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9 May 1974
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United Nations Industrial Development Organization

In-Plant Training Workshop on
the Production of Refractories

Pilsen, Czechoslovakia

11 - 28 June 1974.

BODY COMPOSITION AND PROCESSING OF
GRAPHITE PRODUCTS, INSULATION BRICKS
AND OTHER KINDS OF SPECIAL OXIDE CERAMICS 1/

K. Engelthaler*

* Institute for Ceramics, Refractories and Raw Materials, Horni Briza,
Czechoslovakia

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BODY COMPOSITION AND PROCESSING OF
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K. Engelthaler*

SUMMARY

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Special papers have been devoted to the body composition and processing of silica and firebricks, magnesite and other basic refractories, castables, mouldables and mortars because these products may be counted among the principal and leading products in the refractories industries. This paper covers the majority of the remaining products which are counted under the group of refractories.

However, graphite products, insulation bricks, zircon and zirconia bricks, as well as high alumina bricks, are also very important refractory products.

Other types of special refractories are also known, such as forsterites, nitrides, borides, etc., but these are not so important for the developing countries since their production is rather intricate and difficult. Therefore it is not recommended to start with such a production in the first stage of developing a refractory industry.

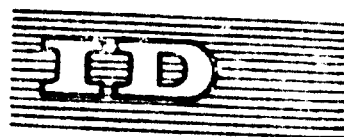
This paper covers the body composition and processing of graphite products, insulation products, zircon and zirconia bricks and high alumina bricks and is divided into four chapters. Each chapter covers one separate problem.

Because the production process - namely the production process including body preparation for producing high alumina bricks or zircon and zirconia bricks - is similar to that of silica or firebricks, the detailed description of body mixing, pressing or hand moulding, drying and firing was not included. Only in such cases where the production process is different are details given to understand the production flow.

Various developmental steps in the technology and the advantages and disadvantages of various types of fuels are the same for these products as for silica or firebricks. Therefore special attention is not devoted to this problem, except in the chapter "Graphite Products", where the kiln atmosphere plays an important role.



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COMPOSICION Y ELABORACION DE LA PASTA PARA PRODUCTOS DE GRAFITO,
LADRILLOS AISLANTES Y OTROS TIPOS DE PRODUCTOS
CERAMICOS ESPECIALES A BASE DE OXIDOS^{1/}

K. Engelthaler*

RESUMEN

Se han dedicado monografías especiales a la composición y elaboración de la pasta para ladrillos de arcilla refractaria y sílice, para productos de magnesita y otros materiales refractarios básicos, compuestos moldeables y morteros, porque se les puede incluir a todos ellos entre los productos principales y de mayor utilización en las industrias de materiales refractarios. La monografía que aquí se resume se refiere a la mayoría de los restantes productos que forman parte del grupo de materiales refractarios.

Debe señalarse, no obstante, que los productos de grafito, los ladrillos aislantes, los ladrillos de zircón y zirconia, así como los ladrillos con elevado contenido de alúmina, son también productos refractarios muy importantes.

Se conocen otros tipos de materiales refractarios especiales, como son las forsteritas, los nitruros, los boruros, etc., pero no son tan importantes para los países en desarrollo, ya que su elaboración es más bien compleja y difícil. Por consiguiente, no se recomienda abordar su fabricación en la primera fase del desarrollo de una industria de productos refractarios.

^{1/} Las opiniones que el autor expresa en este documento no reflejan necesariamente las de la Secretaría de la ONUDI. La presente versión española es traducción de un texto no revisado.

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La monografía abarca la composición y elaboración de pasta para productos de grafito, ladrillos aislantes, ladrillos de zircón y zirconia y ladrillos con elevado contenido de alúmina, y está dividida en cuatro capítulos, cada uno de los cuales se refiere a una cuestión diferente.

Debido a que el proceso de producción -es decir, el proceso de producción, inclusive la preparación de la pasta, para fabricar ladrillos con elevado contenido de alúmina o ladrillos de zircón y zirconia- es similar al que se sigue con ladrillos de arcilla refractaria o de sílice, no se incluye en el estudio la descripción pormenorizada de la mezcla, el prensado o el moldeado manual, el secado y la cocción de la pasta. Sólo se dan detalles para comprender el proceso de producción cuando éste es diferente.

Las diversas etapas del desarrollo de la tecnología, así como las ventajas y desventajas de los diversos tipos de combustible, son los mismos en el caso de estos productos que en el de los ladrillos de sílice o de arcilla refractaria. Por consiguiente, no se dedica atención especial a este problema, excepto en el capítulo sobre "Productos de Grafito", ya que en su caso la atmósfera del horno desempeña un papel importante.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards even though the best possible copy was used for preparing the master fiche

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CHAPTER No. 1.

Graphite and fireclay - graphite products.

The name refractories covers also special products produced from graphite, clays, silicon carbide, ferrosilicon and other different components such as silica sand, grog etc. The best known products from this field are stopper-heads in different qualities and crucibles. Both of them are used in steel and metallurgical industry.

Before coming to the body compositions of stopper-heads and crucibles it will be necessary to say a few words about the raw materials used for their production.

Graphite and carbon: Carbon is a material with a high resistance to thermal shock, a low coefficient of thermal expansion and its strength increases with temperature. It is chemically inactive, is not wet by most molten metals, and is resistant to abrasion and erosion. Graphite, in addition has very high thermal conductivity, high electrical conductivity, and is a high strength material. This unique combination of physical and chemical properties has resulted in countless industrial applications for carbon and graphite where no other materials would do the job.

These applications include lighting carbons, carbon, graphite and metal-graphite brushes for motors and generators; electrodes used in electrometallurgical and electrochemical industries; carbon, graphite and impervious carbon and graphite pipes, fittings, valves, pump towers, heat exchanges, rashig rings, tubes and special structural shapes for handling and processing corrosive materials; highly porous carbon and graphite products for filtration and gas dispersion. Activated carbon is used for solvent recovery and for the desorption of odors and vapors.

In addition carbon and graphite products have many important metallurgical applications. These include carbon linings

for hearth and wall sections of blast furnaces and ferro-alloy furnaces, aluminium pot linings, graphite crucibles for induction and resistance melting, graphite stopper-heads and nozzles as well as static cast rods and other simple castings, etc.

Nuclear grades of graphite are used as moderators, thermal columns, reflectors and shields in nuclear reactors.

Graphite is known as a natural and synthetic mineral. Melting point is above 3700°C , softening temperatures are $2500-2600^{\circ}\text{C}$. Natural graphite is widely distributed throughout the world with the best sources being Sri Lanka, Canada and Mexico. Graphites have a specific gravity of 2,1 - 2,5 as mined, but purified material is close to the theoretical value of 2,26.

Ideally, graphite should behave as a metalloid in two directions and as ceramic in the third. Thus for flake graphite or other polycrystalline graphites in which the crystals are well oriented, the thermal and electrical conductivities are high in two directions and low in the third. Material such as Sri Lanka chunk graphite consists of disordered crystals and has properties which are nearly isotropic. Natural graphites are unctuous and soft /Mohs hardness of $1/2 - 11/2/$, burn slowly, are chemically inert, and have a sublimation temperature greater than 3500°C . It is used in clay bonded refractory applications and in some cases is glazed to prevent oxidation. Thermal conductivity for normal commercial graphite at room temperature is about $0,3 \text{ cal.cm/sec.cm}^2/^{\circ}\text{C}$. The tensile strength of commercial graphite increases with temperature from maximum values of about $120 \text{ kp/cm}^2 / 1700 \text{ psi/}$ at room temperature to $240 \text{ kp/cm}^2 / 3400 \text{ psi/}$ at 2450°C .

Because of its outstanding high temperature properties, graphite is used as a good refractory material.

Silicon carbide: Silicon carbide, SiC , is produced in the electric resistance furnace from a mixture of silica sand, coke, sawdust, and salt. An electric current passes between permanent electrodes located at both ends of the furnace and th-

rough a graphite core produces a temperature of approximately 2200°C where crystals of silicon carbide form from the sand and coke in the charge. The sawdust burns out keeping the mass porous and the salt assist in the removal of impurities through the formation of volatile chlorides. The duration of the furnace run is about 36 hours. Dense recrystallized body has excellent thermal conductivity and it is electrically semiconductive. It does not melt at normal pressures but dissociates at over 2800°C. Oxidises very slowly in air and it is serviceable to 1550 - 1650°C for many uses. Silicon carbide is unattacked by acids; reacts readily with fused caustic, halogens and certain metal oxides at high temperatures. CTE is $5,2 \times 10^{-6}$ °C from 25 to 1500°C.

