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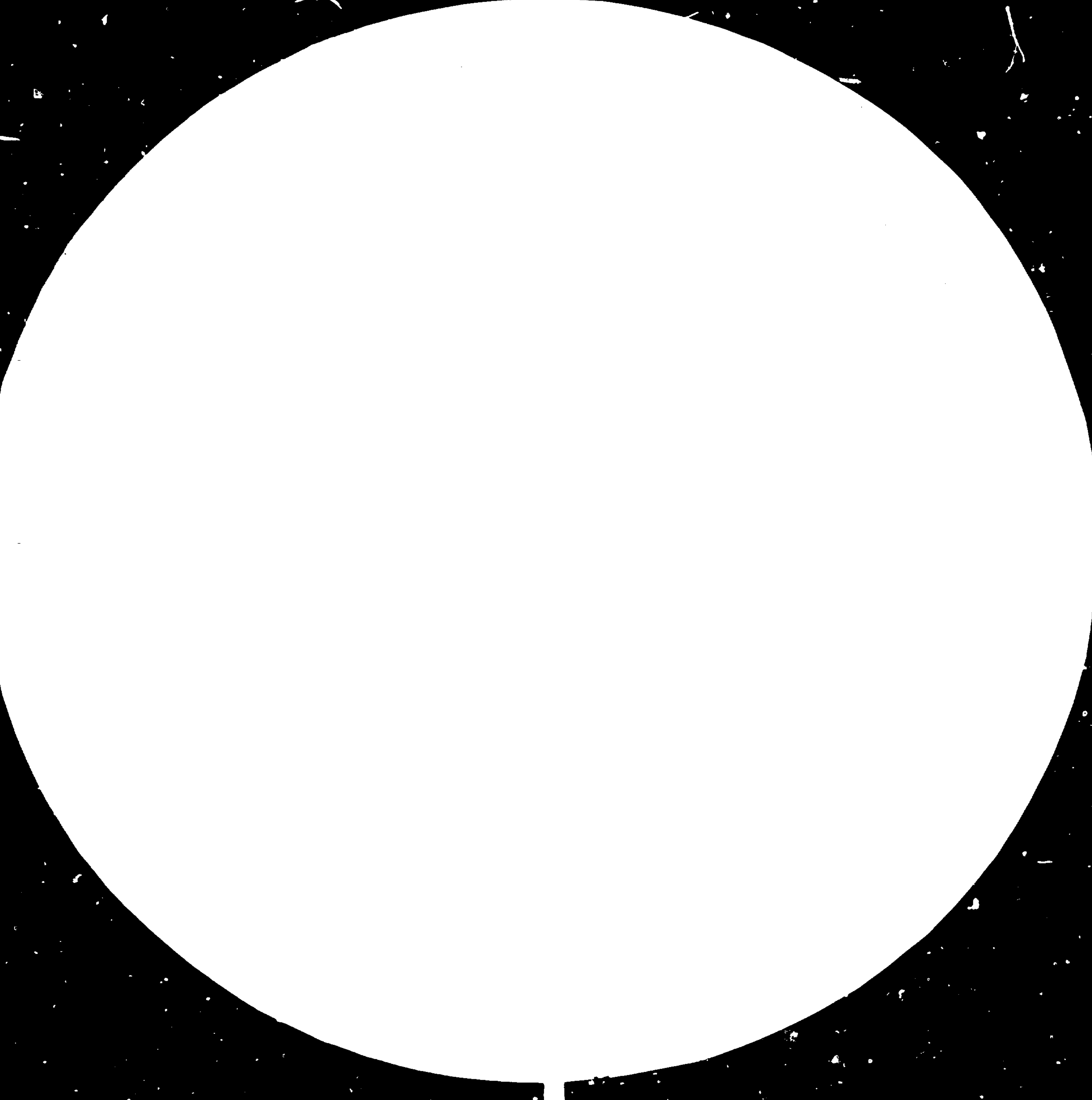

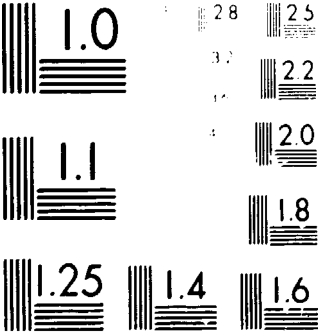

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SILICA - Silica Raw Materials
for Refractories, Ceramics, Glass and Building Materials

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I. INTRODUCTION - SCOPE OF THE LECTURE

Silica is one of the most widespread minerals in the earth´s crust. The content of silicon as an element in the earth´s crust is 26% and, therefore, the element is on the second place, after oxygen whose representation is 49.19%. Silicon never occurs free in the crust, always in compounds, most frequently in the form of silicates. There where its amount is superfluous in a rock, it occurs as silicon oxide SiO_2 /quartz/. This mineral adopts various petrological forms and polymorphous modifications in nature.

Most commonly, silicon oxide occurs as a rock-building mineral, quartz, in a variety of effusive, metamorphed and vein rocks. In the course of weathering processes, quartz as the most resistant mineral accumulates in sediments. During its subsequent solidification, its most important deposit modifications are formed, such as sandstone and quartzite. Through chemogenic and/or organogenic processes, various amourphous or microcrystalline modifications of silica are constituted, such as flint, lydite, limnoquartzite and diatomite.

The uses of silica are manifold. They can be divided as follows:

/a/ technological processing - refractories, ceramics, glass, building materials

/b/ metallurgical processing - alloys and carbides, such as ferrosilicon, metal silicon, silumine, silicon carbide etc.

/c/ direct use of mined silica raw materials, mainly in building industries - mortars, concrete: sands for various technical purposes - filter sands, foundry sands, furnace linings of quartzite etc.

/d/ miscellaneous used - optical quartz crystals, piezoelectric crystals, gemstones

The paper will deal with the first group in which the use of silica is conditioned by its technological, most frequently thermal processing. The group comprises:

1. special acidic refractories /dinas - silica bricks/ production based on the utilization of refractory properties of pure SiO_2: the raw materials for this type of production are usually quartzites, occasionally some silicates /flint, limnoquartzite, lydite/ or quartz and sands /used as admixture/
2. ceramics production /china, sanitary ceramics, tiles, earthenware/: silica used here either as calcinated vein quartz or flint /mainly in the china production/ or as quartz sands
3. glass industry /coloured and white container glass, sheet glass, structural glass, artificial jewellery, optical glass, crystal glass, clear fused silica and UV glasses/: the raw materials used are either glass sands /gained by mining and dressing of sandstones/ or rock crystal and specially dressed vein quartz: also, some types of sand and quartzites can be used
4. building industry: production of building materials of silica sands /lime-sand bricks or expanded silica materials - cellular silicates/ in which reject silica sands of kaoline and/or ore dressing plants can be advantageously used: production of diatomite-based expanded and/or insulation materials

II. MINERALOGY

1. Silica Group of Minerals

Although silica is chemically an oxide /SiO_2/, the general structures and properties of its various forms seems to be related more closely to those of silicates. The silica group of minerals comprises structures consisting of three-dimensional lattices of SiO_4 tetrahedra in which all four oxygens of each tetrahedron are shared by adjoining tetrahedra. This, of course, does not apply to the natural silica glass, lechatelierite.

There are three main crystalline polymorphs of silica /quartz, tridymite and cristoballite/, several high-pressure varieties /notably coesite/. a single cryptocrystalline variety /chalcedony/ and an amorphous variety /opal/.

Table 1: Crystalline polymorphs of silica

Name	Thermal stability range at 1 atm, °C	Symmetry
quartz	below 573	hexagonal-P; trigonal trapezohedral
high-quartz	573 - 870	hexagonal-P; hexagonal trapezohedral
low-tridymite	below 117	orthorhombic
middle-tridymite	117 - 163	hexagonal
high-tridymite	163 - 1470 /stable 870 - 1470/	hexagonal; dihexagonal dipyramidal
low-cristobalite	below 200	tetragonal; tetragonal trapezohedral /?/
high-cristobalite	200 - 1720 /stable 1470 - 1720/	isometric; tetratoidal /?/
keatite	metastable at ordinary conditions	tetragonal; tetragonal trapezohedral
coesite	metastable at ordinary conditions	monoclinic; prismatic
stishovite	metastable at ordinary conditions	tetragonal; ditetragonal dipyramidal

2. Quartz

The name quartz, first used in the Middle Ages in Saxony for massive vein quartz, did not become an inclusive designation for the coloured and fine-grained varieties of this mineral until about the end of the eighteenth century. The mutual identity of these varieties was established partly on morphological grounds, here with reference to amethyst, smoky quartz /morion/ and rock crystal, and partly by qualitative chemical and physical tests. An adequate background for the systematic treatment of the chemistry and crystallography of silica, however, was not available until the first half of the nineteenth century.

In this period, the chemical composition of quartz and the chemistry of silicon in general were established by Berzelius and others, and the morphological crystallography and optical behaviour became known through the work of Herschel, Biot, Weiss, Rose and Des Cloizeaux.

Common quartz /alpha-or low-quartz/ is stable up to 573°C, and is a common mineral in all kinds of rocks and mineral veins. Crystallographically, it is trigonal trapezohedral. When quartz crystals occur showing trapezohedral faces, a division can be made into left-handed and right-handed, according to the position of the "indicator" faces. Many coloured varieties have been named as follows:

violet/purple	amethyst
brown	cairngorm
yellow	citrine
pink	rose quartz
white	milky quartz
clear/transparent/	rock crystal

A characteristic feature of quartz is the absence of cleavage and the presence of a well-developed conchoidal fracture: its hardness is normative for degree 7 of Mohs' Hardness Scale.

At 573°C, low-quartz gives place to high-quartz /beta-quartz/, which is hexagonal trapezohedral. When high-quartz occurs in crystals, the prism faces common in low-quartz are absent. Many of the reported occurences of beta.quartz crystals have been found to consist of pseudomorphs of low-quartz after high-quartz. High-quartz has been reliably reported in acid volcanic rocks where it is presumably metastable.

High-quartz is stable at 1 atm from about 573°C to 870°C. At higher temperatures, it converts to tridymite, but the conversion of the reconstructive type is extremely sluggish and high-quartz can be heated up to its melting point. The melting point value is somewhere near 1460°C. On cooling, high-quartz undergoes a displacive or high-low type of inversion to low-quartz /ordinary quartz/ at about 573°C. The inversion varies considerably in temperature at 1 atm, as a function of compositional variation.

High-low inversion was recognized by Le Chàtelier in 1889 and the first extended effort to identify high-quartz in nature was made by Wright and Larsen in 1909.

3. Tridymite

Above 870°C, high-quartz inverts to tridymite, which is very probably hexagonal holohedral. Tridymite, the first polymorph of silica to be recognized in addition to quartz, was described by vom Rath in 1868, and cristobalite was described by him in 1884. Both substances were originally found in an igneous rocks in the Cerco San Cristobal, Mexico. High-quartz was observed during laboratory experimentation by Le Chatelier in 1889 and was later shown to occur in nature. Tridymite has been found to include a group of three separate polymorphs closely related in crystal structure, called high-, middle- and low-tridymite. The high and low forms were first observed by Merian in 1884.

In the classical interpretation, tridymite is a stable form of silica, at temperatures between 870°C and 1470°C. At higher temperatures, it converts into cristobalite, at lower temperatures into high-quartz. The transformation is of a reconstructive type and is extremely sluggish. The process can be accelerated by mineralizing or fluxing agents, such as alkali oxides or halides and sodium tungstate.

High-tridymite can be heated over 1470°C to its melting point /1670°C/ and can be supercooled below 870°C. On cooling, it undergoes two displacive or high-low inversions; at about 163°C to middle-tridymite which on further cooling inverts at approx. 117°C to low-tridymite. Tridymite also can crystallize directly as a metastable form at temperatures below 870°C.

The two low-temperature inversions are both subject to supercooling and, further, show a significant variation in the temperatures at which they occur, depending on the content of other elements in solid solution and on the amount of structural disorder present /see cristobalite/.

The inversion between the high and middle forms has been observed as low as 125°C and that between the middle and low forms at 100°C. Disordered material containing three-layer cristobalite sequences may show an additional inversion near 240°C /cristobalite/.

Tridymite is only fround in acid volcanic rocks where it is metastable. In other cases, quartz pseudomorphs after tridymite are known.

4. Cristobalite

At 1470°C, tridymite inverts into cristobalite which is cubic. It is probably even rarer than tridymite and occurs in somewhat similar environments.

