OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

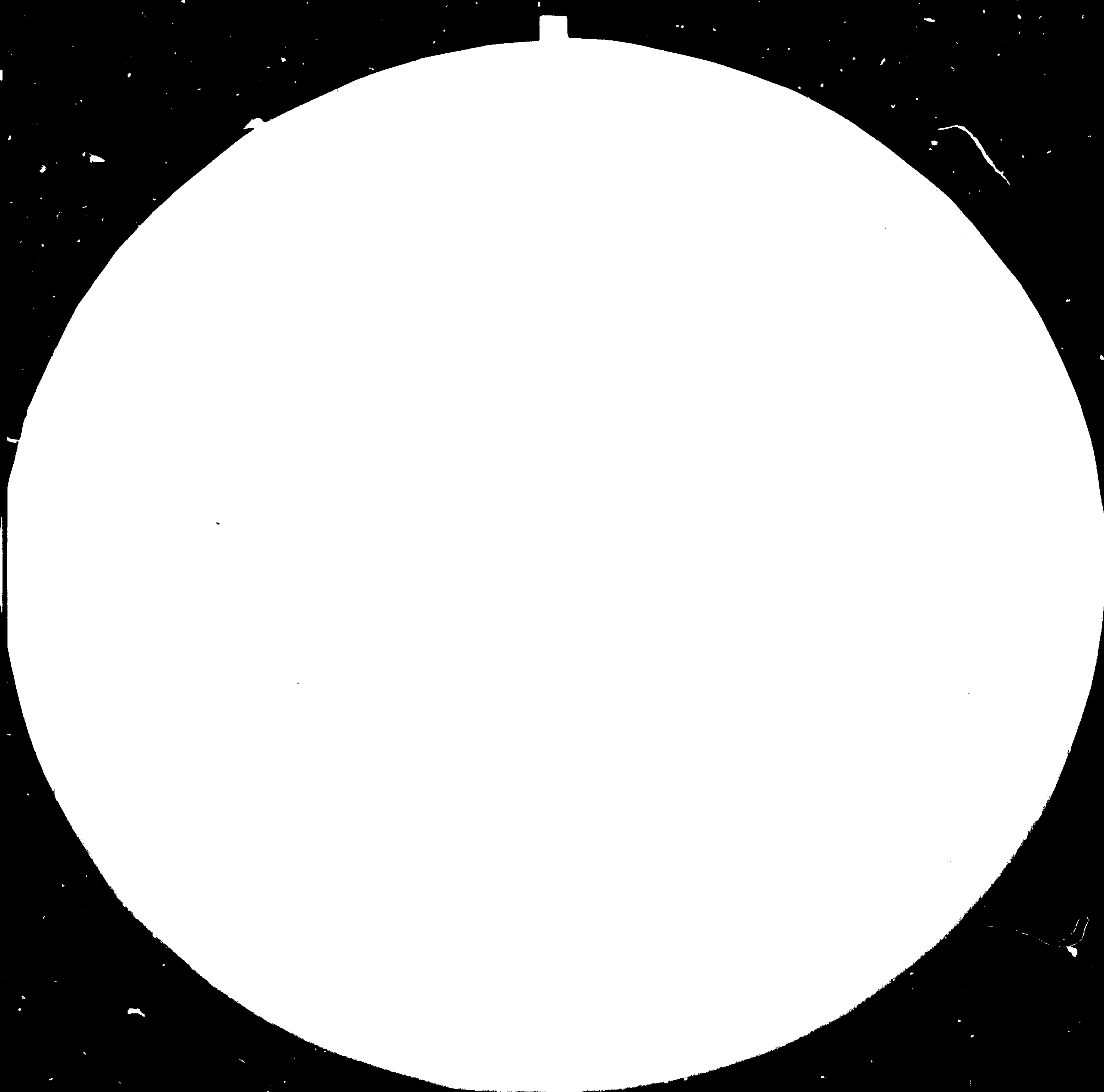
FAIR USE POLICY

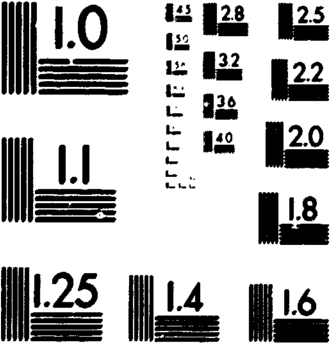
CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

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
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No 2)

14089

UNIDO-Czechoslovakia Joint Programme
for International Co-operation in the Field of Ceramics,
Building Materials and Non-metallic Minerals Based Industries
Pilsen, Czechoslovakia

Distr.
LIMITED

JP/80/81
May 1981

ORIGINAL: English

→ Maria Dietrich

NON-METALLIC RAW MATERIALS,

SOURCE OF ENERGY CONSERVATION

by: Z. A. Engelthaler

A lecture elaborated for UNESCO Scientific Seminar
NEMIRAM 1981, Karlovy Vary, Czechoslovakia

2914

NON-METALLIC RAW MATERIALS, SOURCE OF ENERGY CONSERVATION

Zdeněk A. Engelthaler, M.Sc., Ph.D.
Director, Research Institute for Ceramics, Refractories and Raw Materials, Pilsen
Chief Executive, UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries, Pilsen, Czechoslovakia

The energy management plays an important role in the ceramic industry which is one of the biggest energy consumers among non-metallic industries. The choice of proper technology and the application of non-traditional non-metallics into different batches can decrease energy requirements distinctly.

