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THE EFFECT OF OXIDE ADDITIONS ON THE HIGH TEMPERATURE PROPERTIES OF MAGNESIA.

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The object of this research was to determine the effect of additions from the CaO-MgO-SiO₂ ternary phase system on the sintering behaviour of high purity magnesia. This system was chosen because it was relevant to the production of conmercial refractory material used in steel manufactur.

Additions of forsterite, monticellite, merwinite, dicalcium silicate, tricalcium silicate and calcium oxide were made to magnesia, having a total impurity content of 27 p.p.m. This was specially prepared by calcining at 800°C magnesium oxalate obtained by chemical means from pure magnesium metal. Mixtures were sintered between 1400° and 1800°C for times between 0.1 and 8 hours, and the kinetics of their densification and crystal growth followed.

The additions were found to have an effect on the densification, porosity and grain growth kinetics of magnesia. Activation energies for the grain growth processes were obtained.

Electron microprobe and X-ray diffraction analyses of the fired compositions containing calcium silicate additions showed that lime was lost from the silicate and entered solid solution in the magnesia phase. The stability of the silicates fired in the presence of magnesia decreased with increasing CaO/SiO₂ mole ratio.

These analyses enabled explanations to be made on the sintering behaviour of the mixtures in this system

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and its relevance to the commercial production of dense nagnesia refractories.

This thesis has resulted in the publication of the following papers:-

- "Sintering behaviour of pure magnesia with additions from the CaO-MgO-SiO_system". D.R.F. SPENCER and D.S. COLEMAN. Presented at "Science of Ceramics" 5th International Cinference of the European Ceramic Association, Ronneby Brunn, Sweden. April 21st, 1969.
- "Densities of silicates in the CaO-MgO-SiO₂ system".
 D.R.F. SPENCER and D.S. COLEMAN.
 Transactions of the British Ceramic Society <u>68</u>, (3) May, 1969.
- (iii) "The high temperature solubility of lime in magnesia from silicates in the CaO-MgO-SiO₂ system".
 D.R.F. SPENCER, T.W. BEAMOND and D.S. COLEMAN.
 Accepted for publication in the Transactions of the British Ceramic Society.

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1.00 INTRODUCTION.

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The work described in this thesis is a project in a series which has the general title: "Investigation of the interrelations between composition, high temperature strength and microstructure in ceramic bodies."

Most commercial ceramic bodies for use in high temperature applications consist of a matrix of grains held together by a ceramic bond developed as a result of a firing process. It is the properties of this bond and its degree of compatibility with the matrix that the performance of the ceramic body ultimately depends. In most cases the bond used is complex and consists of several components, which are present naturally, or intentionally added. It is usually difficult to sort out from this multi-phase system the contribution of the individual components to its high temperature physical properties. Whilst the high temperature properties of some pure single crystal and polycrystalline materials are known, little information is available about the way in which the high temperature strength is influenced by such factors as composition, grain size and residual porosity.

The broad aims of this project were to determine the influence of specific additions on the properties of certain pure oxide matrices such as magnesia, alumina, silica and zirconia by using each addition individually in known amounts and then in various combinations. The

effect on the properties due to the additions could then be compared with the properties of those of commercial materials with similar compositions. In this way it would be possible to assess the contribution of each additional component in the commercial material, to its physical behaviour.

Magnesia was selected for investigation as the first material of the series due to its growing use as a refractory material? The growth in the manufacture of higher purity magnesia extracted from sea-water, has been hampered by a lack of knowledge of the effect of impurities on its sintering, grain growth and high temperature strength behaviour.

There are two commercial sources of magnesia, the naturally occurring magnesites (MgCO₃ from Greece, Austria, etc) and the magnesia already mentioned above, which is extracted from sea-water. The naturally occurring material normally has a MgO content of approximately 90% compared with sea-water magnesia which can be produced to over 98% MgO purity. The latter material has the greater refractoriness and, unlike the naturally occurring material, does not have to be imported into Britain. In the following paragraphs a brief summary is given of the developments in the progress of magnesia containing refractories in order to put the present investigation into perspective.

The loss of cohesive strength of magnesia refractories at elevated temperatures has been regarded as the principal cause of their breakdown in service.

The chrome-magnesia brick, containing a major proportion of chrome ore, was developed to overcome this low In these bricks the grains of magnesia and strength. chrome ore were bonded together on firing solely by low melting point eutectic phases formed by the reaction of many impurities, mainly silicates, that can be found in the raw materials. Hayhurst⁴ found liquid to be present in chrome-magnesia refractories at 1360°C. In service, the strength of this refractory is lost as soon as this phase begins to soften? Firing in excess of 1550°C led to the development of the direct bonded brick. Here the grains of magnesia and chrome ore are bonded directly together, the liquid phase migrating into small sinks at the grain boundaries. In such a bonded brick, much of the strength of the refractory is maintained when the silicate phase softens.

The development of the oxygen steelmaking processes led to higher steelmaking temperatures and the requirement of a higher refractoriness than could be obtained from the chrome-magnesia refractory. To obtain a material capable of withstanding these higher temperatures, the percentage of chrome ore in the brick has been gradually decreased, until at the present time 100% magnesia bricks are being used. Problems are now encountered with the sintering and high temperature strength of high purity sea-water magnesia owing to the low level of a bonding liquid present at the firing temperature.

The main impurities in sea-water magnesia are the

oxides of aluminium, calcium, iron and silicon with traces of boron, manganese and alkali oxides. The equilibrium phase assemblage of the 5 component system formed by the major impurities with magnesia was investigated by Brampton et al? They found that the spinels and silicates formed were solely dependent on the lime to silica ratio. Because of the importance of this ratio it was decided to investigate the effect of specific additions of single phases from the ternary system: CaO-MgO-SiO₂ on the sintering, microstructure and high temperature strength of pure magnesia.

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The phases that are present in the system: CaO-MgO-SiO₂, given by Levin et al⁸, are shown in Figure I. The phases that are compatible with magnesia in this system are forsterite, monticellite, merwinite, dicalcium silicate, tricalcium silicate and calcium oxide.

The effect of additions of these compatible phases on the densification and grain growth of fine pure magnesia between 1400° and 1800°C is presented in this thesis. The determination of the high temperature strengths of the sintered products was initially considered in this project and an apparatus was designed and built for this. The development of the sintering investigation was far greater than expected, so that the determination of the high temperature strength of ceramic bodies such as magnesin with silicate additions, has been left for another investigation on a separate project. However, the apparatus that was designed and

built is explained in Appendix I with descriptive diagrams and photographs.

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2.00 REVIEW OF LITERATURE

- 2.10 General Considerations of Sintering
- 2.20 Mechanism of Material Transport
- 2.30 Sintering Mechanisms
 - 2.31 Initial Sintering Stage
 - 2.32 Intermediate and Final Stages of Sintering

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- 2.40 Sintering in the Presence of a Liquid Phase
- 2.50 Kinetics of Grain Growth

- 2.51 Continuous Grain Growth
- 2.52 Discontinuous Grain Growth

2.10 General Considerations of Sintering.

The term "sintering" is used to refer to the process by which compacted crystalline or non-crystalline powders are consolidated into strong and usually dense aggregates, by heating at temperatures below the melting point of the bulk phase. Metal powders start sintering when the ratio of the firing temperature to the melting point (in degrees absolute) is approximately 0.6. Sintering is the normal fabrication process for ceramic materials, where for oxide systems this ratio is usually slightly lower. However, the presence of impurities in the system can greatly affect the temperature at which sintering starts. .- ··

Physical and sometimes chemical changes can occur in the compacted phase during the firing process. For example, chemical decomposition or phase transformations may take place on heating initially. Further heating of a fine-grained porous compact normally produces three major changes which are as follows: increase in grain size, change in pore shape, and change in pore size, resulting in decreased porosity. As heating continues many of the pores can be eliminated completely. It is these phemonena to which sintering theories have attempted to describe and postulate the mechanisms of In systems containing more than one phase, the process. such as when impurities are present or additions of other phases are made, liquid phases may be formed at

the sintering temperature. These phases may react to form different chemical compounds or solid solutions with the bulk phase. Phases may also decompose to the gaseous state. All these processes make it very difficult or impossible to identify in many practical systems the densification process with that predicted by theories, which are derived from model or ideal systems.

The driving force, that causes densification and grain growth, is the tendency to decrease the surface area of the system and hence lower the surface free energy by the elimination of solid-vapour interfaces. This results in the formation of new lower energy solid-solid interfaces, the number of which will decrease as grain growth proceeds. The surface energy of a solid arises from unsaturated chemical bonds at its surface and exists as a property of both solids and liquids. In liquids it is the measureable surface tension. In natural processes, systems will always change in such a manner as to minimize their total free energy. Normally, these reactions are not spontaneous and energy has to be supplied. In the sintering of ceramic powders, heat energy is supplied which overcomes an energy barrier (known as the activation energy) so that the sintering process will proceed. The resultant sintered system will have a lower free energy then that of the original pressed powder compact.

Many theoretical and subsequent practical investi-

gations have been made, to provide a greater understanding of the sintering process. These investigations have mainly been based on model systems with the objective of understanding quantitatively the fundamental steps of the sintering process. Determination of the variables and their effect on the process has enabled sintering mechanisms to be proposed. The resultant objective being to quantitatively predict the behaviour of the complex systems met in practise. But, owing to the complexity of many of the practical systems and the difficulty in controlling the many variables, a full understanding of many of the processes is difficult. For example, the simultaneous grain growth with densification during the later stages of the sintering process make it difficult to follow either process using theoretically derived expressions. Research has however shown the important variables and indicated their effect on the different stages of sintering.

Only a general introductory discussion of the sintering process is presented here. There have been many recent review articles, such as those by Coble and Burke⁹ and by Thümmler and Thomma¹⁰, which give detailed accounts and discussions of the sintering theories and their applicability to experimental observations on real systems. These review articles include all the necessary references to the original papers on all known mechanisms involved in the process.

The purpose of the work presented here is a

phenomenological study of the effect of additions, mentioned in the previous chapter, on the densification and grain growth of high purity magnesia, rather than a fundamental approach to the application of sincering theories. A brief survey of the processes that can occur in sintering is presented here, with the major emphasis on the processes most applicable to the present investigation. 2.20 Mechanism of Material Transport.

In order to predict how the changes will occur during sintering, it is necessary to identify the mechanisms by which the important atom or ion movements occur and to define the effect of the significant variables upon the rate of sintering.

The transport of material during sintering in the presence of a liquid phase is discussed later in section 2.40 of this chapter.

The mechanisms by which material transport occurs are considered to be the following:-

- (i) Viscous or plastic flow
- (ii) Volume diffusion.
- (iii) Surface diffusion.
- (iv) Evaporation and condensation.

Mechanism (i) involves the bulk movement of material compared with movements of individual lattice structural components in the other three mechanisms.

These mechanisms can be divided into two types: those that can produce shrinkage, and those that cannot.

For shrinkage to occur it is necessary for the centres of contacting grains to approach each other. Viscous flow, which will occur in systems with a liquid phase at the sintering temperature; or plastic flow, caused by internal stresses in the solid compact, can both cause shrinkage. The matter at the contact area between the adjacent grains may be transported to pores or the surface by a diffusion process, so the grains approach each other. These are the only processes which will cause a decrease in the porosity of the aggregate.

The process involving evaporation from high vapour pressure sites, and subsequent condensation on lower vapour pressure sites, will only predominate in systems where the vapour pressure is appreciable at the firing temperature. A similar rearrangement may occur by diffusion over solid-vapour surfaces. These mechanisms will cause changes in the shape of pores, but unless pores are continuous to the surface, no shrinkage will be observed. Both processes can cause the growth of a neck or contact area between two sintering particles during the initial stage of sintering and hence increase the strength of the compact.

More than one of these material transport mechanisms may operate simultaneously. For example, a compact may increase in density by a diffusion process and at the same time pores may be rounded by an evaporationcondensation mechanism. The resulting decrease in surface area would decrease the driving force for all

material transport processes and would decrease the rate of shrinkage by the diffusion mechanism.

Most of the evidence from detailed studies of sintering processes supports the view that in a single phase crystalline material having a low vapour pressure, sintering usually occurs by a diffusion process, where grain boundaries act as sinks for diffusing vacancies and pores.

2.30 Sintering Mechanisms.

In most systems of particle compacts it is observed that the rate of shrinkage of the compact changes as the process proceeds. It is thought that the process of material transport is the same throughout sintering, but since changes in the geometry of the system occur, various stages in the sintering process can be identified. The earliest workers in the field defined the stages of the process in terms of changes in strength or electrical conductivity. The stages of the sintering process are now defined in terms of the position of pores and grain boundaries.

Coble¹¹ defines the process of densification of compacts as occurring in three stages:-

(i) The initial stage of sintering is the formation of a neck between adjacent particles. This was first analysed by Kuczynski,¹² whose work has had a great impact on the recent investigations on sintering models.

(ii) An intermediate stage is considered to exist

after some grain growth has occurred. In this stage the pores are a continuous channel and all the pores are intersected by grain boundaries.

(iii) During the final stages of sintering the continuous pore channels become discontinuous, pores may be isolated from the grain boundaries and trapped within grains, especially when discontinuous grain growth occurs.

In the present investigation measurements were taken on the compacts that had reached the latter stages of sintering when grain growth was occurring.

2.31 Initial Sintering Stage. Here a "neck" is formed between adjacent particles so that their midpoints approach only slightly. This corresponds to a small contraction, but a marked decrease in surface activity takes place, although the powder particles retain their individual shape.

Kuczynski analysed the simple model of spheres sintering to a flat plate and conducted measurements of neck growth between the species. He derived the following expression for growth of the neck:-

 $x^n/a^m = Kt$ (1) where K is a temperature dependent constant, t the time, x the radius of the neck and 'a' the radius of the sintering sphere. The values of n and m depend on the mechanism of material tran-port. He found that glass sintered by a viscous flow mechanism with n = 2 and m = 1, whereas copper sintered by a lattice

diffusion mechanism with n = 5 and m = 2. It was assumed that lattice vacancies were created at the 'neck' and were transported away from that site by lattice diffusion. Grain boundaries act as sinks for the diffusing vacancies, and during the elimination of porosity, the grains move closer together and hence the compact shrinks.

Measurements made by Kingery and Berg¹³ during the initial sintering of sodium chloride showed that the neck growth kinetics were consistent with an evaporation-condensation transport mechanism. Coble¹⁴ found that the shrinkage, during the initial stages of sintering of alumina, indicated a bulk diffusion mechanism of material transport.

2.32 Intermediate and Final Stages of Sintering. From a practical aspect, the most important stage in the sintering process is the intermediate stage in which most of the densification occurs and the particles lose their identity.

If a diffusion mechanism operates during sintering, one would predict that pores which lie on grain boundaries must disappear more rapidly than those which lie in the centre of grains. Alexander and Baluffi's¹⁵ investigations on the sintering of copper wires and Coble's investigations on the sintering of alumina, have shown that the pores only shrink and disappear when they are connected to a grain boundary during this intermediate stage. The

grain boundaries either short circuit the diffusion paths or act themselves as vacancy sinks. Burke¹⁶ noted that in the early stage of sintering, pores must lie on grain boundaries, because they are regions where the initial particles are not in contact. Pores isolated inside grains, by the process of controlled and discontinuous grain growth, was one of the reasons for the stopping of sintering before theoretical density is attained. Pores at or near grain boundaries can be removed on further heating, but those far removed from the grain boundaries persist for indefinite periods.

At the beginning of the intermediate stage of sintering, the grain boundaries are pinned within their circumscribing pores and the grain diameter remains constant. As the pores reduce in diameter, they begin to lose their continuity and the grain boundaries are no longer pinned as strongly. Grain growth begins and pores are left stranded, being no longer connected to a grain boundary. At this stage only those pores which pin a grain boundary, reduce appreciably in size until the grain boundary breaks away and is pinned by another pore. This is due to the diffusion along a grain boundary being 2 or 3 times faster than within the grain itself. At this stage of sintering the change in the shrinkage rate of the compact becomes increasingly slower and for practical and commercial purposes sintering may be considered to te complete.

It is very difficult to predict the shrinkage kinetics in practical systems, because of the simultaneous changes in grain size, pore geometry and pore location.

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In the final sintering stage the isolated pores become increasingly spheroidised. Further densification proceeds slowly so that it is often impossible to decide whether the residual porosity is permanent or not. In cases where gases are enclosed in the residual pores, being unable to diffuse out, further densification becomes impossible when the pressure of the gas equals the negative pressure due to the surface tension of the enclosing solid. The sintering atmosphere is thus critical in the sintering process. Cohle¹⁷ has shown that nitrogen, argon and helium physically inhibit the sintering of Al_2O_3 to theoretical density, which can be obtained in oxygen, hydrogen or a vacuum. In the present investigation, air was the sintering atmosphere.

During the final stage of sintering, grain growth is either continuous or discontinuous. In continuous or normal grain growth the size of all the grains is approximately equal, but in discontinuous grain growth, markedly mixed grain sizes arise. Discontinuous grain growth is common in high purity and dense alumina and has been observed by Brown,¹⁸ and Lowrie and Cutler¹⁹ in high density pure magnesia.

2.40 Sintering in the Presence of a Liquid Phase.

In the present investigation small amounts of

liquid will be present in some of the mixtures at the higher sintering temperatures. This is due to the formation of liquid from the silicate and the bulk magnesia phase. A brief discussion is presented here on theories concerning the sintering mechanisms involved under such conditions.

This form of sintering is governed by the degree of wetting of the solid grains by the liquid. For oxide grains, this wetting is governed by its surface energy and its constant angle. If the contact angle is greater than 90° , the grains will not be wetted by the liquid phase and hence greater solid-solid bonding will occur between the grains. On the other hand, if the contact angle is less than 90° , the grains will be wetted and the degree of penetration of the liquid phase between the grains will be determined by the surface energies of the liquid and solid phases. The equilibrium contact angle formed by the solid and liquid interfaces is known as the dihedral angle.

A detailed discussion of sintering in the presence of a liquid phase is given by Kingery.²⁰ Comments here will be limited to that of sintering of reactive solid-liquid systems, where the solid phase shows a limited solubility in the liquid at the sintering temperature. This will be the case for the compositions in the present investigation.

Kingery describes three stages that can be distinguished in the process.

Firstly, rearrangement of the residual solid phase by viscous flow in the liquid during which rapid shrinkage occurs. This relieves stresses induced during the compaction of the particles and produces a more stable system.

Then a process of solution and reprecipitation of the solid in the liquid starts, during which densification occurs more slowly.

Finally, a coalescence process proceeds where incomplete wetting of the solid grains is present. The solid grains are partly in contact without complete penetration of the melt.

In such systems, after the completion of the first stage, the processes that are found during sintering in the absence of a liquid take place, which become rate determining. Cannon and Lenel²¹ suggested that the requirements for complete densifications are: an appreciable amount of liquid, an appreciable solubility of the solid in the liquid and complete wetting of the solid grains. The solubility of the solid in the liquid phase is therefore the critical factor upon which the sintering process depends in these systems.

The generally accepted explanation to this process was originated by Price, Smithells and Williams.²² They suggest that very fine particles have a higher solubility in a liquid than larger particles. During Liquid-phase sintering, the fine particles dissolve in the liquid; but because of the lower solubility of

solid phase in liquid near the larger particles. this material is redeposited on these larger particles. Thus, the fine particles shrink and disappear, while the larger particles grow larger. Kingery disagrees with this mechanism. He points out that because of packing requirements, transfer of material to form larger spheres cannot lead to complete densification, unless the liquid content is larger than that experimentally found to be necessary. In the later stages of the process, densification continues even after the solid particles are quite large. Finally, although samples with large liquid contents show isometric grain growth and rapid densifications, observations of sintered samples with smaller amounts of liquid indicate that the particles do not remain spherical but grow to the shape required for maximum density.

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Kingery concludes that the process is better understood by considering the forces acting on the system due to the surface energies involved. Compositions containing large amounts of liquid at the sintering temperature solidify rapidly due to: surface tension forces, flow of the liquid, and solution of some of the solid giving a moderate to fine grain size with equiaxial particles. For small amounts of liquid, solution occurs at the contact points because of hydrostatic pressure arising from the liquid surface tension and not related to differences in solubility at the radius of curvature of the particles.

The grains tend to grow into shapes which will fill the volume most efficiently. In either case, complete wetting and penetration of liquid between the particles is necessary. If this is not the case, the powder compact will sinter by a process analogous to solidstate sintering.

2.50 Kinetics of Grain Growth.

Kingery²³ describes the terms "recrystallisation" and "grain growth" as occurring in three distinct processes:- recovery, primary and secondary recrystallisation.

Recovery is the relief of stress within a heavily deformed crystalline matrix with no change in the microstructure, at a temperature below the minimum recrystallisation temperature for the material. This process is very common in metals and alloys which can undergo heavy deformation, but for ceramic materials which (because of differences in atomic and ionic bonding) cannot easily be deformed, this process is usually ignored.

Primary recrystallisation is the process by which nucleation and growth of strain-free grains occurs from the "recovered" matrix. Grain growth is the process by which the average grain size of strain-free or nearly strain-free grains increases continuously during heat treatment without a change in the grain size distribution.

Secondary recrystallisation, sometimes referred to as discontinuous, abnormal or "cannibal" grain

growth, is the process by which a few large grains are nucleated and grow at the expense of other finer grains. The latter two processes are the predominant ones in the latter stages of sintering of ceramics.

2.51 Continuous Grain Growth. Whether or not primary recrystallisation occurs, an aggregate of fine grained crystals increases in average grain size when heated above its minimum recrystallisation temperature. As the average grain size increases, some grains must shrink and disappear. If all the grain boundaries are equal in energy they will meet to form angles of 120°. In a two dimensional system. angles of 120° between grains with straight sides can occur for only six sided grains. Grains having fewer sides will have boundaries that are concave when observed from the centre of the grain. Since grain boundaries migrate towards the centre of curvature, grains with less than six sides will tend to grow smaller and grains with more than six sides will tend to grow larger.

For any one grain, the radius of curvature of a side is directly proportional to the grain diameter and therefore the rate of grain growth is inversely proportional to the grain size. Thus at constant temperature:-

dD/dt = k/D (2) On integrating this equation becomes:-

 $D^2 - D_0^2 = K(t - t_0)$ (3)

where D is the average grain diameter at time, t, D_0 the grain diameter at time, t₀ (which is usually O) and K the constant of grain growth rate.

Since D_o is normally small compared with D, the grain growth equation is often represented in the form:-

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When log D is plotted against log t a straight line is commonly observed at least for moderate amounts of grain growth. For a variety of reasons, usually associated with impurities, the value of n in equation (4) is often found to be greater than 2 and is frequently about 3. This is thought to be due to impurities segregated at grain boundaries inhibiting the grain growth at constant temperature. The squared relationship of equation (3) has been verified experimentally by Daniels et al²⁴ and by Spriggs et al²⁵ for fully dense magnesia, and by Budnikov and Charitonov²⁶ for magnesia with hafnium oxide additions.

The cubic relationship (i.e. n = 3) has been found for grain growth of ceramic materials in the presence of a liquid phase²⁷⁻³¹ Greenwood³² in a study of the growth of uranium particles in lead-uranium and sodiumuranium slurries, derived the following relationship based on diffusional flow for the change in particle size.

 $D^3 - D_0^3 = 3 d S 2M \delta t / RTp^2$ (5) where d is the diffusional coefficient, S the solubility, M the molecular weight of the solid, λ the inter-

facial tension and p the density of the solid.

Investigations have shown that grain growth can be limited to a size controlled by second phase inclusion, which includes porosity. From grain growth equations it would be expected that the process would continue to produce a single crystal which is the thermodynamically most stable state of the system.

