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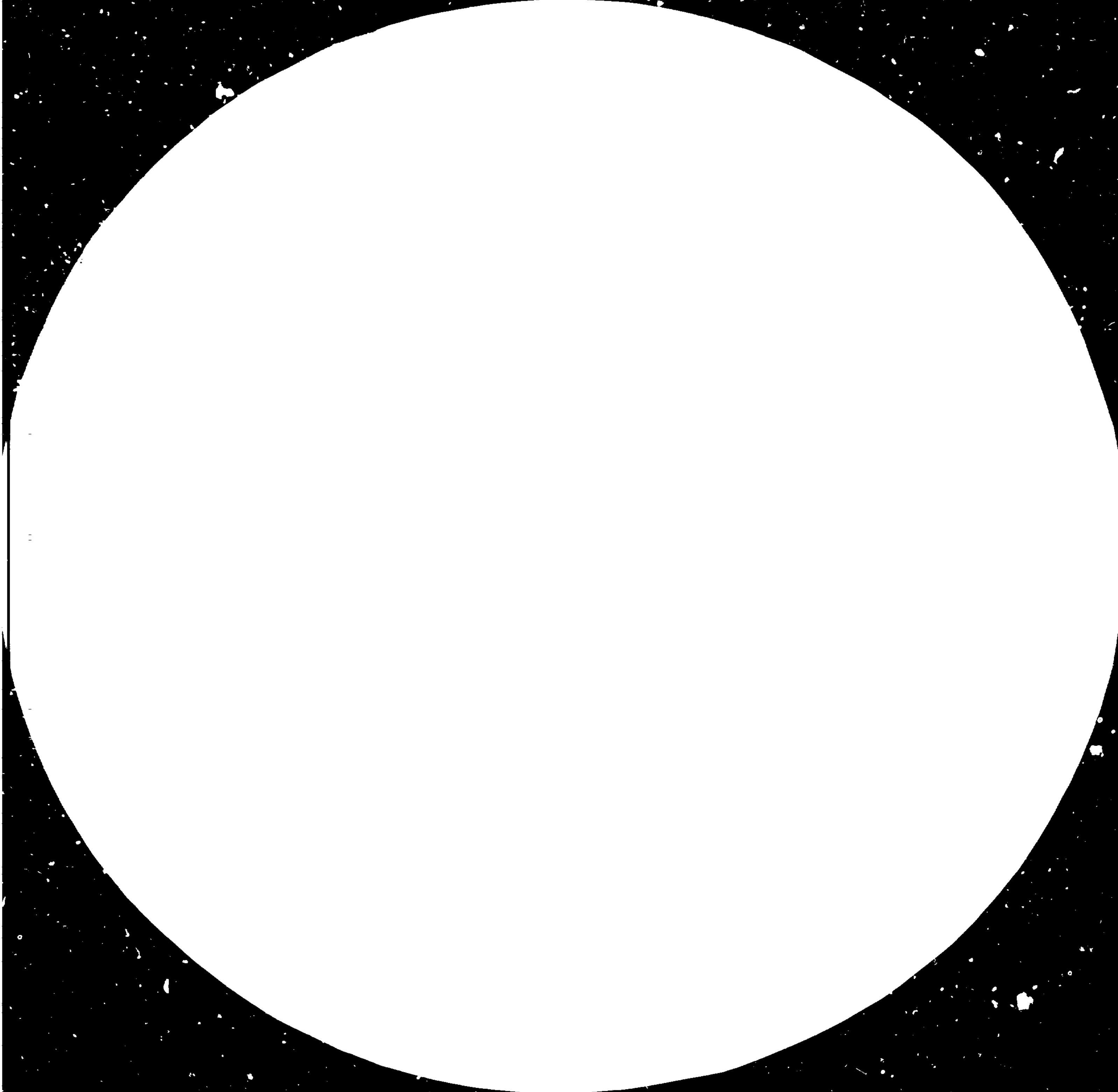

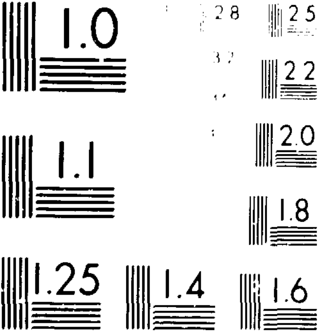
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→ Maria Dietrich

