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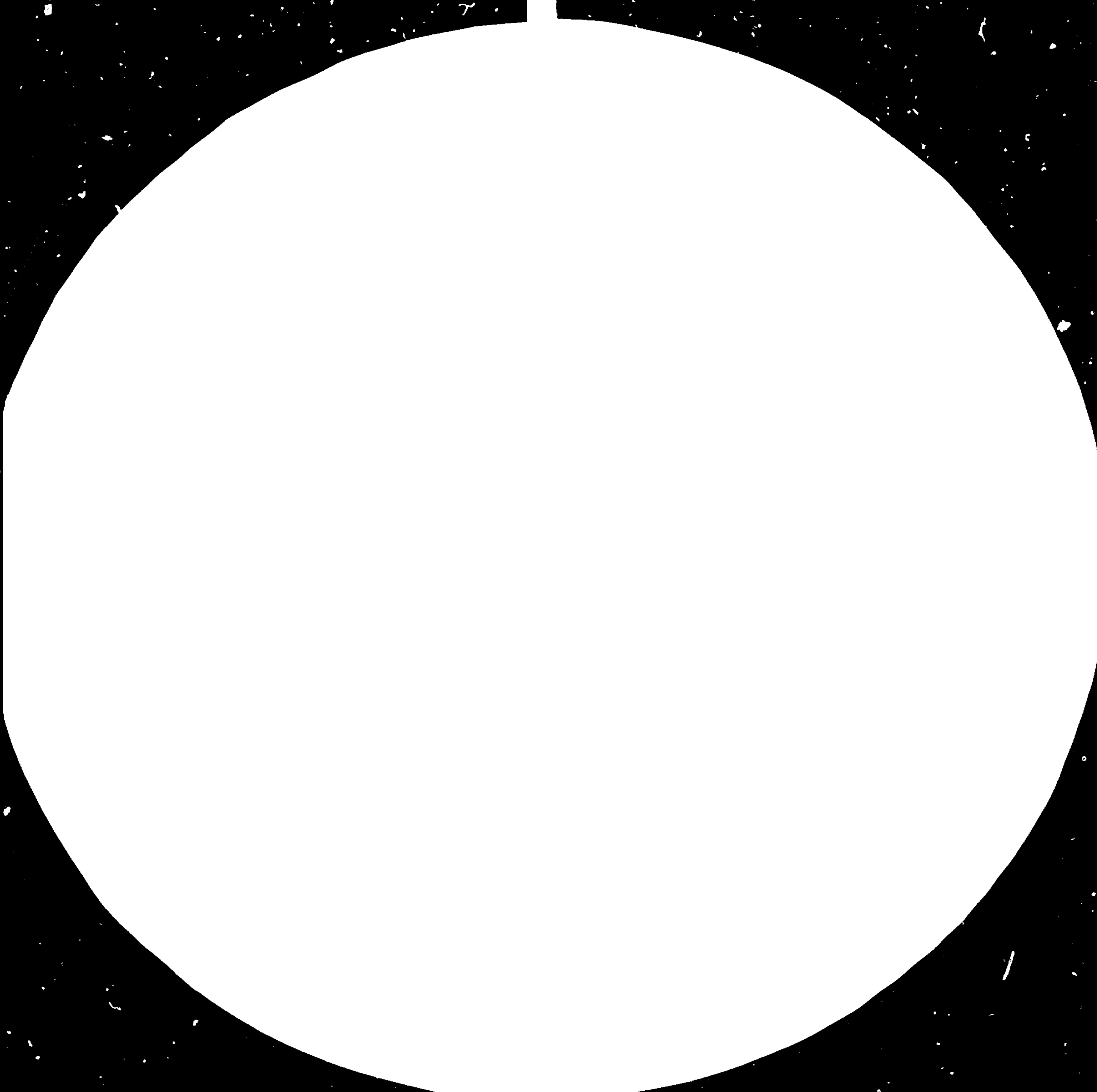
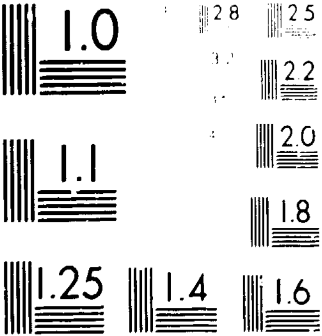
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org





MICROCOPY RESOLUTION TEST CHART

[illegible]

12872 → M. Dietrich

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ENERGY SAVINGS
IN COMPOSING CERAMIC BODIES

by: Z.A. Engelthaler

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ABSTRACT

Ceramic and refractory products are classified. They are mostly based on the alumo-silicate chemistry. The composition of their bodies in view of energy requirements is discussed from the physical-chemical and from the technological aspects. Product aspects are analyzed in details following particular ceramic and refractory products with the main defining factors and with the view of body compositions and their corresponding firing temperature. The paper is concluded with main guidelines to be kept in elaborating ceramic technologies in developing and least developed countries.

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I. INTRODUCTION

Ceramic products are those produced from inorganic matters by grinding, shaping, drying and hardening, which takes place mainly during the firing process. Traditional ceramic raw materials are:

clays and kaolins, which enable the easy shaping of products

siliceous materials, which control the shrinkage of green blends

fluxing materials, which regulate the firing temperature and influence basicly the properties of fired bodies.

The task of any ceramic technology is to develop the manufacturing process which will create, from local non-metallic raw materials at minimum production costs and energy consumption, a product with the required homogenity and properties, i.e. the product which corresponds International Standards.

Ceramic industry is one of the leading consumers of thermal energy. Its consumption consits in average of 86% production consumption /usually 22% for drying and 64% for firing/ and 14% overhead. Practically the majority of ceramic products is fired once or several times to be finished. This fact demonstrates the dependence of the ceramic industry on energy sources as well as on the world energy tendencies. This issue shows the necessity to realize all possible changes and arrangements which may positively influence the energy consumption and which may improve the prospects of ceramic industry in the future.

The complex analysis of the heat consumption in the ceramic industry shows the following possibilities for energy conservation

1. <u>Non-investment arrangements,</u> i.e. energy diagnosis of existing thermal units or of those which are newly put into the operation, improvements of heating units, verification of new technologies in the field of raw materials and components, lowering the firing temperatures, simplifying the manufacturing process, such as single and double firing process, decoration on raw glazes etc., single layer firing and different new drying and firing processes.

2. <u>Investment arrangements</u>. The decision for new heating equipment has to be based on a complex analysis, new equipment has to satisfy the future trends.

This paper deals with a part of non-investment arrangements which are possible to conserve the energy and which are related to <u>the body composition</u> of different ceramic and refractory products in view of local raw materials in developing countries. Physical-chemical, technological and product aspects are taken into the consideration as the basic for the proper body and glaze compositions of different ceramic and refractory products.

General principles which must be observed by the technologist while composing ceramic bodies, are complicated by the wide range of products assortment and different technological processes applicable in the ceramic manufactures. Therefore proper combination and selection of related aspects leads to the successful and most economical manufacture.

Table 1 Ceramic Products Classification

Porous body ← → Vitrified body

Heavy-clay ceramics ← → Fine ceramics

Brick products	Refractories	Earthenware	Stoneware		Vitreous China	Porcelain
Single firing	Single firing	Double firing	Single/double/ firing		Single firing	Double/single/ firing
Coarse grained body	Coarse grained body	Fine grained body	Coarse grained body	Fine grained body	Fine grained body	Fine grained body
Bricks Roofing tiles Drainage Ceramic prefabricates Ducts	Silica Fireclay High alumina Refractory insulations Magnesite Dolomite Chromium-magnesite	Wall-tiles Tableware Artistic ceramics Glazed floor-tiles Kitchenware	Sewage pipes Agricultural stoneware Chemical stoneware Artistic ceramics Facade tiles Industrial tiles Paving tiles Ducts Garden ceramics	Chemical stoneware Floor-tiles Facade tiles Tableware Artistic ceramics Glazed wall and floor-tiles	Sanitary ware Tableware Artistic ceramics	Tableware Electro-porcelain Chemical ware Dental porcelain Artistic ceramics

II. CERAMIC PRODUCTS CLASSIFICATION

Ceramic products represent a wide range of products which can be classified from different aspects with regard to the body preparation, product manufacture and properties and to its use. A simplified classification of industrial ceramics is presented in Table 1.

The classification of ceramic bodies observes the classical terms of heavy-clay and fine ceramics in the relationship to the porosity of products.

