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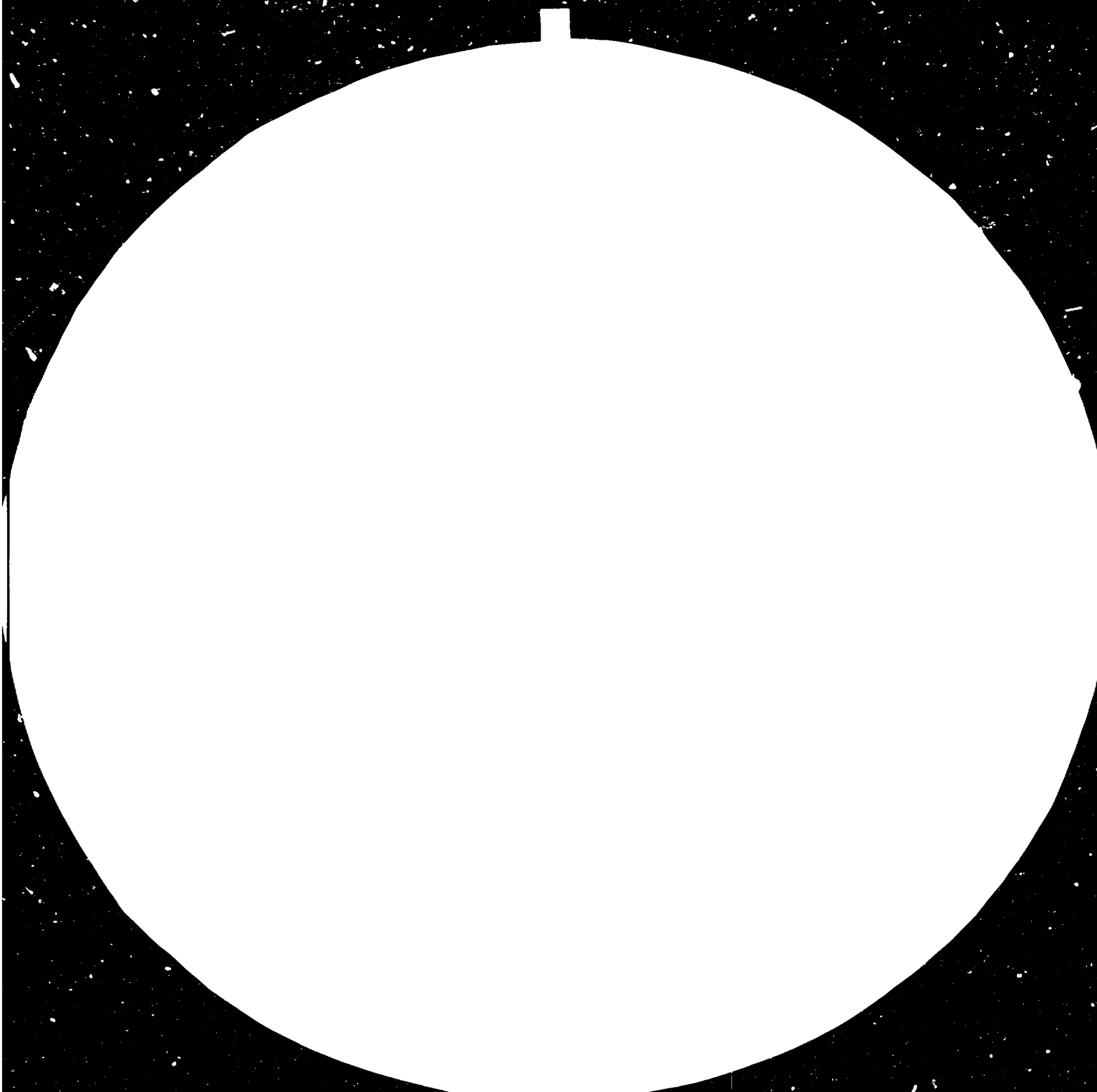
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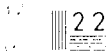
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- THEIR CONTRIBUTION TO ENERGY CONSERVATION .

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## Introduction

Recent rapid increases in energy costs have forced many manufacturers to initiate development research on their raw materials. It covers a great many different industrial activities starting from metallurgical, ceramic, glass and building industries up to the production of plastics, engineering, transport, etc. The present development of science, technology and production has arrived at a paradox situation - the energy consumption along with the ever growing industrial production, increasing world population and growing living standard spirals up enormously. On the other hand, however, it is well known that the energy reserves being used in today's production are limited and practically unrenewable. Obtaining new energy sources is in the stage of research or experimental verification. Besides trying to find new types and sources of energy and efforts to minimize energy losses the extensive research conducted in the majority of world countries is aimed at searching for new types of raw materials that would reduce the energy consumption in the technological processes without losing or deteriorating the utility value of products. There is also endeavour to introduce wasteless technologies and utilization of secondary or non-balanced raw-materials.

It is the objective of this paper to get acquainted with new possible application of various types of fluxes in the

ceramic and glass industries, new types of fillers and extenders in the production of plastics and other raw materials in the refractory materials and building industries. Because of the fact that most of the non-metallic raw materials are yet to be dressed before final processing an improvement of the existing dressing processes from their energy demands point of view is rather important.

#### Fluxes for ceramic industry

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Feldspars and feldspathic rocks, feldspar - silica mixtures, nephelinitic syenite, phonolite and, lately, petalite belong among the most important fluxes used in the ceramic industry.

A number of eruptive rocks, metamorphic rock and rock-forming minerals contain silica and alkalis (first of all sodium, potassium and from the group of alkaline earths there are calcium and barium). The group of feldspars represents sodium-, potassium-, calcium- and barium aluminosilicates belonging to the most important rock-forming minerals in the earth's crust. Albite -  $(\text{NaAlSi}_3\text{O}_8)$ , orthoclase -  $(\text{KAlSi}_3\text{O}_8)$ , anorthite -  $(\text{CaAl}_2\text{Si}_2\text{O}_8)$  and, finally, celsian -  $(\text{BaAl}_2\text{Si}_2\text{O}_8)$  belong among the most important members of the feldspathic group of minerals. It is an isomorphous series of minerals in which the ions of alkalis and alkalic earths can substitute each other in various ratios depending upon the chemism of the parental magma and on the thermodynamic conditions of originating. The subgroup of plagioclase for example is formed by albite rich in sodium and a series of chemically different interstages up to

anortite rich in calcium. A similar series of chemically and crystallographically varying forms does exist also between the orthoclase rich in potassium up to the albite. In the orthoclase for example potassium may be substituted by barium to some extent though the resulting minerals - hyalophane and celsian, are very rare when compared with the potassium, sodium or sodium-calcareous feldspars.

Apart from more or less pure feldspars - mainly orthoclase and albite in some countries even feldspathic earth such as e.g. aplite is used in their ceramic industries. It is a fine-grained form of granite made of silica, sodium and potassium feldspar and admixtures of light mica - muscovite. The so called "Cornish stone" used in the ceramic industry of Great Britain is in fact an aplitic, weakly kaolinized granite with an admixture of fluorite occurring in the area of large kaolin deposits of Cornwall. This raw material is extracted in the vicinity of St. Austell on the Isle of Man and a very similar rock is extracted even in France on the locality of St. Yrieix, south-west from Limoges. Similar composition has the raw material extracted and used in Japan under the name of "Teseiki". A synthetic mixture formed by kaolin, silica, feldspar and fluorite and named as "Carolina Stone" is used in the ceramic industry of the U.S.A.

N e p h e l i n i t i c s y e n i t e is a silicafree rock formed mainly by nepheline and various types of feldspar and stands at the end of the rock series starting with granites rich in silica followed by granodiorites, syenite in which the content of silica and feldspars is approximately in

a balance. The theoretical chemical composition of nepheline is  $\text{NaAlSi}_3\text{O}_8$  but it always contains certain amount of potassium when found in the nature.

