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United Nations Industrial Development Organization

In-Plant Training Workshop on
the Production of Refractories

Pilsen, Czechoslovakia

21-28 June 1974

REFRACTORY RAW MATERIALS SPECIFICATION AND POSSIBILITIES IN THEIR DRESSING[1/]

J. Konta *

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REFRACTORY RAW MATERIALS SPECIFICATION
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J. Konta [*]

SUMMARY

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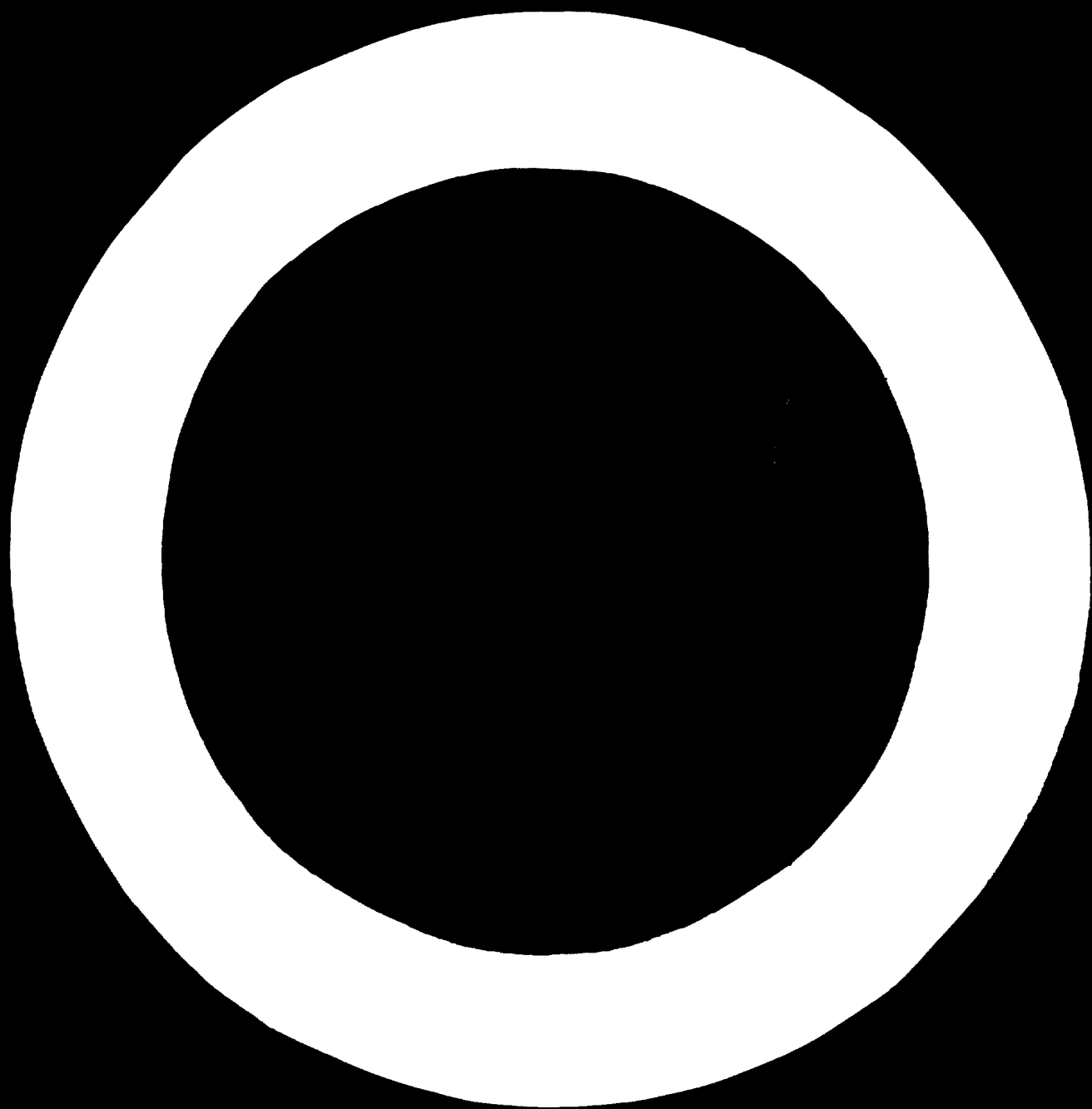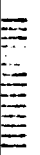
Eight groups of refractories are classified according to their main chemical characteristics and the mineral composition of their raw materials. Silica refractories or acid refractories /SiO_2 ? 95 %/ are manufactured from cement quartzites, microcrystalline silicaceus sediments, fine grained orthoquartzites /ganister/ and silcrete; semi-silica refractories /SiO_2 85-93 %/ are produced from quartz sand with an admixture of kaolinite clay or low-grade quartzites; acid fire clay refractories /SiO_2 below 85 %, Al_2O_3 10-30 %/ and fire clay refractories /Al_2O_3 30-45 %/ are manufactured from kaolinite claystones and clays or raw as well as washed kaolins with various admixtures of quartz, minor amounts of other minerals and substances low in flux; high-alumina refractories /Al_2O_3 45-99 %/ are manufactured from aluminium hydroxides bearing kaolinite clays and claystones, bauxitic clays and claystones, bauxites, or from sillimanite, andalusite, kyanite, dumortierite, topaz and corundum; basic refractories /magnesite r. with $MgO \geq$ 80 %, magnesite-chrome r. with MgO 80-55 %, chrome-magnesite r. with MgO 55-25 %, chromite r. with MgO 15-25 %, $Cr_2O_3 \geq$ 25 %, Fe_2O_3 10-17 % and Al_2O_3 15-33 %, forsterite r. with MgO 47-55 %, SiO_2 33-39 % and Fe_2O_3 0-11 %, dolomite r. with a high concentration of $CaMg(CO_3)_2$/ are produced from dead-fired magnesite or MgO from sea water, chrome-containing ore, natural olivine and dead-fired dolomite; special refractories are prepared from zircon or baddeleyite or flake graphite; insulating refractories are manufactured from diatomite or vermiculite and fire clays or kaolin.

Mineral and chemical specifications for raw materials depend on the requirements of the industry and the available natural sources. Various dressing possibilities are based on the state of induration of the raw material, its mineral and chemical composition, textural characteristics, and specifications demanded by the industry.

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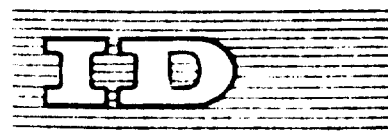
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Curso práctico de capacitación en el trabajo
sobre fabricación de productos refractarios.
Filsen (Checoslovaquia)

11 - 26 junio 1974

ESPECIFICACION DE MATERIAS PRIMAS REFRACTARIAS Y POSIBLES PROCEDIMIENTOS DE PREPARACION MECANICA [1]/

J. Korta [*]

RESUMEN

Se clasifican ocho grupos de materiales refractarios atendiendo a sus principales características químicas y a la composición mineral de sus materias primas. Los materiales refractarios silíceos, o materiales refractarios ácidos $[SiO_2 = 93\%]$ se fabrican a partir de cuarcitas cementadas, sedimentos silíceos microcristalinos, ortocuarcitas de grano fino (ganister) y cuarcita calcedónica, los materiales refractarios semisilíceos $[SiO_2 85-93\%]$ se obtienen a base de arena cuarzosa con una mezcla de arcilla caolínica o cuarcitas pobres, los materiales de arcilla refractaria ácida $[SiO_2$ inferior a 85%, Al_2O_3 10-30%$]$ y los materiales de arcilla refractaria $[Al_2O_3$ 30-45%$]$ se fabrican partiendo de piedras arcillosas y arcillas de caolinita o de caolines brutos y refinados con diversas mezclas de cuarzo, pequeñas cantidades de otros minerales y sustancias de bajo contenido de fundente; los materiales
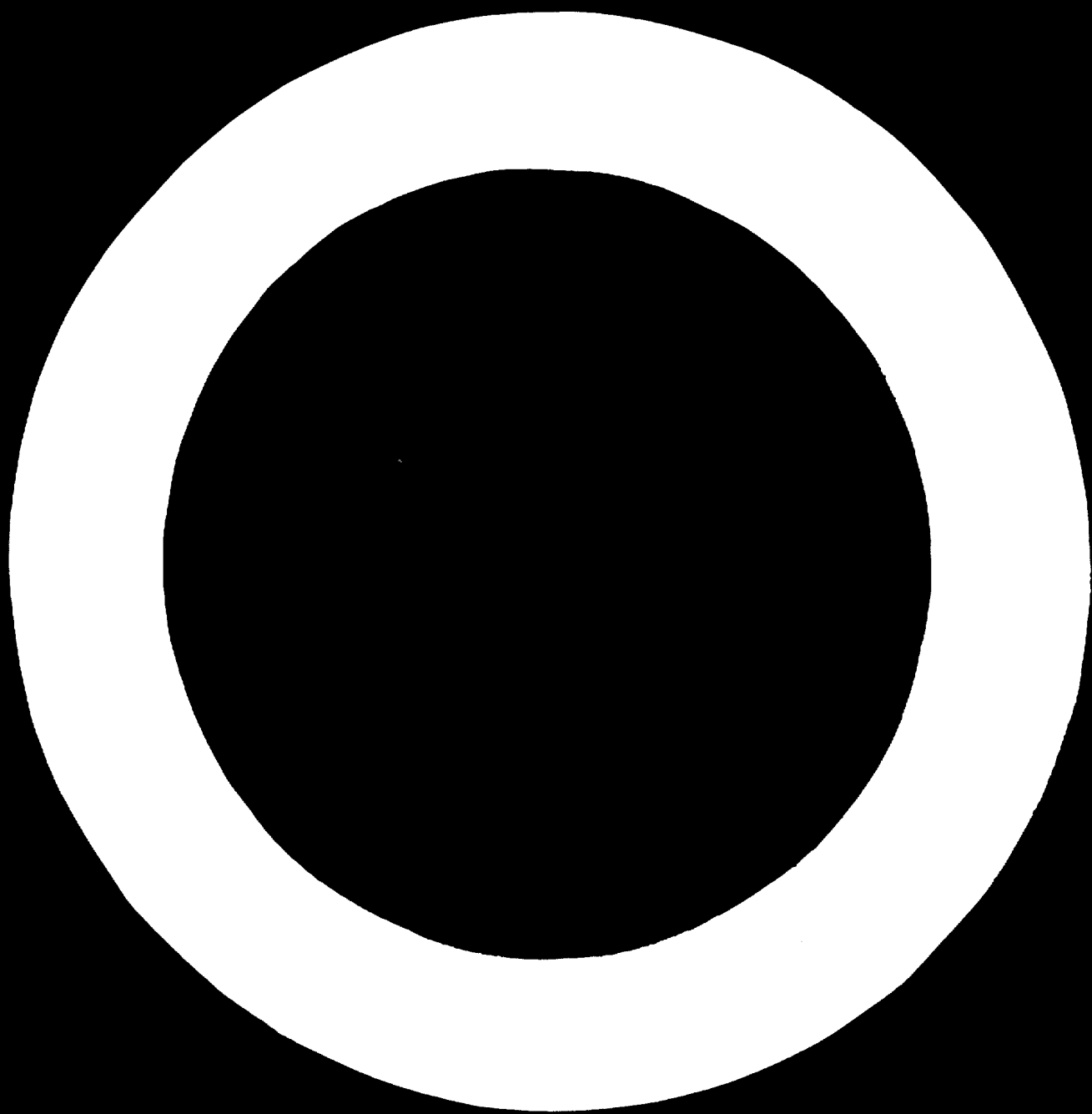
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[1]/ Las opiniones que el autor expresa en este documento no reflejan necesariamente las de la Secretaría de la ONUDI. La presente versión española es traducción de un texto no revisado.

