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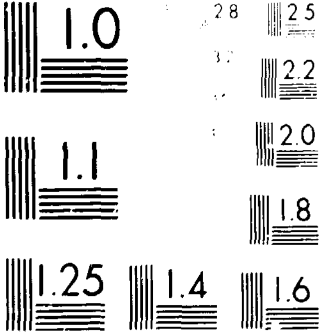
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CERAMIC INDUSTRY - REDUCING THE ENERGY REQUIREMENTS IN TECHNOLOGICAL PROCESSES

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I. INTRODUCTION

Ceramic industry can play a significant role in the national economy of developing and the least developed countries because it shows its positive influence in the following fields

- industrial exploitation of local natural resources which are available more or less in all countries around the world
- housing and general level of living standard depends on the availability of different ceramic products
- ceramic products and raw materials can be considered as strategical ones as promoting or stipulating the establishment and development of other industrial activities
- the benefits of the selected ceramic industries are significant from the viewpoint of national economies
- ceramic industry promotes the development of social relations

The ceramic industry provides the market with a large assortment of different products and raw materials, such as building and structural ceramics, industrial ceramics, refractories, insulating materials but also refined and upgraded kaolins, clays, sands, fillers and others.

The manufacture of ceramics and non-metallics participates in the consumption of total energy available, in spite of the fact that in developed countries the biggest energy consumer is the iron and steel industry which consumes about 23% from total energy consumption. The non-metallic industries such as cement, glass and ceramics are much lower in their requirements on energy inputs, as, in average, they consume about 3.5% energy from total. Refractories represented mainly with fireclays, consume about 0.5% to 1.0% from total energy available. But the energy consumption in processing of non-metallics much exceeds that one needed in other types of industries such as in textile, shoe, food, furniture and housing industries.

To manufacture ceramic products, relatively high energy consumption is required due to firing, drying, pressing, milling and other technological processes. Therefore, the energy management in the field of ceramics and ceramic raw materials can bring considerable savings not only from the point of energy but also from the point of general manufacturing costs.

Ceramics as a whole with cement come top of the list when energy cost is expressed as a proportion of gross sales. Table 1 shows that in many cases the energy costs can reach up to 50% of gross sales and it is the highest proportion from all industrial activities.

This paper presents a review of basic precepts of energy management for the ceramic industry. In detail, the technological processes are analyzed as one of the potential sources for energy conservation. In preparing suitable blends by applying non-traditional materials with the fluxing effect, in applying new methods of body and glaze compositions and in new firing and drying processes, the ceramic industry can play an active role in the rational use of energy resources in all countries. On the other hand, the ceramic, refractory and other non-metallic industries can intensify energy conservation in other industrial activities as insulating materials, fillers and substitutes.

Table 1 Approximate Energy Costs as a Proportion of Gross Sales

	%
Bricks, Pottery, Glass, Cement	30 - 50
Chemicals	20 - 30
Coal and Petroleum Products	20
Metal Manufacture (excl. Steel)	10 - 20
Paper, Printing, Publishing	10 - 20
Textiles	7.5
Food, Drink, Tobacco	5
Mechanical Engineering	5
Electrical Engineering	5
Vehicles	2.5

II. SCOPE

The presented lecture deals with the following energy conservation possibilities in the ceramic technologies:

1. Energy management plays an important role in the ceramic industry which is one of the potential energy consumers amoung non-metallic industries. Main steps of energy management in the energy consumption are defined.

2. Specific energy consumptions in different ceramic technologies are presented, needed to transform the natural raw material into the product of required properties.

3. The role of fluxes in ceramic technologies, if properly understood, opens lot of possibilities for energy conservation.

4. Main non-metallic minerals with the fluxing effect in the ceramic technologies are discussed. While developed countries looked after such natural resources during the past decade, developing and the least developed countries have not yet paid enough attention to their industrial exploitation and to their application in energy conservation attempts.

5. The practical utilization in the ceramic technologies of the following minerals and rocks is discussed: Tuffs, Tuffites, Nepheline Syenite, Phonolites, Perlites, Calcites, Marls, Basalts and Albite.

6. Ceramic glazes with different maturing temperatures can help to save energy.

7. Practical examples of energy conservation in ceramics and refractories are analyzed from the point of view of body composition in the brick, earthenware, single fired wall tile, porcelain and stoneware manufacture. To simplify the technology can also be a step towards energy conservation. The role of refractories in energy conservation implies decreasing of energy requirement in the manufacture and proper choice and application of refractories by the buyer.

The aim of this lecture is to turn attention of all technicians and managers from the ceramic industries to the problems of energy conservation in own factories, furthermore, to the industrial application of non-traditional raw materials in the processing and the development and application of new methods and technics which have not yet been common in the ceramic industries.

III. ENERGY MANAGEMENT IN CERAMICS

The energy supply and utilization has become one of the most important world problems for the next two decades not only in terms of competition for scarce resources between the industrialized and developing world or between particular countries but also in terms of allocating these resources among the direct consumer sector, transport, agriculture and industry. Scientific, technical and manufacturing capacities are being mobilized in order to discover non-traditional energy resources and to develop new ways for energy conservation. Energy management has become one of the important activities of any enterprising.

The ceramic industry is one of the biggest energy consumers among non-metallic industries. The survey has confirmed that drying and firing of ceramics consume more than 50 times of energy compared with winning and transport of raw materials and more than 15 times of energy compared with mass preparation and shaping. Therefore, the application of main steps of energy management for the energy consumption during the firing and drying processes is very important. To save energy in the ceramic industry, the following steps are to be taken into consideration:

1. Development of non-traditional technologies
   with the reduced energy requirements. The technological processes are undergoing a violent development at present which, on one hand, enables and, on the other hand, it demands a diversion from traditional to

non-traditional raw materials in order to lower the firing temperatures, to shorten the firing cycles and to simplify the technological processes. Each raw material with fluxing effect may be applicable in the ceramic technology either directly or after having been dressed. Single firing technology of wall tiles, porcelain, dinnerware, floor tiles, sanitary ware etc. enables the producer to save up to 40% - 60% of thermal energy when compared with the double-firing process. On-glaze decoration of ceramic products applied on raw glazed semi-products shows new effects and saves energy. Defined grain composition of glass sands as far as the maximum grain size is concerned can bring during the glass melting energy saving about 20% from total.

2. Optimum of heat processes according to limiting conditions of the products and according to the output of the thermal unit.

During the firing process ceramic raw materials undergo different crystallographical and mineralogical changes. Quartz modifications are transformed to modifications of cristobalite and tridymite, kaolinite changes to metakaolinite and mullite, in presence of other oxides, different minerals can be created in the ceramic body. Many of newly created minerals cause volume changes in the ceramic body during their critical temperatures. Therefore, aside the size of the product, also mineralogical changes are limiting factors during our attempt to shorten the firing cycle of a ceramic product. The knowledge of the critical (theoretical) firing curve is important in order to determine the minimum possible time of firing.

