PROPERTIES OF HEAT TREATED DIATOMITE

by

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We accept this thesis as conforming to the
required standard

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ABSTRACT

The density, strength and thermal conductivity of diatomite compacts were determined after heating the specimens in the temperature range between 200 and 1050 °C. The linear dimensional change of these specimens on heating was also measured. All properties changed during heating with the increase in firing temperatures and especially above 800 °C.

The reduction of density, strength and thermal conductivity of diatomite compacts on firing at up to 600 °C can be attributed to the mass loss due to decomposition of the constituents such as hydrated silica, carbonates, etc. Heating these compacts above 600 °C resulted in shrinkage with a concomitant increase in bulk density, strength and thermal conductivity. Attempts were made to evaluate the fundamental factors which may be contributing to this change of properties during heat treatment.

Analyses of data have been made using a sintering model, which assumes that after decomposition diatomite particles are composed of a large number of microspheres and that the change of properties (i.e., increase in density, strength and thermal conductivity) can be attributed to the growth of interparticle contact areas (similar to neck growth during sintering).

Equations for shrinkage, thermal conductivity and strength are all related to the bulk density and weight loss of the compacts, and are given by:
For shrinkage,

\[
\frac{\Delta L}{L_o} = \frac{1}{3} \left(1 - \frac{\rho_{Bo} W}{\rho_B W_o}\right)
\]

For thermal conductivity,

\[
K = N \alpha K_s \left[\left(\frac{\rho_B W_o}{\rho_{Bo} W}\right)^{2/3} - 1\right] + K_o
\]

For strength,

\[
S = C \left[\left(\frac{\rho_B W_o}{\rho_{Bo} W}\right)^{2/3} - 1\right] + S_o
\]

The validity of these equations has been tested with the experimental data of shrinkage, bulk density, weight loss, strength and thermal conductivity of pure diatomite compacts. The good agreement between the experimental results and the equations may be indicative that it is the increase in interparticle contact areas during the heat treatment which results in the increase in strength, bulk density and thermal conductivity.

The general applicability of the equations, developed in order to explain the change in properties of pure diatomite compacts, was further tested with experimental data obtained from a commercial brand of diatomite insulating bricks.
# TABLE OF CONTENTS

1.0 Introduction ......................................................... 1

1.1 Insulating Refractory Bricks ........................................ 1

1.2 Diatomite and Diatomite Insulating Bricks ......................... 2

1.3 Literature on the Fired Properties of Diatomites ............... 6

2.0 Objectives of the Research .......................................... 11

3.0 Experimental .......................................................... 12

3.1 Raw Materials .......................................................... 12

3.2 Sampling and Grinding ................................................ 12

3.3 Equipment .............................................................. 16

3.4 Specimen Preparation .................................................. 26

3.4.1 Shapes and Sizes of Specimens ................................... 26

3.4.2 Firing ................................................................. 27

3.5 Test Procedures ....................................................... 28

3.5.1 Shrinkage Measurements .......................................... 28

3.5.2 Density Measurements .............................................. 28

3.5.3 Thermal Conductivity Measurements ............................. 31

3.5.4 Strength Measurements ............................................. 31

4.0 Results and Discussion on Properties of Fired Diatomite ....... 33
4.1 Experimental Results on the Effect of Grinding and Compacting ........................................ 33

4.2 Experimental Results on Shrinkage and Density ................. 36
4.2.1 Shrinkage and Density Changes of Diatomite .............. 36
4.2.2 Mineralogical Changes of Diatomite ..................... 38

4.3 Discussion on Sintering of Diatomite ......................... 46
4.3.1 Sintering of Diatomite ................................... 46
4.3.2 Weight Changes of Diatomite ............................ 47
4.3.3 True Density Changes of Diatomite ..................... 48

4.4 Development of Shrinkage Equations .......................... 50
4.4.1 Development of Density Equations ....................... 61
4.4.2 Testing of shrinkage and Density Equations ............ 65

4.5 Results and Discussion on Thermal Conductivity .............. 65
4.5.1 Experimental Results of Thermal Conductivity .......... 69
4.5.2 Development of Thermal Conductivity Equations .......... 69
4.5.2.1 Correction for Mineral Transformation ............. 77
4.5.3 Testing of Thermal Conductivity Equations ............. 78
4.5.4 Porosity Effect on Thermal Conductivity ............... 84

4.6 Results and Discussion on Strength .......................... 94
4.6.1 Experimental Results of Strength ....................... 94
4.6.2 Development of Strength Equations ....................... 94
4.6.3 Testing of Strength Equations ........................... 102
4.6.3.1 Experimental Values of "C " ......................... 102
4.6.3.2 Evaluations of Results with Strength Equations .......... 104

5.0 Verification of Equations with Data of Commercial Diatomite Bricks ........................................ 107
5.1 Results and Discussion on Shrinkage and Density of Commercial Diatomite Bricks ............................................. 109
5.1.1 Experimental Results of Shrinkage and Density on Commercial Diatomite Bricks ............................................. 109
5.1.2 Testing of Shrinkage and Density Equations with Commercial Diatomite Bricks ............................................. 112

5.2 Results and Discussion on Thermal Conductivity of Commercial Diatomite Bricks ............................................. 112
5.2.1 Experimental Results of Thermal Conductivity on Commercial Diatomite Bricks ............................................. 112
5.2.2 Testing of Thermal Conductivity Equations with Commercial Diatomite Bricks ............................................. 112

5.3 Results and Discussion on Strength of Commercial Diatomite Bricks ......................................................... 117
5.3.1 Experimental Results of Strength on Commercial Diatomite Bricks ......................................................... 117
5.3.2 Testing of Strength Equations with Commercial Diatomite Bricks ......................................................... 117

6.0 Summary and Conclusions ......................................................... 121

Appendix: The Results of the Experiments Carried out by E.L. Calacal ......................................................... 124

References ......................................................... 132
# LIST OF TABLES

I. Typical Properties of Insulating Refractory Bricks .................. 3

II. Chemical and Physical Properties of Quesnel Diatomites ........... 15

III. True Density Changes of Diatomites on Firing ..................... 42

IV. X-ray Diffractometer Analyses of Diatomites ....................... 43

V. d-Spacings of Tridymite and Clay Minerals ......................... 44

VI. The Calculated Values of $\frac{a}{R}$ (from the shrinkage data) .... 67

VII. Geometric Parameters for Various Packings ......................... 79

VIII. The Calculated Values of "N" .................................. 81

IX. The Calculated Values of "k_s" .................................. 83

X. Equations for Thermal Conductivity of a Porous Body ............... 89

XI. Geometric parameters (β) of various packing (Kakar)$^{(25)}$ ....... 99

XII. The Calculated Values of "C_i" .................................. 103

XIII. Properties of Commercial Diatomite Bricks ....................... 108
LIST OF FIGURES

1. Quesnel diatomite: fossilized diatoms ........................................ 5
2. Quesnel Diatomite Pit .............................................................. 13
3. Lumps and saw-cut specimens of Quesnel diatomite .................... 14
4. Laboratory extruder used for extrusion ..................................... 17
5. Tinius Olsen Compressive Testing Machine ................................. 18
6. Ferro Enamel Electric Furnace ................................................. 20
7. Thermal conductivity apparatus ............................................... 21
8. Set-up of the thermal conductivity apparatus ............................. 21
9. Details of the brass plate and disk for the thermal conductivity apparatus ........................................... 23
10. Methods and positions for the dimensional measurements of bricks .................................................................. 29
11. The effect of compaction on the shrinkage behaviour .................. 34
12. The effect of compaction on the bulk density of fired specimens ................................................................. 35
13. The experimental shrinkage data of pure diatomite specimens .... 37
14. The experimental weight loss data of pure diatomite specimens .. 39
15. The experimental bulk density data of pure diatomite specimens ........................................ 40
16. Pores in diatomite compact ................................................................. 49
17. The proposed model of the diatomite shell wall .............................. 51
18. The SEM photo of diatomite shell wall (from Calacal) ............... 51
19. Diatom showing minute cellular structure .............................................. 53
20. Shrinkage of diatom shell on firing, maintaining the original geometric shape ......................................................... 55
21. A schematic illustration of the weight loss of diatomite .......... 57
22. The geometry of Frenkel's Model for the initial stage of sintering by viscous flow ................................................................. 59
23. The geometry of unit cell incorporating of a microsphere ......... 60
24. The experimental shrinkage data of pure diatomite specimens, normalized to the 600 °C firing ......................................................... 66
25. The theoretical shrinkage plot as a function of relative density and weight loss. Experimental shrinkage data are also included ................................................................. 68
26. The experimental thermal Conductivity Data of Pure Diatomite Specimens ................................................................. 70
27. The geometry of two spheres in contact and the equivalent electrical network (after Ramanan) ................................. 72
28. Spheres in a two dimensional cubic array and an equivalent electrical network (after Ramanan) .............................. 72

29. Heat flow through a sphere in a simple cubic model .............. 73

30. The experimental data and the theoretical (simple cubic packing) thermal conductivity plot ........................................ 85

31. The experimental data and the theoretical (orthorhombic packing) thermal conductivity plot ........................................ 86

32. The experimental data and the theoretical (b.c.c. packing) thermal conductivity plot ................................................. 87

33. The effect of porosity on the thermal resistivity of graphite (after Wagner)\(^{(31)}\) ......................................................... 90

34. Dimensionless thermal conductivity vs. fractional porosity for polycrystalline graphite (after Rhee)\(^{(32)}\) .......................... 90

35. The experimental data of thermal conductivity vs porosity ...... 91

36. The experimental relationship between relative density \((\Delta \rho/\rho_0)\) change and thermal conductivity \((\Delta K/K_0)\) change .......... 93

37. The experimental compressive strength data of pure diatomite specimens ................................................................. 95

38. A model for the breakage of bricks during the compressive strength test ................................................................. 96

39. The experimental data and the predicted strength .................. 105
40. The experimental shrinkage data of commercial diatomite bricks . 110

41. The experimental bulk density data of commercial diatomite bricks ........................................ 111

42. Evaluation of the shrinkage equation using the experimental data of commercial diatomite bricks ........................................ 113

43. The experimental thermal conductivity data of commercial diatomite bricks ........................................ 114

44. Evaluation of the thermal conductivity equation using the experimental data of commercial diatomite bricks ........................................ 116

45. The experimental strength data of commercial diatomite bricks .. 118

46. Evaluation of the strength equation by using the experimental data of commercial diatomite bricks ........................................ 120
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1.0 INTRODUCTION

The primary function of high temperature furnaces, built of refractory materials, is to confine and utilize heat energy. Furnaces, however, lose a considerable proportion of the supplied heat energy through the refractory wall, which then dissipates into the surroundings. Such a heat loss can be minimized by a layer of insulating refractory bricks which provides a desired temperature drop across a furnace wall.

1.1 Insulating Refractory Bricks

Insulating refractory bricks derive their low thermal conductivity from the air enclosed in their pores\(^{(1)}\). The insulating effect is principally due to the presence of a series of air spaces between an alternate series of solid boundaries. Accordingly, the more air present, and the less solid, the lower the thermal conductivity.

Air spaces in the bricks are produced by incorporating one or more different manufacturing techniques. The techniques are (1) using porous raw materials such as fused alumina bubbles, expanded vermiculite, diatomite, light weight aggregates made from fireclay, etc., (2) using combustible additives within bricks and subsequently burning them off during the final firing stage and (3) foaming clay slips and stabilizing them during the moulding process. In most cases the amount of pores that can be generated is limited, as the introduction of a large volume fraction of pores results in a brick of poor mechanical strength.
In spite of the difficulty of making these bricks there is a wide range of insulating refractory bricks currently available in the market. Typical porosity values of insulating refractory bricks commonly used in industries are shown in Table I\(^{(2)}\). Diatomite insulating bricks occupy a significant segment of insulating brick usage, because they are inexpensive and have relatively high strength with low thermal conductivity value.

1.2 **Diatomite and Diatomite Insulating Bricks**

Diatomite is a siliceous rock of sedimentary origin\(^{(3)}\). Diatom skeletons, the fossilized remains of microscopic single-celled aquatic plants, are the main component of diatomite. The living diatom organism has the capacity to extract silica from its aquatic habitat and to form a shell structure which consists mainly of a biologically precipitated amorphous silica. When the organism dies, it sinks as a sediment. Under favorable conditions residues accumulate and upon subsequent compaction these become potential diatomite deposits.

The term diatomite is used for the mineral rock deposit whose main constituent is diatomaceous silica, the substance of silica shell itself. The terms diatomaceous earth and kieselguhr are synonymous with diatomite. Other names such as infusorial earth, tripoli and tripolite are obsolete today.
<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Service limit, °C</td>
<td>900</td>
<td>1300</td>
<td>1500</td>
<td>1300</td>
<td>1800</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>71</td>
<td>71</td>
<td>72</td>
<td>81</td>
<td>63</td>
</tr>
<tr>
<td>Crushing Strength, kg/cm</td>
<td>34</td>
<td>28</td>
<td>16</td>
<td>10</td>
<td>65</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kcal/mh C</td>
<td>0.14</td>
<td>0.22</td>
<td>0.22</td>
<td>0.14</td>
<td>0.61</td>
</tr>
<tr>
<td>(W/m.K)</td>
<td>(0.16)</td>
<td>(0.26)</td>
<td>(0.26)</td>
<td>(0.16)</td>
<td>(0.71)</td>
</tr>
</tbody>
</table>
Mineralogically diatomite, a form of hydrated silica resembling opaline, has a unique physical structure which contains inherently a large volume fraction of pores. No other natural or synthetically produced material has been found to have the same physical characteristics (Figure 1).