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Non-traditional Ceramic Raw Materials

Enabling Savings in Energy

by: Z. A. Engelthaler

Non-traditional Ceramic Raw Materials

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List of Contents:

By: [illegible]

A Traditional Raw Materials in Ceramics

The traditional raw materials in ceramics are based on the following minerals:

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
- controlling shrinkage
- expansivity
- refractoriness

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

Orthoclase

$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$

characteristic properties

- grog
- fluxing agent - 1200°C
- shrinkage

china ware
sanitary ware
stoneware
glazes

B Non-traditional Ceramic Raw Materials Enabling Savings in Energy

1. Development of the ceramic industry

The ceramic industry belongs to those industrial branches in which the properties of final products are achieved by heat treatment. Hence, it is a branch of high energy consumption both in the form of electric power and, prevailingly, in the form of thermal energy.

Reducing the firing temperature, accelerating the firing process and simplifying the production technology are some of the methods to save energy in the ceramic industry, e.g. by switching over from the double-fire production process to the one-fire one.

The following tables 1 and 2 illustrate the development in the porous wall tile manufacture:

Table 1 Development in the Firing Temperatures of the Double-Fired Wall Tile Production

	Biscuit, °C	Glaze, °C
After the World War II.	12[illegible]-1300	11[illegible]-1150
Early 60'	1220-1250	1100-1120
Contemporary	1050-10[illegible]0	1020-1040
Prospects till the year 2000	1000-1020	960- [illegible]

Table 2 Development in the Firing Cycles of the Double-Fired Wall Tiles

	Biscuit, 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

Table 3 gives a review of the specific heat consumption in selected ceramic technological processes.

Table 3 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
one-fire	1040-1100	3560-4800
Floor tiles		
semigres bisque	1100	3350-5000
glaze	1050	2500-3800
one-fire	1100	3800-4600
one-fire mosaics	1180	7100-8000
Building bricks		
common bricks	960	1700-2900
Fireclay		
normal bricks	1350-1450	2700-5000
Stoneware		
pipes, traditional composition	1280	5100-9000
floor tiles	1090	3800-5000

The widely ranging specific heat consumption proves the variety of demands for thermal energy by various plants and the changes being made in the world.

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

a) progressive firing equipment that enables the construction of production lines when firing is performed in a single layer,

b) switch-over to the non-traditional body composition in which more efficient fluxes are applied in the basic body composition that may form suitable eutectics requiring lower eutectic temperatures. It means that the rule according to which the firing temperature is proportionately reduced while the addition of a fluxing agent is increased is no longer applicable.

Volcanic fluxes belong among the non-traditional fluxing agents enabling the reduction of the firing temperatures.

Effusive rocks consist of many minerals having primarily crystallized from the glowing magma while secondarily they were formed by the transformation of primary minerals by the action of vapours and hot gases, high pressures and temperatures. The absolute majority of these effusive rocks is formed by silicates containing alkalis and calcium. Silica content fluctuates from 30 to 80% and scarcely drops below 30% (classification of rocks into aciduous, medium and basic). Effusive rocks also contain sometimes a considerable amount of alumina, the content of which may reach as high as 30% particularly in rocks rich in nepheline. The content of bivalent and trivalent iron oxides in the nature is rarely below 1% but it may reach as high as 20%. Magnesium oxide ranges from traces up to 45%, calcium oxide up to 20%. Alkaline oxides may occur in similar amounts while sodium oxide prevails quite distinctly. Almost all these rocks contain certain amount of combined water.

The lecture points out to some effusive rocks being an indispensable raw material in solving energy conservation in the technology of ceramic production.

2. <u>Tuffs and tuffites</u>

<u>Tuffs</u> are bulk or secondarily consolidated sediments of volcanic ash or small sized fragments of material of neovolcanic origin. Hence, they are [illegible] for stones containing fragments of rocks and glass. When tuffs have been transferred and mixed with admixtures of nonvolcanic material they are called <u>tuffites</u>. In technical routine under the name of tuffs we understand that there are also volcanic agglomerations of fused, porous basalt, phonolite and andesite materials. According to the hardness scale tuffs belong among soft minerals being thus easily groundable.