Cristobalite has been found to include two related polymorphs, called low- and high-crystobalite.Both the high and low forms of cristobalite were first observed by Mallard in 1890. The stability relations of these polymorphs of silica were comprehensively studied by Fenner in early 1900´s.

High-cristobalite is an isometric, high-temperature form stable from 1470°C to the melting point at 1728°C at atmospheric pressure. However, its metastable form exists, too, down to about 268°C at which it converts into low-cristobalite.

Low cristobalite, a tetragonal metastable form, exists at lower temperatures. The conversion from high-cristobalite to tridymite at 1470°C is of the reconstructive type and is extremely sluggish in the absence of fluxes. The high-low inversion temperature at 268°C varies over a wide range, depending on the amount of structural disorder present and on the chemical composition of the sample. Highly ordered high-crystobalite with the ideal composition SiO_2 inverts at about 268°C. With increasing disorder and amount of material present in solid solution, the inversion temperature may be as low as 130°C or less. Often it has been found to range between 175°C and 250°C. The inversion is subject to marked supercooling. The amount of supercooling apparently tends to be greater in highly ordered material, amounting to 30° or more, giving the actual high-low inversion much below 268°C on cooling /but at 268°C on heating/. In highly disordered material, an additional inversion may be observed and the dilatometric curves tend to round off.

5. Coesite, keatite, stishovite

The three additional polymorphs of silica were obtained by laboratory synthesis: coesite, synthesized in 1953 by L.Coes, keatite, synthesized in 1954 by P.P.Keat, and stishovite, synthesized in 1961 by Stishov and Popova. Two of these polymorphs, coesite and stishovite, have been since identified in nature.

Coesite is a monoclinic polymorph of silica which develops at very high pressures /20 kilobars/. Although originating as a laboratory substance, it was subsequently found in quartzose rocks in craters formed by the impact of large meteorites.

6. Chalcedony and Opal

Chalcedony is a cryptocrystalline variety of silica, consisting essentially of fibrous or ultrafine quartz; some opal, together with water, which is either enclosed in the lattice or in the macrostructure of the mineral. It is possible that some of the quartz has had oxygen ions replaced by those of hydroxyle group. There occur a large number of chalcedony varieties. Banded varieties include agate, onyx and sardonyx: reddish or brownish ones are called sard or carnelian while green are labelled prase or chyrsoprase. Jasper is a red, chert-like variety. Chalcedony is usually regarded as a low temperature material, occuring mainly in sediments, low temperature hydrothermal veins, and as an amygdale filling. Several varieties of chalcedony are used as semi-precious stones.

Opal is hydrated amorphous variety of silica, derived from a silica gel. It contains more water than chalcedony and is considerably softer than quartz. Opal occurs mainly as a secondary deposit formed by the action of percolating ground waters: shells of various types are known in which the replacement of their material by opal has occured. Silica deposited by hot springs

/siliceous sinter and geyserite/ is virtually opaline in character. Sponges, radiolaria and diatoms secrete opaline skeletons. Precious opal is a well-known gemstone showing a typical colour play. Diatomite /kieselguhr/, a rock made up almost entirely of diatom skeletons is important due to its insulating properties and as an abrasive or a filtering agents.

III. RAW MATERIAL TYPES AND THEIR CHARACTERISTICS

In the last decades, the economic interest has concentrated upon the following raw material types: vein quartz, quartzite, silicates, sandstone and quartz sands and pebbles.

1. Vein quartz

According to their genesis, vein quartzs can be divided into several groups:

/a/ Vein quartz deposite located in pegmatites which are either with a coarse-crystalline block zone or possessing a quartz core. This quartz type is usually very pure, suitable for the china production, and after its necessary processing, even for the production of special glass. It is this genetic type that occurences of rock crystal are related to, which is the basic raw material for the transparent silica glass production as well as for other special purposes.

/b/ Quartz ramparts, essentially silicified disconformity zones, represented by vein systems with a number of solid, lenticular quartz veins containing ample resistant inclusions /mica, feldspar, kaolinized rocks/. A typical feature of this genetic type is a lower content of SiO_2, as well as of Fe_2O_3, while that of Al_2O_3 is relatively high. The type finds its principal uses in ceramics.

/c/ Hydrothermal quartz veins related to granitoid massives, which were originally ore veins and subsequently silicified, the process resulting in the formation of barren quartz veins. Several generations of quartz can usually be observed. The quality is variable: however, even very pure, high-quality quartz may be found. This quartz type frequently contains gaseous and liquid inclusions due to which it cannot be used in the transparent silica glass production. If the hydrothermal quartz veins were, together with the neighbouring rocks, subject to metamorphic processes in the course of which the gaseous and/or liquid inclusions were removed, the conditions for its use in the transparent silica glass production would be achieved /providing the material were properly chemically dressed/.

/d/ Secretional type is represented by quartz of variable granularity which contains a negligible amount of small inclusions and, accessorically, biotite and graphite. It is generally very pure and was used as a principal raw material for the glass production in the past. However, it is not exploited at present as these deposits are characterized with a small volume, irregular position and do not fulfil the requirements of the industrial-scale mining.

The quality of vein quartz is evaluated regarding the possibilities of its use in the ceramics and glass productions. For the production of ceramics, the maximum Fe_2O_3 content equal to 0.3% and white fired colour are required. Prior to its use in the ceramics, quartz is calcinated, i.e. burnt at 600^o to 800^oC. During this operation, it converts to high-quartz. At the same time, its volumetric change occurs which would, if acting in the final product, cause shrinkage and other flaws. Also, the calcinated quartz is easier to grind. The minimum SiO_2 content required is usually 96%. A higher content of Al_2O_3 is not generally a negative feature, if it is not too variable and/or bound to some pollutants /e.g. chlorites/. During mining, quartz is sorted, frequently even washed, and its finer-grained /below approx. 40 mm/ fraction is rejected as it contains more pollutants

At present, quartz is used in the glass industry only for the production of special items, such as silica UV radiation tubes, clear silica glass elements /which are extremely resistant to sudden temperature changes over a wide temperature interval/, high-quality optical glass etc. All these products require the raw material to be capable of dressing to high-quality parameters. The respective processing technologies are given in the chapter on the glass production. According to the Czechoslovak standards, the quartz raw material used for the transparent silica glass and UV glass productions should show the following parameters /after processing/:

SiO_2	99.98 - 99.99%
Fe_2O_3	$1 . 10^{-4}$%
TiO_2	$4 . 10^{-5}$%
Al_2O_3	$5 - 8 . 10^{-4}$%

Optical grade glass require the maximum Fe_2O_3 content to be equal 0.005 - 0.010% The processibility evaluation is generally based on the assumption that such raw material which does not contain any visible solid inclusions and whose content of pollutants is max. 0.5% is compliable. An indispensable part of a raw material quality and usability evaluations is the processibility test /chemical leaching + electromagnetic separation/ as well practical pilot tests. The clear silica glass production requires only such materials which melt limpidly, i.e. without any bubbles and turbidities. The production capacity of plants producing such special grade glasses usually does not exceed several hundred tons. Therefore, even small deposits /up from 50000 tons of reserves/ can be considered economically exploitable. However, the effectiveness of their use is rather low as up to 9/10 of the raw material is rejected in sorting selective mining and dressing.

2. Quartzite

According to genesis, age and petrological composition, the following groups can be distinguished:

/a/ The so-called cement quartzites which occur at the basement of Tertiary series in Central Europe /Bohemia, Germany/. They are composed of fine, eroded quartz grains cemented with superfine matter. Representing the most typical dinas raw material, they are also known as "dinassic" or "amorphous". The cement in natural state contains mineralizers which enable the metamorphosis of crystallographic modifications of SiO_2. A typical locality in Bohemia is Skršín /at present, the deposit has been already finished/. Several deposits in the Most area /Kamenná Voda/ are drawing near the end of their operation, too. In Germany, this type represents still the most important dinas raw material. These deposits were formed in the course of secondary silification acting on surface parts of Upper Cretaceous and Tertiary sediments, in favourable climatic conditions and on large areas. Generally, their degree of tectonic disturbation is rather high and their mining conditions quite difficult.

/b/ Quarzites of the Cretaceous age which were formed by mineralization and recrystallization of Cretaceous sandstones /Upper Cretaceous - Turonian/. At present one of the deposits of this type is Lahošť - Jeníkov which originated by silification of the Turonian sandstones situated at the Ore Mts. foothill, near the nothern margin of the brown-coal basin, in the immediate vicinity of the Teplice siliceous porphyry. This raw material type is suitable, provided the technology is modified and proper mineralizers added, for the dinas production, too. The Research Institute of Ceramics, Horní Bříza, Czechoslovakia, has developed a super-duty dinas production based on the utilization of this raw material.

/c/ Hydrothermally metamorphed quartzites are known mainly from Slovakia /e.g. Šobov/. These are microcrystalline, intensively hydrothermally silicified, Lower Triassic quartzites. Quite often, they are labelled as secondary quartzites or hydroquartzites, and represent a suitable dinas raw material /dinas is produced in Bánská Belá/. Those basal quartzites which have not undergone the hydrothermal metamorphosis cannot be used in the dinas production.

/d/ Paleozoic quartzites which are, from the genetic viewpoint, fine-grained, silica sands of the shelf type cemented by recrystallizative SiO_2. In Bohemia, these quartzites are found mainly from the Ordovician Barrandien unit while in Moravia, they occur in the Jeseníky Mts. /Devonian/. Their typical features are a low cement content and a variable Al_2O_3 content caused by the presence of sericite and kaolinized feldspar. Quartzites containing little Al_2O_3 are suitable for the production of some types of dinas. In the Ruhr area, FRG, Carboniferous quartzites /so-called "garnister"/ are known which serve as a dinas raw material. Similar quartzites are found in the Ostrava Basin, too; however, their composition does not provide any grounds for their industrial utilization.

/e/ Metaquartzites are such rocks which have been metamorphed to such an extent that they have adopted a quartz-like appearance. One of their advantageous features is a low content of both gaseous and liquid inclusions. Provided they can be purified to possess the required parameters, they are a good raw material for some special glasses. These rocks are usually Pre-Cambrian in age /in Africa, they constitute a part of the so-called Basement Complex/.

The quality of quartzite, regarding the production of refractories /dinas/, is determined on the basis of its mineralogical-petrological composition and chemical composition. Very coarse-grained, crystalline quartzites are far from being in demand as their heat transformation is very slow. Moreover, also the presence of various minerals,/mainly of the mica type/ such as sericite, pyrophyllite and muscovite/, should be regarded as a negative feature. These minerals are the main Al_2O_3 and alkalies bearing media and their presence unfavourably influences the properties of the dinas produced. According to their chemical composition, quartzites can be classified as follows:

SiO_2	min. 96%
	min. 97.5% for higher-quality dinas
Al_2O_3	max. 1 - 1.5%: it is a fluxing agent and a very effective transformation inhibitor: even a 0.69% content is noxious
TiO_2	it acts essentially favourably; however, if the Al_2O_3 content is higher, its role reverses
Fe_2O_3	max. 1.5%; a very effective catalyst speeding up the transformation rate: it must be finely dispersed throughout the quartz mass
CaO+MgO	should not exceed 0.4%: they do not act negatively if dispersed and not forming melts: catalysts boosting the transformation

alkalies - act as a very noxious pollutant, increasing the liquid melt content: cement quartzites have from 0.02 to 0.09% of alkalies, other types even as much as 0.5%: the dinas produced from such quartzites whose alkalic content is about 0.5% cannot be used for high-temperature, heavy-duty furnace linings

Determination of the silica raw materials´ heat transformation rate:

According to the heat transformation rate of a silica raw material which is suitable as far as its chemical composition is concerned,a proper technology can be selected. Contrarywise, for a given technology optimum raw materials can be chosen.

In practice, the heat transformation rate and extent are determined on the basis of the firing expansion of a burnt sample or on the basis of the secondary expansion if the burning is repeated. The burning temperature and the duration of the process is chosen appropriate to the given raw material type.

The production capacity of smaller plants producing dinas is about 10,000 tons/year, that of medium-sized plants from 30,000 to 40,000 tons/year. As economically exploitable, a deposit whose reserves are approx. 500,000 tons can be considered. In practice, the mining losses are from 20% to 40% as the fraction below 40 mm is usually rejected due to its high content of pollutants. The best raw material type, cement quartzite, are mined even if the overburden is considerably thick /stripping ratio 10 : 1, even more/. However, crystalline quartzite exploitation requires more favourable conditions /stripping ratio 1 : 1/ as the respective technology is more demanding and costly.