Orthosite is a rock used in some cases as a flux in the ceramic industry. It is a coarse granular plutonic rock formed of more than 90 % of sodium-calcareous feldspars.

Phonolite is a fine-grained igneous rock formed chiefly by nepheline mineral.

#### F e l d s p a r s

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Feldspars nowadays are the most often used flux in ceramic bodies with a prevailing component of clayey mass mostly, however, in the utility and technical porcelain and in sanitary ceramics. The main role of feldspars as fluxes in ceramic bodies is, first of all, in densification of a ceramic body during the firing process so as to make a silicate glass phase. The ceramic bodies of this type are generally fired within the range of 1473 to 1673 K (1200 - 1400 degrees centigrade). The melting temperature of sodium feldspar albite ( $\text{NaAlSi}_3\text{O}_8$ ) is given at 1393 K (1120° C). The incongruent temperature of disintegration of potassium feldspar orthoclase or sanidine ( $\text{KAlSi}_3\text{O}_8$ ) is 1423 K (1150° C). When ceramic body containing feldspar is fired the following process takes place when briefly described:

Point-type eutectic drops of molten mass are formed at the contact between the grains of feldspar and silica as early as at the temperature of 1223 K (950° C). They are comparable with



spot welding of metals. It may be explained by the well known reduction of melting temperature in case of mixtures of chemically varying compositions. The initial contact melting takes also place at the contact points between feldspars and particles of the present clayey minerals because when the thermal decomposition of the clayey minerals takes place within this temperature a very reactive silicic acid is liberated. To the contrary, however, no initial contact melting happens between the silica grains and the clayey mass being disintegrated- the respective eutectic temperature lies much higher - at 1873 K (1600° C).

Though melting temperature of the present feldspar is far from being reached a quick formation of the vitrification phase takes place as early as at the temperature of about 1273 K (1000° C) in the ceramic body which begins to be of a more or less densified nature. When the temperature is being raised the amount of the eutectic molten material rises, too. It has been formed by melting of feldspar, silica and calcined clayey minerals. The maximum attainable amount of the vitrification phase corresponds to every temperature provided that the appropriate chemical or molar body composition is adhered to.

The more contact points are provided between the individual minerals by the foregoing dressing of the ceramic body, the quicker is the vitrification phase achieved and the quicker the above mentioned maximum is attained. Finely ground, thoroughly mixed homogenous ceramic bodies which are even densified by a suitable pressing process (when products are formed by a dry-pressing method), they can vitrify faster. In such a case

various deformation effects are also eliminated. The final vitrification phase gets faster completed when the feldspar melting temperature is reached. Easily movable ions of alkaline metals get among the particles of the disintegrated clayey minerals during the firing process supporting thus the formation of mullite. The diffusion of multivalent ions of alumina and silica within the temperature of 1473 K (1200° C) is rather unimportant. Hence, mullite is formed at this temperature in such places where sufficient material is available for its crystallization. Its formation is chiefly concentrated in areas in the disintegrated clayey material where highly reactive silicic acid and some liberated alumina ions are available. Therefore also the primarily formed mullite has a flaky shape. Very much movable ions of alkaline metals activate also the mobility of the other ions being present. The primary mullite gets gradually recrystallized in a needle-shaped secondary mullite. In this stage the boundaries of crystal growth of the secondary components substantially overwhelm the limits of the primary minerals. Primary mullite is also formed in the contact zone of the vitrification phase (of the molten mass). The technological firing process is performed both thermally and timely so that the required final technological properties of a product could be achieved.

Cristobalite, the only stable silica modification does not get formed usually in porcelain products under the existing normal thermal and thermodynamic conditions. Ceramic products containing high amount of silica dioxide are an exception.

Fluxing efficiency of feldspars thus can become obvious first of all by the formation of eutectic spot melts at the points of contact between feldspar grains and quartz particles and clayey minerals within the temperature below 1273 K (1000° C). When temperature is further raised the proportion of melt being formed by melting the present solid phase rises, too. In case the temperature for the melting of the present feldspar has been reached and its grains are not yet melted local spots of the melt are formed. The easily moveable ions of alkaline metals penetrate into the disintegrated clayey body and activate the recrystallization of the primary mullite into a secondary mullite. During cooling small needles of secondary mullite are formed in the melt. Cristobalite is formed on the surface of the quartz grains which have not been touched by the melt in porous ceramic products. While firing the ceramic bodies consisting of quartz, feldspars and clayey material it is necessary to keep in mind that the melt of potassium feldspar has a higher viscosity than that of sodium feldspar under identical thermal conditions. The temperature of a perfect melting of a body rich in silica dioxide can be reduced more distinctly by using potassium feldspar than by an application of sodium feldspar.

When feldspathic minerals are applied as a flux in the production of ceramic materials there is a rule that for reducing the firing time and firing temperature it is of extraordinary importance to grind the material finely that should be also achieved in grinding the present quartz.

N e p h e l i n i t i c   s y e n i t e  
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Commercial types of nephelinitic syenite are formed by a medium-grained homogenous mixture of various proportions of albite, orthoclase, microcline and, first of all, by nepheline. The mineral raw material - nephelinitic syenite contains generally a small quantity of accessory minerals such as amphibole, biotite, magnetite, limonite, calcite, garnet, zirconium and, sometimes, even corundum. Deposits of nephelinitic rocks can be found in many countries all over the world; they only differ in genesis and in geological occurrence. Most important deposits of nephelinitic syenite are in Canada and in Norway owing to their high mineralogical purity and homogenous petrographic composition. The raw material from both these regions are used in ceramic and in glass industries, similarly as fillers in the paint and plastics industries. Vast fields of nephelinitic rocks in the North of the USSR are utilized in the production of aluminium, Portland cement and some chemical compositions. Their utilization in the glass and ceramic industries represents a smaller part only of their industrial application.

From the point of view of industrial utilization the nephelinitic syenite should be coarse - or medium - grained, from the petrographic point of view its composition should be homogenous, the content of nepheline must not drop below 20 %, the content of feldspathic minerals must be higher than 60 % and the content of accessory minerals in average must not

exceed 5 %. The content of iron expressed in terms of  $Fe_2O_3$  should be lower than 0.1 % even though it may be higher for a number of industrial uses. Nephelinitic syenite from the Canadian deposit in Ontario (Blue Mountain) and from the deposit of Stjernoya Island near the northern coast of Norway are of the greatest industrial importance from the point of view of their application in the ceramic and glass industries. The exploitation in the Canadian deposits is performed by an open-cast mining and mostly dry dressing methods are applied in its dressing such as electrostatic separation and flotation though the major part of the raw material is supplied without any special dressing in a crushed form.

The extraction in the Norwegian deposit is carried out underground, the raw material is crushed, sorted and dried in rotary driers and subjected to a high-intensity magnetic separation that enables to cut down substantially the content of contaminating admixtures. Though there is ample occurrence of nephelinitic rocks all over the world there has not yet been found a deposit of nephelinitic syenite comparable in purity and homogeneity with those of Norway and Canada. It is quite well known that transport costs of nephelinitic syenite in many cases are much higher than those of its winning and dressing. Despite the ever spiralling cost of dressed nephelinitic syenite the demand for it increases both in the glass and especially in the ceramic industries in most of the industrially developed countries.

In the future, probably, political interests will play more important role than nowadays in the exploitation of mineral raw materials deposits and it seems to be sure that nephelini-

tic syenite will not be an exception in this context. Though the demands for this mineral raw material are met at present in the future supplies the political and national interests might play more important role on them than it has been so far.

The world production of nephelinitic syenite rose from 226000 t in 1961 to 666000 t in 1972.

