Technology of refractory materials and heat insulating materials

Study Support

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1. CLASSIFICATION OF REFRACTORY MATERIALS .......................... 4  
   1.1 Basic terms .......................................................................................... 4  
   1.2 Incorporation and classification of refractory materials (RM) as ceramic products .......................................................... 4  
   1.3 Classification of refractory materials ....................................................... 5  

2. METHOD OF TESTING AND CHARACTERISTICS OF REFRACTORY MATERIALS .............................................................................. 7  
   2.1. Criteria of dense.................................................................................... 7  
   2.2. Mechanical characteristics .................................................................... 9  
   2.3. Thermal properties .................................................................................. 10  
   2.4. Thermomechanical properties ................................................................. 13  
   2.5. Thermomechanical and thermophysical properties ................................. 14  

3. ALUMINOSILICATE MATERIALS (SILICA) ........................................ 16  
   3.1 Silica ....................................................................................................... 16  
   3.2 Manufacture of shaped refractory materials .............................................. 17  

4. FIRECLAY AND HIGH ALUMINA ....................................................... 19  
   3.3 Basic terms ........................................................................................... 19  
   1.1. System SiO₂ – Al₂O₃ .............................................................................. 19  
   1.2. Aluminosilicate raw materials ............................................................... 20  
   1.3. Technology of production of compact shaped fired aluminosilicate products ................................................................. 23  
   1.4. Combined products containing aluminosilicate ...................................... 25  

5. BASIC REFRACTORY MATERIALS ......................................................... 27  
   5.1 Basic terms ........................................................................................... 27  
   5.2 Magnesium oxide – periclase ................................................................... 27  
   5.3 Sources of mgO and production of sintered magnesia ............................. 27  
   5.4 Periclasis carbon refractory materials .................................................... 29  
   5.5 Magnesite – dolomite products .............................................................. 30  
   6.1 Magnesite – chrome products ............................................................... 31  

6. HEAT INSULATING REFRACTORY MATERIALS ................................. 32  
   6.2 Technology of production of porous materials ........................................ 32  
   6.3 Castable .................................................................................................. 33  
   6.4 Heat insulating fibrous materials ............................................................. 34  

7. LITERATURE ......................................................................................... 38
INSTRUCTIONS FOR STUDYING

You have received study materials for extramural studies for the subject Refractory materials and heat insulating materials of 2nd semester of following master’s study field.

PREREQUISITES

There are no prerequisites set for the studies of this subject.

AIM OF SUBJECT AND OUTPUTS OF STUDIES

The aim is to gain knowledge about the classification of refractory and insulation materials, their chemical and physical properties, conditions for their use and application. After studying the module, the student should well-versed in the use of suitable refractory materials and thermal insulation materials for the type of equipment in practice and be able to design the possibilities of solving their application.

AFTER STUDYING OF THIS SUBJECT, STUDENT SHOULD BE ABLE TO:

Outputs of knowledge:
- Student will be able to recognize refractory material
- Student will be able to characterize refractory ceramic material and will be use to praxis

Outputs of skills: for example
- Student will be able to analyze classification signs of refractory materials
- Student will be able to divide refractory materials according to their characteristics
- Student will be able to decide about application of refractory ceramic materials in practice

WE RECOMMEND THIS PROCEDURE DURING STUDYING OF EACH CHAPTER:

To understand stated text, to look for further information in recommended literature and to study stated problematic.

WAY OF COMMUNICATION WITH EDUCATORS:

Educator will give assignment of semester project for given topic from the area of economics and management at the beginning of the semester. Project will be checked by educators within two weeks after handover and results will be sent to students by email through the IS EDISON.

CONSULTATIONS WILL BE WITH GUARANTEE OF THE SUBJECT OR WITH LECTURER

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1. **CLASSIFICATION OF REFRACTORY MATERIALS**

### Time for studying

4 hours

### Aim

- general knowledge of the definition of refractory materials and basic terms in the field of this special grade of ceramic materials and products,
- find explanation of using selected oxides for production of refractory materials,

### Definition

#### 1.1 BASIC TERMS

Refactory materials (RM) are defined:

- As inorganic non-metallic materials,
- Their refractoriness is $\geq 1500^\circ$,
- They belong to coarse-grained ceramics,
- Their microstructure is composed of large grains,
- The basis of body is coarse-grained grog joined by fine materials,
- They are mainly used as refractory lining for furnaces and heat installations.

#### 1.2 INCORPORATION AND CLASSIFICATION OF REFRACTORY MATERIALS (RM) AS CERAMIC PRODUCTS

Refactory products are a specific sort of ceramics that differs from any “normal” ceramics mainly with their coarse-grained structure being formed by larger grog particles joined by finer intermediate materials (bonding).

**Basic characteristics of refractory materials (RM):**

- Ability to withstand high temperatures,
- All solid phases that occurred in larger quantities have got higher melting temperature than the temperature of use is,
- At this temperature a liquid alloy may occur only in such amount and with such viscosity to prevent any deformation,
- Vast majority of the refractory products create oxides and their combinations,
- High melting point and thermodynamic stability at high temperatures are necessary there.

The highest melting temperatures from the well-known compounds have got carbides, nitrides, borides and oxides. From these oxides listed above only six oxides are of great significance to industrial production of refractory materials: $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{MgO}$, $\text{SiO}_2$, $\text{Cr}_2\text{O}_3$, $\text{ZrO}_2$, and their compounds, some combinations of oxide-containing components with carbon, or with covalent compounds, namely with SiC. Possible combinations are shown in the pyramid of basic components and compounds by Barthel.
1.3 CLASSIFICATION OF REFRACTORY MATERIALS

Refractory materials are classified namely according to the content of major components, i.e. according to their chemical composition as follows:

Classification of refractory materials can be briefly summarized as follows:

1. **According the principal base features**:
   - Oxide-containing → they are namely based on oxides and their compounds, the most important oxides are $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{MgO}$, $\text{SiO}_2$, $\text{Cr}_2\text{O}_3$, $\text{ZrO}_2$.
   - Non-oxide ones → carbon-based refractory materials, and carbides, nitrides, borides, silicides. This group included also sialons – the silicon nitride sinterable derivatives.

2. **According to the content of major components, i.e. according to their chemical composition**:
   - acid → as the main phase they contain $\text{SiO}_2$ (silica, low alumina fireclay),
   - alkaline (basic) → as the main phase they contain $\text{CaO}$, $\text{MgO}$ (magnesite, periclase, chrommagnezite, dolomite, etc.),
   - neutral → as the main phase they do not contain either $\text{SiO}_2$ or $\text{CaO}$ and $\text{MgO}$, but $\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$, $\text{Cr}_2\text{O}_3$, C (fireclays, corundum, mullite, carbon materials).
3. **Besides chemical composition there are other aspects according to which the refractory materials can be classified:**
   - Shaped products → piece products which are characterized by a precisely defined shape (bricks, slabs, blocks, fittings, wedges,...),
   - Unshaped products → fibrous linings, some mixtures from which a monolithic lining can be created (fluid mixtures, crushed materials).

4. **Another possible classification by compactness (porosity):**
   - Dense refractory product is material with their true porosity less than 45%,
   - Insulating refractory materials material with their true porosity more than 45%.

5. **By their heat-resisting quality:**
   - Refractory 1580 – 1770 °C
   - Highly refractory 1770 – 2000 °C
   - Extra-high refractory above 2000 °C

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### Summary of terms

- refractory oxides,
- refractory material, refractory product,
- classification of refractory materials, classification criteria,

### Questions

- Define the term the “refractory material”.
- How are the refractory materials different from other kinds of ceramic materials?
2. METHOD OF TESTING AND CHARACTERISTICS OF REFRACTORY MATERIALS

Section 2

Time for studying

6 hours

Aim

- be well versed in methods of testing of refractory materials,
- familiarize yourselves with single tests, included criteria of compactness, mechanical and thermal properties, and so on

Definition

2.1. CRITERIA OF DENSE

Compactness means a grade of filling the space with solid phases and it is expressed in percentage of the volume of solid phases, or as a proportion of volume weight to density. Unfilled spaces, i.e. pores in refractory products, reduce weight of a volume unit, enlarge surface of solid phases, and thus significantly affect mechanical and thermal characteristics and resistance to chemical effects of the environment. The quantity, as well as the shape of pores is determined by the technological process of manufacture.

When evaluating the compactness criteria there shall be measured:

- number of pores (open, closed, both),
- size of pores,
- continuity of pores.

