MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE

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FUNDAMENTALS OF CHEMICAL PRODUCTION TECHNOLOGY FOR WALLING, FINISHING AND PROTECTIVE MATERIALS

Lecture notes
in two parts

Part 2

Chemical production of materials for thermal insulation, waterproofing and wall construction finishing

for applicants at first (bachelor) level of higher education of the speciality 161 "Chemical technology and engineering" the specialisation "New technologies and design of modern wall and finishing materials"

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Rudenko I.I.

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Contains the fundamentals of chemical processes in the technologies of materials for thermal insulation, waterproofing and finishing of wall structures.

It is intended for students of the speciality 161 "Chemical technology and engineering" the specialisation "New technologies and design of modern wall and finishing materials" of full-time education.

Руденко І.І.

Р83 Основи технології хімічних виробництв стінових, оздоблювальних та захисних матеріалів: конспект лекцій в 2-х частинах. – Частина 2. Хімічні виробництва матеріалів для тепло- і гідроізоляції та оздоблення стінової конструкції / І.І. Руденко, О.П. Константиновський, О.Ю. Бердник. – Київ: КНУБА, 2025. – р.

Містить загальні положення хімічних процесів в технологіях отримання матеріалів для теплової ізоляції, гідроізоляції й оздоблення стінової конструкції.

Призначений для зобувачів ??????? спеціальності 161 «Хімічні технології та інженерія» спеціалізації «Новітні технології та дизайн сучасних стінових та оздоблювальних матеріалів» денної форми навчання.

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INTRODUCTION

The discipline “Fundamentals of chemical production technology for walling, finishing and protective materials” is basic discipline in the professionally oriented training of specialists in the speciality “Chemical technology and engineering”. This speciality provides students with essence of chemical processes during processing raw materials into artificial materials, and, taking into account specialisation, mastering the basics of the latest technologies and design of modern wall, finishing and protective materials. That is why the purpose of the lecture course is to provide systematic knowledge of material formulations, disclosure of the nature, features and technological conditions of chemical processes that form the basis of their production.

In order to improve the learning of the discipline, a shortened lecture notes in the form of two parts, subordinated to the work programme, are offered.

The first part includes lectures on the general principles and fundamentals of the chemical production of walling, finishing and protective materials, and the analysis of the functional role of wall construction elements. Techniques for obtaining the required material structure and chemical processes that determine the structure of the wall material are described. The chemical and technological bases for the production of wall materials and products of the entire modern nomenclature are revealed.

The second part of the course includes lectures on the peculiarities of the chemical production of materials for thermal insulation of wall structures, as well as for their waterproofing and finishing.

Each lecture is accompanied by control questions for the students to confirm their understanding of the main points of the lecture.

After studying the discipline, students should know nomenclature, properties and peculiarities of application of modern walling, finishing and protective materials, have theoretical knowledge of the principles and technological basis of processes for the production of such materials, be able to develop their formulation and make an economically sound choice of raw materials, optimise technological solutions in production conditions, calculate the parameters of chemical processes in production technologies, have the skills to use the regulatory framework to control the quality of raw materials, ensure compliance with process parameters and assess the quality of finished products.

Lecture 11

MATERIAL STRUCTURE AS A BASIS FOR CONTROL OF ITS THERMOPHYSICAL PROPERTIES

Plan

11.1. The essence of thermophysical parameters of wall material and product: thermal conductivity and thermal resistance.

11.2. The role of the chemical nature of raw materials - organic, inorganic - in assessing the possibilities of creating a fibrous, cellular, granular structure of the material in terms of thermal properties.

11.3. Chemical conditions to obtain a given density of the material, the role of water and the influence of water content on the thermal conductivity.

11.1. The essence of thermophysical parameters of wall material and product: thermal conductivity and thermal resistance

Thermal insulation is understood as technical and economic measures aimed at preserving thermal energy, ensuring its rational use for heating, regulatory sanitary and hygienic parameters of the indoor microclimate, and the durability of wall structures during the operation of buildings and structures.

One of the most important characteristics of building envelope insulation is its *thermal performance*, the requirements for which are regulated in DBN B.2.6-31:2021 “Thermal insulation and energy efficiency of buildings”. The coefficient of resistance to heat transfer of a wall structure and thermal conductivity are the defining characteristics of thermal insulation materials and products (TIM).

The heat transfer resistance ($R_{\sum}$, $m^2 \cdot K/W$) of a thermally homogeneous part of building unit is determined by formula (2) in DSTU 9191:2022 “Thermal insulation of buildings. Method for choosing of insulation material for insulation of buildings”.

Thermal conductivity coefficient (λ, W/m·K) - reflects the proportionality between the heat flux density along its vector and the temperature gradient (numerically equal to the amount of thermal energy required to change the air temperature by 1 K with a material thickness of 1 m). All building materials are characterised by l values greater than air (0.02 W/m·K), which determines the need for a reasonable choice of building

material and the search for an effective structural solution for the wall The thermal conductivity of a material is largely determined by its structure. Since gases, including air, are characterised by very low thermal conductivity, the higher the material's insulating ability, the higher its porosity. However, heat transfer within the pores decreases with a decrease in their diameter, since at a certain diameter, the minimum thermal conductivity can be achieved.

The reduced resistance to heat transfer ($R_{\sum pr}$, $m^2 \cdot K/W$) characterises the area-averaged density of heat flow through a fragment of the building unit under stationary heat transfer conditions, which is numerically equal to the ratio of the temperature difference on sides of the building unit to the area-averaged density of heat flow through this fragment under stationary heat transfer conditions. For a thermally inhomogeneous building unit, the value of $R_{\sum pr}$ is calculated using formula (1) in DSTU 9191:2022.

Determination of linear and point heat transfer coefficients should be based on calculations of two-dimensional and three-dimensional temperature fields, respectively. The calculation methodology is established in accordance with DSTU EN ISO 10211:2022 “Thermal bridges in building construction – Heat flows and surface temperatures – Detailed calculations”.

In the mentioned DSTU 9191:2022, the calculated thermal and physical characteristics of building materials are given in Annex A, the calculated values of the heat transfer coefficients of the inner and outer surfaces of the building envelope are given in Annex B, the thermal resistance of closed air gaps is given in Annex C, linear heat transfer coefficients are given in Annex D, point heat transfer coefficients are given in Annex E, and the calculation of the minimum permissible heat transfer resistance of the internal building envelope of premises is given in Annex F, calculation of the coefficient of thermal homogeneity of the building envelope - in Annex G, calculation of the equivalent temperature of the outside air - in Annex I, calculation of the temperature difference between the temperature of the inside air and the reduced temperature of the internal envelopes of the premises - in Annex K, calculation of the minimum permissible reduced heat transfer resistance of translucent structures in the external envelopes of premises with a glazing coefficient of more than 0.30 - in Annex L, calculation of the building compactness index - in Annex M.

In the factory, the average density of the material, which is related to thermal conductivity, is determined. The curves of hyperbolic dependence of the thermal conductivity coefficient on the average density and porosity of granular materials are a mirror image of each other.

Artificial heat-insulating materials and products (TIM) are those that are manufactured in a factory. The properties of TIM are regulated by the relevant regulatory documents. According to DSTU B GOST 16381:2011 "Thermal insulating building materials and products. Classification and general technical requirements", the thermal conductivity of the materials should not exceed 0.175 W/(m·K) at t= 25 °C and the average density should not exceed 500 kg/m^3.

11.2. The role of the chemical nature of raw materials - organic, inorganic - in assessing the possibilities of creating a fibrous, cellular, granular structure of the material in terms of thermal properties

According to DSTU B GOST 16381:2011, thermal insulation materials and products (TIM) are classified by the type of basic raw material, structure, shape, flammability, and binder content.

According to the chemical nature of the main raw material, TIM are divided into organic and inorganic. Products made from a mixture of *organic* and *inorganic* raw materials are classified as inorganic if the amount of the latter in the mixture exceeds 50 % by weight.

Inorganic materials are used to insulate equipment and pipelines with an insulated surface temperature above t= 100 °C. The use of materials containing organic substances for thermal insulation of surfaces with a temperature above 100 °C is permitted provided that the relevant instructions are provided in standards or technical specifications.

To ensure the specified thermal properties, the structure of thermal insulation materials should be porous and characterised by a certain type of porosity - cellular, fibrous or granular.

The cellular structure is formed by pores whose shape is close to spherical.

The fibrous structure consists of inter-fibre porosity and the porosity of the material fibres themselves.

The granular structure is determined by the porosity of the material grains (e.g. aggregate) and the intergranular void space.

While the cellular structure can be achieved with both organic and inorganic raw materials, depending on the type of insulation material or product, the fibrous and granular structure is characteristic of materials based on inorganic raw materials only.

11.3. Chemical conditions to obtain a given density of the material, the role of water and the influence of water content on the thermal conductivity

The chemical conditions for creating a given average density of the material are implemented in the following ways: gas formation; foaming; high water mixing method; creation of granular porosity (mechanical dispersion); creation of a fibrous framework; swelling of mineral and organic raw materials when heated; method of burning out additives.

The gas formation method implements chemical processes of gas release in the material when special gas generating agents, such as aluminium powder and pastes based on it, are added to the main raw material. Gas (hydrogen) is released as a result of the interaction of aluminium powder with calcium hydroxide. This method is used in aerated concrete production technology. The possibility of using a particular gas generating agent is determined by the relevant requirements - gas generation should be uniform, as close to theoretically possible as possible and occur at the optimum viscosity of the masses to be swollen. Gas generating agents must be chemically stable, non-toxic, and available for use. The most common gas-forming agent is aluminium powder with the following characteristics: active aluminium content - 87...98.5 %, specific surface area - 8000...8500 cm^2/g; covering capacity - 5000...5900 cm^2/g. When using the powder, it is necessary to remove the paraffin layer from its surface. This is done by treatment with surface-active substances (surfactants).

The foaming method is based on reducing the surface tension of a liquid (water) by adding surfactants (foaming agents) according to DSTU EN 934-2:2019 “Admixtures for concrete, mortar and grout – Part 2: Concrete admixtures – Definitions, requirements, conformity, marking and labelling” and is implemented in the foam concrete production technology. Intensive mixing creates foam, which is then mixed with the porous mass.

The high water mixing method is based on the formation of a pore structure due to the evaporation of excess water. This process is carried out during the drying of moulded products. As a result, a significant number of pores are formed. The main technological characteristic of this method is the high water-solid ratio (W/S) of the raw material mixtures. The high water mixing method is used, in particular, in the production of wood-fibre boards with hydromasses containing 1...2 % fibres, and rigid mineral wool boards

with masses containing 20 % fibres. The high water mixing method produces materials not only with a fibrous structure, but also with a cellular structure. The porosity of cellular concrete produced in this way reaches 85 %. Suspension stabilisers (e.g. liquid glass) are used to prevent stratification of the masses. The average density of the material is regulated by the amount of water added to the mixing of the components. For example, to obtain materials with an average density of 500 kg/m^3, the water consumption is 200 %, and for 300 kg/m^3 - about 400 %.

The method of creating granular porosity (mechanical dispersion) is carried out by adjusting the granulometry of the charge. The essence of the method is to obtain dispersed granular materials. This is how backfill is produced. The starting materials used are diatoms, trepels, and limestone.

The method of creating a fibrous framework is based on the use of air, which is fixed by fibres of mineral and organic origin. These fibres create the material's backbone. This method makes it possible to produce products made of mineral and glass wool, asbestos-containing materials, fibreboard, etc. The porous structure in them is created by the interweaving of fibres. Air pores are mostly large, connected, and heterogeneous in shape and size. Long fibres give TIM its strength.

The method of swelling of mineral and organic raw materials when they are heated sharply is realised by evaporation and expansion of chemically bound water in the form of vapour and an increase in the volume of the material under such conditions. Perlite rocks, vermiculite, and clay minerals have the ability to swell. An example of organic materials that swell when heated is polystyrene.

The burning additives method ensures the formation of porosity by burning out organic additives in the raw material charge. It is used to produce porous ceramics. Fine-ground coal, sawdust, expanded polystyrene, etc. are often used as burning agents.

The choice of a method for obtaining a highly porous structure with control of the average density of TIM depends on the characteristics of the composition of the mixtures and the technology of their processing.

Taking into account the general dependence of thermal conductivity on the average density of the material, the thermal conductivity coefficient can be roughly determined by the empirical formula of B.N. Nekrasov for materials with natural moisture content (about 7 %):

$$\lambda = 1{,}16\sqrt{0{,}0196 + 0{,}22 \cdot \rho_m^2} - 0{,}16$$

where ρ_m – is the average density of the material, t/m^3 (g/cm^3).

The thermal conductivity of materials increases significantly when moistened. This is due to the fact that the thermal conductivity of water (λ = 0.58 W/(m·°C)) is 25 times higher than that of air (λ = 0.02 W/(m·°C)). The freezing of water in the pores with the formation of ice significantly increases the thermal conductivity, since for ice λ = 2.3 W/(m·°C), i.e. four times higher compared to water. Therefore, TIM must be protected from moisture. Within certain limits, the thermal conductivity increases in proportion to the increase in volume humidity (W_o), which allows us to calculate the thermal conductivity of a wet material (λ_w) using the formula:

$$\lambda_w = \lambda_c + \delta \cdot W_o$$

where λ_c – is the thermal conductivity of dry material, W/(m·°C);

δ – is the increase in thermal conductivity by 1 % of the volume humidity, which is equal to 0.002 W/(m·°C) for inorganic materials at a positive temperature and 0.004 W/(m·°C) at a negative temperature; for organic materials, respectively, 0.003 W/(m·°C) and 0.004 W/(m·°C).

W_o – is the volume humidity, %.

Questions for the self-control

1. Explain the relationship between the thermal conductivity and thermal resistance of a wall material.
2. Justify the principles of choosing the chemical nature of raw materials to create a fibrous, cellular, granular structure of the material in terms of thermal and physical properties.
3. What are the factors influencing the creation of a given average density of the material?
4. How is the average density of a material related to the thermal conductivity coefficient?

Lecture 12

CHEMICAL AND TECHNOLOGICAL BASES OF MACROSTRUCTURE CREATION TO ENSURE THE DESIGN THERMAL AND PHYSICAL PROPERTIES OF THE MATERIAL

Plan

12.1. The optimised macrostructure of materials according to the criteria of thermal properties: packing of spherical pores.

12.2. Creation of honeycomb porosity.

12.3. Non-stationary and stationary grain structure.

12.4. Pores in fibrous material.

12.5. Polymerisation and polycondensation, and the application of these processes.

12.1. The optimised macrostructure of materials according to the criteria of thermal properties: packing of spherical pores

The optimal macrostructure of an insulating material is one characterised by maximum porosity values with a uniform distribution of pores and aggregate over the volume.

In general, when using binders to produce heat-insulating materials, a prerequisite is to ensure a continuous layer of binder with a minimum water-solid (water-cement) ratio.

Optimal cellular, fibrous and granular structures have a number of specific characteristics when they are formed.

Optimisation of the cellular structure. If the pores are represented as balls of the same diameter (ideal case), then there are two types of their densest packings – hexagonal or cubic face-centred.

The porosity (*P*) formed by *balls* without taking into account the thickness of the partitions is determined by the following relationship:

$$P = \left(\frac{\pi D^3}{6} \Big/ \frac{\sqrt{2} D^3}{2} \right) \cdot 100 = 74{,}05\,\%,$$

where D – is the pore diameter.

All other possible packages are characterised by lower porosity.

The minimum average density without taking into account the thickness of the pore spaces is 330 kg/m^3 for organic materials and 735 kg/m^3 for mineral materials. In the latter case, this is significantly higher than the maximum permissible average density of insulating materials and products (500 kg/m^3). Further reduction of the average density and increase of porosity is possible due to the arrangement of smaller diameter pores between nodes of larger diameter pores to form two- and three-dimensional lattices. It is actually possible to create porosity characterised by a four-dimensional lattice. Thus, insulation materials must have pores of different diameters to achieve maximum porosity.

In industrial conditions, it is not possible to achieve an ideal macrostructure with the exact number of pores of the required size. It is only possible to obtain pores with an uneven diameter distribution. In this case, areas with the highest distribution density (so-called *modes*) will appear. There can be one-, two-modal, etc. porosity. With a four-mode distribution of pores by size, the maximum porosity is 81.2 %.

12.2. Creation of honeycomb porosity

Further increase of the porosity of thermal insulation materials is achieved by direct deformation of the pores into regular polyhedra to obtain *a honeycomb structure* with a minimum thickness of the partitions.

In real materials, capillary and gel pores are formed in the inter-pore partitions. For example, in cellular concrete, the share of capillary porosity is 5...12 %, and the gel porosity is 1.5...2.5 %. The number of these pores increases with cement consumption. The presence of capillary porosity reduces the construction and operational properties of thermal insulation products, while its effect on thermal properties is insignificant.

Thus, for cellular materials, the optimal structure is one with evenly distributed polydisperse closed pores that are deformed into regular polyhedra. The shape of the pores should be close to a regular dodecahedron (twelve-sided polyhedron).

The lowest porosity and highest strength are achieved by inter-pore partitions with a glossy surface, followed by materials with a dense pore surface and the lowest strength materials with a loose pore surface.

12.3. Non-stationary and stationary grain structure

There are two types of grain structure: unsteady and steady.

A non-stationary granular structure is created in backfill insulation materials. The strength of the system is determined by the forces of mechanical friction between the particles.

A stationary granular structure is formed in heat-insulating materials and products produced with the participation of a binder. The strength is determined by the adhesive and cohesive properties of the binder in the areas of contact with the grains. The use of very fine grains or grains with a rough surface is impractical in this case, as binder consumption increases.