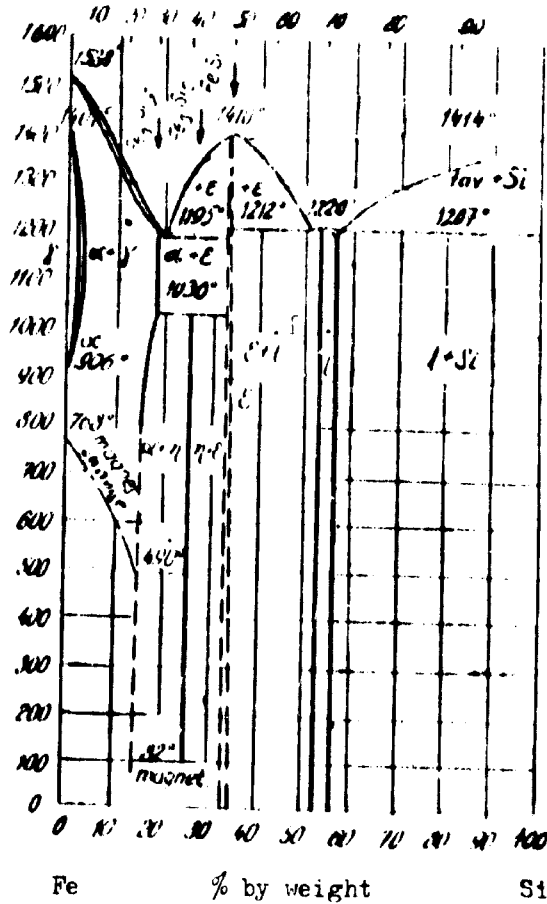
Manufactured in many complex bonded shapes utilized for super refractory uses such as setter tiles and kiln furniture, muffles, retorts, hot cyclone liners, rocket nozzles and skid rails; also for erosion or corrosion-resistant uses such as check valves, orifices, slag blocks, as additive to the body mixture in the production of graphite crucibles and stopper heads, etc.

ferrosilicon: Silicon dissolves in iron in different ratios and build silicides. The diagram Fe - Si /see picture No 1/ shows, that three chemical compounds are known: Fe₃Si₂ with 25,1% Si; FeSi with 33,4% Si; and Fe₃Si₅ with 55,7% Si. Also Fe - Si alloys are known. The following table shows specific gravity of Fe - Si alloys in different ratios:

Si content in %	40	50	60	70	80	85	90
Sp.gr. of the alloy g/cm ³	5,61	4,75	4,00	3,51	3,03	2,78	2,55

The industrial production of ferrosilicon is actually a reduction of high silicious sand with charcoal in presence of iron sawdust. Some producers of silicon carbide or graphite-silicon carbide stopper-heads and crucibles use ferrosilicon instead of ready silicon carbide. For such purpose is suitable ferrosilicon alloy with a content of Si above 90% and grain-size up to 0,30 mm.

Atomic % of Si



Picture NO 1. Fe - Si diagram

Plastic clays: For the production of graphite respectively fireclay graphite goods are used plastic clays as bonding material supporting the plasticity of the body and after firing increasing the mechanical strength of the products. very suitable are plastic clays which are very fine because usually the finesse ensures a good plasticity and a high strength after firing.

It has been said all about the clays which are used in the refractories production in previous lectures and therefore

it is not necessary to repeat it once again. All information about plastic clays given in these lectures is also valid for the production of fireclay graphite goods.

Other raw materials: Under this group of raw materials may be counted most raw materials which play the role of non plastic in the body composition as silica sand, fireclay grog, feldspar etc.

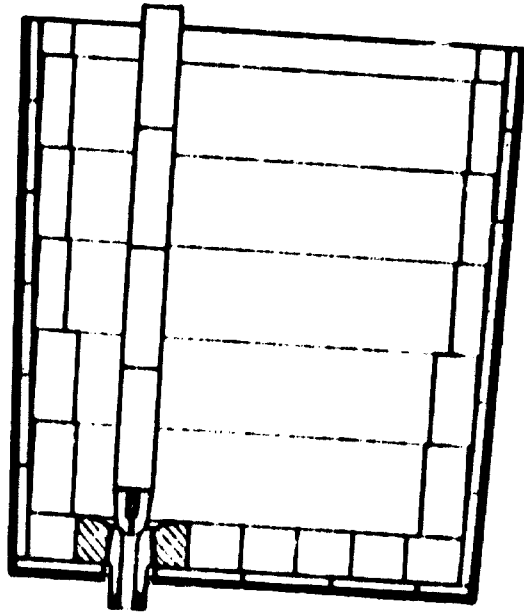
Also raw materials which are used for the frit or glaze preparation in the production of crucibles as dolomite, limestone, caustic soda, iron oxide etc. may fall under this group. However, it is not necessary to discuss these materials deeper because it is not recommendable to produce the glaze on the spot but use it from an established producer.

A. S t o p p e r - h e a d s

Stopper-heads are used in the steel industry and it may be said that they are the most important items in the process of steel pouring. The quality of casted products depends on the quality and perfect montage of a stopper-head. Picture no 2. shows a schematic view how is a stopper-head exposed in the steel production in the period of pouring.

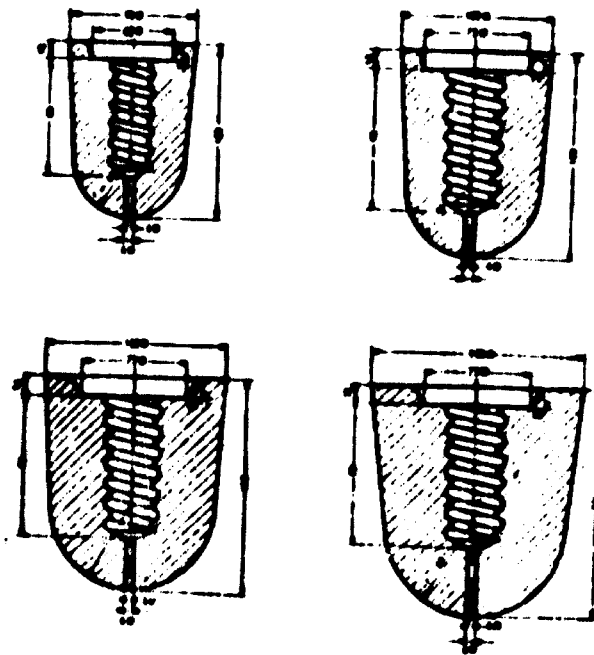
The stopper-head covers a nozzle and the pouring of the metal starts when the opening of the nozzle is free. When the mould is filled with poured metal the opening of the nozzle should be closed again perfectly with the stopper-head. The most important thing is to avoid leakage of melted metal during the time when the ladle is transported to another sand-mould. This operation repeats several times and number of openings and closings depends on the capacity of the ladle and of course on the sizes of the moulds. The following pictures no 3. and 4. show few different shapes and designs of stopper-heads including their sizes which are used through the whole world.

In the production process the raw materials are charged by volume according to the body composition and mixed to -

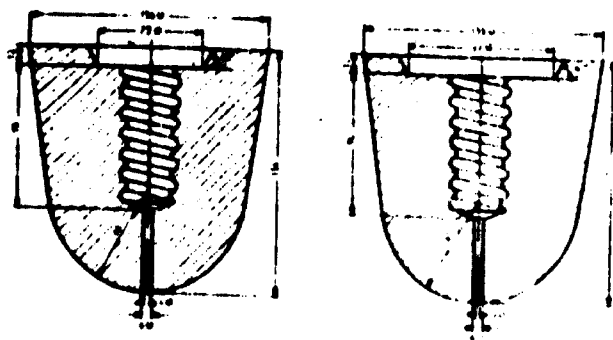


Picture no. 2.

gether in a mixer. Table no. 2. shows examples of body mixtures of fireclay - graphite stopper - heads.



Picture no. 3.



Picture No 4,

Table No 2,

		Example No 1	Example No 2
graphite	%	12 - 20	20 - 30
grog	%	30 - 50	20 - 40
plastic clay	%	20 - 30	20 - 30
feldspar	%	0 - 25	-
silicon carbide	%	-	10 - 30

The mixed body is pugged in a pugmill with the round mouth. The diameter of the mouth should be slightly smaller than the diameter of the pressed stopper head. The pugged body is cut to pieces which should correspond in their weight to the weight of a green stopper-head or it may be slightly higher. In any case it is not allowed the weight of the pugged piece to be lower than the weight of a green stopper-head because the product pressed from two pieces will be definitely rejected. Friction presses are used for pressing of the goods. Simultaneously with the pressing the spindle is poked into the body to shape the tread in the stopper head.

After pressing two different production methods are used. The first one leaves the spindle in the pressed stopper-head during the period of drying up to the stiff body, it means approximately up to the body moisture 12%. Then the stopper-head

is repressed in order to decrease the porosity of the products, increase its cold crushing strength and to give the stopper-head as perfect shape as possible. After repressing the spindle is unscrewed and the products dried and fired in the reduction atmosphere.

The second method does not leave the spindle in the pressed stopper-head, it means that the spindle is unscrewed immediately after pressing when the upper die goes up. The pressed stopper-head is then taken out from the mould, dried up to the moisture below 2% and fired in the reduction atmosphere. The firing temperature for both ways of production is about 1300-1400°C and depends on the body composition.

The advantages and disadvantages of both ways mentioned above is that for the repressing process are necessary many spindles and their number depends on the daily production. On the other hand the final shape and sizes are exactly what is necessary for a good closing of the nozzle in the ladle. However, both ways are used in the existing productions.