Number of pores

Number of pores can be characterized by the following criteria:

- **Absorptivity** (NV) – Proportion of the weight of absorbed water to the sample weight expressed in percentage by weight of a dried sample:

  \[ NV = \frac{m_w - m_s}{m_s} \cdot \frac{\rho_n}{\rho_m} \cdot 100 \ (\%) \]

- **Apparent porosity** (PZ) – Proportion of the volume of open pores of a testing sample to its volume, including pores and cavities expressed as a percentage of the volume of a sample:

  \[ PZ = \frac{m_w - m_s}{m_n - m_m} \cdot \frac{\rho_v}{\rho_m} \cdot 100 \ (\%) \]

- **Volume weight** (OH) – volume weight of a dried sample inclusive of open and closed pores being expressed in g.cm\(^{-3}\):

  \[ OH = \frac{m_s}{V} = \frac{m_s}{m_n - m_m} \cdot \rho_v \ (\text{g.cm}^{-3}) \]
- **Density** ($\rho$) – weight of the sample volume unit without pores being expressed in g.cm$^{-3}$:

$$\rho = \frac{m_s}{V_0} \text{ (g.cm}^{-3}\text{)}$$

- **Apparent porosity** (ZH) – weight of the sample volume unit inclusive of closed pores being expressed in g.cm$^{-3}$:

$$ZH = \frac{m_s}{m_s - m_n} \cdot \rho_{w, v} \text{ (g.cm}^{-3}\text{)}$$

- **True porosity** (PS) – proportion of a volume of the sample open and closed pores to its volume inclusive of pores being expressed in the sample volume percentage:

$$PS = \left(1 - \frac{OH}{\rho}\right) \cdot 100 \text{ (\%)}$$

Where:

- $m_s$ weight of a dried sample (g)
- $m_n$ weight of a sample saturated by a liquid and weighed in air (g)
- $m_{n,v}$ weight of a saturated sample weighed in a liquid (g)
- $\rho_w$ density of water (g.cm$^{-3}$)
- $\rho_n$ density of a liquid for saturation (g.cm$^{-3}$)
- $\rho_v$ density of a liquid for hydrostatic weighing (g. cm$^{-3}$)
- $\rho$ density of material (g. cm$^{-3}$)
- $V$ sample volume, including cavities and pores (cm$^3$)
- $V_0$ sample volume without cavities and pores (cm$^3$)

To determine quantity of pores in compact shaped building materials / pieces refractories: dried and weighed samples shall be saturated by water applying vacuum (while hydrating substances by other liquid), then they shall be weighed and their absorptivity will be calculated. The volume of samples shall be determined by hydrostatic weighing and then their volume weight, apparent porosity and apparent density will be calculated.

**Size of pores**

Study of pores with regards to distribution of their sizes is of great significance when examining processes of corrosion and resistance to sudden temperature changes of refractory materials. There are used methods of the capillary depression of mercury and / or capillary elevation of water.

**Continuity of pores**

Continuity of pores in refractory products is reviewed and assessed by determining gas permeability which is defined as a property of porous bodies to leak gas at a gas pressure difference on the opposite sides of a body.
2.2. MECHANICAL CHARACTERISTICS

Due to action of external forces there some tensions can arise in rigid bodies which cause their deformation. When a body can behave elastically, deformation ($\varepsilon$) is directly proportional to tension ($\sigma$):

$$\sigma = E \cdot \varepsilon$$

where: $E$ is modulus of elasticity (Pa)  
$\varepsilon$ is deformation (1)

In real refractory materials the direct proportionality between acting tension forces and induced deformation is not mostly true. As a consequence of the structural heterogeneity there are both elastic and inelastic (non-recoverable) deformations due to acting external forces. With rising tension forces the rate of inelastic deformations usually rises too. This deformation is mostly time-dependent, i.e. the determined strength and particularly elasticity always depend on test conditions, namely on the rate of rise of the acting tension.

**Strength**

Thanks to their strength the refractory materials must withstand without breaking any tension occurring during their manufacture, transport, but particularly during their use. Within the operation of thermal installations in the lining the compressive stresses can arise due to weight of the masonry or due to gripping by thermally expanding linings in the steel casing, or due to tensile and shear stresses in the unevenly heated masonry as a consequence of thermal expansion/dilatation of materials. According to the strength values it is possible to judge other characteristics of the products, such as abrasion resistance.

1. **Compression strength (PTL)** – acting force (F) per unit of a testing piece (S) cross section at the moment of its crushing down.
2. **Bending strength ($\sigma_b$)** – stress at which a testing piece subjected to bending stress is broken. There is used a three-point bend, the testing piece is placed on two supports and in its midpoint it is loaded evenly with rising force.
3. **Torsion strength (in torsion)** – when exposed to shearing stresses this test is used only rarely for refractory materials. The torsion method is mainly used when determining the shearing modulus (G) and stress relaxation at elevated temperatures.
4. **Compression strength - tearing** – it is not determined at refractory materials by means of this test. However, the method of determining tensile splitting strength on rollers or rings is applicable there. When pressure forces act on a cylindrical part of the testing piece surfaces the maximum tensile strength evolves in the middle of the roller or on the inner side of the ring and the testing piece breaks in the direction of the tensile forces acting.

**Elasticity**

The modulus of elasticity belongs to important material constants of refractory building materials. Its knowledge is needed for:

- calculations of designs of refractory linings,
- determining permissible rates of heating,
- cooling refractory products,
determining the resistance to sudden changes of temperatures.

As for using it is desirable so the values of modulus of elasticity of refractory building materials would be as low as possible. High values of the E – modulus indicate a reduced ability of building materials to deform elastically. These materials are more prone to cracking when exposed to temperature changes.

2.3. THERMAL PROPERTIES

Refractoriness

The refractoriness shall be determined with the aid of comparative methods. Simultaneously there are heated up a testing pyrometric cone and the standard one finding out the pyrometric compliance \( \rightarrow \) the identical pyrometric deformation of both testing and standard pyrometric cones at the known temperature of the pyrometric deformation. The pyrometric cones shall be heated according to the conditions stipulated in the standard, in the crucial thermal zone the velocity of \( 2.5^\circ C \cdot min^{-1} \) to bring to such temperature at which the pyrometric cone will bend. The pyrometric deformation is achieved at the moment when the pyrometric cone will bend over in an arc touching with its tip the horizontal base pad to which it is usually stuck. Laboratory pyrometric cones are of a triangular shape with the height of 30mm and with the edges of the lower base 8 to 9 mm and the upper base 2mm, approximately. The refractoriness of testing pyrometric cone is stated by the number of the standard pyrometric cone of the same pyrometric deformation equal to pyrometric deformation in degrees centigrade divided by ten (e.g. the pyrometric cone with the number 158 has got temperature of pyrometric deformation \( 1580^\circ C \)). Even though it is not possible to determine a temperature of refractory material suitability and applicability that can be significantly lower, it is a very useful test applicable and usable namely for evaluation of aluminosilicate raw materials, semi-products and final products.

Dimensional changes when heated

Heating-up causes reversible or irreversible changes of the refractory material dimensions

- Reversible dimensional changes – they are namely caused by change of the distance of single atoms in a solid substance due to thermal energy increase (in general - with raising temperature interatomic distances enlarge too), or these are reversible phase transformations.
- Irreversible dimensional changes – they are caused namely by sintering processes, as well as by irreversible phase transformations in refractory materials.

Reversible volume changes can be detected by thermal expansion determining, irreversible changes can be find out by determining permanent changes on heating.

Thermal expansion

Thermal expansion is most often determined by methods based on measurements of changes in length of the testing piece when it is evenly heated up. From the results of measurements there are calculated:

\[ a) \text{coefficient of mean longitudinal thermal expansion (KTR)} \ - \ \alpha_{t_1 \ t_2} \text{ defined as a change of the unit of the piece (}\Delta l\text{) related to the original length (}l_0\text{) at the temperature change by 1}^\circ \text{C in the given temperature range:} \]

10
The relative linear temperature expansion (\(D_{t_1 - t_2}\)) should express the percentage change of the testing piece length (\(\Delta l\)) to its original length (\(l_0\)) when heated in the given range of temperatures:

\[
D_{t_1 - t_2} = \frac{\Delta l}{l_0} \cdot 100 \quad \text{(\%)}
\]

The method of determination of the linear temperature expansion for refractory materials is specified in the Standard ČSN 72 6031. For determining, there are used testing pieces with the length 50 to 120 mm in the shape of a roller of its diameter 25 mm, as a maximum, and/or a prism of its cross section max. 20*30 mm. The testing piece is to be heated at a constant speed, that is \(5^\circ \text{C.min}^{-1}\) as a maximum, and temperature is measured with accuracy of \(\pm 5^\circ \text{C}\) (above 1000°C \(\pm 10^\circ \text{C}\)), and changes in length with accuracy of 0,01% of the piece length.

The thermal expansion depends on expansion of individual phases that are present in refractory materials, however, these are not additive quantities. Knowledge of thermal expansion is very important when designing any refractory linings, mainly in the aspect of dilatation joints sizing, as well as when calculating stress and strain states of linings. In addition to the above mentioned facts also resistance to sudden temperature changes depends on thermal expansion.

**Permanent changes on heating**

In general the refractory materials shall provide the greatest possible dimensional stability at long-term exposure to high temperatures. At high temperatures and the burnt building materials have tendency to further shrinkage during sintering process or they may expand due to phase transformations. Dimensional stability of refractories at high temperatures but without mechanical strain shall be checked by the method of determining permanent changes on heating. The ground of the testing technique is warming-up measured testing pieces using the prescribed procedure in a furnace with oxidizing atmosphere up to the defined temperature with the defined dwell time. After cooling down and re-measurement permanent changes should be calculated, such as shrinkage / negative value/, or expanding /positive value/.

Permanent changes on heating depend mainly on testing temperature and the dwell time. Testing temperature is prescribed individually for single kinds of products. The dwell time at the maximum temperature is prescribed in the ISO standard for compact products and it is 5 hours (or 12 or 24 hours), according to the ČSN standard it shall be 2 hours, at least. Lightweight products shall be exposed to the prescribed temperature for 12 hours.