By applying such critical (theoretical) firing curve into any industrial kiln, depending on the type of kiln, the critical (theoretical) firing curve is extended. The highest output of the kiln is achieved, the lower specific heat consumption is needed.

3. Energy diagnostics of thermal units is very important. The determination of all important measured points of a kiln under operation always shows the way how to regulate the kiln to the optimum of energy input, how to balance its preheating and firing process, its draft, how to achieve the balance between different parts of the kiln, how to optimize the cooling, etc. It enables the technician to reduce all heat losses. Furthermore, energy diagnostics always shows proper way for the intensifying the firing process, what results into the increasing of the kilns and driers output, into the lowering the reject and increasing of quality grades of ceramics produced.

4. Thermal units play an important role in energy conservation. The technical level and many times necessary modernization of older kilns and driers can bring considerable saving of heat energy. Therefore, new types of kilns are rapidly developed by all world suppliers in order to meet requirements for the minimum heat consumption. One layer firing kilns are developed, high efficient thermal insulations are applied as walling materials (such as refractory fibre, foam fire-clay materials, etc.), packages kilns are supplied enabling very quick erection or replacing a demadged part of the kiln, high velocity burners enable to achieve a uniform temperature accross

the section of a kiln, weight of the kiln is lowered in order to have more flexible kilns with lowest possible heat capacity, etc.

5. Exploitation of secondary heat resources can play an important role in energy conservation. Waste heat utilization in the drying process decreases specific heat consumption especially in processes with muffle kilns where smoked gases to the chimmey show the temperature much higher above the due poir .

6. Climate conditions can also reflect the heat consumption. In dezert countries, dry technology can replace a wet processing. Instead of drying green products in an artificial drier, open air drying can be applied. Taking into consideration total energy consumption of a plant, there will be lower energy consumption in hot countries compared with cold ones.

The foregoing six steps of energy management in the energy consumption during the processing of ceramics are the main directions which must be taken into consideration before a ceramic plant is established as well as during its operation or its expansion.

IV. ENERGY REQUIREMENTS OF THE CERAMIC INDUSTRY

The ceramic industry belongs to those industrial branches in which the properties of final products are achieved by heat treatment. Table 2 shows a review of the specific heat consumptions in selected ceramic technological processes.

The following conclusions are made from Table 2:

1. Ceramic products of the same nature can be produced in variable firing temperatures which differ even by 240°C.

2. The specific heat consumption of the same product differs up to 100% from total.

3. Different producers manufacture the same ceramic products consuming different amounts of heat.

In the ceramic industry, the energy conservation can be achieved by lowering the firing temperature, by shortenning the firing cycle, by simplifying the technological processing, etc. The development of firing temperatures and cycles of the double fired wall tiles is presented in Table 3 and 4.

The revolutionary development in the ceramic technological processes is subject to two fundamental factors:

a) modern firing units that provide uniform temperatures, high flexibility and firing in a single layer,

b) non-traditional blends in which more efficient fluxes are applied.

Table 2 Specific Heat Consumption in Various Ceramic Technological Processes

Product	Firing temperature, °C	kJ/kg of products
Wall tiles		
bisque, non-traditional composition	1040-1070	3150-6300
bisque, traditional composition	1250-1280	6000-10100
glaze, gas-fired tunnel kiln	1020-1060	2900-5200
glaze, electric tunnel kiln	1020-1060	1250-1700
single firing technology	1040-1100	3560-4800
Floor tiles		
semigres bisque	1100	3350-5000
glaze	1050	2500-3800
single firing, glazed	1100	3800-4600
single firing, glazed mozaics	1180	7100-8000
unglazed	1090	3800-5000
Building bricks		
common bricks	960	1700-2900
Fireclay		
normal bricks	1350-1450	2700-5000
Stoneware		
pipes, traditional composition	1280	5100-9000
pipes, non-traditional composition	1180	4200-5800

Table 3 Development in the Firing Temperatures of the Double Fired Wall Tiles

	Bisque, °C	Glaze, °C
After the World War II	1280-1300	1120-1160
Early 60`	1230-1250	1100-1120
Contemporary	1050-1080	1020-1040
Prospects till the year 2000	1000-1020	900- 980

Table 4 Development in the Firing Cycles of the Double Fired Wall Tiles

	Bisque, hrs	Glaze, hrs
After the World War II	60 - 120	24 - 48
Early 60`	24 - 68	3 - 24
Contemporary	1 - 48	1 - 24
Prospects till the year 2000	0.5	0.5

V. THE ROLE OF FLUXES IN CERAMIC TECHNOLOGIES

In ceramics, the traditionally applied raw materials are based on the following minerals:

Kaolinite	$Al_2O_3.2SiO_2.2H_2O$
Quartz	SiO_2
Orthoclase	$K_2O.Al_2O_3.6SiO_2$

Table 5 shows their main properties and applications.

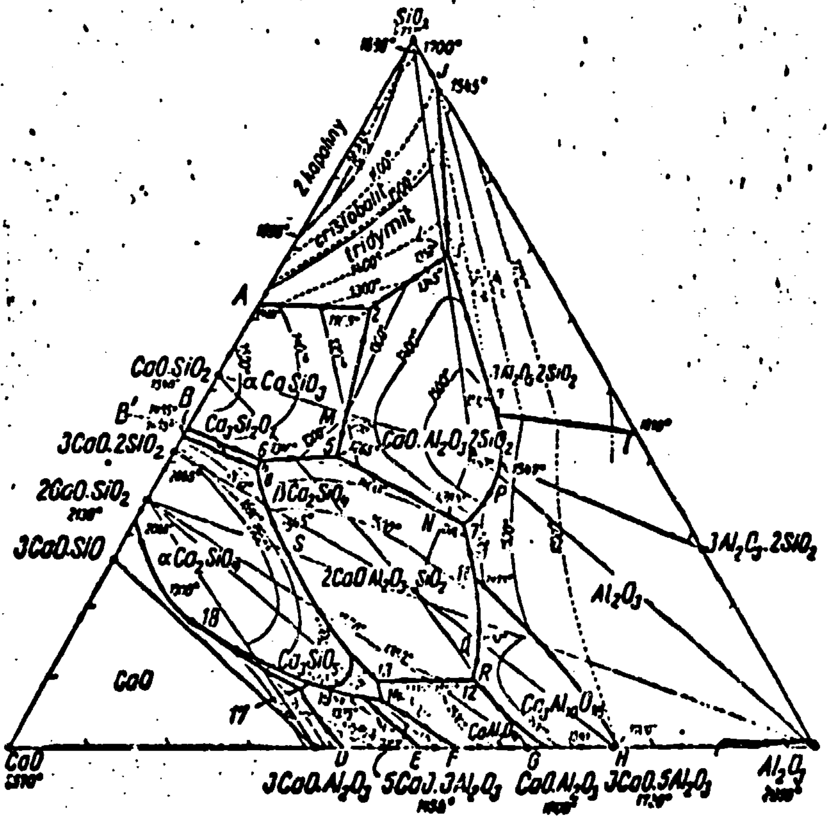
The function of kaolinite and quartz in newly developed blends is based on the same principles as in the traditional technologies. The most important influence to the energy conservation play fluxes. The potassium feldspar has always been considered as the most suitable flux as in ceramic blends it has always caused a wide interval between the vi[illegible]tion and deformation. When sodium fluxes are [illegible], physical and structural changes of the ceramic body are speeded due to the smaller diameter of sodium. Ceramic blends with the potassium feldspar always need higher firing temperature compared with sodium and/or calcium fluxes.