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refractarios con elevado contenido de alúmina $\sqrt{\ }$ Al_2O_3 45-99% $\sqrt{\ }$ se obtienen a base de arcillas y piedras arcillosas de caolinita que contengan hidróxidos de aluminio, arcillas y piedras arcillosas bauxíticas y bauxita o partiendo de la silimanita, la andalucita, la cianita, la dumortierita, el topacio y el corindón; los materiales refractarios básicos $\sqrt{\ }$ r. de magnesita con MgO $\geq$ 60%, r. de magnesita-cromo con MgO 60-55%, r. de cromo-magnesita con MgO 55-25%, r. de cromita con MgO 15-25%, Cr_2O_3 $\geq$ 25%, Fe_2O_3 10-17% y Al_2O_3 15-33%, r. de forsterita con MgO 47-55%, SiO_2 35-39% y Fe_2O_3 0-11%, r. de dolomita con una elevada concentración de $CaMg(CO_3)_2$ $\sqrt{\ }$ se obtienen a partir de magnesita calcinada o de MgO procedente de agua del mar, mineral con contenido de cromo, olivino natural o dolomita calcinada; los materiales refractarios especiales se preparan a partir del circonio o de la badeleyita o del grafito laminar, los materiales refractarios aislantes se fabrican partiendo de la diatomita o vermiculita y de arcillas refractarias o caolín.

Las especificaciones minerales y químicas de las materias primas dependen de las necesidades de la industria y de los recursos naturales disponibles. Los diversos procedimientos posibles de preparación mecánica se basan en el estado de induración de la materia prima, su composición mineral y química, las características de su textura y las especificaciones exigidas por la industria.

CONTENTS

I. DEFINITION AND CLASSIFICATION

Clark and McDowell /1960/ define refractories as "materials having the ability to retain their physical shapes and chemical identities when subjected to high temperatures", or as "nonmetallic materials suitable for the construction or lining of furnaces operated at high temperatures".

Radczewski /1968/ applies the following definition: "Feuerfeste Erzeugnisse sind solche keramische Produkte, deren SK-Fallpunkt oberhalb SK 18 /1500 °C/ liegt, sie gelten als hochfeuerfest, wenn ihr Segerkegelfallpunkt SK 36 /1790 °C/ übersteigt. Ihre Brenntemperatur liegt zwischen SK 10 und SK 18 /1300-1500 °C/. Sie werden im allgemeinen nach keramischen Verfahren oder durch Heraussägen aus geeigneten Rohstoffen /z.B. aus Sillimanit/ bzw. durch Vergießen aus dem Schmelzfluß /z. B. Corhartsteine/ hergestellt".

According to Campbell and Sherwood /1967/ "By definition, a refractory material is distinguishable from other materials by its ability to resist heat. In too many cases, these materials are chosen only on the basis of 'temperature' and without sufficient consideration of the characteristics discussed and conditions of service". Definitions of many other authors are very close to the ones quoted.

While resistance to 'high' temperatures is thus the primary requirement for refractory materials, it is by no means the sole requirement. They must be able to withstand /a/ thermal shock resulting from rapid heating or cooling, /b/ other stresses induced by temperature change, /c/ pressures from the weights of furnace parts or contents, /d/ mechanical abrasion resulting from movement of furnace contents, /e/ chemical attack by heated solids, liquids, or gases.

Refractories of many kinds are needed for the many and widely diversified industrial applications. Those in greatest demand are classified on the basis of composition or proper-

Table 1. Types of refractories, their basic chemical requirement and corresponding raw materials

Type /and temperature of initial deformation, t_α/	Basic chemical requirement Wt. %	Raw materials
SILICA REFRACTORIES or ACID REFRACTORIES /t_α 1660-1700 °C/	$SiO_2 \gtrless 93$	Cement quartzites, siliceous sediments, fine grained ortho-quartzites /ganister/, silcrete /= siliceous residue/
SEMI-SILICA REFRACTORIES /t_α 1400-1660 °C/	SiO_2 85-93	Mixtures of quartz sand with kaolinite clay, low-grade quartzite etc.
ACID FIRE CLAY REFRACTORIES /t_α 1300-1420 °C/	$SiO_2 < 85$ Al_2O_3 10-30	Mostly kaolinite clay-stones and clays, or raw as well as washed kaolins with a various admixture of quartz, minor amounts of other minerals and substances low in flux
FIRE CLAY REFRACTORIES /t_α 1460-1530 °C/	Al_2O_3 30-45	
HIGH-ALUMINA REFRACTORIES /bauxite t_α 1550-1600 °C/ /mullite t_α 1670 °C/ /sillimanite t_α 1600 °C/ /corundum t_α 1600-1650 °C/	Al_2O_3 45-99	Aluminium hydroxides bearing kaolinite clays and claystones, bauxitic clays and claystones; bauxites; sillimanite, andalusite, kyanite, dumortierite, topaz; corundum

Tab. 1 continued:

BASIC REFRACTORIES

Magnesite refr. /t_α 1500-1700 °C/	MgO $\geq$ 80	Raw magnesite or MgO from sea water
Magnesite-chrome r. /t_α 1400-1500 °C/	MgO 80-55	Chrome containing ore and dead-fired magne-
Chrome-magnesite r. /t_α 1500-1600 °C/	MgO 55-25	site + kaolin + fire clay
Chromite refr. /t_α 1500 °C/	MgO 15-25 Cr_2O_3 $\gtrless$ 25 Fe_2O_3 10-17 Al_2O_3 15-33	
Forsterite refr. /t_α 1600-1650 °C/	MgO 47-55 SiO_2 33-39 Fe_2O_3 0-11	Natural olivine, dead- -fired magnesite
Dolomite refr. /t_α 1480 °C/	high concen- tration of $CaMg/CO_3/_2$	Raw dolomite and sea water

---

SPECIAL REFRACTORIES

Zircon /t_α 1480 °C/	$ZrSiO_4$	Zircon sand, mostly separated from heavy
Zirconia	ZrO_2	sands; similarly bad- deleyite
Graphite	C 90	Flake graphite, an-
/Carbides, Silicides, Borides, Nitrides/ /t_α above 2000 °C/	esp. SiC	thracite-based carbon + fire clays or ball clays

---

INSULATING REFRACTORIES

Diatomite	High % SiO_2	Soft as well as hard diatomites
Vermiculite	No special requirement	Vermiculite bearing rocks + fire clays or kaolin

---

ties into three principal groups, known as silica, alumina silica, and basic refractories. In each of these groups there are several types classified usually according to chemical composition. In addition there are several transition refractories between the types mentioned, and various special refractories, e.g. zircon, silicon carbide, carbon and others. Another special group is represented by insulating refractory materials. Table 1 shows one of the practical ways of the classification of refractories and their raw materials. A greater portion of refractories compiled in table 1 have a good. or excellent resistance to spalling and volume stability.

Table 2 shows the proportional world production of different types of refractories approximately during the last 20 years.

Table 2. World production of refractories

Type of refractory product	% Production by weight
Silica refractories	10 - 16
Fire clay refractories	60 - 70
High-alumina refractories	5 - 6
Basic refractories	18 - 6
Special refractories	7 - 2

II. SILICA REFRACTORY RAW MATERIALS

A. Mineral composition and textural characteristics

The raw material used for the manufacture of silica refractories is a dense, mostly fine-grained to microcrystalline quarts rock of sedimentary or metamorphic origin with SiO_2 content above 95 per cent. The greatest part of the raw

materials belong to the sedimentary series: orthoquartzite -
- quartz siltstone - consolidated microcrystalline silicite
/see fig. I/; further relatively common raw materials are
metaquartzite /= metamorphosed quartzite, with mosaic, gra-
noblastic or suturated texture/ and silcrete /= siliceous
weathering crust/. Consolidated microcrystalline silicites are
known under the terms e.g. chert, lydite, flint. Several mi-
xed species in fig. I can be designated by the abbreviated
term cement quartzite, which means a sedimentary rock with
clastic quartz grains cemented with ultramicrocrystalline
quartz /crystals below 4 microns in size/. A sort of fine-
-grained orthoquartzite is called ganister.

The ideal raw material contains the largest amount of
ultramicrocrystalline /or ultramicrograined/ quartz as pos-
sible /fig. II, III/, has a high mechanical resistance, a low
porosity /0 to 10 %/ and only accessory admixture of other
minerals as muscovite, hematite, graphite or combustible or-
ganic substance, chlorite and others; a slow or medium slow
recrystallization of quartz into cristobalite and tridymite
at 1450 $^\circ$C/1 h is also advantageous, since a rapid recrystal-
lization usually leads to a greater porosity and potential
penetration of melts and gases into the bricks. Table 3 shows
the main quality requirements for the silica raw materials,
which differ slightly in different countries.

Table 3. The main quality requirements for silica
raw materials

Property	Superduty silica	Conventio- nal silica	Not ac- ceptable
Refractoriness $^\circ$C	1750	1730-1750	<1730
SiO_2 %	>97	96-97	<96
Al_2O_3 + TiO_2 + alkalies %	<0.5	0.5-2.50	>2.5
Firing expansion /1480 $^\circ$C/ %	<4	4-6	>6
Suction capacity after firing /1480 ^{o}C/ %	≲2.5	2.5-4.5	>4.5
Density /transformation through firing 1480 ^{o}C/ g/cm^3	<2.37	2.37-2.42	>2.42

A compact structure of bricks and no cracks after firing is the primary requirement of any quality grade.

The speed of firing of a raw material is another important factor which must be carefully determined according to the textural features of a raw stone. The ideal curve of the firing program of silica is that by Mieler published by Singer et al. /1966/. The relatively most rapid firing occurs in the region between 900-1500-900 $^{\circ}$C; the total firing time including the cooling is about 10 days.

B. Chemical composition

The limits of Al_2O_3 + TiO_2 + alkalies given in table 3 are the highest admitted. The content of alkalies should be as low as possible since their presence causes a considerable decrease of the refractoriness. On the other hand a small content of iron oxides is favourable for they act as a catalyst in transmitting heat and thus promote the equable transformation of quartz into cristobalite and tridymite. The chemical composition of several well known quartzites and cement quartzites is given in table 4.

