous or cellular, and of light weight. This process is quite widely used for the production of low-temperature insulating refractories. In this case, it is customary to use one of the natural light-weight materials such as diatomaceous earth, expanded vermiculite, and most recently so-called "bubble alumina" for the porous additive. Most of the writings covering this process have been of the popular variety appearing in the trade papers\(^6\). Several patents covering the manufacture of refractories by this process give compositions and methods of manufacture\(^7\) but very little in the way of properties.

4. The addition of chemicals which react to liberate gas at some stage of the plastic mixing or forming. This process, which is frequently referred to as the chemical bloating process, has been the subject of many patents\(^8\) and a fairly comprehensive publication has appeared covering the fundamental aspects of the method\(^9\).

5. The development of a foamy mass by agitation, or the addition of a previously prepared foam to a clay slip. This process, particularly the addition of a foam to a slip, has been covered by several patents\(^10\). A few cover the development of a foamy mass "in situ". The patents of Hobart are most revealing in this regard\(^11\). A few technical papers on this process were published in Russia, but they do not provide any fundamentals of the process\(^13\). An excellent description of the process wherein a foam is added to a slip is given by Nicholson and Bole\(^14\).
6. The bloating or swelling of a ceramic mass heated to a temperature at which it is pyroplastic. This process has been described by Weyl\textsuperscript{15} as well as by Nicholson and Bole\textsuperscript{14}. It has also been written about extensively in both the popular and technical press\textsuperscript{16,17}. A very extensive patent literature gives a great many details of the process\textsuperscript{18}.

Inasmuch as the strength-density ratio and the electrical properties of a low density body are of chief concern in the development of electro-magnetic windows, many of the above methods were automatically eliminated. Insulating refractories, for example, have values of specific strength of about 330 psi while dense alumina bodies have values approaching 10,000 psi. Specific strength as used here is the ratio of the modulus of rupture to the apparent specific gravity. This spread is generally representative, although there are some materials designed for maximum insulating value which will have specific strengths below 300 psi. On the other hand most dense ceramic bodies will have specific strengths ranging from 2500 to 5000 psi. Few low density ceramics will have a specific strength as high as 1000 psi, and this only when the bodies are approaching an apparent specific gravity of 1.

An examination of the various commercial low density ceramics will show that those in which the burning out of a combustible is the means of achieving low density are those having the lowest specific strength, on the average. This is not surprising when we realize that the pore structures of these bodies is made up of a series of open channels, usually interconnecting, which results in a minimal amount of continuity in material cross-section. On the other hand those products made by generating a gas by chemical means either in a pyroplastic
body, or in a clay slip which is subsequently dried and fired, tend to
give the strongest bodies. Here we can trace the strength, insofar as
structure is concerned, to the continuity of solids in the cross-section
as provided by the discrete-pore system. Where combustibles in the form
of spheres or short blocky pieces approaching cubes are used the pressure
developed by the products of combustion tends to break the cell walls.
This leaves the piece much weaker than where a gas alone causes and
occupies the pore. The pyroplastically expanded bodies almost invariably
contain elements which result in compositions which have poor electrical
characteristics. As a result we find that the maximum performance as
structural and electrical components some kind of foaming process would
be desirable. There are two methods whereby one can generate a foamy
ceramic mass and both have been described in the technical literature
or in patents. Neither one has received much publicity but the method
about which most is known is the process wherein a slip and a foam are
prepared separately after which they are mixed together and poured into
a mold. Nicholson and Bole\textsuperscript{14} describe this process and report on some of
the properties of bodies made in this manner. The other foaming process
envisions the development of a foam "in situ". That is, all of the solid
ingredients are added to a liquid which contains the foaming agent and
then the mass is levigated by mechanical agitation. Both methods give
bodies with more uniform pore structures than can be attained by other
processes. There is much to be said for either method but the simplicity
inherent in the method of development of a foam "in situ" coupled with the
paucity of information about this process was the major factor leading to
the decision to study this method of foaming ceramics.
It will be the purpose of this investigation to study the factors involved in the forming, stabilization, and firing of low density ceramic bodies made by the foaming process based on the development of a foam "in situ", and also to examine certain properties of the fired products to determine to what extent they can be predicted from the composition and properties of the dense material.
II. THE FOAMING PROCESS

Theory

A foam is a gas dispersed in a liquid to such an extent that the volume of gas greatly exceeds that of the liquid. As a consequence the liquid, which is the continuous phase, is so extended that it exists as extremely thin laminae separating discrete volumes of gas. Because of the great extent of the liquid surface in these films and the gas-liquid interfacial phenomena these systems constitute one of the eight types of colloid dispersions suggested by Ostwald, namely, a dispersion of a gas in a liquid. Interestingly, the final product of a foamed ceramic may be a ceramic foam if the cell walls vitrify and become impervious. In this case we have another of Ostwald's dispersions, that of a gas in a solid.

It might be well to point out here that "foamed ceramics" and "ceramic foams" are not synonymous. A "foamed ceramic" is one which is made to have a low bulk density through the beating or blowing of air into a liquid-solids system and the subsequent retention of a vesicular structure through drying and firing processes. The liquid used is usually water. These foamed ceramic bodies will ordinarily have porous walls and because of fragility prior to firing will almost invariably have numerous broken cell walls. "Ceramic foams", on the other hand, are solid equivalents of gas-liquid systems wherein the gas is enclosed by a continuous wall of liquid. Since one of the conditions for a foam is that the wall structure remains intact it appears likely that the only true "ceramic foam" would be a body
formed through the release of a gas within it while the body was in a pyroplastic condition. From this it can be seen that "foamed ceramics" are more truly designated by the term "porous ceramics" and they will require a surface coating of vitreous slip or glass to render them impervious to liquid penetration. "Ceramic foams" are by the very nature of their definition impervious, and barring annealing cracks in cell walls require a surface treatment only to render them smooth or more aesthetically pleasing. In this investigation we will be dealing with "foamed ceramics" and not "ceramic foams".

The more one examines the literature on foams and foam systems the more evident it becomes that very little of a quantitative nature has evolved in the century since Plateau wrote down his observations on film formation and bubble stability.

During this interval Freundlich and Foulk have indicated that pure liquids will not foam. This has been confirmed by all who have taken the precaution to insure freedom from contamination during their experimentation. Surface tension is recognized as playing an important role in film formation and foam stability, but the exact role is still not quite clear. Whether the lowering of the surface tension is necessary or not may be debatable, but practically all workers concede that it is helpful. Foulk, for example, states that whether the surface tension is raised or lowered is a matter of indifference to foam generation. In his opinion it is the fact that the surface tension of the surface is different from that of the bulk of the liquid that is of importance. It is now believed that a sharp increase in concentration of surface active
material in the liquid surface leads to increased foam generation\textsuperscript{25}.

In the development of a stable foam the stability of the system is equally as important as the production of the foam itself. Here it is found that two theories of long standing assist in an explanation of foam persistence. The first, due to Marangoni\textsuperscript{26,27}, states that when a needle moves in a surface contaminated with an insoluble or slowly soluble substance the surface film in front of the needle is compressed while that behind it is expanded. The compressed layer having a greater concentration of contaminant will have a greater surface tension while the expanding surface, having a decreasing concentration, will exhibit a lower surface tension. The difference in tension $\Delta \sigma$ opposes the movement of an oscillating needle causing an effect as of a high surface viscosity. From this it is easily seen that if the surface of a dilute solution of a surface active agent expands there will be a decrease in concentration and a resulting higher surface tension than the static value for the solution. A compressed surface, conversely, will develop a lower temporary tension than its surroundings. The Marangoni effect acts to oppose longitudinal or transverse mechanical disturbance in the bubble film and thus prevents rupture.

The second theory is that of Gibbs\textsuperscript{28}. He defined the elasticity of a foam film as the "infinitesimal increase of the united tensions of its surface divided by the infinitesimal increase of area in a unit of surface". If $E_A$ is this elasticity and $A$ is the surface area of the film then $E_A = 2A \frac{d\sigma}{dA}$. It must be pointed out that these Gibbs elasticities refer to a hypothetical equilibrium state. Under dynamic conditions, such as prevail during foam formation, $\sigma$ will be higher
during extension and lower during compression than the equilibrium values. In other words, the Marangoni elasticity is superimposed on the Gibbs elasticity so that the effective restoring force is a function of the rate of extension as well as of the thickness.

These properties acting together are called by Kitchener "film elasticity" and are responsible for the immediate stability of bubble films. When two gas bubbles come together in a liquid it is this property of "film elasticity" which causes the intervening liquid to thin down to a thin lamella instead of rupturing at the point of closest approach.

A final factor in the stabilization of two-phase foams is viscosity. Viscosity makes foaming more difficult but once a foam is formed the more viscous the laminae the more persistent is the foam. Some proteins when exposed to air in thin layers will coagulate, thus giving rise to quite durable foams.

These theories of foam formation will not predict the amount of foam to be expected from a given solution of foam-producing substance. As Ross points out the device used to produce the foam as well as the properties of the foaming solution determine the volume of foam secured. The stability of the resulting foam is primarily a function of the liquid in all-liquid systems. When solids are introduced to form a three-phase system the stability of the foam no longer relies solely on the liquid but is dependent on many factors. The most important of these factors are, according to Alexander and Johnson:

a. The magnitude of the surface tension

b. The variation in surface tension in the stabilizing film
c. The diffusion of foaming agent out of the surface

d. The mechanical properties and cohesion of the stabilizing film

e. The ageing effects in the surface film

f. The magnitude of the bulk viscosity

g. The potential of the surface film

h. The size of the bubbles

i. The rate of drainage of liquid from film

j. The presence of finely divided solids

k. The action of protective colloids

l. The moisture content of the atmosphere

Since a foamed ceramic mixture is a three-phase system, only those foam stabilization factors in the above list which have a pronounced bearing on such systems will be considered. The remainder either do not figure in the stability of three-phase systems or if they do the extent and the manner of their contribution cannot be specifically detected. In addition to being three-phase systems, foamed ceramic masses also involve several components. This further increases the complexity of the stabilization phenomena. It is not sufficient to say that one or the other of the possible stabilization factors alone is involved, but the results of the interaction of two or more of these factors must be considered. Since the presence of ceramic materials as finely divided solids is the immediate cause of the three-phase system it seems that their contribution to the stability of the foam system should be considered the most important. A further justification of this viewpoint is the fact that none of the other
factors can be investigated without simultaneously considering the behavior of the solids. Another reason for placing the ceramic solids in first place is the large amount present. In most foam systems in which finely divided solids act as stabilizers the quantity of such material is small compared with the amount of liquid present. In foamed ceramic bodies, however, this quantity is substantial and in many cases will exceed sixty per cent by weight of the total batch.

