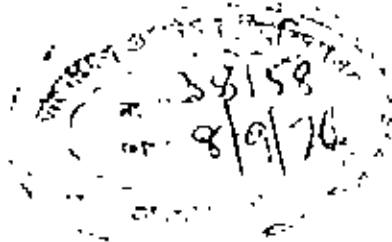


T. 49

REFRACTORY MATERIALS FROM LOCALLY AVAILABLE DEPOSITS

A thesis submitted to the Department of Metallurgical Engineering B.U.E.T., Dacca, in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Metallurgical).



July, 1976



By
Shahjohan Mridha
B. Sc. Engg. (Met.)

CERTIFICATE

This is to certify that this thesis work has been done by me under the supervision of Dr. Mohammed Ibrahim, Professor and Head, Department of Metallurgical Engineering, BUET, Dacca and it has not been submitted elsewhere for award of any other degree or diploma.

Countersigned.

M. Ibrahim

Supervisor

Amir Sha

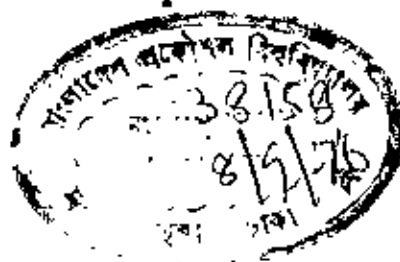
Signature of the author.



July 28, 1976

The undersigned Examiners appointed by the Committee of Advanced Studies and Research (CASR) hereby recommend to the Department of Metallurgical Engineering the acceptance of the thesis "REFRACTORY MATERIALS FROM LOCALLY AVAILABLE DEPOSITS" submitted by Mr. Shahjahan Mridha B.Sc. Engg. (Met.) in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Metallurgy).

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ABSTRACT

Refractory materials are used in almost every industry in which heat is employed and they are the principal construction materials of the domestic fireplace as to that of the largest furnaces employed in Steel-making. In all pyrometallurgical processes of metal extraction, refining and other hot-working processes, high temperature furnace is a must. Lining or refractory material is the deciding factor of using the furnace for a particular purpose. The property, nature and manufacturing methods of these widely used materials are yet so little known, that few people are aware of their enormous importance.

Like other developing countries Bangladesh has got a large number of Industrial furnaces in different Industrial Units for Metallurgical operations and other processes. Most of the lining materials of these furnaces are of fireclay type which are locally manufactured

from Mymensingh clay. No other refractory bricks of high or superduty types are made here and they are imported when needed. Silica brick is one of the high temperature refractory material and is widely used as high temperature construction material for Metallurgical furnaces. It has great mechanical strength, resistance to abrasion, and it retains its rigidity almost upto the melting point.

This research is an attempt to study the suitability of the local silica deposits for manufacture of refractory bricks. Attention was given primarily to the deposit of Shahajibazar, Chatrain and Noayapara of Sylhet district. Initially some fundamental properties of these raw materials were studied so as to know whether these raw materials can be used for making Silica Bricks.

It is essential to have raw materials in abundance for manufacturing any Refractory Bricks. Fortunately the deposits of Sylhet and Mymensingh are in abundance and their chemical compositions satisfy some of the fundamental requirements of the Refractory materials. During experiment some blending was necessary to enhance the binding property of the materials.

Few experiments were conducted initially in an Electric Furnace which showed some cracks. These cracks were subsequently minimized by adding grogs. The final experiments were conducted with standard size Silica bricks in the laboratory Kiln. Since coal, when imported

becomes a costly fuel, an experimental Kiln has been designed and constructed so as to fire the bricks by using natural gas which is abundantly available in Bangladesh. The bricks made with some binding materials and grogs were fired in this Kiln. The burnt bricks were found sound and they resist fusion temperature upto 1450°C . The impact test shows that the brick can resist impact of 2.34 lbs weight for a height of 118 inches.

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CHAPTER / 1

INTRODUCTION

The term refractory is applied to any material that has high resistance to fusion and is suitable for use as lining for industrial furnaces, converters, ladles, hot-metal storage mixers, furnace runners, fire boxes and other apparatus operated at high temperature (usually above 1000°C). Although the primary function of refractories is to withstand high temperature, they are usually called upon to resist one or more of the following destructive influences: abrasion by charges of material, a rapid temperature fluctuation, pressure, corrosion by slags and fluxes or chemical action by molten metals. Various combinations of the following physical properties of refractories are important in determining their utility: softening and fusion temperature, density, porosity, crushing strength, thermal conductivity, electrical conductivity, specific heat, dielectric properties and coefficient of thermal

expansion¹. As in all application of Engineering materials, the initial and upkeep costs are of prime importance in the selection of refractories for a particular purpose.

More than one hundred elements are widespread over the surface of the earth in different form of deposits and only a few of the deposits have both abundance and the ability to form stable refractories. These are silicon, aluminum, magnesium, calcium, chromium, zirconium, carbon etc². The compound of these elements, particularly oxides: SiO_2 , Al_2O_3 , MgO , ZrO_2 , Cr_2O_3 , CaO etc. are the refractory materials. The oxides of chromium is volatile and that of calcium is unstable in the atmosphere; however, they may be combined into useful materials such as dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$ or $\text{Cr}_2\text{O}_3 \cdot \text{MgO}$, the basic spinel. Carbon may be used directly after graphitization, or combined with silicon to form silicon carbide. Fortunately many of these compounds are found in deposits on earth's crust in sufficient purity to enable direct use as refractory material.

The earliest type of refractory used in the furnace was stone mainly silica rock or schist mica. The iron furnaces or forges were constructed mainly of this material in U.S.A. The first furnaces were built in Virginia, but it is quite certain that they were never completed. The first successful furnace was built in 1643 at Sanguis, Massachusetts, and the next year another was operated at Breintree². They were probably made from local stone, although there were no satisfactory deposits in this region. The building of furnaces and forges spread rapidly in the next hundred years, and considerable stone must have been quarried.

Stone was used for the building of furnaces and forges late in the nineteenth century because of the higher cost of firebrick. Even now, stone is used for lining Bessemer converters². A number of the old stone or stone and Brick furnaces are still standing at various part of the world. Two interesting ones stand on Furnace Brook in Bennington, Vermont in U.S.A.²

Record shows that sandstone was used as refractories for the walls of Kiln burning furnaces. Probably many of the early glass furnaces were built of stone. In fact Robert Hewes of the Temple Glass Company Temple, New Hampshire, states in a letter dated 1781, "I shall have to send sixty miles for stones to build my melting furnace, which will take eight teams". It is believed that these stones came from Uxbridge, Massachusetts, which is about sixty miles from Temple. Samples from the old furnaces confirm this².

The first silica bricks are believed to have been made by W.W. Young from Dinas rock in South Wales about 1842. A little later he made brick of ganister. Probably the first silica bricks made in the United States were manufactured by J.P. Alexander of Akron, Ohio, about 1866, but a patent was granted to Thomas Jones in 1858 for a lime bonded silica brick, and he may have manufactured before Alexander. In England lime-bonded silica brick was made even before this. J.R. Thomas made silica brick for the Steel Industry at Niles, Ohio, about 1872. He used quartz pebbles and a Sharon conglomerate and called the bricks "Dinas silica" as they were similar to the European brick of that name. A. Hall of Perth Amboy made some silica

bricks in 1875, but apparently there was no great demand for them. The modern silica brick of lime-bonded ganister is a very recent development. In the year 1899, the first silica-brick plant was started at Mt. Union in U.S.A, which later became a great centre. Silica brick were made later in Chicago district².

Probably the first clay refractories used were glass pots. They were probably made from English or German clays. This was mentioned by J.B. Felt in 1638. J.C. Booth in 1841 stated that a white plastic clay was wrought and exported for manufacture of crucibles and glass pots. Porcelain crucibles were made of Kaolin from Connecticut by a goldsmith in about 1807². Owing to the early development of iron and glass manufacture it was assumed to be used at an early date. And Firebricks appeared in the commercial market for furnace linings and other industrial purposes in 1827.

Lime often made from shells accumulated in the shore, was used in forges walls from very early times. There are references to a very early lime kilns².

Chromite, mainly in the forms of bricks, began to be used by the steel manufacturers about 1896, chiefly in a neutral zone between the acid and basic courses².

Magnesite as a steel-furnace lining was suggested in Europe as early as 1860 but did not come into regular use until 1880 when it was found that the Austrian material could be fitted down into a

good bottom. The brick was used commercially successfully by Carnegie Phipps and Co. at Homestead in 1888. Chemically bonded magnesite, magnesite-chrome and tar-bonded MgO have been made for a long time, but the direct bonded basic brick with a low amount of glass phase came into use in the late 1950².

High-alumina refractories were made after the discovery of bauxite. This was perhaps at the end of eighteenth century. In U.S.A. the first bauxite discovered near Rome, Georgia, during 1888².

One of the important development of refractories was the hot-face insulation or insulating firebrick. This product was pioneered by the Babcock and Wilcox Co. in the mid-1920. In the last 10 years, the use limit has been extended above 1650°C².

Alumina has been melted for abrasives since the beginning of this century. In the early 1920 Dr. Fulcher of Corning Glass works (USA) started making glass factories by fusion and casting. Alumina silica refractories were made at first but in mid 1930 Zirconia was added. This was disclosed in 1942 in USA. In the late 1950 basic fusion cast blocks became available to the steel industry².

Glass and mineral fibers have been in use for a long while as insulation, but demand for a higher use limit encouraged experimentation with more refractory silica-alumina glasses. U.S. patent by Harter, Norton, and Christie seems to be the earliest disclosure of a new highly successful method of forming wool from fused kaolin².

Recently synthetic and plastic refractories appeared in the commercial level for industrial use. Synthetic product is the latest development of Refractories. This has drawn the attention of the manufacturers and users of refractories because of the inaccessibility of raw material of the previously used for refractory bricks.

There are few Industrial Concerns in Bangladesh who are manufacturing Refractory Bricks using the local deposits as raw materials. Some local Ceramic Industries are using Mymensingh clay for manufacturing Fireclay bricks. But these bricks are not of super duty type. So the author took interest to find out some other deposits to manufacture high quality bricks.

It is found from the Geological Survey data that the chemical compositions and other properties of Sylhet Sand is near to that of Quartz. But this deposit lacks some binding property which may be enhanced by adding some binders. Lime and Clay which are locally available can usually be added as binding materials for the manufacture of Silica Bricks.

Since both Oil and Coal are imported fuels, attempt, therefore, has been made to fire the bricks with natural gas which is abundantly available in Bangladesh.

OBJECTIVES

The objective of the present Thesis work will be to study the suitability of the locally available deposit for the manufacture of refractory materials. For this work, the chemical composition of different deposits will be reviewed and if there be any lacking of binding materials the various deposits will be then blended to enhance the bonding property.

CHAPTER / 2

LITERATURE REVIEW

Refractory materials are usually found in the form of mineral substances, but artificial or synthetic substances of the same composition are also used and the term refractory material is also applied to bricks, retorts, crucible and other articles made of refractory materials.

Most of the commercial refractory materials are composed of oxides of different elements. It may be single oxide or associates of more oxides. It is to be remembered that pure-oxides have high refractoriness and any inclusion of other oxides or elements, decreases refractoriness. The fusion point and some other properties of few refractory materials are given in Appendix-B and Appendix-C.

Classification of refractories: According to J. Newton⁶ the refractories may be classified on the basis of the chemical nature.

Acid refractories: Alumina-siliceous materials. These materials occur in three forms:

- i. Natural rock
- ii. Prepared mass (fireclay)
- iii. Burned brick (firebrick)

Siliceous materials: This consists mainly of SiO_2 and must be low in metallic oxides and alkalis. They are commonly used in the following forms:

- i. Natural rock
- ii. Prepared mass
- iii. Electrically fused quartz
- iv. Quartz furnace sand (genister)

Basic Refractories:

A. Aluminium oxides: There are two important classes of these which also includes some high alumina refractories:

- i. Bauxite
- ii. Alundum (Electrically fused bauxite)

B. Oxides of Ca, Mg, and Ca: The common form are produced by calcining:

- i. Magnesite ($MgCO_3$) to give magnesia (MgO)
- ii. Limestone $CaCO_3$ to give lime (CaO)
- iii. Dolomite to give a mixture of lime and magnesia ($MgO.CaO$)
- iv. Magnesite-chromite

- v. Chromite magnesite
- vi. Chromite
- vii. Fosterite ($2\text{MgO} \cdot 5\text{SiO}_2$)

C. Iron oxides: These are used principally in the manufacture of wrought iron:

- i. Hematite
- ii. Magnetite
- iii. Blue Billy, a product consisting of Fe_2O_3 and Fe_3O_4 .

Neutral refractories: The aluminium silicate refractories are sometimes classified as neutral refractories, but they show an acid reaction when exposed to basic slag.

A. Forms of carbon:

- i. Graphite
- ii. Charcoal
- iii. Coke.

B. Chromites:

C. Artificial refractories: Most of these are manufactured in electric furnaces and are used for special purposes. Three typical refractories are as follows:

- i. Zirconium oxide
- ii. Titanium oxide
- iii. Silicon carbide

D. Rarer refractories: These are chiefly used in crucibles for experimental work. The following is a list of a few of these with their approximate melting points:

| | |
|----------------------------|--------|
| 1. Be_2O_3 | 2200°C |
| 2. CeO_2 | 1950°C |
| 3. La_2O_3 | 1840°C |
| 4. Ta_2O_5 | 1875°C |
| 5. ThO_2 | 2470°C |
| 6. TiO_2 | 1350°C |
| 7. Y_2O_3 | 2400°C |
| 8. ZrO_2 | 2570°C |

Budnikov⁴ has classified refractories as in Appendix-D.

Norton² has mentioned the mineralogical compositions of different types of refractory materials as in Appendix-E to Appendix-I.

Budnikov has also shown that Fosterite refractories are those containing from 35 to 55% MgO with MgO : SiO_2 ratio of between 0.94 and 1.33.

| | | |
|--------------------------------|-----|----------------|
| <u>Magnesium metasilicate:</u> | MgO | SiO_2 |
| | 40 | 60 |

Dunite:

| | | | | | | | |
|------------------------------|---|---|---------------------------------------|------------------------------|-----------------------------|----------------------------|--------------------------------|
| $\frac{\text{SiO}_2}{34-35}$ | $\frac{\text{Al}_2\text{O}_3}{0.1-0.7}$ | $\frac{\text{Cr}_2\text{O}_3}{0.3-2.0}$ | $\frac{\text{Fe}_2\text{O}_3}{2-6.1}$ | $\frac{\text{FeO}}{0.2-5.0}$ | $\frac{\text{CaO}}{0.12-1}$ | $\frac{\text{MgO}}{35-45}$ | $\frac{\text{MnO}}{0.14-0.22}$ |
|------------------------------|---|---|---------------------------------------|------------------------------|-----------------------------|----------------------------|--------------------------------|

Alc: It is one of the most widely used type of raw material for ceramic works. Its chemical composition is

| MgO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ +FeO | CaO | Calcining loss |
|------------|------------------|--------------------------------|-------------------------------------|-----------|----------------|
| 26.15-34.7 | 30.9-35.89 | 1.4-4.99 | 7.99-10.4 | 0.63-7.01 | 15.57-26.38 |

Dinas is a refractory material containing at least 93% SiO₂ made from quartz rocks with lime or other binder, and fired at temperature ensuring polymorphic transformation of the silica (quartz) into tridymite and cristobalite.

Silica, SiO₂ by far the most plentiful of all the refractory oxides is without doubt, the most important material in the ceramic industry. Its melting point is about 1726°C. As a high temperature refractory, silica brick has been manufactured for a century and is the standard construction material for many furnaces. To meet increased demands, improved silica refractories are now made and it may be used at higher temperatures than the old standard grades. This has been accomplished primarily by increasing the purity of the silica.

Twichert³ has stated that silica owes its acid characters and is mainly of two kinds: those composed mainly of silica and those composed mainly of aluminium silicates (Appendix-D). Silica, itself occurs in several forms. Quartz and chalcedony are common silica minerals while quartzite, sandstones and sand are composed largely of free silica in the form of quartz. Gneiss is another name for quartzite.

Modifications of silica and their properties

It is reported that silica exists in a number of allotropic forms. The form stable at room temperature is quartz; at about 870°C, this alters to tridymite and at about 1470°C the tridymite alters to cristobalite. Quartz can also exist in the form of an amorphous quartz glass (vitreous silica or fused quartz). The reverse changes of these allotropic forms are very sluggish, and it is possible for tridymite, cristobalite and vitreous quartz to exist infinitely at room temperature. Quartz has a density of about 2.65, but the densities of cristobalite and tridymite are 2.26 - 2.30, when quartz is heated, therefore, there is a considerable volume expansion caused by the allotropic changes over and above the normal expansion caused by heating.⁴

Budnikov has shown that the most abundant form of SiO_2 in nature is found as quartz sand, quartzites, different kinds of rock crystal, as an integral part of igneous rocks, sandstones, and as an impurity in clays and kaolines.