Diatomite, being a mineral rock deposit, always contains such impurities as organic matter, oxides of aluminum, iron and titanium along with compounds of sodium, potassium and calcium. Because of the chemistry of diatomite minerals containing mainly SiO₂, it is highly suitable for the manufacture of low temperature insulating refractories.

Diatomite insulating bricks are manufactured from mixtures of raw diatomite and sawdust, and sometimes some plastic clays are also added into the mixtures. The porosity of diatomite insulating brick, which is due to the inherent porosity of diatomite itself, can be further adjusted by changing the amount of sawdust and fireclay in the mixture. The moulding conditions, such as the moisture content of the brick and nature of the extruding vacuum also contribute to the porosity of the final products.

In recent years the industrial use of diatomite insulating brick has increased significantly due both to today's high energy cost and to the use of high operational temperatures to improve the productivity of industrial furnaces. Sales in Canada and the western United States are estimated at 8 million bricks/annum, with a market value exceeding
Figure 1  Quesnel Diatomite; fossilized diatoms. (800X)
$5 million. In the North American Continent there are only two major suppliers of diatomite insulating bricks, Skamol Skarrehage Molervaerk A/S of Denmark and Clayburn Refractories Ltd., in Abbotsford, the latter utilizing local diatomite from Quesnel, B.C.

To be successful in sales of diatomite insulating refractories, one of the most important elements is to have the capability of manufacturing these products with high strength and low thermal conductivity value. These requirements appear to be contradictory, as high porosity, necessary to achieve a low thermal conductivity, results in poor strength of the brick. It is not surprising that these requirements have been difficult to achieve. It is, however, hoped that with a fundamental understanding of the sintering behaviour of powder compacts, it might yet be possible to develop the desired high strength in a brick and still maintain the thermal conductivity value at a low level.

1.3 Literatures on the Fired Properties of Diatomite

One of the most important properties of diatomite bricks is the thermal conductivity, which largely depends on the amount of air space within the brick. Similarly, strength - the other important property also depends on the extent of porosity contained within the bricks. The more the porosity, the lower the thermal conductivity and the strength. It is generally considered that thermal conductivity and strength are proportionally related to the density of diatomite compacts. Barrett(4), however, noted that diatomite bricks showed remarkable deviations from a linear relationship between thermal conductivity and density owing to the difference in structure and pore size in diatomite bricks.
A literature survey reveals that in 1941 Oliver and Rigby studied the effect of increasing heat treatment on the properties of a diatomaceous insulating brick but there has been no recent publication on this subject and no published data on the change of physical properties such as strength, conductivity etc. that occurs in diatomite compacts on firing. There are only a few reported studies on the mineralogical changes and the pore size changes in diatomite compacts on firing. One of these studies, which is perhaps the most extensive, is that of Calacal for his doctoral dissertation in the University of Washington, Seattle, U.S.A. He considered sintering as a thermal process which resulted in the reduction of the surface area of fine diatomite powder. He analyzed the sintering characteristics of diatomite compacts by measuring the surface area of the compacts after firing them at elevated temperatures. His experiments involved the firing of diatomite compacts (12.65 mm diameter x 0.2 to 0.3 mm thick) under isothermal conditions at temperatures between 700 and 1300 °C, and then measuring the surface area, the midpore diameter and the total pore volume of specimens after firing. Mercury porosimetry was used to obtain data of pore size - as small as 120 Å. Nitrogen absorption was used to back up surface area data measured by Hg porosimetry. Calacal did not attempt to utilize existing sintering models because of the specific geometric conditions normally imposed on these models. Particularly the data obtained in sintering diatomite can not fulfil the basic assumptions used in deriving sintering equations. These basic assumptions are:

(1) The conservation of the mass of solid particles during sintering, and
(2) the conservation of the volume of solid particles during sintering.
Consequently, he developed a sintering equation of diatomite compacts by using the volumetric changes of cylindrical pores and relating them to the changes of the surface area of diatomite compacts as follows: The total surface area of a number of cylindrical pore is

\[ A = 2\pi r l \]

where

- \( A \) = total surface area
- \( P \) = number of pores
- \( r \) = average pore radius
- \( l \) = pore length

The total volume (\( V \)) of the cylindrical pore is,

\[ V = \pi r^2 l \]

The total pore volume, the pore radius and the total surface area can be related by the following equation.

\[ \frac{A}{V} = \frac{2\pi rl}{\pi r^2 l} = \frac{2}{r} \]  

(1.1)

The natural logarithm of Eq. 1.1 is,

\[ \ln A = \ln 2 + \ln V - \ln r \]
Differentiation of this equation with respect to time gives

\[ \frac{1}{A} \frac{dA}{dt} = \frac{1}{V} \frac{dV}{dt} - \frac{1}{r} \frac{dr}{dt} \] (1.2)

The equation predicts the change in surface area with change in pore radius and pore volume. After introducing the capillary force acting in the pore and then on integration, the final form of Eq. 1.2 (when there is no change in the number of pores during sintering) can be expressed by

\[ r_o - r = \frac{1}{2} \frac{\gamma}{\eta} t \] (1.3)

And when pore coalescence occurs, the following equation is applicable:

\[ \frac{1}{m-1} \left( \frac{A_o}{A} \right)^{m-1} = \frac{1}{m-1} + K't \] (1.4)

where

\[ K' = K \frac{A_o^{m-1}}{A} = \frac{1}{2} \frac{\gamma}{\eta} \frac{1}{r_o} \]

\[ m = \text{the exponent in the Eq. } \frac{dA}{dt} = -KA^m, \text{ which was proposed by Kuczynski for the ripening of pores} \]

\[ \gamma = \text{surface tension} \]
\[ \eta = \text{viscosity} \]

Calacal did not use these equations for analysis of the sintering characteristics of diatomite but he applied these equations when evaluating the high temperature viscosity of diatomite.
Calacal concluded that:

(1) Ignition losses of diatomites resulted in pore creation due to gas escape during the initial stages of sintering.

(2) The compaction pressure affected the midpore diameter and total pore volume of sintered diatomite but did not influence the surface area measured by a Hg-porosimeter. Whether the powder was sintered before compaction or compacted before sintering, had no effect on the surface area of pores, which ranged in size from 120 Å (0.012 μm) to $10^6$ Å (100 μm) irrespectively.

(3) Surface area measurements by Hg-porosimetry alone was found not to be a powerful tool in sintering studies, unless it was used in conjunction with some other method capable of measuring the surface area of very fine pores, such as nitrogen absorption.

(4) The results obtained by Hg-porosimetry showed that there must be four stages in the sintering of diatomite. These stages are:

First stage: Surface area, midpore diameter and total pore volume increase.

Second stage: Surface area increase and midpore diameter and total pore volume decrease.

Third stage: Surface area decrease, midpore diameter increase and total pore volume decrease.

Fourth stage: Melting.

Some of Calacal's experimental data are shown in the Appendix of this thesis.
2.0 OBJECTIVES OF THE RESEARCH

The project was aimed at investigating the physical property changes of diatomite compacts that occur on heating to elevated temperatures and correlating these changes to the microstructural changes that also occur during sintering. This was done in order to understand the origin of the strength and the thermal conductivity in diatomite insulating bricks.

The procedures adopted for this study were:

(1) Measurement of shrinkage along with weight and density changes of compacts on heating. This was to allow analysis of the sintering characteristics of diatomite.
(2) True density measurement and X-ray diffraction analysis to identify mineralogical changes in the diatomite.
(3) Determination of cold crushing strength and thermal conductivity values of diatomite compacts and then the correlation of these properties with sintering.

These measurements were carried out on specimens fired at predetermined temperatures between 200 and 1050 °C. The range of temperature that is commonly used in manufacturing diatomite insulating bricks is 800 to 1000 °C.
3.0 **EXPERIMENTAL**

3.1 **Raw Materials**

The source of diatomite used in this series of experiments is a Quesnel deposit owned by Clayburn Refractories Co., Abbotsford, B.C. The Quesnel Diatomite pit is on a hill lying on the west bank of the Fraser River seventeen miles downstream from the city of Quesnel, B.C. The pit is approximately 20 feet deep and 150 feet wide. The colour of diatomite changes locally from white to light grey and to brown. Preliminary investigations indicated that the white material was the purest, and therefore, this material was used for all experiments. Photographs of the deposit site and the diatomite lumps are shown in Figures 2 and 3. The chemical analyses of three types of diatomite found in the deposit are shown in Table 2. Data of X-ray diffraction analyses of the white diatomite are also included in Table II.

3.2 **Sampling and Grinding**

Lumps of white diatomite were picked up from the Quesnel quarry site and brought back to the Abbotsford plant. After being dried overnight in a convection type laboratory dryer at 100 °C, the lumps were ground using a small laboratory jaw crusher, then hand-screened through an eight-mesh Tyler Screen. The minus eight-mesh diatomite powder was stored in plastic bags for future use. Small 2 1/2 x 1 1/2 x 3/4 - in. (63 x 38 x 19 - mm) specimens were also saw-cut from dry lumps to investigate the effects of grinding and compacting the diatomite, which was necessary for preparation of test specimens.
Figure 2  Quesnel Diatomite Pit.
Figure 3  Lumps and saw-cut specimens of Quesnel Diatomite.
## TABLE II
Chemical and Physical Properties of Quesnel Diatomite

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>White</td>
<td>Light Grey</td>
<td>Brownish Grey</td>
</tr>
<tr>
<td>Chemical Analysis (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica $\text{SiO}_2$</td>
<td>83.67</td>
<td>75.32</td>
<td>74.22</td>
</tr>
<tr>
<td>Alumina $\text{Al}_2\text{O}_3$</td>
<td>7.12</td>
<td>9.50</td>
<td>9.90</td>
</tr>
<tr>
<td>Iron $\text{Fe}_2\text{O}_3$</td>
<td>1.41</td>
<td>3.81</td>
<td>1.45</td>
</tr>
<tr>
<td>Titania $\text{TiO}_2$</td>
<td>0.30</td>
<td>0.46</td>
<td>0.37</td>
</tr>
<tr>
<td>Calcium CaO</td>
<td>0.50</td>
<td>0.85</td>
<td>3.55</td>
</tr>
<tr>
<td>Magnesium MgO</td>
<td>0.15</td>
<td>1.46</td>
<td>1.40</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>4.97</td>
<td>6.08</td>
<td>7.44</td>
</tr>
<tr>
<td>Total</td>
<td>98.16</td>
<td>97.48</td>
<td>98.33</td>
</tr>
</tbody>
</table>

Loose Bulk Density $\text{lb/ft}^3$ | 17.9   | 22.6   | 25.2   |
$\text{(g/cm}^3)$ | (0.287) | (0.362) | (0.404) |

X-ray Mineral Analysis

| Major Phase | Amorphous | - | - |
| Minor Phase | Quartz | - | - |
| Trace | Possibly clay minerals having $d = 9.6\text{Å}$ | - | - |

Note: Loose bulk density was measured at the Clayburn plant by the standard quality control procedure which uses a measuring cylinder to determine the volume of dry diatomite powder.
3.3 Equipment

The preparation of test specimens and all the physical tests were carried out in the R & D and Quality Control Laboratory of Clayburn Refractories Co., Abbotsford. The X-ray determination of phases and S.E.M. studies were made in the Metallurgical Engineering Department at the University of British Columbia. The equipment used for these experiments are listed below. Photographs of some of the equipment are included in this thesis as these are not available at U.B.C.

3.3.1 Dryer

The dryer used was a model LEB 2-20 made by Despatch Ind. Ltd., which has a 23 cubic foot capacity (0.65 m$^3$) and a 204 °C max. temperature limit.

3.3.2 Laboratory Extruder

A Vac-Aire Experimental Auger Machine Model 492H made by International Clay Machinery Co. was used for fabricating the specimens (Figure 4).

3.3.3 Tinius Olsen Testing Machine

A Tinius Olsen 300,000 lb. Super "L" Compressive Testing Machine was used for compaction of the specimens and for testing the strength of
Figure 4  Laboratory extruder used for extrusion.
Figure 5  Tinius Olsen Compressive Testing Machine.
3.3.4 Kiln

A Ferro-Enamels Electric Furnace Model #2 with Automatic Controller was used for firing specimens (Figure 6). The kiln has 30 cm W x 30 cm D x 33 cm H inside capacity with 1260 °C max. working temperature and uses a type "R" platinum-rhodium thermocouple for temperature detection and control. The temperature variation during holding periods was ±4 °C.

3.3.5 Thermal Conductivity Apparatus

The apparatus is essentially a home-built model based on the device designed by Blakeley and Cobb [7] for low temperature thermal conductivity measurements. The apparatus uses the difference in temperature (1) of the air, (2) of a dull black surface on the top of the test brick which is radiating and convecting freely to its surroundings and (3) of the hot face. These give a measure of heat flowing through the test brick. A schematic diagram of the apparatus is shown in Figure 7 and the overall view in Figure 8. A brass block 9 x 4.5 x 0.25 - in. (229 x 114 x 6-mm) with a 2-in. (50.8 mm) hole at the center acts as the guard ring of the calorimeter. A brass disc 1/4-in. (6.3 mm) thick x 1 15/16-in. (49.2 mm) diameter is held in this 2-in. (50.8 mm) hole by insulating fibres rammed into the 1/32-in. (0.8 mm) gap. A 3/32-in. (2.4 mm) hole extends horizontally along the minor axis of the block to the center of the brass disc. This hole receives a copper-constantan thermocouple so that the junction is at the center of the disc (Figure 9). The surface of the block,
Figure 6  Ferro Enamels Electric Furnace
Figure 7  Low temperature thermal conductivity apparatus.