The theory of foam stabilization by fine solids has been most fully developed in the field of mineral flotation. The actual function of the solid is to armor or strengthen the liquid film which constitutes the bubble wall. To do this it must get to and remain in the gas-liquid interface. When a liquid containing a foaming agent and finely divided solid matter is agitated with sufficient energy to cause the formation of bubbles the solid particles will be carried into the gas-liquid interface. In order for them to remain there and strengthen the bubble wall it is necessary that the contact angle between solid and liquid be between 0° and 180°. The diagrams in Figure 1 illustrate the measurement of several contact angles between these limits. It is readily seen that at either extreme the particle has moved out of the interface and is completely enveloped in the liquid or gaseous phase. Gaudin presents this argument in the form of an equation relating the interfacial tensions involved and the contact angle. This equation, for the system at equilibrium, is

\[ T_{MA} = T_{MW} + T_{AW} \cos \theta \]

where \( T \) represents interfacial or surface tension and the subscripts M, A, and W represent mineral, air, and water. \( \theta \) is the contact angle.
Figure 1. Mineral - Water Contact Angles
between mineral and water. When \( \theta = 0^\circ \) the mineral is completely wetted by water and there is perfect adhesion of mineral to water. This is expressed,

\[
T_{MA} \gg T_{MW} + T_{AW} \tag{2}
\]

When \( \theta = 180^\circ \) the mineral is not wetted by water and there is perfect adhesion of mineral to air. This condition prevails when

\[
T_{MA} \ll T_{MW} - T_{AW} \tag{3}
\]

Variation of the surface tension has a bearing on the amount of mineral picked up by the foam, as pointed out by Adam. Too great a lowering of the surface tension will cause the foam to become barren, containing little or no mineral. This can be seen from the formula,

\[
W = E_{LA} (1 - \cos \theta) \tag{4}
\]

Where \( W \) is the work required to detach reversibly, 1 sq. cm. of solid surface from a bubble, \( E_{LA} \) is the surface energy of the liquid-air interface and \( \theta \) is the contact angle between the mineral and liquid. Since \( E \) and \( T \) (surface tension) are the same numerically this equation can be written

\[
W = T_{LA} (1 - \cos \theta) \tag{5}
\]

\( T \) is readily measured while \( E \) is not, hence the use of equation (5) for practical evaluation.

Since all of the ceramic body raw materials give zero contact angle with water, are completely wetted, it is necessary to assume that some other factor is also operating in the foaming of a ceramic body. It has been found that there are very few naturally floatable substances. Among these are such diverse materials as native hydrocarbons, sulfur, graphite, boric acid, and talc, all of which are
hydrophobic in character. The inference is readily drawn that the hydrophilic character of the ceramic materials must be altered if satisfactory foam stability is to be secured. This involves another of the factors in foam stability, namely, the ionic effects. If an organic substance having a polar and a nonpolar part is added to the mixture the polar end, provided it is of the proper sign, is attracted to the polar mineral. This gives rise to an oriented coating which adheres strongly to the mineral with the nonpolar end projecting out towards the water. With the hydrophobic surface thus attained the contact angle becomes of sufficient magnitude to satisfy the relationship expressed in equation (1) and the particle remains in the interface, rendering the foam stable. Such organic substances are called "collectors" in the field of mineral flotation. Because most foaming agents are heteropolar they serve in the dual role of foamers and collectors. The foregoing theory is predicated upon static equilibrium. Actually, however, the mass is in a state of continual agitation during the foaming process and is therefore also subjected to frictional and centrifugal forces. Depending upon the mixing speed and dimensions of the mixing blade or beater it is possible to get forces acting on the particles as great as sixty times the forces of gravity. Detailed calculations of these forces and the changes necessary in the contact angle to offset them are given by Gaudin. To what extent these theories are applicable to ceramic masses is problematical. There seems to be no question but what they apply to the early stages of the mixing process when the bubbles are first produced but it seems that bubble size, degree of mineralization (reflected by viscosity), and thixotropic effects are the controlling factors in the final
stabilization of foamed ceramic bodies. It is in the latter stages too that there is a divergence of views on the end product desired. Both the mineral flotation and ceramic viewpoints coincide on all questions related to the entrapment of air and getting solids into suspension, they diverge when it comes to the length of life of the foam and the kind of foam generated. The mineral flotation operator does not want a persistent foam, nor does he want one too filled with solids. Since his objective is to separate two or more different minerals by causing one to be carried in the foam while the other falls out, a foam which is heavily mineralized will carry mechanically trapped undesirable material. Finally, after effecting the separation, it is desired to recover the foam-carried mineral and accordingly the foam should be "tender" enough to break down soon after leaving the flotation cell. The ceramist on the other hand desires the diverse minerals of his body composition to be intimately mixed and equally suspended in the foam. After removal from the mixer he requires further that the air-filled mass retain the maximum volume possible until dry and ready for firing. Any tendency for the foam to break up at this point defeats his purpose. These different aims bring out another point, namely, the choice of foaming agent. For foaming ceramic bodies it is necessary to seek a material which will, hopefully, suspend all of the minerals in the batch equally well.

Another factor in the stability of foamed ceramics is the bubble size. When agitation is first commenced the bubbles formed are of fairly large size and not particularly stable. With continued beating more and more solids are carried into the foam walls and at the same time the shearing action of the beater reduces the large bubbles to a number
of smaller ones. Because the shearing action of the beater is continuously forming small bubbles from large ones it might be expected that bubble size would be a function of time. Uniformity of bubble size is also a function of time at medium and low mixer speeds. The relationship between time and bubble size is shown qualitatively in Figure 2.

The role of viscosity in foam stabilization is exactly the reverse of the part it plays in foam generation. Low viscosity is desirable in forming a foam because this permits the air to be entrained more easily. At the same time this low viscosity permits the air to escape more readily. Hence to keep the air in place and render the foam more permanent a high viscosity is best. The ideal for purposes of foamed ceramics would be a system which had initially a low viscosity changing with time into a high viscosity system.

Thixotropy is a property possessed to a greater or lesser degree by many ceramic materials such as clays and certain oxides. This property, whereby the mass readily flows when stirred but quickly stiffens, in many cases sets to a gel, when stirring ceases is a decided factor in stabilizing a foamed ceramic mass. Even though the ceramic materials themselves are not pronouncedly thixotropic the foam system containing them exhibits marked thixotropic properties. This property is of more interest than viscosity because during the beating to promote aeration it offers no deterrent to the incorporation of air, yet as soon as the mixing ceases it causes the mass to undergo a large increase in viscosity thus effectively trapping the air.

While emphasis was placed on the reduced size of bubble as an aid in stabilization and while a reduced size of pore in the final
Figure 2. Relationship Between Bubble Size and Time
product increases the strength of light weight ceramic bodies it is well to note that decreased pore size may lead to increasing density. It can be shown that a low density body having spherical pores of constant wall thickness has a bulk density which is inversely proportional to the pore diameter. If certain assumptions, closely approximated in practice, are made it is possible to derive a mathematical expression relating pore diameter and porosity. When the specific gravity of the solid portion of the body is known this can easily be converted into a relationship between pore diameter and density. White and Walton\textsuperscript{36} worked out the formulae relating per cent solids and per cent air for all types of spherical close packing of solids. By assuming that a foamed light weight ceramic body is made up of a number of hollow spheres arranged in tetrahedral closest packing it is possible to apply White and Walton's calculations for the interstitial voids. This volume added to that of the pores gives the total porosity of the piece to a reasonably close approximation. Observation of foamed bodies shows that either pyramidal or tetrahedral packing will closely approximate the actual arrangement found. Since either method leads to the same interstitial pore space, 25.95 per cent, tetrahedral packing may be assumed. Measurements made on commercial foamed glass indicate that the practical lower limit for wall thickness is about 0.0025 cm. and that all walls are shared. In deriving the formula for porosity, therefore, the effective wall thickness of the hollow spheres is taken as one half of the measured wall thickness.

For tetrahedral packing the number of spheres, \( N \), in one cubic centimeter is given by the formula,

\[
N = \frac{1}{4} \frac{1}{r^3 \sqrt{2}}.
\]
where \( r_2 \) is the effective radius of pore, i.e., actual radius plus one-half the wall thickness. The volume of air in each pore is given by the formula,

\[
v = \frac{4\pi r_1^3}{3}
\]

where \( r_1 \) is the actual radius of pore. By combining (6) and (7) a simplified formula giving the volume of air in the pores can be derived.

\[
V = Nv = \frac{4\pi r_1^3}{12 \sqrt{2} r_2^3} = 0.7405 \left( \frac{r_1}{r_2} \right)^3
\]

If we further assume that the material of the pore wall also fills the interstices (8) then gives a value for the volume fraction of the pores. Multiplying by 100 gives immediately the per cent porosity. The other possibility is that the interstices are devoid of solids in which case the per cent porosity would be increased by the additional volume due to the open space in tetrahedral packing, namely, 25.95 per cent. The formula for this case is

\[
P = \left[ 0.7405 \left( \frac{r_1}{r_2} \right)^3 + 0.2595 \right] \times 100
\]

Neither one of these cases is quite correct. The interstices do contain solids and the bubble walls do contain voids. The correct expression lies somewhere between the two extremes. For purposes of showing how the porosity is reduced as the pore diameter is made smaller either equation is satisfactory. Four curves shown in Figure 3, labelled A, B, C, and D give the porosity as a function of pore diameter for pores having wall thicknesses of 0.001 cm, 0.0025 cm, 0.005 cm, and 0.0075 cm, respectively.
Figure 3. Relationship Between Pore Diameter and Porosity
Foaming Ceramic Bodies

The few references available on the foaming method of forming light-weight ceramic products which list the raw materials used are patents. From these patents it is found that the early foaming materials used were organic materials of indeterminate composition. In a patent issued in 1929 mentions soap bark, licorice, glue, soap, etc. as being satisfactory foaming agents. The first reference to a synthetic organic surface active agent was by Nelson in a patent issued in 1932. He does not make any mention of ionic activity. There have been two patents granted since then in which synthetic organic surface active agents are specifically mentioned. None of these inventors considers these agents as anything other than foam producing compounds. In 1947, Grim et al. for the first time recognize the possibility of ionic surface active agents playing a role other than that of simple foam formers. In that year they published two papers, in the first of which they reported work done on the reaction between clay minerals and organic cations. In the second of these papers they describe the production of a refractory insulating brick through the use of organic cations. The materials they used were for the most part cationic surface active agents. In this investigation only synthetic organic surface active agents were chosen as foaming agents. This was done because natural substances are of too indefinite composition and action. It would, therefore, be difficult to properly evaluate their behavior in the process. The synthetic materials, on the other hand, are made under close chemical control and have much more definable properties.
III. METHOD OF INVESTIGATION

Selection of Composition

Virtually all references to low density ceramics formed by the entrapment of a gas recommend the use of plaster of Paris to stabilize the levigated structure until the mass dries enough to be stable. The formulations used call for substantial amounts of plaster; a minimum of 15% and a maximum of 35% constitute the range. There must be enough plaster introduced to form a fairly strong framework to support the other ingredients. Such materials would not be expected to be very refractory.

In the initial selection of a composition or compositions to be used in this study the ease of foam stabilization through the use of plaster was of prime importance, but at the same time the well-known problems which arise when small amounts of CaO are incorporated into vitreous ceramic bodies could not be overlooked. In spite of the disadvantages it was felt that there was an excellent chance of accomplishing two things simultaneously if a satisfactory body could be developed in which lime was the principal if not the sole flux. A paper by Rigerink and Grisdale had shown that so-called alkaline earth porcelains were much more desirable for electrical use at very high frequencies than were the traditional alkali feldspar-fluxed bodies. It appeared then that a foamed ceramic body using plaster as a means of stabilizing the foam could at the same time result in a fired composition having excellent electrical characteristics.
The question was whether the amount of CaO which would be added to the composition by the necessary plaster would at the same time preclude the fabrication of an acceptable fired product.