B. Crucibles

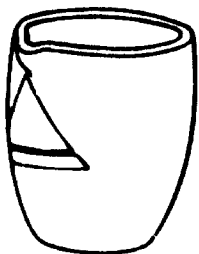
Graphite crucibles are used in the metallurgical industry for melting of different metals and alloys. In the crucibles metals or alloys are melted, mixed, refined and finally poured in moulds.

Crucibles are produced in different shapes and designs, as is visible in picture No 5. Special shapes according to customers order may be also produced.

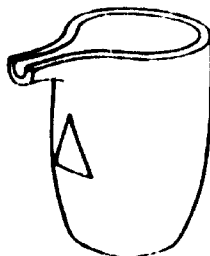
Two different types of graphite crucibles as far as their quality is concerned are now available on the world market. The first type is bonded with plastic clays, the second one with pyrolithic graphite.

Plastic clay bonded crucibles are actually well known graphite or graphite-fireclay crucibles which, in addition to graphite and good plastic clay, sometimes also contain a little silicon carbide and of course other refractory raw materials such as silica sand, grog, etc.

for
LIFT-OUT
FURNACES



for
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EXTERNAL DIMENSIONS											
Height		Top Dia.		Bulge Dia		Bottom Dia		Spout Length		Capacity to Top	
in	mm	in	mm	in	mm	in	mm	in	mm	lb. Water	liters
16	405	12½	314	13	330	9	229	5½	130	49.2	17.8
16½	425	14½	362			9½	250	5½	130	48.0	17.8
18½	472	14½	375			10½	267	4½	108	55.0	20.0
20½	508	15	381	16½	413	11½	302	8½	216	81.0	30.8
22	558	16½	417	17½	435	13	330	6½	168	102.0	36.4
25½	643	17½	454	20½	512	14½	367	6½	168	100.0	37.2

Picture No 5.

Examples for the body compositions are as follows:
Table No 3.

		<u>Example No 1.</u>	<u>Example No 2.</u>
graphite	%	55	50
plastic clay/s/	%	30	30
silica sand	%	6	-
grog	%	5	4
dressed kaolin	%	4	5
silicon carbide	%	-	11

The addition of silicon carbide supports the resistance against the mechanical wearing and such crucibles therefore have a longer life. Some producers use glaze in order to protect the outside surface of the crucible from the oxidation of graphite. However, the glaze does not hold on the crucible

perfectly because graphite does not react with its components. Therefore it happens very often that the glaze falls down namely when a cold crucible is put into a hot furnace. In such a case when the CTE /coefficient of thermal expansion/ of the glaze and the body, which actually happens very often, differs too much the glaze cracks or crazes, builds eggshells or falls down. Then of course the graphite which is present in the body mix is exposed to the oxidising flame and will slowly burn out.

Graphite or pyrolitic graphite bonded crucibles contain graphite and a relatively high content of silicon carbide and are also known for a longer time. The first products with the graphite bond were too breakable and their edges crumbled very easily.

However, the development in last few years overcame these imperfections and nowadays the modern graphite bonded crucibles give excellent results and long life services. They are more resistant against the thermal shocks in comparison with plastic clays bonded crucibles and the glaze held perfectly on the body and does not flake off. Therefore it is possible to heat them quicker.

The following body compositions may be used as examples for graphite bonded crucibles:

Table No 3.

		<u>Example No 1.</u>	<u>Example No 2.</u>
graphite	%	40	50
silicon carbide	%	40	35
ferrosilicon	%	5	-
silicon	%	5	5
resin or tar	%	10	10

Because the body has a high content of silicon carbide, usually between 30 and 50%, the crucibles are very resistant against wearing. It may be said that these crucibles have at least twice a long life of service. Also thermal conductivity of such a crucible is better and therefore melting of the me-

tals and different alloys goes quicker and consumption of the heat is lower.

In the production process the raw materials should be charged according to the body composition and mixed together to a plastic body on a mixer and further pugged on the pugmill. Blocks of the weight of approximately 5,0-7,0 kg should be cut from the pugged body. These blocks will be given on a jigger-head and shaped to a cake one after another so long as the heap which has the shape of a cone is high and heavy enough for shaping of a crucible.

Plaster of Paris mould and a profile is used for shaping. The body prepared as mentioned above is thrown in the mould which is fixed on a jigger-head. During the rotation the profile is pushed down into the mould and the crucible is shaped. After partly drying the green crucible may be taken out from the mould and perfectly dried.

The green crucible may be covered with the glaze and fired in the reduction atmosphere or straight fired without glazing. The firing temperature varies from 1100°C to 1400°C according to the body composition and produced quality.

For the production of graphite bonded crucibles also iso-static pressing or other kind of pressing may be used.

From this ordinary way of the production of crucibles different producers are using slight variations in the production process in order to improve the quality of final products. These variations depend usually on the used raw materials or requested structure of the body. Of course it is not possible to discuss all these possibilities in this paper but a skilled expert will definitely be able to find the best production way in the production process.

Besides graphite crucibles and stopper-heads, graphite fireclay blocks are also produced. These are used for linings of hearth and wall sections of blast furnaces and ferro-alloy furnaces, and aluminium pot linings. For this production graphite, grog and tar are used. Because tar is used as bond, mi-

ring and pressing of the body mixture should be done in steam heated machines and presses to avoid sticking of the body. The green products should be fired in a reduction atmosphere or covered with coke or graphite.

Coming to the conclusions in this chapter concerning graphite products it may be said that the main raw materials are graphite, silicon carbide and plastic clays. The production is rather highly specialized and the price of the goods is also very high. Therefore some of the necessary raw materials may be imported from other countries and still the production might be economic and profitable. The price of the goods allows the products to be exported to the whole world.

CHAPTER No. 2.

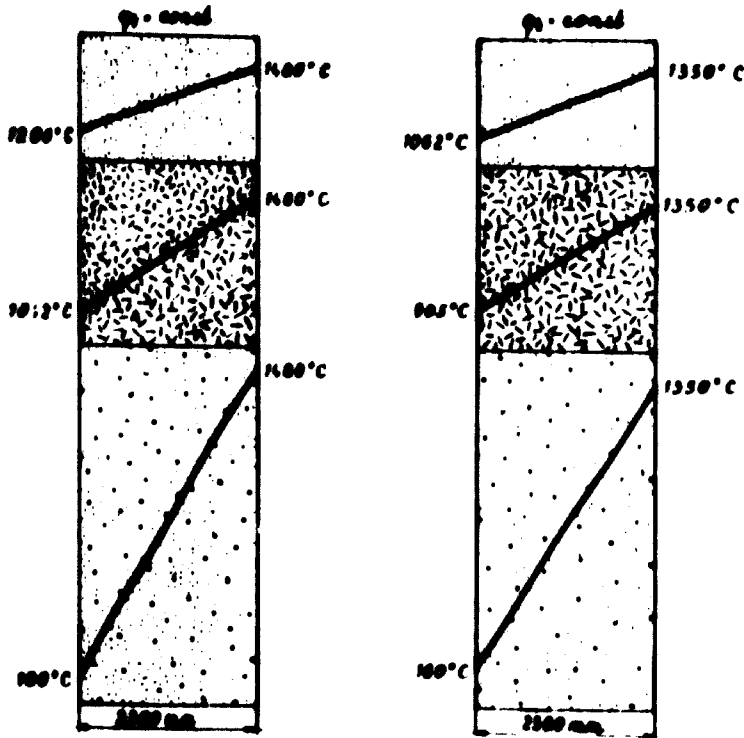
Insulation refractory products.

In the very beginning it is necessary to say a few words about the importance of the production of insulation bricks.

Ordinary refractories, let us say, high duty firebricks with approximately 40% of Al_2O_3 show the thermal conductivity 0,9 to 1,2 kcal.m.h. $^{\circ}C^{-1}$. It means that approximately one kilocalorie will pass through a wall which is 1m thick during one hour when the difference in temperatures between the inside and outside surface of the wall is one degree centigrade. This one kilocalorie is actually totally lost because the wall is from outside cooled by the air.

An insulation refractory product with the bulk density of 0,8 g/cm³ has the thermal conductivity only 0,2 to 0,3 kcal.m.h. $^{\circ}C^{-1}$ what is actually four to five times less.

The following picture No 6. shows the differences in tem-



Picture No 6.

peratures for three various refractory materials, namely high alumina bricks with 80% Al_2O_3 , high duty firebricks with 40% Al_2O_3 and high alumina light weight refractories with a bulk density of $1,0 \text{ g/cm}^3$ and content of 60% Al_2O_3 . On the right sides of the walls on the picture is mentioned temperature 1480°C and 1350°C respectively for all three tested refractories. In our case, when the thickness of the wall is 230 mm will be the temperature on the other side of the wall for dense high alumina bricks 1205°C , for firebricks 1012°C and for high alumina insulation bricks only 180°C or 905°C , 1062°C and 160°C for the second example.

It is evident that the insulation products have the following advantages:

1. Decrease of thermal losses on the conductivity and heat accumulation and therefore saving of 30 - 50% of energy.
2. Decrease of the thickness of the refractory masonry two to three times and therefore saving of investment costs.
3. At intermittent kilns shortening of firing cycles up to 60% and therefore increase of the output of 40-50% more.