(A) thermocouples, (B) test brick, (C) brass plate, (D) diatomite brick, (E) diatomite powder, (F) heating element

Figure 8  Set-up of the thermal conductivity apparatus.
including the center disc, is painted with a heat resistant flat black paint ("Tremclad" High-heat Enamel-650 °C manufactured by Tremco Ltd. Toronto). The center disc acts as a calorimeter, whereas the rest of the block acts as a guard ring as mentioned before. The heater for the hot face of the test brick was made by winding nichrome ribbon in the grooves of a firebrick tile 9 x 4 1/2 x 3/4-in. (229 x 114 x 10-mm) which is covered by a 9 x 4 1/2 x 3/8-in. (229 x 114 x 9-mm) firebrick lid. A platinum-rhodium thermocouple is placed on the top of the heater to record the hot face temperature of the test brick.

The apparatus was placed in a 20 L x 16 W x 7 H-in. (508 L x 206 W x 178 H-mm) insulating box lined with diatomite bricks. The gap between the box and test brick was filled with calcined diatomite powder. The temperatures of the hot face and the cold face of the test brick were detected by the thermocouple as mentioned before and it was assumed that the heat passing through the test brick escaped from the blackened surface of the plate and that, at least in the central portion of the test brick, the heat flow is linear. Since the thickness of the brick and the temperature drop across it are known, the conductivity can then be readily calculated from the heat flow equation.

The apparatus was placed on a bench in a closed room to maintain a still atmosphere. The electric current for the heating element is regulated by a controller made by Robert L. Stone Co., Texas, U.S.A. The air temperature was measured by a mercury thermometer placed two feet away from the apparatus.
Figure 9  Details of the brass plate and disk for the thermal conductivity apparatus.
The current to the heater was switched on and the readings of air temperature, hot face temperature and cold face temperature were taken after thermal equilibrium was attained. Blakeley and Cobb stated that it took 127 minutes for a 6.20 cm thick brick to attain thermal equilibrium. In the present experiments the readings were taken 24 hrs after the electric current was switched on. The temperature gradient across the sample was calculated from the readings of the hot and cold face temperatures and the brick thickness. The heat flow through the brick was derived from the difference in temperature between the central disc of the block surface and the air as follows:

The heat loss (H) from the surface is the sum of the losses due to convection ($H_c$) and to radiation ($H_r$). Taking the values of Griffith and Davis (8) for the heat loss from a horizontal plane surface facing upward,

$$H = H_c + H_r$$

$$H_c = 2.19 \left(T_c - T_a\right)^{1.25}$$

$$H_r = 4.82 \left[\left(\frac{T_c + 273}{100}\right)^{4} - \left(\frac{T_a + 273}{100}\right)^{4}\right]$$

where $T_c$ and $T_a$ are the cold face temperature and the air temperature in degree centigrade, respectively.
Heat transfer equation is,

\[ \dot{q} = -kA \frac{\Delta T}{\Delta x} = -kA \frac{T_h - T_c}{x_1 - x_2} = kA \frac{T_h - T_c}{x_2 - x_1} \]

where,

- \( \dot{q} \) = heat flow (= heat loss, H) (Cal/cm\(^2\).S)
- \( A \) = area of heat flow (cm\(^2\))
- \( K \) = thermal conductivity (cal/cm.S°C)
- \( T_h \) = hot face temperature (°C)
- \( T_c \) = cold face temperature (°C)
- \( x_2-x_1 \) = thickness of specimen (cm)

\( \frac{T_h - T_c}{x_2 - x_1} \) = \( T \) grad i.e. temperature gradient in specimen

\[ K = \frac{\dot{q}}{T \ \text{grad A}} = \frac{H}{T \ \text{grad A}} \]

Using "A" for a unit area,

Thermal conductivity \( (K) = \frac{\text{Heat loss (H)}}{\text{Temperature gradient (T grad)}} \)

\[ K = \frac{2.19(T_h - T_a)^{1.25} + 4.82\left[ \frac{T_c + 273}{100} - \frac{T_a + 273}{100} \right]}{\frac{T_h - T_c}{x_2 - x_1}} \]
Accordingly, thermal conductivity can be calculated from the measurements of (1) the thickness of specimen, \( X_2 - X_1 \), (2) hot face temperature, \( T_h \), (3) cold face temperature, \( T_c \), and (4) ambient temperature, \( T_a \).

3.3.6 X-ray Diffraction and Scanning Electron Microscope

X-ray diffraction patterns of raw diatomite and diatomites after firing were obtained using a Norelco X-ray diffractometer with a Cu target and Ni filter at 40 KV - 15 mA and a speed of 1° 20/min. For microphotographs an ETEC-Autoscan scanning electron microscope was used.

3.4 Specimen Preparations

3.4.1 Shapes and Sizes of Specimens

The minus eight-mesh dry diatomite was thoroughly mixed with 50 weight % (wet base) of water, then extruded through a Vac-Aire Auger Machine. Due to a lack of lubrication between diatomite particles, the extrusion was difficult. Although the mix appeared to be too dry to be extruded, the product from the die mouth was excessively wet and soft, but despite these difficulties complete extrusion was achieved. The specimens had many extrusion cracks and the corners of the specimens were rough. It was, however, the original plan to fabricate specimens by re-pressing the extruded bricks because the laboratory extruder was too small to make specimens large enough for the experiment. The extruded bricks were crushed by hand to approximately ~ 5 mm size then stored in plastic bags to keep the moisture in.
The specimen sizes that were fabricated by re-pressing were 9 × 4 1/2 × 2 1/2-in. (229 × 114 × 63-mm) full size bricks to determine thermal conductivity and 7.5 × 1.2 × 1.0-in. (190 × 30 × 25-mm) small size bricks to determine shrinkage, density and strength.

A steel box was set on the Tinius Olsen Compressive Testing Machine, the box was then filled with extruded material and 300 p.s.i. (21.1 kg/cm²) uniaxial pressure was applied to the 9 × 4 1/2-in. (229 × 114-mm) top face. The steel box was then turned over and 150 p.s.i. (10.5 kg/cm²) uniaxial pressure was applied to the bottom face of 9 × 4 1/2-in. (229 × 114-mm). The bricks, after being removed from the steel box, appeared to be uniformly pressed. A large number of full size and small size bricks were prepared by this method. The green bulk densities of bricks were 80.8 ± 0.2 p.c.f. (1.294 ± 0.003 g/cm³). The bricks were air-dried at room temperature.

3.4.2 Firing

After being air-dried the bricks were placed in the dryer at 100 °C. Several full size and small size bricks were fired in the electric furnace at each pre-determined temperature. Eleven different firing temperatures were selected between 200 and 1050 °C.

The temperature was raised at a rate of 5 °C/min. up to the designated temperature and held at the temperature for 24 hours. After the holding period the kiln was switched off and allowed to cool down to room temperature in 18 hours.
Some of the specimens cut from the dry lumps obtained directly from the quarry (see page 12), were also fired along with the laboratory-prepared specimens. This was done to see the effect of grinding and compacting the diatomite on their firing behaviors and other properties.

3.5 Test Procedures

3.5.1 Shrinkage Measurements

The dimensions of the bricks were measured with a micrometer to an accuracy of ± 0.001 in. (0.0025 cm.). To obtain reasonable data on the dimensions, the length of the brick was measured at the four corners and at the center along the longitudinal axis and the average of the five measurements was used as the length of the brick (Figure 10). The other dimensions - width and thickness were measured by the same method. The dimensions of the brick were measured both before and after firing. The linear shrinkage at the firing temperature was calculated by,

\[
\text{Shrinkage} \left( \frac{\Delta L}{L_0} \right) = \frac{\text{original length} \ (L_0) - \text{fired length} \ (L)}{\text{original length} \ (L_0)}
\]

3.5.2 Density Measurement

A) Bulk Densities

Bulk density was calculated using the formula below.
Figure 10  Methods and positions for the dimensional measurements of bricks.
Bulk density \( (\rho_B) \) = \( \frac{\text{weight of brick}}{\text{volume of brick}} \)

\[
= \frac{\text{weight of brick}}{\text{length x width x thickness of brick}}
\]

The measurement of the weight of the brick was difficult since the diatomite brick quickly absorbed moisture from the environment. Initially the bricks were weighed and approximate values were obtained. The bricks were then dried in a dryer and were placed in a desiccator overnight to cool. The digital weighing balance was set at the predetermined approximate weight, and the brick was re-weighed within 15 seconds of being taken out from the desiccator.

B) True Densities

The true density was measured by the Pycnometric method. The procedures followed the method of J.I.S. R2616\(^9\) (Japan Industrial Standard), since no pycnometer bottle described in ASTM C135-66\(^10\) was available. The measurements were repeated and checked to within 0.03 g/cc.

C) Relative Densities

The relative density \( (\rho) \) was calculated from the ratio of the bulk density \( (\rho_B) \) and the true density \( (\rho_T) \).
3.5.3 Thermal Conductivity Measurements

Fullsize bricks of 9 x 4 1/2 x 2 1/2-in. (229 x 114 x 63-mm.) were used for the measurement of the thermal conductivity. After firing at various temperatures, the densities of the full size bricks were measured and confirmed that they matched the densities of the small size specimens fired at the same temperature. The faces of the brick, 9 x 4 1/2-in. (229 x 114-mm) were then ground to form smooth parallel planes and to a thickness of 2 1/2 inches (63-mm.) using a silicon-carbide brick grinder. After drying overnight in a dryer, the brick was placed in the thermal conductivity apparatus, and the heater was switched on. The brick was left twenty-four hours to reach thermal equilibrium after which the temperature readings were taken. To determine the thermal conductivity at a higher temperature, the current to the heater was slightly increased and again the brick was equilibrated for another twenty-four hours before a further conductivity determination was made. The thermal conductivity at 300 °C mean temperature, i.e. approximately 500 °C hot face temperature and 100 °C cold face temperature, was obtained by the interpolation of the readings taken slightly below 300 °C mean temperature and slightly above 300 °C mean temperature.

3.5.4 Strength Measurements

The dimensions of the specimens for the compressive strength test were 1.5 x 1.2 x 1.0-in. (38.1 x 30.5 x 25.4-mm) and these specimens were cut from 7.5 x 1.2 x 1.0-in. (190.5 x 30.5 x 25.4-mm) small size specimens.
A loading rate of 1000 lbs/min. (454 kg/min.) was applied to the 1.2 x 1.0-in. (30.5 x 25.4-mm) faces by the Tinius Olsen Compressive Testing Machine. The average of several compressive strength tests was used as the value of the strength, which varied ± 8% (for 600 °C specimens) and ± 14% (for 1050 °C specimens) from the average value.
4.0 RESULTS AND DISCUSSION ON THE PROPERTIES OF FIRED DIATOMITE

4.1 Experimental Results on the Effect of Grinding and Compacting

The shrinkage and the bulk density of diatomites versus the firing temperatures are plotted in Figures 11 and 12.

The starting density (i.e. dry density) of the specimens obtained from the natural lumps was 35.58 ± 0.17 p.c.f. (0.570 ± 0.003 g/cc). The starting density of the specimens which were prepared by grinding and compacting was 41.71 ± 0.25 p.c.f. (0.668 ± 0.004 g/cc).

From the results shown in Figure 11, it is apparent that the shrinkage behavior was not affected by the laboratory practice of grinding and compacting. The laboratory compaction only increased the starting density but did not affect the overall densification behavior of the compacts during firing. This conclusion agrees with Calacal's findings that (1) compaction pressures normally used in industries did not have significant effect on the sintering behavior of diatomite, (2) mechanical pressure alone could not enhance mass transport to fill pores within diatomites and consequently, could not cause loss of surface area and (3) the mechanical compaction, therefore, only allowed the particles to approach one another, resulting in the lowering of the total pore volume and the midpore diameter, but never really decreasing the number of pores.
Figure 11 The effect of compaction on the shrinkage behaviour.
Figure 12 The effect of compaction on the bulk density of the fired specimens.
which is an inherent property of the diatom itself. Whittemore, Ayala and Castro\(^{(11)}\) studied the effect of compaction on sintering of two commercial Brazilian diatomites. Their results showed that the surface area of the fired specimens was not affected by compaction pressure applied during fabrication, and that compaction pressure alone could not change the pore population. Therefore, it does not really matter whether the specimens are prepared by compacting the powder or not. As long as the specimens are sintered at the same temperature, the overall density change remains the same.

Following these observations it was decided to carry out further experiments on laboratory compacted specimens which were of suitable size and uniformity.

4.2 Experimental Results on Shrinkage and Density

4.2.1 Shrinkage and Density Changes of Diatomite

Figure 13 shows the shrinkage of the diatomite specimens plotted against their firing temperatures. The linear change was calculated by \(\Delta L/L_0\), where \(\Delta L\) is the change in length during firing and \(L_0\) is the original length.
Figure 13  The experimental shrinkage data of pure diatomite specimens.
Figure 14 shows the weight changes of the same specimens plotted against the firing temperatures. The weight change was calculated by $\Delta W/W_0$, where $\Delta W$ is the change in weight of the specimen during firing and $W_0$ is original dry weight.