In the belief that the simpler the initial composition selected the easier it would be to account for observed differences in behavior a decision was made to make use of the CaO - Al₂O₃ - SiO₂ phase equilibrium diagram in the selection of body compositions, providing it could be shown that equilibrium was approached within a reasonable time. To this end the writer suggested to one of his graduate students that he study the approach to equilibrium of selected compositions in the high alumina portion of the CaO - Al₂O₃ - SiO₂ system.

Accordingly such a study was carried out by S. A. Vitolo under the writer's supervision. The results of this study indicated that compositions in which the first liquid formed was the Gehlenite-Anorthite-Corundum eutectic tended to approach equilibrium during a six hour hold at temperature.

To assist in the selection of compositions for study where a definite amount of liquid was desired the Isoliquidus Diagram was devised. This is a simple means of graphically portraying the equilibrium conditions existing within a given compatibility triangle at any equilibrium temperature selected.

As early as 1937, Lagerqvist, Wallmark, and Westgren had indicated that there was a compound much richer in alumina than any before reported. This compound which they indicated was 3CaO·16Al₂O₃ received scant attention in this country. In 1949, Filonenko and Lavrov also reported on a calcium aluminate having a very high
alumina content. They reported the composition as CaO·6Al₂O₃, calcium hexaluminate. Lagerqvist and co-workers had also described another compound, CaO·2Al₂O₃, which they said was the proper formula for 3CaO·5Al₂O₃ shown on the accepted equilibrium diagrams. Goldsmith verified this in 1948. While this took care of one compound the composition and stability range of the other was still in doubt in the early 1950's. Some of the writer's students in a series of minor investigations determined that the high-alumina compound was CaO·6Al₂O₃ and not 3CaO·16Al₂O₃. By this time it was apparent that the compositions selected using the isoliquidus diagram based on the 1933 version of the CaO - Al₂O₃ - SiO₂ equilibrium diagram would not be expected to have the same equilibrium phases as originally predicted. While this proved to be discouraging from the standpoint of the original concept, nevertheless it in nowise detracted from the subsequent work. Neither does it alter the merit of the idea that, given accurate information about the equilibrium conditions in a system, the phase equilibrium diagram can be used as a convenient starting place for ceramic body development.

The compositions made up using the isoliquidus diagram and which were selected to give 10 or 20 per cent liquid at 1400°C are given in Table 1. Both the oxide composition and the batch composition are given. In Table 2 are given the modulus of rupture, absorption, and bulk density of each of these compositions after it was made into a bar at a pressure of 2000 psi and fired to 1400°C and held for 12 hours. Despite the apparent lack of validity of the predicted amounts of liquid based on the most recent diagram it is interesting to note that those bodies predicted to have 20 per cent
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<th>Compositions Giving 20% Liquid</th>
<th>Modulus of Rupture (psi)</th>
<th>Absorption (%)</th>
<th>Bulk Density (gms/cc)</th>
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liquid actually are stronger and have higher densities than those predicted to have only 10 per cent liquid.

Table 3 gives the compositions studied by Vitolo. Table 4 gives the fired properties of these bodies. It will be noted that the bodies were formulated in two ways. The first used potters flint as the source of the silica so that, in effect, these specimens were made from the oxides. The second manner of batching substituted Georgia kaolin as a source of the silica. These specimens while basically of the same oxide composition as the others contained in addition about 1.8 per cent of impurities mainly in the form of $\text{Fe}_2\text{O}_3$ and $\text{TiO}_2$. It is interesting to note the marked increase in strength of those specimens made with kaolin.

After these preliminary tests the two compositions from Vitolo's work which had the highest content of alumina were selected and designated A and B, respectively. Another composition having a higher alumina content than any studied by Vitolo was designated C. This composition on the basis of the original isoliquidus diagram would contain 10% liquid at 1400°C. Another composition D is included because it was used for both compression and flexural tests. Finally, a composition called E which contained 95% alumina, the maximum amount that could be used and still give a reasonably strong piece at a maximum firing temperature available, 1500°C. Both the oxide and batch compositions of these bodies are given in Table 5. It will be noted that whereas bodies A, B, C, and D were made up using plaster of Paris as the source of the CaO, body E uses calcium aluminate cement. This material, manufactured by the Aluminum Company of America, is composed of calcium dialuminate to which an extra one-half mole of alumina
### TABLE 3

VITOLO’S HIGH ALUMINA COMPOSITIONS

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<th>Batch Composition</th>
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TABLE 5
OXIDE AND BATCH COMPOSITIONS OF BODIES INVESTIGATED

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<th>Composition No.</th>
<th>Oxide Composition</th>
<th>Batch Composition</th>
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<td>CaO</td>
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<td>10%</td>
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<tr>
<td>B</td>
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<td>C-1</td>
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<td>91</td>
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<tr>
<td>D</td>
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<td>E</td>
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<tr>
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</table>
is added. Calcium dialuminate is similar to tricalcium aluminate in its ability to hydrate and form a hydraulic bond. While it does not have the strength of the latter its much greater refractoriness has caused it to be widely used in the manufacture of refractory castables. As a substitute for plaster in the stabilization of a foamed body it has the advantage of introducing a large amount of alumina while the CaO increment is relatively small. With plaster, on the other hand, the maximum amount which could be used in the 95% alumina body was 5.57%. Because of the low silica content the kaolin addition was limited to 5.79%. This combination of low plaster and low clay would not give a stable foamed body.

The initial studies were made using composition A almost exclusively because it contained the greatest amount of plaster and hence was the easiest to foam. It also contained more clay than the other compositions and as a consequence gave a greater dry strength. When the plaster became as low as 10% it required more than 15% clay to provide sufficient dry strength to permit handling. Below 10% plaster it became increasingly more difficult to stabilize the foam system and when the plaster was reduced to 5% the bodies could no longer be stabilized.

After the development of methods for foaming and stabilizing the calcium alumino-silicate bodies a few compositions containing calcium titanate were foamed to provide specimens for the dielectric constant studies. These compositions are given in Table 6.

**Raw Materials Used**

The raw materials used in this work were all commercial grade except where noted.
### TABLE 6

**CALCIUM TITANATE COMPOSITIONS**

<table>
<thead>
<tr>
<th>Oxides</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO$_3$</td>
<td>100%</td>
<td>56.76%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
<td>23.51%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td></td>
<td>13.83%</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>5.88%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plaster</td>
<td>18.9%</td>
<td>21.56%</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>70.7</td>
<td>38.90%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>10.4</td>
<td>4.89%</td>
</tr>
<tr>
<td>Ga$_2$-Kaolin</td>
<td></td>
<td>25.37%</td>
</tr>
<tr>
<td>A-2,-Alumina</td>
<td></td>
<td>9.26%</td>
</tr>
</tbody>
</table>

**Equilibrium Composition of Body G**

- CaTiO$_3$ - 56.78%
- Anorthite - 29.10%
- Mullite - 4.46%
- Corundum - 9.66%
Calcium Carbonate (CaCO₃). Reagent grade obtained from Fisher Scientific Company, Silver Spring, Md.
Calcium Carbonate (CaCO). Obtained from Phipps & Bird Company, Richmond, Va.
Plaster of Paris (CaSO₄·½H₂O). Three brands, Industrial White, Hydrocal White, and Hydrocal B11 were obtained from The U. S. Gypsum Company, Chicago, Ill.
Calcium Titanate (CaTiO₃), Strontium Titanate (SrTiO₃), and Titanium Dioxide (TiO₂) were obtained from The Titanium Alloy Manufacturing Co., Div. of National Lead Company, Niagara Falls, New York
Calcium Aluminate Cement. Obtained from the Aluminum Company of America, East St. Louis, Mo.
Aluminum Oxide (Al₂O₃). A-2, minus 325 mesh. Obtained from the Aluminum Company of America, East St. Louis, Mo.
Kaolin, Pioneer Georgia Kaolin. Obtained from the Georgia Kaolin Company, Patterson, N. J.
Aresket 240. 40% solution of monobutyl biphenyl sodium monosulfonate. Anionic surface active agent. Obtained from The Monsanto Chemical Company, St. Louis, Mo.
Armac 8D through Armac 18D. Homologous series of amine acetates. Cationic surface active agents. Obtained from

Forming Procedures

There are three types of surface active agent, anionic, cationic, and non-ionic, and for this study a representative sample of each type was chosen. Surface active agents which ionize in water are called colloidal electrolytes and according to the disposition of the charge they are called anionic or cationic. In addition to the physical effects, such as adsorption, it might be expected that they would display chemical effects similar to those of inorganic electrolytes.

Anionic colloidal electrolytes carry a negative charge on the hydro-carbon chain while the positive charge is on the hydrophilic portion, usually a monovalent cation such as sodium. The cationic surface active agents on the other hand have a positively charged hydrophobic portion while the water-soluble part is usually a monovalent or one-half a divalent anion. In addition to these colloidal electrolytes there are a few water soluble non-ionic surface active agents. Since there is no ionic group, several hydrophilic groups are necessary to produce a molecule with the properties of a colloidal electrolyte. It may be stated that, in general, all of the colloidal electrolytes have 8 or more carbon atoms with those of greatest activity having from 12 to 16. When the carbon chains become much longer than this solubility decreases to the point where they are no longer satisfactory for use in aqueous media.
The anionic surface active agent chosen for use in this investigation was monobutyl diphenyl sodium monosulfonate. It was prepared as a 40 per cent solution marketed as Aresket #240. The cationic agent selected was dodecylamine acetate sold under the trade name Armac 12 D. The non-ionic agent was polyethylene glycol tertdodecylthioether produced as a commercial product called Nonic 218.

In the discussion of foam formation it was indicated that the volume of foam developed increases with the concentration of surface active agent up to a maximum. At the same time the surface tension of an aqueous solution of surface active agent decreases until at a relatively low concentration it reaches a nearly constant value.

It has been pointed out by Kitchener [29] that there is no standard test for foamability and that the amount of foam generated is a function of the test method. For purposes of this study several of the more widely used test methods were tried but none gave wholly satisfactory results. A beating method wherein a foam was developed in the mixing bowl of a kitchen mixer and then transferred to another vessel for volume determination was too complicated and resulted in a loss of foam during the transfer [49]. A method patterned after Ross's method of bubbling air through a long column containing the solution was simpler to use but the results were not applicable to the method of foaming to be used in this study. The answer was found in a simple test which made use of a Hamilton Beach malted milk mixer. The metal cup of the mixer was replaced by a 500 ml capacity, tapered graduate and a small variable transformer was used to control the speed of the mixer. Plate I shows a photograph of the mixer arrangement used for
PLATE I
MODIFIED HAMILTON BEACH MIXER
evaluating the foaming power of the surface active agents.

The amount of foam increased with the speed of the propeller shaft but at high speeds there was a pulsating action which gave erratic results. A speed of 7500 r.p.m. was, therefore, arbitrarily selected. This speed developed an adequate foam volume with good foamers. One hundred ml. of a 0.20% solution of any one of the surface active agents used in this work developed between 300 and 350 ml. of foam at this speed.