Properties of silicabrick

According to Cahel⁵, silica is polymorphous and the crystalline inversions which occur places definite limitations on the manner in which silica refractories may be used. Refractories of silica is an excellent and widely used refractory and it is used in construction of many high temperature Metallurgical furnaces; it has great mechanical strength and resistance to abrasion, and it retains its rigidity almost up to the melting point of the cristobalite. It has

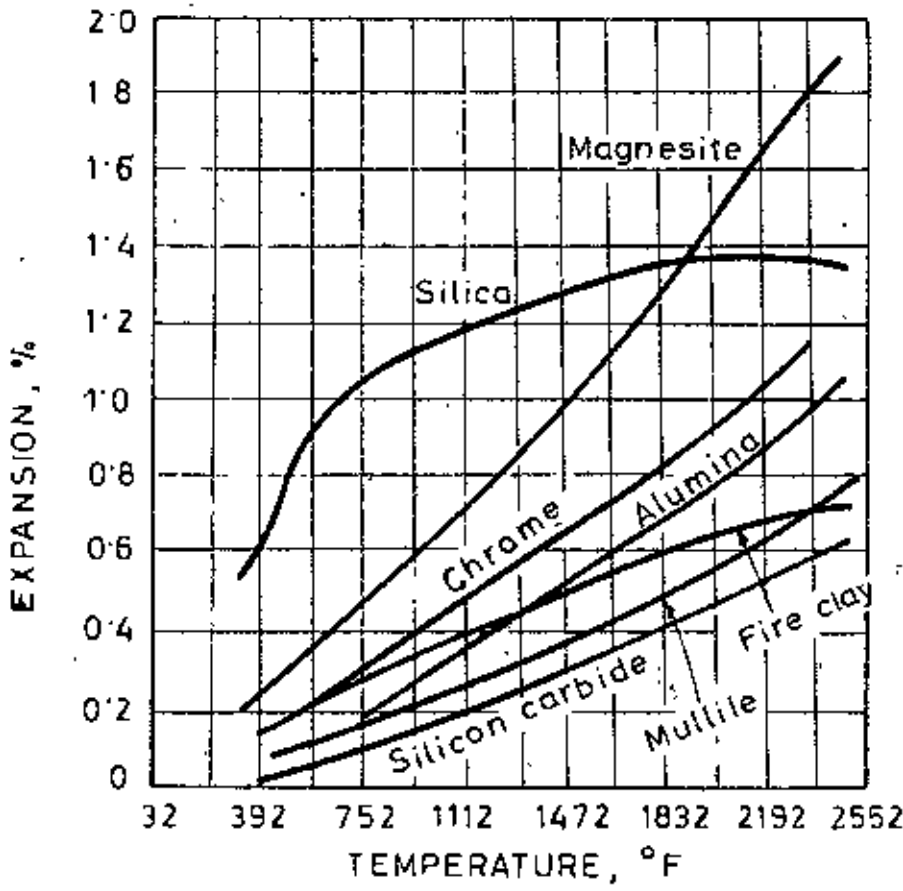


FIG. 21 THERMAL EXPANSION OF HIGH TEMPERATURE MATERIALS.⁵

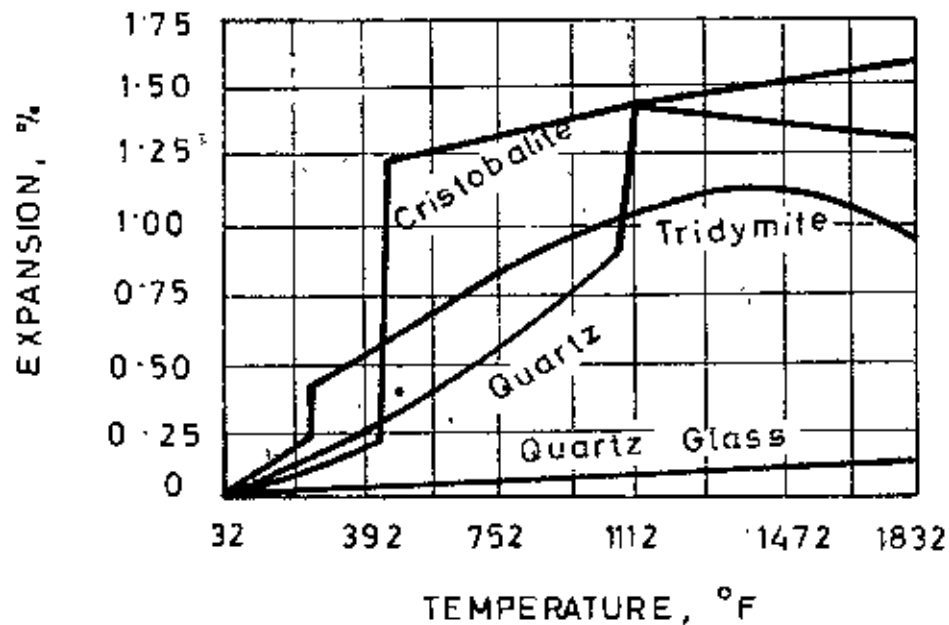


FIG. 22 THERMAL EXPANSION OF DIFFERENT TEMPERATURE OF SILICA.⁵

a comparatively high thermal conductivity and a high resistance to corrosion by acid slags. Silica refractories have excellent thermal resistance for example, in certain temperature ranges because of negligible thermal expansion (see Fig. 2.1 and Fig. 2.2), but very poor thermal shock resistance in other temperature ranges because of large volume changes associated with crystalline inversions. Vitreous silica, however has excellent thermal-shock resistance at all temperatures because of its very low thermal expansion. Silica can not be used at high temperature under reducing conditions owing to the formation of the volatile product, and this limits the use of silica refractory.

Raw material

It is reported that the basic raw materials for making dines are quartzites of the cement and crystalline varieties, containing atleast 95% SiO_2 . All the properties of quartzite are of important in the production of dines. They include type, fracture, microstructure, chemical composition, refractoriness, porosity, mechanical strength and susceptibility to firing.⁴

It is also reported that Ganiater is the most commonly used silica mineral for refractories. It is a common name for quartzite. Not all the quartzite are suitable for making refractories, as they must be of high purity and have good mechanical strength. A few typical analyses of quartzites are shown in Appendix-A. The fusion point of quartzite is very close to 1700°C and it shows

little softening below its melting point. This is its chief value when used as refractory, as it retains its resistance to load at high temperatures than fireclay materials. Most silica refractories are made in the form of bricks or special shapes, but some gneiss is used in rammed furnace bottom².

Lime: Budnikov has stated that for binding the quartzite grains in the green ware, for obtaining a strong product during firing, and for speeding up transformations of the quartz from one modification into another, lime is usually added in the form of milk of lime. The amount of lime added, in terms of CaO , ranges between 1.5% to 2.5% depending on the purpose for which the product is intended and its specifications as to refractoriness. For low temperature refractory, the addition of lime may be high but for high temperature brick it must be a minimum amount.

Investigation has shown that the lime has to be completely slaked so that no unslaked lumps are left in the milk. The accumulation of lime in the form of lumps is dangerous, since it is converted into CaO during firing, and if the lime is stored for a long time where moisture from the air can affect it, the lime begins to slake intensively, increasing in volume and causing the development of cracks.

Poorly slaked lime may also cause cracking of the green ware through hydration, particularly during drying. Unslaked lime is delivered in lumps at least 50 mm in diameter. The amount of fine and slaked

lime permitted in it is not more than 5%. The colour of the crushed large lumps should be the same inside as outside. Unslaked lime should not contain any impurities, pieces of slags, coal, ash, or anything else⁴.

Mineralizers: It is said that a number of different mineralizers are added to dinas charge in order to bind the quartz grains into a monolithic mass and also to speed up alteration of the quartz into high temperature modification (cristobalite and tridymite). If there are no mineralizers, 'dry' alteration occurs accompanied by a considerable expansion in the volume and loosening of the dinas.

Budnikov has pointed out that lime is a fairly strong mineralizer. The use of water-dissolved mineralizers is limited by the fact that when the green ware is dried and fired they emerge onto the surface of the part, where they melt out and form discolouration.

According to F.H. Khan⁷ the mineralogical compositions of some important refractory deposits at different places of Bangladesh are as in Table No. 2.1 to Table No. 2.4. From the mineralogical composition it is found that the deposits of Bijaypur of Mymensingh and Sahajibazar, Chhatrain, Noyapara, Balijuri of Habiganj subdivision under Sylhet district are very important and useful.

Mymensingh deposit

According to the classification and requirements of refractory materials it appears⁸ that the deposit of Mymensingh can be used

for the manufacture of chamotte exclusively. With the addition of Bauxite i.e. increasing alumina content, this deposit is made suitable for fire clay refractories of different grade. Since Bauxite is not available in this country, it has to be imported and thus increasing the cost of product. Fireclay refractories are already being made for long years by blending bauxite to this deposit. Bricks of low grade and medium duty can be made without blending. Addition of bauxite may be discarded by dressing the deposit and thereby increasing alumina content. The manufacturers of fireclay refractories are mainly Mirpur ceramic works Ltd. and Dacca refractory Ltd.

Sylhet deposit

Minerological investigations show that the deposits of Shahajibazar, Moyapara and Chhatlain are very close to that of quartz and sand and according to the requirements for silica brick these deposits are suitable for the manufacture of silica brick. Since no attempt has yet been made to use this sand for refractory purpose. The author took these deposits for his research project. Lime as a binder is abundantly available in Bangladesh.

For experimental purpose about half a ton of the deposits were collected. These sands are washed products from the Hills near Chhatlain, Shahajibazar and Moyapara. The deposit is abundant. So it could be used as a raw material for any industrial purpose if found suitable in composition and other properties.

Table No. 2.1The chemical composition of white clay from Hilsipur, Nymensingh

| SiO_2 | R_2O_3 | Fe_2O_3 | Fe | Mg+Ca | Alkali |
|----------------|------------------------|-------------------------|-----------|-------|-----------|
| 57-83 | 18-40 | 1.59-1.80 | 1.11-1.56 | Trace | 0.30-0.70 |

Ferruginous Conglomerate

| Total insol. (SiO_2) | R_2O_3 | Fe | CaOMgO | Loss in pigment |
|---------------------------------|------------------------|-------|--------|-----------------|
| 46-65.15 | 28-42 | 17-25 | Trace | 6-10 |

Ferruginous sandstone

| Total insol. | R_2O_3 | Moisture |
|--------------|------------------------|----------|
| 64.55 | 35 | 0.60% |

Table No. 2.2Chemical composition of Sylhet glass sand.

a) Balizuri glass sand which covers about 14 square miles. The total reserves is about 3,30,000 tons.

| SiO_2 | Al_2O_3 | Fe_2O_3 | CaO. MgO. |
|----------------|-------------------------|-------------------------|----------------|
| 98.10 to 98.87 | 0.014 to 1.09 | 0.15 to 0.29 | 0.007 to 0.014 |

b) Novapara-Chhatiaia sand

| SiO_2 | Al_2O_3 | Fe | TiO_2 | CaO | MgO | Loss |
|----------------|-------------------------|--------------|----------------|--------------|--------------|--------------|
| 95.08 to 95.52 | 3.01 to 3.03 | 0.10 to 0.13 | 0.15 to 0.20 | 0.05 to 0.06 | 0.28 to 0.35 | 0.40 to 0.48 |

Water washed sample

| <u>SiO₂</u> | <u>Al₂O₃</u> | <u>Fe</u> | <u>TiO₂</u> | <u>CaO</u> | <u>MgO</u> | <u>Loss</u> |
|------------------------|------------------------------------|-----------------|------------------------|------------|------------|-----------------|
| 95.04 to 96.40 | 2.48 to 2.57 | 0.06 to 0.07 | 0.15 to 0.17 | Trace | Trace | 0.28 to 0.40 |

c) Nayapara - Shahaji Daxar

| <u>SiO₂</u> | <u>Al₂O₃</u> | <u>Fe</u> | <u>TiO₂</u> | <u>CaO</u> | <u>MgO</u> | <u>Loss in Ignition</u> |
|------------------------|------------------------------------|-----------|------------------------|------------|------------|-------------------------|
| 95.52 | 3.01 | 0.13 | 0.20 | 0.06 | 0.35 | 0.40 |
| 95.08 | 3.03 | 0.10 | 0.15 | 0.05 | 0.28 | 0.48 |

Water washed sample

| <u>SiO₂</u> | <u>Al₂O₃</u> | <u>Fe</u> | <u>TiO₂</u> | <u>CaO</u> | <u>MgO</u> | <u>Loss in Ignition</u> |
|------------------------|------------------------------------|-----------|------------------------|------------|------------|-------------------------|
| 96.40 | 2.48 | 0.06 | 0.15 | Trace | Trace | 0.28 |
| 95.84 | 2.57 | 0.06 | 0.15 | " | " | 0.40 |

Table No. 2.2

Chemical composition of the sand deposits of Chaudhgrem police station in Comilla.

a) Joyantingar - Nayapara area

| <u>SiO₂</u> | <u>Al₂O₃</u> | <u>Fe₂O₃</u> | <u>CaO</u> | <u>MgO</u> |
|------------------------|------------------------------------|------------------------------------|------------|------------|
| 95.94 | 2.22 | 0.48 | Nil | Trace |
| 96.90 | 1.74 | 0.32 | " | 0.04 |
| 97.12 | 2.24 | 0.06 | " | 0.10 |
| 96.06 | 2.52 | 0.17 | 0.04 | 0.07 |
| 97.32 | 1.93 | 0.33 | Nil | Trace |
| 97.86 | 1.50 | 0.10 | Nil | Trace |

b) Jagannath Dighi, Duttasagar area

| <u>SiO₂</u> | <u>Al₂O₃</u> | <u>Fe₂O₃</u> | <u>CaO</u> | <u>MgO</u> |
|------------------------|------------------------------------|------------------------------------|------------|------------|
| 94.32 | 3.80 | 0.72 | 0.25 | 0.12 |
| 94.90 | 3.80 | 0.36 | 0.22 | 0.04 |
| 95.12 | 3.63 | 0.29 | 0.30 | 0.04 |
| 91.48 | 5.16 | 0.64 | 0.04 | 0.10 |
| 97.34 | 1.63 | 0.21 | 0.01 | 0.17 |

Table No. 2.4

Chemical composition of the sand deposit of Brahman Baria Bhatar area, Maulvi Bazar Subdivision in Sylhet.

| <u>SiO₂</u> | <u>Fe₂O₃</u> | <u>Al₂O₃</u> | <u>CaO</u> | <u>MgO</u> |
|------------------------|------------------------------------|------------------------------------|------------|------------|
| 96-98.17 | 0.01-0.22 | 0.50-3.27 | 0.09-0.99 | 0.03-0.29 |

Washed sand

| | | | | |
|-------------|-----------|----------|-----------|-----------|
| 92.24-96.83 | 0.24-1.28 | 1.5-3.63 | 0.11-1.82 | 0.12-0.72 |
|-------------|-----------|----------|-----------|-----------|

CHAPTER / 3

KILN USED FOR BURNING REFRACTORIES

Kilns have been used for many thousands of years, as their remains are frequently found in the excavations of ancient sites of early civilization. The primitive kilns were without any type and in most cases, consisted only of a firing chamber, a perforated floor, and a wall. The construction of a permanent kiln was too much of a structural problem for most of the early potters, and recourse was made to a temporary roof of green poles and raw clay, which would hold in place long enough for the very low temperature of firing used at that time. There is, however, one exception, as a kiln was found in Tepe Gawrat that was believed to have had a permanent roof at a period as early as 4500 to 4000 B.C.².

Fuels for Kilns: In the ancient period kilns were fired by fire wood. Recently they are fired with coal because of its availability, low

cost and because the refractories are not particularly sensitive to impurities in the kiln gases that might arise from using coal as a fuel. The coal is generally burned in furnaces with sloping or flat grates as shown in Figure 3.1. The manufacturers of refractories generally prefer for the kilns a good grade of bituminous coal giving a long flame; also a low ash content and a high fusion point of the ash are desirable².

Oil has many advantages as a fuel for firing refractories; and in some localities the cost compares favourably with coal. Advantages of oil are better temperature control, higher temperature, a generally cleaner kiln atmosphere, and smaller labour requirements. Oil, of course, obtainable in a number of different grades; but from the cost standpoint, the heavier grades of oil are generally used. For oil fired kiln, special type of burners are used. They break up the oil into a spray of fine particles and intimately mix it with the air blast. The heavier oils have to be heated and must be kept hot until they actually reach the burner; otherwise the viscosity will become so great that proper spray is impossible. A good filter that will permit cleaning without shutting down the oil flow is necessary². The arrangement of firing over the charge by means of downdraft is shown in Figure 3.2.