Thus, the optimal non-stationary grain structure is formed by small highly porous grains of monofractional composition; the optimal stationary grain structure is formed by highly porous grains of increased size of monofractional composition with a spherical compacted surface.

Optimisation of the grain structure. The porosity of granular materials consists of the porosity of the grains themselves and the intergranular space. In efficient granular materials, the contribution of the intergranular porosity and the porosity of the grains themselves to the total porosity is approximately equal. The porosity of grains is most often closed cellular (glass pores, expanded polystyrene grains) or open cellular (swollen perlite and vermiculite). The first type is considered preferable. The surface condition (smooth or rough) has little effect on the intergranular void space, although it could be expected that grains with irregularities would create a smaller intergranular void space. In this case, loose packing is achieved by roughness. In this case, the intergranular void content of granules in the form of balls is 40...50 %, and that of crushed stone is 43...48 %. The presence of intergranular cavities with small pore diameters reduces the thermal conductivity of the material and increases its strength.

12.4. Pores in fibrous material

Fibrous materials are considered to have pores that form between the fibres. These pores have no defined shape and are a system of interconnected air cavities. The size of the fibre cross-section has a significant impact on the properties of fibre materials. Reducing the diameter of the fibre reduces the number of defects in its structure. This causes an increase in the strength of

the fibres and, as a result, an increase in the strength of, for example, mineral wool carpet. At the same time, the number of fine fibres per unit volume of the entire material increases. The pore size decreases and, as a result, the average density, convective heat transfer, and thermal conductivity decrease.

Conventional mineral fibres have an optimum diameter of 6...8 microns. The cross-section of the fibres should be round. In this case, the average density of the material and the proportion of contact thermal conductivity are reduced. A smooth surface of the fibres without thickening, kinks, or cracks increases their strength.

Thus, for fibrous materials, the optimal structure is one with a minimum solid phase content, which is created by fibres of the optimum diameter and should ensure elasticity under load.

The rational length of the fibres is determined by the technology of their manufacture, and the diameter is determined by the strength and elasticity of the substance from which they are made.

12.5. Polymerisation and polycondensation, and the application of these processes

Methods of obtaining a porous material structure were discussed in the previous lecture.

The highly porous structure of products is fixed as a result of: particle adhesion during moisture evaporation; polymerisation processes; polycondensation of organic binders; hydration and contact curing of mineral binders; sintering of masses.

To carry out or accelerate these processes, various technological methods are used, depending on the type of binder: drying; steaming; autoclave processing; and burning.

Questions for the self-control

1. How to characterise the optimised macrostructure of materials in terms of thermal and physical properties?
2. Describe the features of the honeycomb porosity of the material.
3. What is the non-stationary and stationary grain structure of a material?
4. What are the features of the pore structure in fibrous material?
5. How are the processes of polymerisation and polycondensation used in the technology of obtaining a material with specified thermal and physical properties?

Lecture 13
CHEMICAL PRODUCTION OF MINERAL WOOL

Plan

13.1. Randomly arranged fibres of vitreous structure as the basis of mineral wool products.

13.2. Varieties of mineral wool insulation products.

13.3. Technical features of mineral wool types made of basalt rock, rock mixtures, and silicate industrial wastes.

13.4. Characteristics of mineral melts obtained from different raw materials.

13.5. Fibre formation processes.

13.6. Binders and methods of their introduction into mineral wool in the production of thermal insulation products.

13.1. Randomly arranged fibres of vitreous structure as the basis of mineral wool products

One of the main types of thermal insulation materials in Ukraine and abroad is mineral wool and products based on it. The idea to create mineral wool was suggested by nature itself. It has long been noticed that volcanic eruptions result in molten rocks forming fibres tangled like wool. In Hawaii, the locals called these clumps ‘the hair of the goddess Pele’, the local fire goddess, which she pulls out when she is angry. It is believed that this natural mineral wool, formed from a complex mixture of silicates, gave rise to the

idea of the possibility of industrial production of fibres from rocks in the nineteenth century.

Mineral wool is a fluffy material consisting of randomly arranged fibres of a vitreous structure, which are obtained from a melted charge of silicate industrial waste or their mixtures, and rocks.

The main characteristic of mineral wool is the fibre diameter, which ranges from 0.5 to 12 microns. The thickness of the wool fibres used to produce thermal insulation products should not exceed 8 μm, as increase causes deterioration in the main thermal and physical properties. The length of the fibres is determined by the chemical composition of the melt and is 2...300 mm. Longer fibres contribute to greater elasticity and strength of the products.

13.2. Varieties of mineral wool insulation products

Depending on the type and degree of processing of mineral wool, the following types of mineral wool insulation products are distinguished: *flexible rolls* – mats and mineral wool insulation cords (DSTU B V.2.7-317:2016); *plates and cardboards* (DSTU B V.2.7-316:2016); *lamellar materials* – boards, mats (DSTU B V.2.7-169:2008); *shaped materials* – segments, cylinders, shells (DSTU B V.2.7-235:2010); *bulk materials* – granulated mineral wool; *cord materials* – harnesses, cords.

The classification of thermal insulation mineral wool products and general technical requirements for them are given in DSTU B V.2.7-167:2008.

13.3. Technical features of mineral wool types made of basalt rock, rock mixtures, and silicate industrial wastes

According to DSTU B V.2.7-318:2016 “Mineral wool. Specification”, the raw material defined the type of mineral wool. For basalt wool in the form of fibre web - microfine (type BMTV), ultrafine (type BUTV), superfine for construction purposes (type $BSTV_b$), superfine for special purposes ($BSTV_{sp}$), glass microcrystalline (type BSMKV). Depending on the type of wool, the density should not exceed 18...30 kg/m^3, and the average fibre diameter should not exceed 0.6...3.0 μm. The limit temperature for use is no more than

850 °C. Depending on the type of wool, the thermal conductivity should not exceed: 0.033...0.040 W/(m·°C) at a temperature of *t*= 25±5 °C; 0.052...0.060 W/(m·°C) at *t*= 125±5 °C; 0.084...0.096 W/(m·°C) at *t*= 300±5 °C.

Wool made from thin basalt fibres with a diameter of no more than 8 μm, i.e. BTV type, is divided into thin (BTV type) and thin degreased (BTV_o type). For BTV type wool, the density should not exceed 40 kg/m^3 and the maximum temperature of use should not exceed 700 °C. The thermal conductivity of BTW wool should not exceed 0.038...0.198 W/(m·°C) depending on the temperature. Thermal conductivity is not standardised for BTVO wool.

For mineral wool made from rocks or their mixtures with silicate anthropogenic waste, fibres are used - with a diameter of 3...8 μm (type BM), superfine with a diameter of 0.5...3 μm (type VMST), thin with a diameter of 3...6 μm (type VMT). In turn, VM type wool is classified as follows depending on the acidity module of basalt raw materials: type A (acidity module MK ≥ 2.0), type B (MK ≥ 1.5) and type C (MK ≥ 1.4). Wool of VMST and VMT types is classified as type A. Depending on the type of wool of the VM type, the density should not exceed 80...100 kg/m^3. The thermal conductivity of such wool, depending on the type, should not exceed: 0.038 W/(m·°C) at *t*= 25±5 °C; 0.040 W/(m·°C) at *t*= 125±5 °C; 0.070 W/(m·°C) at *t*= 300±5 °C. In contrast, the density of wool of VMST and VMT types is measured under a specific load of (98 ± 1.5) Pa and should not exceed 30 kg/m^3 (for VMST) and is not standardised (for VMT). The thermal conductivity of wool of VMST and VMT types is measured and standardised only at *t*= 25±5 °C and must be within 0.041 W/(m·°C). The limit temperature for using wool of VM, VMST and VMT types is no more than 700 °C.

The porosity of mineral wool is up to 96 %, which determines its high thermal insulation properties. Due to the open nature of the pores, it is necessary to protect the wool from moisture, as its thermal conductivity increases dramatically when it gets wet. The water absorption of mineral wool when immersed in water is high - up to 600 % by weight, hygroscopicity – 0.2...2 %.

Due to the vitreous state of the fibre substance, high operating temperatures contribute to the development of the crystallisation process, which, depending on the fibre composition, can occur as early as *t*= 500 °C. With the development of this process, the thermal properties of mineral wool deteriorate.

13.4. Characteristics of mineral melts obtained from different raw materials

The raw material mixture used to produce the silicate melt from which mineral wool is then manufactured is often multicomponent. According to the generally accepted methodology, the composition of the charge is designed to ensure that the *modulus of acidity (Mk)* of the fibre is not less than 1.5 for the highest quality category and not less than 1.2 for the first category, which is determined by the formula:

$$M_к = \frac{\mathrm{SiO}_2 + Al_2O_3}{CaO + MgO} \geq 1{,}2 \ \ (\geq 1{,}5).$$

Fibres with Mk = 1.5...2.5 are characterised by increased service life, and fibres with Mk < 1.2 are not water resistant. The acidity modulus Mk is directly dependent on the content of SiO_2 and Al_2O_3 in the charge, but an excessive amount of them can dramatically increase the viscosity of the silicate melt, thereby reducing the productivity of the melting unit. Therefore, it is necessary to look for alternative solutions and appropriate melt-to-fibre processing technologies to ensure the main process parameters that determine the quality of the material.

When calculating, it is necessary to take into account not only the value of Mk, but also *the viscosity modulus (Mv)*, which more accurately characterises the state of the melt and is determined from the following relationship:

$$M_v = \frac{M_{\mathrm{SiO}_2} + 2M_{Al_2O_3}}{2M_{Fe_2O_3} + 2M_{FeO} + M_{CaO} + M_{MgO} + M_{K_2O} + M_{Na_2O}},$$

where M_{RmOn} is the molecular weight of each oxide.

The viscosity modulus of the silicate melt should not exceed 1.2, and in the case of the bath method of mineral wool production, it should not exceed 1.4.

Components that turn into a liquid state at temperatures above 1500 °C are refractory. In any case, a pilot melting is carried out to adjust the composition of the charge and specify the technological mode of operation of the equipment.

Rocks of gabbro-basalt type and their analogues, sedimentary rocks, volcanic slag, industrial waste such as crushed stone from blast furnace slag,

ash, ceramic and glass scrap, silicate brick scrap, etc., as well as mixtures of the above components and other raw materials that ensure the production of mineral wool in accordance with the requirements of DSTU B V.2.7-318:2016 and have undergone radiological control are used for the production of rock wool.

It is quite rare to use raw materials without a charge that ensures the required chemical composition of the melt. The starting materials must ensure a low melting point, the required melt viscosity and the performance characteristics of mineral wool. The components of the raw material charge must be in short supply and easy to prepare. Grinding the raw materials helps to accelerate the silicate formation reactions and melt homogenisation, which is necessary to obtain stable fibre properties.

13.5. Fibre formation processes

The mineral wool production technology involves the following basic operations: preparation and loading of raw materials into a melting unit (cupola, bath furnace, etc.); melting of raw materials in the melting unit; processing of the melt into fibre using a centrifuge or other method; deposition of mineral fibres, and formation of a mineral wool blanket.

As the temperature in the smelting unit rises, physical and chemical processes of interaction between the components of the charge begin, leading to silicate and glass formation.

According to the concepts developed by J.I. Frenkel, melting is not a transition of a substance from a crystalline to an amorphous state, but only its partial amorphisation, which is associated with the disturbance of the ‘far order’ while maintaining the ‘near order’ in the structure. Melting is in many ways similar to the transition of a substance into another modification. At sufficiently low temperatures, the liquid (melt) is crystalline in structure (similar to a microcrystalline solid).

Silicate complex ions $(Si_xO_y)^-$ are able to take on the role of compounds that form structural groups in a silicate melt due to their extremely strong covalent bond –Si–O–Si–, which persists even under these extreme conditions and creates the anionic framework of the melt.

The main properties of the melt that affect the characteristics of the resulting mineral fibres include surface tension, viscosity, and the tendency to

crystallise. These properties depend primarily on the chemical composition of the raw materials and the melt temperature.

The production of cotton wool is virtually independent of the type of melting unit. The feasibility of using a furnace of a particular design depends on the type of raw material, its composition and physical state, granulometry, melt viscosity requirements, mineral fibre quality and the area of its use.

The main industrial methods of processing silicate melt into fibre are blown, centrifugal and combined.

Blown methods can only be considered as a fundamental basis for combined methods. The principle of the method is the horizontal or vertical action of the energy carrier at a high speed of 400...600 m/s on the melt jet.

Centrifugal methods are based on the use of centrifugal force arising from the high speed of rotation of rolls or discs of the fibre-forming unit, when the melt is gradually detached from the surface and distributed in the form of thin filaments.

Combined methods combine both blowing and centrifugal forces.

13.6. Binders and methods of their introduction into mineral wool in the production of thermal insulation products

The main purpose of the binder in mineral wool products is to create contacts between individual mineral fibres to fix the fibrous macrostructure of the dispersed system. In the technology of mineral wool products, binders have certain requirements: high adhesion and the ability to spread evenly over the fibre; sufficiently high cohesion of the binder after it has hardened; water solubility in the preparation of working solutions or the ability to form stable emulsions; water and heat resistance in the cured state; durability; non-toxicity; low shrinkage, which prevents the appearance of cracks in the material.

Mineral binders, despite their lower cost, availability and non-toxicity, are not popular due to their low adhesion to mineral fibres, low strength and high average density of products obtained by using them. The use of such binders is possible in certain cases when it is necessary to obtain a rigid, inelastic macrostructure without particularly strict restrictions on the average density.

Organic binders meet most of the above requirements and are the most suitable for the mineral wool-based insulation industry. The group of such

substances includes synthetic resins, bitumen, dextrin, starch, etc. The solvents of the binders are water, alcohols, ethers, petrol, benzene, xylene and others. The most common synthetic binders used in the production of mineral wool products are phenol-formaldehyde resins, such as thermosetting phenol alcohols and urea resins.

The most widely used binders are *multicomponent binders* in the form of a composition of resins with various plasticisers, which increases the elasticity of mineral wool products. Thanks to the use of binding compositions, it is possible to produce mineral wool products with average density and thermal conductivity even lower than that of the original mineral wool.

There are several *ways to introduce binders* in the production of mineral wool products: *by spraying; watering with pushing-off and vacuuming; and producing hydromass (wet method)*.

By *spraying*, a solution or emulsion of the binder in the form of an aerosol is applied to the mineral wool in the fibre deposition chamber. The binder is sprayed using nozzles through the steam manifold of a centrifugal blower or through the centrifuge shaft. In the latter two cases, the binder is distributed more evenly. The higher the degree of atomisation, the more evenly the binder will cover the individual fibres, and the higher the quality of the bond. However, due to high binder losses during spraying, this method is only cost-effective for soft, semi-rigid boards and coiled material with a low average density. To give the boards hydrophobic properties, nozzles for spraying temperature-resistant oil are installed in the same places.

When *watering with pushing-off and vacuuming*, the binder falls in the form of a continuous flat jet onto the moving mineral wool blanket. The blanket is then further compacted, squeezed free of excess moisture and vacuumed to optimise the moisture content of the material. The excess binder is pumped back into the watering bath with a chute after it enters the pool. The method is used to produce rigid and hard mineral wool boards.

When *producing hydromasses*, there are two ways of forming mineral wool products – *pressing method* and *casting method*. In both cases, a dry mineral wool blanket is fed from the fibre deposition chamber into a mixer, where a binder solution is supplied. The mixed mineral wool with the binder solution and other components is laid out in a layer on a continuously moving conveyor, after which it is vacuumed and subjected to heat treatment.

The main distinguishing feature of the methods is the difference in the ratio of ‘solid phase – liquid’. The pressing method allows the use of hydromasses with a ratio of mineral wool to mortar from 1:3 to 1:10, while the casting technology requires a higher consumption of binder.

The pressing method produces mineral wool products with higher technical and economic performance than the casting method; slabs made from hydromasses are distinguished by their stiffness and compressive strength. The properties of the products are the same in all directions due to the random rather than oriented distribution of fibres.

Questions for the self-control

1. What is the structure of mineral wool products?
2. What are the types of thermal insulation products made of mineral wool?
3. Describe the features of the properties of mineral wool obtained from basalt rock, a mixture of rocks and silicate industrial waste?
4. What are the differences between mineral melts of different raw materials in the production of mineral wool?
5. Describe the differences in the processes of fibre formation in different ways during production of mineral wool.
6. What is the reason for the choice of binders and methods of their introduction into mineral wool in the production of heat-insulating products?

Lecture 14
CHEMICAL BASIS OF PRODUCING CELLULAR GLASS FROM SILICATE MELT

Plan

14.1. General technical and thermophysical characteristics of cellular glass.

14.2. Conditions for obtaining and processes during the melting of raw materials of various origins.

14.3. Influence of gas-forming agent on the pore structure.

14.4. Dependence of the average density of foam glass on the foaming temperature and its influence on performances of the material.

14.1. General technical and thermophysical characteristics of cellular glass

Depending on the raw materials used, there are *two types of cellular glass*: the material produced using solid finely ground glass (*foam glass*) as the main starting component; and *materials based on liquid sodium glass*, finely ground fillers and special additives, which will be discussed in the next lecture.