Brick products, such as bricks, roofing tiles, drainage pipes, ceramic prefabricats and refractory products, such as fireclay, silica products, magnesite, chrom-magnesite, dolomite, etc., belong distinctly under the term of heavy-clay ceramics. Thermal insulations, based upon coarse-grained raw material processing, are also the typical representatives of heavy-clay ceramics. All these products possess a distinctly porous body with the absorption capacity of appr. 5 to 60%.

The group of earthenware products represents the body composition with a non-vitrified porous body, however, as far as the fineness of raw materials milling is concerned, they belong rather among the fine ceramics - than heavy-clay products. Wall tiles, double-fired floor tiles, utility and artistic ceramics with a non-vitrified body are included into this group, too.

Earthenware products create, hence, a transition type of ceramics since they belong among fine ceramics products with regard to their character and fineness of milling, however, the physical properties of the body classify them with earthenware products.

Stoneware products form another transitting type between heavy-clay products and fine ceramics in consideration of body preparation and structure. Coarse-grained stoneware products, such as sewage, agricultural facade and artistic stoneware products, paving and industrial tiles, pertain distinctly among heavy-clay ceramics products. Stoneware bodies, if fine-grained, are counted among fine ceramics products. Chemical, utility, facade, artistic stoneware products and floor tiles form this group of products. Low absorption capacity and body vitrification is the common mark of all stoneware products which diferenciates them from all earthenware products.

Vitreous China is the term used for the products with a typical fine-grained and vitrified body without transparency. Products of sanitary, utility and artistic ceramics based on the properties of Vitreous China belong to this group of products.

Porcelain products are typical representatives of fine ceramics with a vitrified and translucent body. Utility porcelain, electroporcelain, chemical and dental porcelain and artistic ceramics made of porcelain bodies fit with this type of products.

Apart from above mentioned basic products of ceramic technology, there are many other new ceramic blends based on non-traditional minerals and oxides, e.g. Cordierite, statite, spinel, wollastonite, alumina, carbides, nitrides, graphite, rutille, ferrites, etc. These are not the subject of this paper.

The presented simplified classification of ceramic products shows the large variety of different products which are produced pending on the market potenciality and local raw materials availability. This classification jointly demonstrates that the ceramic technology is not an easy or simple one. To comprise the whole field, it is necessary to know not only all theoretical laws but also to gain practical experience in the application of the theory in the manufacturing processes.

III. PHYSICAL-CHEMICAL ASPECTS

In composing ceramic bodies, physical and chemical aspects are to be applied in the connection with the availability of local non-metallic raw materials. First of all it is necessary to take into account the chemical and mineralogical composition of products and to determin which of the three basic groups of minerals will influence decisively the production technology and the properties of final products. The majority of ceramic products belongs to the alumosilicate chemistry, as the prevealing oxides in ceramic blends are silica SiO_2 and alumina Al_2O_3. Depending on locally available raw materials the following three groups of minerals can be taken into the consideration

Kaolinite	$Al_2O_3.2SiO_2.\ 2\ H_2O$
Silica	SiO_2
Fluxes	Na_2O, K_2O, CaO, MgO bound in the molecules with alumina, silica and carbonates

1. Refractories

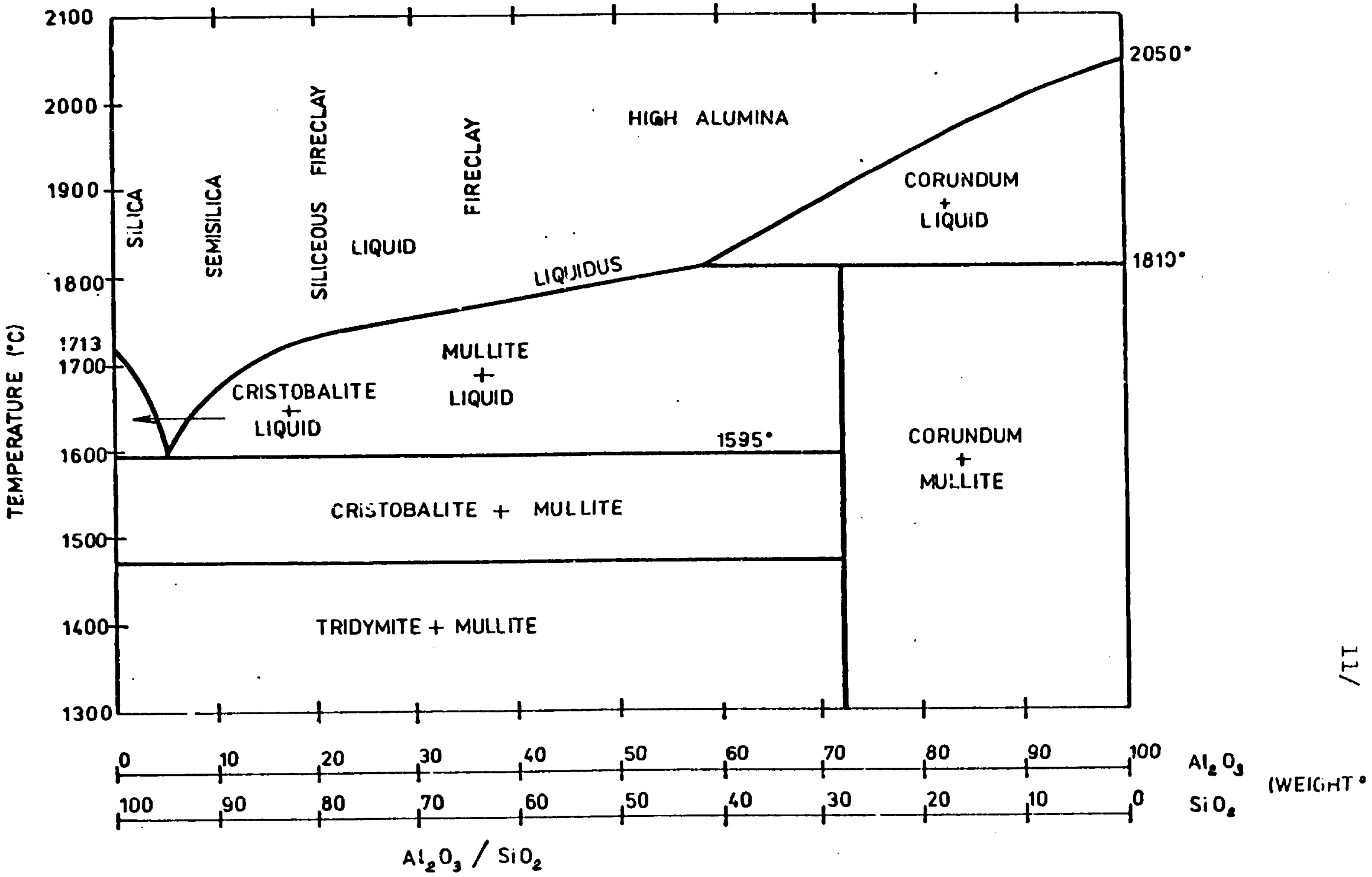
Considering the first two minerals, i.e. Kaolinite and Silica, which occur frequently in developing countries, the characteristic refractory oxides are

Al_2O_3 .... alumina
SiO_2 .... silica

The influence of mutual relations of these refractory oxides in the blend with regard to the equillibrium state between the liquid phase and the solid one, is determined by the SiO_2 - Al_2O_3 diagram, which, in its classical form according to N.L. Bowen and J.W. Greig, is presented in the Table 2.

Table 2

EQUILIBRIUM DIAGRAM : Al_2O_3 – SiO_2 SYSTEM



This diagram shows the Eutectic point with the composition of

94,5% SiO_2
5,5% Al_2O_3

which is the least advantageous for the manufacture of refractories based on silica and alumina oxides.

The Eutectic point is an invariant point on an equilibrium diagram. The eutectic temperature is that at which an autectic composition solidifies when cooled from the liquid state. The eutectic composition has been defined as that combination of components of a minimum system having the lowest melting point of any ratio of the components; in a binary system it is the intersection of the two solubility curves.

The silica products, which are based on the predominant content of SiO_2 must contain the SiO_2 content higher than that one which corresponds to the composition of the Eutected point. Due to the steepness of the curve in the direction to 100% of silica, each decrease in Al_2O_3 and increase in SiO_2 contents influences very much the refractory properties of silica products. Therefore the best silica products contain less than 1% of alumina.