Permanent changes on heating are the basic indicators of quality of refractory building materials. The knowledge of permanent changes on heating is necessary when designing refractory linings and estimating maximum permissible temperatures for using refractory building materials, and for dilatation joint sizing at further expansion. When using the results of measurements it is necessary to keep in mind that further shrinkage or expansion of refractories under isothermal conditions.
conditions depends on time, hence due to the limited temperature dwell time it is only possible to approach the maximum values of linear changes.

**Thermal conductivity**

*Thermal conductivity* is defined as a density of heat flow at the given temperature gradient and it is expressed by the coefficient of thermal conductivity \( \lambda \) (W.m\(^{-1}\).K\(^{-1}\)) being defined as the amount of heat \( Q \) in joules (J) that passes per the unit of time (s) through the unit layer of material (m) with the unit cross section (m\(^2\)), at the unit temperature difference (K).

The coefficient of thermal conductivity is:

- very important physical constant for refractory building materials,
- necessary for calculations of heat transfer through refractory linings,
- necessary for calculations of permissible rates of heating,
- necessary for cooling of refractory building materials,
- necessary to assessing the resistance to sudden temperature changes.

The thermal conductivity of porousless crystalline substances usually decreases with increasing temperature, while the thermal conductivity of glasslike substances increases.

The thermal conductivity of real refractory materials as heterogeneous systems comprising crystalline and glassy phases and pores depends mainly on the porosity and on the phase composition. The porosity significantly reduces thermal conductivity, especially at low temperatures. At higher temperatures (above 600 to 800°C) the porosity influence is lesser, because the heat transfer by radiation is applied to a greater extent.

The coefficient of thermal conductivity of refractory materials at higher temperatures can be determined in more ways which can be sorted as *absolute* (heat flow is measured directly), *comparative* (heat flow is measured with the aid of a comparative body which thermal conductivity is known), as well as *stationary* (measurements at constant heat flow), and *non-stationary* (heat flow changes with time).

**Specific thermal capacity**

The specific thermal capacity is defined as an amount of heat required for heating a mass unit of material by the unit of thermal difference that is expressed in J.g\(^{-1}\). K\(^{-1}\).

Good knowledge of values of a specific thermal capacity of refractory materials is required for calculations of accumulated heat in linings, as well as for calculations of non-stationary heat transfer through linings. The specific thermal capacity depends on phase composition, however, it is an additive value, which means that the specific thermal capacity of a multiphase system can be calculated on the basis of specific thermal capacities of individual phases. The specific thermal capacity is mainly determined with the aid of calorimetric methods. It can be calculated from values found out when measuring thermal conductivity, using a method of wire warming at parallel arrangement.

**Thermal conductivity**

*Thermal conductivity* is characterized by the rate of change of thermal field in solid bodies. The thermal conductivity (\( \alpha \)) of ceramic (porous) materials can be calculated from the thermal conductivity (\( \lambda \)), volume weight (OH) and the specific thermal capacity (c) according to the following formula:
\[ a = \frac{\dot{\lambda}}{OH_C} \quad (m^2.s^{-1}) \]

As for (porous) ceramic materials there the density is to be substituted by the volume weight \((\rho v, OH)\).

### 2.4. THERMOMECHANICAL PROPERTIES

Refractory materials are used at very high temperatures at which some inelastic, thus irreversible and time dependent deformations begin to occur markedly.

**Methods for determining thermomechanical properties**

That is why the thermomechanical behaviour of refractory materials shall be evaluated on the basis of examination of correlation of four quantities:

- **tension**
- **deformation**
- **temperature**
- **time**

When increasing the load evenly, that means the tension in a testing piece at constant temperature it is possible to determine strength. And when recording simultaneously stress and strain states it is possible to calculate the modulus of elasticity, or to define some inelastic behaviour. Uniform rise of temperature at constant load makes determination of resistance to deformation and peak heat load capacity possible. By measuring deformation in dependence on time and with constant load and constant temperature it is possible to determine creeping. By this test it is possible to determine quantitatively the size of inelastic deformations during long-term mechanical stress of refractory materials at high temperatures. Measurements of stress relaxation at rising temperature is limited to cases where constant deformation can be kept, because thermal expansion of a material allows it (e.g. it is not the case of torsion). Determination of strength at uniformly increasing deformation is a very useful test, by which the material reversibility capacity, that is, the ability to deform without destruction can be assessed and evaluated.

**Rheology of refractory materials at high temperatures**

Rheology – it is a discipline dealing with plastic properties of real materials. Its task is the mathematical expression of relations between the stress and strain in relation to time. These relations are to be evaluated focusing on behaviour of refractory materials at high temperatures. Thermomechanical measurements indicate that at high temperatures the refractory materials behave as viscoelastic solid bodies, that is, partly as elastic materials deforming according to Hooke’s Law of elasticity, with the very well-known relation between the stress \((\sigma)\) and the strain \((\varepsilon)\): \( \sigma = E \varepsilon \)
, where \(E\) is the modulus of elasticity, and partly as the Newtonian fluids with the following relation between the stress and strain:

\[ \sigma = \eta \varepsilon \]

where: \(\eta\) ... viscosity.
**Thermal shock resistance**

In the refractory product thermal gradients induce tension caused by different changes in the length. Resulting thermal stresses can disrupt the structure of building material. Resistance to this disruption is called the resistance to sudden thermal changes.

Refractory materials can ensure very good resistance to cracking if they have got:

- high strength,
- high temperature, resp. thermal conductivity,
- low modulus of elasticity
- low coefficient of thermal expansion.

Refractory building materials are heterogeneous systems consisting of crystalline and glasslike phases and pores, while the pores can be the sources, “the germs” of cracks. The resistance to temperature changes should be therefore assessed not only with respect to formation of cracks, but also with respect to their enlarging.

### 2.5. THERMOMECHANICAL AND THERMOPHYSICAL PROPERTIES

When using the refractory materials they are exposed to chemical and physical effects of ambient environment. At high temperatures some mutual reactions may occur among solid bodies, i.e. the linings, and liquid, and even gaseous substances presented in a furnace interior and exterior that may cause wear – corrosion of refractory materials. In the given case, the corrosion caused by melts is a complicated thermomechanical and thermophysical process. The basic chemical phenomenon there is the interaction between some components being contained in refractory materials and some component being contained in corroding melts (slag, molten glass). This reaction depends on a chemical composition of refractory materials, as well as a melt. The corrosion of refractory and heat insulating materials always consists in chemical reactions in polycomponent systems, but because there are no equilibrium diagrams available for estimation of mutual reactions it is necessary to use simplified, three-component or four-component systems at the most which contain basic components of refractory materials and a melt. However, it is true, that a smaller reactivity is in systems in which both mutually reactive substances are chemically related ones.
Summary of terms

- mechanical, thermomechanical, properties,
- thermal conductivity, thermal shock resistance, thermal expansion, refactoriness, strength,

Questions

1. How the testing methods of refractory materials can be classified? Give reasons for using selected oxides of a larger set of high-melting oxides for manufacture of refractory ceramics.
3. ALUMINOSILICATE MATERIALS (SILICA)

Time for studying

4 hours

Aim

- to define process for production of silica
- to describe technology of production of silica

Definition

3.1 SILICA

Silica is fire-resistant material which contains more than 93 % SiO₂. It is typical representative of acidic fire-resistant. It is produced from natural silica containing around 96% SiO₂ mostly in the form of silicae, which during firing changes by decreasing of density into cristobalite and tridymite. It is fired at temperature providing polymorph changeover of silicae (SiO₂) into tridymite and cristobalite. This is besides rests unchanged silicae first crystal phases of product, which is produced during volume expansion, or by growth of porosity during firing. By sintering there are volume changes by modifications of SiO₂.

Raw materials

- basic: silicae, sands, ganister fractions, cobbles
- helping raw materials: lime or lime hydrate (binder)
- plastificators which enhance processability of production mixture, for example sulphite lye,
- mineralisators for quickening of changeover of silicae into high-temperature modifications.

Typical characteristic of silica

- acidic character, resistance against acidic melt
- besides fire-resistance it also has positive fire-technical characteristics – resistance against deformation in heat, capacity in heat (also above 1680 °C),
- high resistance against sudden changes of temperatures above 600 °C,
- high volume stability or (at lower level of changeover) tendency for additional expansion by high-temperature use (compared to further shrinkage which is common by other FRM).
Low resistance against changes of temperature above 600°C, caused by volume changes by modification of SiO₂, lack of suitable raw materials and damaging effects on human organism during its production (silicosis).

Combination of advantageous characteristics makes ganister a classic material for self-supporting vaults of furnaces for high temperatures. While in steel furnaces was ganister in this direction substituted by basilar materials, it is even today important material for vaults and some parts of walling of glass melting furnaces. For walling of places of thermal aggregates which are very stressed as are vaults and walls of furnaces and glass furnaces, for walls of coke ovens, regenerators (for example heaters of air for blast furnaces), electric arch furnaces and also for example in sintering belt of rotation furnaces by production of cement.