Each of the three surface active agents was evaluated at different concentrations for both foam volume developed and surface tension lowering. These data are plotted in Figures 4, 5, and 6 for the anionic, cationic, and non-ionic agents, respectively. A duNouy Tensiometer was used to determine the surface tension of the solutions at different concentrations. Calibrated against water this instrument is sufficiently precise to demonstrate the relationship between surface tension lowering and the foam volume developed. Each foaming agent appears to develop a maximum foam volume regardless of its concentration. The principal effect of increasing concentration of surfactant is to increase the rate of foam development. It was also found that the maximum foam volume reached by satisfactory foaming agents occurred in two minutes or less. A mixing time of two minutes was therefore used for foam volume measurements.

In addition to the foam volume measurements made on simple solutions the effect of additions of kaolin, silica, and alumina singly and in mixtures to solutions of each of the three surface active agents was examined. In virtually all cases there is a decrease in the foam volume
Figure 4. Surface Tension Decrease and Foam Volume Increase with Increase in Concentration of Surfactant - Aresket 240
Figure 5. Surface Tension Decrease and Foam Volume Increase with Increase in Concentration of Surfactant - Armac - 12D
Figure 6. Surface Tension Decrease and Foam Volume Increase with Increase in Concentration of Surfactant - Nonic 218
with increase in the ratio of solids to liquid. At very low concentrations of solids there was some selective increase in volume. An addition of 10 per cent of kaolin to a 0.20% solution of the anionic surface active material produced an increase of 22 per cent in volume. Larger amounts of kaolin produced a continual decrease in volume. When a mixture of kaolin and 10 per cent plaster was added to a 0.20 per cent solution of the anionic foaming agent there was an immediate decrease of 30 per cent in volume with the addition of 10 per cent of the mixture. Further additions produced a recovery of the foam volume until a total of 22 per cent of the mixture of kaolin and plaster was incorporated. At this point the volume developed was about 20 per cent less than that at the maximum and thereafter it fell with further additions of solid. For foam evaluation in the Hamilton Beach mixer a solids content of 30 per cent was about the maximum that could be handled satisfactorily. Above this amount the propellor shaft simply spun ineffectively after a relatively small volume increase.

Actually it was unnecessary to evaluate the foaming agents using a large concentration of solids. It was found that any combination of foaming agent and solid, such as kaolin, silica, alumina, or a mixture of these, would result in a satisfactory foamed body if a volume increase of 100 to 200 per cent could be gained within the first two minutes of mixing. This is with a 20 to 30 per cent concentration of solids. Because of the whipping action of the beater in the equipment used for making the foamed bodies, much higher concentrations of solids can be successfully handled than is possible with a mixer of the propellor type. It is only necessary, therefore, to secure an
initial quick increase in volume before the mass becomes too pasty and thereafter the action of the beater will work-in sufficient air to reach the desired volume. It frequently happened that too much levigation was secured, resulting in a body that was too light. The mixing cycle was found to be just as important as the batch ingredients in developing a satisfactory body.

Beginning with a hand operated egg beater many mixers were tried. As indicated in the foam evaluation studies propellor-type mixers are limited to mixtures that are quite fluid. Thick and pasty mixes cannot be levigated beyond a very low initial volume which is reached before the bulk of the solids are caught up in the foam. For these mixtures a beater-type mixer proved to be most satisfactory. Either a conventional egg beater type of kitchen mixer or one using a wire whip give excellent foam volumes. A household mixer known as the "Kitchen Aide" was finally selected because the manufacturer, the Hobart Manufacturing Company, makes a line of large commercial mixers which duplicate the mixing action of the small domestic model. It was felt that test batches developed in the small mixer could be more readily scaled-up in equipment having the same characteristics. Small batches were made in either a K-3 or a K-4 model Kitchen Aide. The former will handle three quarts and the latter four quarts. Larger batches were made in a Model A 120 which has a capacity of 12 quarts. The K-4 and the A120 are shown in Plates II and III, respectively.

Although the mixing action in the smaller Kitchen Aide was the same as that of the A 120 commercial model, there was a real difference between the mixing action as a function of speed in the small versus the
PLATE II
K-4 HOBART MIXER
PLATE III
A-120 HOBART MIXER
large mixer. The former was powered by a universal motor controlled by a rheostat while the larger model was driven by an induction motor running at a uniform speed. The A 120 had three speeds, provided through a set of reduction gears. Because the maximum output speed of the Kitchen Aide was higher than the A 120 there were, initially, problems when scaling up from small batches to those of larger size. This difficulty was surmounted by locating one of the 12 quart mixers which had been designed for shipboard operation and was outfitted with a direct current motor. By means of a rheostat and making use of the three gears, an almost infinite range of speeds was possible.

The unique mixing action of the Hobart mixers makes speed designations meaningless as a method of describing mixing patterns. The mixing whip, or beater, is moved about the bowl by means of a head which has a planetary motion. To further confound attempts to rationalize the precise mixing action in terms of conventional speed descriptions the beater rotates in a direction opposite to the motion of the planetary head. This rotation is constant while that of the beater itself is varied. For laboratory reproducibility the rheostat settings were used in lieu of speed designations. In the case of larger quantities made in the A 120 mixer a method was devised which describes the mixing speed in terms of one of the three fixed gear ratios, i.e., 1, 2, or 3 and a voltage, e.g. 100 volts. While admittedly crude as a way of indicating the speed for the various cycles it proved, nevertheless, to be quite satisfactory as a means of reproducing the mixing conditions from one experiment to another. Furthermore, it is not possible to specify a given operating characteristic of one mixer of
this general type which can be translated directly into a similar characteristic of another make.

In batches containing several different raw materials it was found to be advantageous to allow the batch to soak for a short time after introducing it into the liquid. This ensures that all of the ingredients are wetted out before the high speed mixing begins. One minute was found to be a satisfactory length of time and all batches were soaked this long before the start of mixing. For the sake of uniformity the subsequent mixing times and speeds were standardized for each mixer. The small mixer had 10 indicated positions. Those marked 1 and 2 were definitely low speed while above 6 were high speeds. The standard cycle for the Kitchen Aide was, one minute soak, then two and one-half minutes on 6, and finally one minute on 2. The total cycle was 4½ minutes. The standard cycle for the A 120 was as follows:

<table>
<thead>
<tr>
<th>Soak</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Speed</td>
<td>2½ 180 V 3</td>
</tr>
<tr>
<td>Low Speed</td>
<td>1 200 V 1</td>
</tr>
</tbody>
</table>

This translates into Soak - 1 minute, High Speed - 2½ minutes at 180 volts on mixer setting No. 3, following by 2 minutes at 200 volts on the same mixer setting and finally, Low Speed - 1 minute at 200 volts on mixer setting No. 1. The total cycle was 6½ minutes. The added time reflects the difference between the two mixers.

Despite the crudity of the mixing cycle descriptions, both gave very good reproducibility. The larger mixer was better in this respect than the Kitchen Aide.
At the end of the mixing cycle the foamed mass is transferred from the mixer to the mold. The molding operation itself is quite simple but the preparation of the pallets on which the mold frames are placed required a good deal of experimentation before satisfactory blocks could be formed. Unlike dense bodies the foamed blocks have virtually no strength at all until they are dry, hence unless the block can move freely on the pallet during drying it will tend to crack in two across the center. Glass plates were used as pallets for the test pieces and the first expedient tried was to oil the surface. This did not prove satisfactory and the next parting material tried was tissue paper. This was an improvement but still there was a considerable loss due to cracking. Also most of the blocks that dried safely had grooves in the bottom where the wetted paper bulged upward into the soft mass of the foamed material. The final solution which eliminated all loss due to cracking and which permitted the stress-free drying of the blocks consisted in first coating the surface of the glass plate with an extremely thin film of silicone grease. Next, a piece of waxed paper was placed on the greased surface of the glass. On top of the waxed paper a small amount of -20, + 30 mesh Ottawa sand was scattered and on this another piece of waxed paper was laid. Now the mold frame was put in place and the block poured. While the foregoing description may appear rather a complicated procedure it is actually quite simple. After the glass plate has been prepared the first time with its silicone and waxed paper coating it is only necessary to cut a single piece of waxed paper for each block and to occasionally replenish some of the sand. The grains of Ottawa sand are very nearly spherical
and permit the contracting block to roll as though on ball bearings.

Even when dry many of the lightweight bodies were quite weak and presented a problem in getting them into the kiln safely. In an attempt to improve the dry strength three plasters were evaluated. They were Industrial White Molding plaster, Hydrocal White plaster, and Hydrocal B-ll plaster. The two Hydrocal's were reputed to be very strong when set and they were examined with a view to replacing the Industrial White Molding plaster which had been originally selected. After making up identical compositions using each of the three plasters and foaming with each of the foaming agents in turn, the Hydrocal B-ll was found to be unsuitable for making foamed ceramics. Both of the others gave stabilized blocks but the Industrial White Molding plaster gave a better structure and dry strength although the Hydrocal White gave slightly more volume. On the basis of this the Industrial White Molding plaster was used throughout.

Compositions A and A-4, identical in oxide content but made up using Georgia kaolin as the source of the silica in A and with potters flint as the source of the silica in A-4, were used to study the drying and firing shrinkages of foamed bodies. Composition A was used to study the effect of the mixing cycle on the volume developed. To this end a special mixing bowl provided with a series of serrated plates in the bottom was secured so that the introduction of air into the batch could be effected during the mixing cycle.

To study the range of liquid within which satisfactory blocks could be made composition A, B, and C were used.
Drying and Firing

Drying. The drying behavior of foamed ceramic bodies turned out to be quite simple once it was realized that the wet mass still maintains the attributes of a foam for several hours after it is formed. Heat, directly applied, will bring about the degradation of a foam system. It is necessary, therefore, to allow the freshly-made ware to air-dry for several hours before applying heat by conduction through a pallet or hot floor. After about six hours at ambient room temperature the pieces can be placed in a conventional dryer without risk of collapse. If, however, a freshly made block is placed directly on a hot object, or on a cool one which is quickly heated up, the cell walls collapse and the piece will squat, forming a shapeless mass. To successfully and quickly dry foamed ceramics a large amount of low humidity low-temperature air should be employed. Drying proceeds rapidly because of the inherent porosity and large surface area of the individual pieces. Once the water has begun to evaporate the temperature can be raised rather rapidly as long as the volume being moved past the ware remains high. A comparison between the same composition dried at a low temperature with a large volume of moving air and at a low temperature (room temperature) with no air movement resulted in the first sample drying completely in seven hours with a shrinkage of 4.7 per cent while the air-dried sample was still damp three days later and had shrunk 6.2 per cent. A careful adjustment of the time temperature cycle should permit the drying of foamed ceramic pieces in as little as four hours.
Firing. All of the bodies, both dense and lightweight, made during this study were fired in electrically heated kilns using silicon carbide heating elements. This limited the maximum firing temperature to 1500 °C. This was no handicap for most of the work as the compositions selected were designed to mature at 1400 °C. It was only in the case of a few mixtures made up with 98 and 99 per cent alumina that the inability to fire to temperatures above 1500 °C was restrictive.