We can conclude that in the range of the existence of silica products aluminium oxide acts as a strong flux with higher effect than for example iron and calcium oxides which are added as mineralizers with the possitive influence on the product properties.

The opposite direction - increasing the Al_2O_3 content above the composition corresponding to the Eutectic point - turns out a continuous succession of compositions from semisilica and silicous fireclays with the silica content increased compared with fireclays, fireclays with different alumina content up to that one which corresponds the alumina content of Metakaolinite, i. e. up to 45,9% from total. Refractories with alumina content above the ratio of $Al_2O_3 : SiO_2$ in the molecule of kaolinite are called high alumina refractories and they are classified usually according to their alumina contant as sillimanite, mullite and corrundum refractories. The increased content of alumina above the kaolinitic ratio is than created either by the addition of Al_2O_3 into the kaolinite blend or by the application of high alumina natural calcined or fused raw materials such as Kyanites, Sillimanites, Andalusite, Bauxites, Corrundum and others. Many times, combination of addition of different high alumina raw materials takes place in the manufacturing technologies.

The high alumina raw materials are described as follows:

Kyanite is a mineral having the same composition $Al_2O_3 . SiO_2$ as sillimanite and andalusite but with different physical properties. When heated, kyanite breaks down at about 1300°C into mullite and cristobalite with an approximate volume expansion of 10%. If applied as a refractory grog, it is, therefore, calcined before use. The chief sources are Virginia, South Carolina in USA and India. Kyanites occur also in different developing countries, such as Suriname, Guyana and Kenya, which start to consider their industrial exploitation.

Sillimanite is a mineral with the composition $Al_2O_3 . . SiO_2$ but it differs in its technological properties from Kyanites and Andalusites. Sillimanite changes into a mixture of mullite and cristobalite when fired at a high temperature of about 1550°C. This change occurs without any significant alteration in volume, what is prefarable compared with Kyanites. The main sources of Sillimanite are South Africa and India.

Andalusite is a mineral having the same composition $Al_2O_3 \cdot SiO_2$ as Kyanite and Sillimanite, but with different physical properties. When fired it breaks down at 1350°C to form mullite and cristobalite; the change takes place without significant change in volume. The principal sources are from South Africa, California, Nevada and New England in USA.

Bauxite is a sedimentary rock consisting of hydrated Alumina $Al/OH/_3$ together with impurities represented in different amounts such as clays, iron oxide and titania. The chief sources are Yamaica, Guyana, USSR, Suriname, France, Hungary and Yugoslavia.

Corrundum is the only form of alumina Al_2O_3 that remains stable when heated above about 1000°C. It occurs naturally, but impure in South Africa and elsewhere. Fused corrundum in its relatively pure form is made in the electric arc furnace and then crushed, ground and screened.

Alumina is the aluminium oxide Al_2O_3 which exists in different forms. It is mostly produced from Bauxites and applied directly or after calcination.

Considering that both SiO_2 and Al_2O_3 are refractory oxides and all their blends lie above the refractory limit of 1580°C /Seger cone No. 26/, raw materials and minerals containig these oxides are the basis for the manufacture of refractories such as silica, fireclays and high-alumina products. The admixture of fluxes in them operates usually negatively, i.e. decreases their refractory properties.

2. Ceramic Products

Refractoriness is not the required property of ceramic products. Therefore, fluxes can be applied in the blends. Their presence, in addition to kaolinite and silica, causes the creation of the glass phase as early as at low temperatures. It influences very positively the porosity and mechanical properties of products, enables the lowering of firing temperatures and the application of speedy firing technology and thus brings energy savings.

Generally it is held true that the lower is the ion diameter of the fluxing element, the more active it is as a flux. It means that the fluxing effect, as far as the commonly used raw materials with alcaline oxides are concerned, falls according to the sequence of the element periodic system. The following are <u>elements from the first group:</u>

Li

Na
K
-------- in cheap natural raw materials
Rb
Cs

Owing to the availability of sodium and potassium fluxes in the whole range of cheap natural raw materials, the choice of fluxes in applied technology is usually confined to the oxides of these two elements. There are mainly the following raw materials

feldspars	$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	orthoclase
	$Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2$	albite
	$CaO \cdot Al_2O_3 \cdot 2\ SiO_2$	anorthite
	$Na_2O \cdot Al_2O_3 \cdot 6\ SiO_2 +$ $+ CaO \cdot Al_2O_3 \cdot 2\ SiO_2$	oligoclase
	$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2 +$ $+ Na_2O \cdot Al_2O_3 \cdot SiO_2$	plagioclase

phonolites - effusive alkaline rocks
tuffs, tuffites - volcanic igneous rocks
nephelines - alumina-sodium silicate
perlites - acidic siliceous effusive rocks
basalts - effusive rocks

Sodium fluxes are successfully applicable in fast-firing technologies /with the firing cycle under 3 hours/, while potassium fluxes in the manufacture of ceramic products of large weight and size such as sanitary ceramics products. In firing them, the deformation in the interval of body vitrification could jeopardize the success of this operation.

Oxides of elements in the 2nd group of the periodic system form very interesting eutectica with alumina and silica oxides.

Be
Mg in cheap natural raw materials
Ca
Sr
Ba

From the second group of the elèment period system, CaO and MgO are the most used fluxes in the ceramic manufacture. They occur abundantly in the nature in the form of the following minerals:

calcite $CaCO_3$ .... sedimented rocks or shells
dolomite $CaCO_3 \cdot MgCO_3$ .... sedimented rocks
magnesite $MgCO_3$ .... sedimented roc

The foregoing fluxes are applied as fine ground additions to the kaolinitic blends. However, there is a lot of natural clays, which contain different fluxing elements already in their composition. Aside the elements from the first and second group of the element periodical system, other oxides can be represented and they can be well exploited in the composition of ceramic blends. Such oxides are mainly iron and titanium oxides, which, being finely dispersed in the clay, can act positively by lowering the firing temperatures of products technology. However, it has to be noted. that products with the increased content of colouring oxides always show after firing a dark body and, therefore, they are never applied in the porcelain and Vitreous China manufacture. On the other hand, such clays can be successfully exploited in the earthenware manufacture, if opaque glazes are applied /such as in the wall tiles or glazed floor tiles manufacture/, or in the manufacture of brick products and stoneware, where the body's colour after firing is desirable or the increase content of colouring oxides is requested due to the salt-glazing technology.

3. Evaluation of Fluxes

a. Lowering of firing temperatures

The function of kaolinite and silica in newly developed blends is shown in Table 3. It is obvious that kaolinitic clays and kaolins are applied in the majority of ceramic technologies as the binding element which provides to the blend the formability and refractoriness. However, clays and kaolins shrink during drying and firing in different limits. To control the shrinkage of ceramic blends, silica is added as a grog, which expands during firing and which is jointly refractory.

The most important role in energy conservation play fluxes.

The potassium feldspar - Orthoclass has always been considered as the most suitable flux due to its ability to create in ceramic blends a wide interval between the temperature of the vitrification and of the deformation. When sodium fluxes are applied, physical and structural changes in ceramic bodies are speeded during the increased temperatures due to the smaller diameter of sodium. Ceramic blends with the pottasium fluxes always require higher firing temperatures compared with sodium fluxes.

Table 3 Technological Application of Kaolinite and Silica

Kaolinite

$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$

characteristic properties

- binding component
- formability
- shrinkage
- refractoriness

technological application

wall tiles
floor tiles
china ware
stoneware
white ware
artistic ceramics
sanitary ware
glazes
fireclay
refractory insulation

Silica

SiO_2

characteristic properties

- grog
- control shrinkage
- expansion
- refractoriness

technological application

wall tiles
floor tiles
china ware
stoneware
white ware
artistic ware
sanitary ware
glazes
silica bricks
acid fireclays

Fluxing effect of elements from the second group of the system is demonstrated on the calcium oxide. If calcium oxide mixed with kaolinite and quartz, complicated mixtures can be created with different melting temperatures and with different Eutectcs, as shown in Table 4. To compose an earthenware body, the aria of existence in lime-siliceous compositions is in the vicinity of the Eutectic point L /see Table 5/, which shows a balanced melting temperature of 1359°C for the following composition

10,5% CaO
19.5% Al_2O_3
70.0% SiO_2

The composition of this Eutectic point L corresponds practically to the composition of the lime siliceous earthenware bodies with the bisque firing temperature of 1040 - 1060°C.