More than 75 % of Canadian production of nephelinitic syenite are exported to the USA, more than 95 % of the total production is exported from Norway. Just for the sake of comparison it may be stated that 1.7 million tons of feldspathic concentrates were produced and consumed in 1972 all over the world. The expected consumption of nephelinitic syenite only from the Canadian deposits will amount to 1.2 to 1.9 million tons in the year 2000. In the case of Norwegian deposits this amount is envisaged to reach 245000 to 390000 tons in the same period.

The final industrial use of nephelinitic syenite is determined by a high content of alkalis, high content of aluminium oxide, practically non-existent silica dioxide and, due to this, high fluxing effect. Producers of wrapping glass, pane glass, insulation glass fibres, some types of utility porcelain and sanitary ceramics start to use more and more nephelinitic syenite owing to its chemical composition and high fluxing ability. Nephelinitic syenite is also used in the production of electric porcelain as well as in the manufacture of dental prothetics. Finely ground and sorted nephelinitic syenite

has been used since 1958 as a filler and an extender in the manufacture of internal and external paints, as a filler into latex for making level signs on roads etc. It has been used ever increasingly since 1960 in the form of microground nephelinitic syenite as filler in plastics and synthetic resins. More than 55 % of feldspathic concentrates and feldspar - silica mixtures produced in the United States are used in the glass industry chiefly for the manufacture of wrapping glass. More than 75 % of imported nephelinitic syenite are consumed by the glass industry in the United States.

The following tables show the basic properties of the characteristic commercial types of nephelinitic syenite. Though nephelinitic syenite forms were 5 to 10 per cent of a glass batch for the manufacture of wrapping glass any variability of its chemical and mineralogical composition and any possible presence of impurities may affect adversely the properties of the products. Similarly, as it is in case of typical feldspathic raw materials, the manufacturers of nephelinitic syenite watch continuously the grain size composition, content of some oxides and dioxides of chemical elements such as e.g.  $Al_2O_3$ ;  $Na_2O$ ;  $K_2O$ ;  $CaO$ ;  $MgO$ ;  $Fe_2O_3$ , content and quality of heavy minerals, loss on ignition and, sometimes even traces of some elements.

Table No. 1: Chemical and grain size composition of commercial types of nephelinitic syenite to be used in glass industry

Chemical components	Canadian nephelinitic syenite percentage		Norwegian nephelinitic syenite percentage	
	Canadian nephelinitic syenite percentage	Norwegian nephelinitic syenite percentage	Canadian nephelinitic syenite percentage	Norwegian nephelinitic syenite percentage
SiO <sub>2</sub>	50.3	55.3		
Al <sub>2</sub> O <sub>3</sub>	23.7	24.2		
Fe <sub>2</sub> O <sub>3</sub>	0.07	0.10		
CaO	0.30	1.30		
MgO	traces	traces		
Mn <sub>2</sub> O	10.5	7.3		
K <sub>2</sub> O	5.-	9.-		
NaO	-	0.3		
SO	-	0.3		
P <sub>2</sub> O <sub>5</sub>	-	0.1		
Loss on ignition (LOI)	0.3	1.0		
typical analysis of grain size	Canadian neph. syenite	Norwegian neph. syenite		
	mesh size according to US standard	mesh size according to Tyler		
	above 25 mesh %	above 28 mesh %		
	30 0.4	32 0.1		
	40 17.-	35 4.3		
	50 43.-	48 30.0		
	60 -	65 52.0		
	100 81.-	-		
	200 98.-	200 69.-		
	undersizes 2.0	undersizes 11.-		



Table No. 2.: Typical mineralogical composition of some types  
of commercially available nephelinitic syenites  
(in terms of percentage of weight)

Minerals	Canada		Norway		USSR
	amphibol.type	biotite type	pyrox.type	biotite type	
albite	48.4	52.0	traces	6.0	20.3
microcline	22.7	16.9		-	37.6
microperthite	-	-	-	-	-
perthite	traces	traces	57.0	55.5	-
nepheline	24.9	24.1	37.-	29.-	26.9
biotite	0.1	2.2	traces	3.5	0.1
amphibol	3.-	-	1.-	-	-
pyroxene	0.2	-	1.-	-	6.1
magnetite	0.4	0.5	1.-	1.5	-
calcite	-	0.1	2.-	5.-	-
muscovite	-	0.7	-	-	-
zeolite	-	-	-	-	8.7

Table No. 3.: Typical chemical composition of some types of commercial nephelinitic syenite (% of weight)

Chemical components	Canada		Norway		USSR
	amphibol.type	biot.type	pyrox.type	biot.type	
SiO <sub>2</sub>	58.8	59.4	52.73	52.37	54.01
Al <sub>2</sub> O <sub>3</sub>	23.0	23.0	23.71	23.22	21.50
Fe <sub>2</sub> O <sub>3</sub>	0.8	0.7	1.9	1.1	2.60
FeO	1.4	1.5	1.89	1.14	1.00
TiO <sub>2</sub>	0.004	0.004	0.51	0.61	1.20
Na <sub>2</sub> O	9.4	9.5	7.78	8.87	9.50
K <sub>2</sub> O	5.2	4.9	8.08	8.30	5.30
CaO	0.82	0.64	2.54	3.11	1.00
MgO	0.04	0.03	0.24	0.25	0.77
MnO	0.049	0.045	0.05	0.09	0.17
P <sub>2</sub> O <sub>5</sub>	0.01	0.01	0.05	0.09	0.09
CO <sub>2</sub>	0.05	0.15	0.77	1.00	--
H <sub>2</sub> O	0.3	0.4	0.28	0.28	1.14
BaO	--	--	0.40	0.47	0.12

In case a raw material is specified for the ceramic industry the grain size composition, melting point, colour of the melt, pH and a series of parameters are to be watched which are specified by individual customers. The respective tests of ceramic-technological properties have been described in detail in the book " Chemistry and Physics of Clays and Allied Ceramic Material " by Grimshaw (4th Edition) and in a monography " Industrial ceramics" by Singer and Singer.

The prospects for further consumption of nephelinitic syenite in view of energy conservation is more than promising. In the coming period it will undoubtedly rise the production of glass fibres for insulation purposes. In this respect nephelinitic syenite has a dominating position. Despite an increased utilization of waste glass by its recycling the use of nephelinitic syenite will grow up in the production of wrapping glass, too. The consumption of this mineral raw material in the production of electric porcelain will increase as well. On the other hand, however, it may be expected that its consumption will be reduced in the production of pane glass by applying the FLOAT method because a glass batch in such a case must contain less aluminum oxide.

From the point of view of good working conditions and air-pollution an extension of industrial utilization of nephelinitic syenite is very much advantageous. Namely, it does not contain harmful admixtures in a harmful quantity.

Though some biotites contain certain amount of fluor the major part of biotite is removed during the dressing process of this mineral raw material because biotite is almost always the bearer of pigment admixtures, mainly of iron.

It is understandable that the less developed countries are interested in providing their own raw material basis. It is supposed that there will be used small, many a time mobile, dressing plants that may enable to exploit industrially smaller deposits of mineral raw materials or at least, to win smaller amounts of the required mineral raw materials in the initial periods. The results of geological explorations undertaken in some regions of Africa and South America show good prospects that in these regions, too, will soon be found deposits of good quality feldspathic raw materials including nephelinitic syenite.

The consumption of feldspathic raw materials including nephelinitic syenite is greatly influenced by the growing use of so called returnable wrapping glass and an industrial application of used waste glass obtained by an organized collection. General and laudable endeavour for energy conservation in ceramic and glass industries results in using raw materials with lower melting point - in this case nephelinitic syenite is literally a bright and positive example.

P e t a l i t e

Just recently only minerals from the group of lithium minerals - petalite has started to be utilized in industrial scale. Its chemical composition -  $\text{Li}_2\text{Al}_4\text{Si}_{14}\text{O}_{35}$  - puts it in the group of aluminosilicates. Its distinct effect on reducing melting temperature and sintering of mixtures in which it is present enables its ever wider use in the glass, ceramic and enamel industries. Petalite as a mineral raw material contains in average 4.3 per cent of lithium oxide, 17 % of aluminum oxide and 78.7 % of silica dioxide.