While many mixtures, particularly those low in clay, are fragile in the dry state they do not present unusual setting problems in the kiln. Most of the test specimens were 8" x 4" x 1¼" and these were set flat. There was some advantage in setting these pieces on the face which was uppermost when the block was formed. There is a greater amount of drying shrinkage in this face with a consequent bowing of the piece. By placing this face down during firing there is counteracting shrinkage during firing which tends to correct this condition.

During the first few firings it was noticed that a copious evolution of sulfur dioxide took place between 1100 °C and 1200 °C. This was considerably lower than the dissociation temperature which had been reported for calcium sulfate. The dissociation temperature was reported by Budnikov and Syrkin to be 1375 °C. Marchal in a series of experiments observed that the presence of kaolin, alumina, etc. caused an increase in the equilibrium pressure. With kaolin, for example, a pressure of 1070 mm was reached at 1170 °C. Newman extrapolated Marchal's figures and arrived at a pressure of one atmosphere for calcium sulfate alone at 1400 °C. Because of the lack of satisfactory thermal data on the behavior of calcium sulfate alone
or in the presence of kaolin, alumina, or silica the writer suggested to one of his graduate student's, W. B. Harrison, that he undertake a study of the effect of both time and added oxides on the dissociation behavior of calcium sulfate. Until the effect of the other raw materials on the dissociation temperature of calcium sulfate was known the kiln was heated to 1100 °C at a rate of 135 °C per hour and then held for 12 hours. At the end of this time the temperature was advanced rapidly to the maturing temperature and held for five hours. Later, on the basis of Harrison's findings, the temperature was raised continuously until the desired firing temperature was reached. After holding at this temperature for 5 hours the firing was terminated, the vents were closed and the kiln allowed to cool to room temperature.

In addition to the problem of the sulfur dioxide fumes which present a health hazard and require that the kiln room be well ventilated, there is also a problem in connection with the thermocouples used for measuring temperature and controlling the firing cycle of the kiln. Because of the temperatures, 1400 - 1500 °C, it was necessary to use platinum-platinum, 13% rhodium thermocouples which were mounted in nominally impervious mullite protection tubes. Three styles of tube were tried, plain vitreous tubes, vitreous tubes glazed on the outside and vitreous tubes glazed both inside and out.

Each type proved to be permeable to sulfur dioxide and after two or three weeks a coating of platinum sulfide was deposited on the insulating tubing at the cool end. Although there was a gradual shift in the reading of the thermocouple this was not serious enough to cause a problem in the firing.
Strength Determinations

Because of the soft nature of the unfired foamed bodies no attempt was made to measure their dry strength. Changes in the dry strength when the amounts and kinds of plaster or clay were changed were readily observable although they were not amenable to measurement.

The first tests made on the fired low density bodies were compression tests. The pieces were so fragile that no available testing equipment had sufficient sensitivity to give reliable breaking-load reading on practical size specimens tested in flexure. To overcome this difficulty a dead load type of transverse strength testing machine was designed and built. Similar to machines used many years ago for testing small pieces and pieces of low strength, it consists of a lever arm giving a three-to-one loading ratio. Unlike most similar pieces of equipment which use lead shot for the load application, water was chosen for use with this equipment. Making use of a solenoid valve in the water line an extremely sharp cut-off was secured by attaching a microswitch to the under side of the loading lever and arranging the actuating mechanism so that a very small movement from the horizontal would close the switch and shut off the flow of water.

This device was very sensitive, responding to as little as one milliliter of water, and proved to be quite satisfactory for determining modulus of rupture breaking loads of less than three pounds. A photograph of this piece of equipment is shown in Plate IV.

Not only the sensitivity of the loading mechanism but also freedom from eccentricity of load application is of great importance
PLATE IV
LEVER ARM LOADING DEVICE
in flexure testing. To ensure freedom of movement in all directions a special loading head was designed for use with this machine. A photograph of this unit with a test piece in position is shown in Plate V. In Plate VI is shown another and earlier loading head designed for use with a Dillon Multi-low Range Universal Tester. This machine which has a loading capacity of 300 pounds and a Tinius Olsen Electomatic machine having a capacity of 12,000 pounds were both used for flexure tests on high alumina bodies. A Tinius Olsen "Petite" machine was used for the compression tests. This machine has two ranges, a low range of 0-1000 pounds and a high range of 0-10,000 pounds. Most of the materials developed in this study were tested using the low range.

A large number of specimens of Body C containing 91 per cent alumina were made with particular care being paid to the homogeneity of the pore structure. The density too was controlled and did not vary by more than 5 per cent. These specimens which were used for a series of round robin tests to develop a test method for modulus of rupture of low density ceramics proved to be quite strong in both flexure and compression. Because of this it was decided to attempt to test in tension an extra set of specimens from the same lot that had been used for flexure testing. The lot of ten specimens which were one-half by one-half inch in cross section necked down to one-quarter by one-half for a gauge length of approximately one and three-quarters inches were tested in tension using the Tinius Olson Electomatic machine. Load versus elongation curves were recorded for each bar.
PLATE V
SPECIAL LOADING HEAD FOR LEVER ARM DEVICE
PLATE VI
SPECIAL LOADING HEAD FOR DILLON MACHINE
**Measurement of Dielectric Constants**

Except for a few exploratory tests made in a home-made condenser all dielectric constant measurements were made at microwave frequencies, 9375MHz to be exact, using the shorted line technique \(^{54}\). The essential equipment consisted of a power supply and square wave generator, a reflex klystron covering the frequency range of interest, a slotted line with travelling probe to detect the minimal positions of the standing wave, a wave meter to check the output from the klystron, a vacuum tube voltmeter to indicate the position of the standing wave minima, and an oscilloscope to visually check the tuning of the klystron.

All of the above equipment with the exception of the vacuum tube voltmeter and the oscilloscope were constructed in the Aeronautical Electronic and Electrical Laboratory of the Naval Air Development Center at Johnsville, Pennsylvania. This equipment proved to be quite stable and with the exception of an occasional vacuum tube failure in the rectifier of the power supply, operated with a minimum of maintenance. The shorting stub was built by the writer after discussions with the personnel at the Navy Air Development Center. Because of the lack of special machining equipment the removable back plate arrangement was not made as originally planned. This led to loss of time with each sample change and some sacrifice of reproducibility between tests. The maximum variation in duplicate runs was approximately plus or minus 5 per cent.

To save time and improve the measurement precision the
specimen thickness was calculated according to the following formula,

\[ d = \frac{0.945}{\sqrt{\varepsilon - 0.51}} \]

Here \( d \) is the specimen thickness, \( \varepsilon \) is an estimate of the dielectric constant and 0.945 is a constant equal to three-quarters of a wavelength in the material in the wave guide. All dimensions are in inches. The interior cross-section of the wave guide for the frequency used is 0.9 inches by 0.4 inches, and a small vise-like jig was made to hold the specimens while they were dressed to size. All specimens were carefully rubbed down, using successively finer abrasive surfaces, until the pieces fitted the wave guide with a tolerance of plus or minus, 0.001 inch. All measurements were made at room temperature.
IV. DISCUSSION

The Foaming Process

The foaming of ceramic bodies is a very complicated process which virtually defies any attempt to explain it in terms of basic phenomena. There are, however, a few fundamentals which are of general application. One of these has to do with the range of water content within which a satisfactory foamed body can be produced. Using compositions A, B, and C, given in Table 5, and varying the percentage of liquid necessary to go from a mixture which was too low in liquid to a mixture which had an excessive amount of solution, it was found that the range is narrow, and the maximum or minimum liquid content is a function of the type of foaming agent, and the amount of clay in the batch. The results of these tests are given in Tables 7 and 8.

When the anionic foaming agent was used the range in liquid content which gave a good block was from 43% to 48%. When the minimum amount of liquid was used the mixtures low in clay gave the lightest bodies. With the maximum amount of liquid it was composition A, the highest in clay, which gave the lightest body. Regardless of the amount of clay, which varied from 8 to 34%, the best bodies were secured with 46 to 48% of an anionic solution. Low clay bodies foam best using the minimal liquid while the high clay bodies foam best using the upper liquid limit. Liquid in amounts greater than 48% can be used to secure even lighter bodies but most of this
<table>
<thead>
<tr>
<th>Composition (a)</th>
<th>Percentage Liquid (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42.4</td>
</tr>
<tr>
<td>A</td>
<td>50.0</td>
</tr>
<tr>
<td>B</td>
<td>52.0</td>
</tr>
<tr>
<td>C</td>
<td>50.0</td>
</tr>
</tbody>
</table>

(a) Batch compositions given in Table 5

(b) Liquid 0.2% aqueous solution of Aresket
TABLE 8

PERCENTAGE OF MOLD FILLED AS A FUNCTION OF KIND OF SURFACE-AGENT (a)

<table>
<thead>
<tr>
<th>Surface-Active Agent</th>
<th>Percentage Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42.4</td>
</tr>
<tr>
<td>Anionic (b)</td>
<td>87.5</td>
</tr>
<tr>
<td>Cationic (c)</td>
<td>50.0</td>
</tr>
<tr>
<td>Non-ionic (d)</td>
<td>29.0</td>
</tr>
<tr>
<td>Mixture of Cationic and non-ionic (e)</td>
<td>50.0</td>
</tr>
</tbody>
</table>

(a) Composition B-Table 5 used throughout
(b) 0.2% solution of Aresket 240
(c) 0.1% solution of Armac 12D
(d) 0.1% solution of nomic 218
(e) 0.05% Armac 12 D 0.1% nonic 218
increased levigation is illusory, being offset by an increased firing shrinkage. Another limiting factor to the use of liquid beyond the 48% point is an increased pore size which leads to reduced strength.

Substituting the cationic surfactant for the anionic agent required more liquid to secure the same increase in volume. The minimum liquid needed for a good block when using a cationic surface active agent was 46%, a significantly greater amount than was needed when using the anionic material. At the upper limit too, a similar increase was noted. The cationic foaming solution had an upper limit of 52% liquid beyond which it was difficult to get a good block. Another characteristic of the cationic material was the very fine pore structure developed in comparison with that produced when using an anionic agent.

The non-ionic surface-active agent which, as shown in Figure 6, produced an adequate amount of foam in a simple aqueous solution was of no value as a foaming agent for a ceramic body. A few experiments were conducted in which the non-ionic material was used jointly with the cationic surface-active agent to enhance its foaming power. But as can be seen from the results there was little or no difference between the volume achieved with the mixture and that attained using the cationic agent alone. To be considered satisfactory a 200 gram batch should develop enough volume to fill one-half of the 8" x 4" x 1½" mold in which the samples are made.

It is in the area of the chemical behavior of the foaming process that attempts to arrive at a quantitative explanation are least successful. Visual observation during the forming of hundreds
of foamed compositions reveals changes which explain much to the
observer but which cannot be readily described. Recognition of the
fact that both the anionic and the cationic surface-active agents
are colloidal electrolytes serves to clarify many of the phenomena
observed during the foaming process. Failure to recognize that
factors other than the setting action of the plaster are even more
important in the development of low density foamed ceramic bodies
has greatly restricted the use of this process.