Examples of chemical composition of the dinas raw materials mined in Czechoslovakia

parameter %	cement quartzite Skršín	cement, quartzite, Kamenná Voda	crystalline quartzite, Lahošť + Jeníkov	microcrystalline quartzite, Sobov
loss of ignition	0.20	0.69	0.42	0.42
SiO_2	96.11	96.98	97.95	98.28

Al_2O_3	0.88	1.02	0.42	0.22
TiO_2	1.16	0.52	0.03	0.74
Fe_2O_3	1.28	0.28	0.40	0.26
CaO	0.20	0.68	0.02	0.22
MgO	0.06	0.09	0.03	0.04

Quartzites can be used as a glass raw material, too. However, in this case they must comply with the qualitative criteria determined for vein quartz.

3. Silicites

Silicites are siliceous rocks of either chemogenic or organogenic origins. They are very variable, both from the viewpoint of their genesis and in their composition. The main component is one of the various SiO_2 modifications - opal, chalcedony or quartz. Their occurences are in a certain way related to geological age /i.e. the degree of their recrystallization/. From the viewpoint of practical use, flint, lydite, limnoquartzites and diatomite are of a certain importance.

/a/ Flint

Flint occurs as modules or chunks in the middle and upper parts of chalk. It consists of a mosaic of small quartz crystals generally less than 5 microns in diameter. Since flint does not occur evenly dispersed in chalk, but preferentially along cracks or joints, it is thought to have formed after chalk was deposited. Flints have a white skin whose composition changes gradually from calcium carbonate to silica and which suggests the replacement origin of the rock. The silica is thought to have been opal sponge spicules which dissolved in water circulating in the chalk, especially along cracks, and was deposited around fossil shells and sand grains, replacing the calcium carbonate of the chalk.

Properties of Flint

Flint is a hard, rock-line mass with no visible cleavage but has a conchoidal fracture. The structure contains small quantities of water together with minute air spaces and interstitial amourphous silica. This special type of structure originated from the unusual way in which it was formed. Siliceous skeletons of sponge-like creatures passed into solution in sea water and subsequently accumulated in patches of solid matter in chalky ooze deposits. Minerals of this type are known as chalcedonic silicas. Flint and chert are the two main forms of this type of "precipitated" silica.

The microstructure of flint makes it much more reactive than quartz in terms of softening point, chemical activity, inversion rate etc. Typical chemical analysis of flint /C.Radford, 1965/:

SiO_2	97.97	CaO	0.62
Al_2O_3	0.39	MgO	0.05
Fe_2O_3	0.06	K_2O	0.02
TiO_2	0.01	Na_2O	0.02

The flint CaO occurs as calcium carbonate within the rock.

Calcination of flint drives off the small amounts of water and organic matter contained within it and loosens the structure. When heated above 870°C, quartz starts to invert to cristobalite and does so from the grain boundaries inwards. After a given firing treatment, flint produces more cristobalite than quartz sand of the same grading, and would be expected to produce a body of a higher thermal expansion coefficient.

Flint is normally calcinated to approx. 1100°C. After this heat treatment, it is friable and this greatly facilitates the grinding process. The specific gravity which was initially 2.63 falls down to an average value of 2.50. The specific gravity value of the final sample provides a valuable indication of the temperature of calcination, the quartz-to-cristobalite inversion and the easy of grinding.

Usage

Flint may be introduced into a body composition in the production of ceramics and refractories /silica bricks/. In ceramics, the objective is to give the ware whiteness and to improve its refractoriness. The body quality is increased in this way and, although opaque, it is similar in general appearance to the porcelain /china/ ware.

The suitability for the production of refractories /silica bricks/ is given by the high silica content and low content of impurities /pollutants/, especially Al_2O_3, CaO, MgO and alkalies.

In England, approximately 100,000 tons of flint are calcinated each year to cover the requirements of the ceramic industry. In GDR, the same raw material is used for the production of silica bricks.

In England, flint is still used in the manufacture of pottery in preference to sand. It is the major constituent of bodies for earthenware, sanitary ceramics and tiles.

Flint comprises less than 5% of chalk and is a by-product of chalk-based cement plants.

/b/ Lydite

Lydites, light-grey to black-grey rocks, occur in the Algonkian series in Bohemia. They represent a so far unexploited source of silica raw materials. The originally fine-grained to compact silicates of organic and chemigenic origin were metamorphed to microcrystalline rocks during recrystallization. Some lydites contain a certain admixture of graphitic and hematitic substance. R. Bárta et al. /1959/ have dealt with the dinas production technology. Either light-coloured, compact, or fine, dark-banded types are considered suitable for the production of dinas. Darker-coloured, lydite and lydite penetrated with secretional quartz veinlets are less favourable in these terms. The usability of lydite is evaluated according to the following criteria:

refractoriness: 34 and over - very good
/Seger Cone/ 33-34 - medium
less than 33 - low

SiO_2 content: over 97% - high
96-97% - medium
less than 96% - low

firing expansion: over 6% - high
4-6% - medium
less than 4% - very low

after-firing absorption capacity: over 4.5% - high
2.5-4.5% - medium
less than 2.5% - very low

heat transformation: less than 2.37 - very good
/density - g/cm^3/ 2.37-2.42 - medium
over 2.42 - bad

/c/ Limnoquartzites

These rocks are the product of the sedimentation of thermal springs rich in silicic acid, i.e. silicites. They are known from Slovakia where they are found in the uppermost parts of the Žiar Basin Neogene filling. They have developed in several layers and their chemical composition is fairly stable: SiO_2 from 95 to 98%, Fe_2O_3 from 0.5 to 1.5%, Al_2O_3 from 0.1% to 0.6%, P_2O_5 from 0.01 to 0.06%. The loss of ignition ranges from 1% /white-coloured types- up to 2.5% /dark-coloured types/, depending on the contents of opal and organic matter.

If a more suitable raw material is lacked limnoquartzite can be used for the production of dinas. However, they require a similar processing as flint /i.e. calcination/. In Czechoslovakia, the raw material is used for the production of ferrosilicon.

/d/ Diatomite

Diatomite is a rock composed basically of opal shells of diatoms: it is either loose or partly to completely cemented. The cement is usually clay or the SiO_2 released in diagenetic processes. Diatomite deposits are usually formed both in marine and sweetwater limnic basins where the $CaCO_3$ content is low and that of suspended alumosilicates is high enough to enable the buildup of diatom shells. As far as their chemical composition is concerned, SiO_2 is prevalent /whose high content is important also from the viewpoint of practical use/. In addition, the raw material contains Al_2O_3 /from 5 to 13%/, Fe_2O_3 /from 2 to 6%/, CaO /from 0.5 to 5%/. The dry bulk weight of the rock ranges from 200 to 900 kgs/cu.m. For its low weight and excellent insulating properties, diatomite is used for the production of lightweight insulating building materials, either in the hardened or fired forms /firing temperature is selected not to exceed 1000°C/. The purest varieties are used as filter materials. Other uses: various fillers, grinding pastes, polishing pastes etc.

In Czechoslovakia, the raw material of the Borovany diatomite deposit is used for the production of lightweight building materials. The pertinent qualitative criteria and the processing technology are given in the chapter on silica-based building materials.

4. Sandstone

Sandstone is a sedimented, cemented, clastic rock, composed prevalently of sand-size particles /i.e. from 0.05 to 2 mms in diameter/. Sandstones are the commonest source of high-quality glass sands. In Europe, such sources are represented by sandstones of the Cretaceous age which provide the raw material from several horizons /Cenomanian, Turonian, Coniacean etc./. Their typical feature is a kaolinite cement /sometimes partly ferrugineous/ whose carbonate content is generally low. Regarding their usability in the glass production, sandstones are evaluated according to the particle size /the 0.1-0.6 mm fraction percentage should be as high as possible, 60% at least/, the content of Fe_2O_3 in the 0.1-0.6 mm fraction, the amount and character of the cement /the kaolinite cemented varieties are the most suitable, those cemented by carbonate are difficult to dress/, the amount and character of heavy minerals. In Czechoslovakia, abundant sandstone deposits of the Bohemian Cretaceous Basin are used for the glass production /Provodín - Srní, Střeleč/. If there is a lack of kaolinite-cemented sandstones even carbonate-cemented types can be used. The latter type is used in the U.S.A. and Canada. However, the carbonate-cemented sandstones require a complex and difficult dressing, consisting in their flotation in an acidic environment through which the heavy minerals´ content is decreases and the sandstone got rid of the remaining carbonate cement.

The glass sand dressing requires a sufficient water resource. The dressing line is fairly complex and is built in Czechoslovakia for a minimum capacity of 150,000 tons/year. Medium-sized plants´ annual capacity is about 0.5 mil.tons, that of large plants even more than 1 mil. tons per year. For this reason, the minimum economic reserves of a glass sand deposit are 5 mil. tons, the optimum value being about 20 mil. tons. More detailed data on the dressing technology are given in the chapter on the use of silica raw materials in the glass industry.

5. Silica Sands and Pebbles

Silica sands and pebbles are very common in Tertiary and Quaternary deposits. However, most of them are either less suitable or unsuitable regarding their use in the glass industry. They can be divided into the following groups:

/a/ From the viewpoint of the glass production, sands building vast complexes of Tertiary basins' filling, particularly those underlying a coal seam or those situated in marginal parts of a basin /beach sands/, are the most suitable. Frequently, they have been secondarily purified /e.g. by action of humine acids/ thus giving way to the formation of high-quality glass sand deposits /e.g. Hohenbocka, GDR, or Dörrentrup, FRG/.

/b/ Quaternary deposits /eolic and fluvioglacial sands/ are favourably fine-grained: however, they generally contain more impurities /Fe-incrustations, heavy minerals, clayey minerals, feldspar and other fluxes/ and are therefore suitable for the production of coloured glasses only. If there is a lack of a high-quality raw material they can be used after the necessary processing /e.g. flotation/. However, to obtain a high-quality glass raw material is always difficult and costly.

/c/ Fluvial sediments are generally unsuitable as a glass raw material, due to their variable granularity and quality. Only sediments in larger deltas can be considered as usable under certain circumstances.

/d/ Kaoline sands which are a by-product of the kaoline washing: their granularity is generally suitable, but their wider use is hampered by a higher Fe_2O_3 content which limits their usability to the coloured glass production. There where other high-quality raw materials are non-existent even those sands can be used for the higher-grade glass production.

/e/ Coarse-grained, weathered silica rocks can be very pure and after their complex processing /grinding, sorting, sieving/, they can serve as a raw material for the highest-quality glass. As an example, the Velký Luh deposit can be given whose Fe_2O_3 content is as low as 0.013% only.

/f/ Silica pebbles sorted out in the gravel mining can be used, after their necessary processing, for the preparation of special glass sands. In GDR, this raw material is added into the dinas mix.

IV. SILICA BASED REFRACTORIES /DINAS/

Dinas /silica bricks/ is a refractory material containing at least 93% SiO_2, made from quartz rocks with lime or other binder, and fired at temperature ensuring polymorphic transformation of silica /quartz/ into tridymite and cristobalite.

1. Modifications of Silica and Their Properties

The chief raw material used to produce dinas is quartz rock. The silica forming it may exist in several crystalline and one amourphous modifications in the rock. The polymorphic transformation of the silica determine both the technological process used and the final properties of the product. Anhydrous silica is known to exist in at least eight modifications. Special resources from the area of silicate technology label them as: alpha- and beta-quartz: alpha-, beta-, and gamma-tridymite: alpha- and beta-cristobalite: and quartz glass.

Some authors, such as Budnikov, use the alpha designation for the forms stable at high temperatures and the beta designation for those stable at cooling. Other, however, resort to reverse designation, i.w. beta for the forms stable at high temperatures and alpha for those stable at cooling /e.g. Chesters, Le Chatelier/. /see diagrams in the Figs. 2 and 3/. In the following paragraphs of this chapter we will stick to Budnikov´s classification.

The most abundant form of SiO_2 in nature is beta-quartz. It is found as quartz sand, quartzite, different kinds of rock crystal, as an integral part of igneous rocks and sandstones, and, last but not least, as an impurity in clays and kaolines.