Use of Natural Gas: Bangladesh lacks both oil and coal as fuels and they are also costly ones when imported. The present price hike of the oil through out the world made its use more difficult. Fortunately Bangladesh has got abundant quantity of good quality natural gas

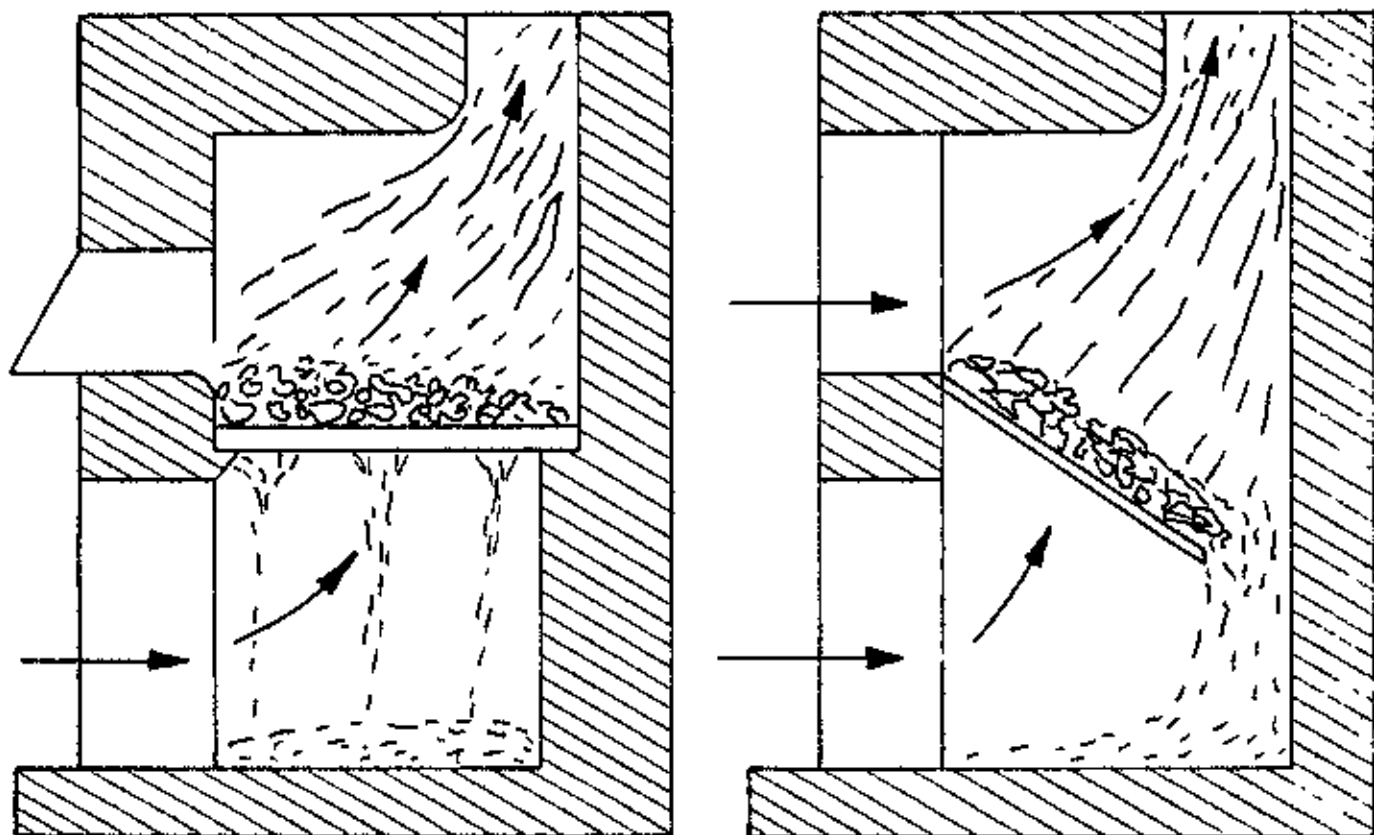


FIG 3'1 KILN FURNACES WITH FLAT & SLOPING GRATE²

which can replace the use of oil and coal in industries with some modification of burners and furnaces.

Natural gas is now available in many countries since the second world war. Many kiln firing refractories now use this fuel often with standby supplies of propane for periods when the gas supply is inadequate. Natural gas is an ideal fuel, as it produces a clean, easily controlled heat. There are many types of natural-gas burners available for the kiln. In the older installation, only primary air was mixed with the gas, while secondary air was drawn in around the burners. This method did not allow a satisfactory control of temperature and atmosphere. To day, all the air is introduced into the burner giving excellent combustion control². A typical burner shown in Figure 3.3.

Design Factors: It is found that in dealing with the early kilns as well as modern ones, four essentials must always be present. 1) a means for producing heat, 2) a support for the ware, 3) a container such as the walls and crown to confine the heat in the working space, and 4) a means to transfer the heat from the source to the ware².

In designing the kiln the following factors are to be taken into consideration.

a) Transfer of heat: One of the most difficult problems in kiln design is to transfer the heat efficiently from its source to the ware. The problem is difficult in the kiln because the ware is

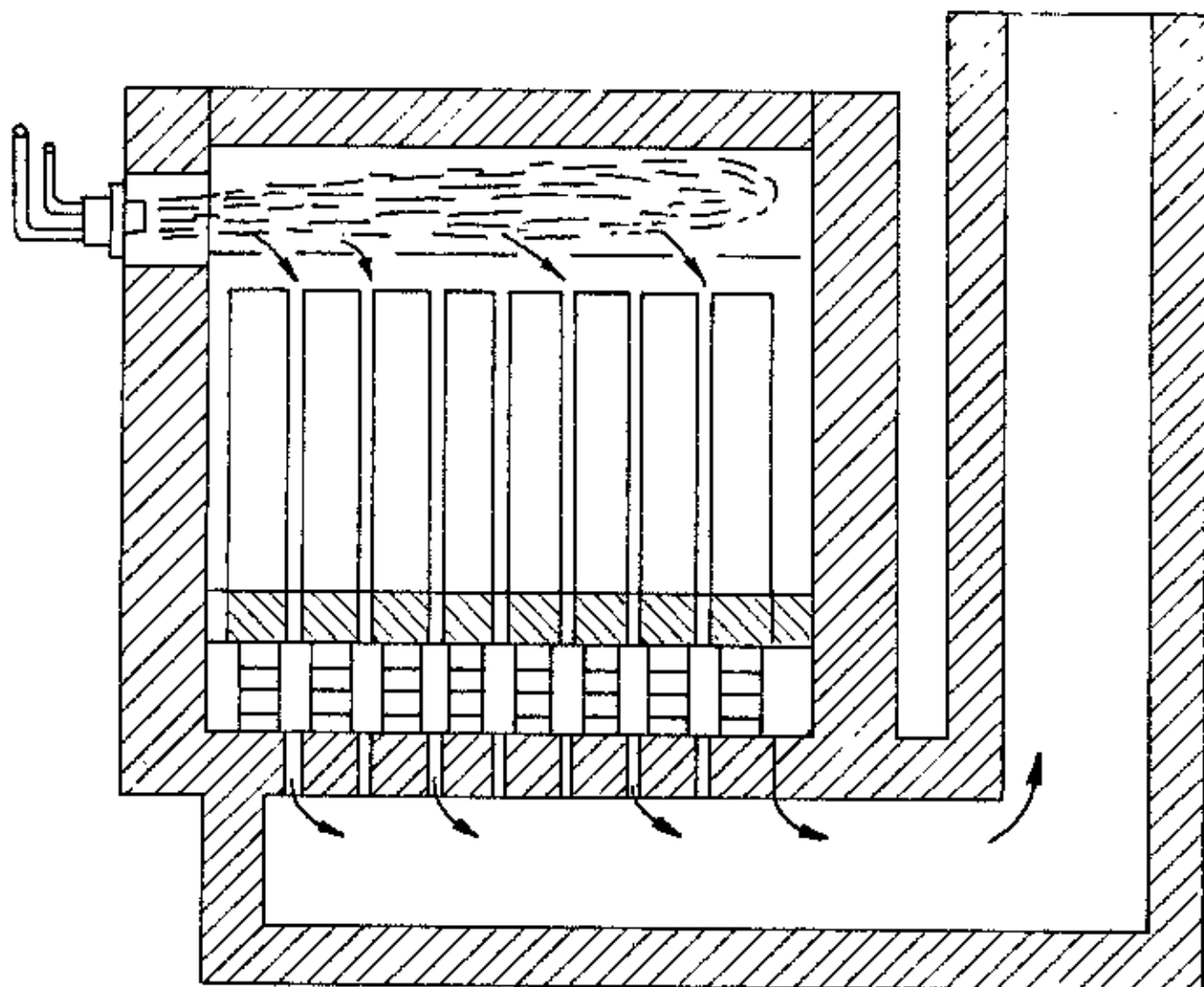


FIG. 3'2 AN OIL-FIRED KILN IN WHICH THE FLAME
PASSES ABOVE THE CHARGE.²

small units stacked into a considerable volume and therefore radiant heat transfer so important in the furnaces such as those used in the Metallurgical industry, can play little part. For the same reason conduction of heat into a bulky charge of small units is of little consequence. Therefore, one must rely entirely upon convection for heating of the charges².

The transfer of heat from a moving stream of gas to a solid surface depends mainly on the temperature between the gas and solid and the velocity with which the gas is passing by the solid. The curve in Figure 3.4, gives an idea of the rate of heat transfer under different conditions between gas and solid. The transfer of heat from the moving gas by radiation from the gas itself and the incandescent particles that it contains are quite important in furnaces of large volume and great flame thickness. However, in this kiln, where the gas stream is divided into relatively thin layers, this radiation can not play a very important part and so radiant heat transfer is not taken into account in designing laboratory kiln².

b) Equalization of temperature: One of the most important problems in kiln design is to produce a uniform temperature throughout the volume of the charge. This is by no means an easy matter. Almost every kiln shows a difference of less than 50°F from top to bottom of the charge. In Tunnel kilns, with small cross section, the temperature uniformity is better; but here again it is apt to vary from place to place in the car by an appreciable amount².

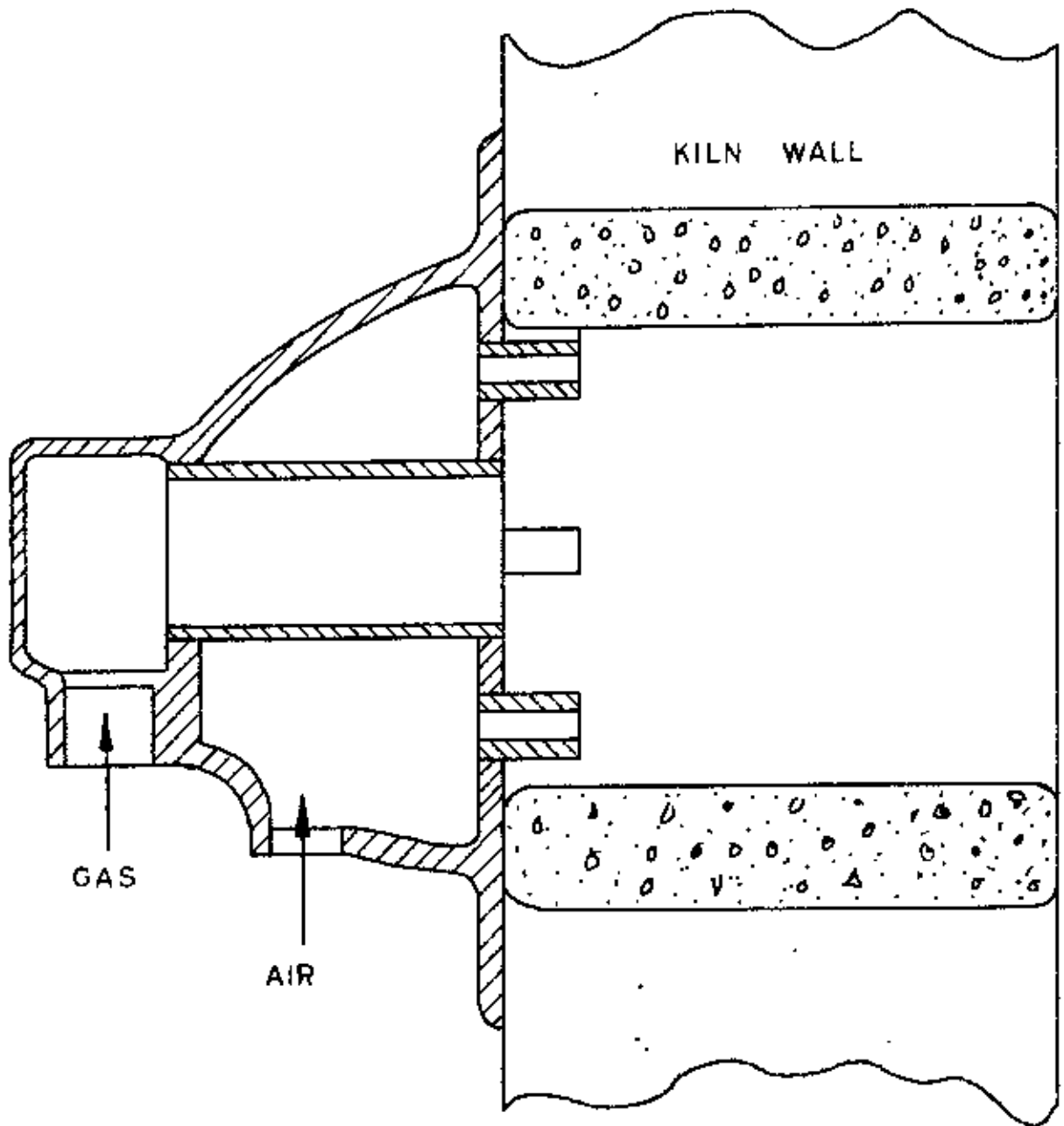


FIG. 33 GAS BURNER²

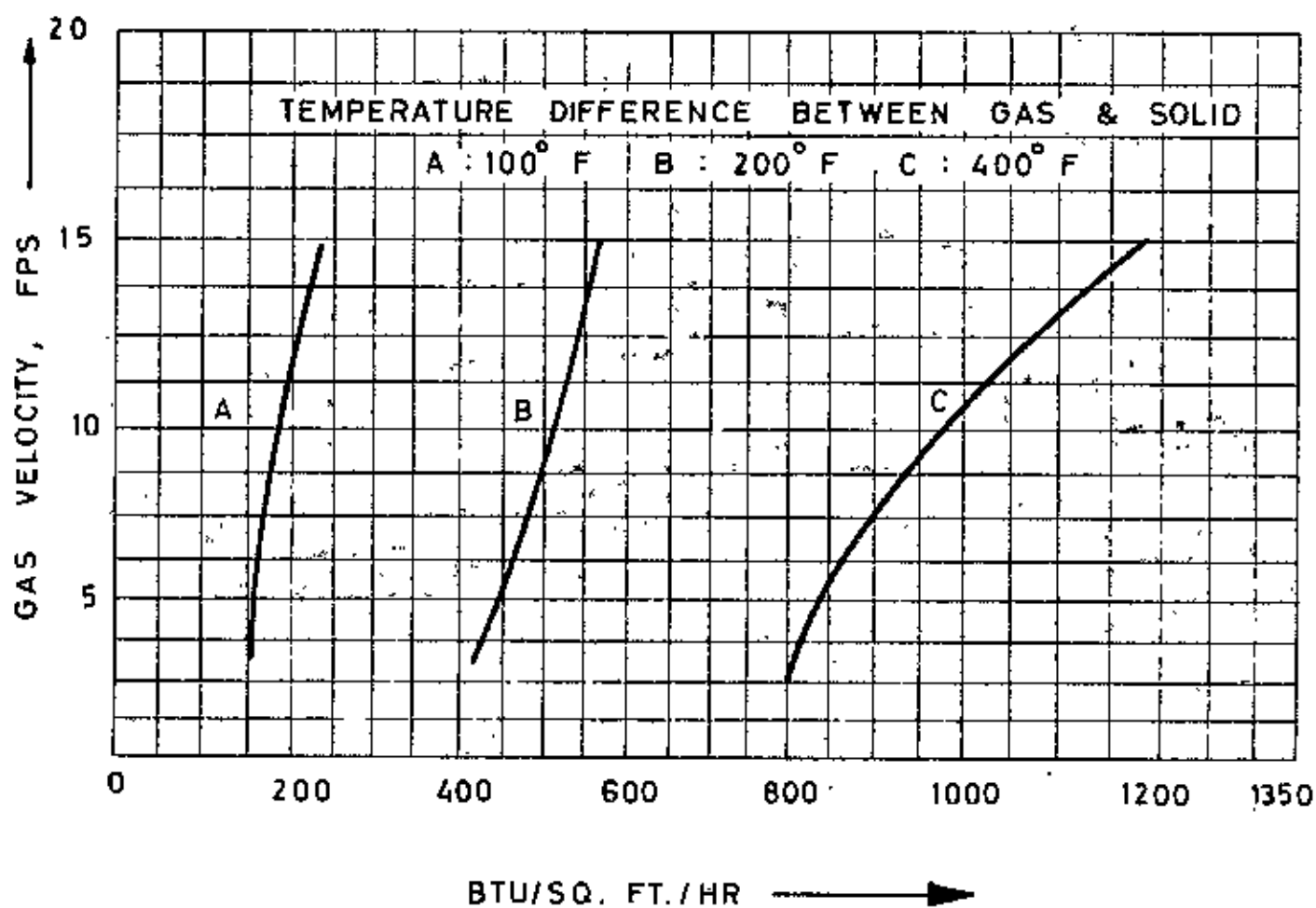


FIG. 3-4 RATE OF HEAT TRANSFER BETWEEN GAS & SOLID²

It may be shown that under equilibrium conditions the temperature difference between top and bottom is related to the mass flow of gases (Figure 3.8).