Five main methods of producing refractory insulating materials are known in the world:

- a. The first method consists of abrupt heating of certain pre-ground materials to 700 - 1000°C, such as vermiculite which expands at these temperatures, or perlite which is expanded also in this way. As a result the volume of the materials is considerably increased. These materials of low bulk density are used as grog and mixed with sodium silicate, Sorel's cement, Portland cement to produce insulating refractories suitable for temperatures up to 600°C. When the light grog is mixed with clay or bentonite and fired, the products are suitable in exceptional cases for temperatures up to 1200°C. The former one using Sorel's or Portland cement as the bond is produced in the ordinary concrete technology, which means that 60-80% of grog is mixed with cement in a mixer and the mixed body is stamped or hand moulded on the spot. The latter one using clay for bonding is produced in the same way as firebricks, with the only exception that light grog is used and the final firing temperature should be accommodated to the refractoriness of the used grog.
- b. Another method is to add combustible matter to a refractory body. This is the oldest method of all in the production of light weight refractories. It is, however, used also presently in the refractory industry and has been modernised in such a way that new artificial combustible additives were developed. Such combustible substances as coke, sawdust, coal, peats etc. may be counted to the classical additives. As a modern additive should be mentioned e.g. foamed polystyrene beads.

Without a special preparation and treatment of the above mentioned classical combustible substances it is very diffi-

cult in production practice to obtain products with a specific gravity much below 0.9 g/cm^3 if the mechanical strength is to be adequate. However, addition of foamed polystyrene beads enables the production of light weight refractories with specific gravity 0.5 g/cm^3 and a good cold crushing strength of the bricks.

The production process is similar to that of the production of ordinary firebricks, which was described in detail in the previous lecture. It must only be added that firing of the products with the addition of coke, sawdust, coal, peats etc. in a tunnel kiln is not possible because in such a case the firing zone will move to the entry of the tunnel kiln due to a low /approximately $300 - 600^\circ\text{C}$ / combustible temperature of this additives.

This way of production is suitable for the production of light weight insulation firebricks, silica bricks, high alumina bricks as well as for the production of other special kinds of insulating refractories.

c. The third method of adding chemicals and then allowing them to volatilize during the drying or firing process from the brick is no longer used in the world and is mentioned briefly only in order to have a complete view of the problems of production of light-weight refractories. Of the volatilize matters the most common one and economically acceptable is naphthalene which is added in amounts of 30-35%. Unfortunately, this substance forms an explosive mixture with air, so that although the method leads to the products of a good quality, the danger of explosion during the volatilization of naphthalene is too high.

On the other hand this method is very cheap because naphthalene is regenerated from the green body and repeatedly used in the production process. However, disadvantages extend beyond advantages and therefore it is recommendable to use another process for the production of light weight refractories.

d. The fourth method of producing porous materials consists in adding chemicals which evolve gases, thus producing very

fine pores. This may be achieved in various ways. For instance, in an alkaline medium powdered aluminium produces hydrogen; hydrogen peroxide breaks down to release oxygen; in an acid medium carbonates give off CO_2 .

Except addition of hydrogen peroxide which breaks down to water and oxygen and which has economic disadvantages, all other methods need addition of chemical components to the body mixture /carbonates, soda ash, sodium hydroxide etc./ which necessarily decrease the refractoriness of final products. However, in spite of these facts and in spite of their apparent production simplicity all these ways show neither qualitative, nor economic advantages over other methods but they may give refractories suitable for temperatures up to $1350^{\circ}C$.

e. The last method is based on the use of foam produced by resin soap or albumen or other foamable organic components. This method enables the production of light-weight refractories of very low densities, for instance down to $0.4g/cm^3$, and the bricks may be used up to very high temperatures depending on the raw materials used for the production. Because also other properties, namely cold crushing strength, are excellent these products may be used not only for the insulation purposes up to certain temperature, but also as construction masonry for temperatures to $1500^{\circ}C$.

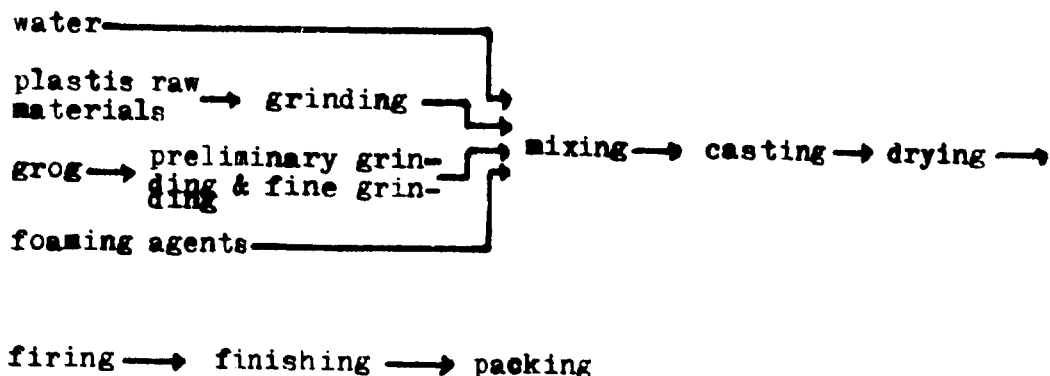
From technical point of view it seems that from the above mentioned five methods only that one using combustible substances and that one using foam are suitable for the mass production; the former one for the production of lower quality, the latter one for the production of higher quality of insulating light-weight refractories.

As mentioned above the production method using combustible substances as coke, sawdust, coal, peats, ricehusks, etc. flows in the same order as the production of dense firebricks, where grog is partly replaced with combustible matters. Because the production of dense firebricks was described in separate lecture I would not like to repeat it once again. However, the method using foam is of great significance for modern

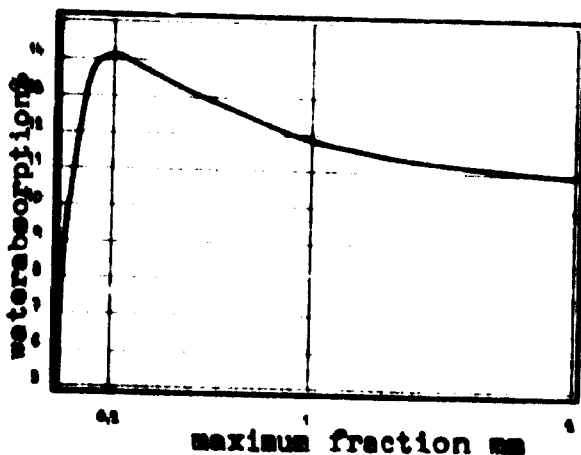
production technology and therefore I would like to describe its basic principles in more detail.

The production process may be simply expressed by the following flow diagram No 1.

Diagram No 1.

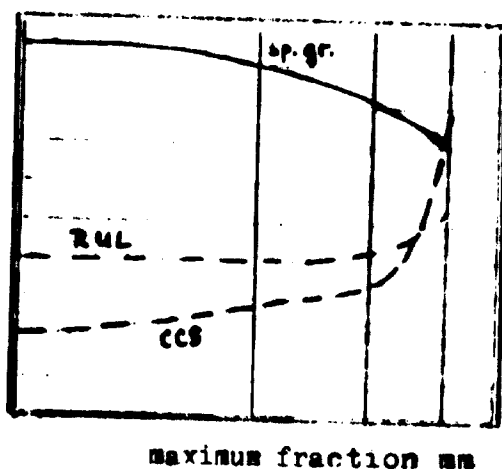


The grain size of the body mix, which is the grain size of the grog and plastic raw materials, is one of the most important factors in the production of foamed firebricks. In view of the fact that the finer the grain size of the mix, the less economical the process /because of the increased power consumption on grinding/, this problem has been extensively investigated. It will be seen from picture No 7. that the water absorption of the products increases with diminish-



Picture No 7. Relationship between water absorption and maximum fraction

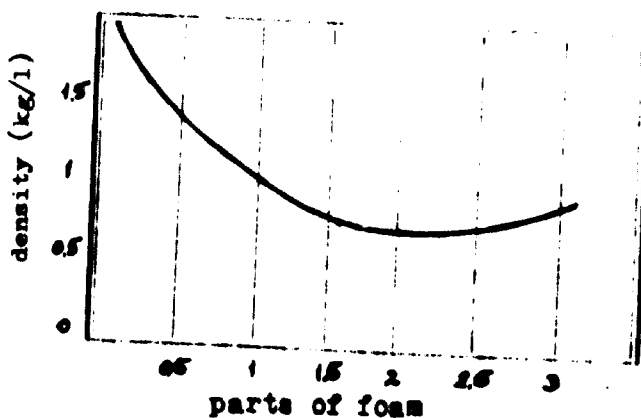
ing maximum grain size to x_0 0.2mm. This maximum grain size, which is totally unsuitable for dense firebricks gives the best results in light-weight products. This is illustrated in picture No 8. showing the properties of one of the prepared



Picture No 8: Influence of grain size of mix on properties of light-weight refractories.