Table 4. Chemical composition of well known quartzites and cement quartzites used as raw materials for manufacture of silica refractories /according to Bárta, 1948/

Components	Neath, Wales, Britain	Hessen, Federal Republic Germany	Medina, U.S.A.	Anzherska, Siberia, USSR	Skršín, Czecho-slovakia
SiO_2	98.31	98.30	97.70	97.25	97.59
TiO_2	n.d.	n.d.	n.d.	n.d.	1.48
Al_2O_3	0.72	1.23	1.67	0.45	0.61
Fe_2O_3 /total/	0.18	0.37	0.44	0.13	0.29
CaO	0.22	0.02	0.03	0.04	traces
MgO	--	n.d.	n.d.	n.d.	--
alkalies	0.14	n.d.	n.d.	0.10	traces
H_2O+	0.35	n.d.	n.d.	0.04	0.10
Total	99.92	99.92	99.84	98.01	100.07

C. Dressing possibilities

Extraneous materials, namely clay or loam deterioration
are removed in washing plants using fresh water. Further be-
neficiation can be achieved by sieving and obtaining those
size fractions which correspond to the highest quality raw
material.

III. RAW MATERIALS FOR SEMI-SILICA BRICKS

The raw materials are usually mixtures of sand with
clay /or claystone/, or quartzites or silicites of lower
quality with an admixture of kaolinite clays of less value.
The properties of raw materials as well as the fired products
are between those of silica and fire clay raw materials and
their refractories. The semi-silica refractories do not
possess the secondary expansion typical for fire clay refrac-
tories and the low resistance to temperature changes of silica
refractories. Table 5 shows chemical analyses of three typi-
cal semi-silica refractories in comparison with those of ty-
pical fire clay and silica refractories.

Table 5. Examples of differences in the refractoriness
and the chemical composition of silica, semi-silica, and
fire clay refractories /Singer et al., 1966/

	Silica refrac-tories	Semi-silica refrac-tories			Fire clay refracto-ries
		1	2	3	
Refractoriness /^{o}C/	1690	1600	1600	1600	1560
SiO_2 %	95.8	88.7	92.3	88.0	53.8
TiO_2 %	0.0	0.4	0.7	0.7	1.6
Al_2O_3 %	0.8	9.1	5.8	7.9	39.2
Fe_2O_3 %	0.9	1.0	0.5	1.2	2.7
CaO %	. 1.6	0.2	traces	0.4	0.3
MgO %	0.3	0.3	0.2	traces	0.7
Alkalies %	0.5	0.4	0.5	0.8	1.4
Loss on ignition %	0.2	--	--	0.3	0.2

IV.   FIRE CLAY REFRACTORY AND ACID FIRE CLAY REFRACTORY
RAW MATERIALS

A.   Mineral composition and textural characteristics

Refractory fire clays and similar materials are dominantly composed of kaolinite with minor proportions of other minerals. Ideally pure kaolinite, $Al_2O_3.2SiO_2.2H_2O$, consists of 39.5 % alumina, 46.5 % silica, and 14.0 % hydroxyl water. At high temperatures the water is driven off, and the resulting product theoretically consists of 45.9 % alumina and 54.1 % silica. However, even the purest of clay raw materials as mined contain small admixtures of other components, as e.g. quartz and minerals containing iron, titanium, potassium, sodium, calcium, magnesium or some of these chemical elements being adsorbed as cations on the clay material, and very often a slight amount of combustible organic substance is also present.

The fire clay raw materials can be divided into the following subgroups:

/1/ Plastic refractory clays and semiplastic refractory clays.

/2/ Raw and washed kaolins /with lower plasticity/.

/3/ Kaolinite claystones, known also under the terms "flint clays", "semiflint fire clays", "hard clays", "Tonsteine", "Schiefertone", "kaolinite argillites", and others. They have the lowest plasticity of all the fire clay raw materials.

P l a s t i c   r e f r a c t o r y   c l a y s satisfactory for the manufacture of refractories are dominantly composed of kaolinite. They are often called "bond clays", "soft clays" or "ball clays". The extremely low amounts of iron, alkalies, and alkaline earths in fire clay raw materials provides the necessary high fusion temperature. The presence of other components than kaolinite tend to reduce refractoriness. They are usually iron oxide pigments /as goethite, hematite, maghemite, akaganeite/, siderite, pyrite, sericite

/fine flaked muscovite and illite/, anatase, rutile, chlorite, montmorillonite and very seldom gypsum, biotite, calcite and others; on the contrary, gibbsite, boehmite and diaspore support the refractoriness. However, there may not be a direct correlation of fusion temperature and the amount of flux. For example, iron components in sizable particles reduce the fusion point less than pigmentary iron. Quartz, the most common admixture and the main component beside kaolinite in acid fire clay refractories, may cause a desirable reduction in shrinkage and plasticity without significantly reducing fusion temperature. Combustible organic substance in plastic fire clays can occur mostly in small but variable amounts, in some kaolinite claystones in larger amounts, up to about 10 per cent. According to Phelps /1959/ the combustible organic substance present in plastic clays can be active or inactive rheologically, and influences also the plasticity property. The active material is soluble or dispersible in alkali. It consists of humic acids in which carboxyl groups predominate, whereas the less active material tends to be more phenolic in nature. But the plasticity behaviour is mostly influenced by the size distribution of clay substance and its delamination ability, where kaolinite pM /pseudomonoclinic, or disordered kaolinite/ tends to higher plasticity than kaolinite T /triclinic, or well ordered kaolinite/. The differentiation between both kaolinites, i.e. pM and T, is easy by means of X-ray diffraction technique /fig. IV/. Other methods, e.g. electron microscopy, chemical analysis and thermal methods are always useful. The plasticity increases with a higher amount of extremely fine flake-shaped particles. This is in agreement with the fact that an increase in the content of illite or especially montmorillonite /or IM interstratifications/ enhances plasticity. Because a slight variation in the mineral composition may considerably influence refractoriness, plasticity, and bonding strength, it is necessary to pay great attention to the determination of all minerals present. It is usually achieved by means of X-ray techniques, differential thermal analysis, microscopic examinations, imbibometric tests and quantitative chemical analysis.

The suitable fire clays are commonly mixtures of kaoli-
nite, illite, and quartz, the kaolinite content has to be
large enough so that the clay is refractory. The "blue clay"
of high bonding strength from Vonšov, Czechoslovakia, is of
Upper Miocene age and has the following semiquantitative
mineral composition /Konta, 1961/: 70 % kaolinite pM, 19 %
illite, 5 % swelling material /IM interstratification/,
2 % quartz, 2 % opal, 1 % anatase, 0.65 % combustible organic
matter. The clays or claystones rich in kaolinite often occur
with coal or not far from coal seams.

Drying and firing shrinkages are usually fairly high.
The refractoriness ranges from 1665 to 1740 ^{o}C for the most
refractory varieties, and from 1620 to 1665 ^{o}C for many clays
of high plasticity and excellent bonding power.

K a o l i n s /sometimes called "primary kaolins"/
are residual rocks resulting from the "in situ" alteration
of feldspathic rocks. They are widely distributed throughout
the world and are an important source of refractory raw mater-
ials. The value of a kaolin deposit depends essentially on
the completeness of the alteration and consequently on the
possibility of producing a washed kaolin rich in kaolinite
/+ other minerals of the kaolinite group, e.g. halloysite/
and of uniform chemical as well as technological properties.

A raw kaolin usually contains large portions of quartz,
micaceous minerals, and admixtures of iron- and titanium-bea-
ring minerals /pyrite, siderite, biotite, iron oxide pigments,
rutile, anatase etc./ which have to be removed, or their
presence reduced to an acceptable minimum. A slight admixture
of combustible organic substance is usually present too.
Figures V and VI show a raw kaolin formed by alteration of
granite in Karlovy Vary area, Czechoslovakia, and fig. VII
shows a washed kaolin obtained from the material in figures
V and VI. The content of clay substance rich in kaolinite
in the raw kaolin is usually between 20-30 per cent. The washed
kaolins of the highest quality are used mostly in the fine
ceramic industry; those with lower bonding strength and lower
plasticity are used in different industrial branches and among

them also in the fire clay refractory industry.

Some sedimentary accumulations rich in kaolinite and quartz grains are called "s e c o n d a r y   k a o l i n s" since they can be beneficiated to yield the washed kaolins in the same way as the "primary kaolins". They usually belong to the sedimentary series sand - silt - kaolinite clay, with variable gravel admixture. It is sometimes difficult or impossible to recognize whether their argillaceous material is of sedimentary origin or has arisen 'in situ'. The same quality requirements are valid for washed kaolins of primary or secondary origin.

K a o l i n i t e   c l a y s t o n e s   /or "flint clays", "semiflint fire clays", "hard clays", "Tonsteine", "Schiefertone", "kaolinite argillites"/ are usually composed of pure, well crystallized, very fine grained kaolinite. The ma/ is hard and nearly nonplastic, but the large concentration of kaolinite and therefore also a high content of Al_2O_3 determine its high refractoriness /34-35 SK/. Most of these claystones break with a conchoidal or shell-like fracture. Their plasticities and drying shrinkages, after they have been ground and mixed with water, are very low. The common impurities are grains or small concentrations of siderite /that have to be removed/, coal substance, mica, quartz, and accessories as anatase, rutile, chlorite and others.

B.   Chemical composition

A high Al_2O_3 content up to 45 per cent in a calcined material and the high refractoriness are the principal requirements. Examples of chemical composition of excellent fire clay raw materials are given in table 6. After firing and subtracting of the loss on ignition, which is normally between 12 and 15 per cent, the contents of all the oxides in table 6 increase. Table 7 informs about the main quality requirements for the washed kaolins used as refractory raw materials, which are based on the chemical composition too.

Table 6. Examples of chemical composition of excellent
fire clay raw materials

Oxides in weight %	1 Highly plastic fire clay /'blue clay'/, Vonšov, Czechoslovakia	2 Washed kaolin /plastic but less bonding product/, Horní Bříza, Czechoslovakia	3 Kaolinite claystone /nearly nonplastic/, Nýřany, Czechoslovakia	4 Kaolinite claystone /'flint clay'/, Missouri, U. S. A.
SiO_2	47.95	50.91	43.1	42.68
TiO_2	0.94	0.80	1.32	2.90
Al_2O_3	32.23	35.30	39.1	38.49
Fe_2O_3	1.60	0.41 t	1.15 t	1.55 t
FeO	0.34	n.d.	n.d.	n.d.
MgO	0.28	0.06	0.50	0.08
CaO	0.89	0.29	0.33	--
Na_2O	0.13	0.15		0.28
K_2O	1.23	1.02	0.40	0.49
H_2O+	12.06	11.52	14.25	14.07
H_2O-	2.16	--	n.d.	--
	99.81	100.46	100.15	100.54

t = total

1. Konta /1963/, analysts Mráz and Adam. Age: Miocene.
2. Unpublished data. Age: Carboniferous to Tertiary.
3. Tománek /1959/. Age: Carboniferous.
4. Keller /1968/, analyst Thornberry. Age: Pennsylvanian.