Beta-quartz, stable at ordinary temperatures, transforms into alpha-quartz at 573°C. At 870°C, alpha-quartz gradually and slowly changes into alpha-tridymite, but only if a strong fluxing agent and a mineralizer are present which are sufficiently finely ground.

Alpha-tridymite is not found in nature, since its stability interval lies between 870 and 1470°C. When cooled, it converts into gamma-tridymite, passing via an intermediate form, beta-tridymite. At 1470°C and above, it begins to slowly change into alpha-cristobalite.

Beta-tridymite is an intermediate modification only, changing extremely rapidly /even at 117°C/ into gamma-tridymite: Its stability interval is, therefore, very narrow /from 117 to 163°C/.

Alpha-cristobalite. When alpha-tridymite is heated above 1470°C it forms alpha-cristobalite extremely slowly, the latter remaining stable up to 1713 ±10°C. At 1713°C, alpha-cristobalite converts into quartz glass without any change in volume. When cooled, alpha-cristobalite in the metastable state turns into beta-cristobalite.

Beta-cristobalite is a metastable form which may exist under ordinary conditions in the nonequilibrium state and virtually for an unlimited amount of time. Hence, it is found in nature, though very rarely.

Quartz /silica glass. When heated to extremely high temperatures, various forms of silica can be melted. The limits of the silica transformation can be represented by the following diagram /after Budnikov/:

$$\begin{tikzcd}
\text{alpha-quartz} \arrow[r, shift left, "870^{\circ}C"] \arrow[d, shift left] & \text{alpha-tridymite} \arrow[l, shift left] \arrow[r, shift left, "1470^{\circ}C"] \arrow[d, shift left] & \text{alpha-cristobalite} \arrow[l, shift left] \arrow[r, shift left, "1723^{\circ}C"] \arrow[d, shift left, "180\text{-}270^{\circ}C"] & \text{fused silica} \arrow[l, shift left] \arrow[d, shift left] \\
\text{beta-quartz} \arrow[u, shift left, "573^{\circ}C"] & \text{beta-tridymite} \arrow[u, shift left, "163^{\circ}C"] \arrow[d, shift left, "117^{\circ}C"'] & \text{beta-cristobalite} \arrow[u, shift left] & \text{quartz /silica/ glass} \arrow[u, shift left] \\
 & \text{gamma-tridymite} \arrow[u, shift left] & &
\end{tikzcd}$$

2. Changes in specific gravity and volume

The most important consequences of the polymorphic transformations of silica affecting the technology of ceramics are the associated changes in specific gravity and volume, which are quite considerable. The variations in volume during the total transformations of silica are shown below.

Modifications of quartz and transformation temperature	volumetric effect of transformation at given temperature, %
beta-quartz $\xrightarrow{573^{\circ}C}$ alpha-quartz	+ 0.82
gamma-tridymite $\xrightarrow{117^{\circ}C}$ beta-tridymite	+ 0.20
beta-cristobalite $\xrightarrow{250^{\circ}C}$ alpha-cristobalite	+ 3.70
beta-tridymite $\xrightarrow{163^{\circ}C}$ alpha-tridymite	+ 0.20
alpha-quartz $\xrightarrow{870^{\circ}C}$ alpha-tridymite	+16.00
alpha-quartz $\xrightarrow{1000^{\circ}C}$ alpha-cristobalite	+15.40
alpha-quartz $\xrightarrow{1723^{\circ}C}$ silica glass	+15.50
silica glass $\xrightarrow{1000^{\circ}C}$ alpha-cristobalite	- 0.90

Volumetric changes determine the behaviour of dinas during firing and service to a considerable extent and must therefore be closely watched, since inconstant volume is one of the most important factors influencing the low spalling resistance of dinas. The more rapid the transformation and the greater the volumetric change, the lower the spalling resistance.
The variations in volume are of utmost importance in ensuring products with accurate dimensions, good spalling resistance, tight fit of brickwork etc.

The speed and degree of slow transformations are functions of temperature /and period over which it is effective/, grain size, microstructure and presence of fluxing agents. Fine-fibred quartz modifications with a dense or "sintered" structure of fine fibrous aggregates /e.g.chalcedony/ decompose more rapidly than coarse lump quartz. The transformation of alpha-quartz into alpha-tridymite can be accelerated by the addition of fluxing mineralizers. The most suitable mineralizers are iron oxides, ferrugineous silicas /particularly ferrous oxide/ and calcium carbonate.

Among the artificial mineralizers are lime, mill scale, pyrolusite and metallurgical slags. Finely dispersed natural mineralizers /impurities in the material/ of specific composition sometimes exert a more favourable effect than mineralizers purposely added. The most common impurity in quartzite is alumina which decelerates the quartz transformation rate.

The negative influence of Al_2O_3 includes also the decrease in refractoriness.

3. Evaluation of silica raw materials for the production of dinas

/a/ Microstructure

High-grade quartzites for dinas production have a dense, sometimes pitted fracture with quartzite grains either visible or invisible to the naked eye, absence of any marked schistose structure, and impurities between the layers. Quartzites of a loose, sandy fracture cannot be classified as first-grade. The microstructure of quartzite is of a great importance, since it makes possible to determine whether or not it is the cement or crystal type, to describe the shape and size of the quartz grains and cement and their ratio, and to get the idea on the mineralogical composition and distribution of impurities. From the microstructure, we can assess some idea on the likelyhood of transformstion. Cement quartzites consisting of quartz and basal cement grains with a very fine structure transform more rapidly. Some impurities play the part of fluxing mineralizers and accelerate the transformations.

Crystalline quartzites retain a fairly dense structure even after firing, though they exhibit the lowest transformation rate. Crystalline quartzites consisting of comparatively homogenous and large quartz grains loosen up more intensively during firing. The combination of quartz grains in the form of serrated seams counteracts the loosening during firing. Finer grinding of the quartzite and the addition of Fe compounds considerably reduces the loosening and accelerates the transformation. Green ware made from well-pulverized crystalline quartzites is more resistant to crack formation during firing than the ware made from the rapidly transformed cement quartzite. Mica, anorthite, alkaline feldspars /often kaolinized/, calcite, clay particles, iron pyrites, carbon particles and sometimes tourmaline, granite and hornblende are found as impurities in quartzites. The coarser-grained types /particularly when layered/ undoubtedly reduce the value of quartzites used for the dinas production. Quartzites with a marked schiatose structure are not very suitable.

/b/ The chemical composition

of quartzites used for the dinas production is characterized chiefly by a high SiO_2 content. Whether or not such quartzites need to be sorted and/or washed depends on the quantity and chemical composition of the impurities, the bulk chemical composition of the quartzite and the requirements placed on the finished product. If there is a dense limestone crust which is difficult to remove, the quartzite is considered unsuitable on the account of the risk of bulges in the brick and cracking through slackening of the free lime. In crystalline quartz, the SiO_2 content is 97% at least.

The amount of SiO_2 in initial quartzite is a function of the required silica content in the dinas:

SiO_2 in dinas /min.%/	content in quartzite SiO_2	Al_2O_3+TiO_2 max.
95	97-98	1.2-1.3
94	96-96.5	1.5
93	95	1.5-2.0

The H_2O content should not be more than 0.25, that of CaO not more than 1% /critical items not more than 0.5-0.8%/. In addition, this substance should not be present in the form of a dense crust. The amount of Fe_2O_3 should not exceed.1%. When making dinas for steel-furnaces, particularly for roof bricks, the amount of Al_2O_3 should be kept to a minimum - below 0.7 - 1.0%.

/c/ Refractoriness

One of the most important properties of quartzite determining its suitability for the dinas production is its refractoriness which should be 1750°C or more. Quartzites of a lower refractoriness /1730°C/ are used as additives.

/d/ Porosity

Quartzites used in the dinas production are typically divided into four groups, according to porosity:

	water absorption, %	apparent porosity, %
very dense	up to 0.5	up to 1.2
dense	0.5 - 1.5	1.2 - 4.0
porous	1.5 - 4.0	4.0 - 10.0
very porous	4.0	10.0

The quartizites of the first and second groups are the basic components of charges for the super-duty dinas items. Quartzites of the third group are either used in mixtures with the first two classes or for less critical elements. The fourth group can be used only as additives.

The porosity classification is secondary in comparison to the overall technological classification.

/e/ The rate of transformation

The technological classification is based on the rate of transformation of quartzite as shown by variations in the specific gravity after firing to 1460°C for one hour at maximum temperature. According to the specific gravity after firing, quartzites can be divided into four groups:

group	specific gravity after firing
rapidly transformating rate	2.4
average transformating rate	from 2.4 to 2.45
slow transformating rate	from 2.4 to 2.5
extremely slow transformating rate	2.5

Quartzites with average, slow and very slow transformation rates which satisfy all the other requirements may be used as the basic raw material for the production of first-grade dinas under the appropriate firing conditions. Rapidly transformating but dense quartzites /chert/ can be used solely under special firing conditions.

4. Technology of the Dinas Production

/a/ Raw Materials

The main dinas raw materials are quartzites, either cement forms or a number of crystalline quartzite varieties. In some countries, other raw materials, such as calcinated flint, are used as well. Also the use of lydite or quartz-pebbles added to other raw materials can be considered. The minimum SiO_2 content should be 95%: however, high-quality products require the minimum value of 96.5%. The suitability of raw materials is evaluated on the basis of their mineralogical-petrological and chemical compositions, refractoriness, heat expansion, specific gravity and secondary expansion of the final dinas product.

Dinas chips: represent an additive frequently used in the production of some dinas materials. However, their addition is limited in order not to decrease the quality of the dinas produced. Their positive influences are: decrease of the firing expansion, lower percentage of insufficiently fired products, lower percentage of rejects. However, they increase the porosity and worsen the body structure.

Sulphite liquor is used for the reinforcement of both the unfired and final products. It is used in liquid state, its dry matter content being 50%. The specific gravity of the solution should fall into between 1.20 - 1.21 kg/l.

Mineralizers are substances which are used in the dinas production to accelerate and direct the transformation of quartz into tridymite and cristobalite. The types used in practice are:

- calcium hydrate: powdery substance whose CaO content in a dried sample should be 65% min.; if sieved through a 0.09 mm mesh, the screen oversize should not exceed 10% of the sample volume
- ferric mineralizer: its composition in a dried sample should be as follows:

loss of ignition	max. 5%
SiO_2	max. 10%
Al_2O_3	max. 3%
Fe_2O_3	min. 65%
screen oversize /0.09 mm mesh/	max. 10%

Composition of dinas materials:

crushed quartzite	80-100%
crushed dinas chips	0-20%
calcium hydrate /CaO in dry matter/	2%
roasted pyrite	1%
sulphite liquor /in dry matter/	1%

/b/ Wet preparation of dinas mixtures

Raw quartzite is sorted, washed and crushed to particles below 6 mms. Dinas chips are crushed to obtain the same particle size.

Calcium hydrate is fed to a blunger where it is stirred together with water in a prescribed ratio.

Roasted pyrite is finely ground in a drum mill /dry grinding/ so as the ground pyrite residue on a 0.09 mm mesh screen would amount to 5% at most.

Sulphite liquor is delivered in a ready-to-use state /liquid, dry matter content 50%/.

Preparation of dinas mixtures:

The preparation of dinas mixtures is carried out in edge mills. The individual components are fed into the mill in the following succession:

The appropriate amounts of water and dinas chips are first fed into the edge mill. The chips are ground in excess water for 3 to 4 minutes. After this period, crushed quartzite, lime milk, sulphite liquor and finely ground roasted pyrite in appropriate amounts are fed into the mill. The subsequent grinding is effected as long until the dinas mixture does not have the granularity required /max. particle size 4 - 5 mms/. The grinding usually takes 40 to 50 minutes to accomplish. The dinas mix prepared in this manner whose humidity is approx. 8.5% is transported to the manual and machine moulding.

Manually, the material is moulded at its original humidity, i.e. 8.5% by tamping into moulds using either electrical or pneumatic rammers. If the mixture is to be machine-moulded it is first allowed to mature to attain approx. 4% of humidity and then moulded using various types of impact pressed. Drying of the semi-products is effected in chambers in order to achieve the residual humidity of approx. 1%. Items up to 20 kgs in weight are usually dried for 8 to 16 hours, those weighing from 20 to 40 kgs for the period of 16 to 36 hours, at the temperature of approx. 30°C. Firing of the dinas items is carried out in chamber kilns. The temperature and duration of the operation depend upon the type of quartzite used and on the dinas grade produced. Generally, dinas is fired to achieve the bulk density of 2.32 - 2.38 g/cucm.