3.2 MANUFACTURE OF SHAPED REFRUCTORY MATERIALS

At present some ternary mixtures are prepared principally. As an inorganic binder there is the calcium oxide CaO. Into mixtures it is added as a milk of lime. A sulfite waste liquor from the cellulose production as an additive to the milk of lime is its efficient liquefying agent. It also ensures the necessary mechanical strength of mouldings. At present it is mostly used a dry powder hydroxide instead of milk of lime and the mixture is to be re-moistened with the sulfite waste liquor. Content of CaO in products is 1,5 - 3 %. Besides to CaO also iron oxides, ferrosilicon and other substances are added into mixtures as mineralizers for controlling conversion of the quartz to tridymite that is in a majority dinas kinds the most desirable modification of SiO₂.

The mixtures are moulded under pressure of 30 – 50 MN.m⁻² of the surface of mouldings with using hydraulic, friction, impact-action presses, and vibration presses, etc. at moisture of 4 - 5%. Due to hardness of quartzites and the mould wall high friction the moulding under applied pressure higher than 50 MNm⁻² can be connected with high maintenance costs and very short lifetime of the mould. However, it is used in manufacture of building materials because there high compactness, mechanical strength and thermal conductivity are the primary requirements.

The mouldings are dried in periodical or continuous drying kilns with warm air gained from burning kilns during cooling the products. The key section of the dinas technology is firing of mouldings. Specific courses of polymorphic conversions and related changes in volume do not allow to implement any universal regime applicable to each kind of quartzite. Enlarging of mouldings, usually by 2 - 3,5% linearly, is the result of several factors acting. Fired wastes of dinas as a part of moulding mixtures can reduce the enlarging of moulding during firing, but they increase porosity of mouldings and products, because the porosity is greater than the porosity of quartzites. Therefore their using for preparation of moulding mixtures is limited. After drying the mouldings are to be fired in tunnel kilns usually 200m long or in truck kilns of their effective volume up to 250m³.

The truck kilns built up to effective volumes of 250 m³ are provided with a heating system with nozzle burners with high flow rates of gases, with intense delivery of heat to moulding being fired. In early stages of firing, at low supply of fuel, there is used multiple air excess in order to ensure above mentioned high flow velocities of gases in the charge. The temperature is increased progressively by refuelling while leaving the amount of air. This procedure shall be kept up to maximum temperature, that is 1430°C-1470°C. When cooling the fuel supply shall be reduced while leaving the amount of air up to temperature range of 350°C - approximately, and then due to some displacive conversions it is necessary to use a special method of cooling slowing down.
The moulding firing is a complex process. The matrix that contains almost the entire amount of added CaO as a binder, 4 - 8%, and moreover even mineralizers and a greater part of accompanying minerals shrinks and becomes compacted thanks to sintering in the presence of the liquid phase. Without it, the bonds among particles of quartzite could not create at normal temperatures and times of firing. The brick would not acquire sufficient mechanical coherence and would crumble. As for the volume changes, the conversions of SiO₂ are realized through processes of contrary sintering, so in fact the moulding cannot become more compacted by way of firing.

For linings of exposed parts of metallurgical and glass furnaces there is used the silica, with sufficiently low porosity at the low contents of Al₂O₃ and alkali. For linings of high-temperature air heaters and as a part of heat transfer fillers there is used dinas with its thermo-mechanical properties at the previous level, with only low additional enlarging, and with density lower than 2.34 g.cm⁻³, that is volume-stable even during a long-term stay in any high-temperature environments, and under permanent effects of pressure. At present the most important kind of dinas is that one used for building of coking chambers. It is characterized by a high degree of conversion, a negligible additional enlarging, high mechanical strength, high compactness and resistance to abrasion.

The antithesis of compact products is a light-weight dinas used e.g. as thermal insulating layers of linings of air heaters in blast furnaces. It is manufactured of fine-grained moulding mixtures with an addition of burnt breaks/chops and burnable additives or substances that are removed from the moulding before firing by sublimation, but leaving there some pores.

The aim is to eliminate free water from formed ceramic product. It needs to be looked for optimal process of drying. Drying of product produces stress in the product, which can cause its destruction.

<table>
<thead>
<tr>
<th>Summary of terms</th>
</tr>
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<tbody>
<tr>
<td>silica</td>
</tr>
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<td>shaped refractory materials</td>
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</table>

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<th>Questions</th>
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<tr>
<td>What basic forming techniques of ceramics are there? Explain the course of the SiO₂, conversions, give changes in volume within conversions, thermal expansion.</td>
</tr>
<tr>
<td>Technology of manufacture of shaped siliceous building materials.</td>
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</table>
4. FIRECLAY AND HIGH ALUMINA

Time for studying

8 hours

Aim

- classification of aluminosilicate materials and classification criteria, the binary system SiO₂ – Al₂O₃,
- raw materials for manufacture of aluminosilicate materials and their characteristics,
- basic technologies of production of compact aluminosilicate building materials focused on preparation of mixtures, moulding, drying and firing,

Definition

3.3 BASIC TERMS

Aluminosilicate refractories contain Al₂O₃ and SiO₂ as principal components, in varying proportions.

According to the content of Al₂O₃ they are divided into two basic groups:

Fireclay
- fireclay Al₂O₃ 10-45%
- low alumina fireclay Al₂O₃ 10-30%

High alumina
- Al₂O₃ 45-98%

Among the aluminosilicate materials also siliceous materials with additives, containing less than 10% Al₂O₃ a 85 - 93% SiO₂ can be included.

Thanks to the natural raw material resources the aluminosilicate materials (mainly fireclay) are the traditional and most common types of refractory building materials. In addition to a wide variety of shaped products – compact and lightweight – the aluminosilicates constitute the basic for refractory monoliths. Also refractory fibrous products can be included to the aluminosilicates thanks to their chemical nature.

1.1. SYSTEM SiO₂ – Al₂O₃
Refactory properties of aluminosilicate products can be assessed from the phase diagram of the system $\text{Al}_2\text{O}_3 - \text{SiO}_2$: 

- The only aluminosilicate compound stable at high temperatures is mullite ($3\text{Al}_2\text{O}_3.2\text{SiO}_2$),
- Actually, with a variable composition in the field of solid solutions,
- Mullite is melted incongruently at $1828^\circ\text{C} + 10^\circ\text{C}$ to obtain a melt rich in $\text{SiO}_2$ and solid $\text{Al}_2\text{O}_3$,
- in metastable conditions the presence of mullite was detected up to $1890 + 10^\circ\text{C}$.

At a lower content of $\text{Al}_2\text{O}_3$ than it is corresponding to the mullite composition in the system $\text{SiO}_2 - \text{Al}_2\text{O}_3$ the first melt is created at $1587 \pm 10^\circ\text{C}$. From the eutectic composition, at about 5.5% $\text{Al}_2\text{O}_3$, the liquidus line is rising together with rising content of $\text{Al}_2\text{O}_3$. For that reason the refractory properties of products containing crystalline phase – mullite improve thanks to the rising content of $\text{Al}_2\text{O}_3$. At a content higher than it is corresponding to the mullite there mullite and corundum coexist and the first melt is created at $1828 \pm 10^\circ\text{C}$.

![Phase diagram of the system SiO$_2$ – Al$_2$O$_3$](image)

**Fig. 3** Phase diagram of the system SiO$_2$ – Al$_2$O$_3$

### 1.2. **ALUMINOSILICATE RAW MATERIALS**

Fireclay building materials are made of natural raw materials. For the production of highly-aluminous building materials there are used both natural raw materials and industrially prepared basic materials of high purity destined for the products of prime quality. And further, there are special raw materials creating the bond.

**Raw materials for production of fireclay building materials**

- Refractory clays – these are fine-grained sedimentary rocks, layered aluminosilicates containing hydroxyllic groups in their structure. Kaolinite ($\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O}$) is the most common mineral, less frequent there are montmorillonite (in bentonites), halloysite or illite. As accompanying minerals in clays there are mainly siliceous sands, feldspars and mica.

  Phasical and technological properties depend on the composition and structure of clay minerals, on the shapes and sizes of particles (up to 70% below 1µm), kinds and quantities of
accompanying minerals. Together with water clays create plastic dough. This property is used for product moulding by traditional methods.

During heating clays of kaolinite type the following conversions occur:

\[ \text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O} \text{ at } 500 \text{ to } 600^\circ\text{C} \rightarrow \text{Al}_2\text{O}_3.2\text{SiO}_2 + 2\text{H}_2\text{O} \]
\[ 2 (\text{Al}_2\text{O}_3.2\text{SiO}_2) \text{ at } 925 \text{ to } 1050^\circ\text{C} \rightarrow 2\text{Al}_2\text{O}_3.3\text{SiO}_2 + \text{SiO}_2 \]
\[ (2\text{Al}_2\text{O}_3.3\text{SiO}_2) \text{ above } 1100^\circ\text{C} \rightarrow 2(3\text{Al}_2\text{O}_3.2\text{SiO}_2) + 5\text{SiO}_2 \]

According to this simplified diagram kaolinite undergoes dehydration to metakaolinite, further to an intermediate with a defective spinelitickou structure, and ultimately to mullite and cristobalite, or resp. rentgenomorfní phase. When warming up the silty clay is sintered and thus considerably shrunked. This shrinkage eliminates manufacture of fireclay products solely from raw clays.

**Burned fereclay** → can be obtained by firing refractory clays, claystones or shales (compacted clays). According to kinds and required quality they are fired in rotary, shaft or chamber kilns at temperature perhaps from 1000 to 1500°C. By firing they are dehydrated, compacted and strengthenendm their dimensional stability increases at re-heating. Burnt shales are used as the grog/non-plastic within the manufacture of fireclay building materials or as stoneware in aluminosilicate refractory monoliths.