It is possible to determine the activation energies of the grain growth process from the values of the rate constant, K, at various temperatures by using the Arrhenius equation:-

In metals of commercial purity, the activation energy for grain growth is comparable to the activation energy for self diffusion in the material. Aust and Rutter,³³ have observed however, that in high purity lead, the activation energy may be very much lower (and the migration rates very much higher) than in slightly alloyed material. The interpretation is that solid solution elements tend to segregate to grain boundaries and slow down their rate of movement.

Kingery and Francois³⁴ observed that as the

majority of the pores remain at grain boundaries during grain growth, pore migration will be accomplished by the same material transport as during densification. The activation energy for grain growth must be consistent with that for densification, but this will no longer be the case for the activation energy of grain growth in porosity-free material.

2.52 Discontinuous Grain Growth. This often occurs when multiple sided grains occur in the structure of a low porosity material. The grain which has many sides will have more strongly curved boundaries, which will be able to move past inclusions and thus be able to grow, although grains having fewer sides will be unable to do so. As this grain consumes its neighbours it will add even more sides, the boundary will become even more strongly curved and its growth potential will increase even more. Coble¹¹ showed that small additions of magnesia to alumina acted as a grain growth inhibitor and prevented discontinuous grain growth from occurring. The resultant effect of the addition on the sintering process is that almost fully dense alumina can be obtained.

3.00 REVIEW OF PREVIOUS RESEARCHES ON THE SINTERING OF MAGNESIA

- 3.10 Sintering of Magnesia
- 3.20 Effect of Additions on the Sintering of Magnesia
- 3.30 Effect of the Lime-Silica Ratio of the Addition on the Fired Properties of Magnesia.

3.10 Sintering of Magnesia.

The term calcination is used to describe the firing process by which the magnesia precursor, usually the hydroxide, carbonate or oxalate, is decomposed to an active fine powder.

Clark and White³⁵ studied the sintering characteristics of calcined magnesia as well as those of powdered soda-lime glass and calcined alumina. They attempted to evaluate the rate constants and activation energies for the sintering process by means of "shrinkage-time" expressions. Further investigations by Cannon, Clark and White³⁶ into the sintering behaviour of calcined magnesia showed that increasing the sintering temperature increased the shrinkage. They found that magnesia calcined at 900°C showed a greater shrinkage on sintering than material calcined at 1450°C.

The effect of the calcination temperature on the sintering of high-purity magnesia was shown by Allison et al³⁷ to give a marked decrease in density of the sintered compacts, where petrographically identifiable periclase was formed on calcination.

Brown¹⁸ described a method for preparing high purity (99.999%) magnesium oxide via the oxalate. This method was used as the basis for the preparation of magnesia in this present investigation. A study of the densification rates of this material between 1300° and 1500°C showed that an empirical equation:-

 $S_a = k \ln t + c \dots (7)$

was obeyed. Where Sa is the sintered bulk density and is taken as a measure of shrinkage, t the sintering time, k the temperature dependent densification rate constant and c a constant. Morgan and Welch³⁸ first proposed this empirical equation between the shrinkage of metal oxide compacts and sintering time. The straight line plots could be predicted from Coble's model for the intermediate stage of sintering. Brown obtained an activation energy for densification of pure magnesia of 27 Kcal, which is considerably lower than the determined values of 62.4 Kcals for the diffusion of oxygen ions or 79 k cals for the diffusion of magnesium ions through magnesia. Brown concludes that this low activation energy could support a mechanism of grain boundary diffusion rather than a bulk diffusion mechanism for material transport.

In an investigation of the sintering and recrystallisation behaviour of pure magnesium oxide, Budnikov et al³⁹ found that zero porosity cannot be obtained with chemically pure magnesia by normal sintering techniques. They suggested that this was due to micro-cracks between individual grains and internal crystalline closed pores.

Bessonov and Semavin⁴⁰ showed that the rate of heating to sintering temperatures of 1650° C affected the final density of the magnesia, as well as the original particle size of the material. For heating rates of between 0.05° and 0.33° C/sec highest porosities
were obtained with the faster heating rates.

Reeve and Clare⁴¹ showed that from Coble's equation for his model of the intermediate stage of sintering, the activation energy for grain growth and densification should be added to give the actual value for the diffusion process responsible for densification. The corrected activation energy for Brown's work would be 85 Kcals which is in better agreement for the diffusion of magnesium ions in magnesium oxide. It should be emphasised that the activation energy of grain growth energy in Brown's work was obtained for small additions of vanadium and in a different temperature range to that of the densification results.

Eastman and Cutler⁴² investigated the effect of water vapour on the initial stage of sintering of magnesia from 800° to 1107°C. They found that the initial sintering occurred by a grain boundary vacancy diffusion mechanism. The diffusion of the Mg²⁺ ions being rate determining. Increasing the water vapour pressure increased the rate of sintering by increasing the number of cation vacancy sites. They obtained an activation energy for densification of 80 Kcals per mole for partial pressures of water up to 5 m.m. and 48 Kcal per mole above this pressure.

3.20 Effect of Additions on the Sintering of Magnesia.

The sintering of magnesia to high density was studied by Atlas.⁴³ He found that small percentages of the halides of the alkali metals, particularly lithium, increased the shrinkage of magnesia calcined

at temperatures below 600° C. He was able to achieve high densities at sintering temperatures below 1400° C. He suggested that the effectiveness of the salts, as sintering catalysts for magnesia, depended on the original surface area and particle size of the magnesia. The catalystic action of the salts was found to be greatest when the particle size of the magnesia was less than 0.5 μ and had a surface area greater than $30 \text{ m}^2/\text{g}$.

The role played by crystal lattice defects in the sintering of magnesia and alumina was studied by Jones et al.⁴⁴ The defects were induced by small additions of TiO₂, Cr_2O_3 , MnO, Fe_2O_3 and ZrO_2 . The mixtures were sintered in atmospheres of O_2 , N_2 and H_2 . The diffusion promoted by lattice defects were observed by measurements of the fired bulk density.

The effect of other additions on the sintering of magnesia were carried out by Layden and McQuarrie.⁴⁵ They selected fourteen metal ions and added each one in turn to basic magnesium carbonate. The magnesia, obtained after calcining the mixture, was fired at various temperatures to determine the effect of the addition on the sintering behaviour. The majority of the additions increased the density for a given firing treatment, but some were without effect and chromic oxide dramatically inhibited sintering. They also suggested that most of the additions, which aided sintering, did so by entering into the magnesia lattice and creating defects.

The influence of CaO, Fe₂O₃, Al₂O₃, TiO₂ and SiO_2 on the sintering of magnesia were studied by Kriek et al. Melt-forming additions such as dicalcium ferrite and brownmillerite (4CaO.Al203.Fe203) were also studied. The sintering was investigated as a function of time, temperature of sintering, and the amount of addition. Lime was found to inhibit sintering to an extent which appeared to depend on the number of points of contact between MgO and CaO particles in the original mixture, and the suggestion is made that this may be related to the magnitude of the interfacial energy between CaO and MgO. All the other additions promoted sintering to some extent, TiO, being most effective and also in promoting grain growth of the periclase crystals. There appears to be an optimum addition of TiO2, Al203 and SiO2 beyond which sintering is inhibited. It was also suggested that TiO2, Al203 and SiO₂, like Fe₂O₃, all aid sintering by promoting cations to the magnesia lattice, with the creation of cation vacancies, and thus enhance their diffusion during sintering.

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Degtyareva et al⁴⁷ showed that additions of up to 0.45% CaO did not affect the sintering of magnesia at temperatures up to 1500°C. They found that the activation energy for sintering varied from 55 to 67 Kcal /mole for different types of magnesia. This indicated a diffusion mechanism and they obtained an activation energy for grain growth of 62 Kcal/mole, which agrees with that obtained by other workers.^{24,25}

Barta and Gorni⁴⁸ found that pellets of dry

magnesium hydroxide could be directly sintered to high densities at 1600° C. Additions of TiO₂ and V_2O_5 enabled the sintering temperatures to be lowered to 1450°C. They found that increasing the rate of temperature rise from 100° to 300° C/hour significantly reduced the sintered densities.

3.30 Effect of the Lime-Silica Ratio of the Addition on the Fired Properties of Magnesia.

Jackson et al^{49,50} have investigated the change in the dihedral angle, which is the angle of the interfaces of the magnesia and calcium silicate phases, with firing temperature and silicate phase compositions. They found that the percentage of solid-solid bonding of the magnesia grains increased as the lime-silica ratio of the silicate phase was increased from 0.5 to 2.0. Fe_2O_3 and Al_2O_3 additions lowered the dihedral angle. The greater the degree of solid-solid bonding i.e. the greater the dihedral angle; then the rate of densification would be expected to be greater and the greater the high temperature strength when the silicate phase softens.

The importance of the lime-silica ratio of the silicate phase has been demonstrated by Kriek and Segal.⁵¹ They found that the constitution of commercial magnesia bricks determined to a major extent their strength at high temperatures. The highest strength was obtained for dicalcium silicate bonded bricks, but additions of ferric oxide lowered the strength substantially and had little effect when the bonding

silicates were monticellite, merwinite and forsterite.

Van Dresser⁵² compared the high temperature properties of magnesia refractories in the purity range of 95 to 99+ % MgO and was able to show the importance of the lime-silica ratio of the silicate phase. Outstanding high temperature creep resistance was obtained on specimens containing more than 98% MgO. He concluded that improved physical properties and chemical erosion resistance appeared to be a function of the MgO content and the type of silicate second phase present.

4.00 RAW MATERIALS AND COMPACT PREPARATION.

- 4.10 Selection of Magnesia Source.
- 4.20 Preparation of Magnesia.

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- 4.30 Properties of Magnesia.
- 4.40 Preparation of the Silicate Additions.
- 4.50 Preparation of the Mixtures.
- 4.60 Pressing of the Pellets.

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4.10 Selection of Magnesia Source.

The effect of small amounts of impurity on sintering characteristics has been discussed in the previous chapter. It is therefore essential to have a high purity magnesia as the starting material for an investigation on the effect of minor additions of phases on its high temperature properties.

The industrial source of magnesia is from the carbonate for the naturally occurring material and from the hydroxide and hydroxycarbonate in the seawater process. It is difficult chemically to prepare a high purity magnesia from these sources. It was therefore decided to adapt a method described by Brown¹⁸ whereby the oxide is prepared by calcining a purified sample of magnesium oxalate as the source of magnesia for this investigation. The particle size of the magnesia will depend on the temperature at which it was calcined. Brown showed that for a calcination temperature of 800°C, well defined cubic shaped crystals were produced having a particle size of around 0.03 µ. Increasing the calcination temperature increases the particle size. Magnesia produced by decomposing the oxalate at 800°C resulted in the highest fired density when compacted and sintered at temperature. Magnesia produced at lower or higher calcination temperatures resulted in lower fired bulk densities. Livey et al⁵³ Eubank⁵⁴ and Coleman⁵⁵ prepared magnesia from magesium carbonate, basic magnesium carbonate and magnesium hydroxide and found

that the optimum calcining temperature was 900° C. The particle size of the oxide from these sources was found by Coleman and Ford⁵⁶ to be between 0.04 and 0.05 μ when calcined in this temperature region.

4.20 Preparation of Magnesia

The following method was used for the preparation of the magnesia. High purity magnesium metal of 99.9% purity was dissolved in nitric acid. Ammonium hydroxide was added to co-precipitate heavy metal hydroxides with a head fraction of magnesium hydroxide. A head fraction of magnesium oxalate was then precipitated, by the addition of ammonium oxalate, and then filtered to remove further impurities. The bulk magnesium was precipitated from the filtrate with a purified oxalate solution. The resulting precipitate was then filtered, washed and dried. All the solutions were mixed and filtered whilst kept as near to their boiling points as possible. The magnesium oxalate was calcined in nickel crucibles for 5 hours at 800°C. The oxalate was heated at a rate of 300°C per hour to the calcination temperature where the furnace chamber was controlled to within $\pm 5^{\circ}$ C. The resulting oxide was stored in sealed containers.

Analysis of magnesia produced by this method showed it to contain 60 parts per million impurity with the major impurity being manganese (30 p.p.m.). The purification process was modified by adding a solution of ammonium sulphide to the alkali solution resulting after the addition of ammonium hydroxide. A grey, buff coloured precipitate resulted, indicating

that manganese sulphide had been precipitated together with other sulphides and hydroxides. Most heavy metal sulphides have a lower solubility in alkali solution than hydroxides. Excess hydrogen sulphide was boiled off from the solution which was then filtered and further processed by the above described method. The addition of sulphide decreased the manganese impurity to approximately 4 p.p.m.

4.30 Properties of Magnesia.

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Four representative samples from each batch of magnesia prepared were analysed spectrographically and the average analysis is given in Table 1.

TABLE 1.

AVERAGE CHEMICAL ANALYSIS OF THE MAGNESIA.

ESTIMATE AS PARTS FER MILLION
3
4
- 3
4
1
4
1
3
2
2
27

Ag, As, Au, B, Be, Bi, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, Li, Mo, Nb, Os, P, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn and Zr were specifically sought but not detected. It was found possible to produce by this method some material with as low as 6 p.p.m. total detectable impurity. 3,0

An ignition loss on the material after calcining at 800°C for 5 hours, resulted in a loss of 0.14% by weight on firing at 1200°C for 2 hours in a platinum crucible. The result indicates that after calcination at 800°C almost complete decomposition of the oxalate to the oxide had occurred. The calcined material, if exposed to the atmosphere, was found to absorb 1.5% by weight of moisture within 3 hours. The hydration kinetics and mechanism involved in the hydration of the particle sized magnesia has been studied by Coleman and Ford⁵⁶ and Chown and Deacon⁵⁷

The surface area of the magnesia was determined using the Haynes Air Absorption Apparatus and was found to be 45 m^2/g .

Particle Shape and Size

Examination of the magnesia, obtained by calcination of the mognesium oxalate at 800° C on the "Stereoscan" Electron Microscope confirmed Brown's observations on this oxide that the material was agglomerates of cubic particles of the oxide.

The cilicates were formed by firing the resultant compacts in an air atmosphere at the following temperatures:-

Fired at 1480°C for 2 hours : Monticellite (CaO.MgO.SiO₂) Fired at 1500°C for 2 hours : Merwinite (3CaO.MgO.2SiO₂) Fired at 1650°C for 2 hours : Forsterite (2MgO.SiO₂) Dicalcium Silicate (2CaO.SiO₂) Tricalcium Silicate (3CaO.SiO₂)

The materials were ground with an agate pestle and mortar to pass through a 300 B.S. mesh sieve (53 µ). The oxides were shown to have fully reacted to form a homogeneous silicate phase by examining them by the X ray diffraction technique. No peaks were observed that could not be assigned to those of the desired silicate. In order to calculate the true densities of the subsequent mixtures, the densities of the silicate phases were determined and checked with those calculated from X ray data⁵⁸ The densities were determined using specific gravity bottles with xylene as the displacement liquid. The density values are summarised in Table 2.

4.50 Preparation of the Mixtures.

Mixtures of the ground silicates and magnesia were made containing 0.5 mole % of the silicate, except in the case of mervinite where a 0.25 mole % addition was made. These additions resulted in a constant 0.73% by weight of silica in all the mixtures containing silicates, which is a level typical of industrially available seawater magnesia. The calcium oxide mixture was made by the addition of the corresponding proportion of calcium carbonate to give a 0.5 mole % calcium oxide content. The carbonate decomposes to the oxide in the temperature range of 750° to 1000°C, well below that of the lowest sintering investigation temperature of 1400°C.

The effect of increasing the additions was investigated by preparing a further series of mixtures with double the amount of the additive phase. The calculated chemical analysis of all the mixtures is summarised in Table 3.

The additions were mixed with magnesia by repeatedly passing through a 72 B.S. mesh sieve.

The mixtures were preheated in nickel crucibles for 2 hours at 600°C before pressing into compacts to remove water absorbed from the atmosphere during the preparation of the mixtures.

4.60 Pressing of the Pellets.

Pellets were pressed in batches of 5 from each mixture. At least three batches from each mixture were sintered in separate firings, so 15 individual results were obtained.

1.5 g. of the powder was pressed at 10 t.p.s.i. in Floating die a 0.5 inch diameter hardened steel mould. A cylindrical compact of approximately 0.25 inch height with a pressed density of 1.58 + 0.03 g./cc. was produced. Six drops of dried carbon tetrachloride was added to the powder in the mould to help suppress laminations occurring during the pressing and ejection of the pellet. The carbon tetrachloride vapour displaces air in the mould chamber due to its greater vapour density and then liquefies when the plunger compresses the powder. The load was maintained on the pellet for 20 seconds. Filter paper discs were placed on the plunger ends to prevent adhesion of the The pellet to the plungers occurring during the pressing.

pellets were dried at 80°C for a few minutes to volatize the carbon tetrachloride and then stored in a desiccator. The maximum storage time of the pellets before firing was one day and they were left for a minimum time exposed to the atmosphere in the furnace chamber.

5.00 APPARATUS AND EXPERIMENTAL TECHNIQUES.

- 5.10 Density, Porosity and Sintering Shrinkage Measurements5.11 Density Measurements.5.12 Porosity Determinations.
 - 5.13 Sintering Shrinkage
- 5.20 Sintering Furnace
- 5.30 Sintering Procedure
- 5.40 Preparation of the Samples for Microscopic Examination
- 5.50 Meaurement of Grain Diameter
- 5.60 Microscopic Identification of the Phases

5.10 Density, Porosity and Sintering Shrinkage Measurements.

5.11 Density Measurements. A Clark-White³⁵ mercury balance was constructed for determining the bulk density of the pressed pellets. A diagram of the apparatus is shown in Figure 2a.

The weight of the specimen Wg. was first found in air. Then the weights required to adjust the stem of the balance to the same position in the mercury, with and without the specimens in the cradle, were obtained. The difference between the weights being the apparent upthrust Ug of the displaced mercury due to the pellet. The volume V of the pellet was calculated from the expression:-

$$V = \frac{W + U}{B_{T}} cc.$$
(8)

where B_{T} is the density of mercury at $T^{\circ}C$. Hence, the bulk density, S_{p}^{-} g./cc. can be calculated:-

$$S_{p} = \frac{W}{V} = \frac{W.B_{T}}{W+U} g./cc \qquad (9)$$

The pressed pellets could be weighed on the mercury balance to within 0.02 g. corresponding to an accuracy of the pressed bulk density of 1.58 ± 0.004 g./cc.

The xylene impregnation method was used to determine the density of the fired pellets. The mercury balance was not used because some of the specimens contained cracks after firing. Therefore the density measured by this method will vary with the time that the cracked pellet is submerged in the mercury. The greater the time of submersion, the greater the penetration of the mercury into the finer cracks; hence the higher the determined density. Tests on uncracked fired pellets showed that the xylene impreg-

nation and mercury balance method gave the same result.

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5.12 Porosity Determinations. The xylene impregnation method also has the advantage that an estimate of the volume of open and closed pores can be made. It should be emphasised, however, that the measured "sealed" porosity may include open pores that cannot be penetrated by the xylene molecule. They may be penetrable to a smaller molecule and therefore porosity values are dependent on the penetrant used.

The bulk densities and porosities of the specimens were determined by the following method. The fired compacts were placed on a piece of paper over a beaker containing xylene in a vacuum desiccator. After evacuating, the desiccator was tilted so that the pellets fell into the xylene which then entered the open pores. They were left standing in the xylene overnight at atmospheric pressure. Then the soaked pellets were weighed on an accurate balance, first suspended from a fine wire cradle in xylene (Wb) and secondly in air (Wc). Care was taken before the latter weighing to remove surplus xylene from the specimen and the wire cradle. Corrections were made for the upthrust on the wire cradle suspended in various depths of xylene. The pellets were dried at 160°C and then weighed in air (Wa). Two density determinations were made on each specimen. Normally the results were reproduceable to within + 0.01 g./cc. The bulk density, Sr, was calculated from the expression:-

 $S_{\mathbf{f}} = \underline{Wa} \times X_{\mathbf{T}} g./cc.$ (10) Wc-Wb

where $X_{\rm T}$ is the density of xylene at T^OC. The apparent solid density Sas, the ratio of the mass of the material to its volume of solid material plus volume of closed pores, was calculated from the expression:-

Sas =
$$\underline{Wa} \times X_{\underline{T}}$$
 g./cc. (11)
Wa-Wb

The true density of the material was calculated from the unit cell dimensions of each phase in the material. The X ray data for the phases is given in section 4.4. The true density St, of the material was calculated in terms of volume from the expression:-

$$\frac{1-x}{3.58} + \frac{x}{P} = \frac{1}{5t}$$
 (12)

where x is the weight fraction of the addition phase having a true density P. The true density of the magnesia was 59taken to be: P = 3.58 g./cc.

The apparent porosity Pa, the ratio of the volume of the open pores to the bulk volume of the material, was calculated from the expression:-

$$Pa = 100 (1-S_{f})_{\%}$$

Sas) (13)

The true porosity Pt, the ratio of the combined volumes of the open and closed pores to the bulk volume of the material, from the expression:-

$$Pt = 100 (1-S_{f}) \%$$
(14)
 \overline{St}

The sealed porosity, Pc, the ratio of the volume of closed pores to the bulk volume, by the definition:-

Pt = Pa + Pc (15)

thus the sealed porosity can be determined knowing Pa and Pt.

5.13 Sintering Shrinkage. The fractional volume shrinkage ΔV of the pellets after sintering can be expressed in terms of the pressed and fired bulk densities Sp and S_p respectively.

$$\frac{\Delta V}{V_{p}} = \frac{V_{p} - V_{F}}{V_{p}} = \frac{1 - \frac{W}{V_{p}}}{W_{F}} = \frac{1 - \frac{Sp}{S_{F}}}{S_{F}}$$
(16)

This method of calculating the volume change was used as small pieces of material were often lost from the pellet after firing,

The densification behaviour of the components is discussed in chapter 7.

5.20 Sintering Furnace.

All the specimens were fired in air using a high temperature furnace described by O'Neill⁶⁰ and loaned by A.E.R.E., Ceramic Division, Harwell. The furnace consisted of a horizontally mounted recrystallised alumina tube carrying a molybdenum wire winding. The winding was sealed from the air and the firing chamber, and a mixture of 97% nitrogen and hydrogen gas passed over the winding to prevent oxidation of the molybdenum at high temperatures. The ends of the tube could be sealed so that the furnace atmosphere could be changed. For all the firings in the present investigation an oxidising atmosphere was main-This was achieved by intermittently circulating tained. air through the furnace chamber to remove any hydrogen that had diffused through the alumina tube at the high firing temperatures.

For firing temperatures up to 1700°C, a 5% Rhodiun/ 95% Platinum - 20% Rhodium/80% Platinum thermocouples were used in conjunction with the corresponding controller to control the furnace temperature and to record the temperatures within the firing zone. At 1800°C, 20% Rhodium/80% Platinum - 40% Rhodium/60% Platinum thermocouples were used with a 0 to 5 millivolt controller, to obtain the maximum accuracy from these thermocouples, since they give lower e.m.f's at temperature than the former mentioned thermocouples. It was possible to control the furnace to within 1°C at temperatures up to 1700°C. At 1800°C the furnace could be controlled to within 5°C. <u>, .</u>,

5.30 Sintering Procedure.

It was not possible with this furnace to inject the pellets into the hot zone at the firing temperature without a considerable loss of heat and disturbance of the distribution of the temperature occuring. No attempt was made to develop a procedure for achieving this since the initial stages of sintering were not being investigated in this research. The pellets were placed in the cold furnace and taken to temperature at constant heating rates and controlled at temperature to the maximum degree of accuracy.