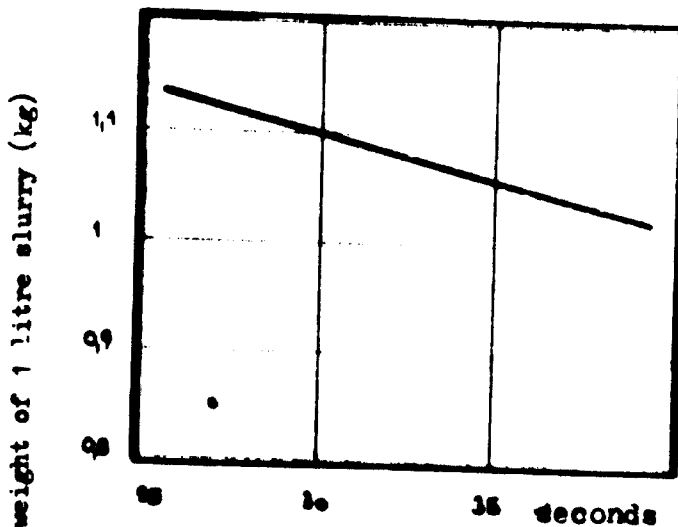
materials plotted against the grain size. Technically it would be feasible to use finer material, but this would unduly increase the production costs.

The relationship between the ratio of foam to body and



Picture No 9: Relationship between foam-body ratio and the density of the finished products.

the density of the finished products is illustrated in picture No 9. The density of the products decreases with increasing of the foam content up to a critical point of 2.5 parts by weight of foam to 1 part by weight of body mix. Beyond this critical point the density increases again. This is partly due to the collapse of the pores ensuing at this stage and partly to a certain compaction of the bricks during drying, since the skeleton of the foamed material does not quite support its own weight even if "stiffeners" are added. Picture No 10. shows how the weight of one litre of foamed slurry decreases with the mixing time.

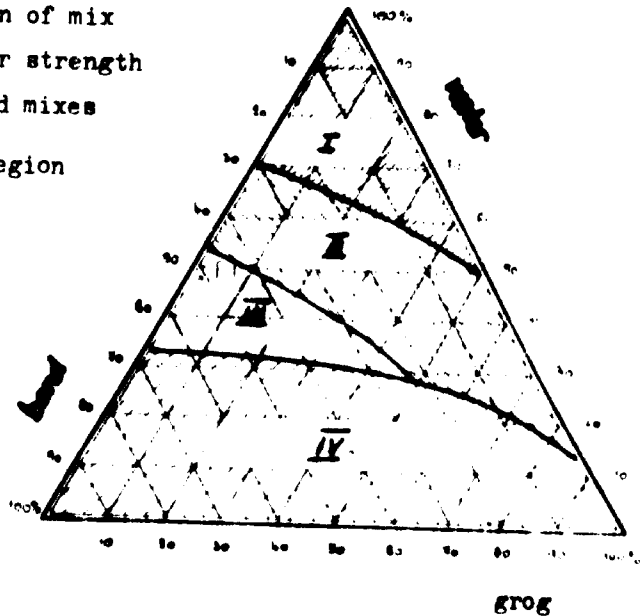


Picture No 10.: Relationship between mixing time and liter weight of the slurry.

The correct proportioning of grog, bond and tempering water is also very important, because the amount of foam which may be added or developed in the body mix depends on the plasticity of the body and also on the amount of added water. The ternary system shows in picture No 11. the results of a great number of practical tests carried out to demonstrate the optimum proportions of the bond, grog and mixing water.

In the original production method the body mixture and the foam were prepared separately and then the foam was introduced into the mixture. Nowadays it is found that it is more

- I Disintegration of mix
- II Region of poor strength
- III Region of good mixes
- IV Non-foaming region



Picture No 11.: Diagram water-bond-grog.

advantageous to produce foam directly in the mix by adding foaming agents to it. This obviates the spoiling of pores of the foam as often occurred in the old method, and the foam is in addition better distributed throughout the brick. This leads to an improvement of the quality, particularly with regard to the density and the cold crushing strength. The optimum mixing time should be determined on the basis of comparison with the properties of the products and varies in time according to the used foaming agent.

Foamed light weight bricks are produced by the casting method. The moulds may be of plaster or metal with the preference to the metal moulds. The manufacture of standard products lends itself to a high degree of mechanization.

The purpose of drying is to obtain a consolidation of the products without destroying the texture produced by the uniform distribution of the pores. The lighter the product, i.e. the lower its density, the greater the temperature gradient arising during drying between the surface and the co-

re of the product. A rapid drying may easily damage the texture of the product.

Under such conditions the humid - air drying is most applicable. This method ensures a uniform drying over the whole cross-section of the product without sealing the surface pores. The only alternative to this would be drying in large open spaces over long periods at low temperatures.

For firing the same kilns are used as in the production of fire clay bricks and high alumina bricks but the firing curve differs as follows:

- a. The cooling has to be slow, since the light-weight products have a very low thermal conductivity, thus giving rise to a great temperature gradient between the surface and the core setting up stresses which can destroy the structure of the products.
- b. In the firing zone the solid-state reactions must proceed uniformly from the surface to the centre. This is important for guaranteeing the customers a low shrinkage in service.

High quality products for special applications must have very accurate dimensions, for which purpose they are calibrated with the diamond or silicon carbide wheels.

Using different raw materials it is possible to produce different types of products which may vary not only in their Al_2O_3 content, bulk density and mechanical strength, but also in their service temperature. The following table gives the properties of two different products produced by the foaming method:

	<u>quality I</u>	<u>quality II</u>
service temperature °C	1300	1500
P.C.E. Seger Cone	34	38
alumina content %	38- 40	60
Fe ₂ O ₃ content %	0.8 -1.0	1.0
CCS kp/cm ²	60	75
bulk density g/cm ³	0.8	1.0
RUL with lkp/cm ² t _a °C	1350	1500
thermal conductivity at 1000°C kcal/m.h. °C	0.35	0.40
shrinkage 4 hours/1300°C %	0.5	-
4 hours/1500°C %	-	0.6

CH A P T E R No. 3.

Zircon and zirconia products.

Shortening of the melting processes in the glass and steel factories leads to a higher wearing of melting aggregates. Increasing of the production temperatures and increasing of the output per one cubic metre in melting aggregates force the ceramic producers to improve their refractory products. From this point of view needs a special attention the glass industry. For the construction of the tanks with melted glass are used in the last years corundum-baddeleyite blocks, or zirconia, mullite blocks etc. either casted or pressed.

Similar attention should be given to the smelting process of special alloys. Zirconia refractories are used in different forms for lining of ladles and for the production of pouring refractory material namely for the production of nozzles.

It is to be mentioned that this type of refractories is, in comparison with fireclay bricks or with high alumina bricks, rather expensive and therefore used for the most exposed places of furnaces or kilns, for melting crucibles, burners, mixing propellers etc.

When zircon is applied as a wash to refractories the life of the latter is considerably increased. It is now common practice to apply zircon washes to the inside walls and roofs of tunnel kilns, as well as to the kiln trucks and furniture. So applied to the roof of a tunnel kiln, the roof itself is protected from hot gases, while the formation of "glaze droppers" is eliminated.

Metals which are exposed to elevated temperatures, such as furnace and kiln fittings, can be protected by a suitable zircon wash. The zircon is made into a wash with approximately 3 per cent by weight of either sodium silicate or

potassium silicate, and the wash is applied to the clean metal surface thinly. Thick layers can be built up by the application of a number of coats, each being dried before the next one is applied.

For the production of this type of refractories zircon and zirconia are used as basic raw materials.

A. Zircon

The mineral zircon, which is $ZrSiO_4$, is widely distributed as an accessory mineral in acidic igneous rocks. Through weathering of these rocks, the zircon appears in sediments as small crystals or sand grains which, because of their high specific gravity, are subject to concentration with other heavy minerals on beaches, or similar wind and water-swept areas. The commercial ores exploited at the present time consist entirely of such beach deposits.

Beach sand zircon is generally associated with quartz, ilmenite and rutile accompanied by minor amounts of garnet kyanite and monazite. The zircon is separated from the lighter minerals by mechanical methods using gravity equipment. Ilmenite is removed by treatment on magnetic separators and rutile is removed by electrostatic separation. While technically suitable zircon is obtained in this fashion, a purer zircon may be obtained by acid leaching.

Reduction to fine sizes is accomplished by the methods usual in the ceramic industry, such as ball milling accompanied by classification. Particle sizes in the ranges of 5 to 50 microns maximum are commercially available in the world. A commercial zircon aggregate carries the following typical chemical analysis:

ZrO ₂	64,98%	CaO	0,12%
SiO ₂	32,54%	Na ₂ O /HCl soluble/...	0,10%
Al ₂ O ₃	1,42%	K ₂ O /HCl soluble/...	0,04%
Ti ₂ O ₃	0,16%	Fe ₂ O ₃	0,052%
MgO ²	0,16%	P ₂ O ₅	0,26%

Zircon of various types alone or in conjunction with other zirconium compounds are used in the manufacture of refractories, in glass opacification, in the manufacture of electrical porcelains, as additions to steatite and cordierite porcelains

in grinding wheel bonds, in precision alloy casting, in chemical and electrical porcelains, electrical resisting cements, in zircon base vitreous enamels etc.