The firing operation is the final and most important phase of the dinas production. By heating, the silica structural properties are changed, giving rise to various silica modifications which differ in terms of their physical and crystallographic properties.

/c/ Dry Preparation of Dinas Mixtures

Crushed quartzite / < 6 cms/ is ground in a dry edge mill whose perimeter is perforated by holes 6 mms in diameter. The quartzite falling through the holes is subsequently sorted using a vibration screen 4 mms mesh. The resulting oversize fraction is fed back to the edge mill, the siftings under 4 mms are transported to hoppers. Also, dinas chips are dressed in the same way.

Preparation of Lime Suspension:

The preparation is effected together with sulphite liquor according to the following formulation:

water	38.5% of weight
calcium hydrate	43.5% of weight
sulphite liquor /50% of dry matter/	18.0% of weight

The lime suspension containing sulphite liquor is prepared by introducing the individual components of the suspension in the succession given in the formulation into a propeller agitator where the suspension must be stirred continually. The bulk weight should be 1.3 kg/l.

Preparation of Ferric Mineralizer:

Formulation:	water	50%
	roasted pyrite	50%

Both components are fed /water first/ into an attrition ball mill. Approximately 1/3 of the mill volume should be occupied by attrition balls. The suspension thus produced should have the volume weight of approx. 1.60-1.62 kgs/l. The attrition requires approx. 4 hours to accomplish.

Preparation of Dinas Mixtures:

Granular components, i.e. ground quartzite and dinas chips, are fed from the hoppers into agitators. Subsequently, the lime suspension containing sulphite liquor and the ferric mineralizer solution are added into the agitators which have already contained the granular materials.

By mixing the granular components and the lime suspension and the ferric mineralizer solution, a dinas mixture containing approx. 2.9% of water is formed. However, a further addition of water is necessary as the mixture must have 3.5% - 4% of water /machine moulding/ and approx. 7% of water for manual tamping. The mixing of the dinas mixture is effected in a muller, its duration being 10 to 15 minutes. The ready-to-mould mixture is transported to the presses in containers. Subsequent technological operations are the same as for the wet preparation.

5. Technology of the Super-Duty Dinas Production

The production of high-quality dinas from crystalline quartzite requires special development works to establish the optimum technology for a given raw material. In Czechoslovaki, these research works have been carried out in the Ceramics Research Institute, Horní Bříza, for the crystalline quartzite of the Lahošť - Jeníkov deposit.

Composition of the quartzite:

SiO_2	min. 97.5%
Al_2O_3	max. 0.7%
Fe_2O_3	max. 0.8%
CaO	max. 0.11%
refractoriness	min. 1730°C

The quartzite should have a uniform structure, without any apparent particle orientation. Particles over 2.5 mms are admissible only when occurring occasionally.

Admixtures:

- dinas chips /of individual types of compact dinas/
- calcium hydrate /powdery; content of CaO min. 65%, oversize residue on a 0.09 mm sieve max. 10%
- agglomeration ore dust, required composition

loss of ignition	max. 5%
SiO_2	max. 10%
Fe_2O_3	max. 65%
oversize residue on a 0.09 mm sieve	max. 10%

- liquid sulphite liquor: dry matter content 50%, volume weight of the solution 1.20 - 1.21 kg/l
- sulphonaphtenic soap: liquid, volume weight 0.92 kg/l, water content max. 1%, mineral oils content max. 80%

The used raw material and dinas chips must be ground more finely than for the ordinary dinas. The grindings are required to have the constant granularity of the 2-3.15, 1-2, 0.1-1 and below 0.1 mm fractions. To obtain the required amount of the 0.1 fraction /approx. 35%/, a part of the raw material is ground in a vibration mill.

The lime suspension and the agglomeration ore dust suspension are processed in an attrition ball mill for some 4 hours. The volume weight of the solution thus prepared should be 1.60 to 1.62 kg/l.

The preparation of dinas mixtures is effected according to the formulations worked out for every specific type of dinas and the raw material used. A special attention is paid to the content of the fine /below 0.1 mm/ fraction and that of the coarse /0.1 - 3.15 mms/ fraction in quartzite. The compact dinas should have from 33 to 35% of the fine fraction, the requirements for the super-duty dinas are even more strict - 35 to 37%.

The further technology /which is very similar to the production of ordinary/dinas/ stresses particularly the effectiveness of moulding. The volume weight of press-moulded dinas items should be 2.20 gs/cu.cm. The firing is at 1380°C. The total firing time is 156 hours, that of cooling 168 to 176 hours. The firing is executed in circular or chamber periodic kilns.

V. SILICA IN CERAMIC INDUSTRY

Silica is one of the basic components of ceramic body. The china production is based on using three basic raw materials: washed kaoline, silica and feldspar /approximate ratio 50 : 25 : 25/. It has been traditionally using vein quartz which must be, prior to its utilization, fired /calcinated/ at 800°C so that its lower forms convert to high ones. The fired quartz is cooled by water, gets cracked and is well grindable. The vein quartz used in the glass industry must be pure, without any impurities which are represented by various inclusions /kaolinized rocks, such as chlorite/, limonitic incrustations or ore minerals. Therefore, quartz is sorted and washed. The quartz quality is determined according to its fired colour which should be purely white, without any colour stains or dots. The standards for the glass quartz usually require the maximum Fe_2O_3 content of 0.3% /as for instance the KI grade/, sometimes 0.2%. The SiO_2 content is usually required to be 99% /min./: however, a lower content is not straightly a mistake if SiO_2 is made up for by another usable raw material /clay, feldspar/, the criteria for the fired colour maintained, and the raw material is of a uniform quality. The most decisive factor is that the china made from the quartz analysed must have a good transparence.

Quartz from vein deposits /pegmatites and hydrothermal quartz veins/ is mined using either the open-pit or underground methods /the underground method is applied if the thickness of a deposit is min. 2 ms/. Quartz pebbles can, under certain circumstances, fully substitute vein quartz. The sorting is executed after calcination in this case because pure quartz can be distinguished more easily from polluted quartz and impurities when this operation is completed. In some countries, flint has been traditionally used. The necessary prerequisite is calcination during which also the water present in this silicite is removed.

As the mining of quartz is costly and, moreover, increased by the necessary firing /calcination/, ways of his replacement by quartz sand are intensively sought. It has been found that it is not difficult to find quartz sand of the chemical composition required. On the contrary, glass sands are very pure, often purer than ceramic vein quartz. However, two difficult problems must be solved: firstly, volumetric changes encountered when uncalcinated quartz is used, secondly, transparence of the produced china.

In evaluation of any type of quartz sand suitability regarding the china production, experimental works cannot be dispensed with. The Czechoslovak experience shows that the genetic character of the quartz plays the most important role in these terms. However, these parameters cannot be expressed using the standard criteria. Since 1968, Czechoslovak china plants have been using the quartz sand of the Velký Luh /Cheb District/ deposit which is virtually the Smrčiny Granite elluvium. The extraordinary suitability of this raw material is attributed to the arrangement of the quartz structural grid whose surface is luckily occupied by silanole groups. This arrangement allows for releasing of the water bound in the grid at higher temperatures.

Other types of ceramic industry, such as the tile, sanitary ceramics and earthenware productions, prefer to use cheaper, multi-component raw materials, e.g. feldspar-quartz sands /such as low-grade feldspar containing 55% of feldspar and 45% of quartz, sometimes labelled as pegmatite, or rou kaoline, typically containing 75% of quartz and 25% of clay - kaolinite/. Also, the fine-grained sandy by-product gained by washing of kaoline can be used. Its granularity is usually from 0.06 to 0.5 mm and it contains approx. 80% of quartz and 20% of feldspar. Occasionally, it is labelles as "pegraf".

The mutual problem for all types of silica material is their grinding whose objective is to achieve such material that is fine enough to fall through a 0.06 mm screen. The most frequently used dry grinding can /and also often results/ in silicosis. Therefore, automatized rotary-type grinding plants must be used. In order not to pollute the ground material, the mill interior must be lined by a non-metallic material, such as silex /i.e. fine-grained quartzite/. Recently, vibration mills have been introduced for fine grinding of quartz sands. Their interior is lined by porcelain material.

In designing new plants, the grinding technology must be paid a special attention. Any improvization in the selection of the grinding equipment is unthinkable. In any case, the grinding plant finally erected must comply with the requirements pertaining to the protection against silicosis which are very rigid.

VI. SILICA IN GLASS INDUSTRY

Silica is one of the most important raw materials for the glass industry. It is used in the form of the finely-ground glass sand of the prescribed granularity /main portion from 0.1 to 0.6 mm/. Moreover, there also exist strict requirements as far as the content of impurities, namely that of colouring oxides and hard-to-melt heavy minerals. The glass sand is prepared from sandy deposits, sandstones, quartzites, quartz pebbles or vein quartz. The methods of its preparation are sometimes quite complex. As the glass sand accounts for 60 to 80% of all the raw materials used in the glass production /sometimes even as much as 100% for some special types of glass/, its quality decisively influences both the production technology and the quali of final products.

1. Qualitative evaluation of glass sands

The qualitative evaluation of glass sand is based both on the material granularity /quartz particle size and their properties - granulometric evaluation/ and on the content and character of various admixtures /particularly colouring oxides which negatively influence the final product colour/.

The granular composition of glass sand can be fixed by dressi In the dressing of granular rocks /sands, sandstones cemented by kaolinite/, the content of the principal fraction /0.1 - 0.6 mm/ is required to as high as possible as it directly influences the economy of dressing. Usually, the minimum content of 60% is required. If other materials are processed /vein quartz, quartz pebbles, quartzites, coarse-grained sands/ it is necessary to monitor the coarse-grained fraction while the fine-grained one /in which impurities tend to concentrate/ is rejected. If these raw materials are used, it is not uncommon to fire the quartz prior to its grinding as its grindability is greatly improved by the operation. After grinding, the raw material is sorted to the fine /0.1-0.6 or possibly 0.1-0.4 mm/ and coarser fractions. The former is ready to use, the latter has to be reground and sorted again. The granularity of glass sands is expressed graphically by granularity curves. Fig. shows the respective curves for the Provodín, Srní, Střeleč and Velký Luh deposits, Czechoslovakia.

It is obvious that the most valued raw material is such that has the granularity required already in its natural state or only a minor dressing operation must be executed /such as removal of clay etc./. These sands are found, for instance, in Belgium, Fontainebleau /France/, Hohenbocka /GRD/, Dörrentrupp /FRG/ etc. The granularity curves /see above/ for the four Czechoslovak deposits show that the raw material of the Střeleč, Srní and Provodín deposits requires the removal of fractions below 0.1 and above 0.6 mm while the sand of the Velký Luh deposit represents the second type, i.e. requires grinding and subsequent sorting.

Properties of silica particles depend on their shape and size. The shape and character of their surface are very important as these parameters influence mechanical adhesion of impurities, such as kaolinite and limonite, and thus have something to say in the dressing technology. The surface pollution is, regarding the main impurity is Fe_2O_3, very grave. Generally, this type of pollution accoungs for approx. 0.01 to 0.02% of Fe_2O_3 present in the raw material.

The particle size plays a major part in the melting process. The larger the particles, the slower they melt, and the effectiveness of the production is thereby decreased. The dressed glass sand should not contain any grains over 1 mm. Also, inclusions of heavy minerals within quartz grains may act negatively, as well as impurities present in microfissures. The fraction below 0.1 mm is usually composed of impurities, too, and effects a negative influence upon glass plaining. However, if this fraction is composed of ground quartz the lower limit may be pushed down to 0.06 mm.

The commonest impurity present in glass sand are so-called heavy minerals. They are accessoric, bind a considerable amount of colouring oxides, and, in addition, some of them are almost infusible, deteriorating the glass matter with unmelted pieces. In sedimentary rocks, these pollutants are concentrated in the finest fraction. Cretaceous sandstones show a relatively stable association of heavy minerals: anatase, rutile, tinatite, brookite and metamorphic leucoxene; also zircon, staurolite and garnet are very common. Spinellids, the minerals most feared by glassmakers /also labelled as chrome-spinels/, are fortunately rare. They are not completely melted in the glass batch, resulting in the formation of the so-called "black stones". According to chemical analyses, heavy minerals contain from 10 to 15% of Fe_2O_3 on average. Thus, even as low as 0.1% amount of heavy minerals present in the raw material infers some 0.01 to 0.015% of Fe_2O_3 into the batch. The removal of heavy minerals is, therefore, one of the possibilities of increasing the quality of glass sands.