In batches containing 15% or more plaster the setting of the
plaster is no doubt the means of stabilizing the foamed mass. When
the plaster is reduced to less than 10% the foam stability becomes
sensitive to the ionic character of the constituents. At this
point it is possible to describe foam stability in terms of froth
flotation fundamentals. Because the clay and any silica present are
negatively charged an anionic surface-active agent tends to enhance
the wettability of these materials thus rendering them non-floatable.
The alumina on the other hand being positively charged can be held
in the foam walls. At the same time the anionic surfactant is also
an electrolyte which deflocculates the clay thus making the dis-
persion more mobile. As a result of these effects it is found that
large bubbles containing very little solids in the walls are quickly
formed when beating commences. With time the slight solubility of
the plaster provides Ca-ions and SO₄-ions which counteract the ionic
effects of the anionic surfactant. The cations first act to further
lower the surface tension which aids in foam generations. The anion
tends to precipitate the surface-active material. It must be
recognized that organic materials present with the plaster and which have been added to act as regarders to the set, as well as the sodium ions present from the small amount of sodium aluminate in the A-2 alumina complicate the picture of the actual behavior of the foamy mass. After approximately one minute of mixing there is a noticeable stiffening of the material in the mixing bowl. Subsequent beating at the same speed reduces the coarse bubble structure while simultaneously increasing the total volume. At this point an increase in the speed of the mixer will substantially increase the volume. At this point in the mixing cycle mixtures very low in plaster partake of the nature of emulsions rather than of foams. In mixtures having little alumina and a large amount of silica, as quartz, there is not the same degree of thickening and after the mass is poured in the mold the cell walls expel the siliceous material with a resulting coalescence and collapse of the foam structure.

The substitution of a cationic surface-active agent for an anionic agent results in quite different behavior. Here the long, water-repellent hydrocarbon chain has the positive ion attached to one end and when introduced into a liquid containing negatively charged particles this positive ion is adsorbed onto the surface of the particle. In this manner the long hydrophobic tails are extended outward into the liquid medium and the coated particle, now non-wetted, is carried in the bubble walls of the foam generated in the liquid. Cationic foaming agents permit the foaming and subsequent stabilizing of mixtures containing silica whereas anionic agents, although developing a foam, do not aid in its
stabilization. It is also noticed that cationic surfactants will
develop stable foams in systems containing substantial amounts of
$\text{Al}_2\text{O}_3$. Since alumina carries a positive charge it would be expected
that with it a cationic agent would behave in much the same fashion
as the anionic agent does with silica. There is another factor,
however, which tends to offset this behavior in real systems. The
clay present being negatively charged is quickly taken into the
bubble wall resulting in a thick mass almost from the very start of
the mixing cycle. As a consequence not only do the cationically-
foamed bodies develop less volume than do those foamed using an
anionic agent but they also have a much finer pore structure. Foams
produced using a cationic foaming agent remain soft longer than do
those made with the anionic foamers. After the mass foamed using a
cationic surfactant is poured into the mold it has a gel-like con-
sistency due to its thixotropic nature. Within a period of 15 to
20 minutes there is a reaction akin to syneresis and water is expelled
from the piece. At this time the mold can easily be slipped off of
the block. The expulsion of the water is the counterpart of the
coalescence of the bubbles in the case of the anionic foaming agent
used with silica. Here it is the alumina which tends to be thrown
from the bubble walls, but because the pores are so very small and
the walls are filled with the stable clay there is no place for the
alumina particles to go and in consequence it is the water which must
leave. It is the clay and not the plaster which does most to give
stability to these blocks. It must not be thought, however, that the
plaster plays no role besides that of another mineral ingredient. In
addition to supplying ions for certain base exchange phenomena it
also crystallizes as gypsum, or sets, and in so doing ties up an amount of water equal to 20% of its own weight. In addition the interlacing crystals help to give reinforcement to the fine-grained materials present and thus minimize the drying shrinkage while the large amount of water used is removed.

Despite the qualitative manner in which most of the phenomena connected with the foaming operation must be explained it is possible to reduce some things to a quantitative basis. Such things as the liquid:solid ratio mentioned at the beginning of this discussion is one of the things which can be expressed quantitatively. Another area in which it is possible to see a reproducible result to which numbers can be applied is that concerned with the mixing cycle. An explanation of the mixing cycle and how it is expressed is given on page 46. In Table 9 are given the changes in slurry bulk density with changes in time of high speed mixing. It is noticed that with increasing time there is a marked drop in density. Tables 10 and 11 show the effect of adding air to the mixing bowl during foaming. In Table 10 the liquid constitutes 45.95% of the total batch and the volume does not increase very much. As shown in Table 11, however, when the liquid is increased to 47.36% of the total batch a marked reduction in slurry bulk density occurs at a mixing cycle of 1 minute soak, 3 minutes at 180 volts on mixer speed 3 (all with air), and 1 minute at 180 volts on mixer speed 1. The data in Tables 9 through 11 were obtained using Composition A and an 0.2% Aresket solution. The data in Table 12 were secured without using air and are for the purpose of showing how well the fired density of the product can be
### TABLE 9

**CHANGES IN SLURRY DENSITY WITH CHANGE IN TIMES OF HIGH SPEED MIXING**

<table>
<thead>
<tr>
<th>Soak Time (Min)</th>
<th>High Speed</th>
<th>Low Speed</th>
<th>Slurry Bulk Density #/cu.ft.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (Min)</td>
<td>Volts</td>
<td>Mixer Speed</td>
</tr>
<tr>
<td>1</td>
<td>2½</td>
<td>180</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>2½</td>
<td>180</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>2½</td>
<td>180</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>200</td>
<td>3</td>
</tr>
</tbody>
</table>

Liquid - 48.72%

Solid - 51.28%

Areskot 240 - 0.5% of total liquid.

*Each value average of two.
### TABLE 10

**EFFECT OF AIR ON VOLUME-LIQUID 45.95%**

<table>
<thead>
<tr>
<th>Soak Time (Min)</th>
<th>Time (Min)</th>
<th>High Speed Volts</th>
<th>Mixing Cycle</th>
<th>Low Speed Volts</th>
<th>Mixer Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2½</td>
<td>180</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>3 (with air)</td>
<td>1</td>
<td>200</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Slurry Density #/cu.ft.</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B77-60</td>
<td>43.4</td>
<td>Increasing</td>
<td>Liquid - 45.95%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>42.0</td>
<td>Air</td>
<td>Solid - 54.05%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>40.5</td>
<td></td>
<td>Aresket 240 - 0.5% of liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>41.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 11
EFFECT OF AIR ON VOLUME-LIQUID 47.36%

Mixing Cycle

<table>
<thead>
<tr>
<th>Soak</th>
<th>High speed</th>
<th>Low speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Min)</td>
<td>Time (Min)</td>
<td>Volts</td>
</tr>
<tr>
<td>1</td>
<td>2½</td>
<td>180</td>
</tr>
</tbody>
</table>

Note: Air was on during different portions of the cycle as indicated for each sample below:

| Sample No. | Slurry Dehshy  
# / cu. ft. |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B77-64</td>
<td>Air from 3½ to 4½ min. of cycle. 34.8</td>
</tr>
<tr>
<td>65</td>
<td>Air from 3 to 4 min. of cycle. 33.5</td>
</tr>
<tr>
<td>66</td>
<td>Air from 4 to 5 min. of cycle. 35.5</td>
</tr>
</tbody>
</table>

Mixing Cycle

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Soak</th>
<th>High Speed</th>
<th>Low Speed</th>
<th>Slurry Density 180 Volts M.S.-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>B77-67</td>
<td>1 min. 4 min. total. Last 3 with air</td>
<td>1 min. 30.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>1 min. 2 min. total. Both with air</td>
<td>1 min. 30.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>1 min. 3 min. total. All with air</td>
<td>1 min. 24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1 min. 3 min. total. All with air</td>
<td>1 min. 25.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>1 min. 2½ min. total. All with air</td>
<td>1 min. 27.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Liquid - 47.36%
Solids - 52.63% Aresket 240 - 0.5% of the total liquid.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Slurry Density</th>
<th>Fired Density</th>
<th>Composition</th>
<th>Slurry Density</th>
<th>Fired Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>53.2</td>
<td>47.6</td>
<td>A20</td>
<td>37.8</td>
<td>35.6</td>
</tr>
<tr>
<td>A6</td>
<td>54.4</td>
<td>48.9</td>
<td>A21</td>
<td>32.1</td>
<td>27.7</td>
</tr>
<tr>
<td>A7</td>
<td>50.6</td>
<td>45.3</td>
<td>A22</td>
<td>42.0</td>
<td>36.5</td>
</tr>
<tr>
<td>A8</td>
<td>48.7</td>
<td>44.3</td>
<td>A23</td>
<td>40.1</td>
<td>35.7</td>
</tr>
<tr>
<td>A9</td>
<td>42.8</td>
<td>40.0</td>
<td>A24</td>
<td>33.0</td>
<td>29.8</td>
</tr>
<tr>
<td>A10</td>
<td>43.5</td>
<td>39.2</td>
<td>A25</td>
<td>42.1</td>
<td>38.2</td>
</tr>
<tr>
<td>A11</td>
<td>44.0</td>
<td>41.0</td>
<td>A26</td>
<td>38.3</td>
<td>36.3</td>
</tr>
<tr>
<td>A12</td>
<td>43.3</td>
<td>41.2</td>
<td>A27</td>
<td>34.5</td>
<td>32.3</td>
</tr>
<tr>
<td>A13</td>
<td>36.7</td>
<td>32.9</td>
<td>A28</td>
<td>45.2</td>
<td>44.8</td>
</tr>
<tr>
<td>A14</td>
<td>38.5</td>
<td>36.5</td>
<td>A29</td>
<td>38.8</td>
<td>38.1</td>
</tr>
<tr>
<td>A15</td>
<td>33.9</td>
<td>30.3</td>
<td>A30</td>
<td>34.3</td>
<td>30.9</td>
</tr>
<tr>
<td>A16</td>
<td>42.8</td>
<td>39.8</td>
<td>A31</td>
<td>30.0</td>
<td>27.0</td>
</tr>
<tr>
<td>A17</td>
<td>38.1</td>
<td>35.9</td>
<td>A32</td>
<td>24.5</td>
<td>22.5</td>
</tr>
<tr>
<td>A18</td>
<td>32.4</td>
<td>27.8</td>
<td>A33</td>
<td>25.0</td>
<td>23.3</td>
</tr>
<tr>
<td>A19</td>
<td>41.8</td>
<td>38.0</td>
<td>A34</td>
<td>27.7</td>
<td>25.4</td>
</tr>
</tbody>
</table>
controlled by controlling the slurry bulk density. Based on thirty
separate determinations using composition A the regression of fired
density on slurry density was calculated and the following equation
was found to hold for a firing temperature of 1350°C.

\[ D_f = 0.918 D_s - 0.04 \]

where \( D_f \) is the fired bulk density and \( D_s \) is the slurry bulk density.

Although the correlation coefficient is not a very efficient
statistic, still the value of 0.9843 found for the fired density and
slurry density is very highly significant and indicates the high
degree of control which can be maintained when making these foamed
bodies. The regression curve of fired bulk density on slurry density
shown in Figure 7 was calculated by the Method of Least Squares which
gives statistically the best-fitting line to the data. The 95% con­
fidence limits, the dashed lines, are also shown.