Cellular glass based on solid glass is often called “foam glass” because this porous material looks like frozen foam with spherical pores separated by thin glass walls. Foam glass is *easy to machine* - it can be sawn, drilled, ground, and nailed into. It is characterised by *high biostability*. The average density of foam glass is 150...800 kg/m^3. The material is characterised by *increased strength* and *structural quality factor* compared to other cellular materials, which is explained by the high strength of the frozen vitreous phase. *The porosity* is 80...95 % of the total volume of the material. The pores are closed, with the exception of soundproof and filter foam glass, which is dominated by communicating pores. The size of macropores that make up the cellular structure of foam glass is 0.1...3 mm. In addition to them, there are micropores that penetrate the partitions between the macropores. The size of micropores is 1...10 microns. For all types of foam glass, a decrease in pore size is accompanied by an improvement in their quality and performance characteristics. Foam glass has a *low thermal conductivity* (0.055...0.085 W/(m·°C)), which is ensured by a high degree of porosity, small pore sizes and a glassy state of the frame. *The sound absorption coefficient* for foam glass with a combined porosity of 0.5...0.65 is 600...1200 Hz, which meets the requirements for acoustic materials. *Frost resistance* is high enough only if the foam glass surface is protected from moisture, where some of the pores are open. *Heat resistance* is determined exclusively by the softening point, which depends on the type of raw glass. The material is non-flammable; the temperature limit for use in conventional industrial glasses is t= 400...500 °C, alkali-free glasses - up to t= 600 °C, and high-silica glasses – up to t= 1000 °C.

14.2. Conditions for obtaining and processes during the melting of raw materials of various origins

The raw materials used in the production of foam glass include scrap container and window glass, glass production waste, specially welded glass granulate, low-melting alkali-containing rocks, and various gas-forming agents. The highest quality foam glass is produced from specially welded glass granulate. Glass waste and scrap produce a material with unstable characteristics. Preference should be given to melts with a wide temperature range of working viscosity, or so-called ‘long’ melts. It is recommended to use glass of the following chemical composition, % by mass: SiO_2 – 70...75; Al_2O_3 – 1...2; CaO - 3...6; MgO - 2...3; Na_2O - 15...16; SO_3 – 0.5...1. The dispersion of glass in the charge is quite high – 500...700 m^2/kg by Blaine.

14.3. Influence of gas-forming agent on the pore structure

The type of gas-forming agent and the chemical composition of the raw glass determine the pore pattern of the foam glass. When using glass with a low crystallisation temperature, the material is dominated by communicating pores. Low water absorption (1...10 % by volume) is ensured by closed porosity. In this case, water is adsorbed only in the surface destroyed open pores of the foam glass. In the case of interconnected pores, water absorption is much higher (70...80 % by volume). The material's resistance to prolonged exposure to water is quite high and depends on its chemical composition.

In turn, the appropriateness of using a particular gas-forming agent depends on the technological parameters of foam glass production (temperature, degree and type of porosity), glass melt properties (viscosity range, surface tension), and colour. Depending on these factors, the following *gas-forming agents* are used: pyrolusite, sodium nitrate, limestone, marble, calcium carbide, anthracite, coke, graphite, and silicon carbide.

14.4. Dependence of the average density of foam glass on the foaming temperature and its influence on performances of the material

The relationship between the strength and average density of foam glass can be expressed by the empirical formula:

$$R_{c.} = 0{,}2 \cdot \rho_o - 20,$$

where R_c is compressive strength, kg/cm^2;

ρ_o is average density, kg/m^3.

In turn, *an inverse proportional (hyperbolic) relationship* is observed between the average density of foam glass and its foaming temperature, depending on the type of gas-forming agent. For example, when anthracite is used at temperatures up to *t*= 715 °C, the average density of foam glass can be achieved at 400 kg/m^3, but at *t*= 800 °C, the average density no longer exceeds 200 kg/m^3. Accordingly, while *the thermal conductivity* at an average density of 150 kg/m^3 does not exceed 0.055 W/(m·°C), at 800 kg/m^3 it rises to 0.085 W/(m·°C).

In addition to the foaming temperature and the type of gas-forming agent, the average density of foam glass depends on the duration of foaming and the degree of grinding of the powdered gas-forming agent and glass.

Questions for the self-control

1. What are the structural features that explain the technical and thermal characteristics of cellular glass?
2. Give the conditions for obtaining and melting processes of raw materials of different origin.
3. Describe the influence of gas-forming agents on the nature of the pore structure of cellular glass.
4. What are the technological factors affecting the average density of foam glass?
5. What processes determine the thermophysical characteristics of foam glass?

Lecture 15
PRODUCTS OBTAINED FROM LIQUID GLASS AND SWELLING ROCKS

Plan

15.1. Chemical bases of obtaining liquid (soluble) glass.
15.2. Swelling processes in the presence of technological admixtures.
15.3. Dehydration and granulation of a sol-glass mixture.
15.4. Processes for swelling of granulate.

15.5. Conditions for ensuring the specified thermal and physical characteristics of the material.

15.6. Chemical swelling ability of rocks of the perlite and vermiculite group.

15.7. Physicochemical and technological features of the perlite swelling process.

15.8. Features and temperature parameters of swelling depending on the granulometry of the rock.

15.9. Thermal and physical properties of the products obtained from swollen raw materials.

15.1. Chemical bases of obtaining liquid (soluble) glass

Liquid glass production methods can be divided into dry and wet.

Dry methods are based on the production of alkaline silicate melts at high temperatures, followed by cooling to a glassy state and dissolution. The dry methods include carbonate, sulphate, carbonate-sulphate, bisulphate, nitrate, alkaline and sulphide methods.

Wet methods are based on the dissolution of various forms of silica in caustic alkalis to produce alkaline silicate solutions (liquid glass) without preliminary cooking of vitreous alkaline silicates (liquor or granulate). Wet methods include alkaline, sulphide, silicon and silicide, and carbide.

Other methods include chloride and silicon fluoride methods.

15.2. Swelling processes in the presence of technological admixtures

Thermal insulation materials based on swollen liquid glass include a wide range of materials, the main structural element of which is the swelling products of hydrated liquid glasses (hydrated alkaline silicates).

According to *the nature of their swelling*, liquid glass materials are divided into thermoset and swollen as a result of the chemical interaction of liquid glass with special substances added to the raw material mixture. Thermoset materials include granular and fired monolithic materials. Chemically swollen materials include casting compositions in which a gas-forming component is added.

Thermal insulation composite materials based on liquid glass are divided into *cold and hot-melt insulation materials* depending on the hardening (polymerisation) of the main component.

In addition to the alkali-silicate component (liquid glass or aqueous suspension of finely ground silicate), the components of raw material mixtures required for *cold-blowing liquid glass* are a foaming agent, a surfactant and an active additive. The manufacturing process typically includes the following stages: a) mixing of the components of the raw material mass; b) swelling; c) curing of the swollen mass; d) drying at t= 20...120 °C. In some embodiments of the technology, similar to the foam concrete technology, the first two stages are interchanged. Metal compounds are most often used as gas-forming agents, the effect of which is based on the heterogeneous reaction of the metal with an alkaline solution, accompanied by the release of hydrogen. The action of chemical-type gas generators is based on a liquid-phase decomposition reaction (H_2O_2 and other peroxides that release oxygen) or oxidation (polyethylhydrosiloxanes that release hydrogen). It is possible to use volatile foaming agents, the action of which is based on the evaporation of a substance insoluble in liquid glass (CCl_4, dry ice).

Hot swelling is ensured by the formation of solid inorganic foam (foam silicate), which acquires the specified size and shape in the process of porosity of the liquid-glass mixture under heating (t= 350...450 °C). By purposefully changing the content of the solid phase in the raw material mixture by introducing various fine mineral fillers, it is possible to obtain foam-silicate products with the required average density.

15.3. Dehydration and granulation of a sol-glass mixture

The technology for the production of *swollen granular products* based on liquid glass includes four main stages: a) preparation of the raw material mixture; b) granulation with simultaneous curing; c) drying of the granulate; and d) swelling of the granulate at t= 300...500 °C.

The preparing a *liquid glass composition (LCC)* for *beads* is carried out in a high-speed mixer by mixing sodium liquid glass, finely ground mineral fillers and special additives. The finished LCC, which is a homogeneous viscous mixture, is fed to rollers or an extruder (a screw press with a hole

nozzle). The tape coming out of the extruder is cut into grains of specified sizes in a knife rotary crusher. In the production of glass beads, Y. P. Gorlov proposed a different type of bead granulation, which consists in using sodium liquid glass in a solution of calcium chloride as a medium for the formation of cheese granules by coagulating it in a solution of calcium chloride. Thus, the prepared LCC is fed to a die and, passing through its holes, is divided into droplets. Liquid-glass droplets fall into a special container with a $CaCl_2$ solution equipped with a conveyor belt. The formation of granules in the solution takes 20...30 minutes. During this time, the granules gain the mechanical strength required for further transport and swelling. When liquid glass is added by spraying into a concentrated $CaCl_2$ solution, the hydrolysis reaction prevails at the interface of the two liquid phases due to the difference in pH values of the solutions. The neutralisation of the anionic charge leads to immediate coagulation of the surface bonds. If the concentration of silicates is high enough, a membrane is formed with a negative charge on the side of the silicate and a positive charge on the side of the calcium chloride solution. When the viscosity of the silicate solution is high, the membrane gradually transforms into a gel-like shell of coagulated silicate with a low concentration gradient created by the walls of calcium from the $CaCl_2$ solution and sodium from the silicate solution.

The moulded raw granules are dried by flue gases from the thermal units to prevent sticking together and are then sent for low-temperature heat treatment.

The raw granulate swelling can be carried out in various thermal units, such as drying drums, tunnel and fluidised bed furnaces, vertical vibratory drying units, etc.

15.4. Processes for swelling of granulate

During the thermal swelling of a liquid-glass composition, water is the main pore-forming agent. The moisture content in raw material mixtures is classified as follows: capillary water, which is retained by capillary forces; adsorption-bound water, which is retained by Van der Waals forces in the amount of two or three molecular layers, is removed at a temperature $t \geq 100$ °C; chemically bound water, which is part of hydrate formations. If such water is bound by basic valences, it evaporates at $t = 300...500$ °C. In

crystalline hydrates, it can be bound in the form of ions or molecules and held in the lattice by coordination bonds, removed at t= 200...300 °C.

Depending on the type of structure-forming components, liquid glass materials are:

- ✓ products of its swelling (silopor, glass porcelain);
- ✓ composite materials that include swollen granular liquid glass and a binder.

Swelling of liquid glass is carried out in moulds or without them in chamber or slit furnaces at a temperature not exceeding 500 °C due to the release of water contained in the beaded glass pore granules when the glass enters a pyrolytic softened state. Although an increase in the amount of water in the beaded glass mat reduces its softening temperature to a known limit, an excessive amount of water contributes to the formation of a large-pore defective structure of the material.

The production of *silopor* differs from *glasspor* production by combining granulation and swelling in one operation, which is performed by spraying a liquid glass mixture in a tower dryer. The resulting swollen granular products are used to make products using various organic and mineral binders or as a filling material for filling voids, for example in honeycomb laminates.

In *materials based on expanded liquid glass*, the type of binder (mineral or organic) determines the name of the composite porous material, for example, glass silicate, glass laminate, glass cement, glass bitumen, glass polymer.

For the production of *glass cement*, fast-setting and especially fast-setting cements are used. Glass cement is produced by mixing glass fibre granules with cement milk, followed by hardening and drying of the moulded products.

Liquid glass or a mixture of liquid glass and special additives is used as a binder in the production of *glass silicate*. Depending on the technology, there are coarse-grained lightweight concrete, fired glass silicate, and cast-in-place glass silicate.

Glass phosphogel is produced from a mixture of glass fibre, liquid glass and orthophosphoric acid, which is subject to heat treatment in a closed volume (in closed moulds). The material is characterised by a coarse porous structure.

For production of *glass bitumen,* glasspor is used as an aggregate and bitumen of BN-IV and BN-V grades as a binder.

Glass phenolic plastic is made from glasspor and phenol alcohols (concentration 80...85 %), which can be diluted with fillers to reduce polymer consumption and improve the thermal performance of products.

15.5. Conditions for ensuring the specified thermal and physical characteristics of the material

The expanded granular products are used to manufacture products using various organic and mineral binders or as a filling material to fill voids, for example, in honeycomb plastics.

The thermal conductivity of the lightest materials (silopor and glasspor) is 0.028...0.035 W/(m·°C). For other liquid-glass foams, the thermal conductivity does not exceed 0.065 W/(m·°C). This is due to the fact that *the porosity* of such materials reaches an average of 98...99.6 %, and the macrostructure is cellular. Practically, in free swelling, non-granulated liquid glass materials have an average density of 10...200 kg/m^3. The average density of granulated materials (in lumps) is slightly higher.

The heat resistance depends on the chemical state of the liquid glass, the type and amount of additives used, and the nature of the porosity. The temperature range for using products based on expanded liquid glass is *t*= -200...+660 °C. An increase in the silicate module of liquid glass increases the heat resistance of the material.

15.6. Chemical swelling ability of rocks of the perlite and vermiculite group

In the industry, the term “perlite” is used to refer to all volcanic glass containing 1...10 % water. Swellable rocks *include water-containing glassy igneous rocks* (pearlites, obsidians, marekanites, vitrophyrites, tuffs, pechstains, etc.), as well as *secondary mica* (vermiculite highly hydrated mica - hydrobiotite, hydrophlogopite), which are formed as a result of physical and chemical transformations in magnesium-iron mica (biotite, phlogopite), in the crystal lattice of which alkalis are replaced by water. Obsidians contain up to 1 % water, perlites - 1...6 %, other volcanic glasses - more than 6 %. A

common feature of swelling rocks, regardless of their composition and structure, is their ability to *significantly increase the volume of rock grains* due to the intensive release of chemically bound water during high-temperature processing.

15.7. Physicochemical and technological features of the perlite swelling process

According to DSTU B V.2.7-157:2011 “Perlite expanded sand and crushed stone. Technical specifications”, the compacted perlite is mainly used in the form of perlite sand (grain size up to 5 mm) and perlite crushed stone (grain size 5...20 mm).

High-temperature processing (burning) of perlite is the main technological operation that determines the main quality characteristics of the resulting material. Swelling of the pre-dispersed rock occurs when it enters a plastic-viscous (pyroplastic) state when heated and is mainly due to the release of chemically bound water in the form of steam and, partially, due to the release of CO_2. The chemically bound water is of a zeolite nature and can be removed without destroying the crystal lattice. *The effectiveness of the swelling process* is assessed by the swelling coefficient, the ratio of the volume of swollen rock to the original, which can be in the range of 8...15. The chemical composition significantly affects *the viscosity* and *surface tension* of the softened rock. For example, the presence of alkalis reduces the softening point, so the content of Na_2O+K_2O in the raw material should be $\geq$4 %. For the swelling process to work properly, it is necessary to increase the viscosity and reduce the surface tension of the mass.

15.8. Features and temperature parameters of swelling depending on the granulometry of the rock

The swelling capacity of *perlite* is inversely proportional (hyperbolic) to its dispersion. The effectiveness of the swelling process is assessed by the swelling coefficient, the ratio of the volume of swollen rock to the original, which can be in the range of 8...15. In production conditions, the coefficient of swelling of grain perlite (grain size up to 1.5 mm) should be at least 6, and lumpy perlite (size 5...10 mm) – at least 4.

The prerequisite for satisfactory swelling of perlite is the content of 1...3 % of the so-called ‘effective’ molecular water. In this case, the raw material is swollen according to a one-stage scheme - it is immediately fed for heat treatment. If the amount of water in the raw material exceeds the optimum amount, swelling is carried out in two stages – first, at t= 200...400 °C, the raw material is heat treated to release excess water to the optimum amount, and then the perlite with the effective amount of water is fed into a high-temperature zone, where it is swollen. An excessively high effective water content disrupts the normal swelling process. In this case, intensive formation of water vapours can occur before the pearlite enters the pyrolytic state. The pressure created by them is so great that it leads to an ‘explosion’ of the rock being burned, with the formation of fine pearlite dust.

The correct choice of temperature for perlite heat treatment is *prerequisite* for obtaining high-quality products. Typically, the temperature of perlite heat treatment, which achieves the required ratio between the softening of the glass mass and the gas phase pressure, which arises mainly due to the evaporation of perlite ‘effective’ water, is in the range of t= 850...1250 °C.

In the swollen state, perlite is a light, loose heat-insulating material in the form of small (sand) or larger (crushed stone) grains with a highly porous structure.

The vermiculite swells due to the mechanical action of elastic water vapour, which is instantly formed during the heat treatment of the grains. In this process, mica plates are split and pushed apart in a direction perpendicular to the plane of adhesion, with an increase in grain volume by 15 or more times. Similarly to perlite, the quality of vermiculite swelling is assessed by the swelling coefficient, which is 4...40.

Reducing the grain size of swollen vermiculite leads to an increase in its average density (hyperbolic dependence). The optimal heat treatment time is 2...3 min at t= 900...1100 °C. Increasing the heat treatment time at such temperatures, although slightly increasing the average density, causes a sharp increase in product brittleness. Particles fr. ≤15 mm are sent for swelling.

Water in raw vermiculite has different forms of bonding (chemically bound, inter-package, adsorbed on the adhesion planes, zeolite, hygroscopic). The main role in swelling is played by the release of inter-package and chemically bound water at t= 200...1000 °C.

15.9. Thermal and physical properties of the products obtained from swollen raw materials

Materials based on expanded liquid glass

The cold swelling provides low energy consumption and a simple production technology. However, it is not possible to produce lightweight materials (with an average density below 100 kg/m^3) with sufficiently low thermal conductivity. This is the reason why cold-swelling insulation is not widely used in production. Another significant disadvantage of low-temperature technology is the reduced chemical resistance (primarily less water resistance) of the compression product.