The nearest lower Eutectic temperature t of 1165°C is in the direction of incresed CaO content with the following composition

23.3% CaO
14.7% Al_2O_3
62.0% SiO_2

The estimated bisque firing temperature of the Eutectic composition t amounts to 900°C. Successfully managed composing of such a body shows the trend of a further possible development as far as the lowering of firing temperatures and energy conservation is concerned.

B. Dimensions accuracy

The accuracy of dimensions of ceramic products can play an important role in their application. Especiously ceramic wall and floor tiles cannot differ in their dimensions in order to provide the esthetic impression after being fixed. Therefore, the influence of different

Table 4 Ternary Diagram $CaO-Al_2O_3-SiO_2$

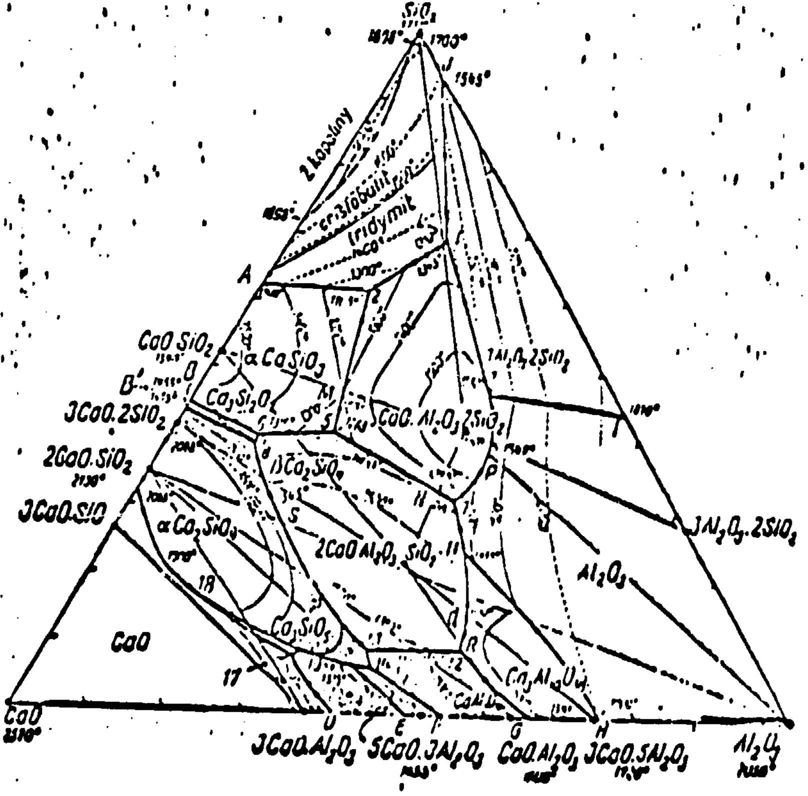
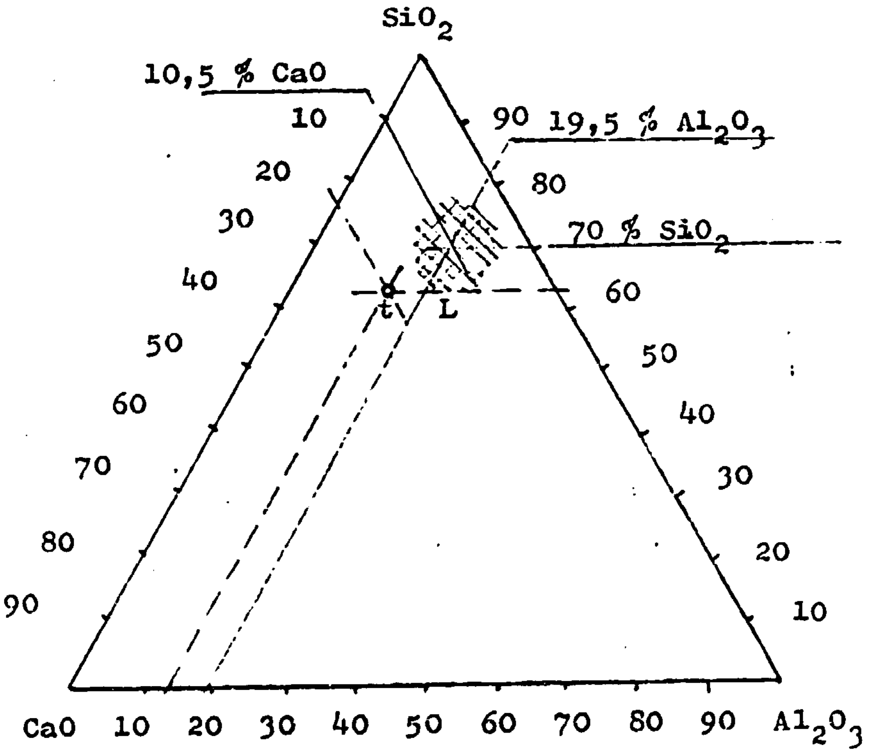


Table 5 Existence of Lime-siliceous Earthenware Compositions



fluxing oxides on the thermal expansion of ceramic bodies must be taken into the consideration.

Table 6 shows the thermal expansion of an earthenware body which contains pottassium, sodium and alcali oxide mix. The diagram clearly shows that the sodium fluxes act at the lowest temperature, the glass phase in the earthenware body starts to be created in the temperature bellow 900°C when the shrinkage of the body is visible. However, the shrinking runs very fast during a relatively short temperature interval. Such bodies, if dimensions accuracy required, must be fired in the uniform temerapture, which, in the majority of industral kilns, canno~~s~~t be obtained.

The pottassium fluxes start to create in the connection with the earthenware body, the glass phase at about one hundert degrees higher temperature and the shrinking of the body does not follow so steeply as with sodium fluxes. Such bodies, however, do not provide accuracy good enough for the ceramic tiles manufacture.

For the manufacture of the vitrified bodies, which must not show accurate dimensions, such as sanitary ware, dinnerware and stoneware, alcali oxides are good enough to reach the required properties of finished products. If sodium fluxes are applied the vitrification point is obtained at the lower temperature compared with pottassium fluxes.

For the manufacture of earthenware bodies the alcali oxides are not the best ones if accuracy in dimensions is required. Better results are obtained with the addition of Calcium and/or Magnesium carbonites. The thermal expansion of such lime-siliceous bodies is presented in Table 7.