**Refined kaolins** → They are acquired by raw kaolin washing when coarse particles, namely siliceous feldspar and sand, are removed. Kaolinite is the basic mineral phase of washed kaolins. Compared with refractory clays the washed kaolins have got a lower content of fluxes (mainly Fe₂O₃ and alkali), however they are course-grained (basic kinds of washed ceramic kaolins contain about 30% of particles smaller than 1µm), but less plastic. Within warming up the same conversions as with clays are carried out. They are used for manufacture of special kinds of building materials where the low content of iron oxide is required, in their natural – raw state as a bond or a grog made by burning out semiproducts most often of plastic in chamber or tunnel kilns, usually up to 1400 to 1500°C (kaolin grog).

**Siliceous sands and slates** → They are a cheap raw material for manufacture of acidic fireclay materials in which they create the grog. Sands being removed within kaolin washing are very suitable. Besides a proper granularity a reasonably low contamination by other minerals carrying fluxes is required.

**Natural high-aluminum raw materials**

The minerals of the sillimanite group (sillimanite, andalusite, kyanite) contain basic components - Al₂O₃ a SiO₂ – in a molar ratio 1:1, i.e. the theoretical content of Al₂O₃ is 62.8%. These materials differ in their structure, as well as in their density:

1. sillimanite 3.23 to 3.25 g.cm⁻³
2. andalusite 3.10 to 3.20 g.cm⁻³
3. kyanite 3.50 to 3.60 g.cm⁻³

When warming up there a phase conversion to the mullite and SiO₂ (cristobalite or roentge amorphous phase) is realized:

\[ 3 (\text{Al}_2\text{O}_3.\text{SiO}_2) \rightarrow 3 \text{Al}_2\text{O}_3.2\text{SiO}_2 + \text{SiO}_2 \]
From the density of reaction products, i.e. of the mullite about 3.03 g.cm\(^{-3}\) and of SiO\(_2\) about 2.30 g.cm\(^{-3}\) it follows, that the conversion is associated with a certain enlarging in volume. The following temperatures and changes in volume for single minerals are given:

- sillimanite at temperature of 1500 to 1550 °C 7 - 8% of volume.
- andalusite at temperature of 1270 to 1500°C 3- 5% of volume.
- Kyanite at temperature of 1240 to 1330°C 16- 18% of volume.

**Andalusite** → can be treated to refractory products without preliminary heat processing, because relatively small changes in volume in a wide temperature range are carried out there. Other raw materials of this group shall be fired in advance to reaching the above mentioned phase change.

In the Czech Republic there is not sufficient amount of these raw materials for the industrial extraction. On the worlds markets there are mainly the South African and French andalusite and the Indian and Californian sillimanite, or the calcined kyanite. The content of Al\(_2\)O\(_3\) in these raw materials is approximately 60 %, the content of fluxes is very low, usually 1to 2%.

**Bauxite** → it is a rock containing mainly various aluminium hydrates (hydrargillite – Al\(_2\)O\(_3\).3H\(_2\)O, böhmite and diaspor – Al\(_2\)O\(_3\), H\(_2\)O) and in a small amount also other minerals, in which besides Al\(_2\)O\(_3\) a SiO\(_2\) can be also found iron and titanium oxides and alkali. Only bauxites with very low content of iron oxide (the limit is about 3%) are suitable for procesing to refractory products. Before their use in refractory manufacture the bauxites shall be fired, usually to 1400 to 1600°C. During firing the raw material is gradually dehydrated and crystalline phases are created (corundum and also mullite) and the sintering occurs thanks to a melt presence. According to the firing conditions the volume weight of the product may range from 2.90 to 3.40 g.cm\(^{-3}\).

**Factory made basic high aluminium materials**

The technical aluminium oxide is most often the initial raw material from which the following materials are manufactured:

- sintered (tabular)
- fused corundum

And from the mixtures with alumino-siliceous raw materials (washed kaolins or clays) the following materials are manufactured:

- synthetic high-aluminium grog (mullite, mullito-corundum)
- fused mullite.

**Technical aluminium oxide** is manufactured from bauxites using various procedures, usually with the aid and through sodium aluminate and aluminium hydroxide. The aluminium oxide emerging by calcination of hydroxide (usually at 1200 to 1300°C) contains porous crystal clusters α - Al\(_2\)O\(_3\) (corundum) and γ - Al\(_2\)O\(_3\) (metastable, structurally diverse cubic form) with a specific surface more than 5m\(^2\)g\(^{-1}\). The specific surface area decreases with the increasing temperature of calcination. When processing the technical aluminium oxide using sintering procedures (sintered corundum, synthetic high-aluminium grog) the technical aluminium oxide is dispersed to single monocrystals.

As for certain kinds of products and methods of processing it is more advantageous to use the recrystallized (mineralized) α - Al\(_2\)O\(_3\), that can be obtained by calcination of a hydrate up to 1050 to 1250°C in the presence of a small quantity of AlF\(_3\). This speeds up the growth of table (shaped)
crystals α - Al₂O₃, the specific surface decreases (to 1 m² g⁻¹ approximately) and the mean crystal size increases (usually from 1 to 10 µm).

Aluminium oxides are evaluated according to the content of Al₂O₃ (more than 98.5 to 99.5%) and polluting oxides (SiO₂ and Fe₂O₃ generally below 0.1%, alkali of ordinary kinds below 0.6% approximately, however with these of superior quality it is below 0.2%), depending on the amount of crystalline phases, i.e. α-Al₂O₃ and γ-Al₂O₃ or according to the granularity.

**Fused corundum** (fused alumina) is made by melting the blocks of technical alumina in electric arc furnaces. Then the product (polycrystalline Al₂O₃) is crushed and ground. Milled iron is removed with the aid of magnetic separation, or by washing in the hydrochlorid acid. It is sorted to the fractions according to the grain sizes. Its main using is in the manufacture of grinding tools.

**Sintered alumina** being also called the "Tabular alumina" is manufactured of a technical alumina with a low content of alkali. The technological procedure is characterized by piecemealing of raw materials with a high degree of dispersity, peltizing or briquetting, firing the pellets or briquettes up to temperatures about 1900°C, followed by crushing, grinding and cleaning of a sintered polycrystalline product. The name “tabular" is based on the shape of crystals that are usually table-shaped, which evidences their preferred growth in two directions.

**Synthetic high-aluminium grog** (mullite about 72% Al₂O₃ or mullite-corundum with a higher content of Al₂O₃, usually over 80%) is produced of a mixture of ground alumina and kaolinitic substances (washed kaolins or refractory clays). The raw materials are mixed when are they dry in the proportion corresponding to the required content of Al₂O₃ in the product. The mixture is usually moistened in a plastic consistency that is pulled on a vacuum de-airing auger. Cut semiproducts are dried and fired according to the content of Al₂O₃ up to 1600 to 1700°C. During the firing the primary mullite occurs at first from the kaolinite substance (see the conversions when heating clays). SiO₂, released during creation of the primary mullite, reacts at 1200 to 1500°C with aluminium oxide to form the secondary mullite. And at 1400 to 1700 °C the growth of mullite crystals, as well as sintering occur. The rate of conversion to mullite depends on the content of Al₂O₃, fineness of input components, the perfection of their homogenization and on the conditions of firing. In the thoroughly conversed grog with the content up to 72% of Al₂O₃ there are only mullite and roentgen amorphous phases. At a higher content of Al₂O₃ there are coexistent mullite and corundum. The amount of roentgen amorphous phase increases together with increasing content of fluxes.

### 1.3. TECHNOLOGY OF PRODUCTION OF COMPACT SHAPED FIRED ALUMINOSILICATE PRODUCTS

There are two basic technological procedures of production of compact fired aluminosilicate building materials, namely:

These two procedures differ by the ratio of basic constituents:
Clays shrink during drying and especially during firing, which means, that during firing the joining and connection between the shrinking clay bond and dimensionally relatively stable grained grog is violated. This increases porosity, reduces strength and conditions for gaining the product accuracy in shape and dimensions could be deteriorated. In semi-dry materials the plastification function of clay is reduced due to lower moisture, so the clay acts only as a fine fraction. Adverse effects of its shrinking during drying and firing can be suppressed by reducing its content and adding fine ground grog into a mixture. This reduces shrinkage of the matrix (clay + fine grog).

In the manufacture of highly-aluminous building materials any greater additions of clay into the mixture are undesirable, because the matrix of a lower quality could significantly reduce the product quality. On the contrary there is an effort to achieve the same quality of the matrix as is the quality of grained fractions. This can be achieved by minimizing the clay content and creating the matrix of fine-grained highly-aluminous grogs.

**Basic technological procedure of production from semi-dry mixtures:**

- separate preparation of raw materials,
- proportioning of fractions by weight in proportions ensuring the compact filling space,
- intensive mixing after adding water and additives,
- high-pressure moulding,
- drying and firing.

This procedure is approaching the manufacture processes of other kinds of refractory materials made solely of non-plastic raw materials. Compared with the plastic manufacturing method it is possible to reach the product of higher quality, accurate dimensions (low shrinkage properties) at lower energy consumption (energy saving drying) with extensive possibilities of automatization of the technological procedures, especially during moulding and handling mouldings (direct placing on tunnel trucks).