The hot swelling produces foam-silicate products with an average density of 50...200 kg/m^3, a thermal conductivity of 0.032...0.065 W/(m·°C) and a compressive strength of 0.08...1.5 MPa. The functional properties of foam silicate are similar to those of foam glass. This material retains its shape and properties when heated to $t \leq 450$ °C, is biostable and environmentally friendly. The only drawback is its rather high water absorption due to a significant proportion of through porosity in the structure. This disadvantage is eliminated by applying protective polymer or inorganic waterproof coatings to the surface of the boards in the form of a continuous film with a thickness of 0.1…0.5 mm. The coating reliably blocks the penetration of moisture into the material and makes it durable. Particularly lightweight types of foam silicate with an average density of 50...75 kg/m^3 have thermal conductivity typical of foams made from organic substances, but the main advantage of foam silicate is that it is a non-combustible material.

Materials from expanded rocks

Two types of materials can be produced from *expanded perlite and vermiculite* using different binders:

- ✓ non-burning – expanded perlite sand, perlite concrete, bituminous perlite, perlite plastic concrete, ligno perlite, vermiculite concrete;
- ✓ firing – ceramic perlite, perlite phosphate, ceramic vermiculite.

Expanded perlite and vermiculite are used to ensure effective insulation, fire safety, durability and environmental friendliness of a construction project. The main technical and operational characteristics of products based on them depend on the average density and fractional

composition of the expanded aggregates, the type and consumption of binder and additives, the water content of the moulding mixtures, and the preservation of lightweight aggregate grains during the preparation of moulding mixtures.

The optimal fractional composition of aggregates is determined based on product requirements. The predominant content of fine aggregates increases strength, average density and thermal conductivity. Coarse aggregates produce lighter but less durable products.

Mineral and organic binders, sometimes hydrophobic and foaming agents, are used as additives to expanded perlite and vermiculite. The choice of binder is determined by the specifics of the product manufacturing process and its operation. *The organic binders* make it possible to produce water-resistant, lightweight, sufficiently strong, but low-heat-resistant products with a service temperature of t= 60...200 °C. *The mineral binders* increase the average density of the products, but also extend the thermal range of their use at high temperatures (up to t= 1100 °C) and increase their mechanical strength.

Perlite insulation is used in the form of polyethylene bags filled with swollen perlite sand, which are pressed for the convenience of further laying of the reinforced screed. The thickness of such a heat-insulating element is about 100 mm, the average density is about 200 kg/m^3, and the thermal conductivity is about 0.065 W/(m·°C). It is used to insulate cold attics and create warm underfloor heating in the horizontal plane.

Vermiculite insulation is used in the form of boards made of swollen vermiculite with an inorganic binder. They are characterised by environmental friendliness, fire resistance, high heat and sound insulation properties, chemical inertness, and decorative properties. They are used for thermal insulation of load-bearing metal structures, reinforced concrete floors, for the manufacture of cable ducts, fireproof partitions, thermal insulation of stoves, fireplaces and chimney systems. The boards are used for thermal insulation of any equipment in the energy sector. Characteristics: average density 350...650 kg/m^3; thermal conductivity 0.09...0.16 W/(m·°C); bending strength 0.5...1.5 MPa; compressive strength 0.6...2.0 MPa; sound absorption coefficient 0.4...0.8; application temperature t= -50...+1100 °C.

Questions for the self-control

1. Describe the chemical processes involved in the production of liquid (soluble) glass.
2. Explain the mechanism of swelling processes in the presence of technological additives.
3. What is the essence of the processes of dehydration and granulation of a sol-glass mixture?
4. What processes accompany the swelling of liquid glass granulate?
5. How are the specified thermal and physical characteristics of materials based on swelling rocks ensured?
6. What is the reason for the ability to swell rocks of the perlite and vermiculite group?
7. Describe the features of the process of swelling of perlite.
8. How does the swelling process depend on the granulometry of the rock?
9. What are the thermophysical properties of materials from swollen raw materials?

Lecture 16
CHEMICAL BASIS OF FIBROLITE PRODUCTION

Plan

16.1. Preparation of raw wood.
16.2. Requirements for mineral binders.
16.3. Features of the influence of mineralising additives on cement hydration processes.
16.4. Processes for obtaining the moulding mixture.
16.5. Chemical processes in the hardening fibrolite.
16.6. Dependence of the thermophysical properties of fibrolite on chemical processes in its production.

16.1. Preparation of raw wood

Fibrolite (from the Latin “fibra”, and Greek “líthos” – stone) is a tile material made using a mineral binder and special wood chips (wood wool).

For the production of fibrolite, the following materials are used: wood wool, binder and mineraliser.

Wood wool is obtained by using non-business wood with the bark previously removed, as the bark contains a significant amount of extractives that negatively affect the hardening of binders. The wood itself also contains a whole range of organic substances – lignin, hemicellulose, resinous and extractive substances, sugar compounds, mineral salts. Some of these substances (e.g. hemicellulose) under the influence of the alkaline environment of the portland cement mortar turn into water-soluble sugar compounds, which can have a very negative impact on the hardening of cement stone and reduce its strength by 5...10 times. After wood has been stored in warehouses for up to 6 months, the content of extractive substances in it decreases due to their oxidation and conversion to a hardly soluble form.

Wood wool is a thin and long wood chip 200...500 mm long, 2...5 mm wide and 0.2...0.6 mm thick. Deviations in thickness downwards reduce the mechanical strength of the products, and deviations upwards reduce the elasticity of the board and increase its brittleness. Wood wool can be partially replaced with ordinary chips from planing and joining machines.

Preparation of wood raw materials includes removing the bark from unused wood, keeping it in the open air for 4…6 months to partially neutralise extractives by converting them into less soluble forms, sawing wood into lengths up to 0.5 m, and obtaining wood wool on special machines. The wool is separated on screens or by air, removing dust and small particles, and then dried to ensure deeper penetration of the mineraliser into the wood and a higher degree of mineralisation. When the mineraliser solution is heated up to t= 40 °C, the mineralisation process is more profound and complete.

16.2. Requirements for mineral binders

The binder in fibrolite can be: cement, magnesia, magnesia-dolomite, cement-lime, lime, lime-treppel and gypsum.

Portland cement or another binder with similar properties used for fibrolite production should be fast-setting, cement grade 400 (strength class 32.5) or higher. To improve the kinetics of strength gain, the cement can be diluted to a higher specific surface area. Cement containing up to 60 % tricalcium silicate (C_3S) and more than 8 % tricalcium aluminate (C_3A) is the most suitable for fibrolite production.

16.3. Features of the influence of mineralising additives on cement hydration processes

Mineralisers are designed to neutralise the harmful effects of sugar compounds on cement stone and improve the adhesion of cement to wool. The mineralisers used are an aqueous solution of calcium chloride $CaCl_2$, soluble glass $Na_2O \cdot nSiO_2$ or alumina sulfate $Al_2(SO_4)_3$, which are used to moisten the wood wool.

The hydration processes of Portland cement in the presence of mineralising additives are accelerated. For example, cations are ranked in the row according to their effect on the acceleration of C_3S hydration (in the case of portland cement): $Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+}$. Regarding the effect of anion, it can be concluded that chloride ion is inferior to sulfate ion, and in general, the accelerating effect of anions decreases in the row: $SO_4^{2-} > OH^{-} > Cl^{-} > Br^{-} > I^{-} > NO_3^{-} > CH_3COO^{-}$.

16.4. Processes for obtaining the moulding mixture

The moulding mixture is often produced using a dry method, in which pre-moistened wool is sprinkled with cement. The wool moisture content should be 140...160 %. If the content of C_3S in portland cement is less than 50 %, the mineralisation operation can be eliminated. Cement dosage depends on the fibrolite grade and wool type and is 1.3...1.9 kg/kg for strength class 32.5 (grade 400). The mixture is produced in mixers that prevent the wool from being compacted and wound on the shaft during the mixing process. From the mixer, the fibreboard mass is distributed by a conveyor with a special loosening device and a roller separator to moulds, which are pressed using mechanical, hydraulic or pneumatic presses. The thickness of the mass layer is higher, the greater the degree of compaction. For example, in the manufacture of fibrolite grades 300 and 350, the layer of mass in the mould is 2.5…3 times higher than the thickness of the finished fibrolite board. In case of fibrolite grades 400 and 500 the layer of mass in the mould is 3.5...5 times higher.

16.5. Chemical processes in the hardening fibrolite

When producing insulating fibrolite, a pressing pressure of 0.06...0.1 MPa is used due to the dead weight of the moulds above in the packages and a special pressure plate. More dense boards are produced by hydraulic pressing at a specific pressure of 0.25...0.4 MPa.

16.6. Dependence of the thermophysical properties of fibrolite on chemical processes in its production

According to applications, fibrolite is divided into: 1 – heat-insulating (with an average density of 250...350 kg/m^3); 2 – heat-insulating, structural and acoustic (351...450 kg/m^3), and 3 – structural (451...500 kg/m^3).

The grade of fibrolite corresponds to its average density, which depends on the consumption of binder and the pressing force during manufacture. Thus, at an average density of 300 kg/m^3, the thermal conductivity coefficient is 0.098 W/(m·°C), but at 500 kg/m^3 it reaches 0.151 W/(m·°C).

Increasing the consumption of binder makes it possible to obtain a more porous and lightweight structure of fibrolite due to loosening of the moulding mass, reduced pressing pressure and greater strength at the points of contact with wood wool. However, only a simple increase in the cement content without changing the technological modes of individual operations will lead to an increase in the average density and thermal conductivity of the material. The bio- and fire resistance of fibrolite will increase with higher dosage of a binder. In addition, the flexural strength significantly depends on the quality and length of the wood wool fibres and the heat treatment regime.

Questions for the self-control

1. Describe the processes of preparing wood raw materials for fibrolite production.

2. Justify the requirements for mineral binders for fibrolite.

3. Explain the effect of mineralising additives on the processes of cement hydration in the manufacture of fibrolite.

4. What processes occur when obtaining a moulding mixture in the manufacture of fibrolite?

5. Explain the essence of chemical processes during the hardening of fibrolite.

6. How do the thermophysical properties of fibrolite depend on the chemical processes in its production?

Lecture 17
POLYMERS AS A BASIS FOR CHEMICAL PRODUCTION OF HEAT-INSULATING MATERIALS

Plan

17.1. Historical background of polymer chemistry.

17.2. Raw materials for the production of polymeric heat-insulating materials.

17.3. General principles for chemical processing of polymeric raw materials.

17.1. Historical background of polymer chemistry

Polymers are organic compounds whose molecules have elementary units that repeat many times. In construction, synthetic polymers obtained by the synthesis of low molecular weight substances (monomers) are commonly used, and their processing has become the basis for obtaining effective materials for protecting wall structures. The emergence of foams (polystyrene, polyurethane, etc.) revolutionised the market of thermal insulation materials in the mid-twentieth century.

Polystyrene was discovered in 1839 by pharmacist Edward Simon. When he distilled benzoin resin from the styrax tree, which grows on the Mediterranean coast in Turkey, he obtained an oily, colourless, aromatic substance that he called ‘Styrene’. After some time, Simon found that the oily substance condensed on its own, turning into a jelly-like substance. He named the resulting substance styrene oxide, as he decided that this transformation was the result of the oxidation of styrene. Simon found no practical application for his discovery and stopped experimenting with it.

In 1845, John Blyth (Germany) and August Wilhelm von Hoffmann (England) conducted their own research and found that the substance becomes jelly-like without access to oxygen. The chemists called the jelly-like styrene they obtained metastyrene. Twenty-one years later, French chemist Marcelin Bertlot named the process of sealing styrene polymerisation.

In 1922, German chemist Hermann Staudinger discovered that heating styrene causes a chain reaction that forms long chains of macromolecules. Staudinger's discovery enabled the production of polymers and plastics.

In 1937, a group of scientists at the laboratory of the present-day Bayer AG (Germany) under the leadership of Otto Bayer produced polyurethane through the reaction between glycol and polyisocyanate. Depending on the speed of the reaction and the degree of substitution of the components between which the synthesis took place, the properties of the resulting material differed dramatically. On the one hand, it was flexible, resilient, but not tensile (laboratory name Perlon U, hence the name 'foam rubber'), and on the other hand, it was dense, hard, strong, but at the same time brittle when bent (laboratory name Igamid U). Based on the experiments conducted in the Concern's laboratory, recommendations were made on the use of polyurethanes for the production of rigid foam, adhesive bases and various coatings. During the First World War, polyurethanes were actively used as aircraft coatings and for impregnating paper capes that protected the skin from mustard gas.

Depending on the method of production, polymers are divided into two types: polymerisation (thermoplastic) and polycondensation (thermosetting, resin).

Polymerisation polymers are produced by a polymerisation reaction that occurs as a result of the opening of multiple bonds in unsaturated low molecular weight substances, or by the destruction of unstable cycles and their connection into long chains. No by-products are released during polymerisation, and the composition of the resulting polymers corresponds to that of the starting monomer.

Polycondensation polymers are formed during the polycondensation reaction, which is accompanied by the release of low-molecular weight by-products (water, ammonia, etc.). The composition of the main polymer formed during polycondensation differs from the composition of the starting monomers.

All polymers are sensitive to temperature and are divided into thermoplastic and thermosetting polymers.

Thermoplastics polymers are the materials with a linear structure whose properties change inversely when they are repeatedly heated and cooled. Such polymers soften when the temperature rises and harden again when it drops. They include polyethylene, polyvinyl chloride, polystyrene, etc.

Thermosetting polymers cure only once and are no longer capable of changing to a plastic-viscous state when reheated. These materials have a spatial structure, the formation of which occurs with a consistent increase in molecular weight. They include phenolaldehyde, urea, polyester, epoxy and other polymers.

17.2. Raw materials for the production of polymeric heat-insulating materials

The following polymers are widely used to produce polymeric thermal insulation materials:

✓ *polystyrene* $[–CH_2–CH–]_n$ is a product of styrene polymerisation, a thermoplastic polymer. The basis of insulating polystyrene is beaded polystyrene, which is a product of styrene polymerisation by the suspension method in the presence of an initiator, porofor, and a volatile foaming agent, isopentane;

✓ *polyvinyl chloride* $[–CH_2–CHC1–]_n$ is a polymerisation product of vinyl chloride, a thermoplastic polymer;

✓ *carbamide resins* – a product of polycondensation of urea $(NH_2)_2CO$ and its derivatives (thiourea, dicyandiamide, melamine) with formaldehyde;

✓ *polyurethanes* – heterochain polymers whose macromolecule contains an unsubstituted and/or substituted urethane group *–N(R) –C(O)O–*, where *R = H*, alkyl, aryl or acyl radicals. Synthetic elastomer. It is obtained by the interaction of compounds containing isocyanate groups with bi- and polyfunctional hydroxyl-containing derivatives;

✓ *phenolaldehyde resins* – the products of polycondensation of phenols (C_6H_5OH) with aldehydes in the presence of alkaline or acidic catalysts. Aldehydes contain a carbonyl group. The simplest type is formaldehyde (CH_2O). When it is used in combination with phenol, phenol-formaldehyde resins are formed.

Foaming agents can be mineral or organic, solid, liquid or gaseous.

Solid foaming agents are divided into the following according to the mechanism of the gas formation process:

- ✓ that emit gaseous products due to reverse thermal decomposition (mineral gas-forming agents – sodium, potassium, calcium carbonates and bicarbonates; ammonium salts of mineral and organic acids, etc.); they don't have a plasticising effect on the polymer, which makes it possible to obtain foams with increased heat resistance; but they are poorly compatible with polymers;
- ✓ that emit gases (N_2, CO_2, NH_3, etc.) during irreversible thermal decomposition (organic substances – nitrogen compounds, nitroso compounds, guanidine derivatives, sulfonyl hydrazides, acid azides, etc.). Their decomposition temperature is close to the softening point of the polymer, they are easily ground and evenly distributed in the raw material composition. However, they are expensive, toxic, and contribute to the plasticisation of the foam with decomposition products, reducing its heat resistance;
- ✓ that interact with each other to produce gaseous products - sodium nitrate with ammonium chloride, carbon dioxide salts with organic acids, etc.
- ✓ that release previously absorbed gases as a result of thermal disturbance of their structure (gas-forming adsorbents – silica gel, activated clays, activated carbon, etc., gas or vapour saturation of which is carried out under pressure).

Liquid foaming agents are low-boiling liquids that do not dissolve the starting polymer and, when boiled or under pressure, can foam the material (benzene, isopentane, water, light fractions of petrol, etc.).

The softened polymer is saturated with *gaseous inert substances* as a foaming agent at elevated pressure. Foaming is performed by heating the gas-saturated polymer while reducing the pressure.

Plasticisers and other components, as a rule, do not interact with the polymer, but are evenly distributed in it.

Polymers are the most expensive component in the production of products made from gas-filled plastics. Reducing their consumption can therefore increase the profitability of production, which is achieved by: introducing fillers into the polymer composition; using technologies that allow for a larger volume of products with a reduced average density at the

same polymer consumption (e.g., foaming, using pre-foamed semi-finished product granules, etc.); increasing the production of high-performance polymeric thermal insulation materials (e.g., sotoplastics), etc.

Fillers are used to give foams certain physical and mechanical properties and to reduce the consumption of the starting polymer. Various organic and mineral substances can be used as fillers: quartz and perlite sand, synthetic rubber, wood flour, glass fibre, asbestos, etc.

Initiators are the substances that significantly accelerate the polymerisation reaction. For example, in the production of polyvinyl chloride foams, ammonium persulfate or benzene peroxide are used as initiators.

17.3. General principles for chemical processing of polymeric raw materials

The press technology for producing foams involves the use of thermoplastic polymers, as a rule, and includes three main operations:

- production of a powdered or paste-like press compound by mixing the polymer with a gas generator and other components;
- pressing of dense billets at elevated temperatures and pressures;
- foaming of workpieces by repeated heating.