The composition of siliceous material used is given by the genesis and is virtually definite. The chemical composition of quartz grains relieved of all the admixtures and surface incrustations represents the limit of dressibility. This value must be known if we are to evaluate the given raw material properly. It may happen that the quality of a relatively pure raw material cannot be by any means substantially improved. On the other hand, a seemingly unusable silica rock may be dressed to obtain the best raw material. In addition, it is necessary to observe the amount and character of gaseous and liquid inclusions present in the rock which influence the properties of melt in the transparent glass production. The best raw materials for this special purpose are rock crystal and some varieties of vein quartz.

Qualitative Classification of Glass Sands:

Almost all countries use the Fe_2O_3 content as the basic criterion in the evaluation of the quality of glass sands. This parameter has been chosen because it is the principal limiting factor of the type of glass for whose production any given glass sand grade can be used. However, the limit values of the Fe_2O_3 for the individual glass types are not identical in all countries, namely for white and semi-white types.

On the basis of qualitative requirements and the type of glass produced, the following categories can be determined:

1/ Glass sands containing 0.035 to 0.050% Fe_2O_3. They are used in the production of ordinary sheet glass, white and semi-white container glass etc. Sometimes, glass sands containing even 0.080% are used, but their dressing is costly /decolouring agents/. Glass sands containing more Fe_2O_3 /from 0.1 to 0.2%/ are used for the coloured glass production if they do not contain any impurities which would negatively influence the melting and plaining process /heavy minerals, mica/. Dressing of the glass sands falling into this category is simple as it consists only in washing and sorting. More complicated dressing methods of glass sands containing 0.035% - 0.050% of Fe_2O_3 /e.g. flotation/ are used only there where it is a shortage of these glass raw materials.

2/ Glass sands containing from 0.020 to 0.035% of Fe_2O_3 are the most important category as they are used for the production of all the types of white glass. In many cases, their dressing is complex /e.g. flotation, rubbing. electromagnetic separation/. Some Cretaceous sandstones, however, provide materials complying with this category only after a simple dressing.

3/ Glass sands containing 0.013 to 0.020% Fe_2O_3 constitute separate layers in some deposits from which these high-grade sands are selectively mined. Large mining plants draw these raw materials from the 1 and 2 categories. The dressing consists mainly in the removal of heavy minerals /flotation, gravity separation, possibly sorting out of a certain grain fraction/, rubbing off of impurities present on the surface of particles, occasionally in chemical processing. These sands are used mainly for the production of crystal glass and some types of optical glass. The world's production is limited to a relatively small number of localities.

4/ Raw material resources for the production of optical glass represent a special category. The required Fe_2O_3 content is between 0.005 to 0.010%, in some cases even 0.001 or 0.002%. In addition, a number of trace elements is observed. This category comprises either the raw material of the preceding category which must be further chemically /leaching in an acidic environment/ and electromagnetically dressed, or extremely pure vein quartz. The ncessary processing of the raw material is frequently carried out directly in glass factories or in specialized processing plants.

2. Mining and Dressing of Glass Raw Materials

Open-pit mining is virtually the sole resort in the glass sand extraction. Tunnel or coyote blasting methods may be combined with high-capacity haulage and conventional crushing. Hydrolic mining is used effectively for kaolinic sandstones. Where near-surface water and geological conditions permit, unconsolidated sands are removed by dredging. Either hydrolic mining or dredging, and the subsequent removal by pumps offer a relative optimum in economy; fluid mechanics, applicable to flow in pipelines, may also provide a measure of attrition /scrubbing/ and prove an aid to beneficiation. Any prospect for the development of a glass sand operation must include a readily accessible source of water. Long established in some areas, regulations which concern the withdrawal of groundwater, diversion of surface water and the possible contamination of either source may be considered nationwide in effect.

The glass sand beneficiation is carried out in a number of ways, mostly taken from technologies for other raw materials, particularly kaoline and ores. The commonest method used is washing plus sorting of the material into individual grain-size fractions. Various type of drum washers, counterflow sorters /e.g. Rheax, Lavodune, in Czechoslovaki VPT 25 etc./, and hydrocyclones. If better glass sands see to be dressed, attrition, flotation, high-intensity magnetic separation or leaching may be applied.

Froth flotation methods are used to remove contaminating metal minerals. Essentially, it is based on the fact that organic compounds of high molecular weight become attached to the metal ions on the surface of the minerals. These particles, coated by what is virtually a hydrocarbon layer, are attracted to air bubbles which are blown through the slurry. This ultimately forms on the surface as a froth which is removed periodically by rotating scrapers. The quartz particles do not absorb the organic reagent used and therefore are not removed in the froth.

Fe_2O_3 can be removed from the surface of the quartz grains by solution in acids, such as HCl. Sodium hyposulphite is also used to create reducing conditions which are found to be most favourable for maximum solubility.

Finally, alumosilicates can be removed from the quartz grain by mechanical agitation of the thick slurry. High-speed impellers cause the quartz grains to be rubbed against each other and this abrasive reaction frees the quartz from the contaminants.

Dressing of Quartz for the Clear Silica Glass Production

Czechoslovak experts have worked out and introduced their own method of the clear silica glass raw material dressing. The product resulting from this technology is capable of substituting Brazil rock crystal which is presently a deficit raw material throughout the world. The technology includes: /1/ washing and sorting of the raw material, /2/ calcination - firing at 850°C for 7 hours, /3/ hand-sorting of the calcinated raw material, /4/ crushing and grinding of the raw material to achieve the final fineness below 0.5 mm, followed by the counterflow sorting out of the 0.1 - 0.5 mm fraction, /5/ magnetic separation, /6/ leaching in a 20% hydrofluoric acid at 60°C in a rotary plastic drum /novodur/ and subsequent washing of the quartz to remove the leaching acid, /7/ drying and delivery of the dressed product, /8/ neuralization of acidic waste water by hydraulic lime-

The dressed product should have the following composition:

	chemical composition	recalculate to oxides
Fe	0.0005%	0.0007%
Ti	0.0003%	0.0005%
Al	0.003%	0.0056%

Ca		0.0015%	0.0020%
Na		0.004%	0.0053%
K		0.0012%	0.0014%
Li		0.0003%	0.00064%
Mg		0.0003%	0.0005%
H_2O	0.06%		

Practically all melting and is sold on a near moisture-free basis and modern plants are equipped with either oil- or gas-fired rotary and/or fluid-bed dryers. Exclusive of mining, initial electric power requirements range from 0.75 to 1.75 connected horsepower per ton of product per day.

In evaluating any raw material resource, we must particularly know:

- chemical composition of the raw material and its processibility
- amount of economically exploitable reserves
- economically justifiable degree and technology of processing
- suitability of the processed product for practical purposes
- mining method and a sufficient water resource nearby
- methods of waste water and other waste products recycling

We must mention that variable quality of glass sand may result in great financial losses in the production. Therefore, the qualitative parameters must be continually monitored by thorough checks and chemical analyses in a laboratory whose equipment is rather costly. All these circumstances must be taken into account if a new glass sand deposit is to be evaluated properly.

The glass sand producer must respond with a melting sand that is /1/ virtually free of refractory minerals which are particularly objectionable in thin-wall container and sheet glass, /2/ screened to exacting specification /oversize quartz grains may remain unmelted, /3/ so beneficiated as to remove practically all components other than quartz.

Future prospects will, then, be concerned with raw materials of the best possible quality - a concern which will probably prove more difficult and surely more expensive to dispatch as markets and product lines are expanded.

3. Investment in Modern Glass Sand Plants

The following observations are pertinent:

1/ The cost of construction as well as the return of investment may be predicted with reasonable accuracy.

2/ Melting sand required by a major glassmaking operation will range from 50000 to 200000 tons/year but less often the larger tonnage.

3/ The development of prospects is solely the result of a significant increase in the demand for melting sand. It does not follow, however, that a given tonnage, area by area, will prove sufficient to warrant the investment.

4/ The minimal capacity is 150,000 tons/year melting sand. A modern glass sand plant might have a capacity in the range of 500000 to 100000 tons/year. Depending upon the nature of the raw material as well as the diversity of products, the cost of such an operation will range from 7 US$ to 15 US$ per ton of annual capacity.

5/ The silica prospect, if considered competent, will include a minimum of 20 years reserves.

By far the major tonnage of glass sand produced is taken from friable sandstones and unconsolidated sands.

The properties of the one body of principal concern to the investigator include /1/ chemical composition of the silica-bearing body, /2/ the nature and diversity of the component grains, and /3/ the grain-size distribution.

From the chemical viewpoint, iron-bearing impurities are particularly objectionable to the glassmaker. Iron oxides usually form either crusts or stains on quartz grains and id-ally should be so weakly bonded as to permit their removal by simple washing methods. Attrition /scrubbing/ is used to remove stubbornly-held crusts and films and in some cases, flotation may be used to remove iron-stained quartz. Again, ideally, clays and the small-size mineral fraction will have been reduced to an acceptably uniform level by the use of conventional washing methods and equipment. Apart from its use in the production of special purpose silica, flotation is seldom a necessary adjunct to the beneficiation of Lower and Middle Paleozoic sandstones. The last-mentioned rocks include a heavy mineral suite of relatively small proportion: this detrital assemblage is consistent in its composition and is rarely objectionable to glassmakers. Coastal plain sediments, and virtually all post-Paleozoic sources of silica sand contain a varied and commonly distinctive detrital mineral suite. This suite includes refractory minerals - particularly beryl, corundum, kyanite, sillimanite, spinel and topaz, which all can prove detrimental in glass melting. These refractories, generally larger than 80 mesh, may remain unmelted an become particularly damaging in the glass batch; ordinarily, the only remedy is flotation.

VII. SILICA-BASED BUILDING MATERIALS

The basic raw materials are silicious sands obtained either by mining of sandy deposits /sands, sandstones, spongilitic sandstones etc./, or as waste products of kaoline dressing /kaolinic sands/, ore dressing /flotation by/products/ or as waste silicious products of some industrial processes. The products can be divided into two groups:

a/ calcium silicate bricks
b/ light-weight building materials - foamed concrete and foamed silicate

The requirements put on the raw material for the first group of the products are limited to the SiO_2 content to be equal 70% /however, occasionally even materials with a lower SiO_2 content are advantageously used/ and to a certain degree of fineness /in case of need the raw materials are either sorted or ground/. The presence of some impurities, such as flotation reagents' remnants, is easily eliminated by various admixtures. The resulting products are characterized by a high strength and extraordinary esthetic properties /they can be used for unplastered walls/. Nonetheless, their thermal insulating properties are not so good.

The second group qualitative requirements are rather more strict /min. 90% of SiO_2, particle size under 1 - 2 mms, min. 50% of the total bulk under 0.5 mm; also, the contents of alkalies in the form of feldspar and mica are limited to 1.6% and the sulphur content to 1% of SO_3, respectively/. The products are very light and have favourable thermal insulating properties. However, their compression strength is usually lower. They are easily workable and suitable even for large-volume panel elements.

The individual manufacturing processes are characterized as follows:

1. Calcium Silicate Bricks Production

The manufacture of calcium silicate bricks can be divided into the four basic stages:

The first one includes the mixing and preparation /dressing/ of the raw material, its haulage into a plant and its grinding to the fineness required. It also comprises the preparation of calcium material. The used lime should be very fine, not dolomitic. The optimum fineness of the lime regarding the calcium lime process is declared to equal 2% of the oversize fraction for the 0.09 mm screen. The most suitable is the lime fired in rotary kilns as the firing process is suitably slow there. Namely, if higher temperatures are involved the lime gets overfired. On slaking, an immediate increase in temperature is required; within three minutes, at least 70°C must be achieved.

In the second stage the lime is slaked together with sand. The lime/sand mixture can be either pre-mixed in reactors and stored in hoppers prior to slaking itself /the duration of the slaking process depends on the lime quality/ or it can be slaked in the course of the mixing process. Sand: ground slaked lime ratio is adjusted at 92-94 : 6-8. During mixing, water is also added. The resulting mix is transferred to a reactor inside of which the slaked lime converts into calcium hydroxide. More water added, the mix is subsequently fed into another mixing machine and is ready to be pressed.