The bulk densities, calculated from the linear dimensions and the weights, are plotted against the firing temperatures in Figure 15. The calculation was done by,

$$\text{Fired bulk density} = \frac{\text{weight of specimen (after firing)}}{\text{volume of specimen (after firing)}}$$

### 4.2.2 Mineralogical Changes of Diatomite on Firing

In order to determine the mineral compositions of the fired diatomite specimens, true density measurements (by the pycnometric method) and X-ray diffraction analyses were carried out. The samples were prepared from the same batch of saw-cut specimens 2 1/2 x 1 1/2 x 3/4-in. (63 x 38 x 19-mm) in size as described in Section 3.2.

The published data of true densities for silica minerals are\(^{(12,13,14)}\) quartz = 2.64 g/cc, cristobalite = 2.33 g/cc, Tridymite = 2.27 g/cc, Opal = 1.9 ~ 2.3 g/cc and raw diatomite = 1.9 ~ 2.3 g/cc. True density of raw diatomite varies from one deposit to another mainly due to the presence of impurities.
Figure 14  The experimental weight loss data of pure diatomite specimens.
Figure 15  The experimental bulk density data of pure diatomite specimens.
Table III shows the experimental results of the true density measurements. It appears that the raw diatomite from Quesnel has the true density of ~ 2.15 g/cc but this value changes on firing at and above 950 °C. The decrease in the true density value between 800 and 950 °C may be due to the decomposition of carbonates and other reactions.

To confirm that the true density change of the Quesnel diatomite on firing at or above 950 °C is due to the crystallization of amorphous silica, X-ray diffraction analyses were conducted on the specimens dried at 100 °C and fired at 850 and 1000 °C.

Tables IV and V show the X-ray diffraction peaks of the specimens and the d-spacings of some reference minerals.

For the diatomite specimen dried at 100 °C, the peak at d = 3.35 Å indicates the presence of α-quartz. A very weak peak at d = 9.6 Å may also suggest the presence of some type of clay minerals, some of which have peaks at ~ 10 Å, e.g. dehydrated montmorillonite and hydrated halloysite. The peaks at d = 4.26 Å, α-quartz (100) and d = 1.82 Å, α-quartz (112) are very weak but recognizable. Other weaker peaks of α-quartz are not clearly discernable. There are also very weak almost unrecognizable broad peaks at d = 4.05 Å and 3.13 Å which correspond to α-cristobalite. There is also a general increase in the background intensities in these areas, indicating the possible presence of very fine particles of these minerals. It is however, known that unfired diatomite is primarily composed of amorphous silica and X-ray diffraction analysis of unfired
<table>
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<th>Firing Temperature, °C</th>
<th>True Density, g/cm$^3$</th>
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<tr>
<td>600</td>
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<tr>
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<td>Peaks at</td>
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**TABLE 5**

*d*-Spacings of Tridymite and Clay Minerals
Diatomite normally produces broad patterns of non-crystalline material\(^{(19)}\).

For the diatomite specimen fired at 850°C, X-ray diffraction patterns showed no extra peaks than those obtained from the dried diatomite specimens, indicating no change in the phases due to firing at this low temperature.

For the diatomite specimen fired at 1000°C, all the peaks correspond to either α-quartz or α-cristobalite. Tridymite and mullite could not be detected in the specimen fired at 1000°C although Calacal reported the formation of these minerals in an impure diatomite from the Washington state. The background intensity was reduced for the specimen fired at 1000°C indicating that some crystallization of the amorphous silica occurred.

It appears that amorphous silica in this Quesnel diatomite changes directly to cristobalite on firing above 900°C. This may be due to the effect of the presence of certain mineralizers which favour cristobalite formation rather than tridymite crystallization.
4.3 Discussion on Sintering of Diatomite

4.3.1 Sintering of Diatomite

A large number of equations are available to interpret the shrinkage data of powder compacts \(^{20,21}\). These are primarily based on particles of simple geometric shape i.e. spheres. Neck growth equations have also been developed for contact points of parabolas and cones on a flat plate and similarly attempts have also been made to develop shrinkage equations for compacts of complex geometric shapes. These models are, however, based on the assumptions that:

1. The mass remains constant during sintering; thus they are not applicable to sintering of decomposable compounds, and
2. There is no transformation, therefore the true density stays the same during sintering.

For diatomite compacts these assumptions are not valid, as during sintering, diatomite looses weight and also crystallographic transformations occur in the system. This means that the physical property changes for diatomite on heating are very complex. The changes that occur on heating diatomite are due to sintering, mass loss and phase change.
These changes can be listed as follows:

(1) from $L_0$ to $L$ in the dimension
(2) from $W_0$ to $W$ in the weight, and
(3) from $\rho^T_0$ to $\rho^T$ in the true density

Although the bulk density (i.e. weight of solid/volume of specimen) changed from $\rho_{B_0}$ to $\rho_B$ and the relative density (i.e. volume of solid/volume of specimen) changed from $\rho_0$ to $\rho$, these values can be calculated from the primary changes in dimension, mass and true density of compacts. The weight and the true density changes are the two special characteristics which have to be taken into consideration while studying the sintering characteristics of diatomite compacts. Accordingly, the nature of these changes has to be clarified before any shrinkage model can be developed for diatomite compacts.

4.3.2 Weight Changes of Diatomite

As mentioned previously, Calacal in his study on the surface area of diatomite compacts, encountered both pore growth and pore creation due to loss of weight resulting from gas evolution. He reasoned that the gas evolution was caused by (1) the escape of water in the opaline structure of diatomite during heating, (2) the burn-off of organic matter in the raw material to form $CO_2$ and (3) the decomposition of carbonates of Mg and Ca to MgO, CaO and $CO_2$ gas. In this present study the same types of weight loss were observed. Accordingly, it was assumed that the weight loss was
due to the gas evolution and this created pores in the solid of diatomite compacts.

The geometry of pores in diatomite compacts is not as simple as most sintering models assume, and furthermore several types of pores have to be considered in the case of diatomite compacts. These are (1) pores which are formed due to mass loss, i.e. by the evaporation of gases and water, (2) pores which exist in diatom shell walls, (3) pores which form the inner cavities of diatom shells and (4) pores which are formed between diatomite particles (Figure 16). The concentration of these various pores in the compacts is related to the weight loss and the density change of diatomite during sintering; therefore, a sintering model for diatomite compacts must represent the various types and sizes of pores in a simple geometry.

4.3.3 True Density Changes of Diatomite

The true density increase of diatomite during sintering is caused by the transformation of amorphous silica into cristobalite. It is expected that a shrinkage of the compact would accompany the increase in true density and the resultant decrease in solid volume. It is assumed that this shrinkage will produce equivalent dimensional reduction of test specimens, without affecting the porosity of the specimens. The validity of this assumption stems from the experimental observations that (1) when the true density increased, the shrinkage also increased, (2) when the
Figure 16  Pores in diatomite compact. (800X)
true density increased, the porosity did not increase and (3) the increase of the true density was small in comparison with the increase of the shrinkage. This implies that the contribution from the changes of true density to the overall shrinkage of the compact was small.

4.4 Development of Shrinkage Equations

With respect to the above mentioned characteristics of diatomite compacts, the following inferences can be made:

(1) The weight loss generated pores.
(2) There were different types and sizes of pores in the compacts.
(3) The density of solid changed during firing.

Any sintering model, to be applicable to diatomite compacts, has to take all these into account and accordingly, a sintering model as shown in Figure 17 is proposed.

It should be noted that the diatomite specimens in this study started sintering at about 600 °C as can be seen in the plots of shrinkage (Figure 13) and bulk density change (Figure 15) with temperature. For this and the consideration that the manufacturing temperatures of commercial diatomite bricks are between 800 and 1000 °C, the discussion in this study will focus on the property changes of diatomite compacts fired above 600 °C. Accordingly, the data were all re-calculated using a base set
Figure 17 The proposed model of the diatomite shell wall.

Figure 18 SEM photo of diatomite shell wall (from Calacal).
arbitrarily at 600°C i.e. $L_0$, $W_0$ and $\rho_{T0}$ are the properties corresponding to firing at 600°C. This should not affect the test procedures as described in section 3.5 and also the shrinkage and the density data as reported in section 4.2.1.

The sintering model developed to interpret the data of diatomite compacts is based on the observations by Calacal and in this study, and can be represented by a typical microstructure as shown in Figure 18. This photomicrograph depicts small beady structures all throughout the solid mass with large hollow spaces. To represent this structure it is assumed that the diatomite shell-wall consists of an array of very small microspheres. Photomicrographs taken by Oliver(22) also show the minute cellular structures of the diatoms as can be seen in Figure 19. Assuming that these microspheres are solid spheres (i.e., no pores inside), a shrinkage equation of microspheres can be derived from the standard sintering equations developed for the neck growth between two spheres. It is also assumed that the mass of these microspheres does not change during firing.

To deal with (1) the weight loss which results in micropore formation in diatomite during firing and (2) the presence of a variety of pore sizes due to different origins of pores, a new approach is necessary. Consider that a three dimensional array of microspheres is arranged, extending throughout the entire diatomite compact, and some of the microspheres are missing from certain locations. A large pore may be equivalent to a region from which a large number of microspheres are missing. A single micropore may be simply a missing microsphere as shown
Figure 19  Diatom showing minute cellular structure. (After Oliver)
in Figure 17. There are pores existing (1) between diatomite particles, (2) in the inner cavities of diatom shells, (3) in diatom shell walls and (4) also formed by the evaporation of gases. All these pores may be represented by groups of missing microspheres. It is assumed that all solid microspheres are of identical size and they are arranged in a pattern which can represent the whole diatomite microstructure. These solid microspheres are contained in cells each identical in size, shape and orientation to its neighbours. Any one of these cells can be called a unit cell and a unit cell can be defined as a unit size and shape of cell which contains a solid sphere and open space surrounding it. It is also considered that missing microspheres constitute vacant unit cells. It is assumed that vacant unit cells shrink in the same manner as occupied unit cells which contain solid microspheres, since the vacant space in powder compact is surrounded by solid microspheres. This can be visualized by the shrinkage of the inner diameter of a hollow ceramic tube built with clay particles, which may also be considered as unit cells. The resemblance of the shrinkage of a single diatom shell to the shrinkage of a ceramic tube is shown in Figure 20, where the shrinkage of the diatom shells have the same geometric characteristics as that of a ceramic tube. For further development of the shrinkage equation the problem can be approached as follows: consider there are "m_o" vacant cells and "n_o" occupied cells per unit volume of a diatomite compact. The total number of unit cells in a unit volume is "m_o + n_o". If N_o is the fraction of occupied unit cells in a unit volume, then
Figure 20  Shrinkage of diatomite shells on firing, maintaining the original geometric shape.
Let this diatomite compact be subjected to sintering. Shrinkage and weight loss occur during sintering. After sintering, the numbers of vacant cells and occupied cells are \( m \) and \( n \), respectively. The loss of mass can be represented by the disappearance of \( q \) microspheres (i.e. \( q \) occupied unit cells turn into \( q \) vacant unit cells). This is shown schematically in Figure 21. As can be seen in the Figure,

\[
\begin{align*}
    m_0 + q &= m \\
    n_0 - q &= n \\
    m + n &= (m_0 + q) + (n_0 - q) = m_0 + n_0.
\end{align*}
\]

Consequently, the total number of unit cells before and after sintering is unchanged. If \( N \) is the fraction of occupied unit cells per unit volume after sintering, then

\[
N = \frac{n}{m + n}
\]

\[
N_o = \frac{n_0}{m_0 + n_0}
\]

\[
N_o = \frac{n}{n_0} \times \frac{x \text{ weight of each microsphere}}{n_0 x \text{ weight of each microsphere}} = \frac{\text{weight of a unit volume after sintering}}{\text{weight of a unit volume before sintering}} = \frac{\text{weight of specimen after firing}}{\text{weight of specimen before firing}} = \frac{(W)}{(W_o)}
\]

\( (4.4.1) \)

Note: the mass of microsphere does not change during firing.
(1) Original unit volume.

\[ n_0 = \text{number of occupied unit cells} \]
\[ m_0 = \text{number of vacant unit cells} \]
\[ m_0 + n_0 = \text{total number of unit cells} \]

(2) Subjected to sintering.

(3) Volume shrinkage and weight loss occur during sintering. Consider the loss of mass can be represented by disappearance of "q" occupied unit cells.

\[ n = \text{number of occupied unit cells after sintering: } n = n_0 - q \]
\[ m = \text{number of vacant unit cells after sintering: } m = m_0 + q \]

Figure 21 A schematic illustration of the weight loss of diatomite.
The conventional spherical geometry for sintering model can now be applied. It must, however, be noted that in the case of diatomite compacts, the neck growth is assumed to follow the sintering model proposed by Frenkel\(^{(23)}\) for viscous flow as shown in Figure 22. Figure 23 shows schematically the change of geometric configuration of the unit cell during sintering. The symbols in this figure have been altered from Frenkel's model in order to match the ones used in this thesis. For developing the shrinkage equation, it is considered that the coordination number with the neighbouring spheres remains constant throughout the sintering process.