An exploration of the temperature distribution along the tube at 1600°C revealed a two inch long hot zone. Specimens were fired within this region on a magnesia plinth. A diagram showing the positioning of the specimens in the furnace is given in Figure 26. Two magnesia

blocks 1.5 inches long were connected to the ends of this plinth, onto which were tied the thermocouples. Two high alumina porous cylindrical plugs 2.5 inches long were placed in each end of the furnace tube 1 inch from the magnesia blocks. The purpose of these was to improve the temperature distribution in the firing zone. They did not, however, prevent the free flow of air through the tube. The control thermocouple was placed in the centre of the pellets and two further thermocouples at the ends of the pellets. The couples were connected to a potentiometer and the standard calibration charts supplied by the manufacturers with each thermocouple were used to convert the e.m.f. output to the corresponding temperature. At temperatures up to 1700°C the recorded temperature along the firing zone did not vary more than + 2°C. Normally the temperature distribution was within 2°C. At 1800° C the temperature distribution was within + 5° C and normally in the region of 5°C. The calibrations of the former thermocouples were guaranteed by the manufacturers to be within $\pm 3^{\circ}$ C at 1700° C and the latter to be + $5^{\circ}C$ at $1800^{\circ}C$.

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The pellets were stood on platinum foil placed over the magnesia plinth. For firing temperatures above the melting point of platinum they were placed on sections of fired pellets of a similar composition. These precautions were taken to avoid migration of impurities from the magnesia plinth into the samples.

The temperature was raised to 1000°C in 2 hours and then the rate of temperature rise was accurately controlled

at 300° C per hour to the firing temperature. The firing temperatures investigated were 1400° , 1500° , 1600° , 1700° , and 1800° C. Specimens were fired at these temperatures for 0.1, 1, 2, 4, and 8 hours. The pellets were cooled in the furnace from the firing temperature to 900° C within 1 hour and then removed from the furnace and air cooled. The furnace cooled from 1800° C to 1500° C within 5 minutes. 1,0

Appendix II contains a complete summary of the average results for the density, porosity and volume changes for each firing of the compositions M1, M3, M4, M6, M7, M8 and M9 given in Table 3.

The mixtures D3, D4, D6, D7, D8 and D9, given in Table 3, containing double the addition of the additive phases were fired at each temperature for 4 hours. The data on these compositions $\frac{are}{4\pi}$ given in Appendix III.

5.40 Preparation of the Samples for Microscopic Examination.

Polished surfaces of the pellets were prepared to examine the distribution of the additive phase in the magnesia matrix, to identify the silicate phase present and to determine the grain size of the magnesia. In this thesis the term "grain" is used to describe a single crystal of the magnesia in the polycrystalline specimens.

Three pellets from each firing treatment for all the mixtures were selected for grain size determinations. One pellet being taken from each of the three separate firings. Most of the samples fired at the lower temperatures and those fired for short periods at higher temperatures had a significant open porosity. It was therefore, necessary to impregnate the specimens with a hard setting resin

before mounting them for polishing. This impregnation helped to prevent pull-out of the grains during the polishing of the samples, and was carried out as follows: Pellets were heated to approximately 120°C on a hotplate and then placed on non-absorbent paper covered with "Araldite" resin (a prepared mixture of AY219 resin, HY 219 hardener and GY 219 accelerator). The cooling of the pellets resulted in resin being drawn into the open pores. They were then allowed to cool at room temperature when the resin set. The 3 pellets of similar composition and firing treatment were mounted together in "Ceemar" embedding resin in 1[‡]" diameter cardboard pill-box moulds.

The mountings were ground on a diamond impregnated grinding wheel until approximately 0.05 inch of the pellet had been removed. The surfaces were then progressively ground on papers coated with grades of 200, 300, 400 and 600 B.S. mesh carborundum grit sizes, using water as the lubricant. Final polishing was carried out with diamond paste, using 6 micron size material followed by 3 micron size and finishing with 1 micron size diamond paste on paper fibre laps. The specimens were polished under a load of 31bs for 30 minutes on each grade of diamond paste. The lap was rotated at 250 r.p.m. for the course grade of abrasive and increased to 400 r.p.m. for the fine grade. The specimens were cleaned with alcohol between each polishing treatment. <u>5.50 Measurement of Grain Diameter</u>.

The polished surfaces of the specimens had to be

etched to produce a well defined grain boundary structure in order to measure their grain sizes. This was achieved by etching the materials containing calcium silicate, which had grain sizes of greater than 15 μ , with cold saturated oxalic acid. Specimens fired at the higher temperatures for 4 and 8 hours were etched for 8 minutes. For the lower firing times and temperatures the etching time was increased up to a maximum of 20 minutes. Specimens of pure magnesia, those containing calcium oxide, and those with calcium silicate additions having grain sizes under 15 μ , were etched in cold dilute sulphuric acid for times which varied between 3 and 10 minutes. The mixtures containing forsterite were the most difficult to etch and in this case 25% sulphuric acid at approximately 80° C was used as the etchant.

Photographs of the etched surfaces were obtained using a metallographic microscope with a camera attachment. Ilford HP4 (400 A.S.A.) 35 mm. film was used. The negatives were enlarged to give 8 x 6 ins. prints. Standard scales were photographed on each film so that the exact magnification of each print could be determined. The magnification on the microscope was arranged, such that the mean grain intercept length (to be described in the next paragraph) was between 5 and 10 mm. It was found that the calculated grain diameter was always greater if the mean intercept length was less than 5 mm. as it was not possible to count all the grains intercepted by the line drawn across the photograph of the polished section. If the inter-

cept length was greater than 10 mm., insufficient grains were intercepted, hence decreasing the accuracy. Magnificiations of between 150 and 1500 were obtained on the prints for the specimens examined.

Fullman⁶¹ derived relationships for the calculation of the mean grain diameter, D, for a section through a random arrangement of equal spherical grains. He showed that for random straight lines drawn across a section of such a system, then the mean grain diameter could be obtained from the relationship:-

 $D = 1.225 L_d$ (18) Buist et al²⁹ showed that results obtained by the two methods agreed to within 3%.

For non-uniform spherical grains Fullman¹⁰ derived the relationship:

where $\overline{\mathbf{n}}$ is the average of the reciprocals of the grain diameters in the section.

Because of the number of grain size determinations required in this investigation, the average intercept method was used to estimate the grain diameters. Straight lines were drawn across the photographs and the mean

intercept length was calculated from approximately 500 intercepts. The mean grain diameter was calculated from equation (17). If the three grain sizes determined for each firing of the mixtures varied by more than 5%, a further specimen was mounted and its grain size determined. The grain sizes of all the specimens are given in the complete summary of the results in Appendices II and III. The grain diameter isothermals were plotted for each mixture at the 5 firing temperatures. These results are fully discussed and analysed in chapter 7.

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It was not always possible to determine the grain sizes of some of the mixtures after firing at 1400° and 1500° C for the shorter sintering times by this method. <u>5.60 Microscopic Identification of the Phases</u>.

This was carried out on the specimens mounted and polished as described in Section 5.40. It was found that silicates in the magnesia matrix were more distinct after polishing with alumina on terylene cloth, than after polishing with diamond paste on paper fibre laps. The former mentioned method gave more relief on the polished surface. Water was used as the lubricant on the terylene cloths, except for samples containing dicalcium silicate, tricalcium silicate and calcium oxide which are etched by water. For these mixtures paraffin was used as the lubricant during polishing.

Etching techniques similar to those described by Insley and Frechette⁶² were used in order to identify the phases present. The materials containing forsterite were etched with dilute sulphuric acid, which cause differences in the reflectivity between the forsterite

and the etched magnesia grains making the phases clearly distinguishable. For those materials containing the monticellite phase, 1% hydrofluoric acid was used, the monticellite appeared as a dark grey phase around the light magnesia grains. Mixtures containing merwinite were etched with 2% Nital (2% nitric acid in alcohol) followed by 1% hydrofluoric acid, which etches the phase to a light grey colour. Materials containing dicalcium silicate and tricalcium silicate were etched with 2% nital alone. The former phase is etched black and the latter is only slightly etched. Mixtures containing calcium oxide were etched with water. Photomicrographs of the freshly polished and etched surfaces of all the mixtures after firing at 1800° C are given in Figures 49 to 54. ي ` تر

Examination of the etched surfaces of the mixtures fired at 1800°C containing merwinite, dicalcium silicate and tricalcium silicate additions clearly showed that a 'silicate having a lower lime to silica ratio than the addition was present in the structure, as well as the original silicate phase. The calcium lost from the silicate phase was thought to have entered the magnesia lattice. An investigation of the polished surfaces of the fired materials was carried out on the electron probe microenalyser in order to determine the calcium content in the magnesia grains.

6.00 ANALYSIS OF THE FIRED MATERIALS BY ELECTRON PROBE

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AND X-RAY DIFFRACTION.

- 6.10 Previous Investigations on the Solubility of Lime in Magnesia.
- 6.20 Electron Probe Analysis.
 - 6.21 Experimental Details
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 - 6.32 Experimental Details
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- 6.40 General Discussion on the Solubility of Lime from Calium Silicates in Magnesia.

6.10 Previous Investigations on the Solubility of Lime in Magnesia

Jones and Melford⁶³ have studied the phases present in commercially available magnesia raw material and in refractory products⁶⁴ using electron probe analysis, electron-microscopy, X-ray diffraction and microscopic techniques. They found only 0.13% CaO in the magnesia grains in sea-water magnesia having a mainly monticellite (with a little merwinite) bond, and up to 1.9% CaO in naturally occurring mægnesias. The latter material had a higher lime and silica content than the former mentioned material, and the lime to silica ratio was greater than 2.0 to 1 compared with the sea-water magnesia which was less than 1.5 to 1.

A sea-water magnesia and three types of naturally occurring magnesias were examined by Obst et al⁵⁵ using electron probe analysis and microscopy to study the distribution of elements in the phases of these materials. They found in them evidence of solid solution formation by comparing optical microphotographs and electron probe Leipold^{66,67} analysis data. showed by electron probe analysis of hot pressed magnesia, that impurities such as the elements: Al, Ca and Si, even present in amounts as small as 30 p.p.m., were segregated mainly at grain boundaries; whereas other impurity elements, such as Fe, appeared uniformly distributed. Investigations of the mutual solubility of CaO and MgO in the binary phase system by Dorman et al showed that solid solutions up Obst 69 to 5 wt.% CaO in magnesia can occur at 1300°C.

found 2.5 wt.% CaO in MgO in a sample of sintered Dolomite $(MgCO_3.CaCO_3)$ fired at $1800^{\circ}C$. These results show that the magnesia lattice can accomodate the larger calcium ions in solid solution and in refractory magnesias there is an equilibrium distribution of the lime at high temperature between the silicate phase and the magnesia grains.

6.20 Electron Probe Analysis.

<u>6.21 Experimental Details</u>. Pellet samples of the materials containing the 0.5 mole % additions (0.25 mole % for the merwinite addition) fired at 1800°C for 8 hours were mounted together with a sample of monticellite, which was used as a standard, since it contained equal molar proportions of Ca, Mg and Si. The sample was polished by a similar procedure described in section 5.40. The polished set of samples was then coated in a vacuum with a layer of carbon estimated to be about 200-300° Å thick. The sample set was mounted in the electron probe analyser and point counts for Ca, Mg and Si taken in the centres of magnesia grains and compared with the standard sample. Counts were taken in the centres of the grains to minimise interferences from the silicate phases at the grain boundaries.

Point counts across large periclase grains showed that there was no appreciable difference in counts for a particular element within a grain. Therefore the phases were assumed to have reached equilibrium within the mixtures.

Further mountings were made containing pellet samples

from mixtures fired at 1800°C for 4 hours with the 1.0 mole % additions of the calcium containing phases (0.5 mole % merwinite addition). Samples containing 0.5 mole % of dicalcium and tricalcium silicates were investigated after firing at 1400°, 1500°, 1600° and 1700°C for 8 hours. The corresponding additions of monticellite and merwinite were investigated after firing at 1600° and 1700°C only.

Measurements were made on mixtures containing 0.5 mole % tricalcium silicate fired at 1800⁰C for shorter times of 1 and 4 hours, as well as 8 hours, to determine the effect of time at temperature.

Each result presented here is the average of at least six individual point counts on different grains. Any unusually high counts on a grain were disregarded because it was assumed that silicate phases, in the grain boundary under the grain being observed, were too close to the polished surface being examined.

The percentage of phases present was calculated from the point counts by comparing the counts given by the standard monticellite with those given by the sample. It was assumed that the counts were directly proportional to the weight percentage of the element in the sample. Hence, since monticellite contains 25.6 wt.% calcium, the percentage of calcium in the sample is given by the relationship:-

Accuracy of counts, allowing for corrections of the background counts, were assessed as having statistical standard deviations of \pm 10% for the very low counts and \pm 1% for the highest counts. Therefore for electron probe analyses which depend on low point counts, such as in the examination of fired magnesia containing a monticellite addition (where the lowest level of CaO in magnesia was detected as 0.09 wt.%) the accuracy is \pm 0.009 wt.%. In analyses determined from higher point counts, such as in the examination of fired magnesia containing 1.0 mole % tricalcium silicate, where the level of CaO in magnesia was detected as 1.48 wt.%, the accuracy will be \pm 0.015%.

The overall accuracy will, however, depend on many factors, particularly the probe stability and standard accuracy. In all cases, these effects should amount to an error representing less than 1% of the amount present.

The level of accuracy is confirmed in the analyses obtained on fired magnesia and lime mixtures where 0.69 wt.% CaO was added and this was determined after firing at 1700° and 1800° C as 0.70 ± 0.02 wt.% CaO in the magnesia grains.

<u>6.22 Results of Electron Probe Analysis</u>. The average point counts made for the elements Ca, Mg and Si showed that in the periclase of the sintered mixtures containing calcium silicate additions, there were measureable amounts of Ca, but no significant amounts of Si.

From the Ca counts were calculated the amounts of CaO in the periclase grains. Since the amount of CaO

present initially in the magnesia was very low, about 0.0006 wt.% CaO (see Table 1.) the lime present in the magnesia grains would come from the additions. Appreciable lime contents were found in the magnesia grains and the values are presented in Tables 4 to 7; where details of each mixture with firing treatment are given. The CaO/SiO₂ ratio in the silicate bond after firing was calculated by subtracting the lime lost from the silicate on firing from that of the original lime content of the silicate, and then redetermining the CaO/SiO, mole ratio. The line contents of the magnesia for the 0.5 mole % silicate addition (0.25 mole % for mervinite addition) after firing for 8 hours are plotted against the firing temperature in Figure 3. Figure 4 shows that the CaO/SiO2 mole ratio of the silicate phase changes with the solution of lime in the magnesia, when mixtures containing 0.5 mole % silicate additions are fired at 1600°, 1700° and 1800°C.

The changes that occur to the lime content in the magnesia and its subsequent effect on the CaO/SiO_2 ratio in the silicate phase after firing at $1800^{\circ}C$ are presented in Tables 4 to 7 for the silicate mixtures containing 1.0 mole % silicate addition (0.5 mole % merwinite). Figure 5 compares the effect of the lime solubility in magnesia with the CaO/SiO_2 mole ratio of the addition for the two levels of addition of the silicate phase. Figure 6 shows the changes in the solubility of the calcium oxide in the magnesia with the increasing addition of each silicate. The plots give an indication of the maximum solubility of the lime in magnesia from

each of the silicate additions at 1800°C.

Examination of the mixtures containing the 0.5 mole % addition of calcium oxide fired at 1700° and 1800° C, and the 1.0 mole % addition fired at 1800° C, showed that all the CaO had entered the magnesia. This was confirmed by microscopic examination of the fired mixtures, where no trace of free lime was found at any stage of the preparation of the polished microstructure.

The effect of the firing time on the solution of lime in magnesia was only investigated for the tricalcium silicate and magnesia mixture fired at 1800^oC. The electron probe analysis gave the following lime contents of the magnesia after 1, 4 and 8 hours at temperature:-

Time at 1800 ⁰ C, hours.	CaO Content of Magnesia, wt.%.
1	0.74
4	0.77
8	0.75

TABLE 8.

This Table shows that there is no appreciable variation in lime contents for firing times greater than 1 hour, within the accuracy of the determinations.

It was not possible to do quantitive analyses on the composition of the silicate phase after firing because of the narrow width of the phase, when interference from the X-rays from the elements in the magnesia grains

either side occurred. A scan across the silicate phase did, however, indicate a CaO/SiO₂ ratio which was the same as that calculated earlier (see Tables 4 to 7). <u>6.30 X-ray Diffraction Examination</u>

<u>6.31 Ionic Size Effect</u>. If the calcium ions go into solid solution in the magnesia lattice, the lattice parameter of the material will be increased as the ionic radius⁷⁰ of the C_a^{2+} ions is 0.99Å compared with that of the Mg²⁺ ions of 0.65Å, which it is replacing in the cubic lattice. A preliminary X-ray examination of the fired materials containing various amounts of lime in magnesia was made to determine the lattice parameters of these solid solutions.

<u>6.32 Experimental Details</u>. Samples of pellets were crushed with an agate pestle and mortar to pass through a 300 B.S. sieve before mounting in the X-ray diffractometer which had previously been standardised using a silicon sample.

Only samples fired at 1800° C containing 0.5 mole % dicalcium silicate, 0.5 mole % tricalcium silicate and 1.0 mole % calcium oxide were examined using a slow scanning speed of 0.3° /min. These were compared with the diffraction peaks obtained with the pure magnesia fired at 1800° C.

<u>6.33 Lattice Parameter Calculation</u>. The investigation was limited to the first order diffraction patterns obtained by reflection from (111), (200) and (220) planes. The interplanar spacing d_{hkl} for each plane (h k l) was calculated from the Bragg equation:-

 $\lambda = 2d_{hkl} \sin \theta \qquad (21)$

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The lattice constant a for the cubic magnesia lattice was calculated using this information in the formula:-

 $a_0^2 = d_{hkl}^2(h^2 + k^2 + l^2)$ (22)

In this preliminary survey no Nelson and Riley⁷¹ correction was made to determine a_0 at an angle of 0° .

The values of a_0 were used to calculate the true densities of the magnesia phase containing CaO in solution. The fraction of CaO in the lattice $\frac{\text{Were}}{\text{being}}$ the amounts presented in Tables 6 and 7. Table 9 presents the values of a_0 and the true densities of the periclase phase in the fired mixtures.

The results show that there are definite changes in the magnesia crystal lattice when it contains lime. Since the a_o values increase when lime is present in the magnesia, this is proof that a true solid solution is formed between CaO and MgO which is to be expected from the previous work described in 6.10.

It must be emphasised that these X-ray diffraction results are only a cursory examination of the effect of Ca^{2+} ions on the crystal structure of the periclase. Therefore no real conclusions can be drawn other than the fact that the lattice parameter does increase when Ca^{2+} inons enter the magnesia grains, which is confirmation that a true solid solution is formed. Although no corrections(Nelson-Riley) were made to the results, the determined a₀ value of pure magnesia 4.211 Å compares favourably with the accepted value of 4.2115 Å.⁵⁹ The mixtures selected for X-ray examination all had similar

grain size.

6.40 General Discussion on the Solubility of Line from <u>Calcium Silicates in Magnesia.</u>

A detailed discussion on the partial decomposition of each of the silicate additions and its subsequent effect on the densification and grain growth of the periclase is given in chapter 7. However, the general implications of the electron probe and X-ray diffraction analyses will be discussed in this section for completeness.

The effectron probe analyses of the magnesia and silicate mixtures after firing showed that there was no silicon, and hence no silicates, present in the periclase phase after cooling. Schlaudt and Roy^{72} report that the solubility of forsterite, M₂S, is more than 11 mole % in magnesia at 1860°C. They do, however, point out that the silicate appeared as globules in the microstructure on cooling. The forsterite in the observed microstructure after firing at 1800°C, see Figure 52a, contained globules of forsterite in the structure although no silicon was detected in the magnesia grains. This suggests that, on cooling in air, the silica is expelled from the magnesia lattice so reforming the forsterite phase.

The analyses do show that there was an increase in the lime content of the periclase and an increase in its lattice parameter after firing in contact with a calcium silicate phase. The lime content varies with firing temperature, the CaO/SiO₂ mole racio of the silicate, and the amount of silicate phase present.

Presented in Tables 4 to 7 are the distribution
coefficient, Q, for the calcium oxide between the <u>silica</u> and magnesia components for the four calcium silicate additions. It is assumed in this calculation that none of the silica enters the magnesia phase, therefore:-

Q wt. = $\frac{CaO \text{ per unit wt. of SiO}_2}{CaO \text{ per unit wt. of MgO}}$ (23)

For a constant level of addition of the silicate, the values of Q will decrease with increasing temperature as more CaO enters the magnesia lattice. Since the different additions give various calcium silicate compounds in the bond, the Q values can only be used to yield information for a particular level of lime and silica in the mixture. The CaO/SiO2 mole ratio must also be calculated. The CaO/SiO2 ratio in the silicate bond was checked on the electron probe with the value calculated using the data on the lime content in the magnesia and the original chemical analysis of the mixture no quantitive data on the exact composition of the silicate phase for the mixtures could be obtained (see 6.22). It is for this reason that the distribution coefficient is based on the silica in the bond and not the silicate.

Figure 3 shows that the silicate phase having a 1:1 CaO/SiO_2 mole ratio is the most stable of the silicate phases in the presence of magnesia at high temperatures, only c.1 wt. % of CaO being present in the magnesia phase at $1800^{\circ}C$. The tricalcium silicate is the least stable with 0.34 wt.% Cao entering the magnesia lat+ice at $1400^{\circ}C$;

and for the 1.0 mole % addition, up to 1.4 ut.% CaO at 1800°C.

Mixtures containing Monticellite. With the monticellite addition, no forsterite was observed in the microstructure, which would be the decomposition product if any of the monticellite decomposed to give free CaO which then entered the magnesia phase. The calcium content in the magnesia is probably the result of isomorphous replacement of the Ca^{2+} ions in the monticellite for Mg^{2+} . At firing temperatures of 1500°C and above, the silicate phase will be liquid and when at equilibrium will be saturated with magnesia. Exchange of Ca²⁺ ions will occur between the magnesia and the silicate phases until the activity of the ion is the same in the two phases, at which point equilibrium is attained. Keyser and Derie⁷³ have shown that the phase monticellite exists over a range of chemical composition between C_{0.64} M_{1.36} S to CMS. In the present investigation the silicate phase, after cooling from the sintering temperature, existed over the composition range C_{0.84} M_{1.16} S to C_{0.92} M_{1.08} S. This range is based on the calculations of the CaO/SiO₂ ratio left in the bond after a given amount of lime (determined by the electron probe analyses) has entered solution in the magnesia.

The low level of calcium in the magnesia lattice from monticellite additions indicates a low activity of lime in the molten silicate, having a 1:1 CaO/SiO₂ mole ratio.

<u>Mixtures_containing Merwinite, Dicalcium and Tri-</u> <u>calcium Silicates</u>. Microstructures of the mixtures

containing additions of merwinite and dicalcium silicate (see Figures 51 to 53) did show the presence of monticellite and merwinite respectively. At firing temperatures for these mixtures between 1400°C and 1600°C, the low level of lime in solution in the magnesia of approximately 0.1 wt.% is probably the result of isomorphous substitution similar to that mentioned for the monticellite additions. The least stable of the silicate additions, mixtures containing tricalcium silicate, showed the presence of dicalcium silicate after firing at 1400°C. In mixtures fired at 1700° and 1800°C, no tricalcium silicate, only dicalcium.silicate, was observed in the microstructures.

Two explanations are possible for the above mentioned observations:

(i) The silicate is partially soluble in the magnesia at the firing temperature. The silica is rejected from the magnesia lattice on cooling and reacts with the remaining rilicate in the bond forming some of the silicate with the next lower CaO/SiO₂ mole ratio. The calcium oxide part of the silicate remained in solid solution with the magnesia on cooling. Although it could be expected that there would be some solubility of silica in the magnesia at the firing temperature, even if only a very small quantity this mechanism does not satisfactorily explain why increasing the addition of the silicate increases the level of the lime in solution in the magnesia. Since some silicate remained in the bond for the lower level of addition, this infers that sufficient silicate was present

to saturate the magnesia.