Although it does not seem possible at present to explain in
a satisfactory manner all of the fundamental factors operating in
the process of foaming ceramics, nevertheless it has been shown that
certain properties of foamed bodies can be controlled and predicted
in a sufficiently quantitatively fashion to permit the use of the
process for the manufacture of low density ceramics. In addition it
is felt that a reasonable explanation has been advanced for those
phenomena not at present amenable to more precise delineation, and
furthermore, the guide lines have been laid down to indicate the
direction in which more fundamental studies should proceed.
Figure 7. Regression of Fired Density on Slurry Density
Strength of Foamed Ceramics

In reviewing the literature on low density ceramics one is struck by the few references to the strength of the products as a function of the density. It is true that strengths are usually listed, along with the other physical properties, but only rarely does an author attempt to relate the strength, either compressive or tensile, to the density. Rarer yet is the author who attempts to formulate such a relationship. One such was Lauritz Andersson who, in a paper dealing with low-density tile, gave the following formula to describe the compressive strength in terms of the bulk density,

\[ C = 1000 \left( \frac{g}{s} \right)^3 \]  

Here \( C \) = compressive strength in kg/sq.cm  
\( g \) = bulk density in gm/cc  
\( s \) = true specific gravity

If, for reasons of uniformity, we substitute \( \rho \) for \( g \), and \( \rho_o \) for \( s \), and at the same time express the strength in pounds per square inch instead of kilograms per square centimeter we obtain,

\[ C = 14223 \left( \frac{\rho}{\rho_o} \right)^3 \]  

The term \( g/s \), or \( \rho_o \), is seen to be the volume fraction of the solids in the piece, and hence the compressive strength as would be expected varies directly with this value. The two constants are empirical and might be expected to vary with the clay, type of combustible used, or any one of a number of factors.
In a paper on porous metal compacts cited by Knudsen\textsuperscript{56}, Bal'shin\textsuperscript{57} proposed that the tensile strength of porous, brittle crystalline materials could be represented by an equation of the form,

\[ S = S_0 D^m \]  

where \( S \) = strength of the test piece
\( S_0 \) = calculated strength of non-porous specimen
\( D \) = relative density
\( m \) = constant

One is at once struck by the similarity between this equation and that of Andersson. The \( D \) in this formula is again the volume fraction of solids present, and using the same terminology as in \((2)\) we have

\[ S = S_0 \left( \frac{\rho}{\rho_0} \right)^m \]  

The only difference between equations (2) and (4) lies in the numerical factor introduced by Andersson to fit his specific data and the term \( S_0 \) introduced by Bal'shin. Andersson does not attempt to hypothesize that his value of 1000 (14223 in English units) represents the strength of the pore-free body. Without a knowledge of the properties of the clay from which the test specimens were made it would be futile to try and equate this number with the pore-free crushing strength.

In 1950, J. M. Watson\textsuperscript{58} wrote a M.Sc. thesis under the writer's direction in which he derived a relationship between strength and bulk density for low density ceramic bodies. This equation too is a
polynomial of the form \( y = ax^b \).

In 1953 Ryshkewitch described the results of tests he had made using low density alumina and low density zirconia cubes tested in compression. Plotting the logarithm of the crushing strength against the porosity he concluded that the relationship between the properties was exponential. Ryshkewitch did not, however, attempt to derive an equation based on his data. This was done by Duckworth in his discussion of Ryshkewitch's paper. From the data Duckworth arrived at the following relationship,

\[
\sigma = \sigma_0 e^{-BP}
\]

(5)

Here \( \sigma \), and \( \sigma_0 \) stand for the compressive strengths of the porous and dense body, respectively. \( P \) is the volume fraction of pores and \( B \) is the slope of the \( \ln(\sigma) \) vs. \( P \) curve. Both Ryshkewitch and Duckworth comment on the departure of the highest porosity values from the exponential relationship. It is to be noted that the maximum porosities studied by Ryshkewitch were in the neighborhood of 50%. Cutler in a paper dealing with the strength of sintered alumina as affected by porosity and grain size could see no evidence of the foregoing exponential relationship. Actually he found that a straight line fitted his data satisfactorily. Cutler attributed the lack of similarity between his data and that of Ryshkewitch to the much smaller pores in his bodies. The fact that his bodies contained only 15% pores was another factor. Coble and Kingery do not give data for material more porous than 60% nor do they, apparently, attempt to derive an
equation to fit the data given in one graph. They do show a wholly empirical equation which appears to have no physical justification. Knudsen in the paper in which he cites Bal'shin and subsequently in another with Parker and Burdick develops equations in which the effect of both grain size and porosity are considered. The second paper appears to get better correlation between flexural strength and the two variables, grain size and porosity, than Knudsen got in his first work. In the equation as given there are three empirical constants. This formula is

\[ S = kG^{-a}e^{-bP} \]

In this equation it will be noted that the term involving porosity is identical with that which Duckworth proposed for Ryshkewitch's data and which is given as equation (5) above. Fryxell and Chandler found rather large discrepancies between calculated and measured values when using Knudsen's relation. Their porosities did not exceed 17%.

In all of those studies Ryshkewitch was the only one who deliberately undertook to create a porous body. Most of the others were made with a view to explaining the decrease in strength of dense bodies with increasing porosity regardless of the source of the pores. None of them, with the exception of Ryshkewitch's, could be called porous, or low density, bodies. The compositions made and studied in this work, on the other hand, were all highly porous, low density bodies with porosities ranging from 66% to a maximum of 89%. The low density bodies of Ryshkewitch did not exceed 62% porosity. It was
this failure to study bodies of high porosity, which led to the belief that the relationship between porosity, or density, and strength is exponential. In Figure 8 a polynomial of the form

\[ R = k \left( \frac{\rho}{\rho_0} \right)^n \]

is plotted on semi-logarithmic coordinates. Here \( R \) = modulus of rupture, \( \frac{\rho}{\rho_0} \) is the volume fraction of solids present, and \( k \) and \( m \) are constants. It will be noted that \( 1 - \frac{\rho}{\rho_0} \) is the porosity as a fraction. The dashed line drawn on the curve indicates how well the low porosity portion of the curve can be fitted using a straight line.

If Ryshkewitch's curves for alumina are examined it will be noted that there is a marked departure from linearity beyond a porosity of 40%. When it is recognized that the points on the curve in Figure 8 were calculated from a polynomial equation it is all the more understandable how experimental points following such a curve could be fitted by a straight line up to a porosity of 40% or even a little higher.

Figures 9, 10, 11 and 13 show the modulus of rupture values for Compositions A, B, C and E and E-1 plotted against the volume fraction solid. Figure 12 gives both the modulus of rupture and compression strength of Composition D as a function of volume fraction solid.

The Method of Least Squares was used to calculate the regression of strength on volume fraction solid. The equations both as polynomials and as linear logarithmic expressions are as follows:

Composition A -

\[ R = 7026 \left( \frac{\rho}{\rho_0} \right)^{1.88} \]
\[
\log R = 3.8467 + 1.88 \log (\rho/\rho_0)
\]
Composition B -
\[
R = 25,200 (\rho/\rho_0)^{2.48}
\]
\[
\log R = 4.40144 + 2.48 \log (\rho/\rho_0)
\]
Composition C -
\[
R = 24,300 (\rho/\rho_0)^{1.90}
\]
\[
\log R = 4.3855 + 1.90 \log (\rho/\rho_0)
\]
Composition D -
\[
R = 19,750 (\rho/\rho_0)^{1.903}
\]
\[
\log R = 4.2957 + 1.903 \log (\rho/\rho_0)
\]
Composition D-l -
\[
R = 23,820 (\rho/\rho_0)^{1.93}
\]
\[
\log R = 3.1991 + 1.93 \log (\rho/\rho_0)
\]
Composition E - (compression)
\[
C = 500,600 (\rho/\rho_0)^{3.65}
\]
\[
\log C = 5.69951 + 3.65 \log (\rho/\rho_0)
\]
Composition E - (flexure)
\[
R = 17770 (\rho/\rho_0)^{2.40}
\]
\[
\log R = 4.24968 + 2.40 \log (\rho/\rho_0)
\]

The individual points shown on the curves are the experimentally determined values. All of the curves are of the form
\[
R = k (\rho/\rho_0)^n
\]
Both Andersson's and Bal'shin's equations are of this form. The latter
sets $k$ equal to the strength of the dense material. Duckworth, too in his formulation for Ryshkewitch's data treats the constant in equation (5) as the dense strength of the material. Andersson makes no claim for his constant value. In the equations calculated from the data developed in this work the values of the constant $k$ range from 14,000 to 25,000 for modulus of rupture data, and for the data in compression for Body E a value of 500,600 was found. These values are interesting from two standpoints. First, they are all of the right order of magnitude for dense bodies containing the same amounts of alumina as these bodies. Second, the moduli of rupture in Tables 2 and 4 for the experimental bars of the same or nearly the same compositions are of the same order of magnitude. The values given in the Tables are lower than those developed in the equations, but the fact that the dense specimens were formed by dry pressing at a pressure of 2000 psi while the low density material was formed by what was equivalent to a slip casting process could readily account for the numerical difference. Had the dense bars been slip cast they might well have shown values of 20,000 to 24,000 psi. If the numerical values of the constant are assumed to be representative of the flexural strengths of the pore-free material the equations for either modulus of rupture or compressive strength can be written,

$$s = s_0 \left(\frac{\rho}{\rho_c}\right)^n$$

where only the meaning of the exponent, $n$, remains to be explained.