If M = weight of gases flowing through the channel in unit time.

S = Heat lost between top and bottom by transfer laterally through walls per unit time, then

$$S = (t_1 - t_2) C_p M, \quad C_p = \text{specific heat of gas.}$$

So it may be concluded that a more even temperature is obtained by a large volume flow, which may be realized by the addition of excess air to the products of combustion. This equation also shows that insulation of the kiln walls will give a more even temperature distribution.

Another method of equalizing the temperature is to recirculate the combustion gases through the charges. In this way a large volume flow is obtained thus decreasing the temperature difference (Figure 3.9). The only difficulty with the recirculation method is the practical problem of handling the high temperature gases. At the lower temperature encountered in heat treating furnaces, gases can be recirculated with water-cooled, alloy fans at temperature upto 2000°F (1100°C); but above this the only possible method is by injection action, a method quite successful in driers but one that has not been developed for kilns at the present time. Recently, recirculation has been used successfully in some tunnel kilns at the preheating end².

- (a) Loss in cooling ware
 (b) Loss through walls
 (c) Flue loss

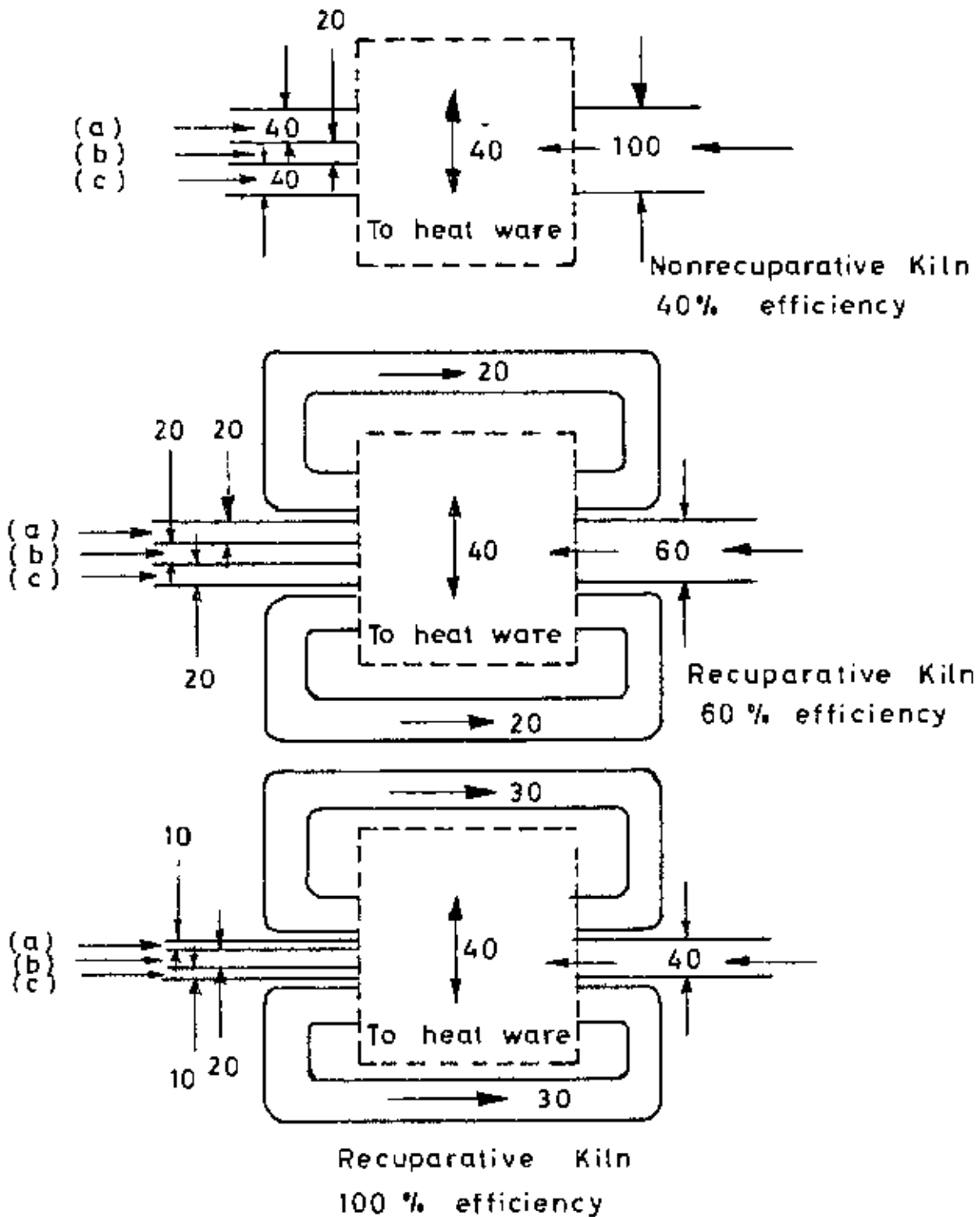


FIG. 3'5 HEAT BALANCE DIAGRAMS²

The equalization of temperature at right angles to the path of flow is readily accomplished by adjustments in the floor openings, so that the hotter areas have the openings reduced and the cooler areas have then enlarged. By trial and error, a very uniform temperature can be attained over the horizontal cross section of the charge².

One often hears the kiln fireman state that he uses a damper or a close-set floor to back up the heat in the kiln and give a more uniform temperature². It is not generally understood, however, just what the effect of dampers and restrictions to the flow accomplish. The curve in figure 3.4 show clearly the great increase in the heat transfer from the gases to the charge with increasing velocities. The point in the kiln where the flow is restricted has an increased velocity, and thereby more heat is transferred from the gas to the charge. As the usual problem is to raise the temperature at the bottom of the charge, it is possible to have a relatively open setting in the charge itself and as small floor openings as are permitted by the available draft. Owing to the high velocity through the floor openings, the heat from the gas will be given upto a much greater extent at the floor than in other parts of the charge and will therefore tend to compensate for the gradual cooling of the gas as it goes down through the charge.

Insulation of the kiln tends to increase the uniformity of inside temperature, because 1) it tends to keep the inside walls of the kiln at a more uniform temperature, and because 2) an insulated

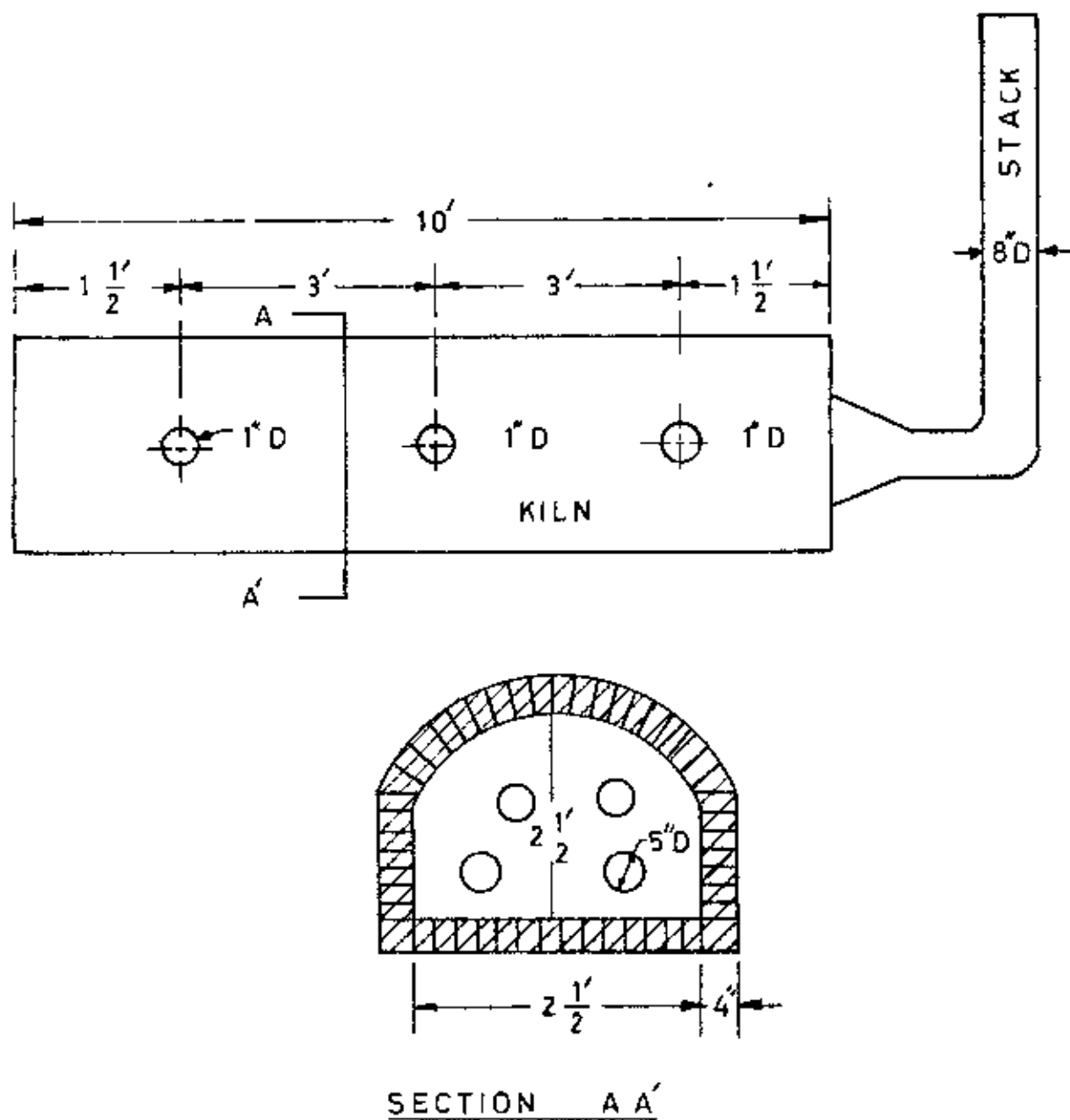


FIG. 3'6 EXPERIMENTAL KILN WITH DIMENSIONS

kiln requires less fuel and therefore, the gases entering the kiln can be at a lower temperature. Also the insulation of the walls of the kiln increases the uniformity of temperature by minimizing the heat loss as the gases pass through the charge².

The Laboratory kiln that has been made for firing refractories is an end-fired one. No other specific factors are considered for temperature distribution in the kiln except the gas velocity. Recirculation method is not applicable for high temperature kiln (above 1450°C). Insulation, bottom openings and damper will be a too complicated and costly proposition for this laboratory kiln. More over the kiln is so small that damper and bottom openings methods for equalizing temperature can not be attained. So the gas velocity is the only temperature uniformity factor in the laboratory kiln.

c) Kiln Efficiency: The efficiency of the kiln is usually defined as the ratio of the heat required to bring up the ware to its maximum temperature divided by the amount of heat supplied by the fuel. This definition is perfectly logical when applied to the periodic kiln; but when it is used under conditions where recuperation occurs, then it may become absurd, as efficiencies of over 100 per cent have been determined on actual kilns. This can be made clear by the set of heat balance diagrams shown in Figure 3.5 beginning with a non recuperative kiln and ending with one having a high recuperative effect. It is seen that the heat required to

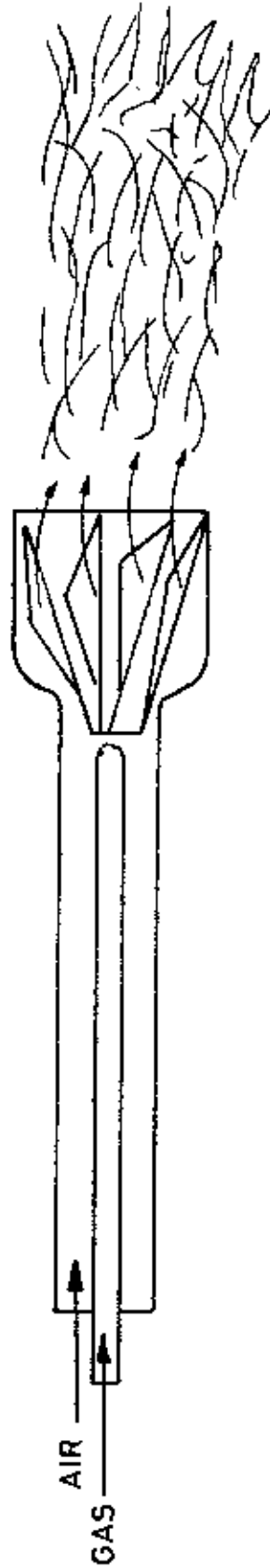


FIG. 3'7 GAS BURNER

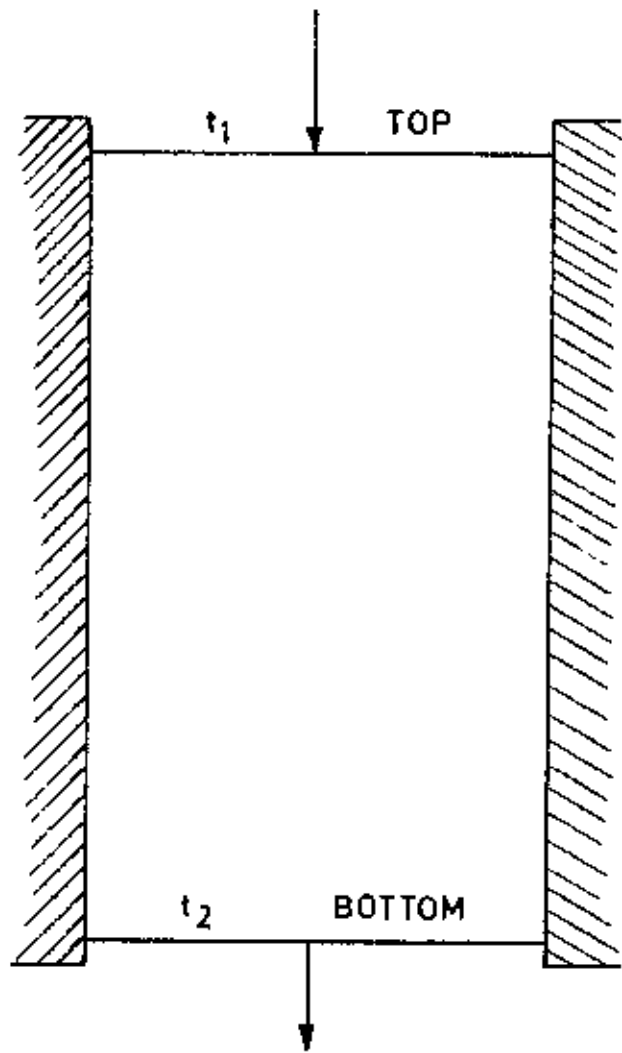


FIGURE. 3'8

bring up the ware upto temperature is the same in each case but the external heat supplied to the kiln becomes progressively smaller as the recuperative action increases².

It should be stated here that a high degree of kiln efficiency is often incompatible with good uniformity of temperature because high efficiency demands a low temperature of the gases and these, in turn, mean a low temperature of the charge at the bottom of the kiln. Only by recuperative action or recuperation a good temperature uniformity can be obtained together with high efficiency. The laboratory kiln used is so small in length (10 feet) that the exhausts carry away large quantity of the heat. Larger tunnel kiln and recuperation system could be designed but the construction would have not been possible for lack of space and materials needed for it.

For experimental purpose a small size laboratory kiln has been designed and constructed. Dimensional details of the kiln have been given in Figure 3.6.

It is obvious that the insulation of kilns will increase their efficiency, but unfortunately very few data are at hand to show just what the saving might be, as there is seldom an opportunity to compare similar kilns, one of which is insulated and the other not.