(ii) The other explanation for the presence of different ofter silicates after firing at temperature, than those initially added, is that some decomposition of the silicate occurs on firing. The decomposition products are free lime, which then enters solution in the magnesia, and the silicate with the next lower CaO/SiO₂ mole ratio. The decomposition reactions of the silicates would then be as follows:-

 $C_3MS_2 + M$ M(C)CMS C₃MS₂ merwinite magnesia monticellite magnesiaunreacted lime solid merwinite solution \longrightarrow C₃MS₂ M(C)CoS М C2S + dicalcium magnesia merwinite solid unreacted silicate solution diealcium silicate

 $C_3S + M \longrightarrow C_2S + M(C) + C_3S$ tricalcium magnesia dicalcium solid unreacted silicate silicate solution tricalcium silicate

This would explain why increasing the level of the addition of the silicate increases the level of the CaO in solid solution, providing that the magnesia has not been saturated with lime at the firing temperature. It also explains why increasing the firing temperature from 1600° to 1800° C for the 0.5 mole % tricalcium silicate additions does not greatly affect the level of the lime in solution with the magnesia. At 1600° C the CaO/SiO₂ mole ratio in the silicate bond is 2.0:1, indicating that all the tricalcium silicate addition has decomposed to dicalcium silicate and lime.

At the higher firing temperatures the silicates will be molten and must be described in terms of their CaO/SiO₂ mole ratio. It is only on cooling that mixtures of separate silicate phases will form in the microstructure.

The CaO will dissolve in the magnesia since this results in the formation of a more stable system. The free energy change, ΔG , for the solid solution forming reactions is given by the relationship:-

The instability of the tricalcium silicate with the ease at which it decomposes to lime and dicalcium silicate is indicated by the binary equilibrium phase diagram of CaO and SiO₂ given by Levin⁸ where this phase is only stable above 1250°C.

The activity of the lime increases with increasing CaO/SiO_2 ratio of the silicate phase. The highest

activity of the lime is in the tricalcium silicate. Hence, when tricalcium silicate is fired in the presence of magnesia, the silicate shows the highest instability of this series of calcium silicates. صر* ء

7.00 EXPERIMENTAL RESULTS AND DISCUSSION.

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- 7.10 Presentation of Results
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- 7.70 Magnesia Containing Tricalcium Silicate Additions
- 7.80 Magnesia Containing Calcium Oxide Additions

7.10 Presentation of Results.

A complete summary of results for all the mixtures of the bulk, apparent solid and true densities; apparent, true and sealed porosities; volume change on firing and mean grain diameter measurements after each firing treatment are presented in Appendices II and III.

<u>7.11</u> Densification. For the purpose of graphical presentation of the densification undergone by each mixture, isothermals are plotted of a volume shrinkage parameter, F_v , at each of the 5 sintering temperatures. The volume change on firing was not plotted directly due to variations in the presend bulk density (1.58 \pm 0.03 g/cc) and in the true densities of the mixture. These variables were incorporated in a volume shrinkage parameter, which is defined as follows:-

- $F_v = Volume change of mixture x 100$ Maximum volume change possible
 - Pressed Bulk Volume Fired Bulk Volume x 100
 Pressed Bulk Volume Specific Bulk Volume

The bulk volumes were calculated from the reciprocals of the corresponding density values which had been determined as described in chapter 4. It was generally found that for a given firing treatment the factor F_v remained constant over the range of the pressed bulk densities

The maximum error in the values of F was $\pm 2.0\%$ for values around 40%. This error gradually reduced with increasing the sintering time and temperature, so that for values of F greater than 90%, the maximum was $\pm 0.2\%$. These error limits are illustrated on Figure 7, which shows the densification parameter versus time at each sintering temperature for pure magnesia.

firing temperature:-

The results based on this densification parameter are included in the tables of results for comparison with the volume shrinkage parameter.

The changes in the grain diameter,D, of each of the mixtures is demonstrated by isothermal plots for the 5 sintering temperatures.

<u>7.12</u> Porosity. The effect of increasing the additive phase from 0.5 to 1.0 mole % (0.25 to 0.5 mole % for merwinite) on the densification of magnesia can be demonstrated by plots of true and apparent porosities against the sintering temperature.

<u>7.13</u> Grain Size. The effect of these two levels of addition on the grain diameter is shown by plots of grain diameter against sintering temperature. The results obtained on the pure magnesia are included for comparison. All these results were for material sintered for 4 hours at temperature.

<u>7.14 Lime/Silica Ratio</u>. In this chapter the results obtained on the individual mixtures will be discussed. A comparative discussion on the effect of the lime-silica mole ratio of the addition on the densification and grain growth of magnesia will be given in the next chapter. 7.20 Pure Magnesia.

A complete summary of the densities and porosities after each firing treatment for pure magnesia is given in Tables 11 to 15 of Appendix II. The isothermal changes in the volume shrinkage parameter and the grain

diameter of the pure magnesia are shown in Figures 7 and 8.

Figure 7 shows that the sintering of magnesia. prepared from the oxalate, is sensitive to the firing temperature and time at temperature, on firing between 1400° and 1700°C for times up to 8 hours. At 1700°C only small changes of shrinkage occurs on increasing the firing time from 4 to 8 hours. The isotherm at 1800°C shows little change in the shrinkage of the compact after firing for times in excess of 1 hour. The sealed porosity remains very low (less than 0.5 %) until the true porosity falls to approximately 10%. This was achieved by sintering at 1600°C for 8 hours, at 1700°C for 2 hours or more and at 1800°C for all the sintering times. The proportion of sealed porosity to apparent porosity increases with increasing temperature and time at temperature, until at 1800°C the greater proportion of the pores are small enough not to be penetrated by the xylene used in the porosity determination. The densities obtained at 1400° and 1500°C are similar to those reported by Brown¹⁸ on magnesia prepared from a similar source.

No grain size determinations could be made on specimens fired at 1400°C or at 1500°C for sintering times of less than 4 hours, because of the very small grain size associated with the high porosities, which were greater than 30 %, of the magnesia compacts. Figure 8 shows that the rate of grain growth increases with increasing firing temperature.

Brown observed that discontinuous grain growth had

occurred in magnesia after firing at 1725°C for 48 hours. The microstructure of the magnesia after firing at 1800°C for 8 hours is shown in Figure 49a. After this firing treatment, no secondary grain growth had occured, the mean grain diameter of the angular grains being $\sim 49 \,\mu$. The microstructure shows rounded pores at the grain boundaries and also isolated within the grains. These entrapped pores would make it difficult to achieve densities greater than the 3.50 g./cc obtained since further heating will cause further grain growth. This could occur as discontinuous grain growth and would be expected from the results obtained by Brown and by Lowrie and Cutler¹⁹ on high density magnesia. The pores would become isolated at larger distances from the grain boundaries making it more difficult to remove them.

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It should be noted that some pores were observed entrapped within magnesia grains in all specimens on which grain size measurements were made. This includes the pure magnesia with and without the additions and for sintering temperatures as low as 1400°C.

7.30 Magnesia Containing Forsterite Additions.

A complete summary of the densities and porosities of mixtures containing 0.5 mole % of forsterite after each firing treatment is given in Tables 16 - 20 of Appendix II. The isothermal changes in the volume shrinkage parameter and grain size measurements are shown in Figures 9 and 10.

Figure 9 shows that between 1400° and 1500°C a large increase in the volume shrinkage parameter occurs. The

forsterite addition has little effect on the shrinkage of magnesia at 1400° C. It is probable that it is not until the compact reaches 1500° C that the forsterite addition, (having a larger particle size compared with the magnesia) has diffused in the compact to produce a homogeneous mixture. At 1500° and 1600° C little shrinkage occurs on increasing the sintering time from 4 to 8 hours. At 1800° C no increase in the density occurs for times at temperature in excess of 1 hour. The maximum volume shrinkage obtained being similar to that obtained at 1700° C after 4 and 8 hours.

Figure 10 shows an even increase in the grain size with increasing time and temperature between 1400° and 1700°C. At 1800°C there is a rapid increase in the grain growth. the grain size increasing from 40 µ after 0.1 hour to 106 μ after 8 hours at 1800°C. This was the only mixture to exhibit this secondary grain growth phenomenon. In this rapid grain growth the grain size distribution remains constant and no cannibal grain growth occurred. Microstructures are shown in Figures 49b and 52a where the nearly angular grains can be observed and the rounded pores are mainly isolated within the grains. The forsterite phase was observed as distinct isolated pockets at the grain boundaries and also within the magnesia grains. It is not homogeneously dispersed around the grains as is the case with the calcium silicates. Schaudt and Roy⁷² report that forsterite has limited solubility in magnesia at high temperatures. It would be expected that both 0.5 and 1.0 mole % additions of forsterite to magnesia would be comp-

letely soluble in magnesia at 1400°C and above providing equilibrium has been attained. The magnesia lattice apparently rejects the silicate on cooling to room temperature.

The results obtained on sintering a mixture containing 1.0 mole % forsterite addition are summarised in Table 46 of Appendix III. Figure 11 shows the change in the true and apparent porosities with the sintering temperature for the 0.5 and 1.0 mole % additions after 4 hours at temperature. The increased addition decreases the porosities at 1400° and 1500°C. The higher silicate content of the magnesia enhances the diffusion of material and accelerates the densification process. At 1600°, 1700° and 1800°C the porosities are approximately the same for the two mixtures. The sealed porosity remains at approximately 4% within this firing temperature region.

Plots of the effect of the two levels of the addition on the grain size of the magnesia is given in Figure 12. The higher addition results in a slightly higher grain size of between 5 and 6 μ after similar firing treatments. The rate of increase with temperature is the same for the two additions. The forsterite additions increases the grain size of the magnesia at 1500°C and above.

7.40 Magnesia Containing Monticellite Additions.

A complete summary of the sintering data on magnesia mixtures containing 0.5 mole % additions of monticellite is given in Tables 21 to 25 of Appendix II.

Figure 13 shows the isothermal plots of the volume shrinkage parameter for the mixture. The parameter inc-

reases rapidly at 1400°C for firing times in excess of 1 In the mixture fired for 0.1 hour at 1400°C small hour. particles of monticellite were observed in the microstructure that had not diffused into the magnesia structure. Once a homogeneous dispersion of the silicate phase had occurred the compact shrinks rapidly to give a density as high as 3.00 g./cc after 8 hours at 1400° C. At 1500° C the silicate phase is molten. At this temperature and above only small changes occur in the shrinkage after firing at temperature in excess of 2 hours. At 1800°C the shrinkage parameter increases with firing times up to 2 hours. On further heating the compact expands and the parameter falls to a level similar to that produced by firing at 1400°C for 8 hours. This expansion is thought to be caused by the pressure of the gas trapped in sealed pores overcoming the surface tension forces of the silicate liquid which wets the magnesia grains and holds the structure together at the high firing temperatures. This phenomenon will be discussed in the rext chapter. The microstructure of the expanded structure shown in Figure 49c shows where the impregnating resin has entered pores that have expanded and become open to the surface during firing.

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The microstructures of the mixtures containing monticellite show that there are less pores isolated within the magnesia grains than in the pure magnesia and mixtures containing additions of forsterite and calcium oxide, which do not form liquid phases at firing temperatures up to 1800°C. The pores isolated within the magnesia

grains in the mixtures containing the calcium silicate are however larger than in the other mixtures and are located almost entirely at the centres of the grains. It appears as though these pores have acted as sinks for diffusing vacancies and have grown at the expense of the smaller pores within the grains. ·· `,>

Figure 14 shows the isothermal change in the grain diameter of mixtures containing 0.5 mole % monticellite. Only small increases in the grain size occur at 1400° C on increasing the firing time from 1 to 8 hours. At this temperature the silicate phase is solid. At the higher firing temperatures even increases in the grain size occur with increasing firing temperatures and times. The grain size $\frac{Was}{Was}$ sensitive to the time at the sintering temperature.

A summary of the results obtained on the mixture containing a 1.0 mole % addition of monticellite is given in Table 47 of Appendix III.

Figure 15 shows the effect of the firing temperature on the porosities of the mixtures containing 0.5 and 1.0 mole % additions. At 1400°C the higher addition decreases the porosity of the compact. At 1500°C the sealed porosity of the material has reached between 6 and 7 % which is maintained for both the mixtures on firing at 1600° and 1700°C. A slight lowering of the apparent porosity is observed with increasing firing temperature to 1700°C. At 1800°C the porosities of both the mixtures increase. The apparent porosity increases due to sealed pores expanding and becoming open to pore networks open to the surface of the compact. The sealed porosity also

increases to between 9 and 10%.

A plot of the grain diameter of the magnesia, for the two monticellite containing mixtures, against the firing temperature is shown in Figure 16. There is a linear relationship between the grain diameter and firing temperature for both the mixtures after 4 hours at temperature. The plots for the 0.5 and 1.0 mole % additions show the same increase of grain size with the firing temperature but the higher addition has grain sizes approximately 4 μ greater than the 0.5 mole % addition, after each firing treatment.

7.50 Magnesia Containing Mervinite Additions.

A complete summary of the sintering data obtained on magnesia mixtures containing 0.25 mole % of merwinite is given in Tables 26 to 30 of Appendix II.

Figure 17 shows the isothermal plots of the volume shrinkage parameter for the mixture. At 1400°C there is a steady increase in the shrinkage parameter for the first 2 hours at temperature whilst the silicate is diffusing in the compact to provide a homogeneous dispersion. Increasing the firing time to 4 hours then produces rapid shrinkage to densities of approximately 2.90 g./cc. Rapid shrinkage also occurs during the first 4 hours of firing at 1500°C. Firing between 1500° and 1800°C for 4 to 8 hours produces only small changes in the volume shrinkage parameter. These changes result in the density increasing from 3.26 g./cc at 1500°C to 3.33 g./cc. at 1700°C. At 1800°C greater shrinkages are observed up to 2 hours at temperature similar to that observed with

the monticellite addition, but on further heating slight expansions occur resulting in a fall of the fired bulk density from 3.36 to 3.30 g./cc. after 4 and 8 hours at temperature.

Liquid is present in mixtures of magnesia and merwinite at 1575°C⁸. Above this temperature line is lost from the liquid silicate and enters solution in the magnesia as described in the previous chapter.

Plots of the isotherms of the grain diameter of the magnesia with a 0.25 mole % merwinite addition is shown in Figure 18. A discontinuity in the positioning of the isotherms occurs between 1600° and 1700°C. This corresponds to the temperature at which appreciable amounts of lime are lost from the silicate to the magnesia (see Figure 3). It also approximately corresponds to the temperature at which liquid is formed in this system.

A summary of the data obtained on sintering mixtures containing 0.5 mole % additions of merwinite is given in Table 48 of Appendix III.

Figure 19 shows the effect of 0.25 and 0.5 mole % additions of merwinite to magnesia on the porosities after firing for 4 hours at temperature. The higher addition results in slightly lower porosities being obtained at the lower sintering temperatures. At 1500°C the sealed porosity is between 4 and 5 % for both mixtures. This increases on raising the temperature to 1700°C. At 1800°C the true porosity increases but a slight decrease in the apparent porosity is observed.

The sealed porosity increases from 5.8 % at 1700° C to 6.6% at 1800° C for the 0.25 mole % addition and increases from 5.5 to 7.8 % over the same temperature range for the higher addition.

Prots of grain diameter after 4 hours at temperature against the firing for the two levels of merwinite addition are given in Figure 20. At 1600° C and above a similar linear increase of grain size with temperature is observed. The higher addition resulting in grain sizes approximately 5 μ greater than for the 0.25 mole % addition. At 1400° and 1500° C, where the silicate phase is solid, the grain sizes of the mixture containing the 0.5 mole % addition are approximately 3 μ smaller than those in the system containing the lower addition. 7.60 Magnesia Containing Dicalcium Silicate Additions.

A complete summary of the sintering data on magnesia mixtures containing 0.5 mole % dicalcium silicate is given in Tables 31 to 35 of Appendix II.

Figure 21 shows the plots of the volume shrinkage parameter against firing time. At 1400° C a rapid increase in the shrinkage occurs and the parameter increases from 42 to 85 (corresponding to an increase in density from 2.05 to 3.02 g./cc.) on increasing the firing time from 0.1 to 8 hours. On increasing the sintering temperature the greater proportion of the shrinkage occurs during the heating to the firing temperature until at 1700° and 1800° C only small changes are observed in the shrinkage parameter on increasing the firing time from 0.1 to 8 hours.

Liquid is not formed in $MgO-2CaO.SiO_2$ mixtures until $1790^{\circ}C^{8}$ but because of the loss of lime from the silicate (see 6.40) at temperatures above $1600^{\circ}C$ to form some merwinite in the silicate phase, liquid will be present at both 1700° and $1800^{\circ}C$.

The plots of the isotherms of the grain diameters of the magnesia for this mixture given in Figure 22 shows a discontinuity between 1600° and 1700° C. At temperatures of between 1400° and 1600° C very little grain growth is observed. Only small increases occur with increasing temperature and time at temperature. At 1700° and 1800° C, when the liquid is present in the system, appreciable grain growth occurs in the system. Figure 54 shows the increase in the grain size on increasing the firing temperature from 1600° to 1700° C.

The sintering data on mixtures containing a 1.0 mole % addition of dicalcium silicate is given in Table 49 of Appendix III.

Plots of the porosity against firing temperature after firing for 4 hours for the 0.5 and 1.0 mole % additions are given in Figure 23. The porosity of the compacts for both the mixtures decreases rapidly with increasing firing temperatures to 1600°C. On firing at higher temperatures only small reductions in the porosities are observed. The higher addition results in slightly lower apparent and true porosities than the 0.5 mole % addition. The true porosities of the two mixtures are similar and gradually increase from 1% at 1400°C to between 5 and 6 % at 1800°C. There is an increase

in the true porosity of the 1.0 mole % dicalcium silicate containing mixture from 5 % to 6.5 % on increasing the firing temperature from 1700° to 1800°C.

Figure 24 shows the changes in the grain diameter of the magnesia with 0.5 and 1.0 mole % additions of dicalcium silicate after 4 hours at temperature. At firing temperatures between 1400° and 1600°C the grain sizes of the two mixtures and the pure magnesia are similar. Small increases in the grain size are observed with increasing the silicate content. At 1700°C the grain size for the lower level of addition mixture increases to 48 µ compared with the 32 µ for the 1.0 mole % addition. This could be caused by the lower CaO/SiO2 ratio of the silicate bond in the former mixture resulting in some merwinite being formed and being molten and the firing temperature. At 1800°C the increase in line content in the magnesia phase has resulted in a further decrease in the CaO/SiO, mole ratio of the silicate bond. At this temperature merwinite is present in the 1.0 mole % mixture after cooling to room temperature. At this temperature, where liquid is present in the magnesia - dicalcium silicate system, the two mixtures give similar grain sizes of 61 µ.

7.70 Magnesia Containing Tricalcium Silicate Additions.

A complete summary of the sintering data obtained on magnesia mixtures containing a 0.5 mole % addition of tricalcium silicate is given in Tables 36 to 40 of Appendix II.

The results obtained on the electron microprobe

given in the previous chapter showed that due to the loss of lime from the tricalcium silicate addition the CaO/SiO_2 mole ratio in the silicate bond changes from 3:1 to 2:1 for 0.5 mole % addition, when the firing temperature has reached 1600°C. The resulting dicalcium silicate will form a liquid phase with the magnesia at 1790°C. Normally, in the MgO-3CaO.SiO₂ system liquid would not be expected below temperatures of 1850°C.

Figure 25 shows the isothermal plots of the volume shrinkage parameter of the mixture containing a 0.5 mole % addition at the 5 sintering investigation temperatures. The shrinkage of the compacts increases with increasing the firing temperature and time. The increases in the shrinkage get ing progressively smaller as the sintering temperature is raised towards 1800°C. At 1400°, 1500° and 1600°C only small changes occur in the shrinkage on increasing the firing time from 4 to 8 hours. At 1700° and 1800°C the densification is nearly complete within the first hour at temperature. Continued heating only produces small changes in the shrinkage parameter. Densities of 3.45 g./cc. were obtained at 1800°C. Only the pure magnesia and the mixture containing 0.5 mole % forsterite gave higher fired bulk densities. The 0.5 mole % calcium oxide addition giving a similar maximum bulk density after firing at 1800°C as the tricalcium silicate addition.

Figure 26 shows the isothermal changes in the grain diameter of magnesia containing 0.5 mole % tricalcium silicate. At 1400° , 1500° and 1600° C only small changes

in the grain size are observed. At 1700° C a greater increase in the grain diameter occurs, but only diameters of 22 μ are obtained after 8 hours at temperature. At 1800° C when a liquid phase is present in the system rapid grain growth occurs. The grain diameter increases from 37 to 73 μ on increasing the firing time from 0.1 to 8 hours. The changes in the microstructures of the fired specimens after increasing the firing from 1700° to 1800° C are shown in Figures 5hc and d.

The sintering data obtained on the mixtures containing a 1.0 mole % addition of tricalcium silicate is summarised in Table 50 of Appendix III.

Plots of the porosities of mixtures containing 0.5 and 1.0 mole % additions of tricalcium silicate after 4 hours at temperature are given in Figure 27. The higher addition results in a greater acceleration of the densification of the magnesia at the lower sintering temperatures. At 1700° and 1800° C the apparent porosities of the two mixtures are similar but the 1.0 mole % addition results in a higher true porosity due to it containing more sealed pores. At 1800° C the lower addition mixture has a sealed porosity of 2.9 % compared with the 4.2 % of the mixture containing the 1.0 mole % addition.

Figure 28 compares the grain diameters of the two mixtures with those of the pure magnesia. Similar results are observed for these systems at temperatures up to 1700°C. The 1.0 mole % addition results in slightly higher grain sizes at 1600° and 1700°C. This could be due to the decreased porosity in this system at these

temperatures. At 1800°C appreciable grain growth only occurs with the 0.5 mole % addition. In this system the magnesia contains 0.76 % CaO (see Table 7) and the silicate phase has a CaO/SiO₂ mole ratio of 1.90:1, the magnesia grain size being 63 µ. This compares with the relatively small grain size of 35 µ in the mixture containing the 1.0 mole % addition, where the magnesia phase containes 1.46 % CaO and the CaO/SiO₂ mole ratio of the remaining silicate phase is 1.99:1. Here, as can be seen in Figure 53b, some tricalcium silicate is retained in the structure after cooling. For the lower addition only dicalcium silicate was observed as can be seen in Figure 51d. The 1.0 mole % addition of tricalcium silicate inhibits the grain growth of pure magnesia at 1800° C, where the pure magnesia has a grain diameter of 40 ju.

7.80 Magnesia Containing Calcium Oxide Additions.

A complete summary of the sintering data on magnesia mixtures containing a 0.5 mole % addition of calcium oxide is given in Tables 41 to 45 of Appendix II. Results for mixtures where the addition is increased to 1.0 mole % are presented in Table 51 of Appendix III.

Figure 29 shows the isothermal plots of the volume shrinkage parameter at the 5 temperatures investigated for the 0.5 mole % calcium oxide addition. The corresponding grain size results on the magnesia mixture are given in Figure 30. Both the shrinkage and grain size plots show discontinuities between 1600° and 1700°C. Both the grain diameters and volume shrinkage parameters show

greater increases within this temperature range than within any other. This may be caused by incomplete solution of the 0.5 mole % line addition in the magnesia at the lower firing temperatures. From the published binary phase diagram of Dorman et al⁶⁸ both the 0.5 and 1.0 mole % additions would be expected to be completely soluble in the magnesia at temperatures of 1400°C and above. The increase in the grain diameter at 1700°C, may be due to the decreased porosity at this temperature. At 1700° and 1800°C little further shrinkage occurs after firing in excess of 2 hours at temperature. This composition also shows the most marked increase of all the mixtures for shrinkage on increasing the firing temperature from 1700° to 1800°C. After 8 hours at the former temperature, the density is 3.37 g./cc. and increases to 3.45 g./cc. after 8 hours at 1800°C. Very little grain growtb occurs in the temperature range of 1400° to 1600°C for firing times up to 8 hours.