The third stage consists in the pressure-moulding of bricks. The ready mix is pressed under some 150 - 300 kp/sqcm into any chosen size. The pressing process can be divided into the four basic operations: filling of moulds, pressing, taking out of the pressed products from the moulds and their deposition onto cars, their feeding into autoclaves. Generally, automatic-feed presses are used for this type of work, such as the Universal II, Model 550, employed in the Příbram brickworks, whose capacity is 4000 bricks per hour.

The fourth stage is curing of the pressed bricks in special autoclaves. This operation is usually accomplished at 8 - 16 atmospheres and 175 - 210°C. It is only during this stage that a calcium silicate brick obtains its high strength preconditioned by the following calcium hydrosilicate formation:

$$/CaO/_x \cdot /SiO_2/_y - /H_2O/_z$$

The formation is effected by the reaction of calcium hydroxide, silicates and silica pressent in the siliceous sand used. During curing, the equilibrium state is not maintained and, therefore, a number of semiproducts, both amorphous and gelous and crystalline, are found in the material. Stable crystalline compounds are formed already at 100°C, their size not exceeding several microns. At 180°C, mainly rhombic tobermorite formation can be observed. Slab-like crystals of tobermorite are the agent influencing the high strength of calcium silicate bricks; therefore, the ultimate strength depends mainly upon the amount of this crystalline phase. Tobermorite originates in the whole range of the $CaO : SiO_2$ ratics used and the minimum temperature necessary to its formation is 115°C.

According to K.H. Büchler /1959/, the reaction takes place as follows:

Ist stage: partial decomposition of silica

IInd stage: formation of phases unstable against CO_2 action

$$SiO_2 + Ca/OH/_2 + X\ H_2O \longrightarrow Ca/H_2SiO_4/$$

$$2\ SiO_2 + Ca/OH/_2 + H_2O \longrightarrow Ca/H_2Si_2O_7/$$

IIIrd stage: formation of tobermorite

$$4\ Ca/H_2SiO_4/ + SiO_2 \longrightarrow /CaOH/2Ca_2/H_6Si_5O_{16}/$$

$$\text{or}\ 5\ Ca/H_2SiO_4/ \longrightarrow /CaOH/4Ca/H_6Si_5O_{16}/$$

IVth stage: long-term transformation of tobermorite into xonothlite

$$/Ca/OH/_2Ca_2/H_6Si_5O_{16}/ + Ca/OH/_2 \longrightarrow Ca_5/H_5Si_5O_{16}/ + 4H_2O$$

The fourth stage cannot be effected in practice as it requires a very long duration of the autoclave process.

According to Neuhaus and Gebhardt, the brick curing during the autoclave process takes place in two stages. The following phases were observed: calcite, aragonite, portlandite, tobermorite, xonothlite, truscottite and $CaCO_3$ x 2/3 H_2O. While calcite and tobermorite are always present, the representation of the other phases varies from sample to sample, depending on the production conditions.

The duration of autoclaving depends upon the processing pressure. If pressurized steam is used, the operation requires some 1.5 hours to accomplish. After the autoclave process has been completed, cars with cured bricks are transported by marshalling conveyors to a cooling station and, subsequently, are ready for delivery.

If waste products from ore dressing are employed as the raw material, which contain a small amount of flotation sulphides, the resulting bricks may be liable to scumming. According to Czechoslovak experience, the impurity can be eliminated by adding of baryum carbonate into the reactor. Free sulphate ions are bound to baryum and insoluble baryum sulphate originates, leaving no sulphur free to form scums. Another possibility of driving back this proneness is to add ground Fe oxides and graphite.

The technology described is capable of producing both standard and hollow bricks of various dimensions, according to customers´ requirements. The Příbram brickwork, for instance, produces the following items

	size	weight
calcium silicate brick, full	240x115x71 mms	3.8 kgs
calcium silicate brick, hollow	240x115x113 mms	4.5 kgs
calcium silicate block, hollow	240x175x113 mms	7.2 kgs

The bricks can be coloured by both artificial and natural dyes. The compression strength of a full brick is from 200 to 300 kp/sqcm, that of perforated bricks and hollow bricks is from 100 to 200 kp/sqcm.

Another plant producing calcium silicate bricks was built in Bzenec /SSR/ on the basis of Quaternary eolian sands. These sands are light-yellow-brown and rusty, their average grain size falls between 0.2 and 0.4 mm, with a coarser fraction up to 4 mms in diameter. For the major part, the sand is composed of quartz particles, with the admixture of feldspar and dark minerals. It is free of humine acid. The typical particle is angular and its corners are rounded. The plant produces:

calcium silicate bricks	290x140x65 mms	20 mil./year
perforated blocks VDK	290x240x113 mms	3.6 mil./year

It consumes:

sand	97300 cums/year
lime	14098 tons/year
water	4300 cums/year

2. Light-Weight Building Materials Based on Silica Sands

The production of light-weight building materials is virtually a new phenomenon within the construction industry. Generally, these materials are designated as porous concrete /foamed concrete/. They are permeated by numerous small pores and are characterized by a low bulk weight and a low coefficient of their thermal conductivity. Usually, the porosity is obtained by adding proper gas-forming or foaming agents. Cement and/or lime is used as a binding agent. These are also the criteria for their grouping. We can distinguish between gas concrete and foamed concrete on one side /if the binding agent is cement/ and gas silicates and foamed silicates on the other /if the binding agent is lime/. A typical feature of porous concrete is that it is produced from the mortar in which, besides binding and gas-forming /foaming/ agents, only fine-grained silica sands /which are usually even -round/ are employed.

An important part of the production of gas silicates, foamed silicates and most of gas and foamed concretes is autoclaving. During this operation, various hydrothermal reactions are encountered, resulting in the formation of various calcium silicates, one of most important of which is tobermorite. It usually constitutes tabular or leaf-like crystals whose size is approx. 1 micron and which are the main strength bearer of the material. Due to the kinetics of the hydrothermal reactions, tobermorite represent only a transitory mineralogical phase, gradually converting into xonothlite.

The raw materials used for the production of porous concrete:

-binding agents /lime, cement/
- siliceous materials /silica sand, sandstone, arenaceous marl, industrial wastes etc./
- gas-forming and foaming agents
- auxiliary raw materials

The requirements on the basic raw materials quality:

a/ Binding agents

Quick /burnt/ lime is the principal binding agents in the production of porous gas silicates. It must be a pure, airy lime. It is used fresh and quick and, therefore, its hydratation hea can be effectively utilized in the technological process:

The lime must comply with the following requirements:

- must come from a single locality
- must be soft-burnt and must not contain any overburnts
- must be rich, its content of unslakeables must not exceed 12%
- the total CaO content must be 90% at least /annealed state/
- most of the CaO should be free and active
- the MgO content should not exceed 5%
- the sulphide sulphur content should not exceed 0.2%
- the loss of ignition should range from 3% to 8% /the H_2O content must not exceed 3%, that of CO_2 5%/
- the slaking temperature should be min. 70°C, the duration of the process between 4 and 10 minutes /standard conditions : 50 gs of lime, 170 mls of water/

Regarding the production of porous concretes, it is most advantageous to employ lump, rich lime, soft-burnt at the temperature slightly over the theoretical value /1150°C at most/ which must be pre-ground for the production of porous concretes.

Cement is used only for some of the large family of porous concretes. All Portland clinker based cements can be used for the production of autoclaved porous concrete. Also, some special cements have been employed, such as the nepheline cement, which is produced in the U.S.S.R. from wastes of the aluminium industry. A certain amount of alkalies is not definitely detrimental. They must be present in soluble forms and in the following amounts: 0.8 to 1.0% of K_2O and 0.2 to 0.5% of Na_2O. They are helpful in adjusting the alkali environment necessary for the optimum gas formation initiated by a foaming agent /aluminium powder/. If not present naturally, alkalies must be added in the form of hydroxides or other alkali compounds.

b/ Siliceous Sands

In Czechsolovakia, either eolian sands or sands from kaoline washing are used. Of course, other siliceous raw materials, such as river sands, fine-ground sandstones, etc., can be used as well. The raw material should contain at least 90% of SiO_2. The content of alkalies /K_2O + Na_2O/ in the form of mica and feldspar must not exceed 1.6%, that of mica itself 0.5%. The quality of siliceous sands is deteriorated by the presence of pyrite, sulphites /S as total SO_3 should not exceed 1%/, and organic matter. In addition, the quality is greatly decreased if the limestone content is over 20%. If the amount of clay is higher than 1.5% it decelerates the curing process and worsens the strength properties of the porous concrete. In addition, the same phenomenon may result in crack formation.

An important factor regarding the ultimate strength of porous concretes. is fineness of the used sand. Sand delivered to the autoclave process should not have more than 10% or max. 15% of its total bulk left on a 2 mm screen. On the contrary, at least 50% should pass through a 0.5 mm screen. It is for purely economic reasons, as the sand must be ground so that 92% to 94% would pass through a 0.09 mm screen.

c/ Gas-Forming and Foaming Agents

Usually, 0.1 to 2.5 kgs of powder metal per 1 cum of porous concrete is used as a gas-forming agent. The metal is most often aluminium /typically 0.3 kg of Al/cum/. In addition, calcium, zinc, magnesium, baryum, lithium, ferrosilica, various blends of hydroxene peroxide and chloric lime, and usea are employed, too. The gases which initiate the concrete expansion are hydrogen, oxygen, nitrogen and acethylene.

The aluminium powder which is the most frequently used gas-forming agent must comply with the following criteria:

- its active Al content should be min. 94% and its variations should not exceed ±1%
- it should be as fine as possible as the finer the powder is, the quicker is the gas formation. All its bulk should be able to pass through a 0.09 mm screen: the oversize left on a 0.063 mm screen should be 35% at most; its specific surface should be between 4000 and 5500 sqcms/g /i.e. under 50 microns of the grinding size/
- the powder should be composed of uniform particles of a scale like appearance and should not contain any clods or spheroidal grains /they react worse/
- the content of fats should not exceed 1.3% /mineral oil is added because of safety reasons as it eliminates the danger of the aluminium powder self-ignition during transport/
- the humidity should not exceed 0.2%

d/ Other Admixtures

Gypsum is employed to improve the strength properties of the products while plaster is used for the time adjustment of the autoclave porous concrete curing. Calcium chloride is sometimes added if unreinforced porous concretes are to be produced. Sugar /technical or molasses/ is added into porous concretes and microporites to delay the beginning of the curing process. Natrium hydroxide is employed mainly in the production of cement gas concrete as it shortens the curing time and acts favourably on the benefit of the solution and chemical activation of silica particles. Water glass is occasionally used as a curing accelerator. Natrium sulphate has similar effects as NaOH. Glue stabilizes the structure of a porous concrete mixture. It also stabilizes the foam formation. Another substance having the identical effect is a glue-resinous emulsion added into gas concretes. Potash soap is used as a defatter of aluminium powder and as a stabilizer in the autoclave concrete production. Copperas /$FeSO_4$, $7H_2O$/ is added if the cement in a gas concrete mix is likely to contain chrome compounds. Also, it is a constituent of some foaming agents.

3. Technology of the Gas Concrete and Silicate Production

The productions of the two main types of light-weight building materials are virtually similar. They both consist of the following operations:

a/ Preparation and Processing of the Raw Materials

Sand is usually wet-ground to obtain sand mud whose bulk weight is 1.54-1.68 g/sqcm and its dry matter specific surface from 1300 to 2000 sqcm/g. A ball tube mill is used /balls made of manganese steel/. Lime is generally dry-ground in order to make use of its slaking heat in the presence of the siliceous component. On the contrary, cement used in the porous concrete production is not pre-dressed at all.

Gypsum is, similarly to lime, dry-ground. Other additives are usually distributed in solutions or suspension of known concentrations.

b/ Preparation of the Gas Concrete Mixture

The mixture composition is determined according to the technological process used and the properties required upon the final product. Typical for any type of light-weight gas concretes or silicates is that its compression strength depends to a great extent upon the bulk weight of the product. Individual components are dosed according to respective specifications in the following succession:

a/ sand mud
b/ plaster, sugar and various regulating additives
c/ part of the emulsion
d/ water
e/ cement /lime/
f/ aluminium powder and the remaining part of the emulsion

c/ Moulding

The term "moulding" designates the processes of casting and curing of gas concretes and silicates. It also includes other operations carried out in the production plant, such as reinforcing and cutting of various building elements. Various types of moulds are used which have been introduced by many companies, e.g. Siporex, Ytong, Durox etc. The mould length is typically fr. 3 to 6 ms, occasionally even 12 ms. In the moulding process, it is necessary to mainatin the specified temperature and the bulk weight of the mixture.

d/ Autoclaving

Prior to the autoclave process, the cast blocks is usually cut to elements having the dimensions required. These are subsequently processed in autoclaves. The success of the autoclave technology depends mostly upon the optimum choice of prope increase, duration and decrease of pressure. The highest autocla temperature is generally determined on the basis of the pressure of saturated steam /8 - 13 atm/. To ensure the quality of produc the autoclaving conditions must be continuously monitored and controlled. The process, therefore, requires sophisticated system of automatic steam pressure regulation, such as those which are computer-controlled.

e/ Storage and Delivery

As the products are fragile, extreme attention must be paid to their storagem delivery and transport. Palletization is often employed. The products must be protected from atmospheric impact namely from precipitations.

f/ Plant Capacity

In Czechoslovakia, plants either of 90,000 or 180,000 cums/ capacity are built.