The polymer is crushed and mixed with a gas generating agent and other components to produce rigid foams in ball mills with a water cooling jacket. The process takes 12...24 hours. To average the paste compositions, the raw materials are mixed in paddle mixers. Dense billets are obtained by pressing the compositions on hydraulic presses in closed-type moulds at a pressure of 12...21 MPa and a temperature of t= 120...180 °C. To reduce the average density without increasing the consumption of the gas generator, it is possible to use such a technological technique as foaming the blanks in the moulds with a smooth release of the pressing pressure at the end of the holding period, and lifting the mould punch due to the pressure of the gases released. This method reduces the average density of the billets by 30...50 %. After pressing, the billet is cooled and removed from the mould. The pressed billets are foamed in chambers at t= 90...120 °C with steam, hot air or water.

The pressless technology. The most common non-press methods of producing foams include:

✓ *pre-foaming polymer granules* saturated with an inert gas, followed by their sintering;

✓ *pouring method* – includes obtaining a raw material mass with polymer, gas-forming agent, hardener and other components; pouring a mould or structural cavity; foaming of the mass due to decomposition of the gas-forming agent; curing of the mass;

✓ spraying method – preparing a mixture of polymer and necessary additives and applying it in a thin layer using special continuously operating machines to a given surface; the applied layer quickly foams and cures, after which the next layer can be applied.

The method of pre-foaming polymer granules is used for thermoplastic plastics, while the method of pouring and spraying is used for thermosetting plastics.

Questions for the self-control

1. What is the chemical nature of polystyrene?
2. What is the difference between thermoplastic and thermosetting polymers?
3. What are the functions of the filler in the production of polymeric thermal insulation materials?
4. What are the non-press methods of producing foams?

Lecture 18

CHEMICAL PRODUCTION OF HIGHLY POROUS POLYMERIC MATERIALS AND THERMAL INSULATION PRODUCTS BASED ON THEM

Plan

18.1. Production of expanded polystyrene.
18.2. Technology of products based on polyvinyl chloride foam.
18.3. Production of foams based on carbamide-formaldehyde resins.
18.4. Production of polyurethane foams.
18.5. Production of phenol-formaldehyde foams.

18.1. Production of expanded polystyrene

For the production of cellular (expanded) polystyrene products, we use emulsion polystyrene, as well as beaded suspension polystyrene, which is produced in the presence of an initiator and isopentane (C_5H1_2) as a cellulating agent.

Expanded polystyrene (EPS) is used as a lightweight aggregate in the production of heat-insulating artificial materials using various binders, as well as products (boards, blocks, shells, etc.) without binders. Cellular polystyrene boards are the most commonly used building insulation.

EPS is characterised by low hygroscopicity (0.05...0.2 %) and water absorption. Diffusion of water vapour in EPS is almost absent. The boards have low water absorption and density and high thermal insulation properties.

According to DSTU B EN 13163:2012 “Thermal insulation products for buildings – Factory made products of expanded polystyrene (EPS) - Specification”, expanded polystyrene (EPS) insulation products are manufactured in the form of boards, rolls or other preformed products, which at an average temperature of 10 °C are characterised by thermal resistance values of at least 0.25 m^2·K/W or nominal thermal conductivity values of not more than 0.06 W/(m·K). This standard establishes requirements for product performance, test methods, conformity assessment, and labelling. For *all areas of application*, products must meet the requirements for thermal resistance and thermal conductivity, geometric dimensions, rectangularity, flatness, dimensional stability, bending strength, reaction to fire, and durability characteristics. For *specific applications*, the following product quality indicators are regulated: dimensional stability at the temperature and humidity specified by the manufacturer; deformation at the specified compressive load and temperature; compressive strength at 10 % linear deformation; tensile strength perpendicular to the plate plane; bending strength; concentrated load; creep; water absorption; frost resistance; vapour permeability; dynamic stiffness; compressibility; density; and emission of hazardous substances.

The main disadvantage of EPS is flammability. Currently, self-extinguishing types of expanded polystyrene are used in construction. The polystyrene foams contain special additives - flame retardants - that suppress spontaneous combustion. EPS is not resistant to ultraviolet rays. Thus, under prolonged exposure to sunlight, the surface of the boards turns brown and

gradually turns to dust. EPS can be protected from UV rays by painting or applying a facing layer.

The following methods are used to produce expanded polystyrene products: pressed, non-press (from foamed granules), and extrusion.

In *the press method*, the raw material is emulsion polystyrene. As a gas generator, we use the porophore (azobisisobutyronitrile $(CH_3)_2C(CN)]_2N_2$), which decomposes at t= 75...90 °C, or a set of gas-forming agents: azobisisobutyronitrile, ammonium carbonate, and sodium bicarbonate. The technology includes the following operations: mixing and grinding of emulsion polystyrene with a gas-forming agent; sifting the powdered composition through a sieve; pressing the blanks on hydraulic presses in moulds at a pressure of 15...20 MPa and t= 140...170 °C; foaming of the blanks in hydraulic chambers; sorting of the products. During hot pressing of the billets in the moulds, the porofoam decomposes. The gases released partially form a fine-pore structure and partially dissolve in the polymer. The pressed billets are foamed in a saturated steam atmosphere at t= 100...105 °C due to the expansion of gases in the polymer. The average density of the products is 35...220 kg/m^3.

The non-press method of producing expanded polystyrene insulation products consists of the following technological operations: pre-foaming of beaded polystyrene granules; drying of the granules and their curing; moulding of the products with final swelling of the granules and their sintering; drying of the blocks; cutting of the blocks; sorting of the products. The raw material is beaded polystyrene, which is produced as a result of suspension polymerisation of styrene in the presence of isopentane and an initiator. The granules swell as a result of isopentane's transition from liquid to gaseous state when heated at $t\geq$ 28 °C. Preliminary foaming of the granules is performed in batch (baths, tanks) or continuous (screw, drum, etc.) machines, for example, in a screw with a steam jacket at a temperature of up to 100 °C for 6...7 minutes. Drying and aging (about 24 hours) of pre-foamed granules is necessary to avoid moisture condensation in the pores during cooling, as well as to eliminate the vacuum formed in the pores during isopentane condensation. It is possible to form polystyrene foams both on batch equipment - moulds, autoclaves, and on continuous equipment - carousel units, packers, conveyor lines.

The extrusion method. Extruded polystyrene boards are a closed-cell material. The pore size ranges from 80...140 microns, with a pore size of 90...100 microns accounting for 80 %. The boards are characterised by: low thermal conductivity (< 0.04 W/(m·°C); low water absorption (< 4 % by volume), which allows the material to be used without additional waterproofing; high strength values that depend on thickness and density; high chemical resistance to most materials widely used in construction (except for organic solvents, anhydrous acids and petrol); and frost resistance. The raw material for the material is beaded (suspension) polystyrene. The first stage involves mixing polystyrene with modifying additives (flame retardants, heat stabilisers and antioxidants to protect against thermal oxidative degradation, abiotic additives to prevent mould, colourants). After mixing, polystyrene is fed into an extruder. Three types of extrusion plants are most common in the industry: single-unit with a single-worm extruder; single-unit with a twin-worm extruder; two-unit or tandem.

18.2. Technology of products based on polyvinyl chloride foam

Polyvinyl chloride (PVC) foams are characterised by reduced flammability compared to polystyrene. PVC foams are produced using both press and non-press methods. Latex polyvinyl chlorides are used as a polymer. When used for thermal insulation, PVC foams can corrode insulated metal surfaces as a result of the release of chlorine ions, which can be formed due to the partial decomposition of the polymer containing chloride compounds. Therefore, these plastics are tested for free chlorine ion.

PVC foam is characterised by a rigid closed cell structure. It is resistant to oil and kerosene, and is highly flammable. The industry produces PCV-1 foam with an average density of 85...115 kg/m^3 and PCV-2 foam with an average density of 150...195 kg/m^3. Thermal conductivity ranges from 0.035 to 0.058 W/(m·°C); water absorption in 24 hours is no more than 4 %. PVC foam is produced in the form of slabs with dimensions of 650×650 mm^2 and 620×620 mm^2 and thicknesses 35…70 mm.

Elastic PVC (PVC-E) foam has a uniform, closed cellular structure. It is a highly flammable material, average density is 125...225 kg/m^3; thermal conductivity –0.046...0.07 W/(m·°C). PVC-E foam is produced in the form of

boards with dimensions of 700x700, 550x550 mm, and thicknesses of 43 and 37 mm.

Rigid PVC foam products are made from polyvinyl chloride polymer using press technology. Isobutyl nitrile, sodium bicarbonate or ammonium carbonate are used as a gas generator. To increase the fluidity of the polymer, methyl methacrylate is added. The components are mixed in a ball mill with a water jacket for 18...20 hours, and the billets are pressed at a pressure of 15...18 MPa and t= 160...170 °C. To obtain foam with an average density of up to 70 kg/m^3, the blanks are foamed in steam chambers in special restrictive moulds that correspond to the configuration and dimensions of the products. Rigid polyvinyl chloride foams are produced in the form of plates and other products with an average density of 60...200 kg/m^3.

The pressless method of producing polyvinyl chloride can be carried out by swelling the compositions using gases released during the decomposition of gas-forming agents. PV-1 foam is made on the basis of polyvinyl chloride and perchlorovinyl with the addition of methyl methacrylate. Poroforum is used as a gas-forming agent. All the solid components (polymers and gas-forming agent) are mixed in ball mills. Methyl methacrylate is added to the mixture before rolling to increase the fluidity of the material. The resulting mixture is used to form sheets on the rollers, which are placed in moulds and heated to t= 100...110 °C in glycerine or in electrically heated chambers. Then, the billet is placed in a cassette (perforated mould) whose dimensions correspond to those of the finished product, heated and held at t= 130...135 °C for 90 minutes. During the heat treatment process, the polymer base of the material softens and swells as a result of the decomposition of the gas-forming agent. The swelling process is considered complete when the entire volume of the cassette is filled with foam. After the cassette has swelled and cooled to t= 25...30 °C, it is removed and the finished product is taken out.

The technology of *elastic* PVC foams is similar to that of rigid foams. A distinctive feature is the addition of plasticisers to the raw material mixture, as well as a slightly lower temperature during pressing and foaming of the blanks.

18.3. Production of foams based on carbamide-formaldehyde resins

Carbamide foams are non-pressure foams that can be used to fill large open cavities with unlimited pouring time, as well as long channels closed around the perimeter. They are distinguished by low cost and availability of raw materials, low average density (25...40 kg/m^3), frost- and biological resistance, low flammability, and resistance to most organic solvents. The disadvantages are low mechanical and adhesive strength, significant water absorption, brittleness, increased technological shrinkage, and the presence of an acidic corrosive environment. For the effective use of urea foams in metal structures, it is necessary to solve the problems associated with shrinkage, crack resistance, adhesion and corrosion protection of metal.

Pinoizol is type of carbamide foams. It is produced using a non-press method with the help of mobile small-sized plants with a capacity of 3…8 m^3/h, which can be used both stationary for the manufacture of boards and directly on the construction site for the insulation of hollow structures. The material is also produced in the form of crushed chips and slabs, the size of which is 500x600x100 mm, and is widely used in residential and industrial construction. However, there are a number of problems associated with the nature of this material that make it necessary to be very cautious about its durability, especially in conditions of humidity and high temperatures.

The group of carbamide foams also includes *mipora*, which is a rigid foam-like material of white or yellowish colour with an open cellular structure. It is made from urea, an aqueous solution of a mixture of formaldehyde (formalin), glycerin, foaming agent and ammonium phosphate. Mipora is produced in grades “M” and “H” in the form of rectangular blocks 950...1100 mm long, 440...500 mm wide, and 200...300 mm high. In the technology of mipora, the raw material preparation involves the production of carbamide-formaldehyde resin and foaming agent. The moulding mass is produced in a foam mixer, where the foam is first whipped and then the polymer is fed. The finished mixture is poured into moulds and cured in special chambers at t= 18...20 °C for 3...4 hours, after which the products removed from the moulds are sent for drying. Mipora products are produced in the form of blocks with an average density of 10...20 kg/m^3.

Products made from casting compositions can be produced using batch or continuous technology. The most promising is *the conveyor technology (continuous)*, and the technological scheme of production is presented and analysed. In this case, the prepared mass is fed from the mixing head to a conveyor, where paper is spread to form a continuous chute. The upper moulding conveyor glues the top layer of paper and calibrates the belt in height. During its passage between the lower and upper conveyors, the mass foams, hardens and is cut into slabs at the outlet.

18.4. Production of polyurethane foams

These products occupy one of the leading positions among polymeric thermal insulation materials. Polyurethane-based foams (polyurethane foams - PU foams) are obtained as a result of complex reactions that occur when polyester, diisocyanate or polyisocyanate, a foaming agent are mixed in the presence of a catalyst, emulsifier and additives. Adjusting the composition of the mixture allows to obtain polyurethane foams with different properties.

To produce PU foams *polyesters* and *polyethers* are used, and depending on their type, rigid or elastic polyurethane foams can be obtained. *Catalysts* are needed to regulate the reaction of polyurethane formation, foaming and curing. *Emulsifiers* are surface-active substances that allow to obtain a uniform structure of PU foams, homogeneous in properties. Additives include *gas-forming agents* to ensure the porosity of the material, *flame retardants* to increase its fire resistance, and *colourants*.

Due to a number of properties (low thermal conductivity and water absorption, sound insulation, and durability), PU foams are used for thermal insulation of industrial and civil buildings, window and door openings, for thermal and waterproofing of roofs, and for insulation of pipelines for various purposes. Products made of PU foams are highly flammable due to the presence of flame retardants in the material, which reduce the access of oxygen during direct fire exposure.

18.5. Production of phenol-formaldehyde foams

Phenol-formaldehyde resins are the most common and cheapest polymers. Foams made on their basis are characterised by increased heat and

fire resistance compared to others. They mainly belong to the group of highly combustible materials; they are chemically resistant materials.

Foams based on phenol-formaldehyde resins are produced using *non-press* or *pouring* technologies. *In the first case*, the composition (semi-finished product) swells and hardens when the moulds are heated in a heat treatment chamber due to the decomposition of the gas-forming agent, polymer curing and rubber vulcanisation. *In the second case*, the swelling of the casting compositions is due to the release of hydrogen when aluminium powder interacts with an acid catalyst or due to the evaporation of light-boiling liquids, such as freons and $CaCl_4$, which swell the composition upon evaporation. The reactions of interaction between the components of the composition are exothermic, which accelerates the swelling and curing process and allows you to do without heat supply from the outside.

Products are made from FF and FS-7-2 foams using *the non-press method*. These foams are made from a mixture consisting of a new-lactic phenol-formaldehyde resin, hardener (urotropin), gas-forming agent (porofor) and fillers (glass fibre, aluminium powder, etc.).

FF foam is a gas-filled plastic with a predominantly closed cellular structure. FF foam is frost-resistant and belongs to the group of highly combustible materials. It is produced in the form of paper-covered boards with uncut and cut ends.

FS-7-2 is a foam plastic made on the basis of phenol-formaldehyde resin SF-121, as well as on the basis of an alloy of resins SF-010, SF-011 and solid furfural acetone resin FA-15 with hardener, foaming agent and filler (glass fibre or swollen perlite). The material is produced in the form of boards coated on both sides with paper or uncoated. Paper-coated boards are characterised by higher strength (0.4 MPa instead of 0.3 MPa) than uncoated boards. The boards are classified as highly flammable.

Foams made by *the pouring method* are produced from a mixture consisting of resinous phenol-formaldehyde resins (FRV-1, FRV-2, FRV-1A, etc.), foaming and curing agents (VAG-1, VAG-2, VAG-3). The boards are used to insulate building envelopes at a temperature of the insulating surface $t \leq 130$ °C. Thermal insulation products should be wrapped in bitumen or tar paper and packed in cardboard boxes. In this form, they can be transported by any type of transport over any distance. Store the products in packaged form in a dry room.

Questions for the self-control

1. What is the effectiveness of polystyrene material?
2. What technology is used to produce foams based on phenol-formaldehyde resins?
3. How is the flammability of polyurethane foam products achieved?
4. What are the ways to produce polystyrene foams?

Lecture 19
CHEMICAL PRODUCTION OF CERAMIC MATERIALS FOR THERMAL INSULATION

Plan

19.1. High-temperature processes for the production of diatomaceous, tripoli, foam diatomaceous and foam tripoli products.

19.2. Requirements for the burning and foaming additives.

19.3. Technological features of ceramic artificial pumice.

19.4. Chemical processes during production of high-temperature liquid ceramic materials with effective thermal insulation properties.

19.1. High-temperature processes for the production of diatomaceous, tripoli, foam diatomaceous and foam trepelite products

Diatomaceous, tripoli, foam diatomaceous and foam tripoli products are made from diatoms and trepels with the introduction of burning or foaming additives, followed by drying and firing at t= 950...1000 °C *(diatomaceous)* and t= 800...850 °C *(foam diatomaceous)*. Products are made in the form of bricks, shaped stones, slabs, shells, segments, etc.

Diatomaceous and *tripoli products* are characterised by an average density of 500...700 kg/m^3, a joint strength of 0.59...0.98 MPa, and a thermal conductivity of 0.14...0.18 W/(m·°C). The moisture content of the products should not exceed 1.5 %.

Foam diatomite products have the same dimensions, but with the same requirements for strength and moisture content, their average density is much lower - 350...450 kg/m^3, which determines the corresponding decrease in

thermal conductivity to 0.13...0.15 W/(m·°C). The permissible moisture content is 5 %.