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Figure 31 compares the porosities of mixtures containing 0.5 and 1.0 mole % additions after firing for 4 hours at temperatures of 1400° to 1800° C. The higher addition causes a greater acceleration of the densification of magnesia at the lower sintering temperatures. At 1600° C the true porosity is 6 % for this addition and only slight reductions occur on raising the temperature to 1800° C. This compares with the gradual reduction of the true porosity from 23 % at 1400° C to 3.6 % at 1800° C. At this temperature both mixtures have an apparent porosity of 1 % but the mixture containing the higher addition

has a sealed porosity of 4.5% compared with 2.5% for the other mixture.

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Figure 32 compares the grain diameters of these mixtures with those of the pure magnesia. The mixture containing 0.5 mole % has similar grain sizes to those of the pure material. At 1600° and 1700°C the 1.0 mole % addition results in grain sizes approximately 8 µ larger than for the pure magnesia. At 1800°C the lime additions inhibit the grain growth of magnesia. The inhibition being more marked for the higher addition.

8.00 DISCUSSION OF THE EFFECT OF THE LIME-SILICA RATIO OF THE ADDITION ON THE GRAIN GROWTH KINETICS, DENSIFICATION AND GRAIN SIZE OF MAGNESIA.

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8.10 Grain Growth Kinetics

8.11 Grain Growth of Magnesia

- 8.12 Grain Growth of Magnesia with Lime Additions
- 8.13 Grain Growth of Magnesia with Additions of Forsterite, Monticellite, Dicalcium and Tricalcium Silicates.
- 8.20 Discussion of the Effect of the CaO/SiO₂ Ratio of the Addition on the Densification of Magnesia.
 - 8.21 Densification of Magnesia with Additions of Monticellite, Dicalcium and Tricalcium Silicates.
 - 8.22 Densification of Magnesia with Additions of Forsterite.
 - 8.23 Densification of Magnesia with Additions of Calcium Oxide.
 - 8.24 The Effect of the Addition on the 'Limiting' True Porosity.

8.30 Grain Growth and CaO/SiO, Ratio.

8.10 Grain Growth Kinetics.

The isothermal grain growth of pure magnesia and the mixtures containing the additions was assumed to be a simple function of time, similar to that given in equation (4) of section 2.51. Plots of $\log_{10}t$ against $\log_{10}D$ were found to be straight lines with slopes approaching 2 for the pure magnesia and magnesia containing calcium oxide, but a slope of about 3 was obtained for the mixtures containing the silicate additions.

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The grain growth equation (4) can be written in the general form:-

where t_0 is some arbitrary zero time and D_0 the grain size at that moment. If this equation is obeyed, when plots are made of $\log_{10} (t - t_0)$ against $\log_{10} (D^n - D_0^n)$ using the appropriate value of n (2 or 3) with various values of $t_0 = 0.1$, 1 or 2 hours the slopes of these lines will be unity. The slopes actually obtained experimentally from these plots are given in Table 10, where it can be seen that the slopes vary between 0.90 and 1.10 with the majority occurring between 0.93 and 1.03.

Plots of D^2 against time, t, for the pure magnesia and magnesia with the lime addition at 1500° , 1600° , 1700° and $1800^{\circ}C$ are given in Figures 33 and 34. From these plots were calculated the grain growth rate constant, K, at each temperature and the values are also given in Table 10.

Similarly, plots of D^3 against time, t, for magnesia

containing each of the silicate additions at 1400° , 1500° , 1600° , 1700° and 1800° C are given in Figures 35 to 39 respectively. These plots compare the influence of the silicate additions on the grain growth rate of the magnesia at the 5 firing temperatures. The slopes of the lines yielded the grain growth rate constant, K, for the influence of the silicate additions, these are also given in Table 10.

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Figure 40 shows the plots of $\log_{10} K$ versus $1/T^{\circ} A$ for the grain growth of pure magnesia which obeys the quadratic relationship (n = 2) of equation (26).

This graph indicates that an Arrehenius relationship as given in equation (6) of section 2.50, holds:

i.e. 2.303 \log_{10} K = constant -E/RT (27) where R cal mole⁻¹ degree⁻¹ is the gas constant and T is in degrees absolute temperature, with E being a phenomenological "activation energy" for the grain growth process.

Also plotted on Figure 40 are the corresponding values for mixtures containing 0.5 mole % lime which also obeyed the relationship for n = 2.

Figure 41 shows similar plots for magnesia with 0.5 mole % (but only 0.25 mole % merwinite) silicate additions, for which the grain growth at each temperature obeys the cubic (n = 3) relationship of equation (26).

The activation energies E (Kcal/mole) obtained from the linear portions of each graph in Figures 40 and 41 are presented in Table 10.

8.11 Grain Growth of Pure Magnesia. Table 10 shows that the grain growth of the pure magnesia followed very closely the relationship in equation (3):-

Time at temperature $K = D^2 - D_0^2$ (28) for each sintering temperature considered, where K is in microns²/hour.

The linear Arrehenius plot given in Figure 40 yields an activation energy of 78 Kcal/mole. A similar value has also been found by Spriggs et al²⁵, who used the same empirical analytical technique to study the grain growth of fully dense magnesia. Their material had a higher impurity level of about 200 p.p.m. compared with the magnesia used in this research, where the impurities were less than 27 p.p.m. (cf. Table 1). They found a value of 81 Kcal/mole for the activation energy of grain growth in dense magnesia.

The value obtained in this research was very close to that obtained by Lindner and Parfitt⁷⁴ of 79 Kcal/mole for the volume diffusion of Mg^{2+} ions in periclase crystals. Oishi and Kingery⁷⁵ found a value of 62.4 Kcal/mole for the activation energy for the slower diffusing 0^{2-} ions in periclase crystals.

The rate of grain growth will depend, among other things, on the relative diffusion rates of the cations and anions, and one would expect the process to have an activation energy similar to the Mg^{2+} ions.

8.12 Grain Growth of Magnesia with Lime Additions. Table 10 shows that the grain growth process for these mixtures still follows a squared relationship of the

grain diameter with time at temperature.

The isothermals in Figure 30 for these mixtures show a break in their sequence between 1600° and 1700° C. This indicates a change in the grain growth mechanism which is seen in Figure 40, as a distinct change in the slope of the Arrhenius plot. Below 1600° C the activation energy for grain growth is 22 Kcal/mole, which means a low temperature dependence for grain growth below 1600° C and is typical of surface diffusion mechanisms. Above this temperature the activation energy is 62 Kcal/ mole, which means that the grain growth is more sensitive to the temperature and is typical of volume diffusion mechanisms.

These mixtures therefore sinter at temperatures below 1600[°]C with very little grain growth. However above 1600[°]C the grain growth increases to a rate similar to that for pure magnesia at the same temperature, as can be seen from the values of K microns²/hour in Table 10.

The discontinuity and change in the activation energy could be due to incomplete solution of the lime addition in the magnesia grains below 1600°C. Concentration of lime at the grain boundaries of the magnesia grains would presumably inhibit grain growth.

8.13 Grain Growth of Magnesia with Additions of Forsterite, Merwinite, Dicalcium and Tricalcium Silicates. The results given in Table 10, for all these mixtures sintered in the temperature range 1400° to 1800°C, show that the grain growth followed closely the relationship:-

Time at temperature $K = D^3 - D_0^3$ (29) where K is in microns³/hour.

This relationship was found to be obeyed for the grain growth of magnesia in the presence of a liquid phase at the sintering temperature by Buist et al²⁹, Nicholson^{27,28} and Brown¹⁸.

From Figure 41, it is seen that there are distinct breaks in the Arrhenius plots. The activation energies determined from each linear part are shown in Table 10 and indicate from those obtainable that these silicates cause grain growth in two stages.

The results of mixtures available for merwinite and dicalcium silicate additions to pure magnesia, show lower activation energies for the high temperature process compared to the lower temperature growth process. The small number of points on the two portions of the Arrhenius plots make it difficult to ascertain that this is a true phenomenon. The activation energies, do however, decrease continuously with increasing CaO/SiO₂ ratio of the addition and with increasing solution of lime, from the silicate, in the magnesia phase.

The breaks in the grain growth mechanism appear to coincide with the formation of a phase change. The temperature range of the change, as shown in Table 10, occurs when a liquid phase is formed. For the merwinite addition the change occurs between 1600° and 1700°C which is higher than expected, since liquid is formed in this system at 1575°C (cf section 7.50). Figure 3 does indicate that in the temperature region of 1600° to 1700°C

there is an increase in the loss of lime from the silicate into the magnesia.

The nixtures containing 0.5 mole % tricalcium silicate have a higher rate constant K at 1700° C than would be expected. This could be due to a small amount of liquid phase being present at this temperature as the CaO/SiO₂ ratio in the silicate phase is below 2:1. The further very large increase in K shown at 1800° C will be due to liquid formation from the dicalcium silicate present forming a eutectic with magnesia.

Mixtures containing forsterite show a grain growth mechanism which has an activation energy of 85 Kcal/mole which is the highest for all the materials and mixtures examined in this research. This high value could be caused by the difficulty in breaking bonds in the magnesia lattice having Si⁴⁺ ions in solid solution. The increase in K at 1800°C, seen in Figure 41, would not be expected since forsterite should all be in solid solution with magnesia at this temperature, as shown by Schlaudt and Roy⁷² and the eutectic temperature for the binary system is reported⁸ as 1860°C.

It might be thought that the low grain growth rate at the lower temperatures for all the silicate mixtures could be due to differences in porosity, the pores inhibiting grain growth. However, this is unlikely since reference to Figures 42, 43 and 44, show that these mixtures have low levels of porosity, i.e. high F_v values at 1500°C and above, and therefore the presence of pores have not had any noticeable effect on the grain growth

kinetics.

Microstructures presented in Figures 49 and 50, show that at 1800[°]C most of the pores are sealed towards the centre of the magnesia grains. Pores within grains were observed in all the microstructures for which grain growth data are presented.

The increase in the grain growth rate when liquid phases are formed is presumably due to the increased solubility and mobility of the magnesia in the liquid phase which accelerates the transport of material. <u>8.20 Discussion of the Effect of the CaO/SiO₂ Ratio</u> of the Addition on the Densification of Magnesia.

In the previous chapter the densification behaviour of individual mixtures was discussed. In this section a comparative discussion is given of the effect of the addition on the densification of magnesia. Plots of volume shrinkage parameter, F_v , against the Ca0/SiO₂ mole ratio of the addition after firing for 1, 4 and 8 hours at temperature are given in Figures 42, 43 and 44 respectively.

8.21 Densification of Magnesia with Additions of Monticellite, Merwinite, Dicalcium and Tricalcium Silicates. It was shown in chapter 6 that, in the presence of magnesia, some lime was lost from these silicates and entered into solid solution in the magnesia phase. The loss of lime resulted in the silicate phase having a lower CaO/SiO₂ ratio and hence forming liquid phases au lower temperatures than those predicted for the original addition. The activity of the lime in the silicate phase

increased with increasing ratio so that the silicate with 1:1 Cao/SiO₂ mole ratio was the most stable, and tricalcium silicate with a 3:1 ratio the least stable phase.

These comments enable interpretation of the densification results, for mixtures containing these calcium silicates, shown in Figures 42, 43 and 44. Comparison of the 1 hour values of F. for the mixtures with those for pure magnesia in Figure 42, show that the addition of 0.5 mole % addition (0.25 mole % for merwinite) of these silicates increased the densification of the magnesia at all temperatures up to 1700°C. At 1800°C the densification of the mixtures was slightly reduced. It should be noticed that the mixtures containing monticellite, merwinite and dicalcium silicate all densified to similar levels. This is probably because they all contain liquid phases at 1700°C and above. Mixtures containing dicalcium silicate also contain mervinite due to the loss of lime from the silicate phase.

According to Levin,⁸ liquid is formed with these silicates in the presence of magnesia as follows:-

Forsterițe	:	1860 ⁰ 0
Monticellite	:	1490 ⁰ 0
Merwinite	:	1575 ⁰ 0
Dicalcium Silicate :		1790 ⁰ 0
Tricalcium Silicate :		1850 ⁰ 0

The increased densification of mixtures containing these silicates, as seen in Figure 43, over the densification of pure magnesia is still shown after sintering

for 4 hours at each temperature up to 1600°C. However at 1700° and 1800°C, the reduction of the densification parameter is more pronounced for the mixtures due to the formation of greater amounts of liquid phase, an effect which increased with time as shown in Figure 44. Here, mixtures containing a silicate phase with a 1:1 CaO/SiO2 mole ratio show a great reduction in density at 1800°C. This is presumably due to liquid phases in the mixtures sealing the pores, which at high temperatures are able to expand. At 1800°C a high degree of wetting of the magnesia grains by the liquid silicate is observed, as shown in Figure 51. This reduces the solid-solid bonding between the magnesia grains, which therefore allows movement due to the pressure within the pores. Jackson^{49,50} showed that increasing the CaO/SiO₂ ratio increased the dihedral angle of the liquid silicate, i.e. increased the solid-solid bonding; and he predicted that this should increase the densification of the system. Reference to Figure 44 shows that at 1600°C and above the densification increases with increasing CaO/SiO2 mole ratio, this phenomenon being more pronounced at 1800°C. Thus, tricalcium silicate additions result in the greatest densification. At 1800°C, at which temperature liquid is first formed in the system, the tricalcium silicate addition results in densification similar to that of pure magnesia.

Douoling the silicate additions from 0.5 to 1.0 mole % (but 0.25 to 0.5 mole % for merwinite) does not affect the densification drastically. Figure 43 shows that the

increase in silicate content has the greatest effect on the volume shrinkage after 4 hours at temperatures of 1400° and 1500° C. At higher temperatures of 1700° and 1800° C, there is no real change in the 4 hour F_v values.

8.22 Densification of Magnesia with Additions of Forsterite. As would be expected, this silicate behaved differently from the others, because it contained no lime component. Additions of 0.5 mole % forsterite to magnesia had little effect on the densification of the mixture at 1400°C. The reasons for this are not clear, but it is probably a diffusion effect since time is needed at lower temperatures for the small amounts of silicate to reach equilibrium with the magnesia phase. This effect is not observed when the silicate content is doubled, as shown in Figure 43, where the addition greatly enhances densification at 1400°C. Figure 42 shows that after 1 hour at temperatures above 1400°C the forsterite increases the densification of magnesia. After 4 and 8 hours at temperatures of 1700° and 1800°C slightly less volume shrinkage occurs with magnesia containing forsterite than with the pure magnesia.

<u>8.23</u> Densification of Magnesia with Additions of <u>Calcium Oxide</u>. Figures 42, 43 and 44 shows that a 0.5 mole % addition of calcium oxide enhances the densification of magnesia at sintering temperatures of 1400° , 1500° and 1600° C for times at temperature of 1, 4 and 8 hours. At 1700° and 1800° C the addition results in a slight reduction in the volume shrinkage compared with that for pure magnesia.
The mixture containing 1.0 mole % lime does show in Figure 43 that at temperatures up to 1600° C there is increased densification compared with pure magnesia and the other silicate mixtures. At 1700° and 1800° C F_v values after sintering for 4 hours were obtained that were similar to those obtained for pure magnesia.

Krick, Ford and White⁴⁶ found that larger additions, than the 1.38 wt. % of lime used in this research, decreased the densification of magnesia when a free lime phase was present.

8.24 The Effect of the Addition on the 'Limiting' True Porosity. Figure 48 shows the plots of the true porosity against the sintering temperature for magnesia with and without the additions after sintering for 8 hours at temperature. At the higher sintering temperatures very little increase in the densification of the mixtures occurred on increasing the time at temperature from 4 to 8 hours. For practical purposes the densification process can be regarded as complete after 8 hours at temperature for the mixtures investigated in this research. Figure 48 shows that although additions of silicates having CaO/SiO2 mole ratios between 1:1 and 2:1 result in lower porosities at 1400°C, they do show a minimum true porosity at 1700°C in excess of 5.5 %. This minimum porosity increases with decreasing CaO/SiO2 ratio. The mixtures containing additions that form liquid phases at 1800°C and above, show minimum true porosities of 3 to 4 % at 1800°C compared with the 2% of the pure magnesia. From the trend of these plots it would be

predicted that the mixtures containing 0.5 mole % forsterite and tricalcium silicate have reached the minimum true porosities at 1800°C and increasing the firing temperature would not be expected to produce further shrinkage of the compacts.

8.30 Grain Growth and CaO/SiO, Ratio.

Figure 45, 46 and 47 show that the average grain diameter, D, of the magnesia after sintering for 1, 4 and 8 hours respectively is dependent on the CaO/SiO₂ ratio at each temperature.

Similar trends are observed for the 3 sintering times, increasing the sintering time accentuates the effect of the CaO/SiO_2 ratio on the grain size. In this section the discussion is limited to the results obtained after 4 hours at temperature given in Figure 46 since this plot shows the effect of increasing the addition from 0.5 to 1.0 mole % (but from 0.25 to 0.5 mole % for the merwinite)

Comparing the D values of the mixtures with those of the pure magnesia, maximum D values are seen where liquid is present at the sintering temperatures.

At 1700°C there is a maximum D value for the mixture containing 0.5 mole % dicalcium silicate due to the formation of a liquid phase, as a result of the loss in lime from the silicate addition. At 1800°C a similar maximum value of D for mixtures containing 0.5 mole % tricalcium silicate is obtained for a similar reason. But doubling the addition to 1.0 mole % of both the dicalcium and tricalcium silicates reduces the liquid

contents at 1700° and 1800°C respectively, since there is more lime available for the silicate phase.

Increasing the silicate contents for the forsterite, monticellite and merwinite additions, slightly increases the grain size of the magnesia. The rate of increase of grain size with temperature for both levels of addition is similar.

Additions of 0.5 and 1.0 mole % lime reduce the grain size of magnesia at $1800^{\circ}C$.

The mixtures that show low grain growth at the lower sintering temperatures result in a greater sintered density being obtained at the higher sintering temperatures.

9.00 GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The work carried out here on the effect of the CaO/SiO₂ ratio in the impurities present in commercial magnesia materials on their densification and grain growth, has produced data that explains much of the behaviour of these materials during their production.

The CaO/SiO₂ ratio of the silicate phase has been known to influence the high temperature strength of magnesia refractories. This work has shown that this ratio also influences the sintering characteristics and microstructure.

The following points summarise the main findings in this research.

- (a) Additions to pure magnesia of 0.5 and 1.0 mole % of the following:- forsterite, monticellite, dicalcium silicate, tricalcium silicate and calcium oxide, (but 0.25 and 0.5 mole % for merwinite) enhances the densification of pure magnesia at sintering temperatures up to 1600°C. For times greater than 1 hour at 1700° and 1800°C, these additions inhibit densification. At these temperatures densification increases with increasing Ca0/SiO₂ ratio of the calcium silicate addition.
- (b) Mixtures containing silicate additions with a CaO/SiO₂ mole ratio of 1:1 and 1.5:1 expanded after sintering at 1800°C for an excess of 2 hours. This phenomenon was more pronounced for the mixture containing the monticellite addition.

- (c) A marked increase occurs in the grain size of magnesia when a liquid phase is formed in the mixture. The mixtures that gave the smallest grain size at the lower sintering temperatures resulted in the highest densities after firing at the higher temperatures.
- (d) The isothermal grain growth of pure magnesia (total impurity 27 p.p.m.) and magnesia solid solutions such as those with a 0.5 mole % calcium oxide addition, followed the relationship:-

Time at temperature ∞ (Grain size)²

(e) The isothermal grain growth of magnesia with additions of each of the above silicates (lower addition), followed the relationship:-

Time at temperature ∞ (Grain size)³

- (f) Activation energies for grain growth of the mixtures decreased with increasing CaO/SiO₂ ratio of the addition. These energies are generally high and similar to those for the bulk diffusion of ions in magnesia.
- (g) Discontinuities occurred in the grain growth of magnesia containing these additions which corresponded to physical and chemical changes within the system. For the calcium silicate additions, these changes generally occurred at the formation of a liquid phase.
- (h) From the additions to pure magnesia of monticellite, merwinite, dicalcium and tricalcium silicate; calcium ions enter the magnesia lattice by solid solution in

varying amounts which increase with the firing temperature. No silicon was observed in the magnesia lattice after firing and subsequent cooling.

- (i) A silicate phase with a CaO/SiO₂ mole ratio of 1:1 is the most stable calcium silicate in contact with magnesia at high temperature. The stability decreases with increasing CaO/SiO₂ ratio, so that tricalcium silicate is the least stable of this group of silicates. These observations demonstrate the increased activity of lime in the calcium silicates as the CaO/SiO₂ mole ratio is increased from 1:1 to 3:1.
- (j) Because of changes in the lime level of the silicate additions up to 1.0 mole %; the CaO/SiO₂ ratio of the fired silicate phase is reduced, resulting on cooling in a mixture containing a silicate phase of a lower CaO/SiO₂ ratio. Hence in calculations of the mineralogical contents of high magnesia bearing taken refractories, account must be made of the level of lime in solid solution with the magnesia phase. This becomes increasingly important for refractories with high CaO/SiO₂ ratios fired at high temperatures.

Two final year undergraduate projects have been carried out to supplement the work described in this thesis. These were as follows:-

- (a) An investigation on the change of the lattice parameter of MgO with lime content from the various calcium silicate sources.
- (b) An investigation of the effect of the sintering atmosphere on the densification and grain growth of

magnesia containing similar additions to those described in this thesis.

The effect of the Ca0/SiO₂ ratio of the silicate additions on the high temperature strength of magnesia is the subject of a project to follow this one.

Future work on both the sintering and high temperature strength properties of magnesia should be concentrated on additions of calcium silicates containing CaO/SiO_2 mole ratios between 0.5:1 and 3.5:1 which covers the whole range of those found in the industrially available material and those likely to be produced in the future.

The effect of additions of Fe_2O_3 and Al_2O_3 in these systems on the densification and grain growth of magnesia would complete the information on the effect of the main impurities present in industrial materials. The effect of the minor impurities such as B_2O_3 , MnO, TiO₂ and the alkali metal oxides could then be determined. It would also be useful to determine whether anions such as chloride and fluoride have any effect on the sintering of magnesia. Such anions are present in the magnesium hydroxide extracted from sea-water.

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TABLE 2.

TRUE DENSITIES OF THE RAW MATERIALS

		DENSITY g./cc.				
MATE CIAL	CHISTAL STRUCTURE	CALCULATED FROM X - RAY DATA	DETERMINED			
Magnes ta Mgo	CUBIC	3.58	3 .53			
FORSTERITE 2Mg0. S10 ₂	ortho RHOMBIC	3.37	3.23			
MONTICELLITE CaO. HgO. SiO2	ortho RHOMBIC	3.04	3.07			
MERLINITE 30a0. Mg0. 510 ₂	ortho RHOMBIC	3.34	3.34			
DICALC IUM	ortho RHOMBIC	2.96	2.93			
2Ca0, S10 ₂	HONOCLINIC	3.30	-			
TRICALCIUM SILICATE 3CaO. SiO2	TRICLINIC	3.14	3.04			
CALCIUM OXIDE CaO	CUBIC	3.37	•••			

TABLE 3.