Compacting pressure at moulding of aluminosilicate products of semi-dry mixtures range widely, from about 30 to 120 MPa. The compacting pressure is governed by the kind of a processed material and required parameters of the product. With the increasing pressure the optimum moisture ensuring the lowest porosity is decreasing. Because the mixtures of the optimum moisture are susceptible to repressing at the given compacting pressure, in the technological practice mixtures of reduced moisture are used, but just enough not to increase significantly the porosity of mouldings. When using plastic materials for manufacture, the moulding process is different. The semiproducts pulled through a de-airing auger can be additionally moulded there with the aid of a low pressure, usually lower than 10 MPa, or they can be moulded by hand.

When drying mouldings of plastics it is necessary to remove water in an amount of 16 - 20% by weight of the mouldings, but for all that there shrinking may occur in dependence on the amount of clay in the mass. That is why drying those mouldings made by the plastic method is very demanding as for energy consumption and the applied technologies. Unlike that, with the mouldings
being moulded from semi-dry mixtures no changes in dimensions occur during drying process and even evaporation of several percents of water proceeds without any technological difficulties even directly on tunnel trucks.

The products acquire their final, definite properties by firing. During the firing process there some phase and structural conversions occur that result in consolidation and compaction of these products.

Temperatures of firing range for particular types of aluminosilicate usually range as follows:

- common kinds of fireclay 1250 to 1400°C
- fireclay superior quality 1400 to 1500°C
- mullite and mullito-corundum products 1500 to 1600°C
- corundum products 1600 to 1700°C

During warming-up the dried aluminosilicate mouldings the chemically bounded water is released from clays. However, there are no sharp dimensional changes, that means, that the rise and drop in temperature can be uniform. The theoretical allowable rate of heating and cooling of individual blocks calculated according to the theory of cracking is relatively high. The real rate depends mainly on a kiln construction and on the method of placing the products in the kiln in term of securing the uniform heating up. Considering the contemporary technical level of firing units the firing process in tunnel kilns lasts usually for 40 to 80 hours, according to the firing temperature (1400 to 1700°C). It comprises about 15 to 30 hours of firing and 5 to 10 hours of soaking at maximum temperature. The cycle of firing in modern truck and bell furnaces is significantly shorter.

1.4. **COMBINED PRODUCTS CONTAINING ALUMINOSILICATE**

Among the combined materials on the basis of aluminosilicates are included mainly the products containing oxide-less constituents – graphite and silicon carbide. The materials in systems Al₂O₃–SiO₂–C and Al₂O₃·SiO₂–C·SiC combine the high thermal conductivity and chemical inertness of carbon and silicon carbide with the chemical and thermal stability of aluminosilicate and corundum. The products are therefore highly resistant to corrosion by liquid metals and the excellent resistance to sudden changes in temperature.

Shaped products containing Al₂O₃, SiO₂, C and SiC (graphite-fireclay, graphite-mullite, graphite-corundum) are used mainly in steel casting as normal or monoblock plugs, submersible and sealing tubes.

Normal graphite-fireclay products are usually moulded from plastic materials, the shaped graphite-highly-aluminium components of higher quality are usually moulded isostatically from semi-dry mixtures. To prevent the graphite oxidation the firing is carried out in such a manner to prevent any contact of a fired product with oxygen. The firing temperature shall be chosen so that a ceramic bond would be created in products. At present the process of quick firing is used and in the kilns there is necessary to ensure a reducing atmosphere at higher temperatures and during cooling the products. Oxidation of graphite can be prevented also by mouldings glazing.

The graphite-corundum products are made also from materials with a bituminous bond. In this case the products are carbonized in reducing atmosphere. The same composition of the system Al₂O₃ · SiO₂ · C · SiC have got some special kinds of refractory monoliths destined namely for troughs serving for transport of liquid metals. Strictly speaking, these are cement-less refractory concretes.
containing micro-additives and dispersing agents allowing processing of mixtures by vibrating at minimum moisture.

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<tr>
<th>Summary of terms</th>
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<tr>
<td>- categorization, classification and classification criteria of the large group of aluminosilicate materials,</td>
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<tr>
<td>- properties of aluminosilicate materials derived from the binary diagram SiO₂ – Al₂O₃,</td>
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<tr>
<td>- raw materials for manufacture of aluminosilicate materials,</td>
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<th>Questions</th>
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<tr>
<td>- Explain categorization and classification of refractory aluminosilicate materials, give the classification criteria.</td>
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<tr>
<td>- Analyse the phase diagram of the system SiO₂ – Al₂O₃ and explain classification of aluminosilicate materials.</td>
</tr>
<tr>
<td>- What raw materials are used for production of aluminosilicate materials, compare their properties.</td>
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5. BASIC REFRACTORY MATERIALS

Time for studying

6 hours

Aim

- be familiarized with categorization and classification of very large group of materials, whose main refractory oxide is MgO,
- after reading-up the successive chapters you will be familiarized in detail with the technology of manufacture of magnesite building materials, either with the content of residual carbon up to 7% or with the content of carbon ranging from 7 to 50%, or even more,

Definition

5.1 BASIC TERMS

The substantial, predominant or functionally important constituent of refractory materials designated as alcaline- ones, the magnesium oxide — the periclase. They are mainly used in metallurgy, in the manufacture of cement, lime and glass.

5.2 MAGNESIUM OXIDE – PERICLASE

Periclase is the only stable modification of MgO. Refractory materials of periclase are resistance to acting of alkaline slags and melts containing iron oxides. This property is based on phase conditions in the systems MgO - FeO and MgO - Fe₂O₃. MgO creates with FeO the full range of solid solutions of magnesiowüstite (Mg, Fe)O. When in the system CAO is replaced by MgO as also strongly alkaline, technically in a pure form easily available oxide with high stability and the melting point at 2625°C. Periklase refractory materials were used successfully in the steel production as furnace linings and containers in which alkaline iron slags are present and act at high temperatures, and why they are better than materials with calcium oxide as a substantial or significant part. Depending on the degree of reactivity the technical magnesium oxide can be distinguished to: calcined, sintered, melted.

5.3 SOURCES OF MGO AND PRODUCTION OF SINTERED MAGNESIA

As a source of MgO there is the magnesite as a rock-forming mineral, sea water with dolomite orlimestone, bischofit, either natural or as an intermediate product and/or a waste from processing the complex potassium magnesium natural salts for potassium fertilizers.
The second group consists of products of MgO obtained by calcination of basic materials at temperatures below 1200°C. They are used in civil engineering, paper and pulp industries, in chemical industry and in agriculture. In the production of refractory materials there are mostly semiproducts.

**Magnesite and its processing**

The mineral magnesite, it is magnesium carbonate – MgCO₃. In theory it contains 47.81% of MgO and 52.19% of CO₂.

\[
\begin{align*}
CaCO_3 + Mg(HCO_3)_2 &= MgCO_3 + Ca(HCO_3)_2 \\
CaCO_3, MgCO_3 + Mg(HCO_3)_2 &= 2 MgCO_3 + Ca(HCO_3)_2
\end{align*}
\]

**Magnesite firing**

Decomposition of magnesite begins at the temperature of 399°C when the balanced, steady partial pressure of CO₂ over MgCO₃ values 101.3 k.Pa is obtained at zero value of standard free energy of reaction. When heating in the air the magnesite begins to be unstable at the temperature of 250°C, due to presence of CO₂ in the atmosphere. As for CaCO₃ there are adequate temperatures (of decomposition/instability during heating) 883/537°C and as for the hydration of Mg(OH)₂ - 277/192°C. These processes are endothermic.

By firing at a temperature below 1000°C it is possible to gain a caustic burnt magnesite of high reactivity. The highest value is achieved by annealing at the lowest temperature required for decarbonisation so that the calcine would contain a small remnant of non-decomposed carbonate. By increasing the temperature above its optimum value these values drop sharply.

Caustic magnesite mixed with MgCl₂ and wood sawdust, ground cork or other fillers is used as Sorel cement for production of floorings and heat insulating boards in civil engineering. When manufacturing the heat insulating boards the mixture of the caustic magnesite, a solution of MgCl₂ and wood sawdust is shaped in the zone that is cured in the heating channel. The process is continuous. Its advantage compared to manufacturing with using the Portland cement as a binder, and with a separate shaping of each board is indisputable. The carriers of mechanical strength of the bond there are hydroxide chlorides. Their structure corresponds to Mg(OH)₂, in which a portion of hydroxyl groups was replaced by Cl ions. Reactiveness of caustic magnesite is a significant parameter for further processing and using in chemical industry, in celulose production, in civil engineering and in production of sintered magnesite.

**Production of sintered magnesite**

Sintered magnesite is obtained by firing magnesite at temperatures of 1500 up to about 1900°C, according to the sizes and arrangement of crystals, content of MgO, accompanying minerals and the content ratios of the individual oxides, especially CaO to SiO₂.

The technologically simplest there is a single-staged firing of piece concentrates in rotary and shaft kilns. Already at the temperature of 1300°C a low-viscosity melt starts to create, which is able to support sufficiently the process of compaction. The firing is usually realized up to the porosity close to 10%.