Table 7. The main quality requirements for the washed
kaolins used as refractories

Fresh, not calcined material	Grade of quality		
	1st	2nd	3rd
Al_2O_3 + TiO_2 % at least	37.5	34	27
Fe_2O_3 /total/ % maxim.	1.6	2	2
CaO + MgO + alkalies % maxim.	1.7	3.0	not followed
Refractoriness, SK	≥ 34	≥ 33	≥ 32

C. Dressing possibilities

The plastic refractory clays are not beneficiated but suitable raw materials are sought directly in nature. Kaolinite claystones can be beneficiated by the following way: Grinding of dry raw material /e.g. 25-3 mm or of other size according to petrographic features/ ———> first kiln /400 °C for 1½ hour/ ———> cooling drum /40 °C/ ———> electromagnets /separation of the iron bearing concentrations/ ———> second high temperature kiln /up to 1400 °C for 1½ hour/ ———> cooling drum /100 °C/ ———> sieving and separation of the fired product into several size fractions ———> milling and further required size separation. About 30-32 kg of black coal of 5000 kcalories capacity are needed for the production of 100 kg of the calcined fire clay.

The high quality refractory clays or claystones can only be ground and directly fired and sieved on a vibration or drum separator into several size fractions, e.g. below 2 mm /or below 4 mm/, 2-20 /or 4-25/ mm and above 20 /or 25/ mm. the milling which follows is carried out according to the requirements of the consumer, who sometimes does the milling himself.

Refractoriness of the high quality fire claystones is 35 SK or 34/35 SK. The medium quality nonplastic fire claystones have a refractoriness of 33 SK or higher and a minimum content of Al_2O_3 42 % after firing. Inferior sorts of fire claystones show a refractoriness at least 32 SK and Al_2O_3 content about 40 % in the calcined material.

In some cases a raw kaolin, poor in iron, alkaline earths and alkalies can be used as refractory raw material without previous dressing. Only homogenisation, drying /or firing/ and milling are the necessary processes and in such cases the economy is usually very advantageous.

The dressing of raw kaolins is normally performed in washing plants. The aim of the beneficiation is to reduce the content of quartz, feldspar, mica, iron or titanium bearing minerals etc. and to enhance the content of kaolinite

/eventually also halloysite/ in the washed kaolins. The washing process needs usually a large investment and well experienced team of experts and workers. The commercial process consists of the following steps:

-- Mining, transportation, homogenization /coarse mixing/, dispersion in water with Na-polyphosphate

-- or direct deflocculation at the mine /using water with Na-polyphosphate/

↓ Grit removal

↓ Slurry storage

↓ Particle size classification

↓ Leaching [/if removal of iron bearing pigments is necessary/]

↓ Flocculation

↓ Filtration and rinsing

either ← → or

Deflocculation ↓ Drying

↓ Spray drying ↓ Milling

↓ High solids slurry preparation ↓ Packing
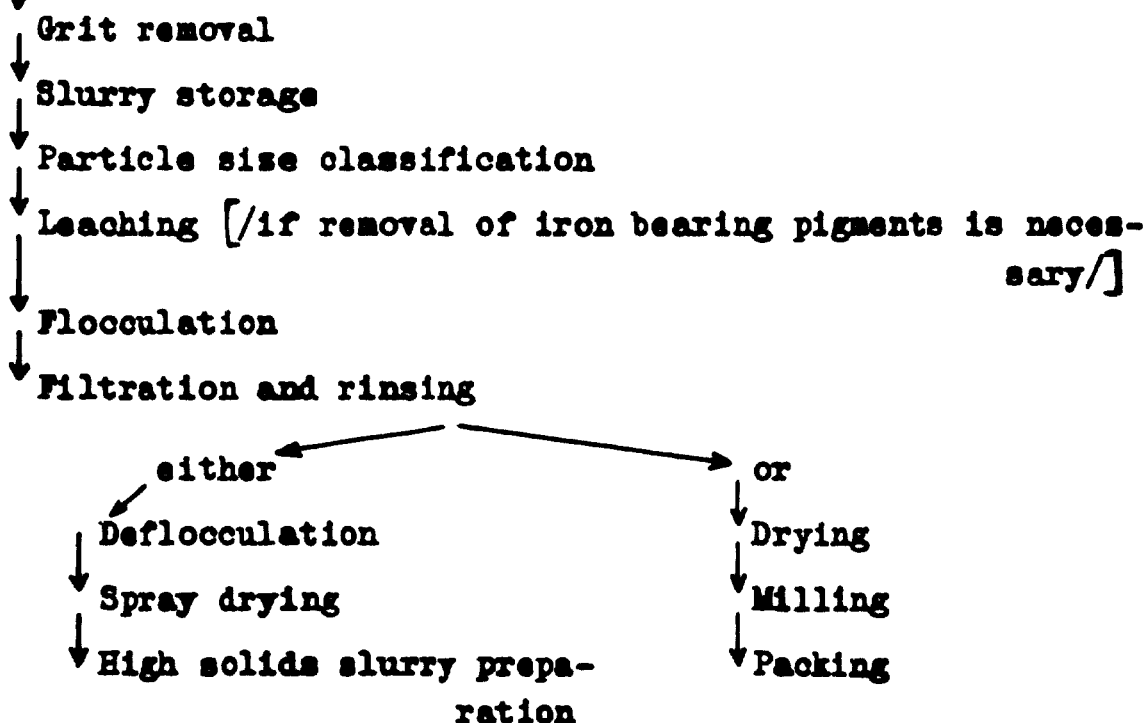
The critical drying temperature of a washed kaolin is 75 °C and must not be overstepped. Dithionite is industrially used for leaching iron from the iron oxide pigments. A good flocculation of kaolinite is usually achieved by means of polyacrylamine or aluminium sulphate if not too much Na-polyphosphate has been used. The carefully directed transportation of the raw kaolin from several pits into the kaolin plant is of the same importance as other steps during the dressing.

One metric ton of a raw kaolin as mined costs approximately $ 3 to 10 and of the washed refractory kaolin between $ 28-35 according to its quality. /The best quality washed kaolin for the china industry costs $ 50-60./

V. HIGH-ALUMINA REFRACTORY RAW MATERIALS

A. Mineral composition and textural characteristics

High-alumina products consisting largely of the mineral mullite in well-developed crystalline form are made from natural minerals and from synthetic mullite; some refractory products are made from electrically fused alumina.

The raw materials used in manufacture of high-alumina refractories include two groups:

/1/ Aluminium hydroxides bearing kaolinite clays and claystones; bauxitic clays and claystones; bauxites.

/2/ Sillimanite, andalusite, kyanite, dumortierite, topaz, corundum.

The raw materials of the first group belong mostly to the sedimentary series: kaolinite clay /claystone/ - bauxite with a small admixture of iron oxide minerals /see fig. VIII/. Some residual rocks of analogous mineral composition can be quantitatively classified in a similar way /cf. Konta, 1973/. The main rock-forming minerals in these raw materials are kaolinite /$Al_2Si_2O_5(OH)_4$/, diaspore /α AlO.OH/, boehmite /γ AlO.OH/, and/or gibbsite /$Al(OH)_3$/; the subordinate or accessory minerals are usually iron oxides /hematite, goethite etc./, quartz, dioctahedral mica, anatase, rutile and sometimes halloysite, alunite and others.

The unconsolidated clays are usually soft and dispersable in water, but some claystones, especially the so called diaspore "flint clays" can be massive and hard. All these types of raw materials rich in alumina have mostly a pelitic texture with a large portion of particles below 4 μm; oolite or pizolite texture is relatively common in bauxites or bauxitic clays and claystones.

Most high-alumina refractories are made from diaspore clay, diaspore claystone or bauxite, either alone or blended with "flint" or plastic clay according to the properties

and alumina content desired in the finished product. On ac-
count of the high firing shrinkage of diaspore clay or bau-
xite, essentially all of it is precalcined before being used
in the manufacture of refractory products.

The raw materials of the second group occur either in
metamorphic or igneous rocks or as a residual debris of
these rocks; topaz occurs also as a pneumatolytic rockfor-
ming product and corundum used in manufacture of high-alumina
refractories is mostly chemically prepared from bauxites.

S i l l i m a n i t e   /Al_2SiO_5/ occurs in felted mas-
ses of long prismatic, needle-like crystals of orthorhombic
symmetry or in subparallel aggregates of white, grey up to
yellowish brown colour in high-grade metamorphic rocks and
sometimes in granites. Its lustre is silky to dull. Sillima-
nite can occur enriched in some gneisses or mica-schists
where it is associated with biotite, muscovite, feldspars,
both orthoclase and plagioclase, garnet, sometimes zoisite,
epidote, hornblende and sphene.

A n d a l u s i t e   /Al_2SiO_5/, also orthorhombic,
occurs as elongate prisms scattered in low- to medium-grade
metamorphic rocks, especially in contact-metamorphosed shales
and also in massive aggregates in some pegmatites. Its colour
is usually grey, reddish, yellow and brown and the luster is
dull to vitreous. It is accompanied by mica minerals, feld-
spar, chlorite etc.

K y a n i t e   /Al_2SiO_5/, triclinic, tabular or bladed
parallel to c axis, occurs in some schists and gneisses
where it is disseminated either as small crystals but some-
times up to several centimetres long; it occurs also in
some pegmatites cutting these rocks. Garnet, staurolite,
corundum and mica are the commonly associated minerals. Kya-
nite is perhaps the most abundant and widespread of the
Al_2SiO_5 minerals.

D u m o r t i e r i t e   /$Al_4[Al_4BSi_3O_{19}(OH)]$/ occurs
as prismatic or fibrous orthorhombic crystals, commonly blue

or violet, in special gneisses, migmatites and pegmatites. The accompanying minerals are quartz, feldspars, micas and cordierite.

T o p a z $/Al_2SiO_4(F,OH)_2/$ occurs as prismatic, orthorhombic crystals, most often colourless or yellow, but sometimes green, pink and brown, of vitreous lustre, in special pegmatites or lithophysae in volcanic rocks. The deposits are relatively rare.

All these minerals and especially kyanite and sillimanite can be accumulated in secondary deposits /river or beach accumulations/.

M u l l i t e $/Al_6Si_2O_{13}/$ is a rare mineral in nature but can be produced by heating any of the preceding five to moderately high temperatures between 1500-1600 °C.

The three Al_2SiO_5 minerals yield 88 % mullite and 12 % silica /mostly as cristobalite/. Dumortierite and topaz decompose to give 95 % or more mullite. Mullite imparts to the products such highly desirable properties as high refractoriness, low thermal expansion with resultant resistance to heat-shock, intermediate thermal conductivity, high load-bearing ability even at high temperature, and resistance to chemical corrosion.

C o r u n d u m $/Al_2O_3/$ used in the manufacture of highest-alumina refractories is made as electrically fused alumina obtained from chemically prepared alumina. The suitable raw materials are bauxites.

B. Chemical composition

The quality of the high-alumina refractory raw materials of both groups increases with the content of Al_2O_3 and decreases mainly with the increasing contents of total Fe_2O_3 + CaO + MgO + alkalies. According to Patterson /1967/, most refractory-grade bauxite purchased for stockpiling in the USA has a minimum bulk density of 3.10 /calcined basis/ and conforms to the following chemical specifications set

forth in National Stockpile Specification P-5c, issued in
1951: Al_2O_3 min. 85.00 %; SiO_2 max. 7.00 %; total Fe_2O_3
max. 3.75 %; TiO_2 max. 3.75 %; loss on ignition max. 0.50 %.
/All numbers mean percent by weight on calcined basis./
The bauxitic clays or bauxitic claystones with lower contents
of alumina may contain still less amounts of iron and titan-
ium oxides. The content of Fe_2O_3 1.75 % is the maximum al-
lowed in not calcined raw materials of the first group.