Fluxing effect of calcium oxide, based on reactions with kaolinite and quartz, is explained in the ternary diagram $CaO.Al_2O_3.SiO_2$ (Table 6).

Table 5 Traditional Minerals in Ceramics

	characteristic properties	technological application
Kaolinite $Al_2O_3 . 2 SiO_3 . 2 H_2O$	- binding component - formability - shrinkage - refractoriness	wall tiles floor tiles china ware stoneware white ware artistic ceramics sanitary ware glazes fireclay refractory insulation
Silica SiO_2	- grog - control shrinkage - expansion - refractoriness	wall tiles floor tiles china ware stoneware white ware artistic ware sanitary ware glazes silica bricks acid fireclays
Orthoclase $K_2O . Al_2O_3 . 6 SiO_2$	- grog - fluxing agent - 1280°C - shrinkage	china ware sanitary ware stoneware glazes

Table 6 Ternary Diagram $CaO-Al_2O_3-SiO_2$



The area of existence of the lime-siliceous body is in the vicinity of the eutectic point L which shows a balanced temperature of 1359°C for the following composition:

10.5% of CaO, 19.5% of Al_2O_3, 70.0% of SiO_2

The composition of this eutectic point corresponds practically with the composition of the lime-siliceous earthenware bodies as a relatively balanced composition.

The nearest lower eutectic temperature of 1165°C is in the direction of increasing CaO content in the following composition:

23.3% of CaO, 14.7% of Al_2O_3, 62.0% of SiO_2

By this fact, too, the practical experience from the manufacture of the lime-siliceous body is confirmed because the addition of CaO into the body must be strictly controlled and kept in correct proportion to SiO_2. The composition of the mixture corresponding with the eutectic temperature of 1165°C may require the bisque firing temperature to be at about 900°C. Successfully managed composing of such a body shows the trend of a further possible development as far as the energy conservation is concerned.

VI. SELECTED NON-METALLIC RAW MATERIALS, SOURCE OF ENERGY CONSERVATION IN THE BODY COMPOSITION

1. Tuffs and Tuffites

Tuffs are bulk or secondarily consolidated sediments of volcanic ash or small sized fragments of material of neovolcanic origin. When tuffs have been transferred and mixed with admixtures of nonvolcanic material they are called tuffites. In technical routine under the name of tuffs we understand that there are also volcanic agglomerations of foamed, porous basalt, phonolite and andezite materials. According to the hardness scale, tuffs belong among relatively soft minerals being thus easy for grinding.

Though tuffs and tuffites may be exploited in many industries, e. g. as light-weight gravel, expanded material in the production of mixed hydraulic mortars, they become an important fluxing admixture in body composition in ceramics. Stoneware body, for instance, may reduce its sintering temperature due to the addition of finely ground tuffs as shown in Table 7.

Table 7 Lowering the Firing Temperature in the Stoneware Pipe Production with the Addition of Tuffs

Body composition,%	Traditional composition	Composition with the addition of tuffs
clay A	50.0	33.0
clay B	45.0	33.0
tuff	-	28.0
fired rejects	5.0	6.0
total	100.0	100.0
sintering temperature, °C	1280	1140

2. Nepheline

Nepheline is an aluminum-sodium-potassium silicate the chemical composition of which is very close to that one of albite (sodium feldspar) but its SiO_2 content is lower. When having 45% of SiO_2 and 34% of Al_2O_3, nepheline may contain as much as 16% of Na_2O and 4 - 5% of K_2O.

Nepheline is a very efficient substitute of feldspars because it can reduce the firing temperature with the minimum risk of deformation of the body because it has a sufficiently broad interval of sintering. It begins to act as a fluxing agent already at low temperatures.

While melting takes place at about 1280°C in case of potassium feldspars, it starts as early as at about 1100°C temperature in case of nephelines.

In the nature, nepheline frequently occurs in the form of nepheline-syenite containing no free SiO_2, composed mainly of feldspars, biotites, amphibole and pyroxenes. The proportion of nepheline proper $Na_2O.Al_2O_3.2SiO_2 = NaAlSiO_4$ represents 28 to 33%. High content of iron oxide stems from the biotite and can be removed by a magnetic separation process to maximum content of 0.1% that is the grade of the best feldspars.

Lately, the industrial utilization of nepheline attracts considerable attention in the world. The natural raw material containing usually large amount of iron must be treated by a magnetic separation. The concentrate so obtained containing less than 1% of iron and about 16 to 19% of alkalis represents a non-traditional but prospective raw material which not only substitutes feldspar but makes further reduction of the firing temperatures feasible. Nepheline in the form of finely ground fluxing agent acts on the sintering of the body as early as at low temperatures within a relatively wide sintering interval so that there is no risk of deformation of a product.

When potassium feldspar is simply replaced by nepheline the firing temperature of a ceramic product can be decreased by 2 to 3 p.c.e. Particularly distinct reduction in the firing temperature may be achieved by a combination of the nepheline concentrate with the other fluxing agents, especially with talc. Such bodies then are the basis for introducing the single firing technology into different ceramic processes.

The addition of 15%, 20% and 30% of the nepheline concentrate into the bodies for glazed wall tiles fired at 1040°C to 1140°C temperature in a single layer firing process at the total 60-minute cycle of the kiln proves that

a) 15% addition of nepheline reduces the water absorption of the products to 4.2 - 5.4%,

b) 30% addition of nepheline reduces the water absorption of the finished product below 1%.

3. Phonolites

Phonolites are effusive alkaline rocks corresponding to nephelinitic syenite with foids, i. e. with aluminosilicates containing less SiO_2 than feldspar.