In rotary kilns there are formed conglomerates and pellets, in shaft kilns compact and airtight blocks are formed. In both types of kilns the proper operation is disabled, and after reaching the
given porosity the firing shall be ended. The compaction and growth of periclase grains continue during firing the moulds in manufacture of shaped building materials. A compact layer is created of very different and various physical properties, so when the temperature is changed the layer is separated from the uncompacted part of refractories. The layer scaling-off is a part of a typical adverse wear mechanism of alkaline linings and their biggest disadvantage. This leads to the sintered periclase with its porosity below 4 % for this kind of initial raw material, but also for all the others. During the sintering process the periclase grains grow continuously and the pores shrink regularly. The porosity of 4% can be gained with the content of MgO of 95 to 97%. The sintered magnesite of this composition is the first-class basic material for production of shaped refractories, especially for linings of oxygen convertors, when it is of low-siliceous type.

5.4 PERICLASE CARBON REFRACTORY MATERIALS

The system MgO – C is not eutectic. No low-melting compounds are produced. The structure and chemical nature of both constituents differ substantially. By their combination it is possible to obtain such products in which the properties of periclase and carbon are joined in peculiar and unique way.

Refractory materials with carbon content up to 7%

Production of unfired periclase building materials containing 3 to 6% of carbon differ from other kinds of alkaline materials with using organic binders leaving after carbonization process a carbon residue that encases magnesite particles, binds them and significantly influences thermomechanical properties as well as the process of the linings wear.

Refractory materials with the content of carbon 7 to 30%

Knowledge of carbon influence in the bond of unfired alkaline materials on wear of linings of steel-making furnaces led to increasing of its content up to 40% and to creation of a new group of shaped periclase-carbon products.

A substantial portion of the carbon component of the building material forms the crystalline flaky graphite characterized by a layered structure in the hexagonal crystalline system. Deformability of the graphite, low inner friction and the mould wall friction within pressure moulding enables making mouldings with substantially lower porosity compared with any basic material used for manufacture of building materials. The graphite differs from periclase by its substantially higher thermal conductivity and by its substantially lower thermal expansion. Both these properties are among those criteria that substantially affect the resistance to sudden changes in temperature.

Periclase-carbon building materials can be characterized by the fact that the ceramic bond is replaced by the carbon bond that is a residue after carbonization of an organic binder. Therefore, the mechanical and thermomechanical properties of products depend on the stability and strength of carbon bonds between the particles of graphite and periclase with applying specific features of the both components.

The disadvantage of carbon is its insufficient resistance to oxygen acting. It started to oxidize since the temperature of 400°C. The disadvantage of periclase is the fact that it reduces with carbon. To slow down the carbon oxidation there were introduced antioxidants as additives to moulding mixtures. These are elements not of metal or of metal, their alloys, or non-oxide compounds with the
high affinity to oxygen. In the operating conditions of linings within the given partial pressures mainly CO and N₂ are capable on their own or through the transient, temporary solid or gaseous intermediate products react with CO to create a stable oxide coexisting with MgO or creating with it some stable compounds. In the final effect they are the means reducing CO released by the carbon oxidation to a new regenerated carbon.

Due to the particularity of the graphite surface and the pitch properties it is very difficult to prepare a moulding mixture capable of being shaped in press, mouldings with sufficiently compact carbon bond and products with required thermomechanical properties with the graphite content over 6%. The solution is using binders of synthetic resins. These are products of polycondensation of phenols with formaldehyde.

Several procedures were developed for preparation of moulding mixtures:

- **Preparation in a cold state** – a binder is the resole there, with its viscosity of 500 to 2500 mPa.s. Sometimes it is combined with the Novolac resin which is added together with the hexyne. When the basic material of mixtures being prepared is a substance containing hydratable CaO, it is used a solution of the Novolak resin as a bond, while its viscosity is 500 to 2000 mPa.s at the temperature of 20°C. The mixtures can be moulded in their cold state.

- **Preparation in a hot state** – as binders there are Novolacs or their solutions, with the viscosity of 500 to 5000 mPa.s and at temperatures of 60 to 100°C. As solvents there are used various kinds of alcohols, ketones, and others. The viscosity at temperatures given above in the text depends on the kind of the Novolac resin, its concentration and a type of solvent. Temperature of a mixture after hexyne adding shall not exceed 80°C to prevent premature starting of polycondensation.

It is moulded at the temperature up to 60°C, preparation at higher temperatures – as a bond there is moulded Novolac. The mixture is usually moulded after cooling and granulation.

The surface properties of graphite and its granularity require compliance with the given measures as for the order and methods of adding constituents and bitumen into a mixer and substantially longer time of mixing. When moulding the pressure increase is slowed down, or pressing-in shall be repeated. By applying a vacuum during pressing it is possible to reduce or prevent cracking due to overpressing. Due to deformability of graphite, increasing the compacting pressure from standard 100 MN.m⁻² to 150 MN.m⁻² significantly reduces porosity of mouldings. High degree of compactness was achieved by pressing in fraction presses that are designed for such a purpose with their compacting pressure 20 000 kN. The compacts are cured at the temperature about 180°C and they become products.

### 5.5 MAGNESITE – DOLOMITE PRODUCTS

Basic product is formed building material, produced from sintered fired dolomite. If we increase content of MgO with help of magnesite, group of magnesite-dolomite products is created. Dolomite, dual carbonate magnesite-lime Mg Ca (CO₃)₂, is rock creating mineral. It is present on many places of Earth surface. Theoretically contains 30,41 % of CaO, 21,86 % MgO and 47,78 % CO₂. Dolomite is decomposed on two levels with annealing treatment. Crude crystal dolomite with low
content of supporting minerals can be fired into dense sintered product only at temperatures above 2000° C. In little crystal type there is enough the temperature about 1600° C.

Firing is done in same devices as by magnesite. Dolomite is processed mainly into products non-fired, bound by black coal rosin containing residual carbon below 7%. In recent years is this method subsidized by phenol bitumen mainly because of the hygiene of work. By fired products form dolomite it is specific technology of precautions against hydration of CaO in presswork. Products from dolomite and from magnesite-dolomite are used by production of steel for walling of pans and containers of pan metallurgy. Other important user is cement industry, where are these products used for walling of fire areas of rotation furnaces.

6.1 MAGNESITE – CHROME PRODUCTS

Magnesite and chrome ore are main materials during production of magnesite-chrome products. Chrome ore as one of the basic materials is basically created by complex spinel. Sherd of magnesite-chrome building material is produced from two composites with very different physical characteristics. Very different is thermal expandability and change of volume by both materials. Specialty of these products is increasing of volume of work layer of walling (so called swell) during work in steel furnaces. Non-fired material with chemical structure (MgSO₄, MgCl₂ or alkali polyphosphate) can be prepared, besides fired building materials. MC building materials can be bound by oleoresin with tar. Building materials are used for walling of exposed parts of convertors for argon-oxygen decarburisation (AOD), containers for degassing of steel in vacuum, RH, DH and some other pan furnaces in ladle metallurgy, especially there, where have effect dross with ratio C/S also bellow 2.

Summary of terms

- magnesium oxide – periclase and its properties,
- magnesium with the content of residual carbon up to 7%,
- magnesium with the content of residual carbon from 7% to 30%,
- magnesium – chromite,
- antioxidants

Questions

- Explain the status of magnesium oxide among steady / resistant oxides with high melting points, describe properties of MgO.
- What are the sources of MgO and what are procedures for preparation of magnesite clinker.
6. HEAT INSULATING REFRACTORY MATERIALS

Time for studying

4 hours

Aim

- classification of thermal insulation refractory materials for: porous shaped materials, unshaped thermal insulating refractory concretes, fibrous heat insulating materials
- technology of production of above listed kinds of heat insulating materials

Definition

The increasing demand for energy saving leads to the development of increasingly sophisticated thermal insulation devices operating at high temperature. Most of the produced heat insulating materials are manufactured on the basis of $\text{Al}_2\text{O}_3 - \text{SiO}_2$ with other additives e.g. CaO, MgO, iron oxides, alkali, TiO$_2$, etc. These additives generally reduce the classification temperature. These materials are further characterized by a low coefficient of thermal conductivity. The lower volume weight of the material, the lower is its thermal conductivity. These materials have their actual porosity of less than 45% (by volume). The shaped insulating materials are obtained by deliberate creation of pores in the material. Basic technological procedures of the porosity increase:

- with the additive of burning-up compounds
- air foaming-up
- addition of volatile substances
- chemical reaction to produce a gas
- Addition of light weighted compounds
- or combination of methods

6.2 TECHNOLOGY OF PRODUCTION OF POROUS MATERIALS

Production of porous materials with the addition of burning-up mixtures

There are usually used for technologies of production of fireclay and high alumina refractory materials, namely of plastic dough or pressing. The basic compositions containing the grog (fired shales, waste scrap by fireclay, high alumina materials, corundum) and a binder (clays) are added burning mixture (pulverized coal, anthracite, coke, charcoal, sawdust, the organic waste material. Preferred are additives with low ash content because they contain harmful oxides of alkali metals, alkaline earth metals and iron.

Production of porous materials by air foaming-up

The principle is pouring foamed-up slurry of refractory fire clay and clay with foaming agents in metal moulds. Thus prepared materials have porosity of 85 to 90%. To stabilize the foam stabilizers are used (carpenter's glue, gelatine, sulphite liquor or protective colloids). And
furthermore, the substance water withdrawing such as sawdust, gypsum, porous clay, which also accelerates the drying process. Products which are prepared in this manner have a higher thermal conductivity and have a substantially higher strength than otherwise prepared products.