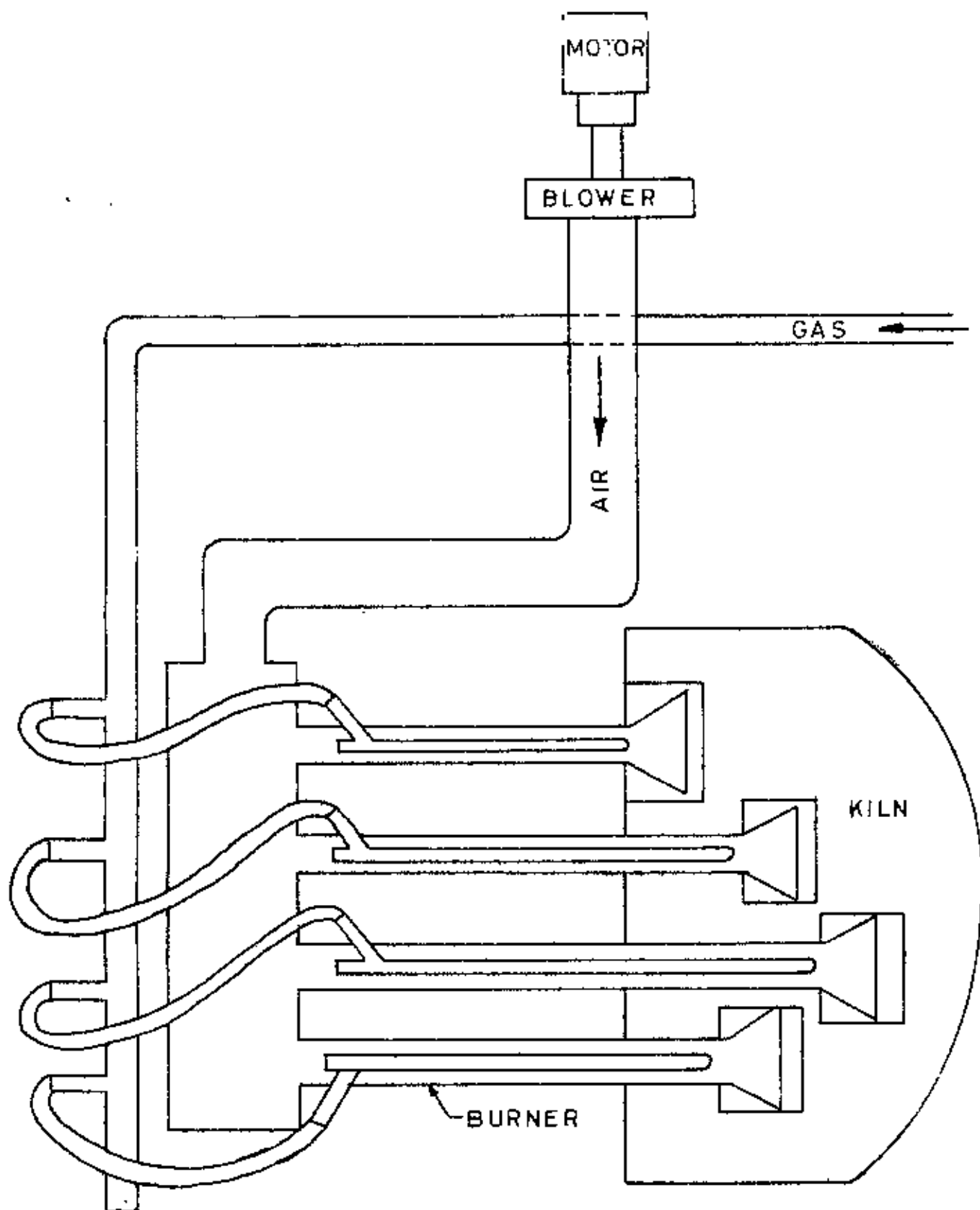


FIG. 3-9 EXPERIMENTAL SET-UP

Burners: Four gas burners of equal capacity are designed and constructed. Since there is no need to atomize the gas as in oil, the gas is sprayed in the furnace by simply passing it through perforated disc tube. No secondary air is supplied. All the air passes around the gas and provision is made to control air and gas individually for individual burners. The air is twisted at the exit of the gas for better mixing. The details of the burners are shown in Figure 3.7. Both air and gas can be centrally controlled and gas supply is recorded from the meter. The schematic diagram of the experimental set up is shown in Figure 3.9.

CHAPTER / 4

EXPERIMENTAL STUDIES AND DISCUSSIONS

Several experiments were carried out just to study the material for its suitability in making refractory bricks. Experiments were carried out in two phases: One in the form of smaller size bricks which are fired in the Silicon Carbide furnace and the other in the form of commercial size bricks which are burnt in a gas fired laboratory kiln.

FIRST PHASE

The furnace used for firing the smaller bricks is shown in figure 4.1(a). A steel mold of 4"x3"x2" inner dimensions was used for making the brick samples. Handles are used for ease of withdrawing the brick from the mold. From the analysis of the sand (Table No.2.2) it is found that both the Noyapara and Shahajibazar deposits contain 2.46 to 2.57% Al_2O_3 and traces amount of CaO .

EXPERIMENTS

1st experiment: Attempts were made to manufacture bricks with the Noyapara sand but it lacks green strength to hold the size and shape of the brick. Moreover on drying it was observed that the brick spalled out to small particles. On grinding the sand in Ball mill to about 100 mesh, no improvement was found in green strength. So the deposit can not be used exclusively as self binding material for manufacturing silica bricks.

2nd experiment: Lime, CaO, was used as binding material upto 2% in addition to the amount present in the sand. The same problem of lack of green strength was found as in 1st experiment. No mechanical press or Hydraulic press was used to press the mixture to the shape. It was manually rammed to the shape in the mold.

3rd experiment: Three bricks of 4"x3"x2" size were subsequently prepared with CaO content of 1%, 7% and 8% with enough water to increase the green strength. The lime added was very fine and was thoroughly mixed. The green strength was enough to hold the shape but on drying it was found very fragile and was not possible to handle conveniently. Of course, the strength after and before drying was apparently found increasing with increase of lime content. The size of the grain remained as that of the original deposit.

After sun drying the bricks were held at 130°C for 4 hours to remove the mechanically held moisture. The bricks were then fired upto 1450°C in the furnace for 25 hours. It was very slowly heated from 300°C to

600°C. Total time required to raise the temperature was 12 hours and held at 1450°C for about 13 hours before being cooled to room temperature. The products are shown in Figure 4.1(b) and 4.2(a).

Almost all the bricks showed cracks of different sizes at different places. These cracks may be due to :- 1) Non homogeneous mixing of the binding material, 2) rapid heating and cooling, 3) Mixture were not well compressed, 4) Crack may originate during drying cycle due to lack of sufficient binding material and other causes.

4th experiment: Experiment number 3 was repeated with finer grain size (100 mesh) and fired at 1500°C for 17 hours. The fired bricks showed trace cracks indicating some improvement. The products are shown in Figure 4.4(a,b,c).

5th experiment: Further grinding of this sand to 150 mesh followed by heating at 1400°C for 20 hours did not show any improvement.

6th experiment: In this experiment Mymensingh clay and Mirpur clay were used individually as binding materials. With increased percentage of clay the bonding property was found improving. With 16% Mymensingh clay the brick showed enough bonding property. It was fired at 1400°C for 18 hours. The colour of the burnt brick was bright ash and some cracks were visible. With 16% Mirpur clay the green strength found better and on burning the bricks showed ash colour and no cracks were found (Figure 4.3(d)). These bricks were found heavier than that of 16% Mymensingh clay and other types. But these types of bricks have

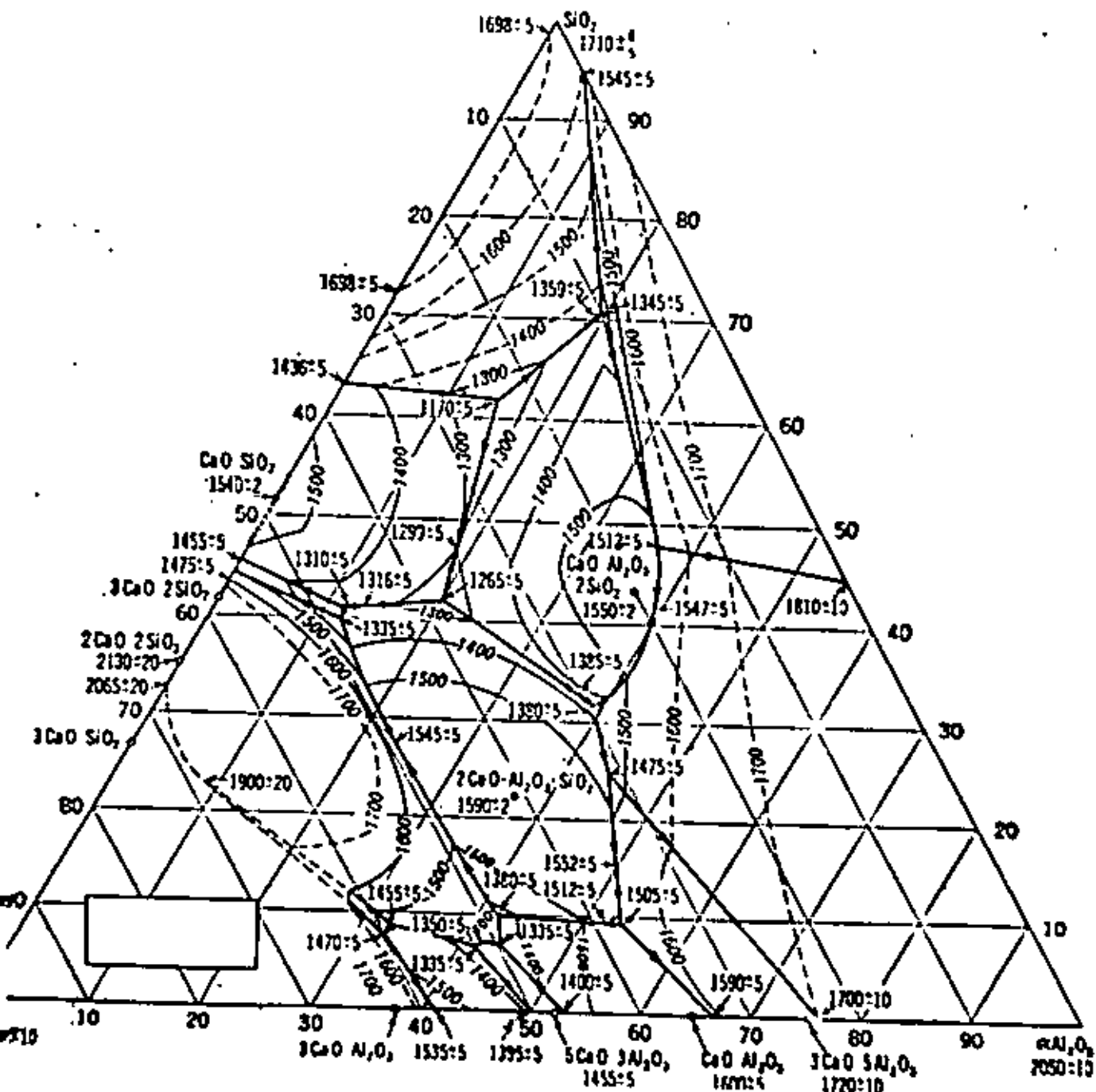


Fig. 4.5 The $\text{CaO-SiO}_2-\alpha\text{Al}_2\text{O}_3$ Equilibrium Diagram

got less fusion point and hence they will not serve the purpose of refractoriness. This is also confirmed from the phase equilibrium diagram of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ (Figure 4.5).

7th experiment: A series of bricks with different types of binding materials and grog were prepared and burnt at a temperature of 1450°C for 30 hours. The percentage compositions of the bricks were as follows:-

| | | |
|--------------------|-------|------------|
| 1. CaO | 10% | |
| Sand | rest. | |
| 2. CaO | 12% | |
| Sand | rest | (10% grog) |
| 3. Mirpur clay | 10% | |
| Sand | rest | |
| 4. Mymensingh clay | 10% | |
| Sand | rest | |
| 5. CaO | 10% | |
| Mymensingh clay | 5% | |
| Sand | rest | |
| 6. CaO | 10% | |
| Mirpur clay | 5% | |
| Sand | rest | |

All the bricks had enough green strength and bricks No. 6 found to have greater strength than others. After burning the bricks made of grog showed little cracks. So the addition of grog has decreased the cracks. The addition of Mirpur clay made the brick heavier and the colour was bright brown. Mymensingh clay also changes the brick into

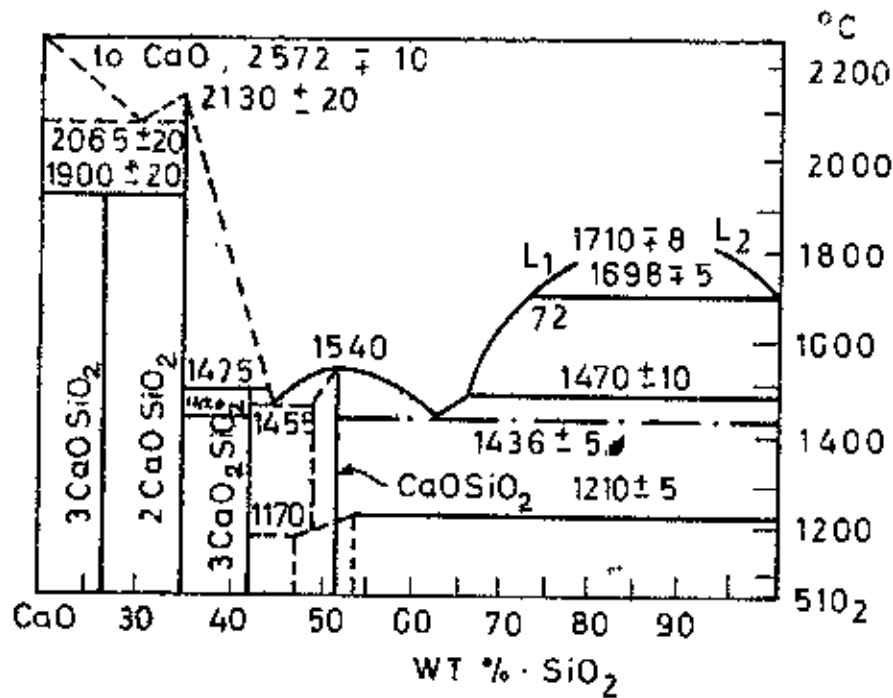


FIG. 4'6 THE SiO_2 - CaO EQUIL. DIAGRAM^B

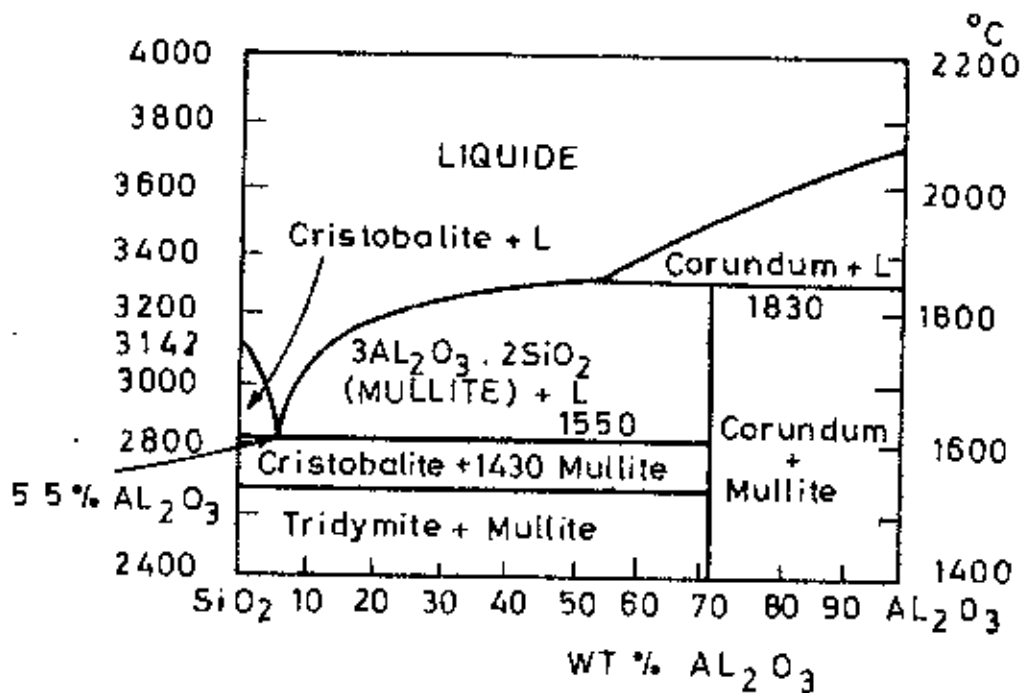


FIG. 4'7 THE SiO_2 - Al_2O_3 EQUILIBRIUM DIAGRAM^B

ash colour. The addition of CaO to Mirpur clay and Mysnasingh clay made the brick stronger on drying but decreased the fusion point. At the furnace temperature of 1450°C, brick no. 6 started to fuse (figure 4.3(c)) but did not show any crack.