The raw materials are *diatomites* and *tripels* - grey or yellowish rocks of organogenic origin with an average density of 400…1000 kg/m^3, consisting of aqueous silica *($SiO_2 \cdot nH_2O$)* and partially containing clay and limestone. The SiO_2 content ranges from 70 % to 95 %, and the content of hydrated water 3…8 %. Silica is in an amorphous state. In terms of mineralogical composition, diatomites and tripels are natural hydrates of silica of the opal group. They were formed as a result of accumulation of dead diatomite shells with a porous structure (80...85 %). The pores are small, mostly closed. Bulk density is 400…900 kg/m^3 (lower than that of diatomites), moisture content – 40…60 %. Diatomites and tripels are characterised by increased water absorption – up to 150 %. When heated, they are converted into an anhydrous silica modification (chalcedony).

The technology of diatomaceous products with burning additives is similar to the production of ordinary bricks. The diatomite or tripoli are pre-crushed and dried in a drying drum if their moisture content is above 70 %. Fine grinding is carried out in hammer or rotary mills. Combining drying and grinding simplifies the production of products. Products are formed on belt presses. To reduce shrinkage and increase the strength of the products, they are pressed: diatomite is dried to a moisture content of 14...25 %, crushed, and pressed under a pressure of 15...40 MPa at an average compression rate of 0.75...4.5 cm/s. The products are dried in chamber or tunnel dryers to a final moisture content of 12...17 %. Drying time for bricks is 8...10 hours, for shells and segments - 14...16 hours. The products are fired in ring or tunnel kilns at t= 800...1000 °C. Due to their low sensitivity to sudden heat, the products are fired in a high-speed mode for 16...20 hours. The 63-metre-long tunnel kiln, where the products are fired, is divided into zones: drying and heating (20 m), firing (18 m), and cooling (22 m). The fired products are calibrated using circular saws and sometimes ground on grinding machines.

The technology of *foam diatomaceous* products, similar to the non-foam diatomaceous products, involves drying and grinding diatomite. The finer the grinding causes the lower dosage of foaming agent and the higher quality of the products. Next, the finely ground powder is used to make diatomaceous grinding powder (60...70 % moisture content), which is mixed with the prepared foam (average density 50...60 kg/m^3). To reduce the shrinkage of products during drying and firing, it is recommended to add up

to 3 % of sifted wood sawdust by weight of diatomite. A homogeneous, stable foam mass is achieved under certain conditions: the average density of the slurry should be within 1280...1330 kg/m^3, a standard cone should be immersed in the slurry to a depth of 10...12 cm; the temperature of the slurry should not exceed $t \leq 25...30$ °C. The prepared foam diatomite mass is *poured* into metal moulds (steel, aluminium), *dried* in the moulds in chamber or tunnel dryers to a final moisture content of 15...20 %. The temperature of the coolant at the dryer inlet is $t = 140...160$ °C for drying bricks and $t = 75...80$ °C for drying shells and segments. Drying time is from 48...50 hours (bricks) to 75...90 hours (segments, shells, etc.). The products are *fired* in ring or tunnel kilns at $t = 800...1000$ °C with a holding time of 1...2 hours at the maximum temperature. The firing time is 17...18 hours (in tunnel kilns) or up to 24...26 hours (in ring kilns). The fired products are *calibrated* on machines, *packed* and *sent to the finished goods warehouse*.

19.2. Requirements for the burning and foaming additives

Burning additives (sawdust, peat, ground carbon, coke sludge, etc.) and *foaming additives* are used: classic - rosin or resin-saponin; modern - PB-2000, PB-Lux, POST, SDO-M, BMK, Lori, Unisell, Foamin-C, etc. The dosage of burning additives depends on the requirements for the products. To obtain products with an average density of 500...700 kg/m^3, cross-cut sawdust, 8...10 mm in size, is added in the amount of 25...35 % by dry weight or about 50 % by volume.

In case of using foaming additives, the foam should not collapse (settle) within 30 minutes from the moment of its preparation.

19.3. Technological features of ceramic artificial pumice

Artificial pumice is produced by swelling clay masses in tunnel kilns. The products are produced in the form of slabs, bars, bricks, and possibly also in the form of crushed stone. The average density of the products is 200...600 kg/m^3. Compressive strength – 1.18...5.88 MPa, porosity – 60...90 %, water absorption – up to 30 %, thermal conductivity – 0.12...0.16 W/(m·°C), frost resistance – 25 cycles. Artificial pumice is fire-resistant, durable, acid- and heat-resistant, and well processed by tools. Artificial pumice is used as an

insulator in the production of exterior wall panels and for insulation of building structures.

The main raw materials used in the production of artificial pumice are low-melting ferruginous clays, which are commonly used in the production of expanded clay, and porous additives. The raw materials are prepared using wet or dry methods.

The wet clay preparation method uses equipment that is used in the production of ordinary bricks. The mass is moistened to a moisture content of 24...27 %. The raw material is formed on a belt press with a mouthpiece 250...450 mm wide and 70...100 mm high. The length of the raw material is from 500 mm to 2.0 m. The raw material is placed on kiln trolleys, pre-sprinkled with a layer of sand 30...40 mm thick, using a vacuum picker, and then roasted.

In *the dry preparation method*, the crushed clay is poured onto kiln trolleys, pre-sprinkled with sand, or into capsules (chamotte or cordierite, collapsible) without preliminary drying. The dry method is simpler and more economical.

In the slip method of producing ceramic artificial pumice, aqueous slurry with a moisture content of 60...70 % and an addition of 0.001...0.1 % by weight of foaming agent is swollen by introducing air, carbon dioxide, or using any chemical compound that forms gas as a result of a chemical reaction. In the process of swelling, gas bubbles remain inside the completely closed pores. In the swelling zone, the material is fired at t= 1150...1250 °C for 2...3 hours. When the final temperature is reached, the material is held for 3...4 hours. For better swelling at the beginning of the zone (heating to t= 300...500 °C), a slightly reducing atmosphere is maintained for 1...1.5 hours. For this purpose, the clay is sprinkled with fine coal or coke.

The cooling zone is conventionally divided into three sections: fast (up to t= 750 °C) and slow (up to t= 350 °C) cooling to the temperature of trolley unloading, which is carried out in the third section at a temperature of up to t= 50 °C. The entire cooling period lasts 17...18 hours, and the full heat treatment cycle takes about 24 hours.

After cooling, the correct geometric shape of the plate is obtained on sawing machines – vertical and horizontal. Waste from sawing and after crushing and screening is used as lightweight crushed stone.

19.4. Chemical processes during production of high-temperature liquid ceramic materials with effective thermal insulation properties

Gas clay is a highly efficient heat-, sound- and structural material produced by chemical swelling of clay materials and subsequent firing in tunnel kilns. The products, in the form of slabs or blocks, have a fine-pore structure and are well processed. The average density of the products is 500...800 kg/m^3 and depends on the amount of gas-forming agent used, the compressive strength is 1.47...3.92 MPa, and the thermal conductivity does not exceed 0.2 W/(m·°C).

The raw materials used are low-melting clays and loams, which are commonly used in the production of bricks and tiles. Aluminium powder and lime serve as gas-forming additives. Aluminium powder contains 87.0...98.5 % active aluminium and is characterised by a specific surface area of 8000...8500 cm^2/g. Before use, it is treated with surface-active substances (surfactants), which are added in an amount of 1...2 % to prevent surface oxidation or calcined at t=180...200 °C.

After preliminary grinding, clay materials are loaded into a propeller mixer and filled with water at t= 60...80 °C in the amount of 75...150 % by dry weight.

From the mixer, the grinding powder is fed into a dosing machine, which also contains 0.15...0.30 % aluminium powder and 4.6 % lime by dry weight. It is mixed for 1.0...1.5 minutes and poured into metal split moulds, which are installed on kiln trolleys.

The swelling process involves the formation of a porous structure of the material as a result of hydrogen release. Since the solubility of hydrogen in water is low, a supersaturated solution condition quickly occurs, with the formation of smaller gaseous spheroidal cells that increase in volume and swell the material in the mould. The rate of outgassing is controlled by appropriate accelerators or retarders.

The slurry takes 30...40 minutes to swell. The mould trolleys are then transported to a tunnel dryer. The drying temperature is t= 90...100 °C and the duration is 40...60 minutes. After drying, the moulds are removed, and the products on the tunnel trolleys are sent for firing. The firing temperature is t=1180...1250 °C and the duration is 22...24 hours.

Questions for the self-control

1. Describe the high-temperature processes used to produce diatomaceous, tripoli, foam diatomaceous earth and foam tripoli products.
2. What is the essence of the composition and action of burning and foaming additives?
3. What are the chemical processes for producing ceramic artificial pumice?
4. Explain the chemical processes for obtaining the specified values of the thermal insulation properties of high-temperature liquid ceramic materials.

Lecture 20
CHEMICAL PRODUCTION OF MATERIALS FOR WATERPROOFING OF WALL. GENERAL CHARACTERISTICS

Plan

20.1. General provisions and historical background of development.
20.2. Raw materials and semi-finished products.
20.3. Fundamentals for production of waterproofing materials.

20.1. General provisions and historical background of development

Waterproofing materials of various types are used to protect the wall from water penetration and ensure normal operating conditions, as well as to increase its reliability and durability.

The development of large-scale panel construction has led to the production of new building materials - *sealants* - which are designed to seal the joints of external wall panels and contribute to the heat, water, sound and airtightness of buildings. Sealing materials must be elastic, durable, water and gas-tight, weatherproof, anti-corrosion, and non-toxic. Since sealants serve as waterproofing, they are included in the general group of waterproofing materials in their classification. Often, the raw materials and manufacturing

technologies for sealants are similar to those for waterproofing materials, and therefore are considered together in a general group.

Waterproofing materials are classified according to several criteria: *by the functional purpose* (priming, coating, putty, insulation, covering); *by the physical state and type of material when used* (liquid, plastic-viscous, elastic-viscous, solid); *by the nature of the main raw material* (organic, inorganic, mixed); *by the type of application* (impregnating, injecting, coating, adhesive, bulk).

The practice has shown that the main classification feature of sealants, according to which they are chosen, is the chemical compound from which they are made. Thus, sealants are grouped into *acrylic, silicone, polyurethane, hybrid, etc*.

The chemical composition of sealing materials largely determines the variety of their properties, namely:

- the material's relationship to the water and steam environment – water resistance, water absorption and hygroscopicity, which are directly dependent on the material composition and porosity; pores can be filled with gas, air, steam or water; the waterproofing material must be absolutely dense or with a minimum of pores;

- mechanical properties – strength, plasticity, elasticity, etc., which at the same time characterise the material's amenability to technological processing;

- qualitative characteristics – show the material's relation to long-term exposure to the external environment and geophysical factors, the stability of the main properties of waterproofing over time (stability); indicators of material stability are swelling, water resistance, frost resistance, heat resistance, chemical and biochemical resistance, weather resistance;

- adhesion – show the ability of the material to adhere to the surface of the structure or to the intermediate layer of the enclosure.

Since thousands of years ago, when people built their first hut or house, they were concerned about making sure that the inside was cosy, warm and dry. Of course, in those days there were no technologies that are used today, and therefore people were forced to use natural materials. The process of extracting and using these waterproofing materials took a lot of time, but the result was often no worse than that of modern specialists.

Many centuries ago, our ancestors used various materials based on both natural tree resin and the product of its heat treatment - *tar*. Most often, it was used to tar boats, ships, ropes and wooden buildings.

Another material known in antiquity was *bitumen*, which was used as a waterproofing and binding material several millennia ago. Of course, it was not the modern artificial bitumen made from hydrocarbons, but *natural bitumen* extracted from asphalt rocks - limestone and dolomite - impregnated with bitumen resins.

It is known that 5,000 years ago, Sumerians living in the Tigris and Euphrates riverside used natural bitumen as a binding and sealing agent. Over time, light hydrocarbons (the same ones that are used today for petrol, kerosene, and gas oil) evaporate, gas is released, and heavy oil fractions remain, which are naturally oxidised. In this way, lakes of natural bitumen (natural asphalt) are formed. The largest known lake is Peach Lake (Trinidad, South America). This is a natural bitumen deposit with an area of about 40 hectares and a depth of up to 75 m. There are also similar lakes in Venezuela, the USA, Peru, Iran.

Already in ancient times, the Sumerians understood the need to waterproof foundations and used such a natural material as bitumen, which became the basis for many modern waterproofing materials. The Sumerians produced a special ‘brick’, which was a mixture of sand, clay, gravel and one third of bitumen.

The use of bitumen waterproofing was discovered during excavations of ritual pools, temples, complexes, drainage canals and other structures in Egypt.

By the middle of the second millennium BC, the Sumerian state was replaced by the strong Babylonian Empire in the Interfluve. And the new inhabitants of modern Iraq continued to use natural bitumen for construction and waterproofing. They passed this knowledge on to their neighbours in the Middle East and Asia Minor - the Assyrians, Midianites, Hittites, and Acadians. The legendary hanging gardens of Semiramis could not be built without waterproofing.

In the 1930s, the production of bituminous roofing material was mastered, based on a special cardboard that was coated with bitumen obtained by *oxidising residual products of direct oil distillation*. *Oxidised bitumen* is significantly superior to conventional bitumen in terms of melting point and elasticity at low temperatures. Such a composite material is called

"ruberoid". However, organic bases are prone to decomposition, so waterproofing was less durability. Although ruberioid was used due to its very low cost.

To increase the service life of soft roofs, synthetic substrates such as glass fibre were used, and special additives were added to bitumen. As a result, the roofing materials became more resistant to decay and stronger, and yet, despite the use of oxidised bitumen, they still had low heat and frost resistance.

In the early 1970s, Italian producers noted the compatibility of pure bitumen and atactic polypropylene (APP), i.e. residue of the isotactic polypropylene (IPP) production process discovered by Nobel laureate Professor Giulio Natta. Bitumen with APP is sometimes called *modified bitumen*. This compatibility made it possible to significantly improve the characteristics of the bitumen mixture. Now the softening point has been significantly increased, and the brittleness of the material at low temperatures has been reduced. In addition to APP, other modifiers can be used, such as SBS - styrene-butadiene-styrene. The use of these modifiers allows achieving very good physical and mechanical characteristics combined with high durability (15...25 years).

Sealants have been known and used as waterproofing materials for a long time. Sealants began to be used on a truly massive scale only in the 70s of the last century, both in construction and in everyday life, and by now they have become firmly established in construction practice. A sealant is a paste-like mass that polymerises when the solvent evaporates.

20.2. Raw materials and semi-finished products

Materials for creating waterproofing and roofing coatings of structures, depending on the specifics of their application, can be divided into three groups: 1 - starting materials; 2 - materials that are prepared in advance in workshops or directly at the site of work; 3 - materials supplied by the industry ready for use.

The group of *starting materials* includes binders and auxiliary materials.

Organic and inorganic *binders* mainly define the properties of waterproofing and roofing coatings. Among *the organic binders*, the most popular for use in waterproofing and roofing are: bituminous materials and

solid fuel processing products (tar materials); synthetic resins; synthetic emulsions, latexes and thiocols. Cements, liquid glass, etc. are used as *inorganic binders*.

Auxiliary materials include those that are introduced to give coatings the desired properties. These include: *solvents* that are added to formulations to improve their technological properties (acetone, toluene, petrol, kerosene, etc.); *plasticisers* to make materials more flexible, and to increase frost resistance, etc. (dibutyl phthalate, pitch distillate, other materials); *fillers* to improve the physical, mechanical and chemical properties of coatings in the form of various powder and fibrous fillers (ground quartz, talc, mica, asbestos, etc.); *reinforcing materials* that improve the mechanical properties of coatings (glass and synthetic fabrics, metal mesh, etc.).

The group of materials that are *prepared in advance in workshops* includes bitumen emulsions and pastes, mastics and mortars. *Emulsions* and *pastes* are distinguished by the size of bitumen particles and the type of emulsifier. *Bitumen* mastics and mortars are divided into hot and cold.

The materials supplied by the industry as *ready for use* include rolled bitumen and tar, synthetic sheet, film and paint materials.

20.3. Fundamentals for production of waterproofing materials

The most common materials used to protect wall structures from moisture are liquid materials, which include: impregnating; injection; film-forming; and primer materials. Their low viscosity is ensured either in a cold or hot state.

The impregnating materials, after free distribution over the surface, wet it well and *self-penetrate* to a certain depth inside, filling the surface pores, forming a more or less thick impregnation layer, protecting the structural element from water penetration into the body of the structural material. The main impregnating material is bitumen. To apply bitumen in a cold or slightly heated state, *liquefied* or liquid *bitumen*, as well as *bitumen emulsions* are used. For hot impregnation, *viscous bitumen* is used.

Liquefied bitumen is produced by dissolving petroleum bitumen in solvents (ligroin-kerosene fractions of oil). Its curing takes from 5 hours to 2 days at t = 18...20 °C.

Viscous bitumen is used in a hot state at t= 150...180 °C. The surface to be treated is preheated (t= 35...40 °C), the impregnation depth is 2...20 mm. *Tar* can also be used for impregnation in non-critical areas.

Emulsions are dispersed systems consisting of two substances that do not mix or dissolve in each other, are in a finely divided state, one of which is a liquid and the other is a liquid or solid. In the preparation of emulsions, weak aqueous solutions of surfactants – *emulsifiers* – are used. Oleic acid, sulfite-alcohol bard concentrates, and asidol are used as emulsifiers. Rosin oil, fatty vaseline, technical fish oil can be used. The content of bitumen in the impregnating emulsion should be at least 50 %, and water-soluble emulsifiers – no more than 1...3 %. The bitumen emulsion at t=18 ± 2 °C should be homogeneous without bitumen aggregates. When passing through a sieve No. 05, the residue on the sieve should not exceed 1 %. The emulsion should be stable during storage and transportation, not prone to re-emulsification, i.e. to re-emulsification when bitumen comes into contact with water (with an excessive amount of emulsifier). To increase the water resistance of bitumen emulsions, special additives are introduced into their composition. The technology for manufacturing bitumen emulsions involves the fine grinding of bitumen in water containing a dissolved emulsifier. The higher the dispersion of bitumen, the more stable and homogeneous the emulsion is. The bitumen is ground or dispersed in homogenisers, colloid mills or paddle mixers of various designs.