Table 6 Thermal Expansion of Earthenware Body with Alcali Oxides

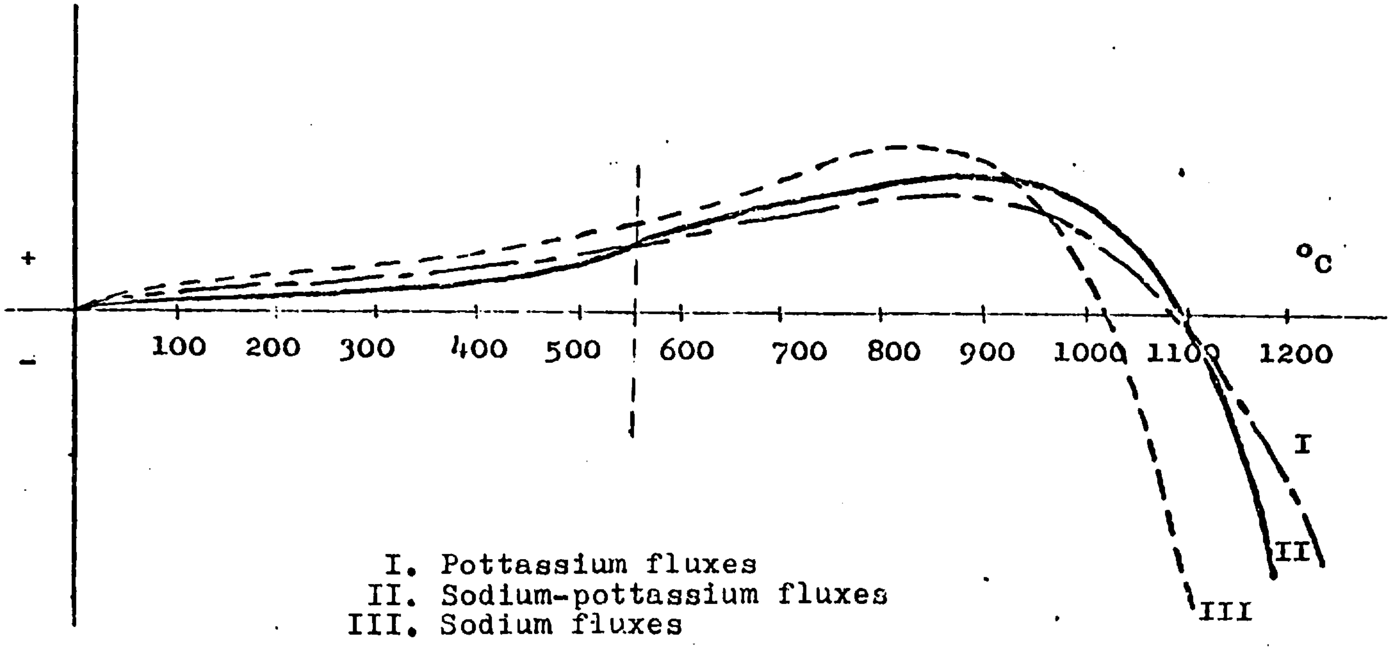
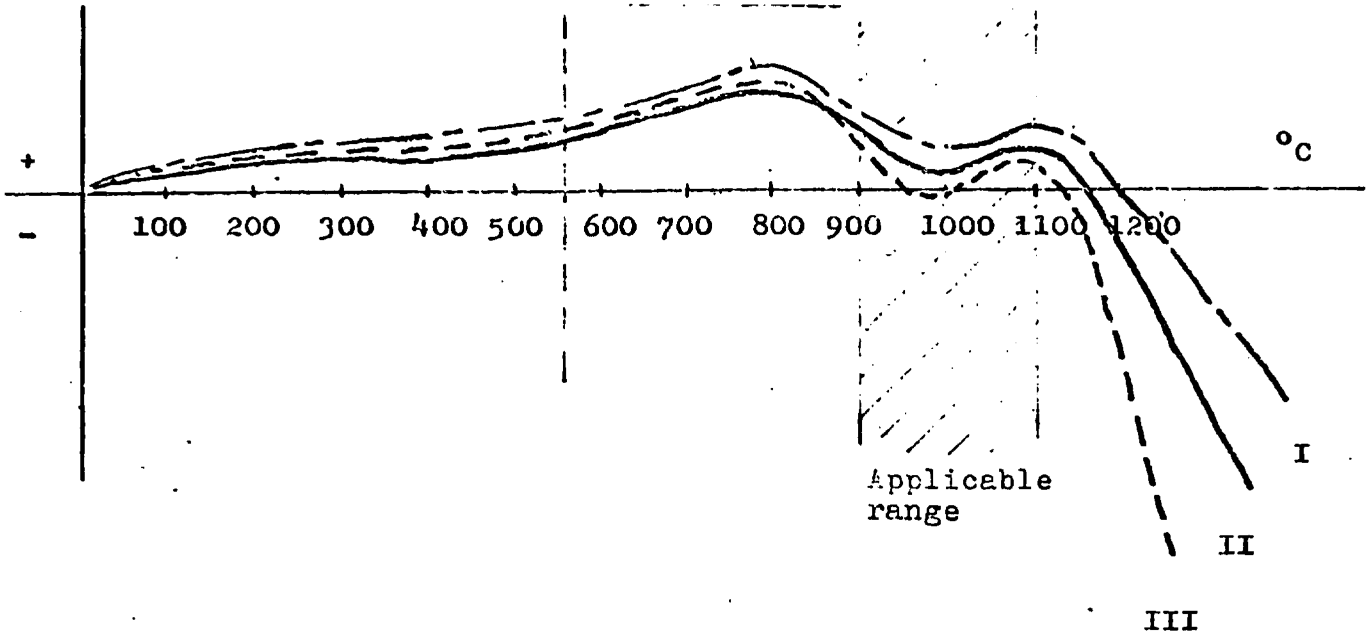


TABLE 7 Thermal Expansion of Earthenware Body with Calcium Oxide



Before lime-siliceous earthenware bodies start to shrink in the bigger extend, the thermal expansion shows the dwelling wave in the temperature interval between 950°C and 1100°C. Different blend compositions I, II and III. show the same effect.

Such bodies keep the same dimensions as green pressed in the temperature interval bigger than 100°C and, therefore, they keep the accurate size during the all manufacturing operations after pressing. The selection of the proper blend and firing temperature depends on the product physical properties requirements, mainly on the porosity and mechanical strength in the connection with plastic raw materials applied.

On the other hand lime-siliceous bodies can never be fired to their vitrification, as the advantage of their thermal expansion is overcome during higher temperature. Therefore, lime-siliceous bodies are recommended for the earthenware composition.

Aside the dimension accuracy the lime-siliceous bodies need the bisque firing temperature of about 1020 - 1080°C only. Compared with the kaolinitic composition with the bisque firing temperature 1280°C, considerable energy saving can be achieved.

IV. TECHNOLOGICAL ASPECTS

Three main technological aspects are to be taken into the consideration in composing ceramic bodies:

1. Workability
2. Drying and firing
3. Properties of final product

Each ceramic product is, therefore, composed of two basic components

a. Binding agent, which is classified as the ceramic, chemical or hydraulic one.

b. Grog, which can be the natural or fired one.

a. The function of a binder is to enable the formation of products of requred shape and size from natural or dressed raw materials. The binder guarantees the workability of ceramic bodies as the basic condition for shaping.

Binding agents in ceramics are prevailingly based on the mineral

kaolinite $Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$

The mineral kaolinite occurs in the nature in the whole range of variants known as different clays and kaolins.

Kaolins and clays occur almost in all parts of the world. Owing to their genesis, two deposits cannot exist in different places of the world containing clays and kaolins of coincident properties. The diversity of properties is conditioned by a series of factors, especially

- particle grain-size
- quantity of particles under 2 microns
- distribution and size of the crystallographic lattice
- kind and quantity of other non-kaolinitc materials, such as montmorillonites, illites, ferric and titanium oxides, pyrites, but also organic materials, remainders of non-converted mother rocks, etc.

Clays and kaolins are, therefore, classified in a series of groups according to different standpoints. As far as the energy conservation is concerned, it is the objective that the lower is the plastic water content in the clay during shaping, the lower amount of water during drying needs to be evaporated and the higher energy saving is obtained. Therefore, different liquifying agents are added to decrease the amount of plastic water in the blend.

Aside from ceramic binders, <u>chemical binders</u> /such as water glass, phosphates, etc./ and <u>hydraulic binders</u> /Such as p-cement, aluminious cement, etc./ are applied in some cases.

However, ceramic binders are prevailing in ceramic technologies since they form a plastic body or casting slip.

Shrinkage occurs in all ceramic binders during drying and firing due to the mutual approach of clay particles in the expulsion of the diluted water during drying and due to the dehydration and desintegraion of the lattice during firing.

b. The basic function of the <u>grog</u> is to control the shrinkage of the binding agent in a ceramic body.

Silica /SiO_2/ is the main representative of natural grogs. It is present mostly in clays and raw kaolins in larger or smaller amounts. It occurs in the nature in the form of silica sand, quartz vein, lydite, quartzites and in many other modifications. All non-plastic fractions of clays and kaolins pertain, however, among natural grogs since they do not give in to dimensional changes during mixing with water and consequent drying. These are e.g. feldspars, pegmatites, micas, igneous rocks, different fluxing rocks, etc.

Fired clays, claystones, kaolins and high-alumina grogs are fired grogs. Fired grogs, being more energy consuming than natural grogs and, therefore, always more expensive, are applied in such cases where the ceramic technology requires other properties than those rendered by natural grogs.

With regard to the fact that available silica raw materials are applied as natural grogs, the enrichment of the body with silica occurs accompanied with the relative decrease in aluminum oxide content. This effect being welcome usually in the bodies of structural and fine ceramics, is harmful in the production of fireclay and high-alumina refractory products. Therefore, fired grogs pravail in the refractory production while natural grogs in the manufacture of fine and structural ceramics and in brick-making. The application of natural grogs has a principle economic significance with some ceramic products.

The firing operation depends closely on the body composition and on properties of final ceramic products. Therefore they are discussed in the following chapter.