From Figure 23,

\[ a^2 + y^2 = R^2 \]

\[ h = R - Y = R - \sqrt{R^2 - a^2} \]

\[ \frac{h}{R} = \frac{R - \sqrt{R^2 - a^2}}{R} = 1 - \sqrt{\frac{R^2 - a^2}{R^2}} = 1 - \sqrt{1 - \left(\frac{a}{R}\right)^2} \]

Shrinkage = \( \frac{\Delta L}{L_0} = \frac{h}{R} = 1 - \sqrt{1 - \left(\frac{a}{R}\right)^2} \) (4.4.2)
Figure 22  The geometry of Frenkel's model for the initial stage of sintering by viscous flow.
Before sintering

After sintering

\[ W \]  Weight of a sphere

\[ V_0 \]  Volume of a unit cell

\[ D_{B_0} \]  Bulk density of a unit cell

Figure 23  The geometry of unit cell incorporating a microsphere.
This equation gives the relation between shrinkage \( \frac{\Delta L}{L_0} \) and relative neck radius \( \frac{a}{R} \), but in case of diatomite the relative neck radius \( \frac{a}{R} \) in Eq. 4.2.2 is impossible to measure experimentally; therefore this equation was modified eliminating \( \frac{a}{R} \) as follows.

### 4.4.1 Development of Density Equations

An occupied unit cell, with the weight of solid \( w \), the length of edge \( l_o \), the volume of unit cell \( v_o \) and the bulk density of unit cell \( D_{Bo} \), is subjected to sintering. After sintering, \( w \) is unchanged, \( l_o \) shrinks to \( l \), \( v_o \) decreased to \( v \) and \( D_{Bo} \) increased to \( D_B \). Rhine\(^{(24)}\) showed that

\[
\begin{align*}
    v_o &\propto l_o^3 \\
    v &\propto l^3 \\

    \frac{l^3}{l_o^3} &= \frac{v}{v_o} \\
        &= \frac{w/v_o}{w/v} \\
        &= \frac{D_{Bo}}{D_B} \\

    \frac{\Delta l}{l_o} &= \frac{l_o - l}{l_o} \\
        &= 1 - \frac{l}{l_o} \\
        &= 1 - \left( \frac{D_{Bo}}{D_B} \right)^{1/3}
\end{align*}
\]
\[
\frac{\Delta L}{L_0} = \frac{\Delta L}{L_0} = 1 - \left(\frac{D_{Bo}}{D_B}\right)^{1/3}
\]

(4.4.3)

By combining Eq's 4.4.2 and 4.4.3, the equation below can be obtained.

\[
\frac{D_{Bo}}{D_B}^{1/3} = \sqrt{1 - \left(\frac{a}{R}\right)^2}
\]

\[
\therefore \quad \frac{D_B}{D_{Bo}} = \frac{1}{\left[1 - \left(\frac{a}{R}\right)^{3/2}\right]} \quad \text{or} \quad \frac{D_B}{D_{Bo}} = \left[\frac{R^2}{R^2 - a^2}\right]^{3/2}
\]

(4.4.4)

The bulk density of compact \((\rho_B)\) is

\[
\rho_B = \frac{\text{weight of specimen}}{\text{volume of specimen}} = \frac{\text{weight of unit volume}}{\text{unit volume}} = \frac{\text{(weight of unit volume)} \div (\text{volume of total occupied unit cells + volume of total vacant unit cells in unit volume})}{(m + n) \times \text{volume of each unit cell}} = \frac{n}{m + n} \times \text{bulk density of each occupied unit cell}
\]

\[
\frac{n}{m + n} \times D_B = \frac{n}{m + n} \times \rho_B
\]

\[
= N \frac{D_B}{D_{Bo}} \quad \text{or} \quad D_B = \frac{\rho_B}{N}
\]

(4.4.5)
In the same way, the relative density of compact \( \rho \) is

\[
\rho = \frac{\text{volume of solid in specimen}}{\text{volume of specimen}} = \frac{\text{volume of solid in unit volume}}{\text{unit volume}} = \frac{\text{volume of solid in unit volume}}{\text{volume of total occupied unit cells} + \text{volume of total vacant unit cells}} = \frac{n \times \text{volume of each solid microsphere}}{(m + n) \times \text{volume of each unit cell}} = \frac{n}{m + n} \times (\text{relative density of each occupied unit cell})
\]

\[= N D \quad \text{or} \quad D = \frac{\rho}{N} \quad (4.4.6)\]

From Eq. 4.4.5

\[
\frac{D_B}{D_{Bo}} = \frac{\rho_B/N}{\rho_{Bo}/N_o} = \frac{N_o \rho_B}{N \rho_{Bo}}
\]

Eq. 4.4.4 is given by,

\[
\frac{D_B}{D_{Bo}} = \frac{1}{[1 - \left(\frac{a}{R}\right)^2]^{3/2}}
\]

\[\therefore \quad \frac{N_o \rho_B}{N \rho_{Bo}} = \frac{1}{[a - \left(\frac{a}{R}\right)^2]^{3/2}}\]
\[ \frac{\rho_B}{\rho_{Bo}} = \frac{N}{N_o} \frac{1}{\left[1 - \left(\frac{a}{R}\right)^2\right]^{3/2}} \]  

(4.4.7)

Eq. 4.4.7 gives the relation between the bulk density of specimen and the relative neck radius.

Combining equations 4.4.3 and 4.4.5 results in

\[ \frac{\Delta L}{L_o} = 1 - \left[\frac{\rho_{Bo}/N}{\rho_B/N}\right]^{1/3} \]

\[ = 1 - \left(\frac{\rho_{Bo}}{\rho_B}\right)^{1/3} \left(\frac{N}{N_o}\right) \]

Substituting for \( N/N_o \) by Eq. 4.4.1 gives

\[ \frac{\Delta L}{L_o} = 1 - \left(\frac{\rho_{Bo}W}{\rho_BW_o}\right)^{1/3} \]

or

\[ \frac{\rho_{Bo}W}{\rho_BW_o} = (1 - \frac{\Delta L}{L_o})^3 \]

\[ = 1 - 3 \frac{\Delta L}{L_o} \]

\[ \therefore \quad \frac{\Delta L}{L_o} = \frac{1}{3} \left(1 - \frac{\rho_{Bo}W}{\rho_BW_o}\right) \]  

(4.4.8)

Eq. 4.4.8 gives the relation between shrinkage, bulk density and weight change, and can be tested with the data obtained in this investigation.
4.4.2 Testing of shrinkage and Density Equations

A plot of the shrinkage of the compacts versus the firing temperature is shown in Figure 24. In the derivation of the shrinkage equation 4.4.8 it is assumed that $R \sim R_\circ$. This approximation is only valid if $R_\circ$ does not change significantly and the boundary condition is that $a/R$ should be less than $\sim 0.4$ (as shown by Kakar\(^{(25)}\)). In order to test this point, the values of $a/R$ were calculated using equation 4.4.2 and the shrinkage $(\Delta L/L_\circ)$ data. These calculated values of $(\frac{a}{R})$ are shown in Table VI. The largest value of $(\frac{a}{R})$ is less than 0.40 which satisfies the above boundary condition that $a/R < 0.4$ and $R \sim R_\circ$.

Equation 4.4.8 can also be used to calculate the shrinkage of the compact from the experimental data of weight loss $(W/W_\circ)$ and bulk density $(\rho_B/\rho_{B\circ})$. Then the calculated values can be compared with experimentally measured shrinkage values. This is shown in Figure 25 to confirm the validity of Eq. 4.4.8. Good agreement between the calculated and the experimental values suggests that the proposed sintering model may be operative in the case of diatomite compacts.

4.5 Results and Discussion on Thermal Conductivity

One of the most important properties of diatomite insulating bricks is the thermal conductivity since these bricks are used as heat insulating material. Another important property beside thermal conductivity is the strength of the brick since they are also used as construction material.
Figure 24  The experimental shrinkage data of pure diatomite specimens, normalized to the 600°C firing.
<table>
<thead>
<tr>
<th>Temperatures of heat treatment</th>
<th>Experimental Results of $\Delta L/L_0$</th>
<th>Calculated $\frac{a}{R}$ from $\Delta L/L_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$600^\circ$ C</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>700</td>
<td>0.0022</td>
<td>0.0663</td>
</tr>
<tr>
<td>800</td>
<td>0.0090</td>
<td>0.1338</td>
</tr>
<tr>
<td>850</td>
<td>0.0147</td>
<td>0.1709</td>
</tr>
<tr>
<td>900</td>
<td>0.0254</td>
<td>0.2241</td>
</tr>
<tr>
<td>950</td>
<td>0.0439</td>
<td>0.2931</td>
</tr>
<tr>
<td>1000</td>
<td>0.0696</td>
<td>0.3667</td>
</tr>
<tr>
<td>1050</td>
<td>0.0782</td>
<td>0.3877</td>
</tr>
</tbody>
</table>
Figure 25 The theoretical shrinkage plot as a function of relative density and weight. Experimental data are also included.
The changes of the thermal conductivity value of diatomite on firing are discussed below while the changes of the strength of diatomite on firing will be dealt with in the next section.

4.5.1 Experimental Results of Thermal Conductivity

The thermal conductivity of diatomite specimens was determined after firing the specimens at elevated temperatures. Thermal conductivity measurements were carried out at 300°C test temperature. Details of the experiments are given in Section 3.3.5 (Equipment) and Section 3.5.3 (Test Procedures) in this thesis.

The experimental results of thermal conductivity measurements of fired specimens are plotted in Figure 26 as a function of the firing temperature of the specimens. The thermal conductivity values were first decreased, on firing up to 600°C, in the same way as the bulk density dropped on firing (Figure 15). These curves, however, are not similar to the shrinkage curve which continued to increase over the whole test temperature range (Figure 13).

4.5.2 Development of Thermal Conductivity Equations

Numerous thermal conductivity equations for porous compacts are available in literature but most of them have been found to be unsuitable to test the present data, because of the peculiar sintering behaviour of diatomite, in which mass loss and mineral transformations occur.
Figure 26  The experimental thermal conductivity data of pure diatomite specimens.
concurrently with sintering. Of these models, the one, which Ramanan derived to relate neck radius after sintering to the electrical conductivity of ceramic compacts, appears to be a suitable model for modification for the testing of the thermal conductivity data determined on diatomite compacts. By combining Ramanan's method and the density equation 4.4.7, and then by applying the vacant unit cell concept developed in a previous section, it is possible to derive an equation relating the thermal conductivity and density of the compacts. The derivation of the equation is as follows.

Figure 27 shows the basic geometry of two spheres in contact and the equivalent electrical circuit as developed by Ramanan. Figure 28 shows spheres in a two dimensional cubic array and the equivalent electrical network. In this present case the electrical current is replaced by heat flow and the electrical conductivity by thermal conductivity. The analogy between the flow of electrical current and heat is well established and has been used by many authors previously. From Ramanan's treatment, the conductivity of the simple cubic cell, \( k_u \) (Figure 29) is given by:

\[
k_u = \frac{\text{area of neck perpendicular to current}}{\text{area of unit cell perpendicular to current}} \times \text{conductivity of particle}
\]

\[
= \frac{A_n}{A_u} k_s
\]

\[
= \frac{\pi a^2}{4y^2} k_s
\]

\[
= \frac{\pi}{4} \frac{a^2}{R^2 - a^2} k_s
\]
Figure 27 The geometry of two spheres in contact and the equivalent electrical network (after Ramanan)

Geometry of two spheres

Two dimensional array of spheres

Figure 28 Spheres in a two-dimensional cubic array and an equivalent electrical network (after Ramanan)
Figure 29  Heat flow through a sphere in a simple cubic model.

- Heat flow
- $2Y$ and $2Y$
- $A_n$: area of neck
- $A_u$: area of unit cell
where \( k_s \) = Conductivity of solid (particle)

\( A_u \) = Area of unit cell

\( A_n \) = Area of heat flow, i.e. area of neck

The general form of this equation for different types of packing is

\[
\frac{k_u}{k_s} = a \frac{a^2}{R^2 - a^2}
\]

(4.5.1)

where \( k_u \) = conductivity of unit cell

"\( a \)" is a geometric constant, whose value is dependent on types of packing.

The value of this geometric constant \( (a) \) will be discussed later. Thermal conductivity of a unit volume \( (K) \) is

\[
K = N k_u
\]

(4.5.2)

where \( N \) is the fraction of the number of solid cells in a unit volume. By combining 4.5.1 and 4.5.2,

\[
K = N \alpha k_s \frac{a^2}{R^2 - a^2}
\]

\[
= N \alpha k_s \frac{1}{R^2 - a^2}
\]

\[
= N \alpha k_s \frac{1}{\left(\frac{a}{R}\right)^2 - 1}
\]
when \( \frac{a}{R} = 0 \) i.e. before sintering started, \( K = K_0 \) i.e. thermal conductivity value before heat treatment (in this case at 600°C).

\[
K = N \alpha k_s \left( \frac{1}{\left( \frac{a}{R} \right)^2} - 1 \right) + K_0 \quad \text{or} \quad K = N \alpha k_s \frac{a^2}{R^2 - a^2} + K_0 \quad (4.5.3)
\]

Eq. 4.5.3 can be rewritten as below assuming that \( N, \alpha \) and \( k_s \) are constants.

\[
K - K_0 = N \alpha k_s \frac{1}{\left( \frac{a}{R} \right)^2 - 1}
= \text{(const)} \frac{1}{\left( \frac{R}{a} \right)^2 - 1}
= \text{(const)} \frac{1}{\left( \frac{R}{a} \right)^2} \quad \text{when} \ a \ll R
= \text{(const)} \left( \frac{a}{R} \right)^2 \quad (4.5.4)
\]

Eq. 4.5.4 shows that the thermal conductivity increases with almost the square of the neck radius (assuming "R" remains constant).