**Production of porous materials by chemical reaction**

The method consists in foaming-up the material by gas being generated during the chemical reaction of present of addition substances. The technology consists in formation of bubbles, their spreading and mixing, and then the fixation of bubble structure.

**Production of porous materials by addition of volatile substances**

The base is to add organic substances into mixtures at elevated temperatures that evaporate or sublimate. As volatile additives are used, for example, naphthalene, paraffin, typically styrofoam. Gases from evaporation, sublimation, and decomposition are then oxidized off the product on CO₂ and water vapour.

6.3 **CASTABLE**

Refractory concretes are kinds of concrete destined for temperatures above 200 °C, at which after a prolonged exposure to higher temperatures the hydraulic bond can convert to a ceramic bond. Disadvantages of products with hydraulic bond can be the strength dropping during the first heating-up, when the decomposition of the hydraulic bond occurs. At higher temperature the sintering of the refractory concrete is realized and the monolith changes its nature into the fired ceramic product, and simultaneously the increase in compressive strength occurs as well.

Refractory concretes with aluminate cement can be divided according to the cement content as follows:

- **MCC** (medium cement castable): >2,5% CaO, >8% cement
- **LCC** (low cement castable): 1-2,5% CaO, 3-8% cement
- **ULCC** (ultra low cement castable): 0,2-1% CaO, <3% cement
- **NCC** (no cement castable): ≤ 0,2% CaO

Stoneware – these are natural or artificial bulk materials, or waste materials /broken away fractions/ that are the main constituent of the refractory concrete.
As binders that after hardening of the refractory concrete compound shall join all solid parts in a compact mass, there are used hydraulic cements: Portlands Portland” slag, aluminous, or high-aluminous or special ones.

Properties of refractory concretes can be affected by additives.

According to the limited temperatures of use we can distinguish refractory concretes up to temperatures: 350, 700, 1100, 1200, 1500 and above 1500°C. According to the volume weight they are specified as standard refractory concretes /20/ and lightweight ones with OH < 1500 kg.m⁻³

Unshaped refractory materials

Unshaped refractory materials are refractory mixture composed of aggregate and binder or more binders, prepared before supplying or then one or more suitable liquids shall be added. These compounds are compact or insulating. They may contain metal, organic or ceramic fibre materials. The advantage of these materials is that there is eliminated any final firing of products in the production process. The firing is realized when putting the thermal unit into operation.

According to the application the materials can be divided as follows:
   a) Refractory monoliths (castable)
   b) Mortars and cements (fasteners – jointing materials
   c) Repair mixtures
   d) Coatings

According to the solidification process they can be divided as:
   a) hydraulic binders - hydraulically curing and hardening at room temperature
   b) ceramic binders – hardening by sintering during firing
   c) chemical binders - chemical curing (not hydraulic) bond at ambient temperature or at a temperature lower than preventing creation of a ceramic bond,
   d) organic binders - creating or harden at room temperature or higher temperatures.

6.4 HEAT INSULATING FIBROUS MATERIALS

As a modern type of insulation materials there are fibrous refractory materials which are produced from the melt or by chemical means for thermal insulation purposes.

They have many advantages over the shaped insulating materials:

- particularly low thermal conductivity,
- low specific conductivity,
- low specific heat capacity,
- high resistance to vibration and shock,
- resistance to temperature changes,
- low volume weight,

As a disadvantage compared to shape the materials of the same composition there is a lower mechanical strength, worse chemical resistance, higher gas permeability and higher price.

Fibrous materials are prepared from the melt of a mixture of raw materials by spraying on a rotating disc or by blowing using a stream of water vapour or air. Another method is using a chemical way. By splashing or blowing the melt kaoline and high-aluminate fibres can be produced. The melt
has viscosity suitable for pulping in the sufficiently wide temperature interval. Production of fibres by
drawing on the organic, organic-inorganic or inorganic bases is used for materials when the melt has
not got a viscosity suitable for splashing or blowing.

For thermal insulation purposes some short monocrystalline fibres (whiskers) can be used, but they are mostly used only for composite materials. While the glass fibres can be used up to 500 ° C, the mineral fibres up to 650 ° C, and special mineral fibres to temperatures max. to 850 ° C and some refractory fibres (ceramic) to temperatures of 1000-1900 ° C.

Classification temperature of ceramic fibres on the basis of the system SiO$_2$ and Al$_2$O$_3$ increases together with the increasing content of Al$_2$O$_3$. It is possible to distinguish two groups: at the content of 43-55% of Al$_2$O$_3$ the classification temperature is 1300 ° C, above 55% the temperature is higher. In the case of fibres from some pure oxides such as ZrO$_2$ the classification temperature is 1900 ° C. The classification temperature is related to the additional linear changes. It is defined the value by 50% higher than the temperature at which the additional linear shrinkage of the test piece after heating for 24 hours does not exceed a specified value (3%). The temperature of using is always lower.

**Production of fibres from the melt**

In this way, the kaolin fibres and high-aluminate fibres are prepared. Fireclay is further
-crushed to a grain size up to 3 mm. The mixture of raw materials is melted in an electric arc furnace
-with carbon or molybdenum electrodes at 1860 - 1960 ° C. The melt is discharged through a hole being cooled by water and it is pulped with a stream of superheated steam and air, or on a cooled rotating disk. By passing the air, the fibres are rapidly cooled and solidified. The fibres being cooled down are now in a glassy state. To improve the fibres structures, surface smoothness and other properties a surfactant – emulsifier is added to the steam. For the pulping also dispersing is used with the aid of the cooled rapidly rotating disc or on several disc system. Into the pulping equipment a steam at supersonic speeds is supplied. In the chamber, where the fibres are taken away by the flow which velocity is reduced and the fibres are deposited on a moving perforated belt. In departure layer, the fibres are poorly oriented and contains significant quantities of alkali and fiber diameter is usually not constant.

Fibres with a low content of SiO$_2$ and a high content of Al$_2$O$_3$ can be created of the melt very difficult. The melt has a high surface tension and low viscosity. From those melts then by flowing can arise very easily rounded shapes, such as alkali. Also, very high viscosity of pure SiO$_2$ do not allow fibres preparing from the melt, therefore, there is preferred a chemical method of the production.

**Production of monocrystalline fibres – whiskers**

Whiskers are threadlike monocrystals. Their diameter is than 10um, fibres reach a length of
0.2 mm to 1 mm, exceptionally 10 mm. For insulating purposes are defined rather longer fibres, so
their use is directed rather to composite materials. Whiskers are prepared mainly by condensation of the gaseous phase in a gradient furnace. The starting materials are placed in a location with the highest temperature, evaporated, and crystallized at the coldest spot in the furnace. It's a slow process. In this manner, whiskers MgO, Al$_2$O$_3$, etc. are to be prepared. Another method of preparing is a chemical reaction which is considerably faster than the preparation of the gaseous phase. Nevertheless, it takes 0.5 - 20 h, until the crystals obtain the appropriate length. Whiskers of silicon
carbide are prepared from hydrocarbons and chlorisilane. From the alumina they are obtained by oxidation of aluminum in wet hydrogen. Whiskers Al₂O₃, SiC and graphite are used for the manufacture of composite materials.

**Advantages and disadvantages of fibrous heat insulating materials**

Fibrous insulating materials represent a major trend in the current development in heat insulating materials.

**Advantages:**

a) low thermal conductivity especially at low temperatures,
b) low heat capacity unit of the lining,
c) resistance to sudden temperature changes,
d) greater resistance of lining against vibration, shock,
e) the possibility of quick and easy fixes
f) absorption of the noise produced during operation of the unit,
g) easy and rapid implementation of the lining or insulation,
h) the possibility of quick commissioning unit to operate without the need for long-term drying and tempering
i) facilitate the possibility of prefabrication
j) the lower cost of the supporting structure of the furnace unit due to a lower overall weight
k) expansion of the fibre allowing a good seal joints and compactness lining.

**Disadvantages compared with shaped materials of an analogous composition are:**

l) a) lower mechanical resistance, ie lower mechanical strength,
m) b) relatively lower price
n) c) somewhat low chemical resistance, especially against a reducing environment due to the greater specific surface area and easy accessibility,
o) d) increased permeability to gases.

**Production of refractory ceramic fibres**

Loose fiber (wool), which is the primary product of production, is used as a material for other products - mats, felts, boards, textiles, shapes, cements, etc. For their production, there are various organic binders which burn out during use, or inorganic which are generally continuous, or mixtures thereof. It is important that the binder used not to increase the volume weight and the specific heat conductivity of the product. Must have good adhesion to the fibress and to ensure sufficient strength of the product. It has to prevent shrinkage and the formation of mullite in the fibres during their use.

<table>
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<tr>
<th>Summary of terms</th>
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<tr>
<td>defined heat-insulating refractory materials,</td>
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<td>production of shaped insulating materials,</td>
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<td>thermally insulating refractory,</td>
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<tr>
<td>thermal insulation fibrous materials,</td>
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Questions

- How can I increase the porosity of shaped insulation products, or castables, describe each technology.
- Describe the technology of fibers and fibrous products.
- What are the advantages and disadvantages of fibrous insulation materials.
7. LITERATURA


[20] KLASSIFIKACIE žárovzdorných výrobkov hutných. Část 1 až 4. ČSN EN 12475 – 1 až 4