No other precise chemical specifications for the high-
-alumina raw materials are available but Clark and McDowell
/1960/ divide the products according to their increasing
alumina content into seven subgroups: 1/ with 99 % Al_2O_3,
2/ with 90 % Al_2O_3, 3/ with 85 % Al_2O_3, 4/ with 80 % Al_2O_3,
5/ with 70 % Al_2O_3, 6/ with 60 % Al_2O_3, 7/ with 50 % Al_2O_3.
The importance of the alumina content from this classification
is evident.

Specifications covering the purchase of the second group
/sillimanite group/ include the permissible limits of varia-
tion in chemical composition, the minimum pyrometric cone
equivalent, and the grain size distribution. No stable agree-
ment exists about the specifications of these refractory raw
materials. According to Foster /1960/ the United States Stock-
pile specifications for kyanite, established in 1950, requi-
red that each lot of lump kyanite or kyanite fines contain
a minimum of 59 % Al_2O_3, a maximum 39 % SiO_2, a maximum of
0.75 % Fe_2O_3, a maximum of 1.00 combined fluxes /CaO + MgO +
Na_2O + K_2O/, and a pyrometric cone equivalent of 37 /1820 °C/
or better. It is necessary to say, however, that some produ-
cers of high-alumina refractories use kyanite or sillimanite
concentrates with a content of alumina up to 55 % only.

C. Dressing possibilities

The raw materials of the rock series of kaolinite clays
bearing aluminium hydroxides, up to bauxites, are usually
not beneficiated but directly selected in the crude state
as mined according to required specifications. Some bauxites

rich in iron oxides or in siderite, used for production of alumina, are beneficiated in the following way:

Crushing /to yield a below 10 cm product/

Washing in scrubbers equipped with vibrating screens
to remove loam and other impurities

Calcining in rotary kilns 60 up to 100 m in length and
3 to 4 m in diameter with heavy refractory linings;
8 to 14 tons of bauxite per hour need 40 to 50 gal
of fuel oil per ton. The calcined material leaves
the kiln at a temperature of 1100 °C.

High-alumina refractories are then produced from ground bauxite or chemically prepared alumina from bauxite by mixing them with a binder /plastic fire clay/, pressing into forms and putting through a firing process. High-alumina refractories, although somewhat more expensive than the fire clay refractories, are much more resistant to heat, abrasion, corrosion spalling, and erosion.

The raw materials of the second group, of which the most common are kyanite and sillimanite, are extremely rare in high-grade concentration and therefore more and more dependence must be put on the low-grade disseminated accumulations. Economic exploitation of such ores necessitates the development and improvement of methods of beneficiation. One of the suitable dressing possibilities is as following:

Primary crushing of the coarse blocks of the mined raw
material in a jaw crusher to yield a 10 cm product
or less

Secondary crushing in a jaw crusher set at 5 cm and a rol-
ler crusher set at 18 mm

Grinding in rod mills set at 28 mesh /0.64 mm/

Froth flotation in several roughing and several cleaning
cells /Flotation concentrates contain the bulk of the
kyanite and the iron minerals, leaving quarts and mica
as tailings/

Dewatering, high temperature drying in rotary kilns at
700 °C convert sulphides into oxides /esp. magnetite/

Previous magnetic separation using drum-type magnets
/reducing   the original iron bearing minerals to
about one third/

High intensity electromagnetic separation /the final
product containing less than 0.5 % Fe_2O_3/

Dry grinding in a pebble mill to finer grades

The price of the final product is about $ 50 to 85 per ton.

VI. BASIC REFRACTORY RAW MATERIALS

A. Mineral composition and textural characteristics

The following raw materials are used in the manufacture
of basic refractories: Magnesite, brucite or MgO from sea
water, chrome containing ore, forsterite or olivine, and do-
lomite. Each of these except chrome containing ore and oli-
vine or forsterite requires a preliminary dead burning to
get a dense, weather-stable periolase MgO. The refractory
products and their main properties are discussed in another
paper. In "magnesite-chromite" and "chromite-magnesite" re-
fractories the component which predominates is named first.

M a g n e s i t e   is a rock of sedimentary, metamor-
phic, hydrothermal or supergene origin and is composed essen-
tially of the mineral magnesite /$MgCC_3$/ which in theoreti-
cal purity would contain 47.6 % MgO and 52.4 % CO_2. Crystal-
line magnesite, occurring in large deposits is more common
than the cryptocrystalline variety. The colour of any magne-
site rock is nearly white or in different light shades. Its
hardness is between 3.5 and 4.0, but its value can rise up
to 5. Other mineral constituents as dolomite, calcite, quartz,
serpentine, talc, palygorskite, pyrite and other accessory
minerals may be present only in small amounts. In general,
commercial deposits of cryptocrystalline magnesite contain

lesser admixtures of accessory minerals than does coarse- or medium-crystalline magnesite.

B r u c i t e /$Mg(OH)_2$/ forms only rare deposits of commercial size. They are of metamorphic or hydrothermal origin. Brucite theoretically contains 69.1 % MgO and 30.9 % H_2O. Its colour is usually white but sometimes greyish blue or green, the hardness about 2.5. Within recent years, chemically prepared magnesium hydroxide has been used commercially in relatively large quantities. It is produced by precipitation from natural magnesium-bearing brines, such as sea water or brine from lakes and wells. The precipitation agent is calcium hydroxide, which is added in the form of slaked high-calcium lime or of slaked calcined dolomite.

C h r o m e - c o n t a i n i n g o r e is composed essentially of chromite /$FeCr_2O_4$/ with a possible admixture of minerals of the spinel group, as chrome-spinel /$Mg(Al,Cr)_2O_4$/, chrome-picotite /$(Mg,Fe)(Cr,Al)_2O_4$/ and others.

F o r s t e r i t e has a theoretical composition Mg_2SiO_4 which corresponds to 57.3 % MgO and 42.7 % SiO_2. The melting point of pure forsterite is 1905 °C. In nature a part of magnesium is substituted by bivalent iron. The mineral with Mg predominating over Fe is often called olivine, usually with the ratio Mg_2SiO_4 : Fe_2SiO_4 around 6 : 1. Forsterite refractories are produced either from olivine igneous rocks or from magnesium hydrosilicates, e.g. serpentine /$Mg_6(Si_4O_{10})(OH)_8$/ or talc /$Mg_3(Si_4O_{10})(OH)_2$/.

B. Chemical composition

No general chemical specifications exist for magnesite, brucite or dolomite. The occurrences of magnesite and especially dolomite are so common that the suitable raw material without larger admixtures of iron-bearing minerals and other fluxes can be found in nature. The magnesite refractory products are composed mainly of 80-95 % MgO /as periclase/ with a melting temperature at 2800 °C and magnesioferrite /$MgFe_2O_4$/. Good dead-burned magnesites contain more than 92 % MgO.

The refractory chrome-containing ores are composed according to Clark and McDowell /1960/ of about 30 to 50 % Cr_2O_3, 12 to 16 % FeO, 14 to 20 % MgO, 13 to 30 % Al_2O_3, 3 to 6 % SiO_2, and up to 1 % CaO. Radczewski /1968/ gives the following chemical specification for the chromite refractories: 30-45 % Cr_2O_3, 14-19 % MgO, 10-17 % total Fe_2O_3, and 15-33 % Al_2O_3. In ores used as refractories the sum of Cr_2O_3 + Al_2O_3 in general is not less than 60 %. Silicate minerals in minor quantities are functioning as a bond.

The forsterite refractories are manufactured from the silicate raw materials which have the following chemical composition /on calcined basis/: 47 to 45 % MgO, 33 to 39 % SiO_2 and 0 to 11 % Fe_2O_3. The chemical formula of ideal raw serpentine corresponds to 44.1 % SiO_2, 43.0 % MgO and 12.9 % hydroxyl water, whereas that of ideal talc corresponds to 63.5 % SiO_2, 31.7 % MgO and 4.8 % hydroxyl water. If forsterite is made by the firing of these raw materials a corresponding stochiometric portion of reactive MgO has to be added.

C. Dressing possibilities

The manufacture of the dead-burned magnesite normally has the following steps:

Crushing in a jaw crusher to yield a 10 cm product or less

Firing in rotary kiln above 1450 °C long enough to form dense, sintered product /dead-burned MgO/

Grinding

Screening

The prices of dead-burned magnesite, ground and screened are between $ 60 - 100 per ton. The prices of the crude material are within the range $ 10 - 20 per ton at the mine and depend upon the quality, ease of mining, scarcity within the marketing area, and the cost of transportation from the mine to the kiln.

Admixtures of pyrite, magnetite and similar minerals can be removed from serpentine, talc or other raw materials

by means of magnetic or electrostatic separations. The prices of crude serpentine, talc or olivine are between $ 8-10 per ton at the mine.

The prices of the chromite ores are several times higher, depending on the Cr_2O_3 content and the Cr/Fe ratio, being between $ 60 - 160 per ton. With continuously increasing steel production an increasing demand on the chromite ore can be expected in future.

VII. SPECIAL REFRACTORY RAW MATERIALS

Special physical properties are characteristic for the special refractories, namely an extreme hardness, extremely high refractoriness and a good or excellent chemical resistance. The cubic BN for example with its hardness of 10 000 kp/mm^2 is very near to diamond. The melting or sublimation temperature of SiC is 2300 $^\circ$C, of ZrC 3420 $^\circ$C, of HfC 3890 $^\circ$C, that of nitrides, e.g. of BN /hexagonal/ is of 3000 $^\circ$C, of ZrN 2980 $^\circ$C; borides have similar high melting temperatures and the silicides of titanium and molybdenum have melting temperatures about 2000 - 2100 $^\circ$C. Graphite, the only soft special refractory, melts or sublimates at about 3800 $^\circ$C. All these and other modern refractories are synthetically prepared, with the exception of zircon and graphite, which are considered as special refractory raw materials.