Petalite is used in the production of TV screens (picture tubes), illuminating glass, technical glass instruments as well as glass oven-ware. In the production of glazes petalite can successfully substitute even lead oxide having been widely spread so far. Since petalite shows some shrinkage while being heated it is suitable for the production of glazes for such products having similar physical properties. The use of petalite enables not only reducing the firing temperature but also higher thermal resistance of ceramic and glass products. Properties being given by petalite to ceramic bodies and glazes enable to accelerate the technological production cycle particularly in the firing phase so that, apart from energy conservation, the total production costs get cut, too, and the technological equipment is thus better utilized. Extensive experiments have proved that the application of petalite in ceramic bodies remarkably increases the mechanical strength of ceramic products.

Apart from the briefly aforesaid characteristics of the most important fluxes for the ceramic and glass industries there exists still a number of minerals and rocks which may enable the temperature of firing or melting and reduce thus strongly the energy consumption. More widely used are ion carriers  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  out of which the most important ones are calcite and dolomite. In recent years even calcium salt of metasilicic acid is used known as wollastonite (it occurs in nature but it is mostly made synthetically). For some ceramic production even talc is applied as a flux. An addition of this raw material enables to reduce the melting interval while cordierite is formed whereby the coefficient of expansivity is reduced distinctly. The addition of talc enables even better adherence of a glaze to the ceramic bisque. The calcareous feldspar anorthite cannot be found in deposits alone but it occurs in rocks called anorthosites and it very often accompanies even potassium feldspars. This raw material is applied particularly in the USA in ceramic bodies which are to be subjected to quick-firing process. Phonolite, too, is important for reducing the melting temperature of wrapping glass and reducing the firing temperature of building ceramics in some regions. It is an effusive alkaline rock with a minimum content of free quartz, relatively high content of nepheline, sodalite, leucite and feldspathic minerals. Since this type of rocks contains a higher amount of ferrite oxide when compared with the nephelinitic syenite and cannot be removed by current dressing methods easily, at high costs and to certain limits only its

practical application is economically advantageous only to a limited range from the deposit.

When we try to sum up the today's situation in the application of mineral raw materials as fluxes in the ceramic and glass industries it is unquestionably obvious that the leading role can only be retained by feldspars and feldspar-quartz mixtures even though their fluxing effect is lower in comparison with the nephelinitic syenite. One of the disadvantages of feldspathic concentrates and particularly feldspars supplied to the customers in an undressed condition is their high variability in chemical as well as mineralogical composition. In order to make good for this shortcoming a flotation process is applied in the dressing of natural feldspathic raw materials that enables to enrich the final product with a feldspathic component and magnetic separation process helps to remove impurities, especially ferrous compositions.

First of all the shortage of industrially exploitable deposits prevents a broader application of mineral raw materials with higher contents of lithium as fluxes. Even though spodumen, petalite and lepidolite occur in some pegmatites in an exploitable quantity the geological reserves are generally small and they can in no case compete with feldspar or nephelinitic syenite. The same applies for other lithium minerals, as well.

It is obvious that further development of production

and consumption of the above mentioned mineral fluxes will depend on geological reserves, on the development of the ceramic and glass industries (and, naturally, on the development of the follow-up industrial branches being the principal consumers of their products) and last but not the least on the energy costs.

### F i l l e r s   f o r   p l a s t i c s

The plastics industry, such as polyethylene, polypropylene, polyvinylchloride and a series of others represents a very important consumer of mineral raw materials applied either as additions in the form of fillers and pigments or as media for reducing inflammability. The use of mineral raw materials as fillers is the subject of an intensive research (may it be fillers in the form of powder or of fibrous shape with a distinct reinforcing effect). Calcium carbonate has been a famous filler into plastics for many years and lately there is a growing demand for wollastonite, talc and especially dressed kaolin. It is obvious that the total volume of sales of mineral raw materials for the above applications are substantially influenced by the rising production of plastics that is realistically expected to grow still more because plastics turn to be ever more an alternative for a great many traditional materials, e.g. metals.



In the present world production of polyolephines (plastics) the filled types represent a smaller proportion only. The results of research and development having been the highest in the USA and Japan in the recent years, however, show that there are ever growing demands by the industries for materials with higher strength, higher rigidity, higher thermal resistance, lower thermal expansivity and cheaper at the same time (with low demands for energy) which can only be met advantageously by using high concentrations of mineral fillers. In the beginning of the eighties it may be realistically spoken of "the age of composite materials" whereby filled plastics are meant unquestionably. It is expected that there will be few cases of application of unfilled polymers in the near future. It ensues from the prognosis published in the middle of the seventies that the world production of plastics in about 1990 should cover at least 20 per cent of materials filled with mineral raw materials having been dressed by various methods. According to the latest opinion influenced chiefly by the quick spiralling of oil costs it is expected that the introduction of mineral fillers will be much faster.

The research in filling plastics with mineral materials in our country started as early as in the beginning of the seventies and it led to a great many achievements both in the technology of the production of the fillers based on calcium carbonate and kaolin and in the processing technology proper in different industrial applications.

There is a number of advantages in introducing the application of filled plastics. In the case of a manufacturer producing polymer-plastics rich in energy consuming oil raw material the substitution of its part with a mineral filler will prove utmost useful by substantial reduction in energy consumption. The energy demand covers first of all the calorific value of the material. In case of a polypropylene e.g. the principal cost item is represented by the cost of washing away catalysers and reclamation of solvents. The energy consumption in the microgrinding of limestone amounts approximately to 0.43 GJ/t that is quite negligible in comparison with the energy demands of polyolefines. Therefore, the volume proportion of the mineral filler added represents practically saving of energy.

Another benefit by the implementation of filled plastics at the manufacturer of polyolefines are lower investment costs in connection with an increase in the production. According to the latest information for instance the investment costs of an increased production of polypropylene by 32000 tons per year would amount to at least 12 million dollars. The investment costs of the production of filled polymers of 40000 tons yearly capacity would reach merely 7.5 million dollars.

While processing filled plastics on an existing equipment the volume of such a production will grow as follows:

- a) shortening of the injection cycles by about 25% owing to the higher thermal conductivity will be distinct mainly in case of large-size products;

- b) higher extrusion speed of boards, foils and shapes is made possible by lower elasticity of the melt by the addition of a filler

An improvement in some utility properties while keeping a low price will enable the application of such plastics in new spheres of use. An increased flexibility module and higher surface hardness bring new applications in the engineering and building industries. Lower inflammability is also a favourable property. The improvement in dimensional tolerances of products owing to smaller shrinkage is particularly important in the engineering industry when metals are replaced with plastics. The improved surface properties will enable easier sticking and printing on the final products.

The flexibility module is connected with the rigidity of the intermolecular bonds which are comparatively weak in the amorphous organic materials. In case of many products being used e.g. for construction of transport means (airplanes, ships, motor cars etc.) it is important that the material could be loaded with maximum force and its weight should be minimized at the same time. For this reason it is necessary to compare specific flexibility modules of the individual types of material. These values and properties are shown in tables No. 4 and No. 5.

From the specific flexibility module point of view it can be seen that glass is equal to steel but its well known

shortcoming is its low rigidity caused by that when elastic energy supplied to it through an outside impact is dispersed in the glass, very slowly and is consumed by breaking of the chemical bonds in the vicinity of the impact.

The data shown in table No. 5 indicate that even by introducing transverse bridges in polar amorphous resins (phenolic resins, polyesters etc.) the flexibility module cannot be increased beyond 4 GPa and these materials cannot compete with iron, glass or cellulose fibres from the hardness point of view. Therefore, lately, the development of so called reinforced plastics has been increased quickly. The anorganic phase in them provides for a component with a high flexibility module and the organic polymer then forms a bonding agent securing high rigidity, i.e. quick distribution of the supplied elastic energy.