V. PRODUCT ASPECTS

Product aspects are the most important ones in composing ceramic bodies. Therefore, in the following, main product aspects are presented in the relationship with the possible technology applied. As far as the technology is concerned, single or double firing technology is discussed with the related firing temperatures. Wide range in firing temperatures, applied for the same product, but achieved through different technologies, shows different ways for energy conservation in different ceramic technologies. Therefore, practical examples are presented in order to orientate the reader to the proper direction for energy saving in the manufacturing process.

1. Tableware

Ceramic tableware can be produced in a large technological variety from which the most important types are negotiated.

a. Stoneware Tableware is produced with a vitreous, but opaque type of the body. The blend contains a naturally vitrified clays, such as stoneware clays or suitable ball clay. Non-plastic constituents to control the shrinkage and to regulate the eoeficient of thermal expansion of the green body and flux to lower the firing temperature and to save energy during firing can be added.

Stoneware tableware can be produced in the single-firing or double-firing technology. The bisque firing temperature fluctuates between 800 - 1000°C, meanwhile the glost firing temperature reaches usually 1250°C. By applying fluxes, the glost firing temperature can be lowered down to 1180 - 1200°C.

At present stoneware is produced on the commercial scale chiefly as cooking ware and some table ware with lowlead, glossy or matt glazes, which are mostly opaque coloured or rarely translucent. Tableware, produced from stoneware, shows high mechanical properties, low porosity and excellent resitence against craking.

Table 8 shows two types of the stoneware tableware possible body compositions with corresponding firing temperatures.

Table 8 Stoneware Tableware Body Compositions with Corresponding Firing Temperatures

Type	Content %				Firing Temperature °C
	Stoneware Clays	Silica	Feldspar	Fluxes as Feldspar, Talcum and Dolomite	
Body I	40-50	45	5-15	-	1250-1280
Body II	60	15	-	25	1200

The increased content of well vitrifying stoneware clays, lower content of silica and higher content of fluxes, in which aside feldspar other fluxing materials are presented, decrease the firing temperature from 1250° - 1280°C down to 1200°C.

b. Earthenware Tableware is produced with the non-vitreous, opaque, off-white or coloured bodies. Different types of the body composition can be applied, in which aside the China clay, ball clay, silica also pottassium or sodium feldspars are the prevailing fluxes or lime siliceous body composition can be developed. Non-traditional fluxes, such as phonolites can be added to lower the firing temperature.

Earthenware tableware is always produced in the double firing technology. If decoration is applied, three or more firings are necessary to obtain the final product. The bisque firing temperature can fluctuate in a wide interval between 980° to 1280°C. The glost firing temperature reaches 900 to 1120°C.

At present earthenware table ware is produced in different developing countries which introduce usually the dinnerware manufacture by the earthenware composition. Leadless or leadlow glazes are applied usually as glossy opaque glazes to cover the colour of the body. Tableware, produced from earthenware, must be carefully balanced to avoid cracking or peeling of glazes due to a poreous body. Earthenware dinnerware always shows high avarage weight of one piece, being usually above 400 gr.

Table 9 shows the earthenware tableware body compositions with corresponding firing temperatures.

Table 9 Earthenware Tableware Body Compositions with Corresponding Firing Temperatures

Type	Content %				Bisque Firing Temper. °C	Glost Firing Temper. °C
	Kaolins and clays	Silica	Feldspar	Limestone		
I.	50-55	35-45	6-12	-	1280	1120
II.	50-55	35-45	-	5-10	1080	980-1020
III.	75-85	15-20	0-5	-	1160	960-1020

The earthenware tableware type I. represents so called hard type as showing lower porosity, but its firing temperatures are the highest. The lime-siliceous body composition in type II. results in higher porosity. The type III. is a compromise applicable in all cases where good plastic clays and kaolins are available in such qualities that they show white or light colour after firing.

c. Vitreous China Tableware is produced with high grade, fully vitrified body. The blend is composed from a mixture of washed kaolins, light - the best white - burning clays and finely ground silica and fluxes.

Vitreous China tableware is produced mostly in the single firing technology, but the double-firing is also applied. If bisque is produced it is fired 1180 - 1250°C, meanwhile glost firing is realized at 1180 - 1280°C. The single firing manufacture is more rational, however it is more sensitive to keep high quality products.

At present the vitreous China tableware is produced on the mass scale specially on the American Continent, where it represents a common type of lower priced tableware and the hotel tableware, as showing thicker body and being less fregile than the porcelain, and, therefore, being more resistant against breakage. Semiopaque, opaque or transparent glazes are applied with the under-glaze and on-glaze decoration and/or with different coloured glazes. The vitreous China tableware shows high mechanical properties, fully vitrified but opaque body and good resistance against cracking of the glaze.

Table 10 brings the vitreous China tableware body compositions with corresponding firing temperatures.

Table 10 Vitreous China Tableware Body Compositions with Corresponding Firing Temperatures

	Content %			Firing Temperature °C
	Kaolins and clays	Silica	Feldspar and Pegmatite	
I.	50	-	50	1250
II.	55	-	45	1300
III.	52	35	13	1250

Body types I. and II. are composed from natural clays and kaolins which contain silica. The difference in the firing temperature depends on the type and amount of flux applied. Type III. is composed from pure components and, therefore, silica is added in the form of a siliceous sand.

d. Porcelain Tableware represents the high quality ware of purest whiteness and considerable transparency. The body is composed from high grade in average from washed kaolins, off-white-burning clays, silica and feldspar.

Porcelain tableware is traditionally produced in the double firing process. The bisque firing of porcelain differs from that of earthenware in these: the first firing is at a low temperature 800 - 1000°C, the body and the non-fritted glaze being subsequently matured together in a second firing at about 1320 - 1450°C, depending on the type of porcelain. The new technologies try to develop the single firing technology when high plastic clays and kaolins can provide mechanical properties of the green body high enough for the glazing and for the manipulation.

The porcelain tableware is produced mostly in the European countries. It is provided by the glossy transparent or rarely by the semi-opaque glaze, being decorated with all possible decorating techniques. Tableware produced from porcelain shows low average weight of one piece, being usually below 200 gr, good mechanical strength of the body, hard scratch resisting glaze, thermal shock resistance and resistance against the crazing of the glaze. It represents the most luxury type of the tableware.

Table 11 shows the porcelain tableware body compositions with corresponding firing temperatures.

Table 11 Porcelain Tableware Body Compositions with Corresponding Firing Temperatures

Type	Content %			Glost Firing Temperature °C
	Washed Kaolins and Clays	Silica	Feldspar	
I.	35-60	20-40	15-25	1350-1450
II.	43-66	12-30	18-33	1350-1450
III.	40-60	20-40	20-30	1300-1400
IV.	25-35	20-45	30-40	1250-1350
V.	25-34	11-45	30-55	
VI.	2-5	15-25	75-81	1100-1200

Types I and II represent the hard porcelain products with highest firing temperature. The hotel porcelain III. is the transitting type between the hard and soft porcelain products. As an example the composition of the dental porcelain is given.All compositions clearly show that the higher is the content of feldspar in the porcelain body composition, the lower is the glost firing temperature.

2. Sanitary Ware

Sanitary ware's body can be blended from different local raw materials and it can be produced in different technologies from which the main important are presented.

a. Vitreous China sanitary ware is produced with the highly vitrified opaque body which shows high mechanical properties. The blend is composed from a mixture of washed kaolins, light-burning clays and finely ground silica and fluxes. Sometimes nepheline, sienite or phonollite is used instead of feldspar.

Vitreous China sanitary ware is produced in the single firing technology. After firing at the temperature 1200 - 1280°C the body will not, even when unglazed, show a mean value of water absorption greater than 0,5% of the ware when dry.

The vitreous China sanitary ware is the prevealing type of sanitary ware produced due to low investment cost and single firing technology. It is also the labour intensive manufacture, being appreciated in many developing countries. The vitreous China sanitary ware is coated on all exposed surfaces with an impervious non-crazing vitreous glaze giving a white or coloured finish.

The Table 12 shows the vitreous China sanitary ware body compositions with corresponding firing temperatures.

Table 12 Vitreous China Sanitary Ware Body Compositions with Corresponding Firing Temperatures

Type	Content %				Firing Temperature °C
	Washed Kaolins and Clays	Silica	Feldspar	Other Fluxes	
I.	40-60	30-40	10-20	-	1250-1300
II.	40-60	25-35	-	15-25	1200-1250

The traditional composition of vitreous China sanitary ware is based on pottassium feldspar as on the fluxing material. If nepheline syenite, phonolites, talcum and other non-traditional fluxes are applied the firing temperature is decreased by 50 - 100°C.

b. Earthenware sanitary ware is produced with a poreous body and less strength than vitreous China ware but more easily made from different clays, washed or raw kaolins, silica and different fluxes such as feldspars, pegmatites, limestone, chalk and others.