Traditional ceramic raw materials are based on the content of Kaolinite, Quartz and Orthoclase. The application of non-traditional non-metallic raw materials containing other types of fluxing oxides creates new eutectic combinations of components of a minimum system having the lowest melting point. If sodium fluxes are concerned, deformation interval is to be observed. However, new types of modern kilns with uniformly distributed temperatures across their cross-section and one layer firing kilns enable the application of non-traditional technologies for many products.

The practical utilization of the following minerals and rocks is discussed: Tuffs, Tuffites, Nepheline Syenite, Phonolites, Perlites, Calcites, Marls, Basalts and Albite. Non-shrinking ceramic bodies and single-firing technologies are other examples showing the possibility to save the thermal energy during the firing process up to 40% of total.

The new technological development with its influence to energy conservation in the field of ceramic building materials is documented by specific energy consumptions of different products related to different firing processes. Summary tables are presented with the estimates on the development of selected ceramic products until the year 2000.

The paper summarizes that non-metallic raw materials are one of the vital factors of the energy conservation as being an important part of energy management.

I. Energy Management

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 application of basic precepts of energy management for the silicate industries has resulted into main steps which are important in view of energy conservation:

1. Development of non-traditional technologies with the reduced energy requirements
2. Optimum of heat processes according to limit ing conditions of the products and according to the output of the thermal unit
3. Energy diagnostics of thermal units related to the energy conservation, intensifying of the kilns and driers output, lowering the reject and increasing the quality grades
4. Thermal units, their technical level and modernization
5. Secondary heat resources, their exploitation within the manufacturing process
6. Climate conditions related to geographical position as well as to the seasonal influence.

This paper analyses the first foregoing way showing that the non-metallic raw materials, if properly considered and exploited, can be a valuable resource for energy conservation in the non-metallic manufactures, as they can be utilized for the development of non-traditional technologies. The application has been made for the ceramic industry, one of the biggest energy consumer among the non-metallic industries.

II. Energy Requirement 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 No. 1 shows a review of the specific heat consumptions in selected ceramic technological processes.

The following conclusions are made from Table No. 1:

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 Nos. 2 and 3.

Table No. 1 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	1260	5100-9000
pipes, non-traditional composition	1180	4200-5800

Table No. 2 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 No. 3 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

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.

III. 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 No. 4 shows their main properties and applications.

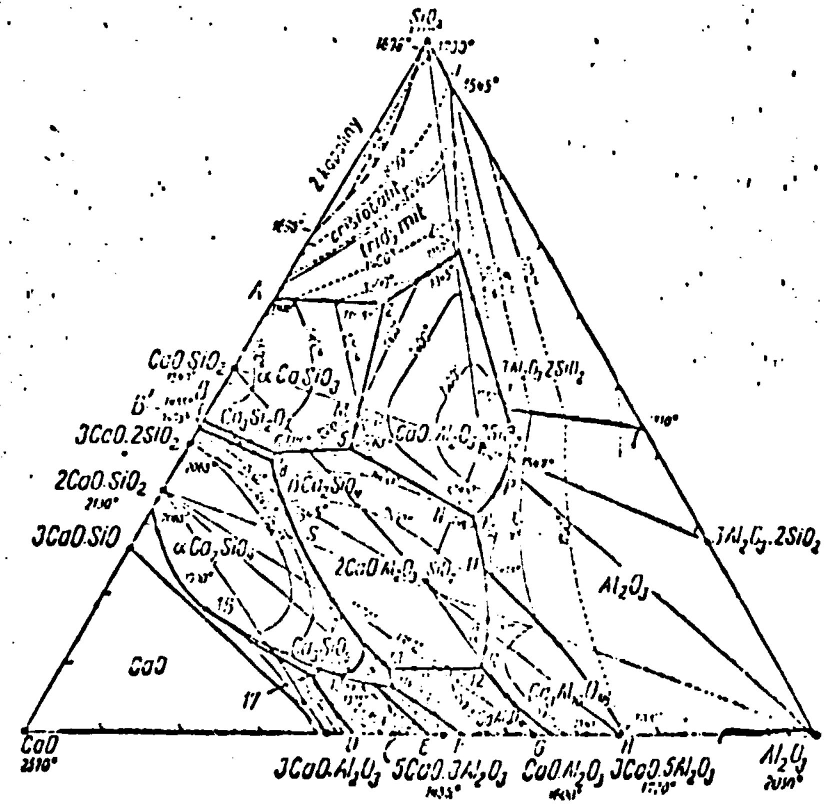
Table No. 4 Traditional Minerals in Ceramics

Kaolinite $Al_2O_3 . 2 SiO_2 . 2 H_2O$ 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
Orthoclase $K_2O . Al_2O_3 . 6 SiO_2$ characteristic properties - grog - fluxing agent - 1280°C - shrinkage	technological application china ware sanitary ware stoneware glazes

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 pottassium feldspar has always been considered as the most suitable flux as in ceramic blends it has always caused a wide interval between the vitrification and deformation. When sodium fluxes are applied, 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 No. 5) .