CREMICAL COMPOSITION OF MIXTURES

R.IF.	MATERIAL ADDED TO MAGN-STA	ADDI	t Ion	CALCULATED CHEMICAL ANALYSIS \$ vt.				
NO.		Bole S	vt. ≸	MgO	CaO	³¹⁰ 2		
KQ.	NO ADDITION		4	100,00	0.00	0.00		
ML	Forstenite	0.5	1.72	99.27	0.00	0.73		
NB	Mon t I CELLITE	0.5	1.91	90 .59	.6 8	0.73		
145	Lagivit.	0.25	2.00	93 ,25	1.02	0.73		
N7	DICALCIUM SILICATE	0.5	2.10	97.90	1.37	0.73		
143	TRICALCIUM GILICATE	0.5	2.77	97.23	2.04	0.73		
N9	CALCIUM OXIDE	0.5	0.69	99.31	0 .69	0,00		
54	Forstlaite	1.0	3.40	93 .55	J•00	1.45		
D3	Hort icell its	1.0	3.77	97,20	1.35	1.45		
D 6	M274 INIT -	0.5	3.94	⊁ •55	2 .01	1.44		
D 7	DICALCIUM SILICATE	1.0	4 .13	95 . 67	2.69	1.44		
DB	TRICALCIUM SILICAT.	1.0	5 •4 0	94.60	3.93	1.42		
D9	CALCIUM OXIDE	1.0	1.38	93.62	1.38	0.00		

II2.

TABLE 4.

THE BOLUBILITY OF CALCIEM ONTOE IN MACRESIA CONTAINING MONTIC ALLITE ADDITIONS.

Calcium oxide content of monticellite 35.9 wt. %; Cal/SiO2 mole ratio of addition 1...:1.

nef.	PONTICILLTL. Additicy	Cao Covrei Op Mixture	FIRING TEMPERATUSE	CaO IN Solution IN	CaO/SiO2 MOLA RATIO IN SILICATE BORD	DISTRIB I LUT COSPFICILINT OF TRO I DIVITIN DIO/I 50.		
NO.	mole 🛱	wt. <i>"</i> %	°C HACKES IA		AFTER FIRING	Q ut.	Q mole	
1368	0.5	0.63	1600	Ů ₊ 09	J.86:1	?))	1340	
11373	0.5	0.63	1700	0.09	0.36:1	3 01	1340	
1388	0.5	0.68	1800	0.11	0.84:1	710	1060	
D3 84	1.0	1.35	1800	0.10	0.92:1	250	1730	

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TABLE 5.

THE SULUBILITY OF CALCINY OF LDE IN MAGNISIA CONTAINING ALCONTES ADDITIONS.

Calcium oxide content of merwinite 51.2 wt. 1; CaO/SiO2 mole ratio of addition 1.5 : 1.

REF.	MER. INIT. ADDITION	CaO CONTENT	FIRING	CaO IN SOLUTION	CaO/DiO MOLE RATIO	JETRIBUTION COEFFICIENT of Cao BLTWEEN SiO2/MgO.		
NO.	cole 🏌	vt.%	°C.	MAGNES IA wt.%	SILICATE BOND AFTLR FIRI'.G	Q wt.	8 mole	
M668	0.25	1.02	1600	0.12	1:32:1	1030	1530	
M678	0,25	1.02	1700	0 .1 6	1:26:1	7 40	1100	
1:688	0.25	1.02	1800	0,22	1:17:1	500	750	
D684	0 .50	2.01	1800	0.30	1:26:1	400	590	

II4.

TABLE 6.

THE SOLUBILITY OF CALETTY OXIDE IN PAGELEIA CONTAINING DICALCHUA SILICARE DETENDED.

Calcium oxide content of dicalcium silicate 65.3 wt. 7; CaO/SiO2 role ratio of addition 2.0:1.

REF.	DICALCIA SILICAP	Cao Cuit Mixita	FIRING FLITERATUR	CaO II COLUTIUN	CaO/3102 NOLE RATIO IN SILICATE BORD	DIJAJI TER GOLFFICLIAN CAD PT MEN AN ART.			
жо.	NO. mole wt.	wt. T	°c.	21ACIELSIA wt.L	AFTSR FIRING.	Q ut.	Q mole.		
1:743	0.5	1.37	1400	0.11	1.85:1	1570	2350		
19753	0.5	1.37	1500	0.11 1.85:1		1570	2350		
11763	0.5	1.37 1600 0.12 1.54:		1.34:1	143~	2120			
H778	0.5	1.37	1700	0.22	1.68:1	720	1070		
H788	0.5	1.37	1800	0.30	1.58:1	400	740		
D784	1.0	2,69	1800	0.51	1.68:1	300	450		

II5.

TABLE 7.

THE SOLUBILITY OF CALCIUM OVIDE IN MAGNESIA CONTAINING TRICALCIU. SILICATE ADDITIONS

Calcium oxide content of tricalcum silicate 73.7 wt. 5; Ca0/Si02 mole ratio of addition 3.0:1.

3

REF.	TRICALUIU: SILICATE CaO content ADDITION MIXTURE		FIRING	CaO IN SOLUTION IN	CaO/SiO2 MOL2 RATIO IN SILICATE	DISTRIBUTION COUPTICIENT OF THE BUTWLEN SiO2/Mg0		
NO.	mole %	wt.%	°C.	MAGNES IA wt.%	BOND AFTER FIRING	ą wt.	Q mole	
M348	0.5	2.04	1400	0.34 2.50 : 1		690	1020	
M358	0,5	2.04	1500	0.50	2.27 : 1	42 0	630	
M868	0.5	2.04	1600	0,72	1.96 : 1	26 0	380	
M878	0.5	2.04	1700	0.75	1.92 : 1	240	360	
M888	0.5	2.04	1800	0,76	1.90 : 1	230	350	
D884	1.0	3.98	1800	1.46	1.99 : 1	130	190	

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CHARGE IS INTERED PARTHITER AND TRUE DENSITY OF MACHINIA ATH LIE COMPANY.

is The Inc	а _о о Л	CaO in LACTAJIA wt. I	CALCULAR JU DUNSITI g./cc.
: U	4.211	0.0	3.534
MgO + 1.0 mole % CaO	4.220	1.30	3.532
:/ʒ) + 0.5 ¬ole % 025	4.214	0,30	3.533
11g0 + 0.5 mole \$ 038	4.216	0.75	3.534

ADDITICN TO 1 GULLIA I.,	INT.MER n IN RELATIONSHIF	LOG ₁₀	SLOPT OF PLOT LOG ₁₀ (t-to)VS.LOG ₁₀ (D ⁿ -Do ⁿ) RATE CONSTANT K							TEMPERATURE RANGE OF CHANGE IN	APPA ACTIV ENE	RENT ATION RGY		
Lole, %	$Kt = D^n$	14000	15000	16000	17000	1800	1400°C	1500℃	1600°C	1700℃	18000	MECHANISM	LUJ FLMP. K. cals	TEMP. Kcals
גסונונתיי טע	2	-	-	0.92	1.03	0.94	-	1.0 x10	2.6 x10 ¹	8.9 x 10 ¹	2.47 x10 ²	NO CHANGE	78	
0.5 FORSELLE	3	-	0.94	0.95	0.95	1.01	_	1.06 x10 ³	3.81 x10 ³	1.23 x10 ⁴	1.28 x10 ⁵	1700 - 1800	85	-
0.5 MONITOLLITE	3	0.97	1.05	1.10	1.01	1.00	1.66 x10 ²	2.73 x 10 ³	1.11 x10 ¹	2.56 x10 ⁴	4.84 x10 ⁴	1400 - 1500	-	73
0.25 Meralnite	3	0.97	0.95	1.01	1.02	0.96	4.08 x10 ²	1.31 x10 ³	3.88 x10 ³	1.54 x10 ⁴	3.21 x10 ⁴	1600 - 1700	70	60
0.5 DICALCIUM SILICATE	3	-	0.90	0.93	0.97	1.00	1.00 x10 ²	2.38 x10 ²	5.63 x10 ²	2.45 x10	4.17 x10 ⁴	1600 - 1700	53	43
0.5 TRICALCIUM SILICATE	3	0.90	0.90	1.03	1.04	0.94	8.25 x10	1.88 ₂ 10 ²	3.13 x10 ²	1.01 x10 ³	4•79 x10	1700 - 1800	47	-
0.5 C/LCIUN OXIDE	2		0.93	0.94	1.00	1.03	-	8.40 x10 ⁰	1.15 x10 ¹	1.28 x10 ²	2.76 x10 ²	1600 - 1700	22	62

TAB ... 2 10.

SUP 1 BY OF THE REFECT OF ADDITIONS ON THE KINETICS OF THE GRAIN GROWTH OF MAGNESIA

FIGURE I

SILICATES IN THE C.O-MgO-SLO2 TERNARY SYSTEM





FIGURE 2A



FIGURE 2B

DIAGRAM OF THE POSITIONING OF THE PELLETS IN THE SINTERING FURNACE



Figure 3.

THE EFFECT OF FIRING TEMPERATURE ON THE SULUBILITY

OF CALCIUM OXIDE IN MAGNESIA FROM THE

CALCIUM SILICATE ADDITIONS.



Figure 4.

PLOTE OF CALCIUM OXIDE CONTENT IN THE MAGNESIA AGAINST THE LIME/SILICA RATIO OF THE SILICATE ADDITION AND SILICATE BOND AFTER FIRING AT VARIOUS TEMPERATURE 3 FOR 8 HOURS.

Mixtures containing 0.5 mole % (but 0.25 mole % for merwinite) of the silicate additions.



LIME-SILICA RATIO OF THE SILICATE

Figure 5. THE EFFECT OF THE LEAS/SILICA RATIO OF THE CALCING

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SILICAT. ADDITION ON THE SOLUBILITY OF CALCIUM

ONIDE IN MAGYESIA

VET_R FIRING AT 1800°C.

Mixtures containing 0.5 and 1.0 mole % (but 0.25 and 0.5 mole % for merwinite) of the calcium silicate additions.



Figure 6.

THE EFFECT OF INCREASING THE ADDITION OF THE CALCIUM SILICATE ON THE SOLUBILITY OF CALCIUM OXIDE IN MAGNISIA AT 1800°C.

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Figure 7.

ISOTHERMAL PLOTS OF VOLUEE SHALLKAGE PARAMETER, F.

AGAINST FIRING TIME, t,

FOR PURE HAGYLSIA.



Figure 8.

ISOTH_ MAL PLOTS OF GRAIN DIALLTER, D, AGAINST FIRING THE, t,

FOR FURE MAGNESIA.



Figure 9.

ISOTHERMAL PLOTS OF VOLUME SHRIMKAGE PARAMETER, F

GAI'ST FIRP'S TEE, t,

FOR MAGNES LA CONTAINING 0.5 mole % FORSTERITE.


Figure 10.

ISOTHLEMAL PLOTS OF GRAIN DIALTER, D, AGAINST

FIRI'S TIPE, t, FOR MAGNESIA

CONTAILT'S 0.5 mole % FORSTLRITE.



Figure 11.

THE EFFECT OF ENCRUASING THE ADDITION OF FORSTENITE TO MAGNESIA ON THE POROSITY AFTER 4 HOURS AT THE SINTERING TEMPERATURE.



Figure 12.

THE EFFECT OF INCREASING THE ADDITION OF FORSTARITE

TO MAGNESIA ON THE GRAIN DIAMETER, D,

AFTER 4 HOURS AT THE SINTERING

TLIPLRATURE.



Figure 13.

ISOTHERMAL PLOTS OF VOLUEL SER DERAGE PARAMETER, F

AGATIST FIRING TEE, t.

FOR MAGNESIA CO TAINING 0.5 mole \$ MONTICELLITE.



Figure 14.

ISOTHERMAL PLOTS OF GRAIN DIMETER, D, AGAREST FIRING TIME, t, FOR MAGNESIA CONFAINING 0.5 molo & MONTICELLITE.



Figure 15.

THE EFFECT OF INCREASING THE ADDITION OF MONTICELLITE TO MAGNESIA ON THE POROSITY AFTER A HOURS AT THE SINTERING TEMPERATURE.



Figure 16.

THE EFFECT OF INCREASING THE ADDITION OF MONTICELLITE TO MAGNESIA ON THE GRAIN DIAMETER, D. AFTER 4 HOURS

AT THE SINTERING TEMPERATURE.



Figure 17.

ISOTHERMAL PLOTS OF VOLUES SHRINKAGE PARAMETER, F_v, AGAINST FIRING THE, t, FOR "AGNESIA CONTAINING A 0.25 mole % MURJENTE ADDITION.

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Figure 18.

ISOTHERMAL PLOTS OF GRAIN DIAMETER, D. AGAINST FIRING TIME, t, FOR MAGNESIA CONTRENIEG A 0.25 mole \$ MERICHITE ADDITION.



Figure 19.

THE EFFECT OF INCREASING THE ADDITION OF MERVINITE TO MAGNESIA ON THE POROSITY AFTER & HOURS AT THE SIMTERING TEMPERATURE.



Figure 20.

THE EFFECT OF INCREASING THE ADDITION OF MERNINITE TO MAGNESIA ON THE GRAIN DIAMETER, D, AFTER 4 HOURS AT THE SEMIERING TEMPERATURE.

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Figure 21.

ISOTHERMAL PLOTS OF VOLUME SHRINKAGE PARAMETER, F, AGAINST FIREIG THE, t, FOR MACHESIA CONTAINING A.O.5 mole %

DIGALCIUM SILICATE ADDITION.



Figure 22.

ISOTHERNAL PLOTS OF GRAIN DIMETLR, D, AGAINST FIRING THE, t, FOR MACHINEL CONTAINING A 0.5 mole \$

DIGALCIUM SILICATE ADDITION.



Atgure 23.

THE EFFECT OF PROBABILY THE ADDITION OF DICALCIUM SILICATE TO MAGNESIA ON THE POROSITY AFTER 4 HOURS

AT THE SINTERING TEMPERATURE.



Figure 24.

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THE EFFECT OF INCREASING THE ADDITION OF DICALCIUM SILICATE TO MAGNESIA ON THE GRAIN DIAMETER, D, AFTER 4 HOURS

AT THE SINTERING TEMPERATURE.



Figure 25.

ISOTHERMAL PLOTS OF VOLUME SHRINKAGE FARAMETER, F_v , AGAINST

FIRING TEE, t, FOR .AGNESIA CONTAINING A 0.5 mole \$

TRICALCIUN SILICATE ADDITION.



Figure 26.

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ISOTHERMAL PLOTS OF GRAIN DIAMETAR, D, AGAINST FIRING TIME, t, FOR MAGYESIA CONTAINING A 0.5 mole %

TRICALCIUM SILICATE ADDITION.



Figure 27.

THE EFF OF INCREASING THE ADDITION OF TRICALCIUM SILICATE TO MAGNESIA ON THE POROSITY AFTER 4 HOURS

AT THE SINTERING TOMPERATURE.


Figure 23.

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THE EFFECT OF INCREASING THE ADDITION OF TRICALCIUM SILICATE TO MAGNESIA ON THE GRAIN DIAMETER, D, AFTER 4 HOURS

AT THE SERTERING TENDERATURE.



Figure 27.

IDOTHLRIAL PLOTS OF VOLUEE SHRINKAGE FARAMETER, F_v, AGAENOT FIRING THE, t, FOR MACHESIA CONTAINING A 0.5 mole %

CALCIUM CXIDE ADDITION.

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Figure 30.

ISOTHLRYAL PLOTS OF GRAIN DIAMETER, D, AGAINST FIRING TIE, t, FOR MAGNESIA CONTAINING A 0.5 mole % CALCIUM GXIDE ADDITION.



Figure 31.

THE EFFECT OF INCREASING THE ADDITION OF CALCIUM OXIDE TO MAGNESIA ON THE POROSITY AFTER 4 HOURS AT THE SINTERING TEMPERATURE.



Figure 32.

THE EFFECT OF INCREASING THE ADDITION OF CALCIUM OXIDE TO MAGNESIA ON THE GRAIN DIALETER, D, AFTER 4 HOURS AT THE SINTERING TEMPLICATURE.

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ISOTHERMAL PLOTS OF D² AGAINST FIRING THE, t, FOR PURE MAGNESIA

AND MAGNESIA CONTAINING 0.5 mole % CALCIUM OXIDE.

Figure 33. AT 1500° AND 1600°C.

Figure 34. AT 1700 AND 1800°C.







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ISOTHERMAL PLOTS OF D³ AGAINST FIRING THE, t, FOR MAGNESIA CONTAINING SILICATE ADDITIONS.

Figure 35	AT 1400°C.
Figure 36	AT 1500°C.
Figure 37	AT 1600°C.
Figure 38	AT 1700 ⁰ C.
Figure 39	AT 1800°C.

All mixtures containing 0.5 mole % (but only 0.25 mole % for , merwinite) of the silicate additive phase.



FIGURE 35





FIGURE 37

FIGURE 38





Figure 40.

PLOTS OF Log K AGAINST ¹/T^OA TO DETERMINE THE ACTIVATION EVERGIES 10 OF GRAIN GROATH OF MAGNESIA.

(i) SYSTERS ODEVING RELATIONSHIP $Kt = D_t^2 - D_o^2$

(A) PURE HgO

(G) MgO + 0.5 mole % CaO



Figure 41.

PLOTS OF Log10K AGAINST 1/T°A TO DETERMINE THE ACTIVATION ENERGIES OF GRAIN GROWTH OF MAGNESIA.

(11) SYSTEMS OBEVING THE RELATIONSHIP $Kt = D_0^3 - D_0^3$

- (B) Mg0 + 0.5 mole % 2Mg0.Si0₂
- (C) Mg0 + 0.5 mole % Ca0.Mg0.Si02
- (D) Mg0 + 0.25 mole % 3Ca0.Mg0.2Si02
- (E) Hg0 + 0.5 mole % 20a0.Si02
- (F) Hg0 + 0.5 mole % 3Ca0.Si02



Figure 42.

PLOTS OF VOLUEE SHRINKAGE PARAMETER F. AGAINST CaO/SiO2 MOLE RATIO OF ADDITION TO PURE MAGNESIA AFTER SENTERING FOR 1 HOUR AT EACH TEMPERATURE.

All mixtures containing 0.5 mole % (but only 0.25 mole % for merwinite) of the additive phase.



Figure 43.

PLOTS OF VOLUME SHARMAGE PARAMETER F. AGAINET CaO/SHO2 'OLE RATIO OF ADDITION TO PURE MAGY SIA AFTER SINTERING FOR 4 HOURS AT EACH TEMPERATURE.

Comparison of mixtures containing 0.5 and 1.0 mole % (but only 0.25 and 0.5 mole % for morvinite) of the additive phase.



Figure 44.

PLOTS OF VOLUET SHRINKAGL P RAMITER F AGAINST CaO/SiO2 MOLT RATIO OF ADDITION TO PURE MAGNESIA AFTLE STUTERING FOR 8 HOURS AT DACH TELEPERATURE.

All mixtures containing 0.5 mole % (but only 0.25 mole % for merwinite) of the additive phase.



Figure 45.

ISOTHURIS OF GIVEN DIALUTUR D (in microns) PLUTTED AGAINST THE CAO/8102 LOLE RATIO OF THE ADDITION TO DURE (ACTUSIA AMPER HER ST G FOR 1 HOUR AP TO PROTECT.

All mixtures containing 0.5 mole \lesssim (but only 0.25 mole \lesssim for mervinite) of the additive phase.



Figure 46.

ISOTHERNS OF GRAIN DIMINTER D (in microns) PLOTTED AGAINST THE <u>C=O/SiO_ HOL_RATIO OF THE ADDITION TO PURE MAGNESIA</u> <u>AFTER SLITERENG FOR A HOURS AT TO PERATURE</u>.

Comparison of mixtures containing 0.5 and 1.0 mole % (but only 0.25 and 0.5 mole % for merwinite) of the additive phase.



Figure 47.

ISOTHARMS OF CARA DIA ATAR D (in microns) PLOTTED AGAINT THE CAO/SiO2 ATHO OF THE ADDITION TO PURE MACUESIA AFTAR ATARI G FOR 8 HOLDS AT THE RATURE.

All mixtures containing 0.5 mole " (but only 0.25 pole " for mervinite) of the additive phase.



Figure 48.

PLOTE OF TAUL LONDERTY ACALLET THE STATURE THE RATURE FOR MAGY SIA MITT AND AITHOUT THE ADDITIONS AFTER SIGHT AND ADDITIONS

- (A) Pure Mg0
- (B) 1130 + 0.5 nole \$ 21'30.3102
- (C) 1'g0 + 0.5 mole 5 CaJ.1';0.Si02
- (D) 170 + 0.25 mole % 30a0.hg0.20102
- (E) Mg0 + 0.5 mole % 20a0.0102
- (F) Mg0 + 0.5 mole ; 30a0.310_p
- (G) Mg0 + 0.5 mole 7 Ca8


Figure 49.

MICROSTRUCTURES OF UNITUMED MATERIALS AFTER SINTARING FOR 8 HJURS AT 1800°C.

- (a) Pure Magnesia. Mote the angular magnesia grains.
- (b) Magnesia with 0.5 mole 5 of forsterite. Note the darker grey isolated areas of forsterite at the grain boundaries and the large magnesia grains.
- (c) Magnesia with 0.5 mole % of monticellite. Note the rounded magnesia grains with the monticellite phase around them. Large black areas are where material was pulled out during polishing. Grey patches are the impregnating resin.
- (d) Magnesia with 0.25 mole 5 meruinite. Note the rounded magnesia grains with the silicate phase around ther.





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ALL X 200





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Figure 50.

HICROSTRUCTURES OF MATERIALS AFTER SINTERING FOR

8 HOURS AT 1800°C.

- (a) Magnesia with 0.5 mole % of dicalcium silicate. Rounded magnesia grains with the silicate phase at their grain boundaries.
- (b) Magnasia with 0.5 mole % of tricalcium silicate. Large rounded magnesia grains with the silicate phase at their grain boundaries.
- (c) Magnesia with 0.5 mole % of calcium oxide etched with dilute sulphuric acid. Note the small angular magnesia grains.
- (d) Pure magnesia etched with dilute sulphuric acid.





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C X 4 0 0

d x 200

Figure 51.

MICROSTRUCTURES OF THE STORED MAGNESIA CONTAINING SILICATE

ADDITIONS AFTLE SI T AING FOR 8 HOURS AT 1800°C.

- (a) Magnesia with 0.5 mole % of monticellite etched with
 1 % hydrofluoric acid. Note the dark etched monticellite
 phase around the magnesia grains. The light grey phase
 is the impreciating rosin.
- (b) Engnesia with 0.25 mole % mervinite addition etched with 2 % Nital.followed by 1 % hydrofluoric acid. Note the light grey mervinite phase and small areas of 'ark monticellite phase around the magnesia grains.
- (c) Magnesia with 0.5 mole % of dicalcium silicate addition etched with 2 % Nital. Note the light grey merwinite phase and dark grey patches of etched dicalcium silicate around the magnesia grains.
- (d) Eurnesia with 0.5 mole % of tricalcium silicate addition etched with 2 % Nital. At the grain boundaries are dark areas which are almost all dicalcium silicate.



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Figure 52.

MICROSTRUCTURES OF THE ETCHED MAGNESIA CONTAINING SILICATE

ADDITIONS AFTER SINTERING FOR 4 HOURS AT 1800°C.

- (a) Magnesia with 1.0 mole % of forsterite etched with dilute sulphuric acid. Note the isolated pockets of light grey forsterite at the grain boundaries and also the large magnesia grains.
- (b) Magnesia with 1.0 mole % of monticellite etched with 1 % hydrofluoric acid. Note the dark monticellite phase at the grain boundaries, also the rounded pores within the magnesia grains and at the grain boundaries.
- (c) Magnesia with 0.5 mole % of merwipite addition etched with 2 % Nital followed by 1 % hydrofluoric acid. Note the light grey merwinite phase and the amall areas of dark grey monticellite.at the magnesia grain boundaries.





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ALL X 400



Figure 53.

MICROSTRUCTURES OF THE ETCHED MATERIALS AFTER SINTERING

FOR 4 HOURS AT 1800°C.

- (a) Magnesia with 1.0 mole % of dicalcium silicate addition etched with 2 % Nital. Note the light grey merwinite and the dark grey dicalcium silicate phase surrounding the magnesia grains.
- (b) Magnesia with 1.0 mole % of tricalcium silicate addition etched with 2 % Nital. Note the small magnesia grains and dark areas of dark grey dicalcium silicate surrounding the light grey tricalcium silicate at the grain boundaries.
- (c) Magnesia with 1.0 mole % of calcium oxide etched with dilute sulphuric acid. Note the small magnesia grains.