A. Z i r c o n

Mineral composition and textural characteristics

Zircon is the most abundant mineral of zirconium and occurs in extensive littoral and placer clastic deposits. Its chemical formula is $ZrSiO_4$, but a small portion of zirconium is usually substituted by hafnium. The accompanying minerals in the sedimentary deposits are quartz, mica, ilmenite, rutile, monazite, xenotime, sometimes baddeleyite and other heavy minerals. The source rocks of sedimentary accumu-
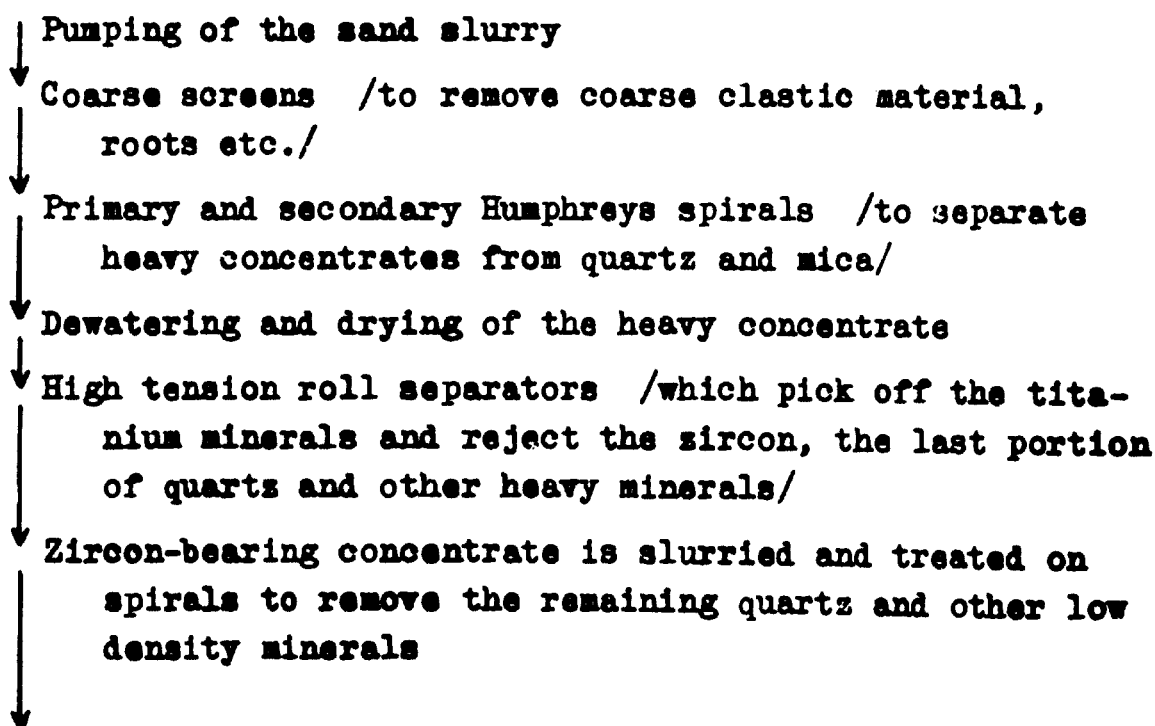
lations of zircon and accompanying heavy minerals were the
acid intrusive igneous rocks like granites, granodiorites,
nepheline syenites and their pegmatites, where zircon occurs
as a minor constituent in the form of prismatic crystals
terminated by pyramidal faces. The size of crystals is mostly
below 1 mm.

Chemical composition

No special chemical specification is required. Zircon
concentrates used as refractory raw materials are composed
of nearly pure zircon. The ideal chemical formula corresponds
to 67.1 % ZrO_2 and 32.9 % SiO_2.

Dressing possibilities

Zircon is obtained as a coproduct of rutile and other
heavy minerals. Beach deposits are the predominant source
of zircon bearing sand. The heavy mineral content of the
suitable beach sands can be 2 or 4 por cent only. In some
alluvial and eluvial deposits in Brazil the mineral b a d -
d e l e y i t e /ZrO_2/ is the predominating heavy mine-
ral. It mostly occurs as radial, fibrous masses and rolled
pebbles. One of the dressing possibilities of zircon or bad-
deleyite bearing sands is the following one:

Pumping of the sand slurry

Coarse screens /to remove coarse clastic material,
roots etc./

Primary and secondary Humphreys spirals /to separate
heavy concentrates from quartz and mica/

Dewatering and drying of the heavy concentrate

High tension roll separators /which pick off the tita-
nium minerals and reject the zircon, the last portion
of quartz and other heavy minerals/

Zircon-bearing concentrate is slurried and treated on
spirals to remove the remaining quartz and other low
density minerals

Drying and calcination of the zircon concentrate

Treating on high tension roll separators and high intensity magnetic separators

Packing of pure zircon

One ton of premium quality zircon with less than 0.1 % TiO_2 costs $ 80-95.

B. G r a p h i t e

Mineral composition and textural characteristics

Graphite is widely distributed in nature but industrial deposits occur chiefly in metamorphic rocks. Graphite is the hexagonal form of crystalline carbon. Two varieties of graphite are distinguished according to the size of flake crystals: /1/ Flake or coarse crystalline, and /2/ ultra-microcrystalline or "amorphous" graphite. The artificial graphite is prepared mostly from coke by electric furnace processes.

There are no standard specifications for the refractory graphite. Flake graphite is preferred in the manufacture of refractories, and among them mainly of crucibles. The better grades of flake graphite must contain 85 % or more carbon and be coarser than 150-mesh /0.10 mm/ with greater portion above 40-mesh /0.42 mm/. From accompanying minerals, especially mica, carbonate minerals and sulphides have to be removed or depressed, as they would cause pinholes and other defects to appear in firing.

Chemical composition

The high quality crucible flake graphite contains more than 94 % C, less than 2.3 % SiO_2, 1.4 % total Fe_2O_3 and 0.3 % S.

Dressing possibilities

The easiest way is handsorting into various grades if the raw graphite occurs in relatively pure masses, e.g. in pegmatites or lenses in metamorphic rocks, surrounded by other minerals. If the flake graphite is dispersed in a meta-

morphic rock and contaminated with quartz, mica and other
minerals, the froth flotation is an essential part of most
current procedures. A wide variety of milling and screening
methods is applied to the beneficiation of raw graphite.
Some raw graphites can be beneficiated by air flotation.

Prices of graphite depend on the shape of particles
and the content of carbon. One ton of the best sort of Ceylon
coarse-flake graphite in hard large lumps and with 97-99 % C
costs about $ 270 to 300, but of a concentrate with 90-92 % C
about $ 180 only.

VIII.   INSULATION REFRACTORY RAW MATERIALS

They are used either alone or mixed with fire clay
refractories. One of the most characteristic advantages of
insulation refractories is a low bulk density.

A.   D i a t o m i t e

Mineral composition and textural characteristics

Diatomite is a sediment occurring in layers or lenses
and is composed mainly of remains /skelets/ of diatoms.
These are microscopic algae of the order Bacillaria. The
main mineral component of diatomites is opal /$SiO_2.nH_2O$/
which occurs in the amount of 90 % or more in the dried mater-
ial. The rest are combustible organic substance, clay minerals,
clastic mica, quartz, iron oxide pigment or calcite, soluble
salts etc. The content of molecular water in raw diatomite
may vary from 10 to 65 %.

Diatomite occurs in nature mixed with other various
sedimentary material, and continuous sedimentary series
e.g. that of diatomite - limestone or diatomite - clay and
similar ones have been described /Konta, 1973/. All consti-
tuents in diatomites are predominantly very fine, mostly
of the size-categories of physical clay and silt. The colour
may vary from whitish yellow or grey to brown, greenish

up to nearly black. The colour tone changes after calcination. Specific gravity of a dry diatomite is between 1.9 and 2.3.

Opal in diatomite is considered as amorphous on the basis of its X-ray patterns since the cristobalite crystallites in it are of extremely small size and are randomly associated. Calcination of diatomite at high temperatures considerably increases the inversion of "amorphous" silica to submicroscopic forms of the cristobalite type which can evoke X-ray diffraction.
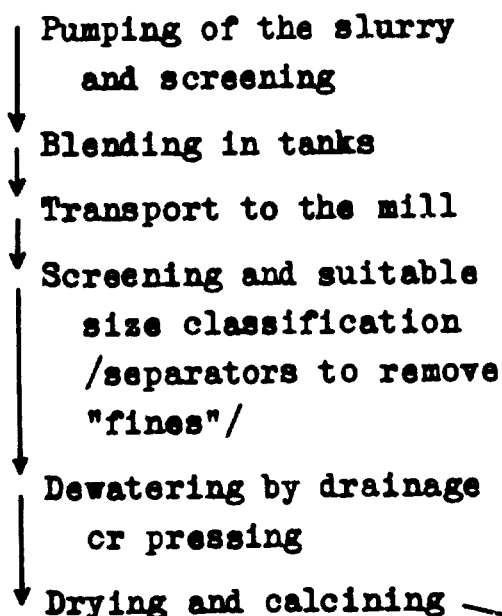
Skelets of diatoms are typical with fine perforation resembling ultrafine sieves, visible under the microscope or much better using the electron microscope. This sieve-like structure and submicroscopic "pores" originally filled with molecular water are responsible for the insulation capacity of diatomites.

The following physical properties specified for the use of diatomite as a refractory insulating material are valid for the raw material: Bulk density of the pulverised product between 350-450 kg/m^3; grains and particles below 0.063 mm have to be 87 up to only about 70 %; the coarsest material /coarser than 0.063 mm/ can be present in some tenths of one per cent only; moisture below 65 %. The more bright and light the diatomite is with simultaneous increase of SiO_2, the better quality can be usually expected. The raw material used for manufacture of insulating refractories may contain a larger admixture of clay or silt and sand, up to 30 or 35 per cent. It means that also a natural clayey diatomite, or silty or clayey-silty diatomite with low amounts of iron oxide /below 1 to 6 % Fe_2O_3/, lime /below 0.4 to 2.5 % CaO/, magnesia /below 0.5 to 3.0 % MgO/, sodium oxide /below 0.5 to 1.0 % Na_2O/, potassium oxide /below 0.5 to 1.2 % K_2O/, and alumina /below 2.0 to 18 % Al_2O_3/ is a suitable raw material. A slight admixture of quartz sand means no problems.
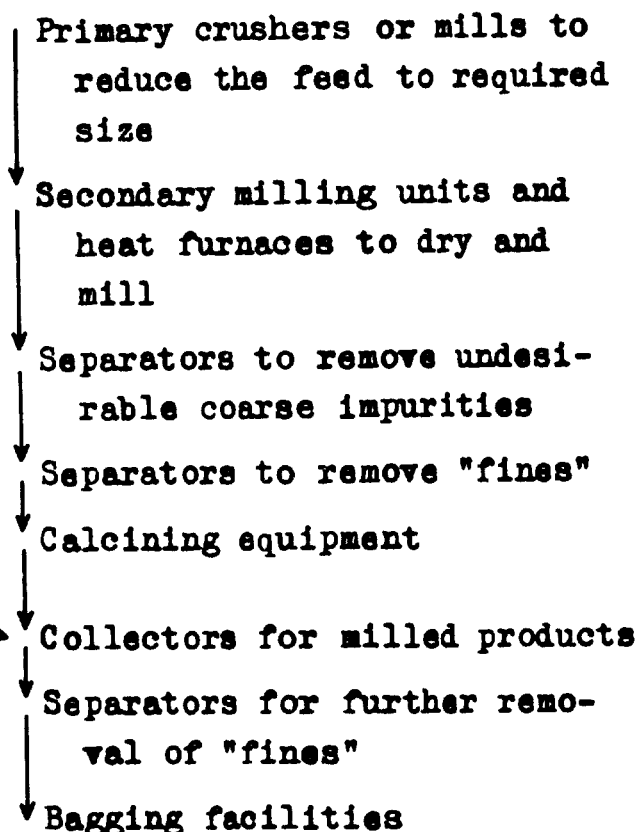
Dressing possibilities

Beneficiation of diatomite is not a simple process.
Two beneficiation ways are applied, depending on the state
of consolidation of the raw material:

Soft /unconsolidated/
diatomite:

Firm /consolidated/
diatomite:

Pumping of the slurry
and screening

Blending in tanks

Transport to the mill

Screening and suitable
size classification
/separators to remove
"fines"/

Dewatering by drainage
or pressing

Drying and calcining

Primary crushers or mills to
reduce the feed to required
size

Secondary milling units and
heat furnaces to dry and
mill

Separators to remove undesi-
rable coarse impurities

Separators to remove "fines"

Calcining equipment

Collectors for milled products

Separators for further remo-
val of "fines"

Bagging facilities

A serious control and prevention of dust has to be established!