Table No. 4.: Basic material properties

-----  
mechanical properties:

flexibility module

rigidity  
-----

chemical properties:

atmospheric stability

uninflammability

chemical resistance  
-----

economic parameters:

high productivity in processing

cheap raw materials

cheap production technology  
-----

Table No. 3.: Flexibility modules and specific flexibility modules of some materials

material	flexibility module (GPa)	specific flexibility module (MPa.m <sup>3</sup> .kg <sup>-1</sup> )
carbon fibre	210 - 420	65 - 170
steel	210	27
glass fibre	70 - 110	20 - 44
hemp, flax	50 - 80	30 - 50
spruce wood:		
longitudinally	13.5	33
radially	0.05	1.7
tangentially	0.70	1.4
fibre of polyethylene- -terephthalate	12	6.7
phenolic resins	2.5 - 4.2	1.3 - 3.2
hard PVC	3.0	2.1
rubber	0.01	0.01
polyethylene	0.9 - 1.2	1.0 - 1.3
polyester laminate	7 - 21	5.4 - 11
polyethylene + kaolin		
40 % weight	2.5	2.0
60 % weight	4.7	3.1

At this opportunity it is useful to mention two ways of development of composite materials:

- a) laminates - in this case a material with high flexibility module forms a continuous phase (fabric, fleece, etc.) and the bonding agent is a thermoset or a thermoplastic material. In such cases high flexibility modules are achieved but their processing is difficult and expensive.

A compromising solution having a quick tendency of development are so called "prepegies" in which the reinforcement is made by glass fibres of several centimetres length only and the bonding agent are mostly the polyester resins. These materials can be shaped by pressing. The productivity of pressing is influenced first of all by the quickness of resin hardening

- b) filled thermoplastics - in this case the filler, i.e. the component with high flexibility module, forms a dispersion phase in the continuous thermoplastic matrix.

It is an advantage that the filled thermoplasts retain their thermoplastic workability. Short glass fibres are the most effective known filler to increase the flexibility module; less efficient are fillers of particle shape though e.g. in case of a mixture of linear polyethylene containing 60 % kaolin the flexibility module was increased seven times against the unfilled one (table No. 5).

Unmodified particle fillers disperse badly in organic polymers and they mostly cannot form firm enough bond with the surrounding polymer matrix that results in low rigidity of composite materials having so been prepared. The research has focused therefore mainly to make such boundary layers between the filler and the polymer matrix that can secure an effective transfer of forces which is a condition for achieving high flexibility module as well as high rigidity.

From the atmospheric stability point of view plastics advantage is that they cannot be attacked with corrosion but their atmospheric stability lays in a wide interval from materials quickly deteriorating up to those being long time stable. The ideal goal of the research in this respect will be to adapt the physical durability to the moral lifetime that is closely connected nowadays with the world's problem of new utilization of wastes.

The influence of fillers on the photooxidation stability of polymers is quite complicated. Briefly said there are two overlapping effects - a photofiltration effect and a catalytic one.

Unless these two effects are separated incorrect conclusions may often be made. The photofiltration effect will appear mainly at high concentration of a filler and when thicker test pieces are used. When we watch the exposure time influence on these bodies and their mecha-



nical properties we usually can see an improvement in comparison with an unfilled polymer because a radiation initiating the photooxidation will penetrate less deep into the sample being examined.

To the contrary, however, in case of very thin foils or small concentrations of fillers the catalytic effect of the filler will occur that may be caused either by the radiation reflected from the filler particles or due to the presence of matters acting as catalyst e.g. compositions of transition metals.

The problem how to stabilize polymers is a field in which the Czechoslovak industry has achieved an international level. It ensues from the aforesaid that purposeful modification of fillers is a very perspective way how to increase or intentionally reduce the life of the polymers.

Incombustibility is one of the main shortcomings of most of the plastics. To achieve a real incombustibility, i.e. a permanent resistance against the action of flames cannot be, of course, achieved in organic materials in view of the present level of scientific knowledge. Due regard is to be paid, however, to the justified requirements of the fire safety to which, first of all, belongs a selfquenching property, i.e. no inflammation should happen from a minor source of heat (a match, a cigarette etc.) or, when a flame is put a bit away, the burning must discontinue. Furthermore, it is necessary

to respect the requirement of nonintoxication and noncorrosivity of burning products (that is a case of phosgene and hydrogen chloride being created when polyvinylchloride is burning). For this reason retarders of burning of chlorated and bromated compositions cannot be taken as satisfactory.

To the contrary, a very much perspective addition reducing the inflammability of organic polymers are some organic fillers out of which the most wide spread lately has been aluminum hydroxide which readily eliminates and releases water at temperatures above 200° C.

It is a known fact that a pyrolysis of polymer to volatile inflammables is a precondition of burning. The flame cannot get wider as long as the decomposition of a polymer requires more heat than the flame can supply. In other words, when the flame is small enough to be able to release sufficient amount of combustible gases.

Another advantage in using inorganic fillers to increase the fire safety is in the fact that no dropping of polymers occurs during burning in case of filled mixtures. It is known, for instance that when ceilings are lined with a foam polystyrene the burning material drops down to the floor whereby the whole room becomes a fireplace.

When plastics are applied in a corrosive environment it is necessary to see that the fillers themselves must be chemically resistant (from this point of view it is ne-

cessary to count beforehand on reduced application of calcium carbonate).

The effect of mineral fillers on the diffusion speed of various chemicals is another much more complicated problem. It is mainly connected with the formation of a suitable structure of interphases at the boundary between filler and polymer. It leads towards reducing the mobility of macromolecular segments.

It is necessary to take into consideration that the high productivity in the processing of various masses and in our case of the plastics it is the main reason for wider use of practical application of filled plastics in the processing industries.

The savings when compared with metals due to the high productivity in the lot production of particularly engineering products are so great that the cost of the polymer is not decisive. Generally, it may be said that in case of precise and complicated products their mechanical properties and workability will be the most important parameters; in case of less demanding products of mass use the cost of the polymer is also very important.

Thermoplastics have a great priority before recotoplastics from their workability point of view. Easy workability, however, stands often against the mechanical properties of products. From the point of view of their properties optimum polymers will usually be those having the highest molecular weight (therefore the use of additionally screened thermoplastics becomes more spread); in order to be easily workable the materials should be

those of high flowability of the melt.

The influence on rheological properties of thermoplastics melts is considerably complicated. It is necessary to realize that the melt of the polymers represents a non-Newton suspension in a non-Newton matrix. When conditions are chosen suitably the highly filled thermoplastics can be worked at high speeds without any difficulty. Possibility of quicker cooling is a definite advantage of using the filled mixtures that is a decisive criterion for the length of the injection cycle especially in the case of large products.

Apart from talc, calcium carbonate and some other non-metallic raw materials also specially dressed kaolins belong to the important mineral fillers into plastics. The world consumption of kaolin has grown three times larger in the recent twenty years and, at the same time, the number of industrial branches and technological processes has increased, too, in which the kaolin dressed in different ways is required and at the traditional customers - paper and ceramic industries the demands for quality have increased substantially.

From the point of view of processing branches in the world scale the sales of dressed kaolins may be specified as follows:

kaolin for paper industry	- 40 %
kaolin for ceramics	- 30 %
kaolin for rubber and cable industry	- 20 %
kaolin for other industrial use	- 10 %

These figures are for orientation only because the industrial application of this raw material grows ever broader. Under the existing trend of production the geological reserves will suffice for tens or even hundreds of years; the geological exploration, however, goes on steadily in the regions of good prospects.