Tuffs occur in the deposits of Bohemian massif in Northern Bohemia, Northern Moravia and in Slovakia northward from Detva and in localities of Žarnovce, Čajkov, Veľká Tŕňa and others.

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, in disposal of radioactive waste 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 4).

Table 4 [illegible]

Body composition,%	Traditional composition	Composition with the addition of tuff
clay A	50.0	32.0
clay B	45.0	33.0
tuff	-	[illegible].0
fired rejects	5.0	[illegible].0
t o t a l	100.0	100.0
sintering temperature	[illegible]°C	1140°C

3. Nepheline

Nepheline is an aluminium-sodium-potassium silicate the chemical composition of which is in the vicinity of albite (sodium feldspar) but its SiO_2 content is lower. Nepheline forms [illegible] developed hexagonal columns of white to clear colour. 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 feldspar because it can reduce the firing temperature without any risk of a premature 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 smelting 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.

Nepheline in the nature occurs in the form of

a) nepheline-syenite containing no free SiO_2, composed mainly of feldspars, biotites, amphibole and pyroxenes. The proportion of nepheline proper $Na_2O.Al_2O_3.2\ SiO_2$ = = $NaAlSiO_4$ represents 28 to 33%. High content of iron stems from the biotite and hornstone and can be removed by a magnetic separation process to maximum content of 0.1% that is the grade of the best feldspars. Table 5 shows the composition of nepheline concentrate produced at the Novozersk beneficiation factory.

Table 5 Composition of Nepheline Concentrate
Novozersk beneficiation factory, USSR

SiO_2	47.42%
Al_2O_3	28.49%
Fe_2O_3	0.94%
MgO	0.13%
CaO	1.76%
Na_2O	13.72%
K_2O	5.01%

b) Nepheline also occurs in nephelinites and in olivinitic nephelites which are known in the mineral association of augite and nepheline or augite, olivine and nepheline. Magnetite is currently present.

Nephelinites and nephelines in our country occur in the Doupov Hills, Krušné hory, České středohoří, at the line between Mladá Boleslav and Jičín, in the locality of Loveš, Hradiště, Vinařická hora, Říp and elsewhere.

c) Abundant occurrence of nepheline is in nephelinitic phonolites in the amounts of 11 to 15%. The largest amounts of nepheline are in phonolites (Bořeň, Želenický vrch, Zlatník, Špičák and particularly at Červený vrch near Braňany).

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 while 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 switching over to an one-fire process.

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%.

4. Phonolites

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

Phonolites can further be classified according to the 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 folds and nephelines.

Nephelinitic phonolites are most important forming a series of effusives in the České Středohoří. There are the hills called Bořeň, [illegible] vrch, Želenický vrch, Červený vrch, Mariánská hora near Ústí, Špičák at Most, Zlatník and others. Table 6 shows the 3 main representatives of phonolites rich in nepheline. It ensues from the table that the types of phonolites shown therein have 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 6 Chemical Composition of Nephelinitic Phonolites

Content of components, %	Želenický vrch	Špičák near [illegible]	Červený vrch at Br[illegible]
SiO_2	56.41	56.1[illegible]	55.81
Al_2O_3	20.70	23.01	23.02
TiO_2	0.26	0.31	0.40
Fe_2O_3	0.56	0.80	2.04
FeO	1.[illegible]0	0.26	0.03
MnO	0.2[illegible]	0.18	0.18
MgO	0.87	1.83	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 7 Reduction of Firing Temperature in the Production of Porous Products

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	1020
Total shrinkage,%	13.9	12.8

Table 8 Reduction of Firing Temperature in the Production of Ceramic Floor Tiles

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	1100
Total shrinkage, %	13.4	12.2

Table 8 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.

5. Perlites

Perlites are acidious 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.[illegible]0 g/cm3. The hardness of perlites fluctuates between 5.5 and 7.0 according to Mohs.

Perlite occurs as a rock in Slovakia near Lhotka pod Brehy, at Byšta and in the locality of Zemplín.

Expanded perlite shows a good sorption capacity, low volume weight, very low coefficient 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 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 9 shows the volume weights and coefficients of thermal conductivity of some materials produced on the basis of expanded perlite.

Perlite plaster+	400 500 600 700	0.116 0.140 0.161 0.186

+ 1 cm of plaster is of identical insulating capacity as

16 cm of stone masonry

10 cm of reinforced concrete

7 cm of Brisolit (commercial name for cement-bound 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.