Eq. 4.5.3 and 4.5.4, however, are not practical to apply to the experimental data of thermal conductivity because the value of \( a/R \) in diatomite compacts is not known. The equations of thermal conductivity and density can however be combined to eliminate \( \frac{a}{R} \) as follows.
Eq. 4.4.7 is modified to

\[ \left( \frac{N_o \rho_B}{N \rho_{Bo}} \right) = \frac{R^2}{R^2 - \alpha^2} \]

\[ \left( \frac{N_o \rho_B}{N \rho_{Bo}} \right)^{2/3} - 1 = \frac{R^2}{R^2 - \alpha^2} - 1 \]

\[ = \frac{\alpha^2}{R^2 - \alpha^2} \]  \( (4.5.5) \)

and then substituted in 4.5.3 resulting in

\[ K = N \alpha k_s \left( \left( \frac{N_o \rho_B}{N \rho_{Bo}} \right)^{2/3} - 1 \right) + K_o \]

since \( \frac{N_o}{N} = \frac{W_o}{W} \)  \( (Eq. 4.4.1) \)

\[ K = N \alpha k_s \left( \left( \frac{W_o \rho_B}{W \rho_{Bo}} \right)^{2/3} - 1 \right) + K_o \]  \( (4.5.6) \)

Eq. 4.5.6 gives the relation between thermal conductivity, bulk density and weight loss of a diatomite specimen. The term \( (k_s) \) in Eq. 4.5.6 is the thermal conductivity of solid diatomite.
4.5.2.1 Correction for Mineral Transformation

In real diatomite compacts the value of $k_s$ changes on firing due to the mineralogical transformation from amorphous silica to a mixture of cristobalite and glass matrix, as observed in the X-ray analyses and true density measurements. It is not possible to know the thermal conductivity of the solid component in diatomite after heat treatment, but by assuming that $k_s$ changes proportionately with fraction of amorphous phase which is crystallized and that this is reflected in the true density change, it is possible to estimate the value of $k_s$ with the extent of crystallization. Fraction of crystallization $= \frac{\rho_T - \rho_{Tg}}{\rho_{Tc} - \rho_{Tg}}$

where $\rho_T = $ true density of test specimen

$\rho_{Tg} = $ true density of glass, in this case the true density of the specimen fired at 600°C where diatomite is amorphous

$\rho_{Tc} = $ true density of crystal, i.e. true density of sintered diatomite, in this case the true density of the specimen fired at 1050°C (after crystallization).

Thermal conductivity change corresponding to the amount of crystallization is,

$$(k_c - k_g) \frac{\rho_T - \rho_{Tg}}{\rho_{Tc} - \rho_{Tg}}$$
where \( k_c \) = thermal conductivity of crystal  
\( k_g \) = thermal conductivity of glass  
when \( \rho_T = \rho_{Tg} \),  
\( k_s = k_g \)

Therefore the thermal conductivity of a zero porosity specimen can be written as,

\[
k_s = k_g + (k_c - k_g) \frac{\rho_T - \rho_{Tg}}{\rho_{Tc} - \rho_{Tg}}
\]

(4.5.7)

Eq. 4.5.7 gives the thermal conductivity value of solid diatomite at different stages of sintering.

The value of "\( \alpha \)" in Eq. 4.5.6 is a constant, but is dependent on the type of packing. The theoretical values of \( \alpha \) calculated by Ramanan for various packings are listed in Table VII.

4.5.3 Testing of Thermal Conductivity Equations

Using the experimental data of thermal conductivity reported in the previous chapter, the thermal conductivity equation (Eq. 4.5.6) can be tested as follows.

\[
K = N \alpha k_s \left( \frac{W_o \rho_B}{W \rho_{Bo}} \right)^{2/3} - 1) + k_o
\]

(4.5.6)
<table>
<thead>
<tr>
<th>Type of Packing</th>
<th>$\alpha$</th>
<th>Relative Density, $D_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>$\pi/4$</td>
<td>0.5236</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\pi/2\sqrt{3}$</td>
<td>0.6046</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$\pi/\sqrt{2}$</td>
<td>0.7403</td>
</tr>
<tr>
<td>b.c.c.</td>
<td>$\pi/\sqrt{3/4}$</td>
<td>0.6802</td>
</tr>
</tbody>
</table>
In this equation $\frac{W}{W_0}$ (the weight loss of specimen), $\frac{\rho_B}{\rho_{B_0}}$ (the bulk density of specimen) and $k_0$ (the thermal conductivity before sintering, in this case the thermal conductivity of the diatomite specimen fired at 600°C) were determined experimentally. But $N$ (the fraction of the number of solid cells in the unit volume) and $a$ (a constant, whose value is dependent on the types of packing) are unknown. Since both $N$ and $a$ are a function of the type of packing, these figures can be calculated theoretically for a variety of packing geometries as follows.

From Eq. 4.4.1 and 4.4.6,

$$\frac{N}{N_0} = \frac{W}{W_0} \quad \text{and} \quad N_0 = \frac{\rho_0}{D_0}$$

Therefore

$$N = \frac{\rho_0}{D_0} \frac{W}{W_0}$$

$\rho_0$ was experimentally determined and found to be equal to 0.3044 at 600°C. $D_0$ is the relative density of the unit cell. This was calculated theoretically by Ramanan and is shown in Table VII. The weight change of diatomite specimens ($\frac{W}{W_0}$) between 600 and 1050°C was less than 1.7%, therefore $\frac{W}{W_0} = 1$. The values of "N" calculated using the above values are shown in Table VIII.
TABLE VIII

The Calculated Values of $N$

\[ N = \frac{\rho_o W}{D_o \frac{W}{W_o}} \quad \text{where} \quad \frac{W}{W_o} = 1 \]

<table>
<thead>
<tr>
<th>Types of Packing</th>
<th>Values of $N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>0.5813</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>0.5035</td>
</tr>
<tr>
<td>b.c.c</td>
<td>0.4475</td>
</tr>
</tbody>
</table>
As mentioned before, Eq. 4.5.7 gives the thermal conductivity value of solid diatomite, which is also necessary to calculate the thermal conductivity of heat treated diatomite compacts. The values of $k_s$ are calculated as follows.

$$k_s = k_g + (k_c - k_g) \frac{\rho_T - \rho_{T_g}}{\rho_{T_c} - \rho_{T_g}} \quad (4.5.7)$$

In this equation

$\rho_{T_g}$ is 2.1543 g/cc (true density of amorphous diatomite, in this case the true density of the specimen fired at 600 °C).

$\rho_{T_c}$ is 2.3807 g/cc (true density of crystallized diatomite, in this case the true density of the specimen fired at 1050 °C).

$k_g$ is $2.3 \times 10^{-3}$ cal/cm.s.C (0.96 w/m K) (thermal conductivity of solid amorphous diatomite, in this case the typical value of crown glass was used).

$k_c$ is $4.6 \times 10^{-3}$ cal/cm.s.C (1.92 w/mK) (thermal conductivity of solid crystallized diatomite, in this case the typical value of siliceous porcelain was used).

$\rho_T$ is true density of test specimen which is shown in Table III.

The calculated values of $k_s$ are shown in Table IX.
<table>
<thead>
<tr>
<th>Temperature of Heat Treatment</th>
<th>Values of $k_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C</td>
<td>0.96 (W/mK)</td>
</tr>
<tr>
<td>700</td>
<td>0.96</td>
</tr>
<tr>
<td>800</td>
<td>0.92</td>
</tr>
<tr>
<td>850</td>
<td>0.92</td>
</tr>
<tr>
<td>900</td>
<td>0.92</td>
</tr>
<tr>
<td>950</td>
<td>1.21</td>
</tr>
<tr>
<td>1000</td>
<td>1.76</td>
</tr>
<tr>
<td>1050</td>
<td>1.92</td>
</tr>
</tbody>
</table>
It is now possible to calculate the value of $K$ from the known and estimated values of $N$, $\alpha$, $k_s$, $\frac{\rho_B}{\rho_{Bo}}$, $\frac{W}{W_o}$ and $k_o$ for specimens heat treated at different temperatures using Eq. 4.5.6. Three different values of $N$ and $\alpha$ were used in the calculation corresponding to three different packings. The theoretical lines and the experimental data are shown in Figures 30 to 32. It appears that the predicted curve for the simple cubic packing fitted best with the experimental values of $K$, indicating that the overall packing geometry of microspheres in these diatomite specimens may be represented by the simple cubic packing. As can be seen in these figures, simple cubic packing is in better agreement with the experimental results for $k_s$ values of 0.96 w/mk up to 900 °C and 1.92 w/mk above 1000 °C.

From this set of data it appears that the thermal conductivity of diatomite compacts increased with the firing temperatures. The increase is likely due to (1) the growth of contact areas between particles and (2) the crystallization of amorphous silica, which is the main structural element in diatomite shells. This increase of thermal conductivity on firing is similar to that reported by Ruh and Renkey(27) who showed that the thermal conductivity of castable refractories increased as ceramic bonds were formed in the refractory concrete.

4.5.4 Porosity Effect on Thermal Conductivity

In the past extensive studies have been made to explain the thermal conductivity of porous bodies(28,29,30). In these studies, consideration has been given not only to the volume fraction of pores but also to such
Figure 30  The experimental data and the theoretical (simple cubic packing) thermal conductivity plot.
Figure 31  The experimental data and the theoretical (orthorhombic packing) thermal conductivity plot.

$k_s = 1.92 \ \text{(w/mK)}$

$k_s = 0.96 \ \text{(w/mK)}$
Figure 32 The experimental data and the theoretical (b.c.c. packing) thermal conductivity plot.
factors as crystalline nature, impurities, lattice imperfection, chemical composition and the size, shape, orientation and emissivity of the pores. Numerous equations are thus available to approximate the thermal conductivity of porous compacts. Some of the well known thermal conductivity equations are shown in Table X and two representative plots are shown in Figures 33 and 34. These equations indicate that the thermal conductivity of a given porous compact can be approximated to a linear function of the porosity of the compact. For instance, Loeb's equation shows that the thermal conductivity changes linearly with porosity, if the geometric effect of the pore is ignored. Loeb's equation is included in Figure 35 along with the thermal conductivity results of pure diatomite specimens and a commercial brand of diatomite bricks. These commercial bricks were used in the latter part of this study.

In Figure 35 it can be seen that the thermal conductivities of diatomaceous compacts (i.e. both pure diatomite specimens and commercial diatomite bricks) increased rapidly with little decrease in porosity; the fractional porosity of pure diatomite specimens decreased from 0.696 (for the specimen heat treated to 600 °C) to 0.654 (for the specimen heat treated to 1050 °C). This is a 6% decrease in fractional porosity. On the other hand, the thermal conductivity of these specimens increased from 0.15 w/mK to 0.30 w/mK, respectively, i.e. 100% increase in the thermal conductivity value. This increase in thermal conductivity is apparently caused by a combination of the increase in contact areas and the crystallization of diatomite particles. This type of increase in thermal conductivity of powder compacts was noted by Kingery(33), that the
### Equations for the Thermal Conductivity of a Porous Body

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(29) Eucken:</td>
<td>$k_p = k_s \frac{1 + 2P(\frac{1 - Q}{2Q + 1})}{1 - P(\frac{1 - Q}{2Q + 1})}$</td>
</tr>
<tr>
<td>(30) Russell:</td>
<td>$k_p = k_s \frac{P^{2/3} + Q(1 - P^{2/3})}{P^{2/3} - P + Q(1 - P^{2/3} + P)}$</td>
</tr>
<tr>
<td>(31) Loeb:</td>
<td>$k_p = k_s (1 - P_c) + \frac{P_c}{P_L k_s \frac{1}{4 \sigma \varepsilon \gamma T_m^3} + (1 - P_L)}$</td>
</tr>
</tbody>
</table>

$k_p$ = conductivity of porous sample
$k_s$ = conductivity of solid sample
$P$ = volume pore fraction
$Q = k_s / k_a$
$k_a$ = conductivity of air
$P_c$ = cross sectional pore fraction
$P_L$ = longitudinal pore fraction
$\sigma$ = radiation constant
$\gamma$ = geometrical pore fraction
$\varepsilon$ = emissivity
$d$ = dimension of pore
$T_m$ = mean absolute temperature
Figure 33  The effect of porosity on thermal resistivity (after Wagner\(^\text{(31)}\)).

Figure 34  Dimensionless thermal conductivity vs. fractional porosity for polycrystalline graphite (after Rhee\(^\text{(32)}\)).
Figure 35  The experimental data of thermal conductivity vs. porosity.
crystalline nature and structure of ceramic materials strongly affect the thermal conductivity of the compact but that these relationships are difficult to assess quantitatively because of the wide divergence in values reported for pure materials.

A detailed curve of the thermal conductivity of diatomite specimens was plotted against the relative density of the specimens in Figure 36. In this figure, the thermal conductivity curve appears to satisfy the relationship: \((\text{thermal conductivity}) \propto (\text{density})^{2/3}\) for specimens heat treated below 900°C. This relationship can easily be assumed by Eq. 4.5.6. On the other hand, the thermal conductivity value of specimens heat treated above 900°C increased drastically with little change in relative density. This behaviour of rapid increase in thermal conductivity appears to coincide with the sudden formation of cristobalites in specimens heat treated in this temperature range.