Injection materials penetrate well into the wall *construction under a certain pressure*, filling pores and capillaries, as well as seams, cracks and other defects. Impregnation with injected materials takes place under pressure, so their viscosity can be higher than that of impregnating materials. Injection is more effective than impregnation, but more complex and expensive. Injectable materials can also be used as sealants.

Questions for the self-control

1. Give the most ancient sealing materials.
2. What are the most common organic binders used in the production of sealing materials?
3. What is the difference between bitumens?
4. What are the characteristics of injectable sealants?

Lecture 21

EMULSIONS AND SEALANTS

Plan

21.1. The processes during the preparation of direct and reverse emulsions.

21.2. Chemical types of sealants, the basics of their preparation and use.

21.3. Modern hybrid sealants, their comparative characteristics and purposes of application.

21.1. The processes during the preparation of direct and reverse emulsions

Emulsions are systems whose production requires the mutual insolubility of the starting substances. One of the substances, *the dispersion medium (*water), is a highly polar liquid. The other substance, *the dispersion phase* (bitumen, oil), is a non-polar substance called "oil". There are two main types of emulsions - oil-in-water (o/w-type) and water-in-oil (w/o-type). Emulsions of the first type are called *forward emulsions,* and the second type is called *reverse emulsions*.

The participation of bitumen in such systems provides the emulsion with the ability to perform waterproofing functions when applied to the surface of a building structure. The system involves an emulsifier that acts as a surfactant and reduces the surface tension at the interface (water-bitumen) by adsorbing in the boundary surface layer. Surfactants, whose molecules consist of polar ("head") and non-polar ("tail") parts, are oriented at the bitumen-water interface in such a way that their "tail" faces the bitumen and the "head" faces the water. As a result of this orientation of the surfactant, a layer is created that equalises the difference in phase polarities and reduces the surface tension at the interface. At the same time, the particles acquire a charge. Charges of the same name repel each other. And the higher the charges, the more stable the emulsion.

Preparation of emulsions. The general scheme for the preparation of a *direct bitumen emulsion* involves the following operations: the oil-bitumen is heated to t= 140...160 °C; the emulsifier is dissolved in heated water (t= 35...55 °C); hot bitumen and emulsifier are fed into a homogeniser. The

preparation of bitumen emulsions can be carried out using homogeniser units of different design and operating principle.

A multi-slotted disperser ensures the formation of an emulsion in narrow gaps between the surfaces of the fixed and movable working bodies. As a result of the friction of the emulsified materials against the surface of the working bodies, the bitumen droplets distributed in the emulsifier solution are stretched into threads, which, upon reaching a certain length, break up into smaller droplets.

The principle of a multi-disc disperser is that bitumen and an aqueous emulsifier solution are forced through numerous holes in a system of moving and stationary discs. The speed of the discs is about 1500 rpm. The smallest bitumen droplets, which are formed as a result of multiple cuts, are stabilised in the emulsifier solution.

A particularly stable emulsion is produced in colloidal mills, in which the material is ground to 0.1 microns.

During the manufacturing process, the temperature of the emulsion should not reach t= 100 °C and is usually within t= 85...95°C. To prevent local overheating, the temperature difference between the bitumen and the emulsifier solution should be kept as low as possible. However, the bitumen must have a sufficiently high temperature (t= 140...160 °C) to allow it to be pumped. For example, for a 60 % emulsion, it is believed that the sum of the temperatures of both phases before mixing should be around t= 195 °C, while the temperature of the finished emulsion at the mill outlet should be around t= 90 °C. Before production begins, the composition is selected to ensure that the emulsion is produced in accordance with the application and technical characteristics.

Emulsions of the reverse type are prepared in paddle mixers with a vertical shaft, which are equipped with a steam jacket or electric heater, a float-type device for dosing materials. In a paddle mixer, the number of revolutions of the shaft and blades is relatively low and amounts to 100...120 rpm. A thin stream of molten bitumen heated to t= 130...140 °C is poured into the water with the emulsifier, heated to t= 85....95 °C. As a result of intensive mixing, the bitumen is crushed and its individual particles are covered with a film of emulsifier. The result is an emulsion with low dispersion and homogeneity. Pastes are produced in this way.

The emulsion can also be produced by acoustic vibrations or ultrasound.

21.2. Chemical types of sealants, the basics of their preparation and use

All sealants are classified as follows. *By readiness for use*: one-component - suitable for direct use – occupy more than 70 % of the market today; two- and more-component – require precise dosing and careful mixing of the components before use. *By the nature of the basic substance*: silicone (also known as siloxane, silicone-organic); acrylic; polyurethane; butyl rubber, butyl, polyisobutylene; thiocene (polysulfide); hybrid based on MS-polymers; bitumen. *By polymerisation characteristics*: non-curing; curing.

The requirements for sealants are very diverse: resistance to ultraviolet radiation; moisture resistance; high adhesion to various materials; environmental friendliness; resistance to cyclic deformation loads; elasticity; wide operating temperature range; ease of application; long service life.

Silicone sealants – are low-molecular-weight polydiorganosiloxane rubbers with end hydroxyl groups as a crosslinking agent. The composition may include fillers and special additives to increase heat resistance, fire resistance, thermal conductivity, and adhesion to various materials. The curing process occurs when the sealant comes into contact with ambient moisture to form a three-dimensional cross-linked structure. Depending on the type of curing agent, silicone sealants are further divided into two more types – acidic (‘vinegar’ – they smell like vinegar during curing) and neutral (amine, oxime, amide, alcohol). Acid sealants should not be used on surfaces that can react with acid - metals (copper, brass, zinc), marble, etc.

Acrylic sealants – are the cheapest, can be diluted in the uncured initial state and easily washed off with water, are well covered with colouring agents after curing, are usually quite waterproof, but ‘age’ within 2...3 years, losing elasticity and becoming brittle. They are mainly used for interior work. They have high adhesion to concrete, brick, wood, PVC products, metals, etc. They do not contain strong toxic substances. Apply with a special gun or directly from the tube with a spatula. They harden completely within 24 hours.

Polyurethane sealants – were developed in response to the need to replace expensive natural cork and rubber. They are obtained by the interaction of polyols and diisocyanates. This type of sealant is an elastic, adhesive, sealing mass that retains its elasticity for a long time. They are used for bonding and sealing any materials – metal, wood, stone, lacquered tin, plastic, ceramics, concrete. They have good adhesion and provide strong

bonding. However, they contain harmful, caustic substances – do not allow them to come into contact with exposed skin.

Butyl, polyisobutylene and butyl rubber sealants – are most often used for primary sealing of double-glazed windows. According to their readiness for use, there are one-component (suitable for direct use) and two-component (requiring mixing of components before use) sealants. The peculiarity of the former is that their polymerisation is carried out gradually from the surface to the depth of the joint and, depending on the type of sealant, can take from two to eight days.

The polymerisation of two-component sealants is much faster, they are characterised by better physical and mechanical properties, but they require very careful preparation when mixing the components, when precise proportions are required.

Thiocene (polysulfide) sealants – are designed for the manufacture of sealing pastes used not only in civil engineering, but also in the aviation industry, shipbuilding, electrical engineering, and radio electronics. They are used for secondary sealing of double-glazed windows. More than 80 % of double-glazed windows for energy-saving glazing of buildings in the world are made with their use.

Usually, these are two-component liquids that are mixed immediately before use. Under normal conditions (air temperature of t= 15...30 °C), the 'viability' of the prepared mixture is no more than two hours, it hardens within 2...3 days, and completely vulcanises in 7...10 days.

Bitumen sealants – have good adhesion to various building materials, such as bituminous surfaces, wood, insulation boards, metal, plastic, concrete, etc. They can withstand low temperatures, but are not suitable for use in places with high temperatures. Application areas: sealing, sealing, filling cracks in roofs, drainage systems, can be used in greenhouses for sealing, sealing and filling cracks in roofs, foundations and plinths.

21.3. Modern hybrid sealants, their comparative characteristics and purposes of application

Hybrid sealants based on MS-polymers are the most promising direction of development in the production of sealing materials. MS-polymer or Silyl Modified Polymer is the main component of modern adhesives and sealants that do not contain isocyanates and solvents. In its essence, MS-

polymer is a polyester compound (polyurethane) with a silanol (organosilicon) group introduced into its structure, which, reacting with air moisture, creates an embedded organosilicon structure, vulcanising the polymer. In this way, the polymer (polyurethane) acquires stabilising properties while retaining its own unique properties.

The production and use of adhesives and sealants based on MS-polymers is growing rapidly. After all, by preserving and enhancing the positive properties of polyurethane compounds (excellent adhesion to any surface, elasticity and strength), the material becomes resistant to ultraviolet radiation, water, acids, alkalis, high temperatures and other critical factors. In Europe, the percentage of consumption of MS-polymer adhesives-sealants reaches 60 % in the industrial sector, and up to 75 % in the construction industry.

The main advantages of adhesives and sealants based on MS-polymers: storage stability (in the absence of moisture as a catalyst, MS-polymers are inert and can be stored for up to 2 years); high durability; ease of application – stable viscosity in a wide temperature range, excellent extrudability even in cold weather; no need for preliminary special surface preparation, since the sealant has excellent adhesion to all surfaces (even wet ones); odourless – MS-polymers do not emit such an unpleasant odour as mercaptan and acetate; fast vulcanization – MS-polymer harden quickly even at low temperatures; colouring – MS-polymer can be painted with any wet-on-wet paints, which does not affect the curing rate; resistance to temperatures within t= 120 °C; does not damage or oxidise surfaces; high bonding strength – MS-polymers allow to obtain the required degree of fixation immediately after application; due to the stable viscosity at low or high temperatures, the material can be easily applied without any problems to any surface (vertical, horizontal, ceiling).

Questions for the self-control

1. What is the difference in the technology of producing forward and reverse emulsions?
2. What is the main purpose of emulsions?
3. Describe the chemical nature of silicone sealants?
4. Name the advantages of hybrid sealants.

Lecture 22

CHEMICAL PRODUCTION OF WATERPROOFING MATERIALS USING CARBON NANOPARTICLES

Plan

22.1. The conceptual principles of waterproofing technologies based on application of nanomodified portland cement systems.

22.2. Chemical and technological basis for the production of carbon nanoparticles.

22.3. Processes of structure formation in the material with the participation of carbon nano-additives.

22.1. The conceptual principles of waterproofing technologies based on application of nanomodified portland cement systems

Traditionally, the conceptual approach to designing Portland cement-based waterproofing mortar formulations involves adjusting the macro-, meso- and micro-levels of the material's hierarchical structure to achieve the required performance properties. This approach has practically exhausted itself, as there is no qualitative improvement in properties and the creation of fundamentally new materials. Therefore, the use of nanotechnology, which allows for the inclusion of the nanoscale (10^{-9} m) in the compositional construction of artificial stone and the systematic and consistent regulation of all components of the hierarchical chain, is considered a promising area that meets the problems of today and the requirements for modern building materials.

In the field of chemical technologies, the use of nanomaterials with particle sizes up to 100 nm over the past 20 years has confirmed the possibility of obtaining special materials with qualitatively different structure and properties, including waterproofing materials due to the increased activity of nanoscale particles in the matrix, including cement.

For waterproofing mortars, which are thin-layer coatings in their hardened form, it is advisable to use elongated carbon nanoparticles (nanotubes, nanofibres) from all existing and studied nanoobjects due to their uniquely high physical and mechanical characteristics, significant surface

energy and ability to act as both crystallisation centres for neoplasms of a certain morphology and dispersed nanolevel reinforcement.

Using the possibilities of nanoscale regulation of the structure and properties of waterproofing solutions also allows solving the problem of coating adhesion to old concrete in the direction of creating a single composite with elements of 'self-healing' of the base, levelling the interface in the 'coating-base' system and extending the service life of the structure.

The scientific conceptual basis for the production of nanomodified waterproofing solutions is the targeted regulation of the composition and structure at all hierarchical levels, taking into account not only the active but also the energy effects, which ensures an increase in the performance properties of waterproofing solutions and waterproof coatings based on them.

The nano-level of structure formation in the chemical technology of producing a waterproofing material based on Portland cement has a decisive influence on the formation of micro- and meso-levels and contains the following elements: crystals of newly formed structures and submicrocrystals, amorphous phases in the form of C-S-H gel globules and other hydrate compounds, globular pores within the gel and interglobular, interlayer pores of the nanoscale level. The use of nano-additives is especially effective in the development of surface-acting waterproofing coatings due to the complex, which includes aluminosilicates of a certain structure and carbon nanosubstances dispersed in the plasticiser. In this case, the positive effect is achieved by creating an ordered dense structure due to the epitaxial growth of hydration products on the surface of carbon nanoparticles, which generally helps to reduce the open porosity of cement stone.

22.2. Chemical and technological basis for the production of carbon nanoparticles

Carbon nanotubes (CNTs) obtained from graphite raw materials and synthesised at special production facilities, for example, at the Institute of Surface Chemistry of the National Academy of Sciences of Ukraine, are most often chosen as a structure modifying substance at the nanoscale. Reducing the cost of the technological solution from the use of carbon nanoparticles is possible by replacing *purified multilayer carbon nanotubes (PMCNTs)* with *unrefined carbon nanotubes (UCNTs)* containing a residual of 6...20 % aerosil and *thermally expanded graphite (TEG)*.

As an additive that modifies waterproofing solutions at the nanoscale, polyhedral fulleride CNTs with interplanar distances of 0.34...0.36 nm and a particle size of 10...40 nm are also used. Carbon nanotubes are extended cylindrical structures, from one to several tens of nanometres in diameter and 1…2 μm long, and consist of one or more hexagonal graphite planes wrapped in a tube and ending in a hemispherical head.

The surface of *purified multilayer carbon nanotubes (PMCNTs)* is a graphene plane containing defects, mainly in the form of oxygen-containing functional groups. The hydrophilic-hydrophobic properties of such materials primarily depend on the concentration of chemisorbed oxygen on their surface. Water interacts with the graphene layer, which is a hydrophobic adsorption centre, by means of weak dispersion forces. Oxygen, which is a hydrophilic adsorption centre, forms hydrogen bonds with water molecules. PMCNTs contain all types of functional groups on the surface; there are water desorption profiles with pronounced maxima at t= 90...100 °C. For PMCNT samples with a significant oxygen concentration, the H_2O desorption profile has a pronounced high-temperature 'tail'. High temperatures of thermal desorption indicate the course of chemical reactions. Reactions associated with the destruction of carboxyl functional groups lead to the formation of gaseous CO_2 at $t \leq 350$ °C.

In the development of materials, just *unrefined carbon nanotubes (UCNTs)* are often used, which have not undergone the acid solution purification stage, which significantly reduces the cost of the final product. This material is homogeneous, and the presence of *aerogel (amorphous silica)* improves the interaction with the components of the cement matrix. The peculiarity of nanotubes is that they are not suspended in water but settle in solution, so it is effective to mix them with surfactants, the choice of which is due to their most effective use in cement matrices to produce solutions.

Thermally expanded graphite (TEG) is a carbon nanoplatelet with a complex pore structure containing micropores (0.72...92 nm), mesopores (1.2...2.0 nm) and macropores (22...25 nm). The plates are subsequently rolled into multilayer tubes. Among the dispersed forms of carbon, TRG occupies a special place. It is formed as a result of structural transformations of graphite intercalation compounds or their hydrolysed forms under rapid heating. In particular, when residual graphite bisulfate compounds ($C_{24+}HSO_4 \cdot 2.5H_2SO_4$) are heated to t= 800...1100 °C, a powder with a specific surface area of 35...75 m^2/g is formed. Consumer properties of composite materials

based on TRG, including physical and mechanical characteristics, are determined by the peculiarities of its crystal structure and phase composition, as well as the strength of bonds between TRG particles arising in the process of material formation. Regulation of the structural state of the surface and volume of TRG particles within certain limits can be achieved by changing the conditions of oxidation and heat treatment of natural graphite.

In general, the requirements for nanoscale substances are united by their actual ability to solve specific technological problems: to act as ready-made crystallisation centres during material hardening; to ensure the most uniform distribution of hydrates in the interstitial space; to ensure physical interaction of carbon nanotubes with the plasticiser surface.

22.3. Processes of structure formation in the material with the participation of carbon nano-additives

The structure of an artificial stone is understood as a certain arrangement in space of individual primary elements (aggregate grains, fillers, crystals of new formations), taking into account their quantitative ratio and the nature of the connections between them. When considering a mortar as a polystructural material, depending on the nature and mechanism of the structure formation processes, the following are distinguished: microstructure (structure of cement stone); mesostructure (structure of mortar as a two-component system ‘fine aggregate –cement stone’); macrostructure (structure of a two-component system ‘coarse aggregate – cement-sand mortar’). The microstructure is characterised by the following components: crystal growth, tobermoryte gel, non-hydrated cement grains and pore space. The mesostructure is considered to be conglomerate with a cement stone matrix, and the macrostructure is considered to be a cement-sand mortar matrix.

The basis for the structure formation of a waterproofing material based on portland cements is the development of the processes of hydration of the clinker component, which are considered as a classical process. The ability of carbon nanotubes to accelerate the hydration processes of the cement matrix of the waterproofing material is confirmed by physicochemical methods of research, including electron microscopic methods. The study of the system in time allowed observing phase formation and identifying its features in comparison with traditional ones, i.e. without the participation of nano-admixtures.