Phonolites can further be classified according to their contents of the main rocks into:

a) nephelinitic phonolites - containing high amount of nepheline
b) trachitic phonolites - containing little nepheline
c) leucithic phonolites - containing leucite
d) tephritic and trachitic phonolites - presence of plagioclase, poor in foids and nephelines

Table 8 shows that the types of phonolites contain a relatively low content of iron so that they can be applied in the ceramic and glass industries even without magnetic separation. The content of alkaline oxides ranges from 12 to 15% while the CaO and MgO oxides content being about 3% so that it constitutes a non-traditional and, at the same time, a prospective raw material for reducing the firing temperature in ceramics.

Tables 9 and 10 clearly prove that the non-traditional composition of the body with phonolite not only may result in reducing the firing temperature but also in a sharp drop of material costs when washed kaolin and feldspar are eliminated from the body at all.

Table 8 Chemical Composition of Selected Czechoslovak Nephelinitic Phonolites

Content of components,%	Phonolite A	Phonolite B	Phonolite C
SiO_2	56.41	56.13	55.81
Al_2O_3	20.70	23.01	23.02
TiO_2	0.26	0.81	0.40
Fe_2O_3	0.96	0.80	2.04
FeO	1.80	0.26	0.83
MnO	0.29	0.18	0.18
MgO	0.87	1.88	0.13
CaO	2.30	1.98	2.73
Na_2O	8.47	8.67	10.02
K_2O	3.76	3.57	5.24
H_2O	2.22	2.22	0.00
P_2O_5	1.14	0.03	0.12

Table 9 Lowering the Firing Temperatures in the Earthenware Production with the Addition of Phonolite

Body composition,%	Traditional composition	Composition with phonolite
clay A	47.0	32.0
clay B	47.0	31.0
phonolite	-	31.0
fired rejects	6.0	6.0
total	100.0	100.0
sintering temperature, °C	1230	1080
total shrinkage, %	13.9	12.8

Table 10 Lowering the Firing Temperatures in the Ceramic Floor Tile Production with the addition of Phonolite

Body composition,%	Traditional composition	Composition with phonolite
clay A	35.0	40.0
raw kaolin	10.0	30.0
washed kaolin	25.0	-
phonolite	-	30.0
feldspar	30.0	-
total	100.0	100.0
sintering temperature, °C	1250	1120
total shrinkage, %	13.4	12.2

4. Perlites

Perlites are effusive rocks containing volcanic glass and 2 to 5% of combined water. After grinding when heated quickly to a suitable temperature of 950 - 1200°C these rocks expand in volume 8 to 20 times whereby their volume weight is reduced from 2.23 to 2.40 g/cm^3 down to 0.06 - 0.20 g/cm^3. The hardness of perlites fluctuates between 5.5 and 7.0 according to Mohs.

Expanded perlite shows a good serption capacity, low volume weight, very low coeficient of thermal conductivity and excellent sound absorption capacity. Due to 5 - 8% of alkaline oxide content and up to 6% of CaO and MgO oxide content and a relatively low content of iron, perlite may be used as a suitable raw material for reducing the firing temperatures of ceramic products.

Expanded perlite is an excellent insulating material the role of which has not yet been fully appreciated. Table 11 shows the volume weights and coefficients of thermal conductivity of some materials produced on the basis of expanded perlite.

Perlite may successfully replace nepheline concentrate in the ceramic wall tile bodies manufacture. The fluxing effect may be increased in combination with ground glass.

Table 11 Volume Weight and Thermal Conductivity of Selected Products Made of Perlite

Name	Volume weight /kg.m-3/	Coefficient of thermal conductivity /W.m^{-1}.K^{-1}/
Expanded perlite	50	0.047
	100	0.052
	150	0.058
	200	0.070
Keramoperlite	250	0.076
	350	0.099
	450	0.116
Perlite concrete	300	0.116
	400	0.128
	500	0.151
Perlite plaster+	400	0.116
	500	0.140
	600	0.161
	700	0.186

\+ 1 cm of Perlite plaster is of identical insulating capacity as

16 cm of stone masonry
10 cm of reinforced concrete
7 cm of Brizolit (commercial name for cement-based plaster)
5 cm of brick masonry

5. Limestone and Marls

Limestone as a sedimented raw material contains very often impurities out of which magnesium carbonate and a proportion of clayey components are important. In relation to clayey mineral content a continuous series of mixed sedimented materials is formed which, in a technical routine, may be classified according to Table 12.

Table 12 Mixed Sediments of Limestone - Clay

	%content of $CaCO_3$	clay, %
high-grade limestone	100 - 98	0 - 2
chemically pure limestone	98 - 95	2 - 5
limestone	95 - 90	5 - 10
marlous limestone	90 - 75	10 - 25
limestone marl	75 - 40	25 - 60
marl	40 - 15	60 - 85
limy clay	15 - 5	85 - 95
clay	5 - 0	95 - 100

All the above mentioned types of limestone-clay combination can be used in ceramics. It is to be noted that high-grade and chemically pure limestone may be suitably dressed as fillers into polymers of cable insulations and other organic matters where they may save as much as 50% of fundamental material which is the product of crude oil.

Fluxing effect of calcium oxide in a ceramic body based on kaolinite and silica is explained in the ternary diagram $CaO.Al_2O_3.SiO_2$ (Table 6).

The principle of using marls as a fundamental ceramic raw material was known as early as in antiquity when the primitive firing methods resulted in fairly good mechanical properties of pottery products. The main favourable feature of the limy marls is the finely dispersed calcium carbonate so that marls act not only as a temperature lowering component but as a plastic component, too. This principle has been applied again, on the basis of the latest research results, in the development of lime-siliceous earthenware body and enables to achieve distinct energy savings in the bisque firing process. Because of the fact that marls and limy marls, due to their sedimentary character, show expressive fluctuation of the fundamental components, i. e. of limestone and clay, the large producers prefer microground limestones which are also very much favourable from the economical point of view. It has been proved that identical results can be achieved by using marls when homogenized after winning.

Good economical suitability of the microground limestones is also the reason why our country is not oriented to the calcium silicate, i. e. to wollastonite which is more advantageous from the technological point of view than carbonates because while its molecule is being decomposed no gaseous phase is released enabling thus a quicker firing process. Under the present conditions the cost of wollastonite is as much as 10 to 20 times higher than that of microground limestones. Therefore, wollastonite is added mostly to glazes but rarely into bodies.

Table 13 shows the different firing temperatures of a traditional body and the Ca-Si body in relation to the different raw material composition.

The non-traditional wall tile technology has not only lowered the firing temperature but also enabled the technologist to apply cheap and low grade raw kaolins instead of expensive washed and burnt kaolins.