4. Properties of Gas Concretes and Gas Silicates

The principal property of gas concretes and silicates is their low bulk weight which usually ranges from 500 to 1100 kgs/ The compression strength is proportionally related to the bulk we ranging from 20-50 kp-sqcm for lower bulk weight values to 80-12 for products of higher bulk weights. A less favourable quality o gas concretes and silicates is their high water absorption, whic ranges from 32 to 52% of their volume. Therefore, the products m be protected from atmospheric impacts.

Thermal properties, namely thermal conductivity, are very important. The lower the bulk weight of a product, the lower its thermal conductivity, i.e. [illegible] to the increase in the product porosity. The thermal [illegible] coefficient values usually do not exceed 0.10, 0.15, and 0.20 kcal/mh°C. Another important property is the fire-resistance. These materials are inorganic and able to withstand temperatures to 1100°C. They also have better acoustic properties than standard concrete; however, they cannot be used specially to damp sound spreading in constructions. In addition, gas concretes and silicates are easily workable /can be cut to various dimensions/.

A similar technology can be used for the production of light-weight building materials from diatomite. However, the choice of possibilities is much wider here. Autoclave curing can be employed. To improve mechanical strength, sawdust is added. Also, these products can be fired at temperatures up to 1000°C. A very light building material can be thus obtained whose mechanical properties are, however, worse. These materials are advantageously used as thermal insulations in various heat units /furnaces etc./.

Recently, there have been introduced a number of inorganic building materials on the basis of silica and plast combinations. These materials usually fulfil the requirements put on their mechanical and thermal insulating properties. However, a more detailed report is outside the scope of my lecture. In addition, it is necessary to mention other raw materials, such as volcanic tuffes, tuffites, light lavas, natural pumice, calcareous tuffas, spongilites etc., and industrial wastes, such as ashes. The family of light-weight building materials represents a progressive trend in the building materials production.

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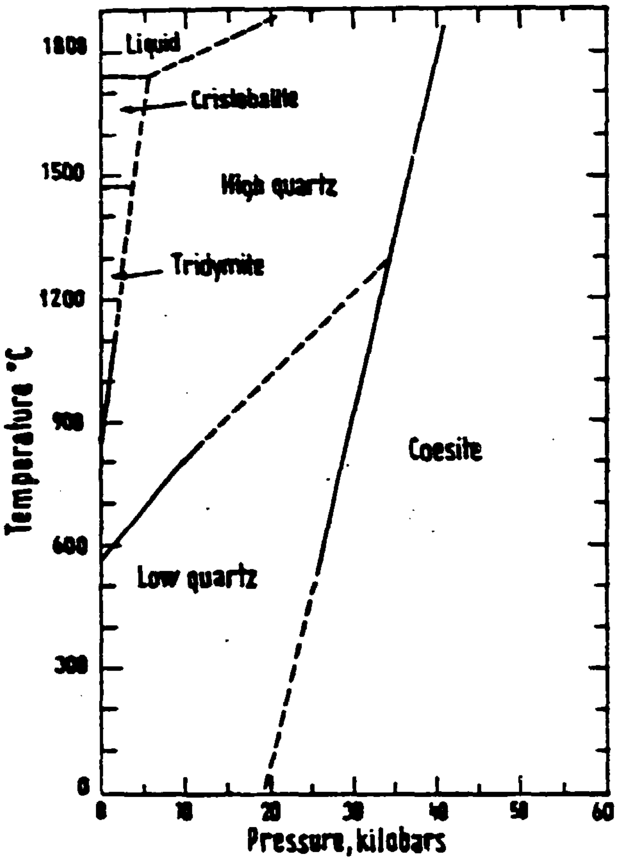

Fig. 1. Pressure-temperature diagram for SiO_2 polymorphs

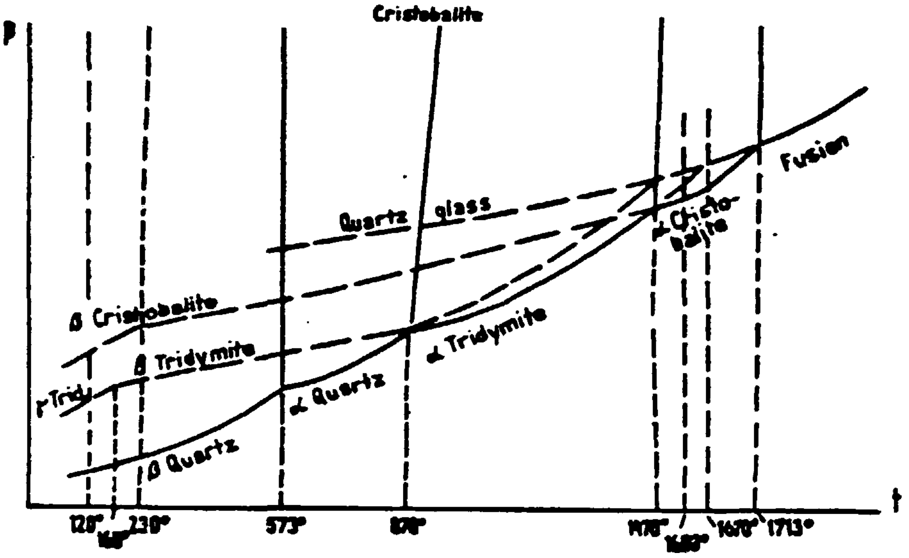

Fig.2. Idealised phase diagram of SiO_2 system

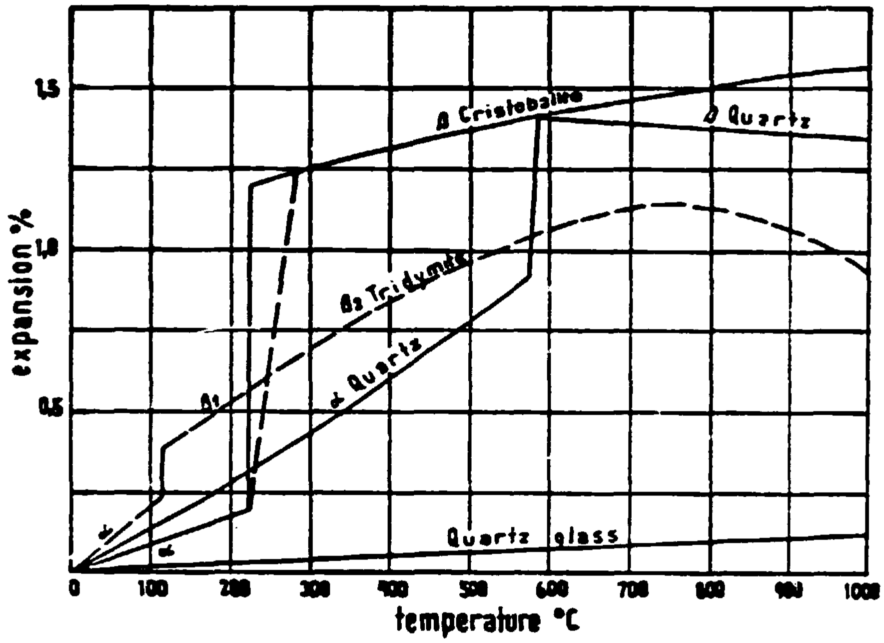

Fig. 3. Thermal expansion of silica minerals /Le Chatelier/

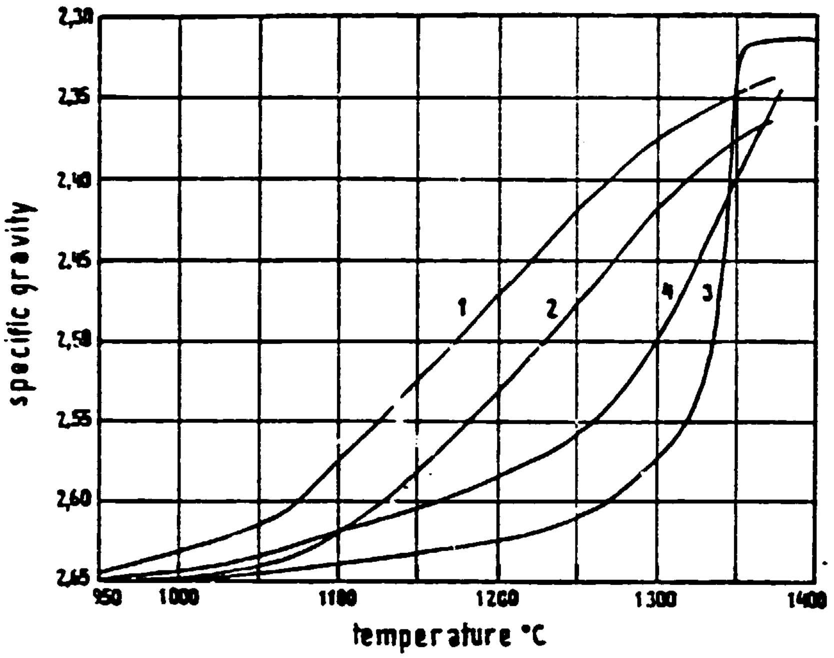

Fig. 4.

Inversion-temperature rolations for various silica rocks /Lynam T.R./

1/ Silcrete

2/ Welsh quartzite

3/ Chalcedonic type

4/ Coarse-grain quartzite of high purity

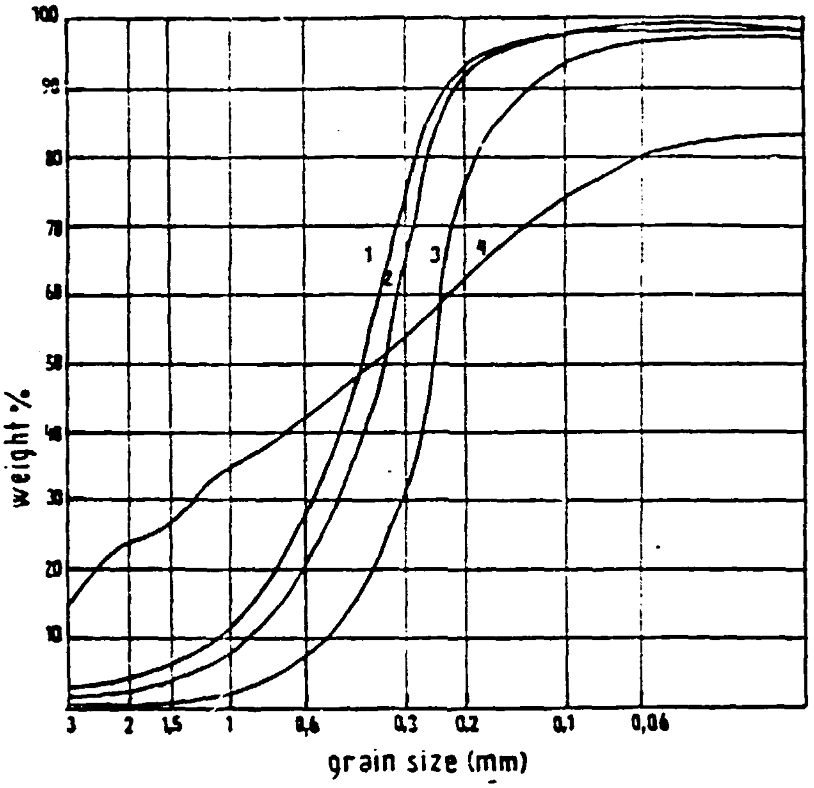

Fig. 5. Granularity curves of Czechoslovak glass sand deposits.

1 - Provodín, 2 - Srní, 3 - Střeleč,
4 - Velký Luh