Apart from volcanic rocks energy may also be saved by using sedimented rocks.

Table 9 Volume Weight and Thermal Conductivity of Selected Products Made of Expanded Perlite

Name	/kg.m-3/ Volume weight	/W.m-1.K-1/ Coefficient of thermal conductivity
Expanded perlite	50 100 150 200	0.047 0.052 0.058 0.070
Keramoperlite	250 350 450	0.076 0.093 0.116
Perlite concrete	300 400 500	0.116 0.133 0.151

6. Limestone (dolomite) and marls

Limestone as a sedimented rock 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 rocks is formed which, in a technical routine, may be classified according to table 10.

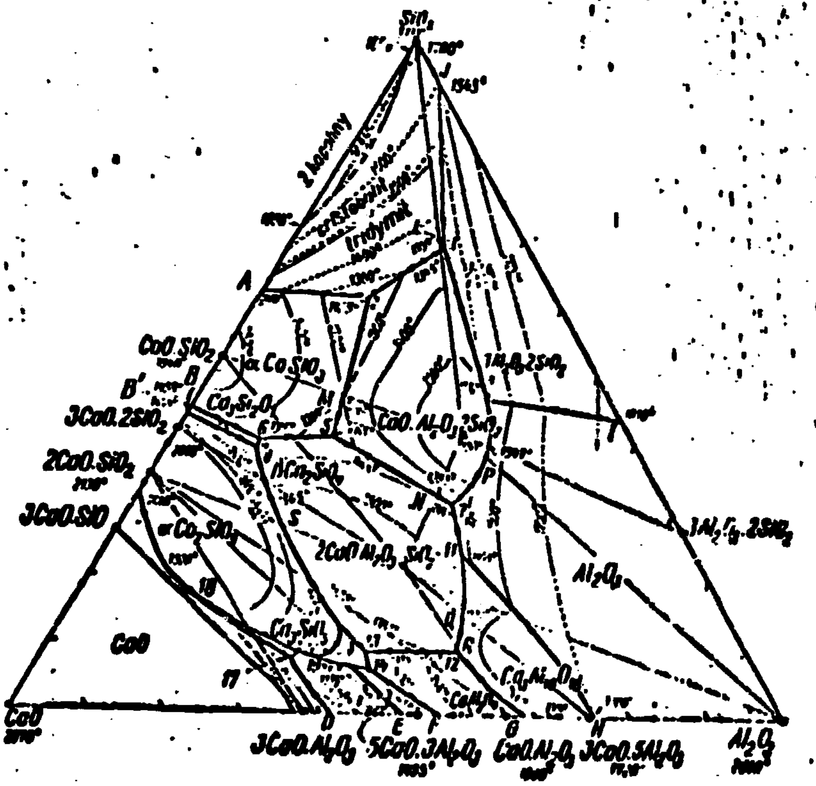
Table 10/ Mixed Rocks of Limestone - Clay

	% 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 rocks of limestone 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 insulation 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 $CaO \cdot Al_2O_3 \cdot SiO_2$ (Figure 1)

Figure 1 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 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. Such a body cannot be practically made due to the low content of clayey material and, hence, due to the pressability and in view of the glost firing temperature and the type of the bisque firing kilns. Nevertheless, successfully managed composing of such a body shows the trend of a further possible development.

<u>The principle of using marls</u> 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. The main favourable feature of the limy marls is the finely scattered 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 body of glazed wall tiles 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 homogenised after washing.

Good economical suitability of the microground limestones is also the reason why our industry 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 20 times higher than that of the microground limestones. Therefore, wollastonite is added to glazes only but not into bodies.

Table 11 shows the different firing temperatures of a traditional body and the Ca-Si body in relation to the different raw material composition.

Table 11 Wall Tile Body Compositions

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 temp. °C	1200	1050-1080	1050-1080

7. 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 12.

Table 12 Average Composition of a Suitable Basalt

	%
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 basalts.

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.

C. Conclusion

In this paper I wanted to point out to the fact that the ceramic 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 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 manufacturing technology of one-fire wall tiles enables to save about 40% of thermal energy when compared with the double-fire technology 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.

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 to 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 be taken into account from this point of view.

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