Table No. 5   Ternary Diagram CaO v Al_2O_3 v 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.

IV. Selected Non-metallic Raw Materials

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 follows (Table No. 6):

Table No. 6 Lowering the Firing Temperatures in the Stoneware Pipe Production with the Addition of Tuffs

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

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 products 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 No. 7 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 temperatures in ceramics.

Table No. 9 proves clearly 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 No. 7 Chemical Composition of Selected Czechoslovakian Nephelinitic Phonolites

Content of components,%	Phonolite A	Phonolite B	Phonolite C
SiO_2	56.41	56.13	55.61
Al_2O_3	20.70	23.01	23.02
TiO_2	0.26	0.81	0.40
Fe_2O_3	0.96	0.60	2.04
FeO	1.60	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 No. 8 Lowering of 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
T o t a l	100.0	100.0
Sintering temperature, °C	1230	1080
Total shrinkage, %	13.9	12.8

Table No. 9 Lowering of 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	-
T o t a l	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 sorption capacity, low volume weight, very low coeficient of thermal conductivity and excellent sound absorption capacity. Due to 5 - 8% of alkaline oxides content and up to 6% of CaO and MgO oxides content and a relatively low lontent 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 No. 10 shows the volume weights and coefficients of thermal conductivity of some materials produced on the basis of expanded perlite.

Table No. 10 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

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

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 minerals content a continuous series of mixed sedimented materials is formed which, in a technical routine, may be classified according to Table No. 11.

Table No. 11 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
lime 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 No. 5/.

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 ov 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 No. 12 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.

Table No. 12 Lowering of Firing Temperatures in the Wall Tile Production with the Addition of Limestone and Marl

Raw material, %	kaolinitic body	lime-siliceous body with limestone	lime-siliceous body 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	1260	1050-1080	1050-1080

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 No. 13.

Table No. 13 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 - 6.0
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.

V. Final Note

The ceramic technological processed are undergoing a violent development at present which, on one hand, enables and, on the other hand, it demands a diversion from traditional raw materials. The up-to-date firing kilns of ever shorter firing time and lower firing temperatures need new types of raw materials which were unapplicable in the traditional technological processes and are often the condition of a successful operation.

In addition to the aforesaid examples I should like to point out also to albite, anorthite and plagioclases. These raw materials are indispensable in composing glazes for quick firing processes.

The single firing technology of wall tiles enables to save about 40% of thermal energy when compared with the double-firing process giving thus further possibilities of application of a series of non-traditional raw materials.

Therefore, each raw material with fluxing effect in the given phase balance may be applicable in the ceramic technology either directly or after having been properly dressed. Some of ceramic producers give preference even to ironese clays which are good for fast firing in lower firing temperatures but which result into dark bodies of ceramic products.

Non-metallics, however, may take share in energy conservation also in other ways. Having been properly dressed they may become good insulating materials to prevent heat losses by conduction or, as fillers into polymers, the latter being crude oil products, in which they may substitute as much as 50% of the polymer and influence its properties in the desired direction at the same time.

Hence, to conclude with I wish to sum up:

Non-metallics are one of the most important sources of energy conservation and they also need to be taken into account from this point of view.

VI. References

Dřevo J., Engelthaler Z.A., Grotte M., Kuna L., Lahovský J., Meinhold L. /1980/: Energy Conservation in Non-metallic Minerals Based Industries, UNIDO

Engelthaler Z.A. /1979/: Technology, UNESCO Scientific Seminar GEO-Nonmetallic, Damascus

Engelthaler Z.A., Krejsa J., Kuna L. /1980/: Non-metallic Raw Materials - Source of Energy Conservation, UNIDO

Engelthaler Z.A., Kuna L. /1981/: Energy Management in the Silicate Industries, SNTL Prague, Stavivo

Engelthaler Z.A. /1975/: Keramické glazury, ČKZ Prague

Engelthaler Z.A. /1981/: The Role of Non-metallics in Energy Conservation, SNTL Prague, Stavivo

Engelthaler Z.A., Haták B. /to be printed in 1981/82/: Keramická technologie, SNTL Prague

Haták B. /1977/: Zkoušky slínovců České křídy, VÚK Horní Bříza

Grotte M., Kuna L. /1979/: The Past-, Present-, Future Trend of Energy Savings in the Non-metallic Minerals Based Industry", UNIDO

Keramické závody, Košice /1977/: Perlit, Košice

Míšek R. /1980/: Vulkanická taviva, VÚK Horní Bříza

UNIDO Energy Task Force /1980/: Report and Proposed Action Programme, UNIDO