From these observations of Figures 30, 35 and 36 it can be inferred that two factors are affecting the thermal conductivity value of diatomite compacts. The first - the amount of pore volume in the compact, which results in lower thermal conductivity value for a lighter brick and a higher thermal conductivity value for a heavier brick. The second - the effect of firing, which influences the thermal conductivity value by changing the size of contact areas and by transforming amorphous silica into cristobalites in the diatomite compact. In this mechanism, thermal conductivity values change with respect to the degree of sintering and the amount of crystals formed in the compact.
Figure 36  The experimental relationship between relative density ($\Delta \rho / \rho$) change and thermal conductivity ($\Delta K / K_0$) change.
4.6 Results and Discussion on Strength

4.6.1 Experimental Results of Strength

Strength is one of the important properties of diatomite insulating bricks because these bricks are routinely used in structural and load-bearing walls.

The measured compressive strength of diatomite specimens were plotted against their firing temperatures as shown in Figure 37. The strength of diatomite was reduced slightly on heating between 200 and 400°C but an increase was observed at about 600°C and especially above 800°C.

4.6.2 Development of Strength Equations

In the previous section, equation of shrinkage, bulk density and thermal conductivity were related to the ratio of neck radius (a) to particle radius (R), \( \frac{a}{R} \). Similarly, it has been found to be convenient to relate the change of \( \frac{a}{R} \) on heating with the increase in strength of diatomite.

Figure 38 shows a simple schematic model of the breaking down of contact areas during compressive strength tests. Consider a unit volume of specimen. It is assumed that particles of diatomite are bonded to one another by necks formed at contact points of particles during the heat treatment.
Figure 37 The experimental compressive strength data of pure diatomite specimens.
Figure 38  A model for the breakage of necks during the compressive strength test.
When the diatomite specimen fractures under a compressive load, the contact areas of the particles fracture.

Therefore,

\[
\frac{Q}{A_f} = \sigma_f
\]

where \( Q \) = fracture load on a unit volume of specimen

\( A_f \) = total fractured neck area on fracture plane/unit volume

\( \sigma_f \) = fracture stress at neck area

\[
\therefore \quad Q = \sigma_f A_f
\]

The total fractured neck area on fracture plane/unit volume (i.e. \( A_f \)) is also equal to (the fractured neck area per particle) \( \times \) (number of particles on the fracture plane).

\[
A_f = A_{pf} \cdot n^{2/3}
\]

\[
= \frac{A_{pf}}{A_p} \cdot A_p \cdot n^{2/3}
\]

\[
= C \cdot A_p \cdot n^{2/3}
\]

where \( A_{pf} \) = fractured neck area/particle

\( A_p \) = total neck area/particle

\( n \) = number of particles/unit volume

\( C \) = \( A_{pf}/A_p \) i.e. fraction of fractured neck area to total neck area/particle on fracture plane.
\[ Q = \sigma_f A_f \]
\[ = \sigma_f C A_p n^{2/3} \quad (4.6.1) \]

"n" is the number of solid (occupied) particles in a unit volume of diatomite compacts. This was defined in Section 4.3.

The fracture strength (S) of a unit volume of specimen is,

\[ S = \frac{Q}{\text{unit area}} \]
\[ = \frac{\sigma_f C A_p n^{2/3}}{\text{unit area}} \quad (4.6.2) \]

A unit area is equal to (the area of one facet of a unit cell) x (number of unit cells on a unit area). Therefore,

\[ \text{A Unit Area} = (\beta^{1/3} y)^2 x (m + n)^{2/3} \]
\[ = \beta^{2/3} (R^2 - a^2)(m + n)^{2/3} \]

where \( \beta \) is a geometric constant. This was defined and calculated by Kakar for various types of packing. The values of \( \beta \) are listed in Table XI. Eq. 4.6.2 thus becomes,

\[ S = \frac{\sigma_f C A_p n^{2/3}}{\beta^{2/3} (R^2 - a^2)(m + n)^{2/3}} \]
\[ = \frac{\sigma_f C A_p}{\beta^{2/3} (R^2 - a^2)} \left( \frac{n}{m + n} \right)^{2/3} \]
\[ = \frac{\sigma_f C A_p}{\beta^{2/3} (R^2 - a^2)} N^{2/3} \quad (4.6.3) \]
### TABLE XI

Geometric Parameter ($\beta$) for Various Packings

(after Kakar)\(^{(25)}\)

<table>
<thead>
<tr>
<th>Types of Packing</th>
<th>Values of $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>8</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$4\sqrt{3}$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$4\sqrt{2}$</td>
</tr>
<tr>
<td>b.c.c.</td>
<td>$32\sqrt{3}/9$</td>
</tr>
</tbody>
</table>
"A_p" in Eq. 4.6.3 can be calculated as follows:

\[ A_p = \text{total neck area of one particle} \]

\[ = \frac{Z}{2} A \]

\[ = \frac{Z}{2} \pi a^2 \]

where \( Z = \) coordination number

\( A = \) area of one neck

\( a = \) radius of one neck

Substituting this in Eq. 4.6.3,

\[ S = \frac{\sigma_f C A_p}{\beta^{2/3} \left(R^2 - a^2\right)} N^{2/3} \]

\[ = \frac{\sigma_f C N^{2/3}}{\beta^{2/3}} \frac{1}{R^2 - a^2} \frac{Z \pi a^2}{2} \]

or

\[ = \frac{\sigma_f C N^{2/3} Z \pi}{2 \beta^{2/3}} \frac{1}{R^2 - a^2} \]

or

\[ = C \frac{1}{\left(\frac{a}{R}\right)^2 - 1} \]  

(4.6.4)
where
\[ C' = \frac{\sigma_f C N^{2/3} Z \pi}{2 \beta^{2/3}} \] (4.6.5)

\( C' \) is a constant because,

\( N \) = a constant when weight loss on firing is very small (above 600°C)

\( \sigma_f \) = fracture stress of neck area = a constant

\( C, Z \) and \( \beta \) = constants

In Eq. 4.6.4 \( S = S_0 \) when \( a = 0 \)

\[ S = C' \frac{1}{\left(\frac{a}{R}\right)^2 - 1} + S_0 \] (4.6.6)

The strength equation 4.6.6 is very similar to the thermal conductivity equation 4.5.3 as shown in Section 4.5.2; thus, the relation between the strength and the bulk density of compacts can also be derived in the same way as the thermal conductivity and the bulk density equation. The final form of the strength and the bulk density equation is given by

\[ S = C' \left(\frac{\rho_B}{\rho_{Bo}}\right)^{2/3} \left(\frac{W}{W_0}\right) - 1) + S_0 \] (4.6.7)
4.6.3 Testing of Strength Equations

4.6.3.1 Experimental Value of "C"

The values of the constant "C" in Eq. 4.6.7 were calculated from the experimental data of strength, bulk density and weight loss. The results of this calculation are shown in Table XII.

The value of C is $4.6 \times 10^5 \text{ g/cm}^2$ and it should be constant as all the factors in Eq. 4.6.5 are constant. For example, $N$ (the fraction of the number of occupied unit cells to total unit cells) was found to vary experimentally less than 1.7% in the temperature range of testing (600 to $1050 \, ^\circ\text{C}$). $Z$ and $\beta$ are functions of the type of packing and, in the development of the sintering theory, these are assumed to be constants. $\sigma_f$ - the stress necessary to fracture the neck region should also be a constant (i.e. stress per unit area). If however, it is considered that there is a reduction in the value of C (Table XII) with temperature of heat treatment above 1000 $^\circ\text{C}$, then this reduction can be attributed to the following:

(1) The transformation of amorphous glass to crystal phase may reduce the strength, if the crystallization is followed by heterogeneous nucleation,

(2) The concentration of impure glassy phase into the neck region, and
TABLE XII

The Calculated Values of $C^-$

<table>
<thead>
<tr>
<th>Temperatures of heat treatment</th>
<th>Values of $C^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C</td>
<td>445 kg/cm$^2$</td>
</tr>
<tr>
<td>800</td>
<td>522</td>
</tr>
<tr>
<td>850</td>
<td>535</td>
</tr>
<tr>
<td>900</td>
<td>510</td>
</tr>
<tr>
<td>950</td>
<td>487</td>
</tr>
<tr>
<td>1000</td>
<td>351</td>
</tr>
<tr>
<td>1050</td>
<td>378</td>
</tr>
<tr>
<td>Av. Value of $C^-$</td>
<td>461</td>
</tr>
</tbody>
</table>
(3) the creation of microcracks at neck areas, which is well known for recrystallization of amorphous silica with significant grain-growth\(^{(34,35)}\).

Specifically, when cristobalite crystals are formed in diatomite compacts, these crystals would tend to invert from the high temperature \(\beta\)-phase to the low temperature \(\alpha\)-phase in the temperature range 200 to 300 °C. This inversion is associated with about a 3 volume % change\(^{(36)}\) which may disrupt the structure, resulting in microcrack formation. Specimens which were cooled rapidly in this temperature range might have poor compressive strength due to this type of crack formation.

4.6.3.2 Evaluation of the Results with Strength Equation

The average value of experimentally determined \(C\) in Table XII is used to calculate the strength of the compact using Equation 4.6.7 and other data on bulk density and weight loss. The calculated strengths are used to draw a line in Figure 39, in which experimental points are also shown. It can be seen that the measured strength of specimens heat treated above 1000 °C are significantly lower than the predicted values of strength. This temperature coincided with the massive formation of cristobalite in the specimen (see Table IV); thus, this may be an indication that the formation of cristobalite may have caused microcrack formation and that this reduced the strength of the diatomite compacts.
Figure 39  The experimental data and the predicted strength.
It can be noted that the strength as well as the thermal conductivity of diatomite compacts increased with respect to the square of the relative neck radius, \( \left( \frac{a}{R} \right)^2 \) (see eqs. 4.6.6, p. 101 and 4.5.3, p. 75). Since both the strength and the thermal conductivity have the same form of equation, it appears that for a given diatomite specimen, the higher the strength, the higher will be the thermal conductivity.

In addition to bulk density and weight changes, both of these equations also contain several different factors some of which are functions of the packing of the particles. Consequently, the change of packing of particles should affect both the thermal conductivity and the strength of diatomite specimen. Besides, it might yet be possible to obtain a specimen with high strength with low thermal conductivity by carefully manipulating the other factors in these equations, such as \( k_s \) against \( \sigma_f \) and \( k_o \) against \( S_o \). For example, some kind of mineralizers such as a mixture of lime and nepheline syenite\(^{(37)}\) may restrict the formation of cristobalites, resulting in a diatomite compact with high \( \sigma_f \) and low \( k_s \). Alternatively the use of compounds of colloidal silica such as sodium silicate solution may increase \( S_o \) without significantly increasing \( K_o \).
5.0 VERIFICATION OF EQUATION WITH DATA OF COMMERCIAL DIATOMITE BRICKS

In the objective of this research project, it was stated that the purpose of this programme would be to develop an understanding of the factors affecting the properties of diatomite during firing so that the knowledge from this research project could be applied to benefit Clayburn Refractories Ltd.

In order to extend this work to commercial diatomite products, attempts were made to test some of the equations developed in previous sections with the data obtained from a commercial brand of insulating refractories, made from the same diatomite materials.

This particular brand of insulating bricks is the heaviest of all diatomite product lines manufactured in the Clayburn plant. The bulk density of these bricks is approximately 1.3 g/cc which is about twice as dense as the diatomite specimens made in the laboratory and tested in this project. Whereas the laboratory specimens were made from one ingredient, "diatomite", the commercial brick is made from mixtures of diatomite, sawdust and fireclay. Table XIII shows the physical properties and the chemical analysis of this refractory insulating brick.

A large number of unfired bricks of the size 9 x 4 1/2 x 2 1/2-in (229 x 114 x 64-mm) were collected from a production run. After being dried in a laboratory oven, the bricks were stored in a dry place.
TABLE XIII

Properties of Commercial Diatomite Bricks
(from published technical data of Clayburn Ref. Ltd.)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk Density</strong></td>
<td>1.20-1.35 g/cm³</td>
</tr>
<tr>
<td><strong>Cold Crushing Strength</strong></td>
<td>176-282 kg/cm²</td>
</tr>
<tr>
<td><strong>Thermal Conductivity</strong></td>
<td></td>
</tr>
<tr>
<td>Mean Temp. (120°C)</td>
<td>0.37 W/mK</td>
</tr>
<tr>
<td>(260°C)</td>
<td>0.41</td>
</tr>
<tr>
<td>(540°C)</td>
<td>0.51</td>
</tr>
<tr>
<td>(820°C)</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>Chemical Analysis</strong></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>67.1%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.2</td>
</tr>
<tr>
<td>CaO</td>
<td>1.1</td>
</tr>
<tr>
<td>MgO</td>
<td>1.1</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The dry densities of the bricks were found to be \(85.2 \pm 0.7\) p.c.f. (\(1.365 \pm 0.011\) g/cc). These bricks were then fired in a laboratory electric furnace at the same heating rate (\(5^\circ\)C/min) and over the same temperature range (between 200 and 1050 °C) as done before with the laboratory diatomite specimens. In this case however, when the firing temperature was higher than 650 °C, the furnace temperature was held at 650 °C overnight (16 hours) to oxidize the organic materials in these bricks. After firing, the following properties were determined: (1) shrinkage, (2) bulk density, (3) thermal conductivity and (4) strength.