6. Basalts

Basalts are volcanic rocks occurring in the nature in a series of various compositions. All types of basalt, however, contain magnetite and augite. From the petrographic point of view they also may contain different amounts of other minerals such as olivine, plagioclases, nephelines, leucites and glass. The chemical composition of a suitable basalt, i. e. basalt with good fluxing effect is shown in Table 14.

Table 13 Lowering the Firing Temperature in the Wall Tile Production with the Addition of Limestone and Marl

Raw material,%	kaolinitic body	lime-siliceous body	
		with limestone	with marl
clay A	20	15 - 20	10 - 15
clay B	20	15 - 20	10 - 15
washed kaolin	10 - 15	0 - 10	0 - 10
raw kaolin	-	30 - 40	30 - 40
burnt kaolin	38 - 43	-	-
marl	-	-	30
limestone	-	15	-
fired rejects	6 - 8	6 - 8	6 - 8
firing temperature, °C	1280	1050-1080	1050-1080

Table 14 Average Composition of Basalt Applicable in the Non-metallic Industries

	%
SiO_2	43.5 - 47.0
TiO_2	2.0 - 3.5
Al_2O_3	11.0 - 13.0
Fe_2O_3	4.0 - 7.0
FeO	5.0 - 8.0
MnO	0.2 - 0.3
MgO	8.0 - 11.0
CaO	10.0 - 12.0
Na_2O	2.5 - 3.5
K_2O	1.0 - 2.5

It ensues from the chemical composition that the fluxing effect in a ceramic body must be achieved mainly by high content of CaO and MgO oxides in combination with iron oxides and alkalis. High content of iron and considerable toughness are the reasons why the use of basalt in ceramics is limited. A priority is given to volcanic rocks which have not such a strong colouring effect on the body as basalt. Hence, the main use of basalts is in the production of fused basalts, mineral wool and aggregates for building purposes. The use of basalts in the glass industry is limited by a series of limiting factors similarly as in the ceramics.

VII. 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. <u>Content of lead oxides</u>
    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 low temperature and earthenware glazes can be leadless or lead containing, usually with the addition of B_2C_3, glazes for ceramic products with higher firing temperature are leadless, some of them contain little or no B_2O_3. Therefore, the suitable raw material availability plays an important role in composing ceramic glazes with different firing (maturing) temperatures.

The glaze fit is, however, a very important factor which must be respected in choosing the type of glaze with lower maturing temperature. If clay products are to be covered by a glaze, the composition of the ceramic body and glaze must be such that their thermal expansions are adjusted to each other. If no harmony between the clay body and the glaze is achieved, stresses are set up between the two which finally can become so great as to shatter one or even both of them. If flat products are glazed, convexity or concavity occurs.(Pictures 1, 2 and 3)

Taking into consideration all physical and technological factors, the most suitable glaze with lowest possible maturing temperature can be applied on the ceramic body. Table 15 shows different glaze compositions related to different firing temperatures.

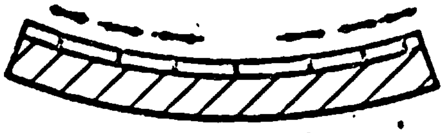
Presented Table shows that a technologist has to pay attention not only to the physical and chemical properties of glazes applied on a clay body but also to different maturing temperatures of glazes which leads to energy conservation. It is understood that, in many cases, the ceramic body must be adjusted according to the glaze thermal expansion in order to reach proper glaze fit.

Picture 1

Thermal Expansion Coeficients of the Body and Glase Are Equal

Picture 2

Thermal Expansion Coeficient of the Glase is Higher than that of the Body. The Tile Is Concave.



Picture 3

Thermal Expansion Coeficient of the Body is Higher than that of the Glase. The Tile Is Convex.

Table 15 Glaze Composition Dependent on Firing Temperatures

1. Temperature 960°C, i. e. 07a PCE

	composition											
	Na_2O	K_2O	MgO	CaO	BaO	ZnO	PbO	B_2O_3	Al_2O_3	SiO_2	SnO_2	ZrO_2
MF	0.25	0.25	-	-	0.50	-	-	0.50	0.25	2.20	-	-
%	5.0	7.6	-	-	24.8	-	-	11.3	8.3	43.0	-	-
MF	0.30	0.25	-	0.45	-	-	-	0.60	0.30	2.30	-	-
%	6.7	8.4	-	9.1	-	-	-	15.1	11.0	49.7	-	-
MF	0.16	0.17	0.25	0.25	0.17	-	-	0.83	0.47	3.42	-	-
%	2.6	4.1	2.6	3.6	6.7	-	-	14.9	12.4	53.1	-	-
MF	-	0.20	-	0.40	-	-	0.40	0.40	0.25	2.1	-	-
%	-	6.1	-	7.2	-	-	28.7	9.0	8.2	40.8	-	-
MF	0.25	0.20	-	0.20	-	-	0.35	0.50	0.28	2.1	-	-
%	4.9	6.0	-	3.6	-	-	24.8	11.1	9.1	40.5	-	-
MF	-	-	-	0.22	-	-	0.78	-	0.29	2.60	0.29	-
%	-	-	-	3.0	-	-	41.8	-	7.1	37.6	10.5	-

2. Temperature 1040°C, i. e. 03a PCE

	composition											
	Na_2O	K_2O	MgO	CaO	BaO	ZnO	PbO	B_2O_3	Al_2O_3	SiO_2	SnO_2	ZrO_2
MF	0.15	0.15	-	0.30	-	-	0.40	0.30	0.24	2.7	-	-
%	2.8	4.2	-	5.0	-	-	26.4	6.2	7.3	48.1	-	-
MF	0.08	0.22	-	0.18	-	-	0.52	-	0.14	1.64	-	-
%	1.9	7.8	-	3.8	-	-	43.7	-	5.4	37.4	-	-
MF	0.10	0.15	-	0.50	-	-	0.25	0.20	0.15	2.30	-	-
%	2.3	5.2	-	10.3	-	-	20.5	5.1	5.6	51.0	-	-
MF	0.15	0.20	-	0.25	0.40	-	-	-	0.19	1.9	-	-
%	3.9	7.9	-	5.9	25.8	-	-	-	8.2	48.3	-	-
MF	0.10	0.15	-	0.65	-	0.1	-	0.45	0.30	3.0	-	-
%	2.0	4.6	-	11.9	-	2.6	-	10.2	10.0	58.7	-	-
MF	-	-	-	0.25	-	-	0.75	-	0.28	2.05	-	0.15
%	-	-	-	4.0	-	-	47.6	-	8.1	35.0	-	5.3