One metric ton of a raw, high quality diatomite /kiesel-
guhr/ costs $ 43 - 65, but of the beneficiated, calcined
diatomite filter-aids $ 140 - 240.

B. Vermiculite

Mineral composition and textural characteristics

Vermiculite is a three-layer phyllosilicate of micaceous
habitus, perfect basal cleavage and usually of deep brown
or greenish colour. When heated it expands and exfoliates
perpendicularly to the basal faces into long wormlike pieces
/therefore the name vermiculite/. The increase in bulk volume

is between 10 to 30 times greater in comparison with the
unheated material. The crystal structure of vermiculite
consists of a layer made up of two silica tetrahedral sheets
/with Al and Fe partially substituting silicon/ and a cen-
tral sheet of oxygens and hydroxyls with magnesium, iron
and aluminium in the centres of the octahedrons; layers are
separated by two layers of water molecules and adsorbed cat-
ions, such as magnesium and calcium. The possibilities for
substitution of silicon in tetrahedral sheets and of the
elements in octahedral sheet are considerably broad. Such
substitution leads to a relatively large electrical charge
of the layer and to a significant capacity for interlayer
cation exchange. This may account for the various chemical
compositions of vermiculites found in nature.

A general crystallochemical formula of vermiculite can
be written in the following way:

$$\underset{\uparrow}{Mg_3} \ /Si, \ Al, \ Fe^{3+}/_4 \ O_{10} \ /OH/_2 \ \underset{\uparrow}{Mg_{0.35}} \ 4.5 \ H_2O$$

$$/Al, Fe^{3+}, Fe^{2+} \ etc/ \qquad\qquad Ca$$

The rocks containing larger accumulations of vermicu-
lite occur relatively rarely. Vermiculite can be connected
mostly with ultrabasic intrusions rich in pyroxene /the
rock is e.g. pyroxenite/ or biotite /the rock is e.g. mi-
netta, zones in different rocks rich in biotite/, or some-
times with dolomite rock. The origin can be supergene as
well as hydrothermal. The possible accompanying minerals
are pyroxene, biotite, "hydrobiotite" /= interstratifica-
tion of vermiculite with biotite/, serpentine, phlogopite,
dolomite, apatite etc. Deposits are considered high grade
if the rock contains 50 % or more, medium grade if between
50 and 30 %, and low grade if less than 30 % vermiculite.

Vermiculite concentrates are tested for screen analy-
sis, ignition loss when expanded, mineral impurities and
bulk density. The specifications are different according
to different patents proposed for specific uses of the

final products. Insulating refractories made as mixtures of fire clay and fire claystones with expanded vermiculite need expanded material mostly between 2 - 0.2 mm.

Chemical composition

Chemical analyses of two vermiculites given in tab. 8 can serve for illustration.

Table 8. Chemical analyses of vermiculite from Bare Hills, Maryland, USA /1/ and Kenya /2/

	1	2	
SiO_2	36.12	34.04	
TiO_2	0.24		
Al_2O_3	13.90	15.37	
Fe_2O_3	4.24	8.01	/1/ Gruner /1934/.
FeO	0.68		/2/ Walker and Milne
MgO	24.84	22.58	/1950/
CaO	0.18		
H_2O- } H_2O }	18.94	19.93	
Total	99.14	99.93	

Dressing possibilities

The expansion and exfoliation of vermiculite crystals can be achieved only if the material is heated quickly. A part of the interlayer molecular water, relatively firmly bonded, is responsible for the effect. The mechanical separation of the layers takes place when the interlayer molecular water is quickly converted to steam. Suitability of the raw material is tested by expanding a weighed sample in an electric muffler furnace at 950-1000 °C for five minutes, or until expansion is complete.

The impurities of nonexpanding materials can be separated by floating off the cool expanded vermiculite with water. Then follows drying, screening, finer crushing, and size classification. The colour of expanded vermiculite

depends on the heating atmosphere.

One ton of a crude vermiculite costs approximately
$ 45 to 55 but of the expanded material about three times
more.

CONCLUSION

Specifications expressed by the mineral and chemical
composition or textural characteristics of the refractory
raw materials are the primary requirements of the cor-
responding industry. They, however, are not necessarily
the major criteria of the commercial utility of refractories.
The methods and conditions of manufacture are at least of
the same importance. It is well known that refractories
of almost identical chemical or mineral composition may
differ widely in their behaviour under similar furnace
conditions. The tradition and the experience of experts
and workers involved in the production of refractories are
an extremely important factor.

REFERENCES

Bárta R.: Keramika /Ceramics/. Part II. Žárovzdorné zboží
/Refractories/. Part I. 701 pp. Edit. Česká spol.
chemická, Praha; 1948.

Campbell I.E. and Sherwood E.M.: High-temperature materials
and technology. 1022 pp. John Wiley and Sons, N. York
- London - Sydney; 1967.

Clark C.B. and McDowell J.S.: Refractories. 39th chapter in
the Monograph "Industrial Minerals and Rocks". 934 pp.
/p. 699-712/. Publ. by The Amer. Inst. of Mining,
Metallurg. and Petrol. Engineers, N. York; 1960.

Grim R.E.: Clay mineralogy. 384 pp. /on p. 373/. McGraw-Hill
Publ. Co., N. York - London - Toronto; 1953.

Gruner J.W.: The structures of vermiculites and their collapse by dehydration. Amer. Min., 19; 1934.

Keller W.D.: Flint clay and a flint-clay facies. Clays and
    Clay Minerals, 16; 1968.

Konta J. : Quantitative mineralogical analysis of 'blue clay'
    from Vonšov, Bohemia: A comparative study by nine laboratories. Clay Minerals Bull., 5, No. 30; 1963.

Konta J.: The quantitative system of residual rocks, sediments and volcanoclastic deposits. 375 pp. Edit. Universita Karlova, Praha; 1973.

Patterson S.H.: Bauxite reserves and potential aluminum resources of the world. Geol. Surv. Bull. 1228, Washington; 1967.

Phelps G.W.: The role of organic matter in slip casting.
    Bull. Amer. Ceram. Soc., 38; 1959.

Radcsewski O.E.: Die Rohstoffe der Keramik. Minerale und Vorkommen. 143 pp. Springer-Verlag, Berlin-Heidelberg-N.
    York; 1968.

Singer F., Singer S.S. and Zimmermann K.: Industrielle Keramik. 3. Band /Die keramischen Erzeugnisse/. 278 pp.
    Springer-Verlag, Berlin-Heidelberg-N. York; 1966.

Tománek Vl.: Fire claystones and technology of their dressing /in Czech/. 247 pp. Edit. Sdruš. kamenouh. dolů,
    Kladno, Praha; 1959.

Walker G.F. and Milne A.: Trans. 4th Internat. Congr. Soil
    Sci., 2; 1950. /From Grim, 1953./

Figure I. Example of a quantitative way of classification
in the sedimentary rock series: /1/ orthoquartzite
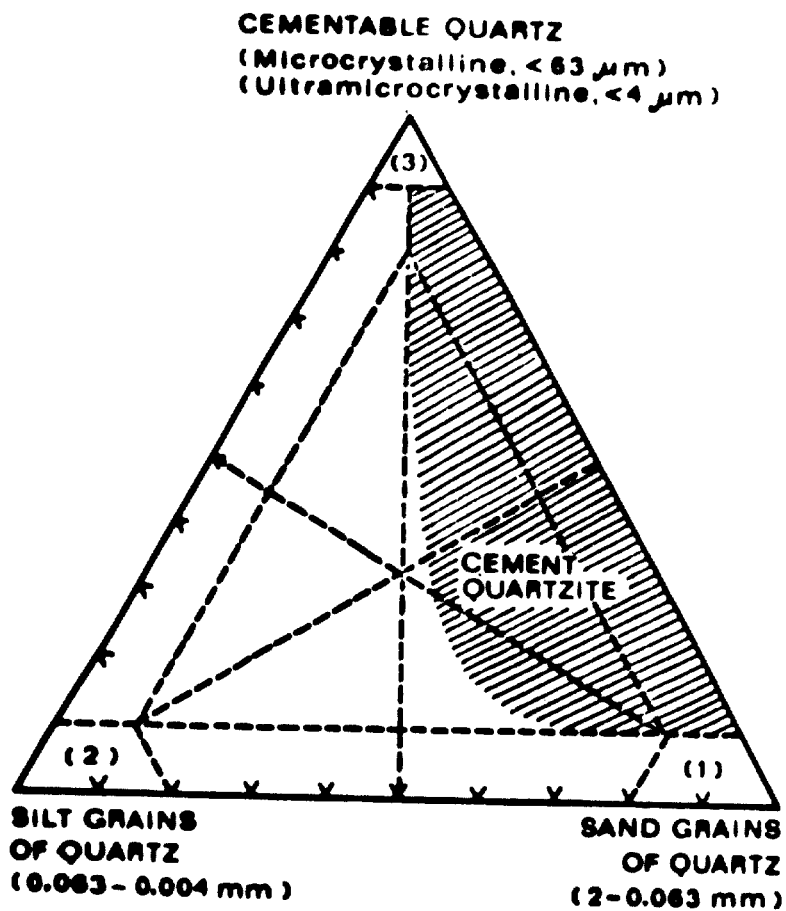- /2/ quarts siltstone - /3/ consolidated quarts
silicite.

CEMENTABLE QUARTZ
(Microcrystalline, < 63 μm)
(Ultramicrocrystalline, < 4 μm)

(3)

CEMENT
QUARTZITE

(2)

(1)

SILT GRAINS
OF QUARTZ
(0.063 - 0.004 mm)

SAND GRAINS
OF QUARTZ
(2 - 0.063 mm)

Figure II/A. Microphotograph of an ideal silica raw
material rich in cementable ultramicrocrystalline
quartz. Polarizing microscope, 1 nicol, 30x. So cal-
led "cement quartsite", Skršín, Czechoslovakia.