5.1 Results and Discussion on Shrinkage and Density of Commercial Diatomite Bricks

5.1.1 Experimental Results of Shrinkage and Density on Commercial Diatomite Bricks

The results of the shrinkage and the bulk density are plotted against their firing temperatures in Figures 40 & 41. As shown in Figure 41, the bulk density dropped significantly between 200 and 500 °C. This was mainly due to the loss of moisture and hydrocarbons from sawdust and diatomite.
Figure 40  The experimental shrinkage data of commercial diatomite bricks.
Figure 41  The experimental bulk density data of commercial diatomite bricks.
5.1.2 Testing of shrinkage and Density Equations with Commercial Diatomite Bricks

The experimental data on shrinkage, weight loss and bulk density can be tested with Eq. 4.4.8 by plotting $\Delta L/L_0$ versus $[1 - (\rho_{Bo}/\rho_B)(w/w_0)]$. This is done in Figure 42. According to the model, the slope of the line should be $1/3$. Experimentally it has been found to be 0.334 confirming the validity of the equation.

5.2 Results and Discussion on Thermal Conductivity of Commercial Diatomite Bricks

5.2.1 Experimental Results of Thermal Conductivity on Commercial Diatomite Bricks

The thermal conductivity data of the commercial diatomite bricks are plotted against their firing temperatures in Figure 43. The drop in the thermal conductivity value up to $600^\circ C$ on heating corresponds to the drop of the bulk density in the same temperature range due to the mass loss from sawdust and diatomite in the raw material mixtures.

5.2.2 Testing of the Thermal Conductivity Equations with Commercial Diatomite Bricks

The thermal conductivity equation 4.5.6 as derived previously is given by:
Figure 42  Evaluation of the shrinkage equation using the experimental data of commercial diatomite bricks.
Figure 43  The experimental thermal conductivity data of commercial diatomite bricks.
\[
K = N \alpha k_s \left( \frac{\rho_B W_o}{\rho_{Bo} W} \right)^{2/3} - 1 \right) + K_o
\] (4.5.6)

In order to plot this equation, the value of \(k_s\) and the type of packing (which gives the values of \(N\) and \(\alpha\)) must be known. It is possible to assume that the value of \(k_s\) used previously for laboratory diatomite specimens may also be applied in the case of commercial diatomite bricks, as chemically and mineralogically they are very similar. On the other hand, it is not possible to determine the nature of the packing for commercial diatomite bricks, from which \(N\) and \(\alpha\) can be calculated, because the packing of particles in this system must be quite complex consisting of a heterogeneous mixture of different materials with different sizes. For these reasons, no attempt has been made to calculate the thermal conductivity values using Equation 4.5.6.

The conductivity data can however, still be tested with Equation 4.5.6 using the experimental bulk density and weight loss data, assuming all factors outside the bracket are constant. The experimental values are plotted in Figure 44.

As can be seen in Figure 44, the distribution of the experimental results of commercial diatomite bricks is almost identical to that of laboratory diatomite specimens. Since \(N\) and \(\alpha\) are almost constant for the temperature range of the tests, the increase in the slope for the specimen fired at 1050°C must be due to the increase of the \(k_s\) value because of the formation of cristobalite. It appears that the identical behavior of
Figure 44 Evaluation of the thermal conductivity equation using the experimental data of commercial diatomite bricks.
thermal conductivity on firing, for both the pure diatomite specimens and the commercial diatomite bricks, suggests that the sintering behaviour, the crystallization and the heat transfer mechanism for both systems are controlled mainly by the diatomite phase itself.

5.3 Results and Discussion on Strength of Commercial Diatomite Bricks

5.3.1 Experimental Results of Strength on Commercial Diatomite Bricks

The Compressive strengths of commercial diatomite bricks after firing at elevated temperatures were determined by the procedures described in previous sections. The results of the strength of these bricks are plotted in Figure 45. Similar to the strength of the laboratory diatomite specimens, the strength of the commercial diatomite bricks reduced slightly on heating between 200 and 500 °C but then increased at about 600 °C and especially above 800 °C.

5.3.2 Testing of Strength Equations with Commercial Diatomite Bricks

The strength and the density equation has been correlated by the following equation for pure diatomite specimens.

\[
S = C \cdot \left( \frac{\rho_B}{\rho_{Bo}} \right)^{2/3} W - 1 + \epsilon \quad (4.6.7)
\]
Figure 45 The experimental strength data of commercial diatomite bricks.
To test the applicability of this equation to the strength data of the commercial diatomite bricks, the strength was plotted as a function of "X" in Figure 46,

where

\[ x = \left( \frac{P_B}{P_{Bo}} \right)^{2/3} - 1 \]

The values of C and S o in Eq. 4.6.7 can be determined respectively from the slope, and the intercept of the line in Figure 46. The values were calculated to be \(1.95 \times 10^3\) kg/cm² and 87 kg/cm² respectively, with a correlation coefficient of 0.99. The corresponding values for pure diatomite specimens are \(4.65 \times 10^2\) kg/cm² and 23 kg/cm² respectively, reflecting that the strengths of the commercial diatomite bricks are higher than those of the pure diatomite specimens. This was expected as there was no extra binder phase present in the laboratory prepared diatomite specimens.

This study shows that the properties of commercial diatomite bricks are primarily controlled by the diatomite phase in the system. Normally, addition of a binder phase to the brick to increase the strength of brick will also increase the thermal conductivity. However, it appears that there may be still some possibility to modify the raw material compositions so that the thermal conductivity may not increase in direct proportion to the increase in strength.
Figure 46 Evaluation of the strength equation using the experimental data of commercial diatomite bricks.

\[ X = \left( \frac{\rho_B W_0}{\rho_{B0} W} \right)^{2/3} - 1 \]
SUMMARY AND CONCLUSIONS

The linear dimensional change, density, thermal conductivity and strength of diatomite compacts were determined after heating specimens in the temperature range 200 to 1050 °C. The mineral constituents in these heat treated specimens were also determined by the X-ray diffraction method, and the true density measurements were carried out using the pycnometric method. The data from these experiments was analysed using a model of sintering which was developed on the basis of observations of microstructural change in diatomite particles on heating. The following conclusions were made:

(1) The experiments on diatomite compacts were not affected by the laboratory treatments of grinding and compacting. The mechanical compaction of diatomite only increased the starting density and did not affect the rate of sintering.

(2) Quesnel diatomite transforms from amorphous silica to cristobalite above 950 °C. This was determined by X-ray diffraction.

(3) The linear dimensional change and the bulk density of diatomite specimens remained almost constant during the heat treatment of the specimen, up to 600 °C, but increased slightly between 600 and 800 °C and more drastically above 800 °C. To interpret the data of the change in the linear dimension and bulk density of diatomite compacts, a shrinkage equation has been developed using a sintering model, in which it is
assumed that after decomposition (i.e. weight loss) each diatomite particle is composed of a large number of microspheres. It has been shown from this model that the shrinkage and bulk density of diatomite compacts can be related by:

$$\frac{\Delta L}{L_o} = \frac{1}{3} \left( 1 - \frac{\rho_{Bo} W}{\rho_B W_o} \right)$$

The validity of this equation was tested with experimental data and it has been shown that the shrinkage can be predicted with reasonable accuracy from the weight loss and bulk density data.

(4) In the case of thermal conductivity, the conductivity value first decreased slightly on firing up to 600 °C and then increased above this temperature.

The thermal conductivity of diatomite compacts can be correlated to the bulk density and weight loss by the sintering equation,

$$K = N \alpha k_s \left[ \left( \frac{\rho_B W_o}{\rho_{Bo} W} \right)^{2/3} - 1 \right] + K_o$$

This has been developed by modifying Ramanan's equation for the electrical conductivity of powder compacts. This equation shows good agreement with the experimental data when the value of N and \( \alpha \) correspond to the single cubic packing. The value of \( k_s \) appears to change on heating due to cristobalite formation from amorphous silica in the diatomite, especially above 950 °C.
(5) The strength of diatomite compacts reduced slightly after heating specimens to between 200 and 400 °C, but increased above 600 °C.

The strength of diatomite compacts also can be correlated to the bulk density and weight loss by an equation similar to the conductivity equation.

\[ S = C \left[ \left( \frac{\rho_B W}{\rho_{Bo} W} \right)^{2/3} - 1 \right] + S_o \]

This equation also showed good agreement with the experimental data for specimens heat treated below 950 °C. The experimental values of strength were significantly lower than the predicted values for specimens heat treated above 1000 °C. This may be due to the microcrack formation during the crystallization of amorphous silica.

(6) Finally to test the general applicability of the equations developed in this research programme, attempts were made to apply these equations to the data obtained from a commercial brand of diatomite insulating refractories. The linear dimensional change, bulk density, thermal conductivity and strength of these bricks, determined after heating bricks in the temperature range 200 to 1050 °C, were tested with the equations developed for pure diatomite specimens. Good agreement was obtained between the strength data and equation, because most probably the added clay phase prevented crystallization of the amorphous silica phase into cristobalite. In the case of the thermal conductivity data, crystallization of the clay fraction into mullite most probably caused the disagreement between the predicted value and experimental data at 1050 °C.
REFERENCES


15. "Alpha Quartz", JCPDS diffraction data card, 5-0490.

17. "Tridymite (Low Form)", JCPDS diffraction data card, 3-0227.


APPENDIX

The Results of the Experiments Carried out by E.L. Calacal
TABLE 1

Sintering Stages of Quincy I Diatomite

First Stage: Pores Coalesce: The surface area by Hg porosimetry increases, pore diameter and total pore volume increase or may remain constant.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
<th>Surface Area Hg BET (m²/g)</th>
<th>Mid Pore Diameter (µm)</th>
<th>Total Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>-</td>
<td>9.9</td>
<td>21.4</td>
<td>0.23</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
<td>10.1</td>
<td>19.7</td>
<td>0.24</td>
</tr>
<tr>
<td>-</td>
<td>4</td>
<td>12.7</td>
<td>18.5</td>
<td>0.24</td>
</tr>
<tr>
<td>900</td>
<td>0.25</td>
<td>10.6</td>
<td>12.0</td>
<td>0.25</td>
</tr>
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<td>11.7</td>
<td>11.9</td>
<td>0.27</td>
</tr>
<tr>
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<td>0.25</td>
<td>11.6</td>
<td>11.6</td>
<td>0.24</td>
</tr>
<tr>
<td>1100</td>
<td>0.5</td>
<td>5.4</td>
<td>9.7</td>
<td>0.37</td>
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<tr>
<td>-</td>
<td>1.0</td>
<td>6.1</td>
<td>8.8</td>
<td>0.40</td>
</tr>
</tbody>
</table>
TABLE II

Sintering Stages of Quincy I Diatomite

Second Stage: The surface area increases. Total pore volume and mid pore diameter decrease.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
<th>Surface Area Hg BET (m²/g)</th>
<th>Mid Pore Diameter (μm)</th>
<th>Total Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>4</td>
<td>12.7</td>
<td>18.5</td>
<td>0.24</td>
</tr>
<tr>
<td>-</td>
<td>8</td>
<td>13.2</td>
<td>17.8</td>
<td>0.21</td>
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<td>11.7</td>
<td>11.9</td>
<td>0.27</td>
</tr>
<tr>
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<td>1</td>
<td>13.0</td>
<td>11.6</td>
<td>0.24</td>
</tr>
<tr>
<td>1000</td>
<td>0.5</td>
<td>6.3</td>
<td>10.1</td>
<td>0.34</td>
</tr>
<tr>
<td>-</td>
<td>1</td>
<td>6.4</td>
<td>9.3</td>
<td>0.34</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>6.5</td>
<td>8.0</td>
<td>0.35</td>
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</tbody>
</table>
# TABLE III

**Sintering Stages of Quincy I Diatomite**

Third Stage: The surface area and total pore volume decrease, mid pore diameter increases.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
<th>Surface Area Hg BET (m^2/g)</th>
<th>Mid Pore Diameter (\mu m)</th>
<th>Total Pore Volume (cc/g)</th>
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<tbody>
<tr>
<td>700</td>
<td>8</td>
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<td>0.21</td>
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<td>6.2</td>
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</table>
### TABLE iv

**Sintering Stages of Quincy I Diatomite**

**Fourth Stage:** The surface area and total pore volume decrease, mid pore diameter increases.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (hrs)</th>
<th>Surface Area Hg BET (m²/g)</th>
<th>Mid Pore Diameter (µm)</th>
<th>Total Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>16</td>
<td>4.8</td>
<td>6.0</td>
<td>0.33</td>
</tr>
<tr>
<td>1100</td>
<td>8</td>
<td>5.1</td>
<td>5.2</td>
<td>0.40</td>
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<td>3.8</td>
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<td>-</td>
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<td>3.0</td>
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<td>-</td>
<td>16</td>
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<td>2.7</td>
<td>3.61</td>
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</tbody>
</table>
Fig. 1: SURFACE AREA BY Hg POROSIMETRY VS TEMPERATURE IN HEATING QUINCY I DIATOMITE AT VARIOUS TIME SCHEDULES.
Fig. ii: PORE VOLUME VS TEMPERATURE IN HEATING QUINCY I DIATOMITE AT VARIOUS TIME SCHEDULES
Fig. iii: MIDPORE DIAMETER VS TIME IN SINTERING QUINCY I DIATOMITE