3. Temperature 1180 - 1200°C, i. e. PCE 5c - 6c

	composition											
	Na_2O	K_2O	MgO	CaO	BaO	ZnO	PbO	B_2O_3	Al_2O_3	SiO_2	SnO_2	ZrO_2
MF	0.12	0.12	0.04	0.25	0.44	0.03	-	-	0.17	2.00	-	-
%	3.1	4.6	0.7	5.8	27.9	1.0	-	-	7.2	49.7	-	-
MF	-	0.20	0.10	0.70	-	-	-	0.10	0.40	3.50	-	-
%	-	5.9	1.3	12.2	-	-	-	2.2	12.7	65.7	-	-
MF	-	0.20	0.05	0.40	0.05	0.30	-	0.10	0.50	4.00	-	-
%	-	5.0	0.5	6.0	2.0	6.5	-	1.9	13.6	64.5	-	-

4. Temperature 1250°C, i. e. PCE 8

MF	-	0.20	0.10	0.70	-	-	-	-	0.45	3.90	-	-
%	-	5.5	1.2	11.4	-	-	-	-	13.4	68.5	-	-
MF	-	0.20	0.10	0.70	-	-	-	0.10	0.50	4.3	-	-
%	-	5.0	1.1	10.3	-	-	-	1.8	13.5	68.3	-	-
MF	-	0.40	-	0.25	-	0.35	-	-	0.60	3.47	-	-
%	-	10.7	-	4.0	-	8.1	-	-	17.5	59.7	-	-

VIII. PRACTICAL EXAMPLES OF ENERGY CONSERVATION IN CERAMICS

In order to illustrate the foregoing considerations on energy conservation in the ceramic industry, practical examples are presented as a guidance for energy conservation in the existing or in the projected ceramic plants.

The energy conservation of mass preparation and shaping, of handling and transport is given by the plant and it is predetermined by the project which must reflect the technology established and the mechanization and automation required. The energy consumption of this part of the manufacturing process of ceramics is much lower than the energy consumed during drying and firing. In developing and the least developed countries this ratio is even lower compared with developed countries. Therefore, the prior attention is to be paid to the drying and firing processes which are influenced by the technology established and raw materials available.

1. Choice of Proper Body Composition

Non-metallic raw materials may be utilized in reducing the energy demand especially in such cases where the body is not composed of single components, i. e. when it is blended of several raw materials. The role and knowledge of a technician become important to choose such a technology which corresponds to the raw material availability of a particular country on one hand and which is the most advantageous from the energy consumption point of view on the other hand.

a) Brick manufacture is usually based on a single-component production technology. In some cases the basic plastic raw material may be corrected by another type of a raw material. This production depends prevailingly on the type of raw materials which is decisive for the main technological operations.

The fineness of raw materials depends on the type of clays applied. If kaolinitic, sedimented clays with finely disperged sands and colouring oxides are used, the grinding to the maximum grain size of 3 mm is sufficient to obtain good quality products. In case of shaly clays, with calcareous inclusions and other rough impurities, the grinding must be directed to the maximum grain size of 1 mm in order to increase the clay plasticity and to disperse calcareous and other unhomogene inserts of such a clay.

The firing temperature is then predetermined by the process of vitrification of the raw material, i. e. its porosity is reduced and the standard mechanical properties are achieved with the increasing firing temperature. Such raw material which indicates a high fraction of kaolinite with finely disperged limestone marl and iron oxides, having minimum content of illite and montmorillonite, at which no cracks occur during the drying process, when there are no indesirable inclusions, is usually the good clay for red bricks and tiles making as its firing temperature is usually lower than 1000°C.

b) Earthenware ceramics manufacture

The term earthenware derives from the early type of ceramic ware that were made from natural clays or earth. Later on the demand has increased for white body ceramic wares which are no more made from simple clays. Instead of natural raw materials there are mixtures of plastic clays, kaolins and non-plastic materials, so called grog. Fluxing materials like feldspar, nepheline, phonolite are added.

Fine earthenware is twice fired. Earthenware is distinguished from vitreous china and porcelain in showing higher porosity and no translucency.

Earthenware ceramics type is applied in the manufacture of crockery, dinnerware, wall tiles and sometimes in the manufacture of glazed floor tiles.

The earthenware manufacture is a typical production process in which the body is blended from a series of raw materials. The technologist has to choose from a number of possibilities the most suitable one which will reflect to domestic raw materials and result into high quality final products at a minimum demand on the technology.

Table 16 shows the selected types of compositions of earthenware bodies classified according to their energy demand.

Table 16 Selected Types of Earthenware Body Composition

	Type of body				
	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 kaolinitic type, in which the content of the mineral kaolinite reaches 80% of total, represents a traditional type which still is produced by some manufacturers. This technology enables the manufacturer to make bisque of rather high whiteness and low consumption of glaze. The disadvantage of this composition implies low dimensional stability which requires the calibration of products, necessity to apply calcined washed kaolin into the body composition to increase the grog content and relatively high bisque firing temperatures. To the contrary, however, lime siliceous body offers good dimensional stability after firing, a reasonable light colour of the body, decreasing of raw material costs and energy savings during the firing process which amounts up to 20% from total heat energy needed to produce kaolinitic earthenware body composition.

c) Ceramic Tiles Single Firing Technology

Single firing in ceramics is known from antique time though only recently it has started to be introduced in mass measures in the production of tiles thanks to non-traditional technologies. First progress has been registered in the production of vitrified glazed floor tiles and facade tiles. This production has been developed so perfectly that the application of double firing processes in these technologies is a vaste of energy.

Such a development with the results obtained have opened the way to realize plants for single firing of wall tiles economically interesting such as already existing for floor tiles.

In the United States the single firing wall tile technology has been introduced on a large scale already in the 30th. Such production has been possible using raw materials as talcum and wollastonite in bigger proportion in the body composition because these two raw materials are available with reasonable prices for the conditions of the American industries in this sector.

The European as well as developing and the least developed countries, however, are mostly missing locally available talcum and wollastonite. The imported ones usually exceed the reasonable price what exclude them from the application in the wall tile body composition. Therefore, new non-traditional technologies for single firing tile technology were developed based on locally available raw materials. These technologies are being disseminated with an increased speed as about 40 - 60% of heat energy can be saved by excluding the bisque firing operation.

Some of the world producers advertize that the establishment of a modern single firing tile manufacture, based on superfast pressing, single-layer fast drying and firing without supporting refractory plates, with a firing cycle of 60 minutes, shows the following savings compared with the traditional double fired tile technology:

Investments	35%
Fuel	60%
Electric energy	30%
Labour	45%
Maintenance	20%

At present, we can distinguish two main types of body for the single firing technology. Both representatives are shown in Table 17.