The obvious explanation is that $n$ is a factor which takes into account the size and shape of pore, the composition of the body, and anything else which might affect the strength. Thus $n$ would be a
typical empirical constant. Because most of the exponents are close to 2, either slightly greater or a little less, there is a strong temptation to speculate that the volume fraction enters as the square modified by a factor which accounts for pore shape or size, for example. Composition changes and thermal treatment would be expected to more directly influence the strength value of the dense portion of the body and hence should be accounted for by an overall multiplying factor. Since there is no real justification for splitting the exponent into two terms a reasonable equation for the modulus of rupture of truly porous ceramics would seem to be,

\[ s = s_0 K \left( \frac{\rho}{\rho_0} \right)^n \]
Figure 8. Modulus of Rupture vs. Volume Fraction Pores
Figure 9. Modulus of Rupture vs. Volume Fraction Solid Composition - A
Figure 10. Modulus of Rupture vs. Volume Fraction Solid Composition- B
Figure 11. Modulus of Rupture vs. Volume Fraction Solid
Composition - C
Figure 12. Modulus of Rupture and Compression Strength as Functions of the Volume Fraction Solid, Composition-D
Figure 13. Modulus of Rupture vs. Volume Fraction Solid Compositions - E and E-1
Dielectric Constant of Foamed Ceramics

Several dielectric constant values as well as the bulk densities and tan \( \delta \) values for compositions A, B and C are given in Table 13. When these values of the dielectric constant along with a few additional values from similar compositions are plotted against the bulk density a linear relationship is indicated as shown in Figure 14. Virtually all of the compositions lying in the region of the \( \text{CaO-} \text{Al}_2\text{O}_3-\text{SiO}_2 \) equilibrium diagram which contain 70% or more \( \text{Al}_2\text{O}_3 \) will fall very close to the dashed line drawn on the Figure. The equation of this line is

\[
\varepsilon = 1 + 0.02d,
\]

where \( \varepsilon \) is the relative dielectric constant and \( d \) is the bulk density in pounds per cubic foot. This equation which was first reported in 1951\(^6\) gave very good results with most calcium alumino-silicate compositions but tended to give low values as the density increased. An almost identical equation proposed by the Cornell Aeronautical Laboratory\(^6\) which contained an additional term rectified the discrepancies. This equation is

\[
\varepsilon = 1 + .02d + .0001d^2.
\]

It is apparent that the first equation is simply the first two terms of the second; which is an expansion of

\[
\varepsilon = (1 + 0.01d)^2.
\]

It is obvious that any equation which relates the dielectric constant to the density must contain a term which accounts for the
### TABLE 13
DIELECTRIC CONSTANTS OF CALCIUM ALUMINO-SILICATES

<table>
<thead>
<tr>
<th>Composition&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Bulk Density &lt;br&gt;#/cu.ft.</th>
<th>Dielectric Constant</th>
<th>Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>23.0</td>
<td>1.58</td>
<td>.0011</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>19.9</td>
<td>1.42</td>
<td>.0007</td>
</tr>
<tr>
<td>A&lt;sub&gt;3&lt;/sub&gt;</td>
<td>16.2</td>
<td>1.34</td>
<td>.0005</td>
</tr>
<tr>
<td>A&lt;sub&gt;4&lt;/sub&gt;</td>
<td>22.5</td>
<td>1.50</td>
<td>.0005</td>
</tr>
<tr>
<td>A&lt;sub&gt;5&lt;/sub&gt;</td>
<td>33.7</td>
<td>1.64</td>
<td>.0008</td>
</tr>
<tr>
<td>A&lt;sub&gt;6&lt;/sub&gt;</td>
<td>34.9</td>
<td>1.76</td>
<td>.0023</td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>57.8</td>
<td>2.16</td>
<td>.0032</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>39.2</td>
<td>1.87</td>
<td>.0009</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>46.7</td>
<td>2.06</td>
<td>.0007</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>44.4</td>
<td>1.92</td>
<td>.0011</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>34.7</td>
<td>1.73</td>
<td>.0005</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>32.8</td>
<td>1.72</td>
<td>.0006</td>
</tr>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>30.4</td>
<td>1.58</td>
<td>.0006</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> - These compositions correspond to those in Table 5
Figure 14. Bulk Density vs. Dielectric Constant. Calcium Alumino-Silicate Compositions.
difference in dielectric constant between materials. In this case the constant 0.01 must be this term. The general expression then, is

\[ \varepsilon = (1 + k \rho)^2. \]

Here \( k \) is a constant associated with a particular compound or mixture of compounds, and \( \rho \) is the bulk density in grams per cubic centimeter. If one now solves for \( k \) the following relationship is established,

\[ k = \frac{\sqrt{\varepsilon - 1}}{\rho} \]

If this relationship is correct then any mutually dependent \( \varepsilon \) and \( \rho \) for the same substance should give the same \( k \), and if the dielectric constant and specific gravity of any ceramic were known it would be possible to calculate a value of \( k \) with which, given the bulk density, the dielectric constant of a low density ceramic could be calculated.

At the time this relationship was developed most workers in the field used the so-called "Logarithmic Mixing Rule" proposed by Lichtenecker. This equation assumes logarithmic additivity and as given by Lichtenecker consisted of two terms. If, as in the case with low density materials, one of the components is air the following equation results

\[ \log \varepsilon = a \log \varepsilon_A \]

Here \( a \) is the volume fraction of the solid which has a dielectric constant equal to \( \varepsilon_A \). For materials having a very small dielectric constant as well as a low density this formula is quite satisfactory and accounts for its wide acceptance by workers in the field of low
density plastics. To resolve the question of which equation is correct for low density ceramics a series of low density bodies composed of calcium titanate were foamed using composition F from Table 6. After firing to 2350° F specimens were prepared and the dielectric constants determined. The results of these tests are given in Table 14 and the bulk density and dielectric constant are plotted in Figure 15. The first column in Table 14 gives the measured values of ε while the second column gives the values calculated using, \( \varepsilon = (1 + k \varepsilon)^2 \).

To make the calculation each measured value of ε was used individually, along with its bulk density, to calculate a value of k. These k values were averaged and the mean value, k = 3.4528 was used to calculate the set of values given in the second column. In the third column are given values of ε calculated, using the logarithmic mixing law. Here a value of 4.10 was used as the specific gravity of calcium titanate to calculate the volume fraction. It is obvious from these results that the logarithmic relationship is not correct.

If one recalls the Maxwell equation which relates the dielectric constant and the index of refraction, \( n^2 = \varepsilon \) then the equation proposed here is found to be analogous to the Gladstone-Dale equation and the value of k corresponds with their "specific refractive energy". The Gladstone-Dale equation along with many others has been used to predict the index of refraction of glasses. When used for this purpose it is necessary to assume additivity of the index contributions of the oxides in the glass. Although not originally contemplated in this study the applicability of the Gladstone-Dale equation to the solid portion of the low density ceramics became of considerable interest.
TABLE 14
DIELECTRIC CONSTANT OF LOW DENSITY CaTiO$_3$

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\varepsilon$ (meas.)</th>
<th>$\varepsilon_i$ (calc.)</th>
<th>$\varepsilon_2$ (calc.)</th>
<th>$\rho$ (gm/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.72</td>
<td>10.13</td>
<td>2.71</td>
<td>0.632</td>
</tr>
<tr>
<td>B</td>
<td>11.51</td>
<td>10.50</td>
<td>2.79</td>
<td>0.649</td>
</tr>
<tr>
<td>C</td>
<td>22.31</td>
<td>21.46</td>
<td>5.25</td>
<td>1.052</td>
</tr>
<tr>
<td>C$^1$</td>
<td>20.65</td>
<td>20.44</td>
<td>5.00</td>
<td>1.020</td>
</tr>
<tr>
<td>D</td>
<td>7.14</td>
<td>7.49</td>
<td>2.22</td>
<td>0.503</td>
</tr>
<tr>
<td>E</td>
<td>21.83</td>
<td>21.21</td>
<td>5.22</td>
<td>1.044</td>
</tr>
<tr>
<td>F</td>
<td>7.81</td>
<td>8.17</td>
<td>2.34</td>
<td>0.538</td>
</tr>
<tr>
<td>G</td>
<td>17.70</td>
<td>22.10</td>
<td>5.44</td>
<td>1.072</td>
</tr>
<tr>
<td>G$^1$</td>
<td>21.36</td>
<td>21.21</td>
<td>5.25</td>
<td>1.047</td>
</tr>
<tr>
<td>H</td>
<td>22.35</td>
<td>22.20</td>
<td>5.47</td>
<td>1.075</td>
</tr>
<tr>
<td>I</td>
<td>9.80</td>
<td>9.73</td>
<td>2.64</td>
<td>0.614</td>
</tr>
<tr>
<td>J</td>
<td>22.35</td>
<td>21.72</td>
<td>5.33</td>
<td>1.060</td>
</tr>
<tr>
<td>K</td>
<td>7.05</td>
<td>7.17</td>
<td>2.15</td>
<td>0.486</td>
</tr>
<tr>
<td>L</td>
<td>18.47</td>
<td>17.21</td>
<td>4.23</td>
<td>0.912</td>
</tr>
<tr>
<td>M</td>
<td>10.12</td>
<td>10.21</td>
<td>2.74</td>
<td>0.636</td>
</tr>
<tr>
<td>N</td>
<td>7.40</td>
<td>8.48</td>
<td>2.40</td>
<td>0.554</td>
</tr>
</tbody>
</table>

$\varepsilon_i$ calculated using $\varepsilon_i = (1 + k \rho)^2$

$\varepsilon_2$ calculated using $\log \varepsilon = a \log \varepsilon_A$
Figure 15. Dielectric Constant vs. Bulk Density. Calcium Titanate
after the good success achieved by using it for the lightweight bodies.

To test the ability of the equation to predict the dielectric constant of a low density body from its oxide composition, Composition G was made up. After foaming it was fired to 2350° F, then made into specimens for dielectric constant measurements. The oxide and batch compositions are given in Table 6 as well as the approximate equilibrium composition calculated from the oxide composition. Three different blocks were made having densities of 35.3, 40.6 and 46.8 pounds per cubic foot, respectively. The dielectric constants measured on these pieces were 4.76, 4.00 and 4.68 while the calculated values for the same specimens were 4.67, 4.04, and 5.46. On the basis of these results the writer has recalculated published results of the dielectric constant of mixtures of powders using Bottcher's and other methods and found that even here the Gladstone-Dale relationship did as well and frequently better than the more involved methods.
V. CONCLUSIONS

From the experimental evidence of this investigation and within the limitations of the materials and methods used it may be concluded that the foaming of ceramic mixtures is a complex process which is based on the laws of physical chemistry, particularly in the area of surface phenomena. Because of the many opposing forces operating together it is impossible at present to single out specific effects and treat them quantitatively. The following general observations may be mentioned.

1. The liquid to solids ratio for good product formation is quite narrow. The minimum amount of liquid is 42% and the maximum is 52%. This range of 10% includes both anionic and cationic surface-active agents and covers a range in clay content from 8 to 34%.

2. The density of the aerated slurry is very highly correlated with the fired density of the ware. The slurry density, therefore, is an excellent control parameter.

3. The role of plaster in foamed ceramics is not simply that of providing mechanical strength due to the crystallization of gypsum. In addition there is an effective exchange of ions to bring about a flocculation of the solids. This effect is of major importance when the amount of plaster used is small, and explains how it is possible to secure stable bodies of low CaO content.

4. The foaming agents themselves, being colloidal electrolytes, play the role of deflocculating and flocculating agents at various
stages of the mixing cycle. The ionic effects are just as important as are the foaming effects provided by the surface-active agents.

5. The strength-density relationship of porous bodies is found to be expressable as a polynomial. An equation relating the volume fraction of solids to the strength of the pore-free material is borne out by experimental evidence noted in this study. The equation is of the form

\[ s = s_0 K \left( \frac{\rho}{\rho_o} \right)^n \]

where \( s \) is the strength of the low-density piece in either compression or flexure, and \( s_0 \) is the strength of the same material, pore-free. The volume fraction solids is given by \( \frac{\rho}{\rho_o} \) and \( K \) and \( n \) are constants.

6. The dielectric constant of low density ceramic materials is found to follow a relationship similar to that of Gladstone and Dale for the index of refraction of mixtures. For materials having both low and high dielectric constants in the dense form the following equation holds,

\[ \epsilon = \left( 1 + k \phi \right)^2. \]

Here \( k = \sqrt{\frac{\epsilon_a}{\rho_a}} - 1 \), and \( \epsilon_a \) and \( \rho_a \) are the dielectric constant and specific gravity of the solid, respectively. \( \rho \) is the bulk density of the low density piece.
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