There may be seen two principal ways in the dressing of kaolins during the last 25 year period. First of all it is an effort to find cheap and highly efficient methods of dressing kaolins of lower quality resting mainly on improvements in the sorting section, dewatering and particularly in removing compositions of iron, titanium and alkalis.

Furthermore, the producers try to find application of kaolin in new processing branches such as in the production of plastics, glass and kaolin fibres, insulation materials, insecticides carriers, various sorbents and catalyst carriers. Besides, the dressing plants of kaolins must be adapted always to the demands of the processing industries for constant technological properties and chemical composition being enforced by the current process of automation of finalizing production processes.

While comparing the kaolin consumption in various industrial branches in Europe and in the USA we may see considerable difference. In the majority of European countries e.g. the use of kaolin for the production of the best quality refractory materials is very small. Kaolin in the industrially developed European countries is used approximately in the following proportions:

Paper filling kaolin	50 %
paper coating kaolin	25 %
ceramic industry	10 %
filler into rubber, paints plastics, insecticide car- riers, fertilizers, catalysts etc.	7 %

Paper industry stands also on the first place in the consumption of kaolin in the USA. It is followed by the production of refractories, rubber and ceramic industries. It is supposed that the greatest growth in kaolin consumption in the USA will be in the paper coating kaolin, filling kaolin in the rubber and plastics industries.

Though there may be noted some trends towards substituting kaolin with other raw materials in some industrial branches there are still many industrial fields in which kaolin could be hardly replaced by other natural or synthetic material and more possible new applications keep occurring. Kaolin is a raw material which can be adapted to the requirements of consuming branches by using the latest dressing processes, often quite nontraditional ones, to keep thus ever growing production assortment.

The producers of kaolin will have to do its dressing and adapting of its parameters much faster than they have done so far to meet the customers' demands and to adapt their technological lines to the quick changes in requirements for the assortment. For instance the Freeport company - Georgia, USA is said to have installed 27 more or

less independent technological lines in their dressing plant in Gordon to be able to produce 58 types of kaolin differing in quality.

High intensity magnetic separation belongs lately to the most progressive methods in the dressing of kaolin (and also of other non-metallic mineral raw materials). It is based on the principle of different magnetic susceptibility of minerals and its theory and practical application change to some extent our opinion we have had so far about the classification of both natural and synthetic materials into ferropara - and diamagnetic ones. This process being an extraordinary step forward in the production of kaolin fillers for plastics resulting in reducing the content of so called transition metals has been thoroughly verified in our production conditions and it enables to obtain a product of remarkably high mineralogical and chemical purity.

As aforesaid earlier when kaolin is added to the linear polyethylene it may get considerably reinforced similarly as in the case of talc. Despite that kaolin as a filler in the production scale has not been applied too much. It has been found out that acidulous centres on the surface of the elementary particles of the majority of aluminosilicates cause a degradation of polymers. They are protonic centres the acidity of which is made weaker by a layer of sorbed water and the acidity shoots up abruptly only at the tempe-

natures of the thermoplastic processing, i.e. within the range of 200 to 250° C when the sorbed water gets eliminated. It is well known e.g. that polyethylene is resistant to 30 % sulphuric acid but gets decomposed very quickly when subjected to the action of 90 % sulphuric acid. New processes of calcined kaolin dressing have enabled to passivate efficiently these acidulous centres whereby the mixtures can be processed without being degraded at the same time.

Silane connecting media have been applied to create a stable connection between the surfaces of kaolinitic and organic polymer. These media get joined with the surface of the kaolinitic filler so that they form a bond of Si - O - Si - R. It has been found out that these media provide for more resistance of the resulting final composite materials against further effects of water.

Because of the worldwide rise in oil raw material costs as well as due to the hopeful properties found in the organic polymers containing inorganic mineral fillers in high concentrations it may be expected that these inorganic fillers will be used in the mass production of plastics in an ever greater extent.



Refractory raw materials and materials

The nowadays's enormous spiralling of costs of all types of energy has forced the manufacturers of refractories to aim an intensive research especially at the field of respective mineral raw materials. A series of refractory mineral raw materials must be fired prior to a further industrial processing. First of all it covers magnesite, bauxite, kaolin and refractory clays and claystones. Owing to the above mentioned energy conservation measures the nearest future will bring about most probably the following changes:

- a) an increased tendency of using green, non-fired clays and claystones into the refractory bodies and mixtures,
- b) an increased interest in uncalcined magnesite,
- c) an increased industrial application of raw materials requiring no calcination in advance such as andalusite, silimanite and adithene.

The most important consumers of refractory raw materials, especially the metallurgical and ceramic industries will have to accept this tendency in the near future.

It may be stated without any exaggeration that the technology of refractory materials has lately reached an important milestone. Years of an intensive research and development have led towards uptodate and rational processing technologies as well as to the discovery of new types of

mineral raw materials and their mixtures. In the past great attention was paid to ever increasing production of various products within the same time mostly without paying due respect to the consumption of energy. Another situation has arisen nowadays, however. After the OPEC consortium has been established the steep rise in the costs of oil and earth gas requires a revision of the technological processes used so far as well as of the choice of refractory mineral raw materials.

The industry of refractory bodies belongs to those demanding the highest amount of energy. The whole ceramic industry is one of the largest consumers of energy within the entire processing industry of a number of industrially developed countries. Therefore, the industry of refractories is affected very strongly by all changes taking place in the field of costs of input energy sources. Energy as it is understood in compliance with the main aspects of this work is meant in the sense of thermic processing of refractory raw materials and, a bit less, in relation to their transportation. Therefore, we shall not closely discuss the dressing operations such as crushing, grinding, separation, sorting, mixing etc.

There is a series of the existing as well as potential energy sources which seem to provide for the industrial development of the mankind till far future. It covers radioactive raw materials and materials such as

water, oil, earth gas, solar and geothermal energy sources as long as we intend to mention the most familiar ones.

Comparatively vivid activity in the energy conservation in the refractories industry may be noted especially in improving combustion equipment and systems as well as in the utilization of so called waste heat.

The following table shows the average values of energy consumption in the preparation (calcination) of a ton of the respective mineral raw material at a standard temperature of firing corresponding with normal industrial conditions.

Table No. 6.: Energy consumption in the firing of various types of mineral raw material

raw material	BTU x 10 <sup>6</sup> per ton
magnesite (natural, synthetic)	6 - 52
siliciumcarbide	23
mullite	19
bauxite 85-90 %	13
bauxite 70 %	9
synthetic corundum	9
bauxitic kaolin	8
kaolin	7
diaspore	5
claystone (shale)	4
perlite	3
vermiculite	1

Out of the raw materials being used in the production of refractories requiring however mostly no heat treatment beforehand belong quartz, chromite, andalusite, sillimanite and diaspore.

It is quite obvious that as long as we can produce refractories from raw materials requiring no high degree of thermal treatment we may achieve important energy savings and, thereby, reduction of production costs in connection with it. In many cases namely the cost of calcination of refractory raw materials before further processing amount to 50 - 75 per cent of their final selling price.

Calcined magnesite for refractory purposes - periclase - is prepared from natural magnesite as well as by a synthetic process. In both the cases the respective technological processes demand large amount of thermal energy. In case of the calcination of natural magnesite in an absolute majority of cases rotary kilns are used for its firing. The rotary kiln proves to be a highly efficient firing equipment in case a microcrystalline type of a raw material is to be calcined. In case of a microcrystalline natural magnesite it is usually necessary to apply a double-stage firing process if we want to obtain the required density of a product.

A single-stage firing process of green magnesite in the rotary kiln offers comparatively limited possibility of optimizing this technological process in relation to the

potential savings of energy. In fact, it is necessary to use a heat exchanger and preheater connected to the rotary kiln. There is quite a number of various designs of the preheaters. The most technicians think that the main effect of the preheaters rests in the utilization of waste heat from the combustion products and from the exhaust gases. This opinion stems out from the experience that the temperature of the exhaust gases is usually lower when preheater has been used. The aforesaid lower temperature of the combustion products and exhaust gases results directly from a much more efficient transfer of heat during the calcination process.