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ALL X400



Figure 54.

(a) and (b) Magnesia with 0.5 mole % of dicalcium silicate addition fired at temperature for 8 hours.

- (a) Fired at 1600°C and etched with dilute sulphuric acid. Note the small magnesia grain size.
- (b) Fired at 1700°0 and etched with 2 % Nital. Note the large rounded magnesia grains surrounded by mainly dark grey dicalcium silicate phase. cf.Fig.51c.

(c)-and (d) Magnesia with 0.5 mole % of tricalcium silicate

addition fired at temperature for 8 hours.

- (c) Fired at 1700°C and etched with dilute sulphuric acid. Note the small grain size of the magnesia.
- (d) Fired at 1800°C and unetched. Note the large rounded magnesia grains.





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APPENDIX I

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HIGH TEMPERATURE STRENGTH MEASUREMENT RIG.

A high temperature furnace has been designed and constructed for the determination of the compressive or modulus of rupture strength, and can be readily adapted for creep measurements of refractory materials at temperatures up to 2000°C. The tungsten element, by which the specimens are heated, will operate in vacuum or low pressure of argon. The furnace is fitted on to an "Instron" physical testing machine capable of applying loads at constant strain or stress rates. The apparatus is illustrated in Figures 55 and 56.

The determination of the effect of additions from the CaO-MgO-SiO₂ phase system on the high temperature strength of magnesia is the subject of a later separate investigation.

Figure 55.

DIAGRAM OF THE HIGH TEMPER TURE FURNACE FOR STRENGTH MEASUREMENTS.



Figure 56.

PHOTOGRAPHS OF THE HIGH TEMPERATURE FURNACE FOR STRENGTH

DETERMINATIONS

- (a) Front view showing position of the furnace on the "Instron" physical testin, rachine.
- (b) Insido view of furnace chowing the heating elements and radiation chields.



(a)



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APPENDIX II

SUMMARY OF THE ISOTHER ALL STUTTEING AND GRAIN SIZE DATA.

- TABLES 11 15 Puro Magnosia
- TABLES 16 20 linguesia Containing 0.5 mole \$ Forsterite
- TABLES 21 25 | Hagnesia Containing 0.5 mole % Honticellite
- TABLES 26 30 Nagnesia Containing 0.25 mole % Nerwinite
- TABLES 31 35 Ingnesia Containing 0.5 mole % Dicalcium Silicato
- TABLES 36 40 Hagnesia Containing 0.5 mole % Tricalcium Silicate
- TABLES 41 45 Magnesia Containing 0.5 mole % Calcium Oxide

TABL'S II

SITT RING DATA ON MACHINA FIRD AT 1400°C.

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עיזק	TIME AT	PPESSED			P 4 (PEPT	IESA	γŢEF	FITTN	G		
	TEMP.	BULK	DENS	SITY g./cc		PO	POSITY %		VOLUME	DENSTATC PA AME	ATION TER	GLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	SIZE µ
1140	0.1	1.56	2.03	3.52	3.58	42.3	43•3	1.0	23.2	23 .3	40.9	-
N141	1.0	1.53	2.21	3.56	3.58	37.9	38.3	0.4	28.5	31.5	51.0	-
M142	2.0	1.58	2.27	3.55	3.53	36.1	36.6	0.5	3 0.24	34•5	54•4	-
1:144	4.0	1.58	2.34	3.55	3.58	34.1	34.6	0.5	32.5	38.0	53.1	-
M148	8.0	1.57	2.39	3.55	3.58	32.7	33.2	0.5	34.3	40.8	61.1	-

TABL 12

SINCE I G DATA ON MAGNICIA FIRED AP 1500°C.

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קקק	TIME AT	PPESSED			P 4 0	регт	IESA	ͲͲΕΡ	FITN	G		
rer.	TEMP.	BULK	DENS	SITY g./co	•	PO	FOSITY %		VOLUME	DENSTRIC PA 'AME	ATION	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANCE %	PENSITY	VOLUME	STZE µ
1:150	0.1	1.53	14	3.55	3.53	39.7	40 . 2	0.5	26.4	23.0	46•3	-
1:151	1.0	1.57	2.36	3.56	3.58	33.9	34 •3	0.4	3 3.5	30.2	57.6	-
11152	2.J	1.56	ť45	3.50	3.53	31.3	31.7	0.4	36.2	43.9	64.2	-
1:154	4.0	1.60	2.57	3.55	3.58	27.3	28.2	0.4	37.7	49.0	63.2	9.0
м153	8.0	1.5.	2.74	3.56	3.53	23.0	23.4	0.4	42.3	5°•0	75.5	11.0

SINTERING DATA ON MAGNESIA FIRED AT 1600°C.

555	TIME AT	PPESSED			P.(ОРЕТТ	IESA	γτΕF	FIRTN	I G		
∩≞r.	TEMP.	BULK	DEN	SITY g./cc		PO	FOSITY 🕉		VOLUME	DENSIL'IC PA AME	CATION TER	GFAIN
NO.	$\frac{1}{100} HR. \qquad DENSITY$	DENSITY g./cc.	BULK	APPAREN'' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSILY	VOLUME	STZE µ
M160	0.1	1.57	2.36	3.58	3.58	34.0	34.0	0.0	33.5	39.3	59•7	5.5
M161	1.0	1.56	2.50	3.57	3.58	30.0	30.2	0.2	37.5	47.5	66.5	8.0
M162	2.0	1.60	2.73	3.57	3.58	23.5	23.7	0,2	41.4	57.1	74.9	10.0
M164	4.0	1.59	2.97	3.57	3.58	16.8	17.0	0.2	46.5	69.3	83.6	12.5
M168	8.0	1.58	3.22	3.55	3.58	9.3	10.1	0.8	50.9	82.0	91.0	14.0

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SINTERING DATA ON MAGNESIA FIRED AT 1700°C.

DED	TIME AT	PPESSED			Ρ.Ο	PEFT	IESA	FTĘF	FTTN	G		
	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY 🕫		VOLUME	DE: STITIC PA 'AME	ATION	GLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S [⊤] ZE µ
М170	0.1	1.60	2.73	3.57	3.58	23.4	23.7	0.3	41.5	57.3	75.0	10.0
171	1.0	1.55	2.99	3.57	3. 58	16.8	16.6	0.2	43.2	70.7	84.8	12.5
M172	2.0	1.57	3.24	3.52	3.58	8.9	9.5	1.6	51.6	83.3	91.8	15.5
1174	4.0	1.60	3.45	3.51	3.58	1.8	3.6	1.8	53.4	93.2	%.9	20.5
11178	8.0	1.60	3.46	3.52	3.58	1.7	3.4	1.7	53.0	93.9	97.2	28.0

TABLE IS

SINTERING DATA ON MAGNESIA FIRED AT 1800°C.

	TIME AT	PPESSED			P.()РЕТТ	IESA	ኮ፲ Ε Γ	FITN	G		
KEF.	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY 🕫		VOLUME	DEI ST, IC PA 'AME	ATION	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'I SOLID	TRUE	APPARENT	TRUE	SEALED	CHANCE %	DENSIGY	VOLUME	S™ZE µ
M180	0.1	1.59	3.32	3.46	3.58	4.3	7.4	3.1	52.1	86.7	93.6	23.0
M181	1.0	1.56	3.40	3.47	3.58	2.0	5.2	3.0	54.2	90.9	95.8	28.0
M182	2.0	1.56	3.44	3.49	3.58	1.5	3.9	2.4	54.6	93.1	%.9	33.0
M184	4.0	1.62	3.48	3.51	3.58	0.9	2.7	1.8	53•4	94•9	97.5	40.0
M188	8.0	1.57	3.49	3.52	3.58	0,8	2.5	1.7	55.0	95.5	98.0	49.0

TIBLE 16

GENT.RING BATA ON MACTISIA CONTAINING 0.5 mole # MONSTLAITE FIRED AT 1400°C.

ספו	TTME AT	PPESSED			Ρ.	ΟΡΕΓΤ	IES A	PTEF	PITIN	G		
NEF.	TEMP.	BULK	DEN	SITY g./cc	•	PO	POSITY %		VOLUME	DENSINTO PARAMI	CATION FIER	CLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANCE %	DENSITY	VOLUME	S™ZE µ
1440	0.1	1.55	1.94	3.50	3.53	44.6	45.3	1.2	19.7	18.8	34.9	-
11441	1.0	1.57	2.03	3.52	3•53	40.9	_. 41.9	1.0	24.6	25.3	43.9	-
M442	2.0	1.55	2.17	3•53	3•58	38•5	39•4	0.9	23.5	30.4	50.3	-
:1444	4.0	1.54	2.24	3.54	3.58	36.7	37-4	0.7	31.4	34.3	55.1	-
1448	8.0	1.56	2.35	3.55	3.58	33.8	34.3	0.5	33.5	39.1	59•4	7.0

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SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole & FORSTERITE FIRLD AT 1500°C.

DDD	TTME AT	PPESSED			Ρ.(OPE T	IES A	FTEF	FILIN	G		
NEP.	TEMP.	BULK	DEN:	SITY g./cc	•	PO	POSITY %		VOLUME	DER STATIC PA ANTE	ATION	GTAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S™ZE µ
M450	0.1	1.54	2.15	3.53	3.58	39.0	39.9	0.9	26.4	29.9	49•9	-
M451	1.0	1.53	2,50	3.54	3.58	29.3	30.1	0.8	36.7	46.0	65.5	10.0
M45 2	2.0	1.57	2.98	3.55	3.58	16.2	16.9	0.7	47.2	70.0	84.1	12.0
M4 54	4.0	1.53	3.19	3•47	3•58	8.1	10.9	2,8	50.4	80.3	90.2	16.0
M45 8	8.0	1.5 5	3.27	3.39	3.58	3.5	8.6	5.1	51.7	84.5	92.5	21.0

GINT.RING DATA ON HUGH DIA CONTAINING 0.5 mole % PORSTERITE FIRED AT 1600°C.

DEM	TIME AT	PPESSED			Ρ.	ОРЕТТ	IES A	FTEF	ΡΙΤΤΝ	I G		
ref.	TEMP.	BULK	DEN:	SITY g./cc	•	PO	FOSITY %		VOLUME	DER ST., TO PA 'AMI	ATION	CLAIN
NO.	NO. HR. DEI g., M460 0.1	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSI'I Y	VOLUME	S ⁻ ZE μ
M460	0.1	1.55	2.46	3.56	3.58	31.0	31.3	0.3	36.8	44.8	65.0	9.5
1461	1.0	1,60	2,80	3.55	3.58	21.0	21.7	0.7	43.1	60.8	77.7	17.5
M462	2.0	1.57	3.12	3.51	3.58	11.2	12.8	1.6	49.7	77.1	88.6	22.0
1464	4.0	1.59	3.33	3.42	3.58	2.6	7. 0	4.4	52.4	87.5	93.9	25.5
M468	8.0	1.58	3.36	3.44	3.58	2,5	6.3	3.8	52.9	83.8	94.8	32.0

SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole & FORSTERITE FIRED AT 1700°C.

		PPESSED			Ρ.()PETT	IES A	FTEF	P T T T N	G		
KEF.	TEMP.	BULK	DENS	SITY g./cc	+	PO	rosity 3		VOLUME	DENST, TO PA 'AME	ATION MER	GLAIN
NO.	NO. HR.	DENSITY g./cc.	BULK	APPAREN')' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSLIY	VOLUME	S⁺ZE µ
M470	0.1	1.57	2.95	3•54	3•58	16.7	17.6	0.9	46.3	68.7	83.5	15.5
M471	1.0	1.59	3.34	3.42	3.58	6.8	11.1	4.3	52•4	87.7	94-1	24.0
M472	2.0	1.56	3.38	3.45	3.58	2.0	5.6	3.6	53.8	90.1	95•4	31.0
11474	4.0	1.59	3.42	3.47	3.58	1.5	4•5	3.0	53•5	92.0	95.2	37.5
M478	8.0	1.57	3.42	3.48	3•58	1.7	4.5	2.8	54.1	92.0	%.4	45•5

SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole % FORSTERITE FIRED AT 1800°C.

	TTME AT	PPESSED			Ρ.	ΟΡΕΞΤ	TES A	FTEF	PITI	IG		
ſÆr.∎	TEMP.	BULK	DEN	SITY g./cc	•	PO	fosity 🖉	<u>;</u>	VOLUME	DERSITI PA 'AM	CATION	CLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHARGE %	DENSITY	VOLUME	S [⊤] ZE µ
M480	0.1	1.60	3.38	3.43	3.58	1.3	5.5	4.2	52.8	89.9	95.3	40.5
M481	1.0	1.61	3.42	3.48	3.58	1.7	4.5	2.8	52.9	91.9	%.2	59.0
M482	2.0	1.60	3.40	3.47	3.58	1.9	4.9	3.0	52.9	91.0	95.8	69.0
M484	4.0	1.60	3.43	3.48	3.58	1.4	4.1	2.7	53.3	92.5	96.5	84.0
M488	8.0	1.60	3.43	3.47	3.58	1.1	4.1	3.0	53.3	92.5	%.5	166

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SINTLANG DATA OF MAGNESIA CONTAINING 0.25 mole \$ MONTICLIAITE FILL AT 1400°C.

	TTME AT	PPESSED			Ρ.	ΟΡΕΓΤ	IES A	FTEF	FTTN	G		
REF.	TEMP.	BULK	DEN	NSITY g./cc	· · · · · · · · · · · · · · · · · · ·	PO	FOSTTY 3	,	VOLUME	DEP STIC PA 'AM	CATION	GFAIN
NO. HR.	HR.	DENSITY g./cc.	BULK	APPAREN'I' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S™ZE µ
>340	0.1	1.60	2.13	3.53	3.57	38.2	39.1	0.9	26.9	29.6	48.7	-
1041	L. 0	1.57	2 .23	3.54	3.57	37.0	37.7	0.7	29.5	33.0	52.7	5.5
N342	2.0	1.57	2.40	3.55	3.57	32.4	33.0	0.6	34+5	41.5	61.6	7.0
1344	4.0	1.53	2.83	3.55	3.57	20.2	21.0	0.8	44.3	60.4	79.5	8.8
M348	8.0	1.59	2.93	3.53	3.57	15.5	16.5	1.0	46.6	70.3	54.0	11.0

SINTLRING DATA ON MAGUESIA CONTAINING 0.5 mole & MONTICELLITE FILLD AT 1500°C.

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ਯਾਜਕ	TIME AT	PPESSED			Ρ.(OPET	IESA	FTET	FTTN	ſĠ		
NEP.	TEMP.	BULK	DEN	SITY g./cc	•	PO	FOSITY 🖇		VOLUME	DER SUFTO PA AME	ATION	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S⊺ZE µ
1350	0.1	1.59	2.83	3.50	3.57	19 . 3	20.9	1.6	43.9	62.5	79.1	10.0
1351	1.0	1.59	2,93	3.42.	3.57	12,8	16.5	3.7	45.6	70.2	84.0	14.0
1352	2.0	1.58	3.06	3.35	3.57	9.1	14.3	5.2	48.5	74.5	87.1	17.5
N354	4=0	1.56	3.10	3.34	3.57	7.2	13.2	6.0	49.7	76.6	88.1	21.0
N 3 58	8.0	1.53	3.13	3.30	3.57	5.2	12,3	7.1	49.6	77.9	89.0	29.0

SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole % MONTICELLITE FIRED AT 1600°C.

ਰਕਰ	TTME AT	PPESSED		P.OPETTIES AFTEF FITTNG										
NO. HR.	TEMP.	BULK	DENSITY g./cc.			POPOSITY %			VOLUME	DESSIFICATION PA AMETER		GFAIN		
	HR.	DENSITY g./cc.	BULK	APPARENT SÓLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSILY	VOLUME	S ^T ZE µ		
M360	0.1	1.60	3.17 -	3.36	3.57	5.6	11.1	5.5	47.6	79.7	89.9	11.0		
N361	1.0	1.60	3.23	3.29	3.57	1.8	9•5	7.8	50.3	82.7	91.6	17.5		
M362	2.0	1.59	3.25	3.29	3.57	1.2	9.0	7.8	51.1	83.8	92.0	26.5		
H364	4.0	1.58	3.25	3.31	3.57	1.8	9.2	7.2	51.2	84.0	92.3	35.5		
M368	8.0	1.60	3.29	3.33	3.57	1.2	7.8	6.6	51.3	85•5	93.0	45.5		

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SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole & MONTICELLITE FIRED AT 1700°C.

REF.	TIME AT	PPESSED		P.OPETTIES AFTEF FIRTNG										
	TEMP.	BULK	DENSITY g./cc.			POPOSITY %			VOLUME	DESSIFICATION PA 'APETER		GFAIN		
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSIAY	VOLUME	S⁺ZE µ		
M370	0.1	1.60	3.22	3.29	3.57	2.1	9.8	7.7	50.4	82.1	91.1	21.0		
M371	1.0	1.57	3.26	3.33	3.57	2.1	3.6	6.5	51.8	84.5	92.6	29.0		
M372	2.0	1.59	3.28	3.34	3.57	1.8	3.0	6.2	51.6	85.6	93.0	36.5		
M374	4.0	1.59	3.29	3.35	3.57	1.8	7.8	6.0	51.7	85.9	93.3	49.0		
M378	8.0	1.58	3.30	3.36	3.57	1.8	7.6	5.8	52.1	86.4	93.6	59.0		

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SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole % MONTICELLITE FIRED AT 1800°C.

	TTME AT	PRESSED		PLOPERTIES ARTER PITTNG										
ner.	TEMP.	BULK	DENSITY g./cc.			POPOSITY %			VOLUME	DENSIFICATION PA APETER		GFAIN		
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	⊤ENSI1Y	VOLUME	S⁺ZE µ		
M380	0.1	1.60	3.28	3.31	3.57	0.9	8.1	7.2	51.3	85.3	92.9	28.5		
M381	1.0	1.60	3.31	3.35	3.57	1.1	7.2	6.1	51.8	86.8	93.7	39.0		
M382	2.0	1.60	3.34	3.36	3.57	0.6	6.4	5.8	52.1	88.3	94•4	50.0		
M384	4.0	1.61	3.16	3.28	3.57	3.6	11.5	7.9	49.0	79.1	89.1	60.0		
M388	8.0	1.60	3.04	3.39	3.57	10.3	≟ 4.8	4.5	47.4	73.1	85.9	73.5		

SINTERING DATA ON MAGNESIA CONTAINING 0.25 mole \$ MERVINITE FIRED AT 1400°C.

ססק	TIME AT	PPESSED		P.OPETTIES AFTEF FILTNG										
NEF.	TEMP.	BULK	DENSITY g./cc.			POPOSITY %			VOLUME	DENSIFICATION PA AMETER		GFAIN		
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'I SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSI'1Y	VOLUME	S™ZE µ		
M640	0.1	1.59	2.11	3.52	3.58	40.2	41.2	1.0	24.7	26.1	4.44	-		
1641	1.0	1.59	2,23	3.55	3.53	35.7	36.4	0.7	30.3	34.7	54•5	8.0		
M642	2.0	1.58	2.34	3.55	3.53	34.1	34.7	9. 6	32.5	38.0	58.1	9.5		
1644	4.0	1.53	2.91	3.50	3.53	18.2	18.7	0.5	45.9	66.5	82.3	12.0		
1648	8.0	1.58	3.07	3.55	3.58	13.5	14.3	0.8	48.6	74•5	86.8	15.0		

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SINTERING DATA ON MAGNESIA CONTAINING 0.25 mole % MERWINITE FIRED AT 1500°C.

	TIME AT	PPESSED		PAOPETTIES AFTEF PITTNG										
KEF.	TEMP.	BULK	DEN	SITY g./cc	•	Poposity %			VOLUME	DENSIFICATION PA 'AMETER		GTAIN		
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TPUE	SEALED	CHANGE %	PENSITY	VOLUME	S ⁻ ZE µ		
M650	0.1	1.60	2.43	3.54	3.58	31.4	32.1	0.7	34.3	42.1	62.0	10.5		
M551	1.0	1.60	3.00	3.50	3.58	14.3	16.2	1.9	46.7	70.7	84•4	13.5		
M652	2.0	1.58	3.16	3.49	3.58	9.3	11.8	2.5	50.1	79.0	89.6	16.0		
M554	4.0	1.60	3.26	3.42	3.58	4.9	9.1	4.2	51.0	83.6	92.0	19.0		
M658	8.0	1.58	3.27	3.41	3.58	4.1	8.7	4.6	51.7	84.5	92.5	23.0		

SINTERING DATA ON MAGNESIA CONTAINING 0.25 mole % MERWINITE FIRED AT 1600°C.

מסס	TIME AT	PRESSED		P.OPETTIES AFTEF FITTNG											
NO. HR.	TEMP.	BULK	DENSITY g./cc.			PO	POPOSITY %			DENSIGICATION PA AMETER		GFAIN			
	HR.	DENSITY g./cc.	BULK	APPAREN'I' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S⊤ZE µ			
M660	0.1	1.57	3.07	3.48	3.58	11.7	14.2	2.5	43.9	74.6	87.1	18.0			
1561	1.0	1.58	3.20	3.43	3.58	6.7	10.6	3.9	50.6	81.0	90.5	20.0			
1662	2.0	1.58	3.25	3.41	3.58	4•4	9.0	4.6	51.5	84.0	92.2	22.0			
1%64	4.0	1.57	3.28	3.41	3.58	3.8	8.4	4.6	52.1	85.1	92.9	27.0			
1568	8.0	1.58	3.31	3.38	3.58	2.1	7.7	5.6	52.2	86.3	93.4	32.0			
SINT RING DATA ON MACH. IA COMPACTING 0.25 mole & MERGINITL FIRED AT 1700°C.

ਸਤਕ	TIME AT	PPESSED			Р.	ΟΡΕΞΤ	IES A	FTEF	P T T T N	ſĠ		
ner.	TEMP.	BULK	DEN	SITY g./cc	•	PO	POSITY 3		VOLUME	DENSUJIO PA 'AM	CATION ETER	CLAIN
NO.	HB.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	change %	DENSITY	VOLUME	S⁺ZE µ
1:670	0.1	1.57	3.22	3.34	3.58	3.6	10.1	6.5	51.2	32.1	91.3	23.0
1671	1.0	1.56	3.24	3.35	3.58	3.3	9•5	6.2	51.3	83.2	91.9	30.0
1572	2.0	1.57	3.30	3.36	3.58	1.8	7.8	6.0	52.4	86.1	93 . 4	33.5
1574	4.0	1.60	3.32	3.37	3.53	1.5	7.3	5.8	51.6	86.9	93.7	42.0
1⁄678	8.0	1.60	3.33	3.38	3.,58	1.5	7.0	5.5	52.0	87.4	94.0	52.0

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SINT NING DATA ON MAGRIDIA CONTAINING 0.25 mole \$ M.R. INTER FLUD AT 1800°C.

DEE	TIME AT	PPESSED			Ρ.Ο) P E D T	IES A	FTEF	FILIN	G		
KET.	TEMP.	BULK	DEN	SITY g./cc	•	PO	FOSITY %		VOLUME	DENSIJIC PA 'ANE	ATTON MER	GTAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSILY	VOLUME	STZE µ
1 6 80	0.1	1.60	3.33	3.36	3.53	0.9	7.0	6.1	52.1	\$7.4	94.0	32.0
1581	1.0	1.61	3 .33	3.37	3.58	1.2	7.0	5.8	51.7	87.3	93.9	40.0
:582	2.0	1.61	3.36	3.40	3 . 5ર	1.2	6.1	4•9	52.1	C3 . 9	94•9	47.0
1584	4.0	1.61	3,30	3.34	3.53	1.2	7.8	6,6	51.2	85.9	93.3	55•5
1%88	3.0	1.59	3,30	3.34	3.58	1.2	7.8	6.6	51.8	26.0	93.2	65.0

SINTERING DATA ON HACHESIA CONTAINING 0.5 mole % DICALCIUM SILICATE FIRED AT 1400°C.