Figure II/B. The same as in fig. II/A but crossed nicols.
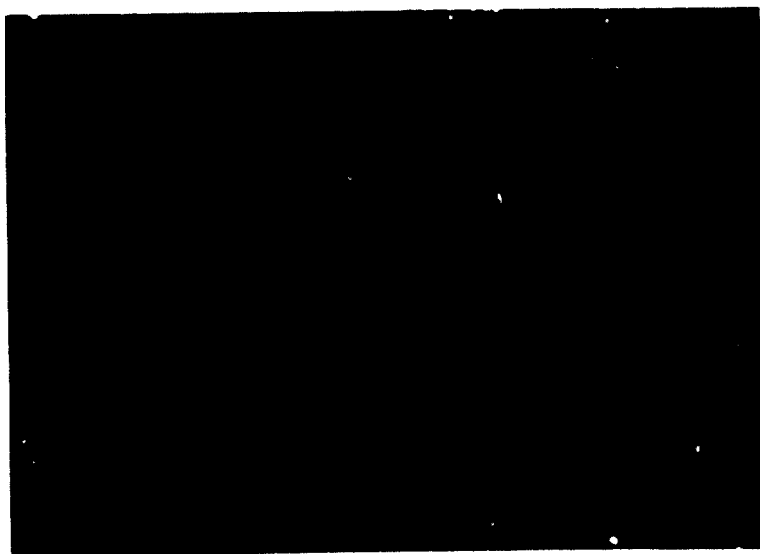
Figure III. Electron microphotograph of the ultramicrocrystalline cementable quarts. Replica of the same material as in fig. II.
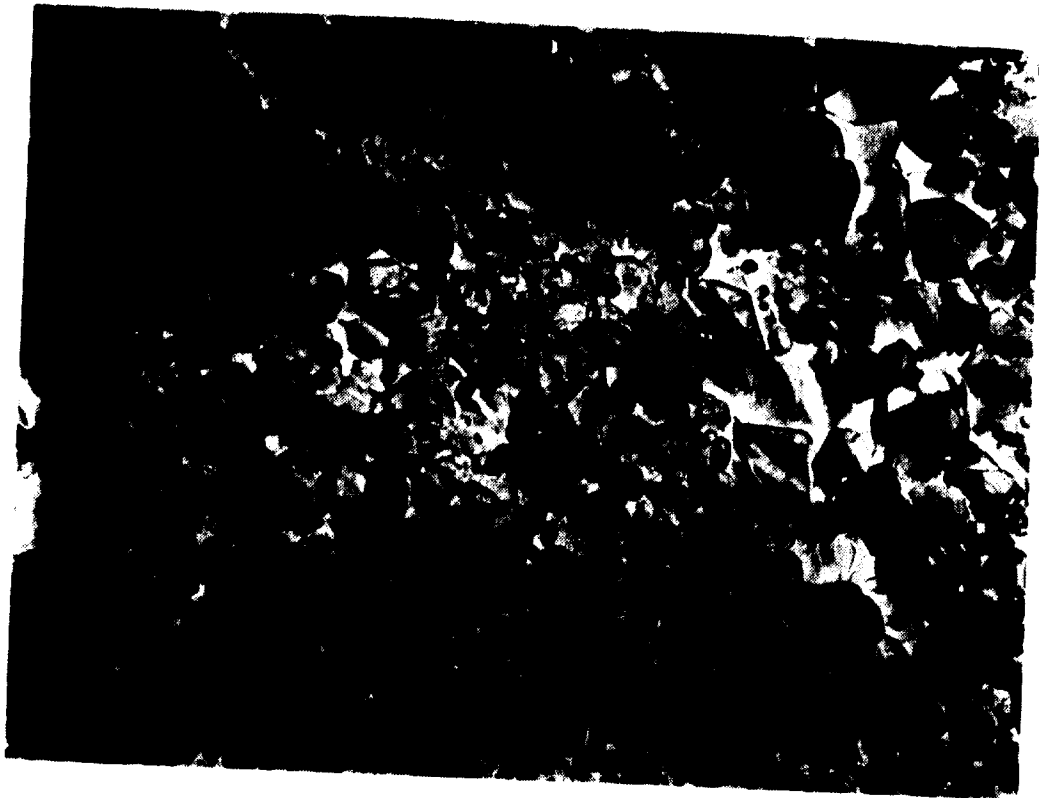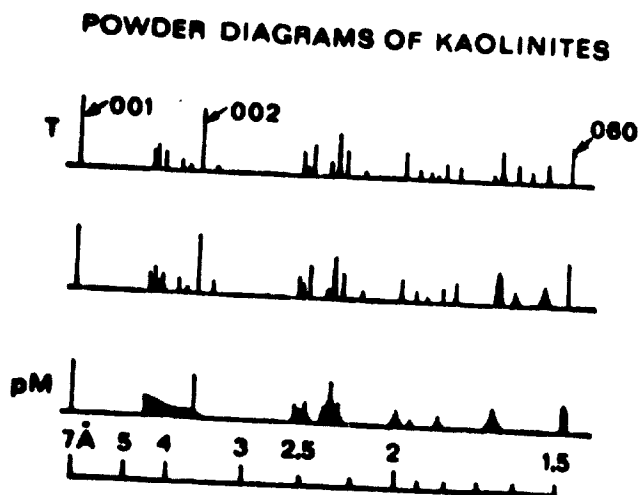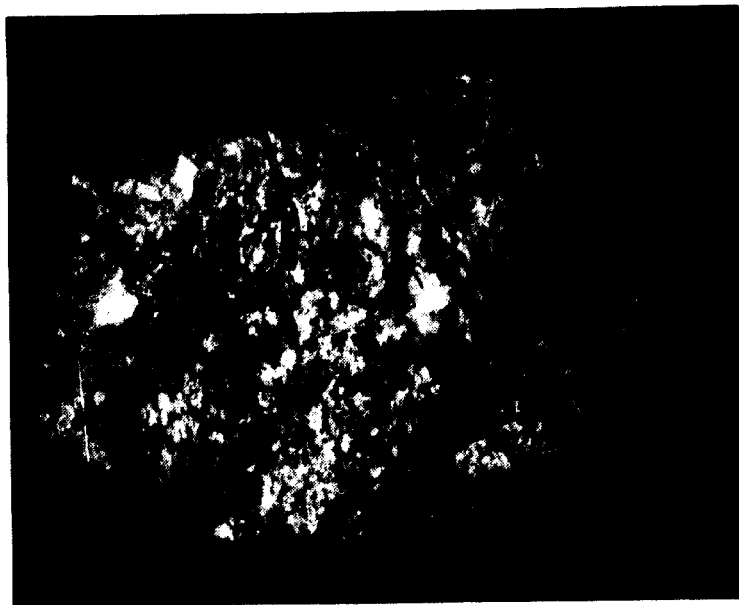

Figure IV. X-ray diffraction patterns of kaolinite pM and kaolinite T and an intermediate form of kaolinite. /According to Murray and Lyons, 1956./

POWDER DIAGRAMS OF KAOLINITES

Figure V. Raw kaolin, Karlovy Vary area, Czechoslovakia.
Natural size.
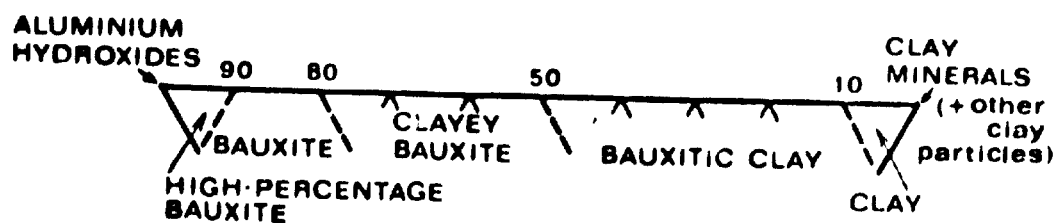

Figure VI. Microphotograph of the raw kaolin, Karlovy
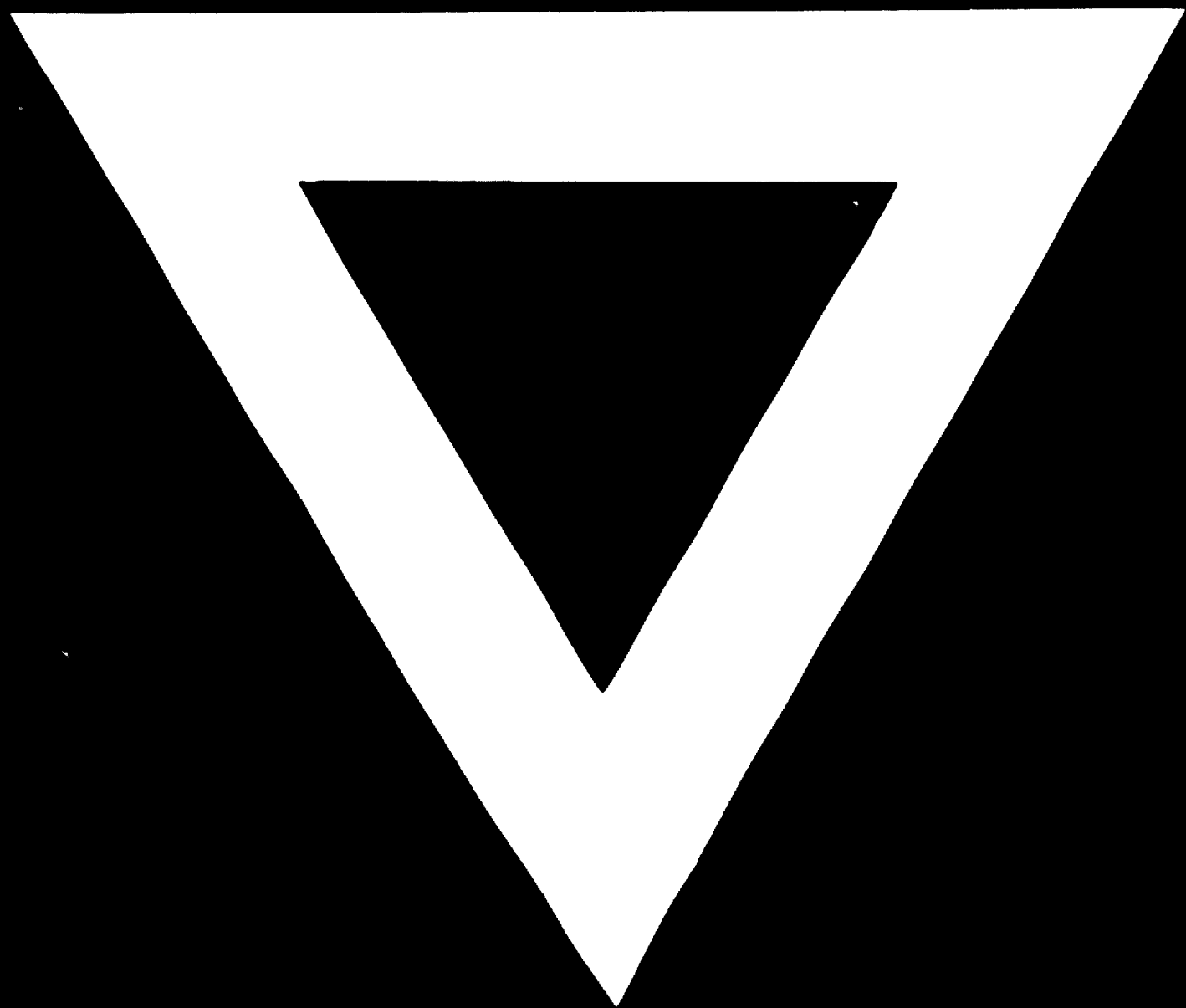Vary area, Czechoslovakia. Polarizing microscope,
1 nicol, 30x.

Figure VII. Electron microphotograph of the washed kaolin,
size fraction below 1 μm, Karlovy Vary area, Czechoslo-
vakia.

Figure VIII. Classification of the high-alumina refractory
raw materials of the sedimentary origin. /According to
Konta, 1973./

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