The highest energy losses in the rotary kilns are caused by:

- a) radiation and convection right from the kiln body
- b) thermal gradient in the calcination zone
- c) nonrecuperative cooling of the product
- d) heat losses through the chimney (unless there are minimized the losses mentioned in the foregoing points, these losses are relatively small).

As long as the work of the rotary kiln preheater is to be really efficient the calcination process must be so controlled that no calcination should take place in the preheating section. The calcination zone, however, must be entered by the raw material the temperature of which being intermediately lower than is the optimum calcination temperature. As far as the heat from the material being

cooled is completely recuperated the radiation heat losses from the kiln body are at minimum level. When these rules are adhered to the losses due to the thermal gradient in the calcination zone are minimized. In case of rotary kilns being not equipped with the preheater a lower thermal efficiency and considerable heat losses may be expected. In order to achieve a maximum efficiency of rotary kilns for a single-stage firing of natural magnesite the following conditions are to be met:

- a) the energy losses caused in the calcination zone by raw material being too cool can be eliminated by incorporating a preheater in the technological process;
- b) using an efficient cooler which will enable the surplus heat from the calcined raw material being cooled to be utilized in the technological process again for example to achieve a maximum temperature of the flamm;
- c) the heat losses by radiation from the rotary kiln jacket can be substantially reduced by incorporating the preheater because this measure alone will reduce the calcination temperature proper;
- d) installation of the preheater enables to use smaller rotary kilns to get identical output - besides others the losses by radiation can thus be reduced due to the smaller square area of the kiln jacket;
- e) and, finally, lower calcination temperature enables to make the kiln lining in the calcination zone of cheaper refractory material while using heat insulating materials

of good quality.

The use of a vertical shaft kiln is an alternative solution for the firing of magnesite. The most serious limitation of this firing method is the required relatively narrow size range of a material to be fired. As far as the raw material can be crushed so that no fine fractions are made being useless for this process or when the fine grained fractions can be used for other purposes the use of the shaft kiln proves to be very attractive. In the case of application of the shaft kiln recuperation is comparatively easy and the combustion products are of relatively low temperature. Besides, the shaft kiln jacket can be easily and efficiently insulated to prevent heat losses - for these reasons the heat consumption related to the same weight unit of the calcined raw material is lower than in the case of the rotary kiln.

To compare the efficiency and energy demands I should like to mention the principal parameters of the above discussed systems:

1. Rotary kilns without a preheater: consumption of about 3 000 000 BTU/MT of the product
2. Rotary kiln with a preheater: about 6 000 000 BTU/MT of a product
3. Shaft kiln: approximately 4 500 000 BTU/MT of a product.



The two stage method of a coarsely crystalline natural magnesite is applied to achieve the required density of a product. In this case the raw material is first calcined in a multistage vertical kiln. After calcination the magnesium oxide having been so made is to be calcined at the highest possible temperature to prevent heat losses and the finished briquettes are transported to the final firing. The briqueted material is calcined either in the shaft or rotary kilns. As far as the shaft kilns are used it is necessary to count with still more heat consumption amounting to 2 000 000 BTU per ton of a product. The rotary kiln, however, consumes another 3 000 000 BTU per ton of a product.

Though chromite is an important refractory material its consumption in the world scale has been dropping down recently. Because, however, it does not require any calcination before the industrial application its consumption in the manufacture of refractories may probably rise again in the near future.

World reserves of bauxite usable for refractory purposes are considerably limited. This material of a characteristic loss by ignition within 25 to 35 % is usually calcined at the temperature of about 1700° C. No substitution of equal value for calcined bauxite exists at present. It seems, therefore, that even the research and development work in this respect are considerably economically limited. For the calcination of this raw material only

in some cases the less energy efficient rotary kilns may be replaced with the shaft ones.

It is well known that bauxite to be used in the industry of refractories containing alumina oxide within the range of 85 to 90 % (after calcination) coming from various world deposits requires different firing temperatures.

Some non-metallic raw materials such as e.g. bauxitic kaolins, diaspor, kyanit (disthene), sillimanite, andalusite contain about 55 to 70 per cent of alumina oxide after calcination. So called bauxitic kaolins are mostly used industrially at present.

Potential changes may be expected in the nearest future in the application of andalusite. This raw material belonging under the same mineralogical group as kyanit and sillimanite contains about 50 to 60 % of alumina oxide and it has been well known as an interesting refractory raw material in various parts of the world for many years. Because of the fact that this mineral does not show practically any changes in volume when heated (loss by ignition is below 0.5 %) it need not be calcined before industrial use.

Andalusite is a typical example of possible expressive change in the application of raw materials in the industrial production of refractories where the reduction in production costs and lowering the energy consumption are the motivation momentum. In this case the economical momentum plays a pre-dominating role. However, it is necessary to take all

circumstances into consideration to which pertains also the durability of the final refractory products under industrial conditions. In the case of andalusite due regard it to be paid to the fact that energy savings stand on one side but the costs of winning and dressing them are on the other. It ensues from this that the manufacturer of refractories has to compare:

- a) the purchase cost of andalusite in relation to the other comparable refractories which can replace this mineral from their chemical composition and physical properties point of view;
- b) the difference in the properties of the final products with or without the application of andalusite;
- c) changes in the life of the final products. It may be supposed that the aspects stated under b) and c) will speak in favour of andalusite.

In the group of refractories containing 55 % to 70 % aluminum oxide kyanit (disthene) and sillimanite are the "close relatives" of andalusite. Though the loss by ignition of these minerals is lower than 1 % and the content of  $Al_2O_3$  ranges within 55 to 60 % their use for refractory purposes has been limited till the recent time. Kyanit is applied in green state as volume stabilizer in the production of refractory mortars, cement, casting, plastic and ramming masses. Green kyanit shows volume changes at the temperatures of 1400 to 1500° C when it changes into the mixture of mullite and silica oxide. This volume change -

expansion - is made use of for eliminating the shrinkage of the other components of refractory mixtures. It is absolutely evident that the applicability of kyanite for the refractory purposes deserves further detail research. When it is used in green state it will bring expressive savings in energy since it can substitute calcined refractory grog to great extent.

The possibilities of energy conservation in case of kaolin and refractory claystones and clays are first of all based on the fact that the mass for making respective refractory products is formed by the mixture of green and calcined refractory clayey refractory raw materials with a typical loss by ignition ranging from 10 to 15 %; enable in this case the production of shapes with a considerable volume stability and satisfactory dimensional tolerances. Some manufacturers of refractory materials still do their production based only on the unfired raw materials and their mixtures. This way the technological stage of high energy demand is eliminated on one hand and, on the other hand, quite outstanding quality parameters of final products can be accomplished especially as regards low porosity and high density resulting of course in substantially prolonged life. The success in the application of this technology (use of clayey refractory raw materials without prior calcination) depends chiefly on the two following preconditions: first it is the procurement of a suitable type of clay the chemical composition and physical properties of which are the presupposition of achieving the re-

quired parameters of the final products and, secondly, a suitable technology and production conditions. It has been proven in the practice that if a suitable mixture of uncalcined raw materials could be found out minimum 25 % of production costs could be saved when compared with standard products having calcined refractory clay or kaolin in the working body.

Pyrophyllite is an aluminosilicate containing about 28 % of aluminum oxide distinct with a low content of alkalis its loss by ignition being about 3 %. This raw material in an industrially important quantity occurs in Japan, Korea, the USA and, lately, also in Australia. Refractories based on pyrophyllite find their main application in the lining of kiln cars, in the production of tanks and ladles in the steel industry. Crushed and sorted pyrophyllite in a mixture with zircon and a binder based on a refractory clay is distinguished by a high resistance against blast furnace slags and by a negligible expansivity. Pyrophyllite in green state is used in the production of monolithic refractories. Since the use of pyrophyllite does not require any precalcination by its broader application high energy conservation can be achieved.