From these experimental data it was found that lime as binding material would not be suitable for making silice bricks as the brick has got little strength after drying and would not be stacked in the kiln for burning. The addition of Mirpur clay or Mysnasingh clay along with lime has overcome the problem. Experiments with sample bricks in the electric furnace showed that some percentage of Mirpur clay or Mysnasingh clay will give better result regarding the bonding property and crack. But the fusion point will abruptly decrease with the addition of these clays. This can be shown from the equilibrium diagrams of CaO - SiO₂ (Figure 4.6) and CaO - Al₂O₃ - SiO₂ (Figure 4.5). So these materials must be added to minimum quantity. From the experimental results it may be concluded that CaO and Mysnasingh clay should be added within the minimum limit of 10% and 5% respectively. Although CaO can be added upto 28% without any change in fusion temperature (Figure 4.5). The grog addition has showed some improvements regarding the burning crack. The second phase and final experiments were carried out with Mysnasingh clay and lime as the binding material and their use were restricted within these maximum range.



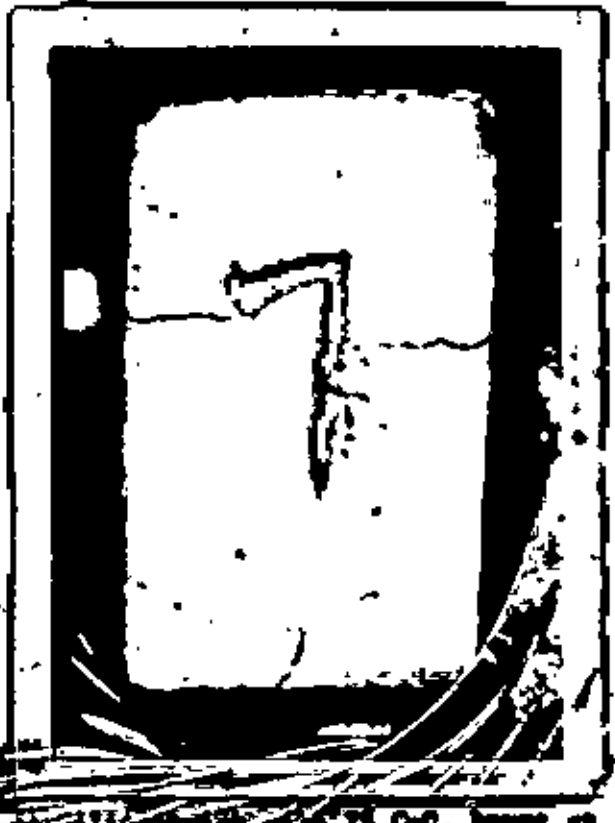
a) Silicon Carbide Furnace.



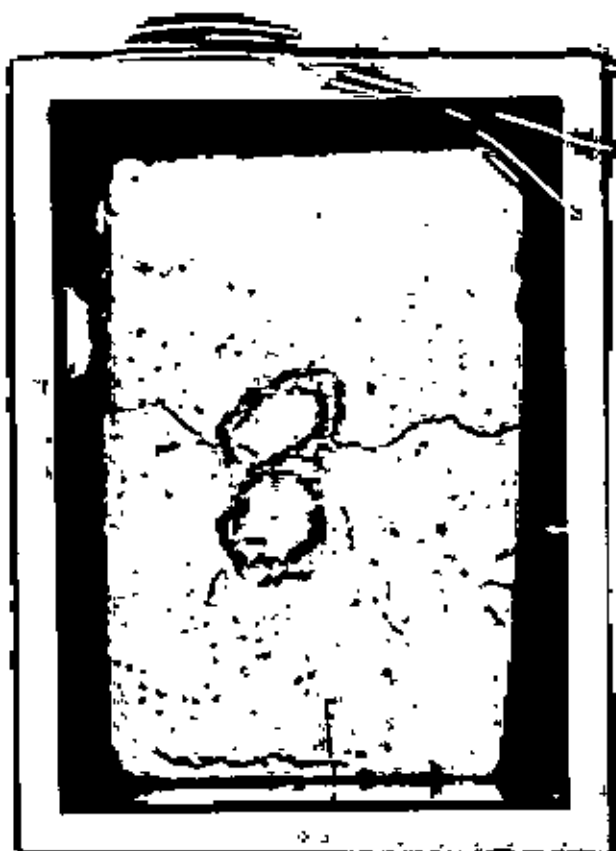
b) Steel Mold



c) Silicon Brick



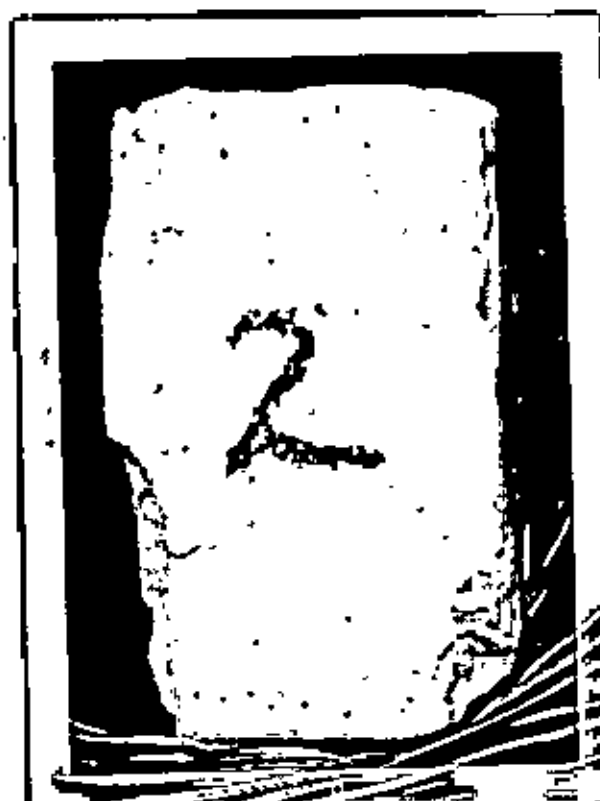
d) Silicon Brick with 7% CaO, burnt at 1450°C.



a) Silica brick with 5% CaO burnt 1450°C.



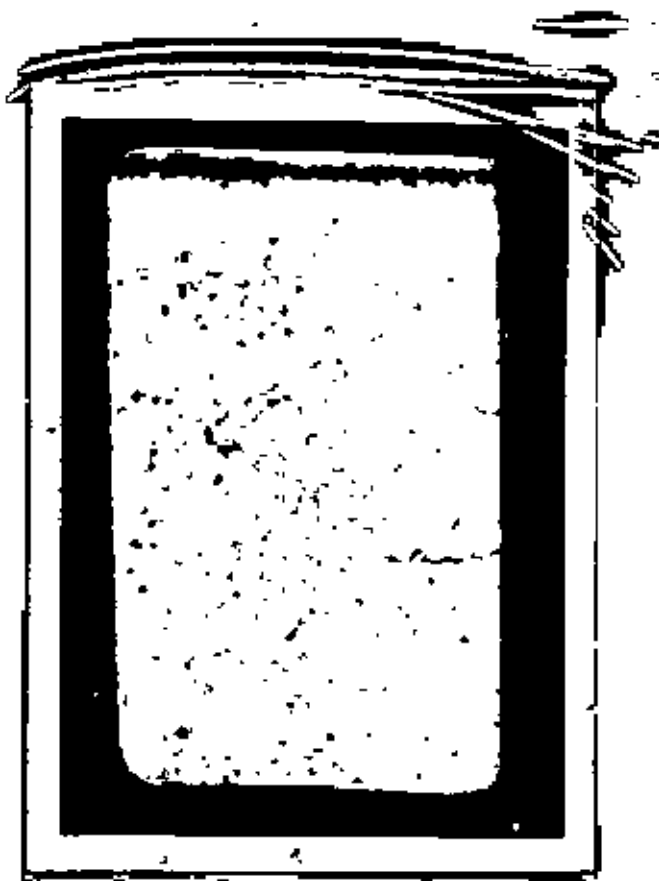
b) Brick containing 10% CaO in Expt. No. 7.



c) Brick containing 20% CaO, Expt. No. 7.



d) Brick containing 40% CaO, Expt. No. 7.



a) Brick containing 10% Hymen Singh clay in Expt. No. 7.



b) Brick containing 10% CaO & 15% Hymen Singh clay.



c) Brick containing 10% CaO & 15% Karper clay.



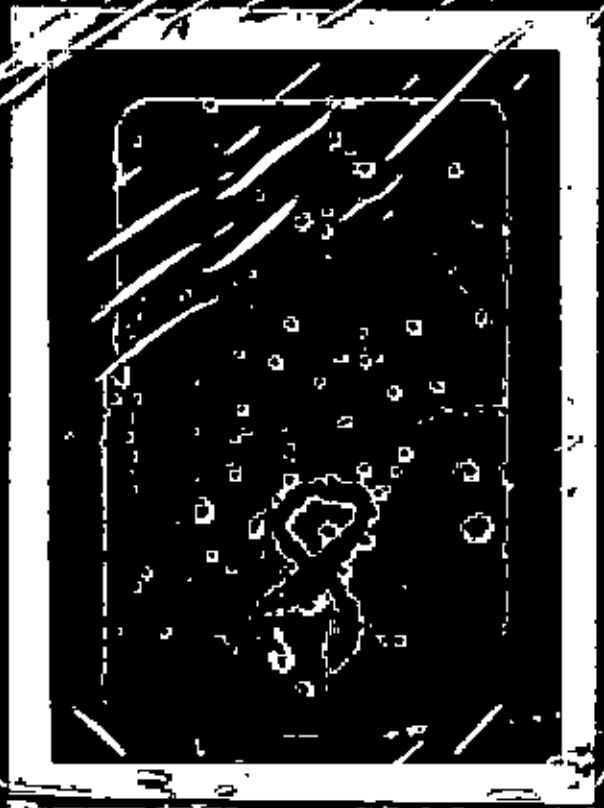
d) Brick containing 10% CaO & 15% Hymen Singh clay.

FIGURE 4.3



a) Silica brick with 3% CaO in Expt. No. 4.

b) Silica brick with 7% CaO in Expt. No. 4.



c) Silica brick with 3% CaO in Expt. No. 4.

SECOND PHASE

The final experiments were conducted in a kiln made of fire clay-bricks for a capacity of about 500 bricks of standard size. The design and the construction of the kiln are given in a separate chapter. Coal is an imported fuel in Bangladesh, hence provision is made to burn the kiln by Titas Gas which is comparatively a cheaper fuel and locally available.

Some experiments about firing of the kiln with burners were made and the length of the flame was accordingly adjusted. Air was introduced with gas and by trial the length of the flame was adjusted within 20" from the mouth of the burner.

1st Experiment: 400 ordinary clay-bricks of commercial size were procured and some firing experiments were made to determine the range of temperature and the quantity of gas and air needed for the appropriate temperature range in the kiln. There had not been sufficient gap in the first stacking of the clay bricks. The burning flame was, as a result, reflected back; the chimney of the kiln was not long enough to create natural draught. The stacking was then corrected and the kiln was fired. During initial firing there happened an explosion in the kiln. It was due to the leakage of gas in the burner that was accumulated in the kiln and on first firing the kiln, the explosion took place causing some damage in the walls and roof of the kiln. To avoid this type of explosion, the kiln is initially purged before firing so that any gas accumulated will thus be removed.

2nd Experiment: The kiln was charged with 150 commercial size ordinary clay-bricks. The bricks were sun dried before they were stacked on the floor of the kiln. Few sand bricks made with 10% lime and 5% Mysoreingh clay of usual size were also placed on the floor of the kiln along with they clay-bricks. The sand bricks were meant to use them as grog for the subsequent experiments in manufacturing the silica bricks. The kiln was then fired with gas without any air except the amount that was sucked along with the gas at the entrance of the burners. Air was blown after three hours and the gas supply was then kept 4 cfm. After about half an hour the front bricks were found to sack resulting a lumpy mass. There was no arrangement to record the temperature of the kiln. The temperature was guessed to be about 1000 to 1050°C which is about 100°C above the firing temperature of ordinary clay bricks.

3rd Experiment: Next experiment was performed with 150 sun dried clay-bricks which were heated for 6 hours with gas supply of 3 cfm. The bricks burned out to be 2nd grade, i.e. 2nd class bricks.

4th Experiment: Commercial size sand bricks with 10% lime and clay 5% were then prepared and dried. This time the kiln was charged with only 16 bricks at about 4'-6" away from the firing end of the kiln. Three holes were provided along the side wall of the kiln at different distances in order to introduce the thermocouple for recording the temperature in the kiln. The gas supply was maintained at 3 cfm. and the temperature was found to be 800°C. The temperature of the kiln was then raised to 1450°C and kept constant for 12 hours. The bricks

was then cooled very slowly in the kiln. The burnt bricks showed some hair cracks at different levels. The bricks were then stacked on the floor in an open atmosphere, the hair cracks were increasing day by day and after few days all the bricks spalled out to small particles. After investigation it was found that the lime and the clay were not thoroughly mixed with the sand particles before they were shaped in the brick mould; the kiln temperature and holding time were not sufficient to cause vitrification and the chemical reaction was delayed due to improper mixing of lime and clay with the refractory sand. Hence during the stacking period, moisture was absorbed from atmosphere through the cracks by the free lime of the bricks resulting swelling and spalling out (Figure 4.8(a,b,c)).

5th Experiment: 60 bricks of standard size were prepared with the following proportions:-

| | | |
|------|---|------|
| CeO | - | 10% |
| Clay | - | 5% |
| Grog | - | 5% |
| Sand | - | rest |

The grogs were of the following sizes

| | |
|-------------------|------|
| 8 to 10 mesh size | 50% |
| 10 to 30 " " | 30% |
| up to 100 " " | rest |

The sand was of the same size as collected from Noyapara and Chhatrain in Sylhet. The clay and lime were of about 200 mesh size. The bonding property was found increasing with thorough mixing of the materials. Grog again decreases the green strength. To avoid the cracking or accumulation of CaO, CaO powder was mixed with proper amount of water and then other materials were mixed with this slurry.

In this experiment both Seger Cones and thermocouple were used for temperature measurement. The Seger Cones were collected from Institute of glass and ceramics and were of the following numbers and temperatures.

| <u>PCE No.</u> | <u>Fusion temperature</u> |
|----------------|---------------------------|
| 05 | 1000°C |
| 08A | 1050°C |
| 1A | 1110°C |
| 3A | 1150°C |
| 6A | 1215°C |
| 8 | 1250°C |
| 10 | 1300°C |
| 12 | 1350°C |
| 14 | 1410°C |

The kiln was fired on February 17, 1975 at 8 A.M. and continued upto 10 A.M. of February 19, 1975 (50 hours). All the cones except PCE No. 14 fused and PCE No. 14 started to bond. So the highest

temperature of the kiln was near about 1400°C . Using radiation pyrometer the temperature recorded to be 1425°C , but in thermocouple it showed only 1330°C . The rate of gas supply in the kiln and the rate of heating and cooling are shown in the table No. 4.12. No extra air was supplied except the amount sucked in the kiln from the entrance of the burners.

During heating cycle the stack of the brick was dismantled and about 60% of the bricks crumbled and the rest burnt sound. (Figure 4.9(a,b)). The crumbling of the stack may be due to the faulty stacking of the bricks and so some part of the bricks carrying the highest load sagged at the kiln temperature.

The bricks showed few hair cracks at different levels. It may be due to the lack of bonding and it may also cause during heating and cooling cycle. The bonding may be improved by thorough mixing and by increasing binding materials. Hair cracks or fire cracks may be eliminated by increasing the amount of grog in the mixture.

6th Experiment: 30 bricks were prepared with 8% grog while other compositions kept constant as the former experiment. The materials were thoroughly mixed for better bonding. After sun drying the bricks were stacked at the middle of the kiln and the temperature was, therefore, recorded at the middle hole. Both Pyrometer and Thermocouple were used to record the temperature. The kiln was fired at 1-30 P.M. of April 10, 1975 and was ended at 7-30 A.M. of April 12, 1975 (42 hours). The highest burning temperature that

Table No. 4.12

Thermocouple readings

| Date | Time | Gas in Cfm. | Temp. in °C | | | Remarks | |
|-----------|------|----------------|-------------|----------|----------|---|-----------------------------------|
| | | | 1st hole | 2nd hole | 3rd hole | | |
| 17.3.1975 | 0800 | 0.80 | | | | Burning started Gas supply increased to 2 cf " 2.5 cfm " 3.75 " | |
| | 1330 | 0.80 | 80 | 80 | 80 | | |
| | 1700 | 2.00 | 170 | 120 | 100 | | |
| | 1915 | 2.50 | 580 | 480 | 300 | | |
| | 2100 | 3.75 | 820 | 660 | 540 | | |
| | 2300 | 3.75 | 900 | 880 | 700 | | |
| 18.3.1975 | 0600 | 3.75 | 980 | 980 | 820 | Gas supply inc- reased to 4.5 cfm " 6.5 " | |
| | 0800 | 4.50 | 1100 | 1080 | 920 | | |
| | 0830 | 6.50 | 1160 | 1200 | 1040 | " 7.5 cfm | |
| | 0900 | 6.50 | 1180 | 1250 | 1080 | | |
| | 0915 | 7.50 | 1180 | 1300 | 1100 | | |
| | 1000 | 7.50 | 1190 | 1320 | 1140 | | |
| | 1015 | 7.50 | 1200 | 1330 | 1170 | | |
| | 1030 | 7.50 | 1230 | 1330 | 1190 | | |
| | 1040 | 7.50 | 1240 | 1330 | 1190 | | |
| | 1050 | 7.50 | 1260 | 1330 | 1200 | | |
| | 1100 | 7.50 | 1170 | 1330 | 1200 | | Gas supply reduced to 5.50 cfm |
| | 1130 | 5.50 | 1150 | 1260 | 1190 | | |
| | 1145 | 5.50 | 1150 | 1240 | 1120 | " 4 cfm. | |
| | 1200 | 5.50 | 1140 | 1220 | 1120 | | |
| | 1210 | 4.00 | 1060 | 1100 | 1100 | | |
| | 1220 | 4.00 | 1060 | 1140 | 1060 | | |
| | 1230 | 4.00 | 1080 | 1100 | 970 | | |
| | 1245 | 4.00 | 1040 | 1060 | 890 | | " 3.8 cfm. |
| | 1330 | 3.00 | 960 | 980 | 850 | | " 2.5 " |
| | 1700 | 2.50 | 870 | 800 | 650 | | " 2.0 " |
| 2100 | 2.00 | 540 | 560 | 470 | " 1.5 " | | |
| 19.3.1975 | 0600 | 1.50 | 430 | 470 | 340 | | " 0.9 " |
| | 0815 | 0.90 | 310 | 310 | 200 | | |
| | 1000 | 0.90 | 200 | 210 | 150 | Gas supply stopped | |

was recorded by thermocouple and by pyrometer were 1300°C and 1400°C respectively. The heating rate and gas supply were as in Table No. 4.13.