		PPESSED		······	P.() P E C T	TES A	ътег	FIRIN	G		
KEF.	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY %		VOLUME	DEN STITIC PA AME	CATION ETER	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'I SOLID	TRUE	APPARENT	TRUE	SEALED	CHANCE %	PENSILY	VOLUME	S⊤ZE µ
M740	0.1	1.56	2.05	3.50	3.58	41.4	42.7	1.3	23.9	24 .2	42.4	-
M741	1.0	1.56	2.30	3.53	3.58	34.8	35.8	1.0	32.2	36.6	57.0	-
M742	2.0	1.59	2.56	3.54	3.58	27.7	28.5	0.8	37.9	48.8	68.2	-
M744	4.0	1.58	2.38	3.54	3.58	18.6	19.6	1.0	45.1	65.0	80.8	8.5
M748	8.6	1.55	3.02	3.54	3.58	14.7	15.6	0.9	48.7	72.5	85.9	10.0

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SINTERING DATA ON 'AGN SIA CONTAINING 0.5 mole % DICALCIUM SILICATE FIRED AT 1500°C

DED	TTME AT	PPESSED			P . C	рет	IES A	FTEF	ртти	G		
NEF.	TEMP.	BULK	DENS	SITY g./cc		PO	FOSITY %		VOLUME	DENSTAIC PA 'ANE	ATION	CTAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S™ZE µ
M750	0.1	1.57	2.42	3.56	3.58	32.0	32.4	0.4	35.1	42.2	62.6	
M751	1.0	1.56	2.76	3.55	3.58	22.3	22.9	0.6	43.5	59.5	77.1	s. 0
11752	2.0	1.58	2.93	3.54	3.58	17.2	18.2	1.0	46.1	67.5	82.4	10.0
М754	4.0	1.57	3.67	3.53	3.58	13.0	14.2	1.2	48.9	74.6	87.1	11.0
M758	8.0	1.57	3.20	3.47	3.58	7.8	10.6	2.8	50.9	81.1	90.8	12.0

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SINTERING DATA ON MAGNEGIA CONTAINING 0.5 mole % DICALCIUM SILICATA FIRED AT 1600°C.

DDD	TIME AT	PRESSED			P at C	PET	IESA	ਸ TE F	FITN	G		
REF.	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY 💋		VOLUME	DENSTITIC PA 'AME	ATTON TER	CFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN') SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	STZE µ
11750	0.1	1.57	2,98	3.55	3.58	16.0	16.8	0,8	47.3	70.2	84.3	6.0
M761	1.0	1.55	3.07	3.50	3.58	12.3	14.2	1.9	49.2	74.8	87.2	9.0
M762	2.0	1.57	3.19	3.45	3.58	7.5	10.9	3.4	50.8	80.6	90.5	11.0
M754	4.0	1.58	3.29	3.41	3.58	3.5	8.1	4.5	52.0	85.5	93.0	13.0
M768	8.0	1.57	3.30	3.41	3.58	3.2	7.0	4.6	52.4	86.1	93.5	15.0

SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole & DICALCIUM SILICATE FIRED AT 1700°C.

סממ	TIME AT	PPESSED			PlC	PETT	IES A	FTEF	ΓττΝ	G		
NEF.	TEMP.	BULK	DEN	SITY g./co		PO	FOSITY 🕫		VOLUME	DENSIFIC PA 'AME	ATION TER	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'I' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S™ZE µ
M770	0.1	1.59	3.25	3.35	3.58	3.0	9.2	6.2	51.1	83.5	91.9	21.0
N771	1.0	1.58	3.27	3.41	3.58	4.0	8.6	4.5	51.7	34.5	92.5	30.0
M772	2.0	1.59	3.30	3.40	3.53	3.0	7.8	4.8	51.8	86.0	93.2	39.0
11774	4.0	1.59	3.33	3.40	3.58	2.0	6.9	4.9	52.2	87.5	94.0	48.0
M778	8.0	1.59	3.30	3.41	3.58	1.5	6.1	4.6	52.7	89.0	94 .7	53.0

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SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole % DICALCIUM SILICATE FIRED AT 1800°C.

DEP	TIME AT	PPESSED			P 1 (DPEFT	IES A	ምጥ ድ F	FITN	G		
REF.	TEMP.	BULK	DENS	SITY g./cc		PO	rosity %		VOLUME	DET STITIC PA 'AME	ATTON DER	CLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S⊺ZE µ
M780	0.1	1.59	3.28	3.37	3.58	2.7	8.4	5.7	51.5	35.0	92.7	36.0
M781	1.0	1.58	3.31	3.38	3.58	2.0	7.5	5•5	52.3	86.5	93.5	43.0
M782	2.0	1.59	3.32	3.38	3.58	1.7	7.2	5.5	52.1	87.0	93.7	50.0
11784	4.0	1.60	3.33	3.38	3.58	1.5	7.0	5 •5	52.0	37.5	93.9	59.5
M738	\$.0	1.59	3.34	3.38	3.58	1.2	6.7	5.5	52.4	88.0	94.2	67.0

SINTERING DATA ON MAGERSIA CONTAINING 0.5 mole & TRICALCIUM BILICATL FIRED AT 1400°C.

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	TTME AT	PPESSED			P , ()PE~T	IESA	FTEF	<u>Γ</u> Τ Τ Ν	G		
KEF.	TEMP.	BULK	DENS	SITY g./co	•	PO	fosity %		VOLUME	DENSTITO PA AME	ATION DER	CFAIN
NO.	HR.	DENSITY g./cc.	BUIK	APPARENT' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S™ZE µ
1.340	0.1	1.60	2.26	3.52	3.57	35.7	36.7	1.0	27.1	33.5	52.8	-
:1241	1.0	1.60	2.52	3.54	3.57	28.8	29.5	0.7	36.5	15.7	66.1	7.0
::342	2.0	1.59	2.66	3.54	3.57	24.7	25.4	0.7	40.3	54.0	72.6	7.5
1:344	4.0	1.59	2.74	3.54	3.57	22.6	23.3	0.7	42.5	53.1	75.6	8.5
1.543	c.0	1.5)	2.80	3.54	3.57	20 .9	21.6	0.7	43.3	61.2	73.0	9.5

TABL: 37

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SI FLAING DATA ON AGALDIA CONTAINING 0.5 mole 5 TRICALCIUM DILICATE - FLD AT 1500°C.

ਰਾਕਰ	TIME AT	PPESSED			P (ОРЕРТ	IES A	FTEF	אייזע	G		
ner.	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY の		VOLUME	DENSITIC PA AME	CATTON MER	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN') SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSILY	VOLUME	SIZE µ
1:350	0.1	1.53	2.47	3.55	3.57	30.4	30.3	0.4	36.2	44.9	64 .8	6.5
1851	1.0	1.60	2.70	3.55	3.57	24.0	24•4	0.4	40.7	55.8	73.8	7.5
¥852	2.0	1.60	2.84	3.55	3.57	20.0	20.4	0.4	43.7	62.9	79.1	9.0
1.854	4.0	1.53	3.04	3.53	3.57	13.9	14.8	0.9	48.1	73.4	86.2	10.5
M <i>8</i> 58	8.0	1.60	3.15	3.50	3.57	10.0	11.3	1.8	49.2	78.6	88.8	12.0

SINTARING DATA ON MAGUESIA CONTAINING 0.5 mole % TRICALCIUM SILICATE FIRED AT 1600°C

DEB	TIME AT	PFESSED			P : 0	ре⊇т	IES A	न्मुम्ह	FILIN	G		
ner.	TEMP.	BULK	DEN	SITY g./cc	•	PO	FOSITY 🕉		VOLUME	DENSIFIC PA AME	ATION JER	CLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'I' SOLID	TAUE	APPARENT	TRUE	SEALED	Change %	DENSITY	VOLUME	STZE µ
11860	0.1	1.62	3.0 3	3.56	3.57	14.9	15.1	0.2	46.6	72.1	C4 .9	8.0
1691	1.0	1.60	3.11	3.55	3.57	12.4	12.9	0.5	43.5	75 .7	83.0	9.0
11862	2.0	1.62	3.21	3.51	3.57	3.5	10.0	1.5	49•9	31.8	90.4	9.5
1.864	4.0	1.59	3.28	3.48	3.57	5.7	8.1	2.4	51.6	85 .5	92.9	11.5
11268	8.0	1.58	3.35	3.45	3.57	2.3	6.1	3.3	52.8	89.0	94.8	14.0

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SINF RENG DATA OF AGYLSIA CONTAINING 0.5 role % TRIDULCIUM CILICAT. I DAT 1700°C.

		PFESSED		·····	P 4 (PEPT	IES A	PTEF	PTTN	G		••••••••••••••••••••••••••••••••••••••
REF.	TEMP.	BULK	DEN	SITY g./cc	•	PO	FOSITY 💋	- <u>,</u>	VOLUME	DENSITIC PA 'AME	ATION MER	GFAIN
NO.	HP.	DENSITY g./cc.	BULK	APPAREN' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S™ZE µ
1:370	0.1	1.61	3.27	3.43	3.57	4.7	8.4	3.7	50.3	34 .7	92.5	10.0
11271	1.0	1.62	3.37	3.43	3.57	1.9	5.6	3.7	51. 9	89.7	95.1	12.0
H872	2.0	1.59	3.39	3.44	3.57	1.7	5•3	3.6	53.1	90.9	95.7	13.5
11874	4.0	1.59	3.42	3.40	3.57	1.6	4.2	2.1	53•4	92.6	%•4	16.0
11878	8.0	1.59	3.43	3.40	3.57	1.4	3.9	2.5	53.8	93.0	%.6	22.0

TAPLE 40

SINTLRING DATA ON MAGNEDIA CONTAINING 0.5 mole & TRICALCIUM SILICATE VIED AT 1800°C.

DED	TIME AT	PPESSED			Р.()РЕ`Т	IES A	FTEF	FITN	G		
NEF.	TEMP.	BULK	DEN	SITY g./cc	•	PO	POSITY 🕉		VOLUME	DENSTITIC PA 'AME	ATION TER	GLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENJ' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSILY	VOLUME	S™ZE µ
11380	0.1	1.57	3.35	3.40	3.57	1.7	6.3	4.6	52.5	S3 .7	94.6	37
M381	1.0	1.57	3.40	3.44	3.57	1.2	4.9	3.7	53.2	91.4	95.9	48
11382	2.0	1.61	3.42	3.45	3.57	1.0	4.2	3.2	52.9	92.3	95•4	53
1534	4.0	1.53	3.44	3.46	3.57	1.0	3.8	2.9	54.0	93.2	%.9	63
11838	8.0	1.57	3.45	3.47	3.57	0.6	3.4	2.3	5414	94.0	27.3	73

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SINTERFIG DATA ON MAGRESIA CONTAINING 0.5 mole & CALCIUM OXID. FIRED AT 1400°C.

תקת	TIME AT	PPESSED			Ρ.	OPET	IES A	FTEF	FITTN	ſĢ		
ner.	TEMP.	BULK	DENS	SITY g./cc		PO	POSITY 🖇		VOLUME	DENSIFTO PA 'AME	ATION DER	GTAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSI4Y	VOLUME	S ⁺ ZE µ
M940	0.1	1.57	2.33	2.50	3.58	33.5	34.9	1.4	33.0	38.1	58.6	-
M941	1.0	1.56	2.50	3.55	3.58	29.6	30.2	0.6	37.6	46.8	66.8	-
11942	2.0	1.53	2.63	3.54	3.58	25.7	26.5	0.3	40.0	52.5	71.6	
M944	4.0	1.53	2.76	3.54	3.53	22.0	22.9	0.9	42.5	59.0	73.6	-
11948	8.0	1.57	2.89	3.54	3.58	18.4	19.3	0.9	45.7	65.7	81.4	7.5

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SINTLAING DATA ON MAGY DIN CONTAINING 0.5 mole & C LUIUM OXIDE FIRED IN 1500°C.

	TTME AT	PPESSED		<u></u>	Ρ.(ретт	IESA	ግ፹E F	FITIN	Ģ		*
REF.	TEMP.	BULK	DENS	SITY g./co	•	PO	FOSITY %		VOLUME	DEI STITC PA 'ANE	ATION MER	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	STZE µ
1:950	0.1	1.60	2.54	3.55	3.58	28.5	29.1	0.6	36.6	47.5	66.3	-
1:751	1.0	1.56	2.60	3.56	3.53	27.0	27.4	0.4	40.0	51.5	70.9	7.0
N952	2.0	1.53	2.75	3.55	3.53	22.7	23.2	0.5	42.5	53.5	73.1	8.0
1:254	4.0	1.60	2.91	3.54	3.53	17.8	16.3	1.0	46.0	66.2	82.0	9.0
м758	8.0	1.53	3.09	3.54	3.53	12.7	13.7	1.0	43.9	75.5	87.5	10.5

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DITTING OF THE OF THE JUNTAINING 0.5 MOLE & CALCIN: OXIDE MILLO AT 1600°C.

היייי	TIME AT	PPESSED			P.(орегт	IESA	FTEF	FITN	G		
REF.	TEMP.	BULK	DENS	SITY g./cc	•	PO	FOSITY %		VOLUME	DENSIJIO PA AME	ATION TER	GFAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'''' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANCE %	PENSITY	VOLUME	S™ZE µ
M960	0.1	1.57	2.67	3.57	3.58	25. 2	25.4	0.2	41.2	54.7	73.4	7.5
M961	1.0	1.58	2.83	3.55	3.58	20.5	20.9	0.4	44•2	62.5	79. 0	9.0
M962	2.0	1.56	2.94	3.5%	3.53	17.4	17.8	0.4	45.3	<i>6</i> 8.1	.83.1	10.0
M964	4.0	1.60	3.07	3.55	3.58	13.5	14.2	0.7	47.5	74.3	86.2	11.0
M968	8.0	1. 53	3.17	3. 54	3.58	10.5	11.5	1.0	50.2	79.5	89. 3	12.5

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SITTRING DATA ON ALL SIA CONTATVING 0.5 POLO & CALDIDA UNIDE FIR D T 1700°C.

DED	TTME AT	PPESSED			P . () P E ¬ T	IES A	TTEF	אייזי	G		
KEF.	TEMP.	BULK	DENS	SITY g./cc	·	PO	FOSITY 3		VOLUME	DEN'S UT IC PA 'AME	CATION	CLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	PENSITY	VOLUME	S⁺ZE µ
M970	0.1	1.56	3.17	3.52	3.58	10.0	11.4	1.4	50.7	79.8	90.0	10.5
M971	1.0	1.58	3.26	3.52	3•58	7.5	9.0	1.5	51.6	83.8	92.2	16.5
M972	2.0	1.57	3.32	3.52	3.58	8.3	7.3	1.5	52.7	e 7. 1	93.9	19.0
м974	4.0	1.57	3.34	3.52	3.58	5.1	6.7	1.6	52.9	88.2	94•4	24.5
M978	8.0	1.56	3.37	3.46	3.58	2.6	5.9	3.3	53.6	89.6	95.2	33.5

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SINTERING DATA ON MAGNESIA CONTAINING 0.5 mole % CALCIUM ONIDE FIRED AT 1800°C.

	TTME AT	PPESSED			Ρ. Ο	PEPT	IES A	FTEF	FITN	G		
REF.	TEMP.	BULK	DENS	SITY g./co		PO	FOSITY 🕉		VOLUME	DER STOTO PA 'AME	ATION TER	GLAIN
NO.	HR.	DENSITY g./cc.	BULK	APPAREN'' SOLID	TRUE	APPARENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	STZE µ
M980	0.1	1.56	3.23	3.42	3.58	5.5	9.9	4•4	51.8	82.7	91.6	18.5
11931	1.0	1.57	3.33	3.43	3.53	1.5	5.6	4.1	53.4	90.0	95.3	22.5
11932	2.0	1.58	3.42	3.45	3.58	0.9	4•5	3.6	53.8	92.0	95.2	26.5
M984	4.0	1.59	3.46	3•49	3.58	0.9	3.5	2.4	54.0	94.0	97.1	37.5
11788	8.0	1.58	3.44	3.47	3.58	0.9	3.9	3.0	54.0	93.0	%.8	49.5

APPENDIX III

SUMMARY OF THE SIMTERING AND GRAIN SIZE DATA, AFTER 4 HOURS AT TEMPERATURE, OF THE MAGNESIA MIXTURES CONTAINING THE INCREASED ADDITIONS.

- TABLE 46 Magnesia Containing 1.0 mole \$ Forsterite
- TABLE 47 Magnesia Containing 1.0 mole % Monticellite
- TABLE 48 Magnesia Containing 0.5 mole % Merwinite
- TABLE 49 Magnesia Containing 1.0 mole \$ Dicalcium Silicate
- TABLE 50 Magnesia Containing 1.0 mole % Tricalcium Silicate
- TABLE 51 Magnesia Containing 1.0 mole \$ Calcium Oxide

SINTERING DATA ON MAGNESIA CONTAINING 1.0 mole & FORSTERITE FIRED AT TEMPERATURE FOR 4 HOURS.

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	EIDING	PRESSED			ΡF	OPERT	IES	AFTEP	FIPI	NG		
NO.	TEMP.	BULK	DEN	SITY g./cc	; .	P	OROSITY	с, ,	VOLUME	DENSIFIC	CATION	GFAIN
	°c.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S ^τ ZE μ
D444	1400	1.58	3.17	3.47	3.57	8.6	11.2	2.6	50.2	79.9	89.9	9.0
D454	1500	1.57	3,33	3.38	3.57	1.5	6.7	5.2	52.8	88.0	94.3	22.0
D464	1600	1.56	3.35	3.42	3.57	2.0	6.1	4.1	53.3	89.1	94.8	32.0
D4 74	1700	1.56	3.38	3.44	3.57	1.7	5.3	3.6	53.6	90.6	95.6	43.0
8 484	1800	1.59	3.41	3.46	3.57	1.4	4.5	3.1	53.4	91.9	%.1	92.0

SINTERING DATA ON MAGNESIA CONTAINING 1.0 mole & MONTICELLITE FIRED AT TEMPE ATURE FOR 4 HOURS.

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DEE	ETDING	PRESSED		· · · · · · · · · · · · · · · · · · ·	PR	OPEPI	SIES	AFTEP	FIPI	NG		
NO.	TEMP.	BULK	DEN	SITY g./cc	•	E	POFOSITY ;	75	VOLUME	DENSIFIC	CATION	GFATN
	°c.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	VCLUME	S [⊤] ZE µ
D344	1400	1.61	2.92	3.50	3.56	16.5	18 .0	1.5	44•9	67.2	31.9	11.0
D354	1500	1.66	3.27	3.32	3.56	1.5	8.1	6,6	49.2	84.8	92.2	23.5
D 364	1600	1.61	3.28	3.33	3.56	1.5	7.8	6.3	51.1	85.6	93.1	39.0
D374	1700	1.62	3.30	3.33	3.56	1.0	7.4	6.4	50.3	86.6	93.2	51.5
D384	1800	1.61	3.14	3.20	3.56	1.9	11.7	9.8	48.3	73.5	89.1	64.5

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SINTARING DATA ON MAGUNSIA CONTAINING 0.5 Hole % MERWINITE FIRED AT TEMPERATURE FOR 4 HOURS.

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		PRESSED			PR	OPERT	IES	AFTEP	FIFI	NG		
NO.	TEMP.	BULK	DEN:	SITY g./cc	•	P	OPOSITY 9	76	VOLUME	DENSIFIC	CATION	GFAIN
	°c.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	STZE µ
D644	1400	1.60	2.99	3.55	3.57	15.7	16.2	0.5	46•4	70.5	84.4	9.0
D654	1500	1.55	3.31	3.41	3.57	2.7	7.2	4.5	53.2	37.2	94.0	16.0
D664	1600	1.58	3.31	3.37	3.57	1.8	7.3	5 •5	52.3	86.9	93.7	32.0
D674	1700	1.58	3.31	3.37	3.57	1.8	7.3	5•5	52.3	86.9	93.7	47.5
D684	1900	1.57	3.25	3.29	3.57	1.2	9.0	7.8	51.7	84.0	92.3	60.5

SINTERING DATA ON MAGNESIA CONTAINING 1.0 mole % DICALCIUM SILICATE FIRED AT TEMPERATURE FOR & HOURS.

ਸ਼ਾਸ	ETDING	PRESSED			PF	ROPEPI	IES	AFTEP	FIPI	NG		
NO	TEMP	BULK	DEN	SITY g./co	2.	F	OPOSITY	%	VOLUME	DENSIFIC	CATION	GFATN
	°c.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	DENSITY VOLUME	
D744	1400	1.60	2.93	3.54	3.57	17.2	17.8	0.7	45•4	67.5	82.2	9.0
D754	1500	1.57	3.19	3.48	3.57	8.3	10.6	2.3	50.8	81.0	90.7	12.5
D764	1600	1.57	3.30	3.41	3.57	3.2	7,5	4.3	52.4	86.5	93.6	17.0
D 774	1700	1.58	3.39	3.43	3.57	1.1	5.0	3.9	53.4	91.0	95.9	32.0
D784	1800	1.57	3.33	3.36	3.57	0.9	6.7	5.8	52.8	88.0	94•4	61.0

SINTERING DATA ON LAGHESIA CONTAINING 1.0 mole % TRICALCIUM SILICATE FIRED AT TE PERATURE FOR 4 HOURS.

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DEE	FTRINC	PRESSED			PI	ROPEPI	TES	AFTEP	FIPI	NG		
NO.	TEMP.	BULK	DEN	SITY g./cc	:.	F	POPOSITY	%	VOLUME	DENSIFI(CATION	GFATN
	°c.	DENSITY g./cc.	Y BULK SOLID		TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S [†] ZE µ
D844	1400	1.61	3.09	3.52	3.56	12.2	13.2	1.0	47.9	S 7. 4	87.4	7.0
D354	1500	1.61	3.31	3.39	3.56	2.2.	7.0	4.8	51.4	73.7	93.7	10.5
DE64	1600	1.59	3.33	3.40	3.56	2.0	6 .5	4•5	52.2	94•5	94.5	18.5
D874	1700	1.53	3.38	3.42	3.56	1.2	5.1	3.9	53.2	95.8	95.8	23.0
D884	1800	1.59	3.38	3.41	3.56	0.9	5.1	4.2	52.9	95•7	95•7	35.0

TABLE SI

SINTAN A DATA ON AGALSIA CONTAINING 1.0 mole & CALOINA OXIDE DIRED AT THAN ATERS FOR 4 HOURS.

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סידים	FIRING	PRESSED			ΡF	OPERT	IÈS	AFTER	FIPI	NG		
NO.	TEMP.	BULK	DEN	SITY g./cc	•	F	OROSITY	%	VOLUME	DENSIFI	CATION	GFATN
	°c.	DENSITY g./cc.	BULK	APPARENT SOLID	TRUE	APPAPENT	TRUE	SEALED	CHANGE %	DENSITY	VOLUME	S [†] ZE µ
D944	1400	1.57	2.36	3.53	3.59	19.0	20.3	1.3	45.0	64.2	80.0	7.0
D 954	1500	1.57	3.75	3.47	3.57	6.1	7.2	3.1	51.º	34.1	92.1	10.5
D9 54	1600	1.55	3.37	3.43	3.57	1.3	6.1	4.3	53.6	37.6	94.9	19.0
D 774	1700	1.57	3.37	3.42	3.53	1.5	5.1	4.6	53.4	37.5	94.9	28.0
<u> 2784</u>	1300	1.53	3.33	3.42	3.57	1.2	5.3	4.6	53.2	90.0	95.1	32.0