Refractories based on silicon dioxide are produced from raw materials requiring no precalcination because they have practically zero loss by ignition. Expressive changes in the use of refractory materials based on silicon dioxide have taken place in recent years. When compared with the year 1950 their present world consumption is by 30 % lower.

The main reason may be found in the fact that the steel industry has switched over from cupola blast furnaces towards oxygen converters and, at the latest, even to a direct reduction of iron ores. On the other hand, however, these materials do not need the precalcination of a raw material so that when new applications of these materials are found it may result in outstanding energy conservation.

Olivine is a magnesium silicate which was used in the production of refractories in many countries of the world as early as more than fifty years ago and to a limited extent it has been used till now.

Furthermore there still exists a small group of minerals raw materials being used in the production of refractory insulating materials. Bentonite with loss by ignition of 6 %, diatomite 5 %, perlite 4 % and vermiculite 9 % are materials the refractory character of which indicates that in the case of an intensive research and development they may become materials requiring no energy demanding predressing. Great possibilities in energy conservation are also in the fact that these materials may serve as a source for the manufacture of highly efficient insulation materials for kilns, furnaces and other thermal equipment. Lately, an increased interest in refractory insulation material can be noted; these materials enable to prolong expressively the life of furnace and kiln linings.

Certain reduction in the production of refractories as a result of the steep rise in oil and earth gas prices is different in various parts of the world - it depends mainly on the extent to which the individual producers have been stricken by the rising prices. The concrete situation is influenced by a number of factors: countries with cheap energy sources earlier producing no refractories and winning no refractory raw materials or, if so, to a small extent only, will certainly think of implementing or expanding this production for local industries and especially for export. The respective feasibility studies must naturally take transport costs into consideration which of course also depend directly on the fuels costs.

Normal, evolutionary development of the majority of industrial branches in the world has been enormously affected by the spiralling prices of energy in the recent years - one of the most important motivation factors of all industrial activity. The production of refractories belongs to those industrial branches being most demanding in view of energy consumption. In many cases, major part of energy is consumed in the calcination of a raw material, more energy than is consumed in the firing of shaped products, prepared of mixtures containing calcined material besides the plastic binding component consisting of green raw material. That is why so much money has been spent lately in the development of new types of technology and products requiring less energy.

Needless to say that expressive changes in technology and refractory products assortment take place all over the world due to the existing energy crisis. These changes of course entail changes in requirements for raw material sources and call for the development of new working masses the most essential viewpoint being the overall energy consumption and production costs. The aforesaid changes do not mean only the reduction in energy consumption and production costs at the manufacturers of refractory raw materials and materials - they affect in the same way their consumers, too.

Insulation materials based on expanded clayey rocks

Demands for light-weight aggregates are growing in the building industry, first of all in the concrete mixing plants and in the panel plants. In most cases it is an expanded granule made of clays and claystones (in many cases the initial raw material for their production being slate rocks from coal mines and wastes from coal washing plants). Expanded clayey material is not important only owing to its low weight but also by its high thermal insulation ability. That is why its use is rather broad and finds its application as aggregate into concrete intended for thermal insulations or in structures of light-weight reinforced concretes.

Expansion ability of a certain clayey material cannot be judged by its chemical composition only. To judge the



usability of a clayey rock for expansion it is necessary to know, besides its chemical analysis, still a series of physical properties and its mineralogical composition. Raw materials to be expanded should meet particularly the following requirements:

- high plasticity
- high proportion of the finest particles - minimum 35 % of particles smaller than 2 micrometers,
- higher proportion of illite to the account of kaolinite, content of calcite and dolomite not exceeding 12 %,
- points of sintering and vitrification must be close to each other, usually below the temperature limit of 1200° C, pyroplastic softening of the body should begin, if possible, at the stage of spontaneous development of gaseous phase,
- the interval of expansion should be in the prevailing majority of cases within the range of 50 to 100° C.

A mixture of expandable clay and power station ashes is used for the preparation of highly strong light-weight fillers applied in the production of light-weight concretes of compression strength exceeding 225 kp/cm<sup>2</sup>.

The granule prepared by various processes can be expanded in different types of kilns the choice of which depends on the characteristic properties of the raw material and on the requirements to be met by the final product. In many cases comparatively slow preheating is used ranging from 400 to 600° C for which grate-type or shaft-type preheaters are used. Following that a greater or smaller thermal shock is applied. Finally, some types of kilns for expansion purposes are equipped with cylinder coolers or by cooling in

a fluid layer. Rotary kilns, however, are most often used for the firing of expandable clayey raw materials. The dwelling time of granules in the kiln moves between 30 to 210 minutes.

On the basis of physical and structural properties the expanded clayey raw materials and light-weight concretes may be applied in many branches of the construction and building industries. Among the application possibilities belong also thermal insulations of old buildings, insulation interlayers in the construction of roads, additions to insulating plasters and mortars, structures of flat roofs, tiling materials, chimney bodies.

The summary of all the possible applications of expanded clays in the building industry can be never complete since new applications are added practically daily.

The consumption of thermal energy per 1 kg of expanded clay drops down in an inverse proportion to the increasing capacity of the plant from 1000 to 650 kcal. Similar proportion applies to the costs of electric power, water, fuel oil, lubricants and spare parts.

While judging the economic profitability of the application of light-weight concrete material costs only are taken often as a basis that may lead towards incorrect conclusions. The material costs namely get lower in relation to the thermal insulation ability of the respective material. The experience gained so far shows that when light-weight aggregate is used in concrete the weight of products in the case of a current type of light-weight concrete is re-

duced as much as by 30 per cent, in the case of an insulation concrete then by as much as 80 %. Out of this other possible savings result than further ones in assembly and transport costs. Though the material costs are higher in case of the light-weight concretes the total costs if it is applied in the project will be lower in comparison with a standard concrete.

Other types of mineral raw materials such as diatomite dressed in various ways, expanded perlite, vermiculite and a broad variety of synthetic fibrous insulation materials of different degree of thermal resistance may also be suitable for application as thermal insulations. The description of their production and physical properties, however, is beyond the range of this paper.

Energy costs and dressing of non-metallic mineral raw  
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materials  
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The rising costs of all types of energy have a direct effect on the costs of the mineral raw materials dressing. It relates particularly to those types of raw materials requiring to be fired. The prices of cement, fired lime, refractory grog which are to be calcined will go up faster than for instance the prices of feldspars, glass and foundry sands and other types of ceramic raw materials. The consumption of some minerals and mineral raw materials will grow because they are used as a source of highly efficient insulating materials. Furthermore, it will also be glass sands and soda for the production of glass fibres for insulation purposes, borates for

the production of boric acid being used as a media for reducing the inflammability of cellulose insulation materials. And, finally, of kaolin and some other raw materials for the production of refractory insulation fibres.

The endeavour to get energy from non-conventional sources there will be ever growing demand for selected types of ceramic and glass raw materials. Glass for solar energy collector, silicon for solar batteries or lithium for electric accumulators are the example of it.

From the production costs point of view the individual processes applied in the dressing of mineral raw materials may be classified as follows:

1. Magnetic separation with low intensity of magnetic field and separation carried out on Humprey spirals.
2. Washing, dressing on jig washers, concentration tables, hydrocyclones, separation in heavy liquids and suspensions.
3. Electrostatic separation.
4. High-intensity magnetic separation.
5. Flotation.
6. Magnetic frying ~~with~~ followed by magnetic separation.
7. Hydro-metallurgical dressing processes and chemical methods of removing ferrous compounds and a surface activation.