All the bricks burnt sound (Figure 4.9(c)) showing no spalling, cracks or sagging. So for commercial purpose Sylhet sand deposit may be used for manufacturing Silica Bricks with addition of some binding materials like CaO and Mymensingh clay and also some grog. These lime and clay additions should not exceed 10% and 5% respectively. Grog must be added over 8%.

Few tests of these bricks have been conducted in the Laboratory and their results are as follows:

| | |
|-----------------------|------------------------------|
| 1. Fusion temperature | above 1450°C |
| 2. Impact value | 118 inches |
| 3. Porosity | 37.40% |
| 4. Apparent Density | 1.11 gm/cm^3 |
| 5. Burning Shrinkage | 3.20% |

Table No.4.13

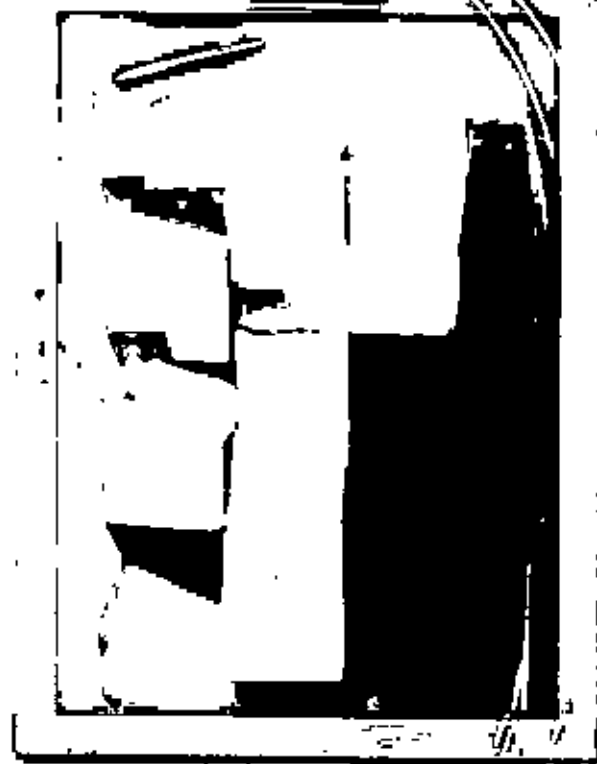
Thermocouple readings and gas supply

| Date | Time | Gas supply in cfm. | Temperature in °C | Remarks |
|-----------|------|-----------------------|----------------------|-------------------------------------|
| 10.4.1975 | 1330 | 1.00 | | Burning started |
| | 1700 | 1.00 | 110 | |
| | 1800 | 1.00 | 120 | Gas supply increased to 1.5 cfm. |
| | 2000 | 1.50 | 300 | " 2 cfm. |
| | 2005 | 2.00 | 340 | |
| | 2010 | 2.00 | 340 | |
| | 2130 | 2.00 | 550 | |
| 11.4.1975 | 0820 | 2.00 | 670 | Gas supply increased to 3.5 cfm. |
| | 0625 | 3.90 | 675 | |
| | 0630 | 3.50 | 680 | |
| | 0805 | 3.50 | 950 | " 5.50 cfm. |
| | 0815 | 5.50 | 1000 | |
| | 0820 | 5.50 | 1040 | |
| | 0850 | 5.50 | 1100 | |
| | 1030 | 5.90 | 1100 | " 7.50 cfm. |
| | 1033 | 7.80 | 1110 | |
| | 1045 | 7.50 | 1200 | |
| | 1135 | 7.50 | 1200 | Air supplied. |
| | 1140 | 7.50 | 1280 | |
| | 1150 | 7.50 | 1280 | Air supply stopped |
| | 1245 | 7.50 | 1300 | |
| | 1250 | 7.50 | 1320 | Gas supply reduced to 4 cfm. |
| | 1430 | 4.00 | 1080 | "3 cfm. |
| | 1700 | 3.00 | 950 | "2 cfm. |
| | 2000 | 2.00 | 700 | "1 cfm. |
| 12.4.1975 | 0730 | 1.00 | 300 | Supply stopped |



a) Brick with 10% CaO & 2% clay in Exp. No. 4. b) Spalling action as a result of slaking.





a) Brick with 10% CaO, 2% clay & 2% spag. b) Brick with 10% CaO, 2% clay & 2% spag.

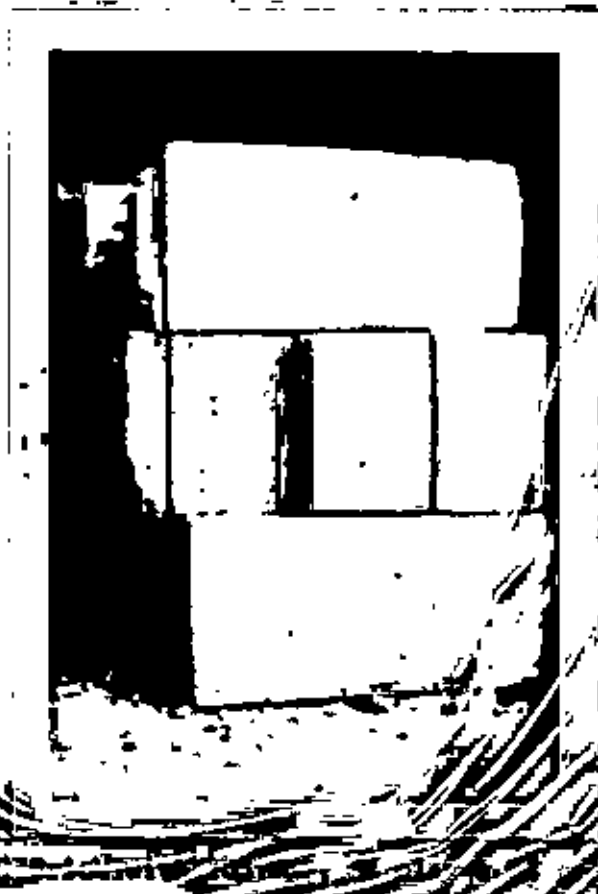
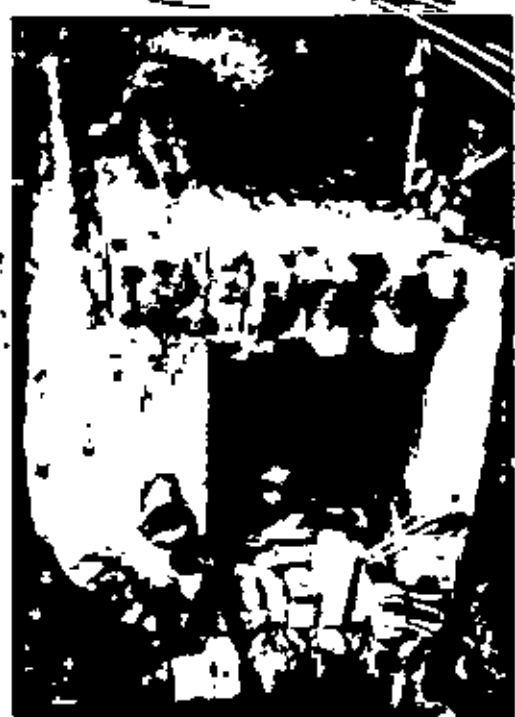


Figure 4.1



a) Gas-fired laboratory kiln.



b) Experimental setup.



a) Experimental setup





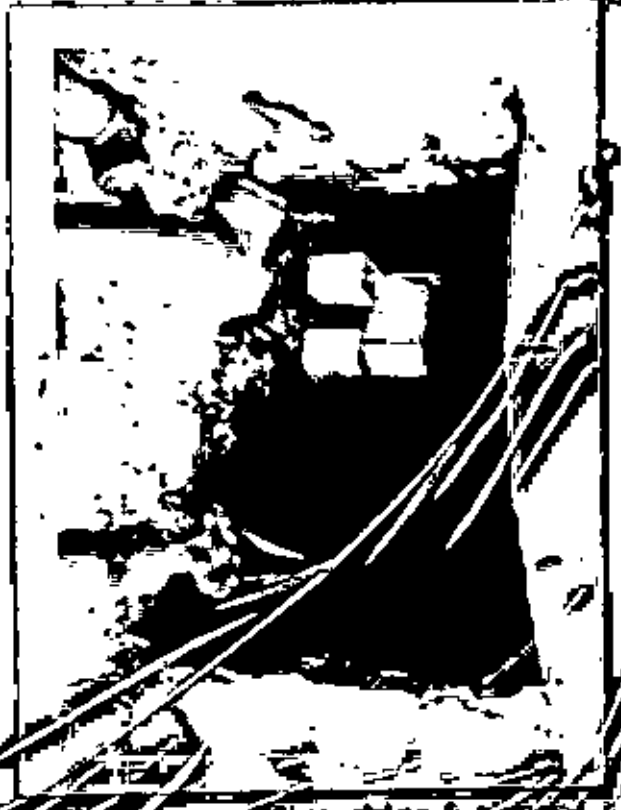
a) Kiln after explosion.



b) A large product of ordinary kiln work at a temperature of 1050 C.



c) Steel door of a kiln after explosion.



d) Fragment of stacking door of a kiln.

Figure 4.11

CHAPTER / 5

CONCLUSION

The informations obtained from the two sets of experiments, of which one set was conducted in a high temperature Silicon Carbide Muffle Furnace while the other was conducted in a laboratory size gas-fired kiln, are summarised below:-

The grain sizes of the both the sands that were collected from Moyapara and Chhatlain in manufacturing experimental bricks were more or less same but both were lacking initial binding properties. Lime was used to improve the binding property. These bricks were burnt in the Muffle furnace for 25 hours to a temperature of 1450°C and were subsequently cooled in the furnace very slowly. Cracks of different sizes were noticed on the surface of these bricks. This experiment was repeated with finer sand and fired at 1500°C for 17 hours. This time cracks were almost absent except few hair cracks.

Difficulty was experienced in handling the bricks with coarse sand grains. It was found that finer sand grains provide better mixing and will definitely help chemical action at the elevated temperature. The cracks that were observed in the first experiment might be due to lack of homogeneity and incomplete chemical action between the binding materials and the sand grains. While the hair cracks that were noticed in the subsequent experiment with finer sand grains might be due to contraction that developed at the time of chemical action and vitrification. The experiments that were conducted with Mirpur clay and Mysensingh clay as binders showed improved binding property and green strength but they lack higher fusion temperature especially Mirpur one. Since the Mysensingh clay contains enough silica (Table 3.1) and it is also found from the Thermal Equilibrium phase diagram of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system (Fig.4.5) that the fusion point of the brick containing SiO_2 near about 90% should be about 1600°C . The bricks made with Mirpur clay were found fused at 1450°C . So it may then easily be inferred that Mirpur clay contains low thermal ingredients and may not be considered suitable as binding materials for manufacturing silica bricks with Sylhet sand. The colour of the bricks also showed a big contrast with those made of Mysensingh clay. To overcome the hair cracks, grog were added in the mixture. Bricks containing different percentage of grog were made and burnt. It was observed that the bricks made with 8% grog showed better results.

The second set of experiment was conducted in a fire clay kiln of capacity for 500 bricks of standard size. The idea of conducting

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this experiment was to conform the result that was obtained in the silicon carbide muffle furnace. The proportion of ingredients and the technique of mixing were more or less same but the size of the bricks were of standard one. After making few experiments with ordinary clay bricks, the rate of heating the kiln was standardized. 16 silica bricks made with 10% CaO and 5% Mirpur clay were prepared and Sun dried. The kiln was then charged with these bricks and the temperature was raised first to 800°C and then to 1450°C and it was then kept steady for about 12 hours. The kiln was allowed to cool slowly, the bricks were then withdrawn from the Kiln and stacked on the open floor. Initial hair cracks were noticed on the surface of the bricks. The hair cracks were found increasing day by day. After about a fortnight most of the bricks were found to spall out to small particles. On investigation it was found that the sand grains were not thoroughly mixed with CaO and clay. The spalling particles showed lacking of mixing and even the particles get separated on finger pressure. It was also revealed that the particles did not show any chemical reaction to each other. The reason might be that the bricks were not kept for sufficient time to initiate the chemical action. Due to bigger size of bricks, the whole section of the bricks might not have been heated uniformly. The gradual increase of the hair cracks might be due to absorption of moisture from the atmosphere by the lime, forming hydrated lime whose volume was gradually increased causing ultimate fracture and spalling.

The 5th experiment was conducted with 60 bricks of 10% CaO, 5% Mysensingh clay and 5% grog. Both the clay and lime were about 200

mesh size. This time the ingredients were thoroughly mixed. To ensure the proper and thorough mixing, lime and clay were first mixed with water and this fine slurry was then added to the sand and was mixed thoroughly before the bricks were shaped into steel mold. The bricks were then dried and charged in the kiln. To be sure about the accurate temperature of the kiln a few Seger cones numbering from 05 to 14 were placed at different places of the kiln. Heating was continued for about 50 hours and temperature was raised to 1425°C . After cooling in the kiln the bricks were withdrawn. Some fine hair cracks were still visible on the surface of these bricks. On stacking the bricks outside the kiln for several weeks no more swelling or spalling was noticed. It was thought that the mixing had been thorough but some more grog might be needed to overcome the cracks caused by shrinkage. The following experiment was repeated keeping all other factors constant except increasing grog by 3% more. The furnace was heated to a temperature of 1400°C and kept for about 42 hours. This time the bricks were found perfect in size and shape. No appreciable cracks were visible and on storing no spalling action was noticed. Some bricks in the 5th experiment of the 2nd phase showed sagging due to load on stacking. Here the firing temperature was 1400°C . Since the kiln was made with locally available fireclay bricks which do not usually stand temperature more than 1425°C , the firing temperature of the kiln was limited within this range. Silice bricks made of ganister containing 2 to 3% binding materials can stand at temperature of 1450 to 1600°C . In this experiment the bricks with 10% CaO and 5% Mysnasingh clay might not

stand at temperature more than 1450°C . For lack of suitable binding materials the experiments were limited to locally available binding materials like CaO and clay.

The work so far done suggests that the physical property, particularly the fusion point of the brick can further be improved by decreasing the amount of binding materials. In the present work, lime and clay were used to increase the green strength of the brick at the cost of fusion point. These could have been avoided to some extent if any mechanical devices were used in mixing the materials and in making the brick mold. Pneumatic pressure will definitely increase the compactness as well as green strength of the bricks and as a result it will decrease their porosity and permeability. Fineness of the sand and binders will also increase the green strength. Temperature as well as duration of heating period are the important factors of vitrification. Generally silica bricks are burnt at 1500°C for at least a week. But because of some limitations of the lining materials of the kiln it was not possible to raise the temperature to that extent. Kiln with high duty refractory lining may help to eliminate this limitations. To apply the thermal equilibrium diagram the percentage of different constituents should be accurately known. Each raw materials should have, therefore, been chemically checked before the final ingredients were made to satisfy the phase diagram.