Table 17 Single Fired Wall Tile Technology, Main Types of Body Composition

Body composition,%	I.	IIa	IIb
Ball clays,plastic clays, china clay	30-40	-	-
Wollastonite Talcum	70-30	-	-
Limestone marl clay	-	15-30	-
Plastic clay	-	10-20	35-45
Limestone,dolomite, chalk	-	-	13-16
Raw kaolins,high siliceous	-	10-15	35-40
Quartz, sand	-	35-40	-
Fired rejects	-	2- 6	5 -10
Firing temperature,°C	1120-1160	1020-1060	1040-1060

In comparing the American with the European technology it is seen that the unique properties of talcum and wollastonite are replaced by the possitive influence of limestone or dolomite raw materials. The only negative influence of the latter ones must be respected in the technology, i. e. they release during the firing process carbon dioxide when the carbonate is decomposed during firing. This handicap must be balanced by an increased firing time.

d) Porcelain Manufacture

Porcelain is the ceramic product which shows white and translucent body. Its body composition can fluctuate within a wide range of rational compositions requesting different glost firing temperature. In general, the lower is the glost firing temperature, the lower is the glaze resistance against scratching. In the reality, porcelain products are excluded from the households much sooner before their glaze is scratched as being broken by washing and manipulation.

Referring to the body composition and firing temperature of porcelain products, three main types can be distinguished as shown in Table 18. A special type of soft porcelain is called dental porcelain.

Table 18 proves that a difference of more than 100°C exists between firing temperatures of porcelain dinnerware with different body compositions.

Table 18 Porcelain Body Compositions

%	Dental porcelain	Soft porcelain	Hard porcelain
Kaolinite	7 - 2	40	55
Quartz	24 - 13	32	22.5
Feldspar	75 - 85	28	22.5
Firing temperature °C	1200-1300	1300-1350	1400-1450

e) Stoneware Products

The possibility and examples of lowering the firing temperatures of stoneware products are negotiated in Chapter VI.

2. Simplifying the Technology

The simplification of the technology can also lead to energy conservation. In case of decoration of ceramic products, there can be either under-glaze or on-glaze decoration applied. If the product is decorated under the translucent glaze, the decorative effect is reached during the glost firing. The on-glaze decoration, however, provides much more possibilities and combinations than the under-glaze decoration, and, therefore, it is preferred around the world.

A ceramic product can be decorated on the fired or applied, not yet fired glaze, which shows the possibility of energy conservation. If the decoration can be realized on the not yet fired glaze, one firing operation will be saved while new possibilities and new effects can be reached.

If the decoration is done on the fired glaze, it is necessary to select such colours, which can be fired and matured at the same temperature. Otherwise, each group of decorating colours requires separated firing starting with the high temperatures, such as Cobalt, and ending with lowest temperatures, such as for Gold.

3. Refractories

Refractories are indispensable materials for the construction of any heat unit. Analyzing the role of refractories in energy conservation, two different points of view must be taken into consideration:

- decreasing of energy requirements in the manufacture of refractories
- proper application of refractories by the consumer in order to avoid heat losses and to reach the maximum of insulation

a) Body composition

Each ceramic body is composed of the grog and binding elements such as clays or kaolins but also such as chemical or hydraulic bonds. Refractories then are composed of refractory grog which is, in many cases, calcined, fired, vitrified or burnt before being blended with the binding substance. The energy consumptions, needed for burning of 1 ton of different types of refractory grog, are presented in Table 19.

Table 19 Energy Consumptions to Produce Selected Refractory Grog

	GJ/ton
Burnt refractory shales or clays	3.0 to 6.0
Rejected fireclay bricks	3.0 to 6.0
Mullite grog synthetic	6.0 to 12
Magnesite clinker	7.0 to 10
Special high temperature magnesite clinker	10.0 to 40

Relatively high energy consumption needed for the manufacture of refractory grog shows two basic ways for energy conservation:

- to apply the technology with such blends which can exploit natural, unfired grog without any preliminary heat treatment, such as
  quartz sands in the manufacture of siliceous fireclays,
  quartzites for silica manufacture,
  cromium ore for the production of crom refractories,
  andalusite or natural corrundum for high alumina production.

  For developing and the least developed countries which start the manufacture of refractories the most easiest way is to produce siliceous fireclays which are easy to be produced, show low energy consumption and can be utilized in many opportunities in the industrial sector.

- to decrease the proportion of fired grog in the refractory blend to a minimum. While the European fireclay technologies apply up to 80 to 85% of fired grog in fireclay masses, the American technologies, in many cases, prefer to blend sometimes 30 to 35% of fired shales only, substituting the remaining part of grog with unfired refractory shales which, as unfired, behave as a bond and are then fired jointly with the clays. The refractory mechanical and physical properties of such products are the same, the accuracy in dimensions is achieved by well defined firing conditions.

b) Assortment of refractories

Total energy needed for the manufacture of different refractories, fluctuates according to their assortment. The experience shows that the highest energy inputs are required in the magnesite and high alumina manufacture. The medium energy consumptions are needed to produce fireclay and silica products. The minimum energy inputs are needed in the manufacture of unshaped unfired refractory masses such as with the ceramic, hydraulic or chemical bonds.

The unshaped unfired refractories are produced, supplied and applied without being fired by the producer. Their firing is made jointly during the period when the heat unit is heated before it is operated with the full output. Their application is very economic as they extend service life, they offer one-piece linings, uninterrupted by numerous joints. Such monolithic constructions are very good as they simplify repairs and they shorten the time of erection. They also show the way for energy conservation.(Table 20)

Table 20 shows the average evaluation of advantages of unshaped monolithic refractory constructions with the traditional lining made from refractory shaped bricks. Insulating properties and energy needed to produce refractory unshaped masses for monolithic constructions offer energy conservation up to 75% from the consumption in the case of fired, shaped bricks. Therefore, during the past decade, this way is being developed. Present production of unshaped refractories in developed countries amounts to about one third from total manufacture of refractories. In developing and the least developed countries this proportion is much lower because of the fact that in spite of relatively easy manufacture (simple assortment, no shaping, drying, firing and completion of orders is required), know-how is needed to prepare blends and to apply them in the heat aggregate. The expected development shows future trends in favour of unshaped masses when they will reach, step by step, up to 70% from total production of refractories.

Table 20 Advantages of Unshaped Monolithic Refractory Constructions

Increased time of service	pending on the type of furnace
Insulating of lining	+20% to +25%
Intenzification of the furnace	+10% to +15%
Energy consumption in the manufacture of refractories	-50% to -75%

c) Liquefying agents for fireclay masses

The manufacture of fireclay products is realized by blending refractory grog and bonds. Sometimes Carboxyl-Methyl-Celulosis or other glueing matters are added in order to increase mechanical properties of green products. Even in developed countries no bigger attempt has been made to mix into green masses liquefying agents in order to decrease the amount of plastic water. However, this is one possible way to conserve energy in the drying process. The addition of 0.2% of a liquefying agent (such as naphtol, pyrocatechine, cresoe) has decreased the amount of plastic water by one third, while the workability of raw fireclay masses was the same compared th the full addition of plastic water without any liquefying agent.