Zircon imparts unusual properties to some types of white-ware bodies. In electrical and chemical porcelains, zircon is used in proportions up to 80% by weight with the advantage of high mechanical strength in bodies maturing as high as Cone 16 and as low as Cone 8. Zircon has a low and regular thermal expansion, making it suitable for use in ceramic bodies that must withstand rapid changes in temperature. In addition, zircon bodies have high dielectric strength at ordinary and elevated temperatures, low electrical loss at high frequencies and are extremely resistant to most chemicals. Zircon is insoluble in all acids except hydrofluoric.

Zircon also is an important constituent in some types of spark plug porcelain. It may be used in compounding zircon - clay - flux type bodies maturing at Cone 12 to Cone 17, or in high fired alumina type bodies. Zircon not only enhances the mechanical and dielectric properties, but aids in lowering the firing temperature when employed in proper proportions in an alumina composition.

B. Zirconia

Zirconia melts at 2700°C and has a low thermal conductivity. Pure zirconia is monoclinic at room temperature and changes to the denser tetragonal form at about 1000°C . Coefficient of expansion for the cubic or stabilized form is $10.5 \times 10^{-6}/\text{C}$ for the monoclinic or pure form is $6.5 \times 10^{-6}/\text{C}$ up to 1200°C . Most manufacturers make a 70-80% cubic material having an expansion of about 8.5×10^{-6} and showing no inversion. However, some ZrO_2 plus stabilizer compositions are being produced with coefficients of linear expansion of $5.1 \times 10^{-6}/\text{C}$.

Zirconia occurs in nature as the mineral "Baddeleyite" which is mined e.g. in Brazil. However, zirconia is usually produced from the mineral zircon which is available in large quantities. Various grades of zirconia are made from zircon;

these grades range from 75% zirconia up to extremely pure hafnium - free material of over 99% purity.

To prepare useful products from zirconia, stabilizing agents such as lime or magnesia must be added to the zirconia, preferably during fusion, to convert the zirconia to the cubic form. Most commercial stabilized zirconia powders or products contain calcium oxide as the stabilizing agent. The "stabilized" cubic form of zirconia undergoes no inversion during heating and cooling.

Zirconia is available in several distinct types. The most widely used form is stabilized in cubic crystal form by a small lime additive. This variety is essential to the fabrication of shapes since the so-called unstabilized monoclinic zirconia undergoes a crystalline inversion on heating which is accompanied by a disruptive volume change.

Stabilized zirconia is used for example for the production of refractories. So-called stabilized zirconia refractories are used where extremely high temperatures are required. The low thermal conductivity ensures low heat losses, and the high melting point permits stabilized zirconia refractories to be used continuously or intermittently at temperatures above 2200°C in neutral or oxidizing atmospheres. Above 1650°C in contact with carbon zirconia is converted to zirconium carbide.

Zirconia is not wetted by many metals and is therefore an excellent crucible material when slag is absent. It has been used very successfully for melting steel alloy and the noble metals. Zirconia refractories are rapidly finding application as setter plates for ferrite and titanate manufacture and as matrix elements and wind tunnel liners for the aerospace industry. Zirconia is also a constituent in fused glass - tank blocks.

With the use of zircon two basic qualities are produced:

- i. Zircon refractories with the clay bond
- ii. Zircon refractories without the clay bond which is replaced with a very finely ground zircon raw material.

i. Zircon refractories with the clay bond are produced from the zircon sand which is finely ground and approximately 10% of plastic clay with a high content of SiO_2 . For the production is used an ordinary process which is used in the production of firebricks or high alumina bricks; it means pressing or moulding of the body mix by use of different kinds of presses or electric and pneumatic moulding equipment. The products are fired to a temperature of 1600°C . During the firing process in the temperature interval $1550 - 1600^\circ\text{C}$ the porosity of the fired products sinks rapidly. Also the possibility to prepare first from zircon and clay a synthetic grog is often used in the industry. Further production process is similar to that mentioned above. When fired to the temperature of $1420 - 1450^\circ\text{C}$ only products with higher porosity will result. Of course, these products will have a lower corrosion resistance but on the other hand they have a higher resistance to the spalling.

This type of products with the clay bond is suitable for lower temperatures and is not suitable for the contact with the melted glass.

ii. Zircon refractories without the clay bond are also produced from the zircon sand where the bond is actually very finely ground zircon. If the grinding or milling process uses steel pebbles it is necessary to dress the finely milled zircon grog with the hydrochloric acid in order to remove the particles of iron from the raw material.

Shaping of such a mixture is rather difficult and therefore it is necessary, namely for hand moulding, to use plasticizers e.g. carboxymethylcellulose, tylose, dextrin, sulphite lye, etc. Hand moulding has been restricted in recent years and replaced by casting to plaster of Paris moulds, by isostatic pressing etc. These production ways give extremely good results, especially good porosity, a high cold crushing strength. Such products may also be further shaped / cut, bored, etc./ in the green stage. The products are fired to the temperature $1600^\circ - 1700^\circ\text{C}$ and the products are not sensitive during the firing period to the kiln atmos -

phere.

Zirconia refractories are produced from ZrO_2 which should be stabilized before use. It does not matter if it was produced by chemical process or by melting. The stabilization may be done by fine milling of ZrO_2 and stabilizer and firing of pressed briquets to the temperature $1700 - 1750^\circ C$.

Usually ball mill which inside surface is covered with rubber or nylon layer is used for fine milling of the body mix in order to avoid increasing of impurities in the body mix, namely iron. Artificial pebbles produced from stabilized zirconia or from metal zirconium are used for this operation. The milled stabilized zirconia should be plastified by:

- i. addition of solution of $ZrCl_2$, $MgCl_2 \cdot 2H_2O$ or other very easy hydrolysed salts.
- ii. function of thin acids or lyes on high fired and finely milled ZrO_2
- iii. addition of extra finely milled $Zr(OH)_2$
- iv. hot pressing

As the bond phosphoric acid, boric acid as well as starch resin etc. may be used. The products are shaped by casting, pressing or hot pressing and after drying should be fired to the temperature $1700 - 2400^\circ C$ according to the used bond.

CHAPTER No. 4.

High alumina refractories.

It has been known for long, in fact since the ancient art of pottery, that kaolinite and clays containing kaolinite undergo certain characteristic transformations when

fired.

Some well-defined reactions take place when kaolin or kaolin-bearing substances are heated. These reactions can be investigated most comfortably by differential thermal analysis.

The characteristics of the enthalpy - change versus temperature plots /DTA curves/ of kaolinite and generally of kaolinite - type clay minerals are as follows:

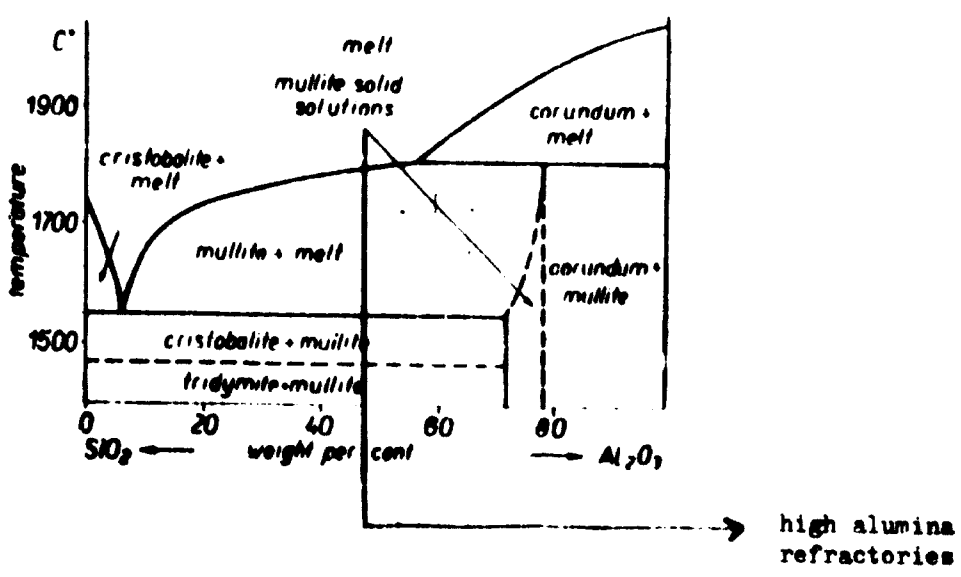
1. A characteristic heat - absorbing endothermic reaction due to the release of hydroxyl ions takes place between 500 and 650°C.
2. A characteristic and sharp exothermic reaction takes place between 900 and 1000°C which can be utilized also for the quantitative determination of kaolinite.
3. Kaolinite - bearing clays show another exothermic effect between 1200 and 1300°C.

The state between the endothermic reaction and the beginning of the first exothermic one is called metastate; thus kaolinite in this state may be called meta - kaolinite. Kaolin, heated above the temperature of the first exothermic peak, already contains crystals. In spite of this, we still have no clear and exact idea of the processes taking place during the first exothermic peak. According to many authors, mullite nuclei are formed from metakaolinite, when fired at the temperature of the first exotherm and later these nuclei begin to grow. The formation of γ -alumina is considered by this theory only an occasional occurrence. No further reactions take place in kaolinite with temperature, because mullite is the only stable crystalline compound in the Al_2O_3 - SiO_2 system; under normal atmospheric pressure or at any pressure exceeding it by a few hundreds only, this compound is produced from every anhydrous or water-containing aluminosilicate.