Sanitary earthenware is produced in the double firing technology. The bisque firing temperature amounts to 1060 - 1280°C pending on the body composition, the glost firing temperature is between 1020 - 1200°C. Shiny fritted or raw opaque glazes are applied.

Due to the sensitivity for crazing of the glaze and due to the poreous body the sanitary earthenware is not introduced to the ceramic industry very much as producers prefer more difficult, but lower cost and higher quality vitreous China technology.

c. Fireclay Sanitary Ware manufacture is applied in the production of large pieces of sanitary ware, i.e. big sinks and urinal stalls, without undue warping. As raw materials, plastic or siliceous fireclays, kaolins,fired grog and silica are applied.

Fireclay sanitary ware can be produced in the single firing or double firing technology. The bisque firing temperatures fluctuate between 1200 - 1300°C, meanwhile the glost firing temperatures reache 1250 - 1300°C.

At present the fireclay technology is not frequently established in the sanitary ware manufacture, as being more complicated and energy intensive compared with the vitreous China type. Fireclay sanitary ware in many cases is provided with the engobe before being glazed with shiny opaque white or coloured glazes.

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3. Stoneware

Stoneware products represent a wide assortment of different ceramics, realized by different technologies but with a large application in any country. Developing countries in many cases, however, do not yet recognize the industrialization possibilities by producing stoneware and bigger movement in this respect is expected in the years to come.

A large number of raw materials can be applied in the stoneware manufacture, such as low vitrifying clays, raw or washed kaolins, silica, feldspar, granite, basalt, phonolites, talcum, zirconia, cordierite and others, depending on the type and technology of stoneware produced.

In general all stoneware products show a low porosity and the opaque body. It can be produced in a double firing technology, however, the majority of products is manufactured in the single firing process. If the bisque is fired, the temperature of about 900°C is applied. The single firing technology shows the firing temperature between 1140 - 1280°C, pending on the body composition. Earthen, raw or salt semi glazes are applied on the majority of stoneware products.

As stoneware products, the following ceramics are produced:

Coarse grained body - drainage, ducts, agricultural and chemical stoneware, paving, facade and indistrial tiles and different types of garden and artistic ceramics.

Fine grained body - chemical stoneware, floor and facade tiles, tableware and artistic ceramics.

Table 13 shows differant stoneware body compositions with corresponding firing temperatures.

Table 13 Stoneware Body Compositions with Corresponding Firing Temperatures

Type	Content %			Vitrifying Temperature °C
	Stoneware Clays and Kaolins	Grog	Flux	
I.	80	20	-	1280
II.	66	6	28	1140

The lower vitrifying temperature of the stoneware body composition Type II. achieved by the blend with the tuff addition. Very positive results are also expected by applying phonolites as fluxing materials.

4. Electroporcelain

The demand for ceramics in the electrical industry has risen very much both in quantity and quality during the period after the War 2. The competition from the glass industry has not depressed the manufacture of electroporcelain. Developing countries usually start with the manufacture of low-tension porcelain, which are used on normal supply and telephone lines. High tension porcelain, applied for the high voltage grid are composed from the same but more pure raw materials and they are fired to a lower porosity.

Ball calys, washed kaolins, silica and feldspars are usual basic raw materials.

Electroporcelain is produced in the single firing technology under the temperature of 1150°C for low tension insulators up to 1420°C for high tension ones. Single fire brown, white transparent, opaque or semiopaque glazes are applied.

Aside the electroporcelain, different other ceramics are applied in the electrical industry such as cordierite, steatite, titanate, zircon and corrundum, which are, however, more specialized types and, therefore, not yet so much developed in developing countries.

Table 14 shows electroporcelain body compositions with corresponding firing temperatures.

Table 14 Electroporcelain Body Compositions with Corresponding Firing Temperatures

Type	Content %			Firing Temperature °C
	Washed Kaolins and Clays	Silica	Feldspar	
I.	35-40	35-45	15-25	1380-1410
II.	40-60	20-30	20-35	1280-1350

The electroporcelain body composition type I represents high tension insulators composition. In order to keep the content of the glass fase in the product as low as possible, the amount of feldspar in the blend is limited and, therefore, the firing temperatures are always relatively high. The low tension porcelain body composition Type II can be blended with the increased amount of fluxes and witn the lowered firing temperatures.

5. Wall Tiles

Wall tiles are mass-produced thin ceramic tiles basicly glazed. They occur in 2 categories, applied in

- interiers with a poreous body
- exteriers with a vitrified body, being usually frostprove.

The difference between glazed wall and floor tiles is of less importance, as wall and floor tiles are used interchangably.

a. Glazes wall tiles with a poreous body are produced as the earthenware technology with white, off-white or coloured body. As the opaque glazes are applied, the colour of the body is less important than earlier when transparent glazes were used. Different types of body composition can be applied depending on the availibility of local raw materials, such as clays, kaolins, silica, feldspar, limestone and shells.

Glazes wall tiles with a poreous body are produced usually in the double firing technology with the bisque firing temperature from 1060 to 1300°C and the glost firing temperature from 960 to 1120°C. The single firing technology is more sensitive against the top quality.

The opaque shiny or matt glazes are decorated with different techniques, mostly based on the screen print. The glazed wall tiles with the poreous body must be accurate in dimensions, high esthetic surface of the glaze can be obtained. Their resistance against glaze crazing and moisture expansion must be carefully examined.

Table 15 shows selected types of wall tiles body compositions with corresponding firing temperatures.

Table 15 Selected Types of Wall Tiles Body Compositions with Corresponding Firing Temperatures

	kaolinitic	semi-kaolinitic	feldspatic	mixed	lime-siliceous
Rational composition, %					
Kaolinite	80	65	55	50	48
Quartz	15	27	35	40	37
Feldspar	5	8	10	3	-
Limestone	-	-	-	7	15
grog,%					
total	60	60	50	55	55
fired grog	46	30	5-10	5-10	5-10
Main components	ball clays, stoneware clays, washed kaolins, fired grog, fired reject	ball clays, siliceous and stoneware clays, kaolins, pegmatite, fired grog, fired reject	ball clays, siliceous and stoneware clays, kaolins, pegmatites, quartz sands, feldspar, fired reject	ball clays, siliceous and stoneware clays, raw kaolins, marls, quartz sands, chalk, dolomite, feldspars, pegmatites, limestone, quartz, phonolite, nepheline, fired reject	ball clays, siliceous and stoneware clays, marls, wollastonite, chalk, dolomite, limestone, raw kaolins, fired reject
Firing temperature, °C					
bisque	1280-1300	1230-1250	1200-1230	1140-1160	1040-1060
glost	1120-1140	1080-1100	1060-1080	1000-1040	960-1000

The foregoing Table 15 clearly demostrates the large variety of main body components which can be applied in order to compose the wall tiles with a poreous body. According to the available local raw materials the right technology with lowest possible firing temperatures is to be choosen.

b. Glazed wall tiles with vitrified body are produced in the stoneware technology. Usually they are used for exteriers, mostly being frostprove. Opaque glazes in different colours with different screen print decoration are applied. As raw materials, low vitrifying clays, kaolins, silica and different types of fluxes are applied.

Glazed wall tiles with the vitrified body are produced in the single firing technology with the firing temperatures between 1080 and 1250°C depending on the body composition.

The manufacture of glazed wall tiles with the vitrified body does not differ from that one applied for the manufacture of vitrified glazed floor tiles, as both products show similar properties and applications. For those developing countries which posses nice, warm weather without frosts, the frostproof glazed wall tiles with the vitrified body are not needed to be produced.

6. Floor Tiles

Ceramic floor tiles are thin tiles applied for flooring. They are produced in two basic types

- unglazed, dense, fully vitrified coloured or white tiles
- glazed, vitrified or poreous, applied with opaque glazes.

a. Ceramic unglazed floor tiles are thin, dense tiles with fully vitrified coloured bodies, frequently the colour of natural clays but also in various colours and textures achieved by additions. They are produced with the smooth surface, others are made "non-slip" by addition of abrasive grains or by a corrugated surface.