The lowering of plastic water in fireclay blends brings the following advantages:

- Energy conservation during the drying process, as for example, in the dry processing of fireclays the addition of plastic water was decreased from 6% to 4.5% only. In the same time, the driers capacity was increased.
- Lowering of reject from drying and firing due to lower plastic water content.

d) Light weight insulating refractories

The application of light weight insulating refractories in the industrial furnaces does not bring energy conservation to the producer but it can play an important role by the buyer. Right application of light weight insulating refractories enables to project new types of light constructions which, in general, show the following advantages:

- Energy conservation by decreasing heat losses thanks to low thermal conductivity of the lining and by decreasing the heat radiation from the kiln surface.

- Energy conservation by lower heat accummulation during the heating and cooling operation of periodically working kilns.

- Lowering the weight of the furnace and of its steel structure.

- Possibility to reduce the thickness of the wall.

Picture 4 shows a practical example in which cross-section of a kiln wall is discussed in case of the application of 2 different types of refractories.

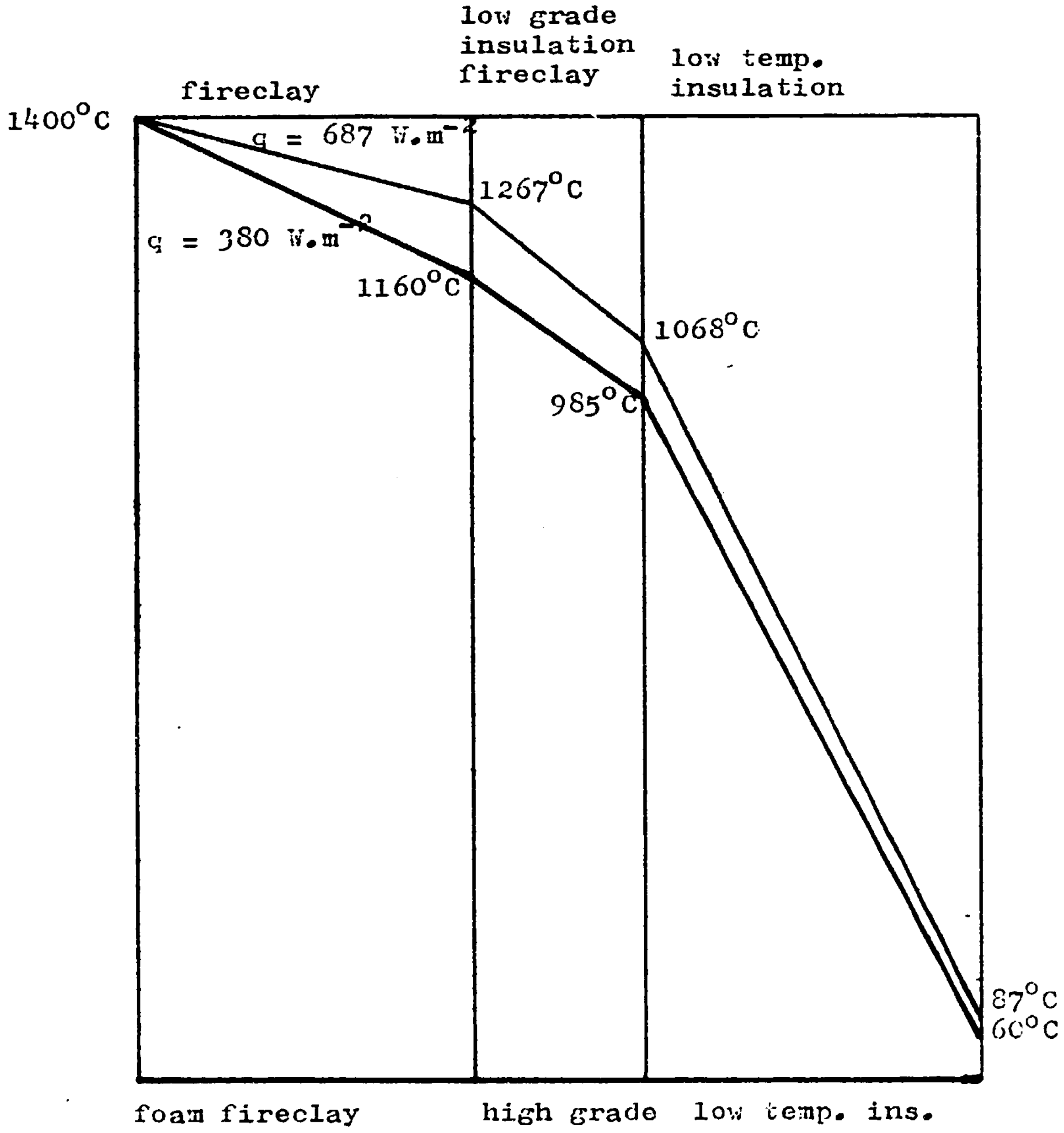
- The traditional wall lining is represented by the 250 mm layer made from dense fireclay bricks, 125 mm from low grade insulating fireclays and 250 mm low temperature insulation.

- The new wall lining is made from 250 mm layer from foam fireclays, 125 mm high grade insulating fireclays and 250 mm low temperature insulation.

If the temperature of 1400°C is reached on the hot face of the wall, then external site of the wall shows 87°C for the traditional lining and 60°C for new construction. Heat losses by conduction represent for the first case 687 $W.m^{-2}$ while 380 $w.m^{-2}$ for the second case. New insulation brings decrease of heat losses by conduction by 45% from total.

By applying modern insulating materials, such as foam fireclays, ceramic fibres, etc., the weight of the traditional lining can be decreased by about 50%. Discontinuously working kilns show the effect of energy conservation even higher.

Picture 4 **Kiln Wall Lining**



IX. FINAL NOTE

Ceramics and non-metallic raw materials represent an important field of the development of any country. In energy conservation, ceramics and non-metallic raw materials play an important role. In order to reach standard properties of ceramic products their green bodies must be dried and fired. New developments show that attention has to be paid to non-traditional raw materials as well as to non-traditional blends which can be applied and result into high quality finished products with lowered requirements on energy consumption. Insulating materials, refractories and different types of non-metallics can also be applied as high efficient insulators and as fillers into polymers in which they may substitute as much as 50% of the polymers which are crude oil products.

As the conclusion, it is possible to say that non-metallics are one of the important sources of energy conservation and they also need to be taken into account from this point of view. Therefore, the ceramic industry has lowered and it has fair prospects for further lowering of energy consumption.

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