Mullite, which has a chemical formula of $3Al_2O_3 \cdot 2SiO_2$, crystallizes in the orthorhombic system, usually in the form of elongated needle-shaped crystals; its density is 3.03 g/cm³, its hardness /according to Mohs/ 7.5. Mullite is rare

in nature; its most important place of occurrence is the Isle of Mull, West Scotland, where it has been formed under exceptional conditions, very similar to those required for the production of artificial mullite. Although rare in nature, mullite is very common in artificial products. Porcelain, fireclay products, stoneware etc. contain certain amount of mullite as well as high alumina refractories where mullite is one of their most valuable constituents.

kaolin itself with its formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ builds the base of refractory clays and has theoretically 39.5% Al_2O_3 , 46.5% SiO_2 and 14.0% H_2O or 45.9% Al_2O_3 and 54.1% SiO_2 without chemical water. Kaolinitic refractory clays as well as kaolin itself are counted under the group of aluminosilicates which are very common throughout the whole world and therefore the limit of 46% of alumina is used to divide fireclay products and high alumina products. Generally speaking, all refractory products with the content of Al_2O_3 higher than 46% fall under the group of high alumina refractories, where mullite and corundum play the top role. The following diagram shows the sphere of high alumina products very clearly.



Picture No 12: Al_2O_3 - SiO_2 diagram

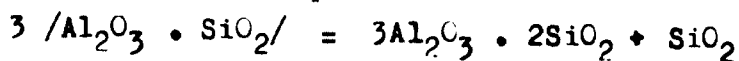
The recognition of the properties of mullite and of their role in fireclay refractories has led to the statement that an alumino - silicate refractory of technical properties surpassing those of fireclay can be produced by reducing the amount of the vitreous phase and by simultaneously increasing that of mullite.

These considerations have induced the production of high alumina refractories. For better explanation it should be said that kaolinite itself when heated changes theoretically to 63.92% of mullite and 36.08% of free silica which is called in practice vitreous phase, contains also all impurities and is the weakest part of the body as far as refractoriness under load and PCE /Pyrometric Cone Equivalent/ is concerned. Figure no 12. also shows that mullite is the single stable crystal phase in high - alumina products below 72 per cent alumina content. Silica above 28% reacts with the accessory minerals of the raw materials /usually called as impurities/ and gives a vitreous grog, softening at corresponding temperature, just as in fireclay products. Getting nearer to the composition of mullite, the percentage of the vitreous phase decreases, and the technical properties of the high alumina product improve. With an alumina content above 72 per cent a liquid is formed /in the absence of fluxes/ only above 1810°C. Below this temperature, only mullite and corundum are present. Mullite decomposed congruently into corundum and into a high - silica vitreous phase.

The following substances are generally used as raw materials for high - alumina refractories:

1. Natural alumino - silicates:

Natural alumino - silicates such as andalusite, kyanite, and sillimanite transform into mullite at 1380 - 1550°C according to the following equation:



Theoretically 88 per cent mullite and 12 per cent silica is formed by this equation. If, however, there are some accessory constituents /usually fluxes/ in the batch, the product

contains a high silica glass besides mullite, with the amount of the vitreous phase considerably lower than in fireclay products, as can be seen from the above formula.

As minerals of the sillimanite group, unfortunately, always contain contaminations from the original rock and its accessory minerals, it is essential to concentrate the rocks. Only a few world occurrences do not need concentration and are used without any dressing. Concentrated products generally have an alumina content of 58 - 62 per cent.

Volume changes due to the transformation of natural anhydrous aluminic - silicates into mullite are of high importance from a technological point of view. All minerals of the sillimanite group have a specific gravity above 3g/cm^3 , while that of the fired product /mullite and amorphous matter/ is below 3g/cm^3 . The increase in volume /expansion/ due to a decrease in specific gravity being considerable, all minerals must be prefired before being manufactured into a refractory product. Exceptions are only some very pure sorts of andalusite. Prefiring temperature should be 1380°C and 1540°C in case of kyanite and sillimanite, respectively. In case of unsatisfactory prefiring, the product will scale with a simultaneous reduction in strength. Mullite is formed from kyanite as low as at 1200°C ; when heated to 1600°C a dense network of mullite crystals appears, surrounded by a vitreous mass.

In order to ensure shaping, some good-quality fireclay is added to the prefired semi-product ground to suitable particle size. The percentage of bond clay is usually 5 - 10 per cent, the minimum firing temperature 1500°C . The properties of the product are determined by its mullite : vitreous phase ratio which again depends on the alumina and flux content of the raw material concentrate.

High alumina refractory products, manufactured from minerals of the sillimanite group, are usually called "sillimanite refractories" even now, although it is well known that they contain no sillimanite, but mullite.

2. Natural alumino hydrates:

natural alumina hydrates such as hydrargillite, boehmite, transform first into gamma, later into alpha-alumina when fired. Artificial alumina hydrate transforms into alpha-alumina as well. The volume of alumina hydrates is greatly reduced when fired. Shrinkage percentages are 60, 33 and 13 % for pure hydrargillite, pure boehmite and gamma-alumina, respectively. Natural alumina hydrates are the chief constituents of bauxite, the accessory minerals present are iron oxide, iron hydroxide, quartz, calcite and sometimes also kaolinite and other minerals.

Some low-iron bauxite sorts of suitable composition were tried as raw materials for high alumina refractories. Bauxite was prefired because of the high degree of volume change, shaped and fired after the addition of about 10% fireclay as a bond. Bauxite refractories, however, have not shown good results in comparison with sillimanite refractories; the firing shrinkage being incomplete even at high temperatures, the products are porous, their refractoriness - under - load properties unsatisfactory in spite of their high alumina content. The reason is to be found in the iron oxide content; even so called low - iron bauxite contains a pretty high quantity of iron compounds / 5-10% /, which make refractory properties poor. Bauxite could not be de-ironed, because the iron-bearing compounds are of very fine distribution and would be removed either by sedimentation or by flotation, only by very expensive chemical methods which are used in industrial production of artificial alumina. In spite of these facts, the bauxite high-alumina refractories are still produced.

Diaspore could be applied better. Diaspore refractories are manufactured from a batch containing about 60 parts of prefired, 40 parts of unfired diaspore and about 10 parts of refractory bond clay.

3. Technical alumina and corundum:

The fragments of electrocast mullite as well as technical

alumina, made by the firing of technical alumina hydrate can also be used as a raw material of high alumina refractories. The latter material is mineralogically alpha-alumina; its chemical composition being 99.0 - 99.5% Al_2O_3 , 0.25 - 0.1% SiO_2 , 0.5 - 0.3% Na_2O and about 0.1% other oxides. As can be seen from these data, the purity of artificial alumina is superior to every natural substance and has a refractoriness of PCE 42.

In lack of natural raw materials, it is most practical to use technical alumina, which is produced usually from bauxite as a raw material for high alumina refractories and to manufacture so-called synthetic mullite products.

The essential points in manufacture of sintered synthetic mullite refractories can be summarized in the following: briquets, pressed from a mixture of technical alumina hydrate, refractory clay and sand in ratio 72% alumina : 28% silica are fired at 1500 - 1600°C, crushed, ground to a suitable particle size, mixed with 10-15% of refractory bond clay, the body gained is shaped into bricks and refired at 1400 to 1500°C.

Another method recommends the following production process: The raw materials of the briquet which are similar to the above are ground to extreme finesse, which means that maximum and average particle sizes should be 2.5 and 1.5 microns, respectively. Mixes in which the particle sizes are quite uniform, give a mixture easily pressed to a briquet and clinckerized as low as at 1500 - 1600°C. No doubt the dry process offers a simplified form of technology.

Natural alumino - silicates, as mentioned, have a maximum alumina content of 60 - 62%. For the manufacture of a refractory, containing only mullite, it is essential that alumina should be added in order to increase the Al_2O_3 content to approximately 72%. No higher enrichment of alumina is necessary since the adding of alumina increases the refractoriness-under-load only until the composition of mullite is reached. Beyond this it becomes ineffective, as it is the par-

tial melting of the mullite phase itself that will soften the product.

4. Corundum:

For the production of high-alumina refractories with the alumina content above 95% corundum may be used. Pure corundum appears in the nature very seldom and therefore it is produced from technical alumina by electromelting. Corundum high-alumina refractories may be also produced from technical alumina by sintering. Addition of 1-2% of TiO_2 to the technical alumina supports better sintering, and the growth of corundum crystals. In this technology the very important moment is the fine grinding of technical alumina. Good results are obtained when technical alumina is ground or milled below 10 microns as a maximum.

Electromelted corundum is used as grog in similar way as grog in the production of ordinary fireclay products. Only the firing temperatures are different and in most cases higher.