Ceramic unglazed floor tiles are produced with a stoneware fine-grained technology. Their firing temperature fluctuate between 1140 to 1280°C depending on available raw materials and on the type of kiln.

Ceramic unglazed floor tiles show high mechanical properties, high resistance to abrasion, to weather, stams and acids.

Table 16 shows floor tiles body compositions with corresponding vitrifying temperatures.

Table 16 Floor Tiles Body Compositions with Corresponding Vitrifying Temperatures

Type	Content %				Vitrifying Temperature °C
	Washed Kaolins and Clays	Raw Kaolins and Clays	Feldspar	Phonolite	
I.	70	-	30		1250-1280
II.	-	70	-	30	1120-1160

The floor tiles body composition Type I. represents the traditional composition of unglazed, fully vitrified ceramic floor tiles with the firing temperature, which, in general, corresponds to firing temperatures of the stoneware. The application of more active fluxes than the pottasium feldspar, such as phonolites, lowers the vitrifying temperatures by 100 to 150°C.

b. Ceramic Glazed Floor Tiles are produced with a vitrified, semiporeous or poreous body. Therefore, they are realized either on the stoneware or earthenware technology with the single or double firing manufacturing process under the similar firing temperatures.

Ceramic glazed floor tiles are used interchangable with ceramic glazed wall tiles and they can be produced on the same manufacturing equipment.

7. Brick Products

Brick products are part of ceramic building materials with a poreous body. They are manufactured in different assortments

a. Common Bricks are mass-produced bricks in which no special care is taken in the manufacture to avoid surface blemishes.

b. Facing Bricks are bricks with a view to the appearance, dimensions as well as structural use.

c. Hollow and Perforated Bricks are bricks or blocks with large regular air spaces surrounded and separated by relatively thin walls. In recent years there has been much development of these bricks in order to produce more economical building methods, better insulation and to meet the competition from concrete blocks.

d. Roofing Tiles are thin pieces shaped to overlap and/or interlock on sloping surfaces, mainly on roofs.

All brick products are produced in the single firing technology. Depending on available raw materials and on the porosity of finished products, their firing temperature fluctuate between 900 - 1160°C. Some of very dense bricks called engineering bricks, can be fired up to 1250°C. But they belong to the stoneware technology more than to brick products.

The firing temperature of brick products are usually predetermined by the behaviour of raw materials during the firing process. Such raw materials which indicate a high fraction of kaolinite with finely dispersed limestone marl and iron oxides, having minimum content of illites, montmorillonites and no content of big grained calcites or other indesirable inclusions, at which no cracks occur during drying and firing, are usually good clays for the brick products manufacture, as their firing temperature is usually lower than 1000°C.

8. Fireclay Refractories

Fireclay refractories are the most common refractories, suitable for many various purposes. Their manufacture is usually the first one from refractories being realized in developing countries as they can be produced in a similar equipment as stoneware or even brick products.

Different types of refractory and/or siliceous clays /refractoriness equals or is higher than 26 Seger Cones/, kaolins and siliceous sands are applied. For high grade fireclays fired grog is blended into the body composition.

The fireclay products are usually fired between 1300 - 1450°C but siliceous, low grade fireclays can even be fired bellow 1300°C.

Fireclays show relatively good spalling resistance and thermal insulation. Fair resistance to acid slags and fluxes, lower resistance to basic slags and fluxes.

Compared with silica bricks, fireclays show lower refractoriness and lower refractoriness under load.

Table 17 brings a review of different alumosilicates refractories with corresponding firing temperatures.

Table 17 Selected Alumosilicate Refractories with Corresponding Firing Temperatures

Type	Firing Temperatures °C
Silica	1350 - 1500
Semi-silica	1300 - 1350
Siliceous fireclays	1250 - 1380
Fireclays	1350 - 1410
Fireclays High Duty	1380 - 1450
Sillimanite	1410 - 1560
Corrundum	1380 - 1700

The different firing temperatures applied in the manufacture of different alumosilicate refractories show that the lowest temperatures can be applied in the manufacture of siliceous fireclays, the highest ones in the manufacture of special corrundum products.

9. Silica Refractories

Silica refractories are acid refractories with a relatively high refractoriness and refractoriness under load. They are free of shrinkage.

They are produced from quartzites with a possible addition of siliceous sands, hydrated lime and other mineralizers. The lower is the alumina content in quartzites, the higher quality of silica can be produced.

The silica refractories are produced in two basic qualities

- for the coke and glass kilns industry with smaller additional volume changes
- for the steel industry with bigger additional volume changes.

Pending on the type of quartzites used and on the type of silica manufactured, the firing temperature fluctuates between 1350 to 1500°C.

The only serious limitation of silica refratories is their sensitivity to thermal shock below 600 to 700°C.

10. Ceramic Glazes

Ceramic glazes belong to industrial activities in which a suitable choice of technology may substantially influence firing temperatures and energy consumption.

The ceramic glaze is a special type of glass which covers a ceramic product of various porosity and thermal expansion. It is vital to always maintain a correct relation between the properties of ceramic bodies and ceramic glazes.

Modern glazes are compounded in order to produce a covering for ceramic bodies which shall be inter alia:

1. Insoluble in water and usual acids and alkalis likely to be met in use,
2. resistant to scratching,
3. as far as possible impervious,
4. suitable for producing certain decorative effects, such as colour, crystal development, carrier for transfers, etc.,
5. resistant to crazing, peeling and similar faults,
6. fusible at predetermined temperature ranges.

Glazes can be classified from different points of view, such as

1. Content of lead oxides
   a) lead containing
   b) leadless

2. Effect produced on the finished article

   a) shiny glaze, white or coloured
   b) crystalline glaze
   c) satin glaze
   d) satin-matt glaze
   e) matt glaze
   f) translucent glaze
   g) opaque glaze

3. Content of fritt

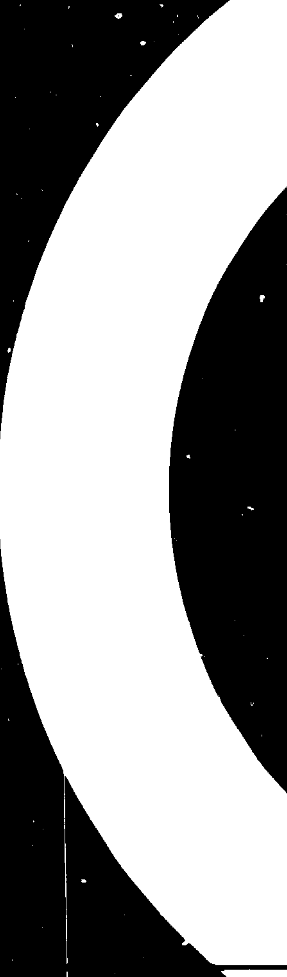
   a) raw glaze
   b) fritted glaze
   c) earthen glaze
   d) salt glaze

4. Maturing or firing temperatures

   a) low temperature glazes, 900 - 1000°C
   b) earthenware glazes, 1000 - 1160°C
   c) sanitary ware glazes, 1160 - 1250°C
   d) stoneware glazes, 1140 - 1280°C
   e) porcelain glazes, 1300 - 1450°C

The maturing of a glaze implies that the glaze is not only melted but that it has flowed smoothly over the surface of the ceramic product. All bubbles and pinholes have disappeared leaving a flawless surface.

In order to save energy, glazes with lower firing (maturing) temperatures are to be preferred. The firing (maturing) temperatures of ceramic glazes are deeply influenced by their composition. While



VI. CONCLUSIONS

1. There are no two deposits of sedimented ceramic raw materials in the world which would be identic in quality factors

2. Ceramic and refractory products are, therefore, produced from different raw materials by applying different technologies but the finished product must always correspond to the international Standard

3. Taking into consideration all aspects of the composition of ceramics and refractories, large variety of technological possibilities exists in each country for the development of ceramic and refractory industries following locally available raw materials. Different non-traditional technologies are applied with non-traditional raw materials in order to decrease the energy consumption.

4. The majority of ceramic and refractory body raw materials is to be available in the country.

5. High alumina additives, fritts, glazes, stains, colouring exides, pastes, reactive glazes, might be imported as their amount necessary for the manufacture is relatively low.

6. Low energy consumption technologies are to be prefered in the connection with locally available raw materials.

7. Closed co-operation between geologists, technologists and industrial economists is to be maintained during the fase of developing or expanding ceramic and refractory industries.

VII. LIST OF TABLES

VIII. LIST OF REFERENCES

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