APPENDICES

Appendix-A

Analyses of Quartzites²

| Constituent | Madina quartzite % | Baraboo quartzite % | Alabama quartzite % | Sharon conglomerate | Washed granites |
|-------------------------|--------------------------|---------------------------|---------------------------|------------------------|--------------------|
| Silica, SiO_2 | 97.8 | 98.2 | 97.7 | 98.0 | 98.6 |
| Alumina, Al_2O_3 | 0.9 | 1.1 | 1.0 | 0.9 | 0.3 |
| Ferric oxide Fe_2O_3 | 0.9 | 0.2 | 0.8 | 0.9 | 0.8 |
| Lime, CaO | 0.1 | 0.0 | 0.1 | 0.3 | 0.1 |
| Magnesia, MgO | 0.2 | Trace | 0.3 | Trace | 0.1 |
| Alkalies, K_2O, Na_2O | 0.4 | 0.1 | 0.3 | 0.2 | 0.1 |

Appendix-B
Properties of pure, Single, Refractory Oxides⁵

| Material | Formula | Melting point in °C | Density, g/cm ³ |
|---------------------------------|--------------------------------|------------------------|-------------------------------|
| Aluminum | Al ₂ O ₃ | 2000 ± 30 | 3.65 |
| Barium oxide(beris) | BaO | 1917 | 5.74 |
| Beryllium oxide(beryllia bro.) | BeO ⁶ | 2550 | 3.01 |
| Calcium oxide(calcia, lime) | CaO | 2590 ± 30 | 3.36 |
| Cerium oxide(Ceria) | CeO ₂ | 2600 | 7.30 |
| Chromic oxide | Cr ₂ O ₃ | 2265 | 5.12 |
| Cobalt oxide | CoO | 1805 | 7.30 |
| Calcium oxide | Ca ₂ O ₃ | 1740 | 6.44 |
| Hafnium oxide(hafnia) | HfO ₂ | 2777 | 9.68 |
| Lanthanum oxide(lanthana) | La ₂ O ₃ | 2305 | 6.51 |
| Magnesium oxide(magnesia Pari.) | MgO | 2800 | 3.58 |
| Manganese oxide (manganosite) | MnO | 1780 | 5.40 |
| Nickel oxide(bunsenite) | NiO | 1950 | 6.80 |
| Niobium oxide | Nb ₂ O ₃ | 1620 ± 120 | - |
| Silicon oxide(cristobalite) | SiO ₂ | 1728 | 2.32 |
| Strontium oxide(strontia) | SrO | 2415 | 4.70 |
| Tantalum oxide | Ta ₂ O ₅ | 1890 | 8.02 |
| Thorium oxide(thoria thori.) | ThO ₂ | 3300 | 9.69 |
| Tin oxide(cassiterite) | SnO ₂ | 1900 | 7.00 |
| Titanium oxide(rutile) | TiO ₂ | 1800 ± 50 | 4.24 |

| Material | Formula | Melting point in °C | Density, g/cm ³ |
|---------------------------|--------------------------------|------------------------|-------------------------------|
| Uranium oxide | UO ₂ | 2820 ± 80 | 10.96 |
| Vanadium oxide | V ₂ O ₃ | 1900 ± 20 | 4.87 |
| Yttrium oxide(yttria) | Y ₂ O ₃ | 2410 | 4.84 |
| Zinc oxide(zincite) | ZnO | 1975 | 5.66 |
| Zirconium oxide(zirconia) | ZrO ₂ | 2770 ± 80 | 5.56 |
| Ferric oxide | Fe ₂ O ₃ | 1548 | - |
| Ferrous oxide | FeO | 1360 | - |
| Ferro-ferric oxide | Fe ₃ O ₄ | 1538 | - |
| Keolinite | - | 1755 | - |

Appendix-CProperties of Some Complex Refractory Oxides⁵

| Material | Formula | Melting point in °C | Density, g/cm ³ |
|-----------------------------------|---------------------------------|------------------------|-------------------------------|
| Aluminum Silicate (Mullite) | $3Al_2O_3 \cdot 2SiO_2$ | 1030 ^B | 3.16 |
| Aluminum titanate | $Al_2O_3 \cdot TiO_2$ | 1655 | - |
| Aluminum titanate | $Al_2O_3 \cdot 2TiO_2$ | 1895 | - |
| Barium aluminate | $BaO \cdot Al_2O_3$ | 2000 | 3.99 |
| Barium aluminate | $BaO \cdot 6Al_2O_3$ | 1860 | 3.64 |
| Barium silicate(orthosilicate) | $2BaO \cdot SiO_2$ | 1755 | 5.2 |
| Barium zirconate | $BaO \cdot ZrO_2$ | 2700 | 6.26 |
| Beryllium aluminate(chrysoberyl) | $BeO \cdot Al_2O_3$ | 1870 | 3.76 |
| Beryllium silicate(metasilicate) | $BeO \cdot SiO_2$ | 1755 | 2.35 |
| Beryllium silicate(phenacite) | $2BeO \cdot TiO_2$ | 1750 | 2.99 |
| Beryllium titanate | $3BeO \cdot TiO_2$ | 1800 | - |
| Beryllium zirconate | $3BeO \cdot 2ZrO_2$ | 2535 | - |
| Calcium chromate | $CaO \cdot CrO_3$ | 2160 | 3.22 |
| Calcium chromite | $CaO \cdot Cr_2O_3$ | 2170 | 4.8 |
| Calcium phosphate(orthophosphate) | $3CaO \cdot P_2O_5$ | 1730 | 3.14 |
| Calcium silicate | $CaO \cdot SiO_2$ | 1900 | 2.91 |
| Calcium silicate(orthosilicate) | $2CaO \cdot SiO_2$ | 2120 | 3.28 |
| Calcium silicon phosphate | $5CaO \cdot SiO_2 \cdot P_2O_5$ | 1780 | 3.01 |
| Calcium titanate(perovskite) | $CaO \cdot TiO_2$ | 1800 | - |
| Calcium titanate | $3CaO \cdot TiO_2$ | 2135 | - |
| Calcium zirconate | $CaO \cdot ZrO_2$ | 2345 | 4.78 |

| Material | Formula | Melting point in °C | Density g/cm ³ |
|------------------------------------|--|------------------------|------------------------------|
| Cobalt aluminate(cobalt blue) | CoO.Al ₂ O ₃ | 1955 | 4.37 |
| Magnesium aluminate(spinel) | MgO.Al ₂ O ₃ | 2135 | 3.58 |
| Magnesium chromite | MgO.Cr ₂ O ₃ | 2000 | 4.39 |
| Magnesium ferrite(magnesioferrite) | MgO.Fe ₂ O ₃ | 1760 | 4.48 |
| Magnesium lanthanate | MgO.La ₂ O ₃ | 2030 | - |
| Magnesium silicate(fersterite) | 2MgO.SiO ₂ | 1885 | 3.22 |
| Magnesium titanate | 2MgO.TiO ₂ | 1835 | 3.52 |
| Magnesium zirconate | MgO.ZrO ₂ | 2120 | - |
| Magnesium zirconium silicate | MgO.ZrO ₂ .SiO ₂ | 1793 | - |
| Nickel aluminate | NiO.Al ₂ O ₃ | 2019 | 4.45 |
| Potassium aluminum silicate(kali) | K ₂ O.Al ₂ O ₃ .2SiO ₂ | 1800 | - |
| Strontium aluminate | SrO.Al ₂ O ₃ | 2010 | - |
| Strontium phosphate(orthophos.) | 3SrO.P ₂ O ₅ | 1767 | 4.53 |
| Strontium zirconate | SrO.ZrO ₂ | 2700 | 5.48 |
| Thorium zirconate | ThO ₂ .ZrO ₂ | 2000 | - |
| Zinc aluminate(gehlinite) | ZnO.Al ₂ O ₃ | 1950 | 4.58 |
| Zinc zirconium silicate | ZnO.ZrO ₂ .SiO ₂ | 2078 | - |
| Zirconium silicate(zircon) | ZrO ₂ .SiO ₂ | 2420 | 4.6 |
| Chromite | FeO.Cr ₂ O ₃ | 2100 | - |

Appendix-D

General Classification of Refractory Materials⁴

| Silica | | Aluminium Silicate | | | Magnesia | | | | |
|----------|--------------------|--------------------|----------|--------------|-----------|----------|---------------------|--------|------------|
| A | B | C | D | E | F | G | H | I | |
| Dinas | Quartz | Semi acid | Chamotte | High alumina | Magnesite | Dolomite | Forsterite | Spinel | |
| Chromite | | Zirconia | | | Carbon | | Carbide and nitride | | Oxide |
| J | K | L | M | N | O | P | Q | R | S |
| Chromite | Chrom magnesite | Magnesite | Zirconia | Zircon | Coke | Graphite | Carborundum | Other | Pure oxide |

Appendix-E

Analyses of Fireclays²

| | Plastic, Lawrence, Ohio | Flint, Cambria, Pa | Flint, Carter, Ky. | Semi-flint, Jackson, Ohio | Semi-flint, Clearfield, Pa. | Plastic Flint, Vinton, Ohio | Flint, Montgomery, Mo. | Siliceous Now Jersey |
|--------------------------------|-------------------------|--------------------|--------------------|---------------------------|-----------------------------|-----------------------------|------------------------|----------------------|
| SiO ₂ | 58.10 | 44.43 | 44.78 | 50.32 | 43.04 | 46.72 | 44.04 | 59.93 |
| Al ₂ O ₂ | 23.11 | 37.10 | 35.11 | 31.53 | 36.49 | 38.06 | 38.03 | 26.95 |
| Fe ₂ O ₂ | 1.73 | 0.46 | 1.18 | 1.02 | 1.37 | 0.68 | 0.63 | 1.24 |
| FeO | 0.68 | 0.55 | 0.74 | 0.35 | 0.83 | 0.55 | 0.22 | 1.24 |
| FeS ₂ | 0.55 | 0.22 | 0.14 | 0.12 | 0.24 | 0.34 | 0.81 | - |
| MgO | 1.01 | 0.19 | 0.55 | 0.18 | 0.54 | 0.19 | 0.12 | 0.07 |
| CaO | 0.79 | 0.60 | 0.77 | 0.80 | 0.74 | 0.61 | 0.40 | - |
| Na ₂ O | 0.34 | 0.10 | 0.29 | 0.07 | 0.46 | 0.42 | 0.10 | Trace |
| K ₂ O | 1.90 | 0.55 | 0.44 | 0.05 | 1.10 | 1.53 | 0.22 | Trace |
| H ₂ O- | 2.27 | 0.80 | 0.84 | 2.47 | 0.82 | 2.21 | 0.78 | - |
| H ₂ O+ | 7.95 | 12.95 | 13.07 | 11.25 | 12.44 | 11.50 | 13.55 | 9.63 |
| CO ₂ | 0.05 | 0.11 | 0.07 | 0.14 | 0.05 | 0.02 | 0.04 | - |
| TiO ₂ | 1.46 | 1.84 | 2.22 | 1.45 | 1.72 | 2.20 | 1.82 | 1.90 |
| P ₂ O ₂ | 0.17 | 0.21 | 0.02 | 0.48 | 0.10 | 0.12 | 0.28 | - |
| SO ₂ | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | - |
| MnO | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | - | - |
| ZrO ₂ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | - |
| Org. C | 0.22 | 0.10 | 0.11 | 0.07 | 0.22 | 0.04 | 0.01 | - |
| Org. H | 0.03 | - | - | - | 0.03 | - | - | - |

Appendix-F

High-alumina Clays Chemical Analyses²

| Clay | Dutch Guiana gibbsite | First grade diaspore ⁺ | Bauxite | Burly flint | Second grade diaspore |
|----------------|--------------------------|--------------------------------------|---------|-------------|--------------------------|
| Silica | 4.5 | 10.9 | 26.0 | 33.8 | 29.2 |
| Alumina | 58.4 | 72.4 | 54.0 | 49.4 | 53.3 |
| Titanium oxide | 2.9 | 3.2 | 2.1 | 2.6 | 2.7 |
| Iron oxide | 3.2 | 1.1 | 1.0 | 1.0 | 1.9 |
| Lime | 0.4 | - | - | - | - |
| Combined water | 30.6 | 13.5 | 16.1 | 12.0 | 12.0 |

Appendix-G

Analysis of Kaolin, Ball Clays, Halloysite, and Pyrophyllite²

| Constituent | Raw Georgia kaolin % | Washed English China clay % | Washed North Carolina kaolin % | Raw Tennessee ball clay % | Raw Kentucky ball clay % | Raw halloysite % | Raw pyrophyllite % |
|-----------------|----------------------|-----------------------------|--------------------------------|---------------------------|--------------------------|------------------|--------------------|
| Silica | 45.8 | 48.3 | 45.8 | 53.9 | 56.4 | 44.3 | 63.5 |
| Alumina | 38.5 | 37.6 | 36.5 | 92.3 | 35.0 | 37.4 | 28.7 |
| Titanium oxide | 1.4 | - | 0.0 | 1.6 | - | - | - |
| Ferric oxide | 0.7 | 0.5 | 1.4 | 1.0 | 1.0 | 0.4 | 0.8 |
| Calcium oxide | Trace | 0.1 | - | 0.7 | 0.4 | 0.2 | Trace |
| Magnesium oxide | Trace | - | 0.5 | 0.4 | Trace | 0.1 | Trace |
| Alkalies | - | 1.6 | 0.3 | - | 5.3 | 0.2 | 0.4 |
| Combined water | 13.6 | 12.0 | 13.4 | 12.8 | 7.8 | 15.1 | 5.9 |

Appendix-MChromite Ore, Refractory Grade²

| Constituent | Philippine | | Tanzania | |
|--------------------------------|------------|-------------|----------|-------------|
| | Lump | Concentrate | Lump | Concentrate |
| SiO ₂ | 5.1 | 2.8 | 2.8 | 0.8 |
| Al ₂ O ₃ | 27.9 | 29.5 | 15.0 | 17.4 |
| FeO | 13.0 | 13.9 | 24.1 | 24.6 |
| CaO | 0.5 | 0.4 | 0.3 | 0.2 |
| Cr ₂ O ₃ | 33.2 | 34.4 | 46.3 | 47.3 |
| MgO | 18.7 | 17.3 | 10.6 | 9.7 |
| Ignition loss | 1.1 | 1.0 | 0.3 | 0.1 |

Appendix-1

DEAD-BURNED MAGNESITES (SEAWATER OR BRINES)²

| Constituent | Michigan | Cape May | Cape May | Lavine | Kaiser | Kaiser |
|--------------------------------|----------|----------|----------|--------|--------|--------|
| SiO ₂ | 0.6 | 4.6 | 1.7 | 1.1 | 2.1 | 0.4 |
| Al ₂ O ₂ | 0.2 | 0.3 | 0.3 | 0.3 | 0.7 | 0.05 |
| TiO ₂ | - | - | - | Trace | Trace | 0.01 |
| Fe ₂ O ₂ | 0.4 | 0.6 | 0.6 | 0.2 | 0.5 | 0.11 |
| CaO | 0.7 | 1.3 | 1.1 | 1.0 | 1.1 | 1.1 |
| HgO | 98.1 | 93.1 | 96.3 | 97.2 | 95.0 | 98.1 |

Dead-burned Natural Magnesites

| Constituent | Austrian | Austrian | Grecian | State of Washington | Manchurian |
|--------------------------------|----------|----------|---------|---------------------|------------|
| SiO ₂ | 5.8 | 1.0 | 6.6 | 4.9 | 3.7 |
| Al ₂ O ₂ | 1.7 | 1.0 | 4.4 | 1.5 | 1.0 |
| Fe ₂ O ₂ | 4.0 | 6.9 | 4.4 | 3.4 | 1.5 |
| CaO | 5.0 | 2.1 | 2.4 | 2.8 | 1.6 |
| HgO | 85.0 | 88.6 | 84.4 | 87.1 | 92.0 |
| Ignition loss | 0.2 | 0.3 | 0.2 | 0.1 | 0.1 |

BIBLIOGRAPHY

1. Robert B. Leighou, *Chemistry of Engineering Materials*, Fourth Edition, New York and London, McGraw-Hill Book Company, Inc. 1942.
2. F.H. Norton, *Refractories*, fourth edition, New York St. Louis San-Francisco Dusseldorf Johannesburg Kuala Lumpur, London, Mexico Montreal New Delhi, Panama Riode Janeiro Singapore, Sydney Toronto, McGraw-Hill Book Company, 1968.
3. Teichert J. Ernest, *Introduction to Ferrous Metallurgy*, Second Edition, Third Impression, McGraw-Hill Book Company, Inc. New York and London 1944.
4. P.P. Budnikov, *The Technology of Ceramics and Refractories*, First Publication, London, Edward Arnold(Publishers) Ltd., 1964.

5. Ivor E. Campbell and Edwin M. Sherwood, High Temperature Materials and Technology, New York, London, Sydney, John Wiley and Sons, Inc., 1968.
6. Joseph Newton, An Introduction to Metallurgy, Second Edition, New York, John Wiley and Sons, Inc. 1955.
7. (a) Khan F.H., Glass Sand Deposits of East Pakistan, Issue of the Journal of CENTO Symposium on Industrial Rock and Minerals, 1962.
 (b) Khan F.H., Clay Deposits of East Pakistan, Issue of the Journal of CENTO Symposium on Industrial Rock and Minerals, 1962.
8. F.P. Hall and Herbert Inley, Issued as part-II of the November, 1947, Issue of the Journal of the American Ceramic Society, Columbus, Ohio,

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