Three different production methods are used in the industry of high-alumina refractories: They are:

- i. semi-dry process using grog
- ii. process of sintering
- iii. process of electroelting

1. Semi-dry process was perfectly described in lecture "Body composition and processing of firebricks" using fired refractory clays as grog and plastic refractory clays as the bond. The same process is also used in the production of high alumina refractories. The only difference is that grog is instead of fired clay prefired kyanite, sillimanite or andalusite or artificial mullite or electromelted corundum. Also prefired bauxite may be used. This grog is bonded with a high quality plastic refractory clay and the production process uses the same production equipment as for the production of firebricks. Also firing temperatures are similar because the firing temperature is ordered according to the quality of the used plastic clay. From the above mentioned reasons it seems not to be necessary to discuss this production method further.

ii. Process of sintering is used for the production of high-alumina refractories with the alumina content above 95%. The principle of this production process is in prefiring of technical alumina to the temperature 1450-1600°C and its fine milling. The prefiring of technical alumina should be done with a view to change gamma-modification to alpha-modification and to obtain crystals of corundum of size 3 to 10 microns. When is so prefired alumina finely milled the surface of particles increases and therefore grows also number of reaction points.

For shaping of recrystallized corundum refractories all modern methods are used: casting of the slip to the plaster of Paris moulds, pressing of the body where pastes or adhesives were added, isostatic pressing or thermoplastic pressing.

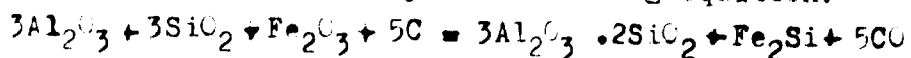
The firing temperature for a perfect sintering of fired body depends on the fineness of milling as well as on the purity of technical alumina and also on the size of corundum crystals. When technical alumina is milled to 2-3 microns, the firing temperature is about 1700°C. However, when additives such as TiO_2 in the amount of 1-5% are used, the firing temperature, which is necessary to the sintering of corundum, goes down to 1500°C.

The advantages of the sintering process in comparison with electromelting process are as follows: The consumption of electric power is lower and the consumption of fuel is also lower. It may be said that the consumption of calories is three to six times favourable for the sintering process. Unfortunately not all products are possible to be produced with sintering process.

iii. Process of electromelting.: Mullite refractories are manufactured also by fusion in an electrically heated kiln and by casting into a suitable form. A batch of 72% alumina content is melted in an electric furnace and the melt is cast into a sand form; a well-defined cooling schedule results in a refractory block of closely interlacing mullite crystals and of very dense texture. The outstanding properties of such refractory blocks are as follows: bulk density

3.0 - 3.1 g/cm³, porosity 5-7%, water absorption capacity 0.5 - 2%, heat conductivity 0.0101 cal/cm.hour.°C /measured at 1200°C/, PCE 38, RUL above 1800°C, temperature of melting 2200°C. The chemical composition of these refractories comes near to that of mullite.

According to this process mullite is melted in an electric arc furnace. The gross process taking place in the furnace can be summarized by the following equation:



Bauxite is also frequently used as a raw material because here the iron oxide content of bauxite, unlike in the case of sintered high-alumina bodies, has no disturbing effect, for at the high temperature of the kiln it gets converted with the coke, added to the batch, into ferrosilicon which, owing to its high density, flows into the bottom of the kiln and may be drawn off separately. However, as can be seen from the equation, the iron oxide content of bauxite is limited. Bauxites of Fe₂O₃ content higher than 10-15% must not be used for the production of electrocast mullite refractories.

The contaminations of bauxite, as titania, calcium oxide, magnesia and alkaline oxides form, together with a slight content of iron oxide, a melt and after the crystallization of mullite remain in a vitreous phase.

Electrocast mullite products can be manufactured from other high-alumina raw materials too, e.g. from a mix of alumina and kaolin. The technological process is always the same: melting in an electric arc furnace, casting into a suitable form and controlled cooling.

The refractory properties of electrocast mullite blocks are favourable even if they have a relatively high silica content, these products have also another precious property: that of high corrosion resistance. It is to be mentioned that the only crystalline component of such high-silica electrocast mullite refractories, which contain the excess of silica in an amorphous or vitreous form, is mullite.

C O N C L U S I O N

New production ways in steel and metalurgical industry as well as atomic and aerospace research and industry need refractories with a high chemical purity, extremely dense and resistant to the temperature changes, with high refractoriness under load and high cold crushing strength.

These properties are more or less fulfilled with refractory products based on pure oxides such as BeO , CeO_2 , CaO , MgO , ThO_2 etc. Oxides before being used as the raw material for the production of refractories should be calcined in order to remove volatile matters as for example chemically bonded water, CO_2 , organic impurities etc

Fine particles will be reached by milling in ball or vibration mills. It may be milled in dry stage or with water or with a suitable organic liquid which does not react with the particular oxide. Ball mills should have rubber or nylon layer and pebbles should be made from the same material in order to avoid increasing of impurities namely of iron oxides.

Products composed from more than one oxide should be prepared in a ball mill by milling of all components together and in such a way ensure a good homogenization.

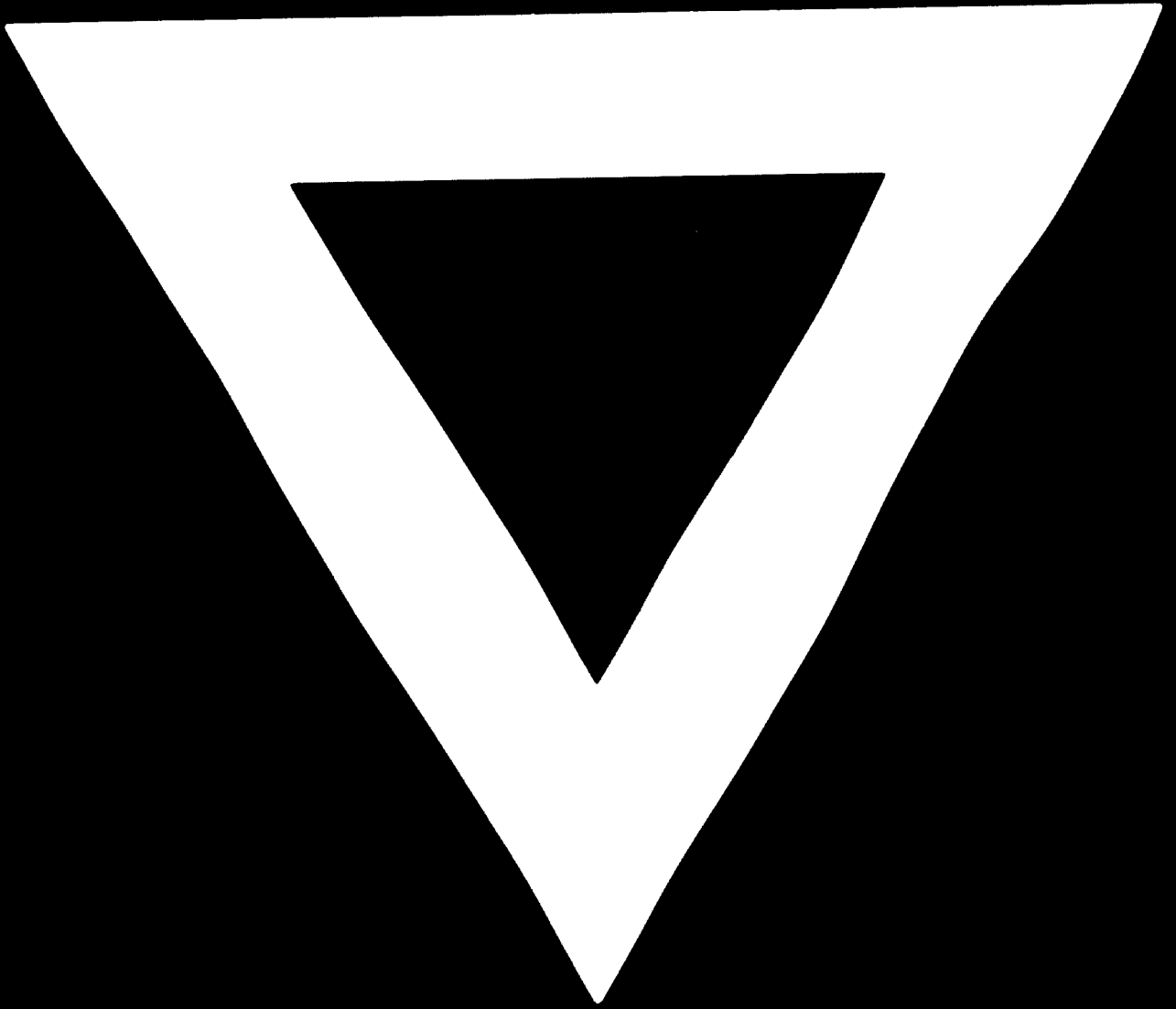
Oxide products are produced by the following processes:

- i. casting to plaster of Paris moulds
- ii. casting in paraffin suspension to steel moulds
- iii. pugging when plastifier is added
- iv. pressing in steel moulds
- v. hot pressing
- vi. isostatic pressing

Firing of the products from oxide ceramic differs according to the quality, size of the product etc. Very often double firing is used. The first one to the temperature $1200 - 1400^\circ\text{C}$; the second one to the temperatures $2000-2200^\circ\text{C}$.

However, these types are mentioned only to complete the view of the refractory products and their production needs highly qualified and skilled experts.





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