During the nanomodification of the cement system, a change in the morphology of crystalline hydrates is observed with the formation of a contact zone of increased density on the surface of the solid phase. In the presence of carbon nanotubes, needle and fibrous formations are formed, which reinforce the cement stone at the nanoscale. Micro- and nanopores are similar in size and are ordered throughout the material field. Carbon nanotubes create uncompensated surface charges. This creates electrokinetic obstacles to the transfer of aggressive substances through the body of the artificial stone, which has a protective purpose. One of the most important properties of the protective material is its active interaction with the surface of the base product, which is determined by the adhesion. The process of forming the adhesive strength is carried out with the active participation of a nanomodifying additive by penetrating ions into the base with the formation of crystalline hydrates of a given composition. The indicators of adhesive strength of a waterproofing solution of permeable action, both early and long-term, were observed. The influence of the nature of the cement matrix on the development of the structure formation process, primarily the participation of such active mineral additives as blast-furnace granulated slag, rocks with minerals of the zeolite group, should be considered separately. The influence of the nature of the plasticising admixture on the structure formation of a permeable mortar is significant.

Generalisation of the results of the development of the waterproofing mortar formulation and the study of structure formation processes allows proposing appropriate technological solutions. Thus, when using *thermosetting graphite (TSG)* as a nanosubstance, its optimal amount is 0.25 % by weight of the plasticiser (0.005 % by weight of cement), and the best dispersion medium for its introduction into the cement composition is lignosulfonate and polycarboxylate plasticisers. For the efficient operation of carbon nanotubes in the cement matrix, it is best to choose cement with a slag content of up to 20 %. The best microfiller is an aluminosilicate with a skeletal or layered structure and high adsorption capacity. These include bentonites (montmorillonites) and zeolites as minerals. They are capable of retaining water in interplanar cavities. Aluminosilicate substances of this composition have the ability to interact with hydrate formations of cement stone with the synthesis of insoluble hydroaluminosilicate compounds that contribute to the formation of a waterproof structure of surface coatings.

Taking into account the above features of nanomodifiers, the material composition of the cement matrix and surface-active substances in the form of plasticisers in the processes of structure formation, it can be stated that the chemical nature of their results is determined by calcium hydrosilicates of the CSH(B) group, hydrogenite C_2ASH_8, etringite and portlandite. Over time, the presence of nanotubes contributes to the complete recrystallisation of needle crystals into lamellas that are arranged one on top of the other and resemble the crystal lattice of graphite.

Questions for the self-control

1. Describe the macro-, meso- and micro-levels in the structure of a waterproofing material.
2. What is the characteristic of the nanoscale in materials science?
3. What are the reasons why material designers have turned to the use of nanoscale particles?
4. What are multiwalled carbon nanotubes?
5. What is thermally expanded graphite?
6. Name the main chemical process in the structure formation of a waterproofing mortar based on portland cement.
7. List the advantages provided by the participation of nanoparticles in the process of material structure formation.

Lecture 23
THE FORMATION OF WATERPROOFING MATERIALS PROPERTIES USING CARBON NANOPARTICLES

Plan

23.1. Functional types of waterproofing materials: permeable materials and surface action materials.

23.2. Interaction of waterproofing coatings with concrete, the adhesion.

23.3 Factors influencing the formation of waterproofing coating properties.

23.1. Functional types of waterproofing materials: permeable materials and surface action materials

Waterproofing coatings differ in the mechanism of interaction with the structure they are designed to protect from the damaging effects of water, including those containing aggressive compounds. This difference is due to the component composition of the cement matrix of the waterproofing material and provides for the production of penetrating waterproofing and surface waterproofing.

Permeable waterproofing material is a new type of coating, a composite cement material that is applied to a wet surface by coating or spraying with a layer thickness of up to 2 mm. In terms of compositional structure, the material is a mixture of cement, quartz sand and a complex of inorganic salts. *The insulating effect* is achieved by filling the pores and microcavities of the base concrete with water-insoluble compounds formed as a result of the reaction of interaction of active chemical components with the cement stone of concrete in the presence of water. This results in a saturated electrolytic solution, which, due to osmotic pressure, promotes the formation of insoluble crystalline hydrates that clog the free space in the concrete structure. The process of sealing the structure occurs in all directions, but the growth of crystals stops in the absence of water and resumes when it appears. The thin-layer waterproofing coating becomes an integral part of the concrete, forming a single, strong and durable structure. Filling the free space in the structure of the artificial stone with needle-shaped water-insoluble crystals prevents water from further passing through the concrete body, while the vapour permeability of the material remains unchanged. *The most important criterion* for choosing this method of waterproofing is the depth of penetration, which depends on the initial water resistance of the concrete. The greater the penetration, the thicker the crystalline layer in the concrete structure that prevents water penetration. Scientific research was the basis for the development of industrial products of various brands such as Penetron, Kalmatron, Viatorn, which are used to increase the water resistance of mineral-based structures (stone, brick, concrete, etc.) in different countries of the world. *The advantage* of such coatings is the ability to restore the structure from the opposite side of the water, and the service life of permeable waterproofing is equal to the service life of concrete, it cannot be broken, as it becomes part of the concrete structure. However, permeable waterproofing

materials have certain *disadvantages* associated with a significant content of active components – electrolyte salts, which in unbound form can cause excessive efflorescence on the surface, as well as unregulated synthesis of crystalline hydrates in the pore space of concrete, which can provoke deformation stress in the structure, which will eventually lead to cracking, reduced density and water resistance of the structure.

Surface action waterproofing material is a coating with a thickness of 5...50 mm applied in several layers using the plaster method. Such waterproofing is characterised by simplicity of execution, low cost, the ability to mechanise work, reliability, durability, even in difficult operating conditions. The hardened coating creates a dense waterproof layer on the surface of the substrate, which prevents moisture from entering the concrete structure. The application of materials allows for additional levelling of the surface of the structure and ensures its tightness, which increases the technical and economic efficiency of plaster waterproofing compared to coating. Such solutions can be used as a stand-alone waterproofing coating applied to a primed base, or as a component in combination with other types of waterproofing to increase the operational reliability of the building structure. *The peculiarity* of the composite cement matrix for surface-acting waterproofing is the modification of the micro level by using mineral additives and redispersed polymer powders, and the meso level is regulated by optimising the particle size distribution of the fine aggregate and adding a fibrous component in the form of fibres of various compositions. *The disadvantage* of surface-acting waterproofing materials is their low crack resistance, which, in the event of a breakdown in the adhesion of the coating to the substrate, leads to a loss of waterproofness of the structure.

In the manufacture of waterproofing mortars, high-quality cements characterised by high activity are usually used as binders, even in the early stages of mortar curing. However, in terms of corrosion resistance and durability, additive-free portland cement is not effective, as its hydration products form highly basic calcium hydrosilicates and water-soluble portlandite. *Cement-based waterproofing materials* have a number of advantages and, unlike organic coatings, are more durable, technologically advanced, vapour permeable, easy to use, cheap and environmentally friendly. Unlike *organic materials*, they do not degrade when exposed to ultraviolet radiation, do not age, and do not require drying of the concrete before application. In addition, due to the related nature of the coating and base

components, the service life of protective materials is similar to that of a concrete structure. It is possible to accelerate the process of their application through the use of mechanical devices (shotcrete machines, sprayers, etc.). At the same time, waterproofing materials based on portland cement, including cement-polymer materials, are characterised by certain *disadvantages*: low resistance to cracking; peeling off from the base in the process of dynamic loading of structures during operation; destruction under the influence of mineralised groundwater. A promising way to improve waterproofing materials with a cement-polymer matrix is to use *nanolayer* to control the structure and properties of the material in order to create a durable and reliable protection of concrete.

23.2. Interaction of waterproofing coatings with concrete, the adhesion

One of the most important results of the interaction of a waterproofing coating with concrete (substrate) is the adhesion index, the adhesive strength. The nature of adhesion is considered on the basis of various theoretical concepts. Let's consider the main ones.

The mechanical theory assigns a decisive role in bonding different materials to the mechanical bonding of the adhesive to the substrate in microdefects and surface pores. However, when studying the problems of bonding heterogeneous surfaces, researchers have come to the conclusion that the chemical structure of adhesives affects the adhesive strength, especially the presence of polar groups. Chemical interfacial bonds were studied, which was reflected in the chemical and colloidal-chemical theories of bonding.

In the colloidal-chemical theory, the bonding mechanism is considered as a process of sol-gel transition and is mostly related to linear polymers, whose long molecular chains are not interconnected by strong chemical bonds. Rather, polymer adhesives are based on *the chemical theory* of adhesion, where strong bonds between materials are formed as a result of chemical reactions of polymerisation and polycondensation.

The adsorption theory explains the formation of a strong adhesive bond as a manifestation of intermolecular interaction due to the presence of free surface energy. It is assumed that the bonding process takes place exclusively on the surface of bodies under the influence of Van der Waals forces, and the degree of bond strength is explained by the direct interaction of functional

groups of adhesive and substrate molecules. According to this theory, the formation of an adhesive joint is considered a multi-stage process, where at stage I, the adhesive molecules move from the solution to the surface of the substrate and the distance between them decreases. At the second stage, adsorption occurs, in which the number of contact points at the interface increases and the distance between them decreases to a minimum. At the third stage, the solvent is removed from the adhesive solution and the adhesive's cohesive strength increases.

The diffusion theory is based on the diffusion of chain molecules or their sections from one phase to another, resulting in a strong bond between the film and the substrate. According to this theory, only the adhesive molecules move when solids are bonded. If the adhesive is applied in the form of a solution, and the joined materials are able to swell and dissolve in the solution medium, diffusion of molecules from one phase to another can occur. This leads to the disappearance of the boundary between the phases, i.e. a mixed layer consisting of adhesive and substrate molecules is formed.

The rheological theory of adhesion explains the strength of an adhesive bond only by the cohesive properties of the materials to be joined. However, the theory does not take into account any influence of the molecular bonds between the adhesive and the substrate on the adhesive strength, and ignores the role of the chemical nature of the adhesive, its polymeric nature, and the specific behaviour of polymers in the boundary layers.

It should be noted that currently there is a convergence of a number of theories on some basic provisions.

For *the permeable waterproofing coatings*, regardless of composition of the cement matrix, the main component that determines the ability to penetrate a porous substrate is active chemicals - a complex of electrolyte salts in a given ratio. When the coating is applied to a porous substrate, conditions are created for the diffusion of ions into the concrete, which bind to portlandite and synthesise insoluble crystalline hydrates that fill pores and cavities. The process of forming the adhesive strength is based on the formation of physical, chemical and donor-acceptor bonds at the interface and is more intense when the substrate is wet and stops when it dries.

Studies of the adhesion strength of penetrating coatings applied to cement-sand specimens, determined by the uniform tear-off method, showed that the failure occurs along the specimen, not along the coating. It can be

assumed that the coating has penetrated deep enough into the substrate and the interface. The coating penetrated deeply enough into the substrate and the interface in the coating-substrate system disappeared. When carbon nanotubes are used, the adhesion of the coating increases by almost 20 % after curing in air-dry conditions and by 40 % after soaking in water compared to the composition without carbon nanotubes.

The surface-acting waterproofing coatings perform the function of protecting concrete from penetration through the forces of physical and chemical interaction. The process of diffusion penetration is less severe; the depth of penetration of the solution into the substrate is about 2...3 mm. The mechanism of action of coatings based on Portland cement is explained by the processes of mechanical and chemical interaction and slight diffusion penetration.

23.3 Factors influencing the formation of waterproofing coating properties

Adhesion strength values are largely related to the overall compressive strength of the cured mortar. Obviously, among the factors influencing the strength, the basic one is the formulation. The meso-level of permeable waterproofing coatings is represented by quartz river sand with a fraction size of less than 0.63 mm. The involvement of the nano-level in the creation of permeable waterproofing coatings is carried out by using as a component of the binder a dispersion of untreated carbon nanotubes in a solution of plasticisers of two types – melamine formaldehyde and lignosulfonate with polycarboxylate esters, since they are known to be the most effective as a dispersion medium for carbon nanosubstances.

It is the use of these plasticisers with dispersed carbon nanomaterials*: unrefined carbon nanotubes (UCNTs)* and *thermally expanded graphite (TEG),* which made it possible to obtain slag-containing cement compositions with the highest compressive and flexural strengths and the lowest open porosity. The material composition of the cement is particularly important for the strength of penetrating waterproofing. Traditionally, such systems consist of pure Portland cements and electrolyte salts; their presence causes efflorescence, delamination, and even leads to the formation of secondary ettringite in the structure of the insulated concrete structure. To eliminate these disadvantages, mineral additives are used that can bind free salts and

provide the required coating properties over time. The compositions of nanomodified materials of permeable action using pozzolanic cements are proposed, the compressive strength of which is 15...17 MPa at 7 days, and 35...37 MPa at 28 days. At the same time, it provides the lowest *water absorption coefficient* of 0.014...0.015 kg/m^2·√h. As electrolyte additives, sodium salts are used, including Na_2CO_3 = 0.8...1.6 %; Na_2SO_4 = 1.2...2.0 %; $NaNO_3$ = 0.4...2.0 %.

The depth of penetration of the nanomodified permeable waterproofing mortar into the cement base is 11...13 cm, and is slightly less than that of the waterproofing mortar without carbon nanoparticles.

The performance indicators (kinetics of strength change, water resistance, sulfate and frost resistance) are positively affected by the presence of natural zeolites in the formulation. The presence of carbon nanotubes in the solution additive leads to an increase in its frost resistance by at least 50 cycles compared to a solution of the same composition but without nanotubes.

Zeolitron can be considered the most effective permeable waterproofing material in terms of its properties, which exceeds the performance of such materials as Penetron and Kalmatron.

The preparation of the dry mixture ‘Zeolitron’ is carried out by mixing the initial components in a ball mill for 1 hour to obtain a mixture with a specific surface area of 3660 cm^2/g. The raw materials (granulated blast furnace slag, natural zeolite, quartz sand) are pre-dried to a moisture content of 1.0...1.5 %. The cement component is modified with a complex nano-additive by adding a liquid component consisting of a plasticiser solution and 1 % untreated carbon nanotubes to the dry mixture under cavitational mixing in a rotary mixer.

Questions for the self-control

1. What is penetrating waterproofing?
2. What are the surface waterproofing coatings?
3. What are the advantages of penetrating waterproofing coatings?
4. What indicator characterises the adhesion of the waterproofing layer to the concrete surface?
5. Name the existing theories of adhesive interaction.
6. List the properties of penetrating waterproofing materials.

Lecture 24

PROPERTIES OF FINISHING MATERIALS, WHICH ARE CAUSED BY CHEMICAL AND TECHNOLOGICAL PROCESSES OF THEIR PRODUCTION

Plan

24.1 Chemical and technological processes for the production of finishing materials.

24.2. Selectivity of finishing materials for wall construction – external and internal application.

24.1 Chemical and technological processes for the production of finishing materials

The general features of the technologies include high-temperature sintering of the raw material mixture (finishing ceramic tiles); homogenisation of dried raw materials (dry building mixtures); and production of water-dispersible materials.

The chemical and technological processes for producing ceramic tiles have their own specific features depending on their intended use. A common feature of the technologies used to produce finishing ceramic tiles is the use of *high-temperature processes (firing)*.

Ceramic finishing tiles are classified according to the following criteria. *By purpose:* for exterior cladding (facade tiles, clinker, and porcelain stoneware); for interior cladding (earthenware, majolica); for floors (cottoforte, cotto, red gres, clinker, etc.). *By the method of forming:* extrusion ceramic tiles produced by plastic moulding with a moisture content of 15...2 5%; semi-dry pressing tiles produced by pressing a powdered mass (press powder) with a moisture content of 5...7 %; cast tiles produced by casting slag with a moisture content of 35...45 %. *By surface appearance:* glazed; unglazed. *By firing method:* double firing (bicotta); single firing (monocotta).

The classification of ceramic tiles made by extrusion and semi-dry pressing and their physical and technical properties depending on the water absorption index (E) is regulated by DSTU B V.2.7-282:2011 “Ceramic tiles. Technical specifications”.

Tiles for exterior cladding (for example, facade tiles). The main raw materials used are white and red fired clays, desalination materials (fireclay,

quartz sand), fusions (pegmatite, nepheline concentrate, perlite, glass, chalk). The chamotte content by weight ranges from 15 to 60 %. Colouring agents are used: chromium iron ore – 2...3 % (grey), chromium oxide – 12% (black), manganese ore up to 3 % (brown). The raw materials can be prepared in the following ways: plastic; semi-dry; and grinding.

The slurry (wet) method is the most widely used, as it allows for the preparation of complex formulations with a lower firing temperature and the products have a good surface quality after pressing. This method involves grinding the raw materials together with water in a mill until a homogeneous mass, or sliver, is obtained. The tiles are formed in a semi-dry or plastic process, depending on the moisture content of the raw material. In the case of the slag method of raw material preparation, moulding can be carried out either by semi-dry pressing or by casting (for example, sanitary or mosaic tiles). In the first case, press powders are obtained from a 45...60 % moisture content of slag obtained by joint or separate wet grinding of clay and non-plastic materials by dehydrating to a moisture content of 7...8 % in spray dryers. After moulding, drying is carried out at t= 120...160 °C to a residual moisture content of 1...2 %. The drying time depends on the initial moisture content of the raw material during moulding. Firing is carried out at a temperature that depends on the type of raw material: for products made of refractory clays – t= 200...1300 °C, refractory clays – t= 1080...1160 °C, low-melting clays – t= 950...1000 °C. Firing time is 40...80 min. Both single and double firing is used.

In the technologies of manufacturing *tiles for interior cladding* (for example, faience tiles), the following raw materials are used as the main raw materials, mass. %: clay –5...75, kaolin –10...26, quartz sand - 10...28, tile fight or fireclay – 5...20, fusions (perlite, nepheline concentrate, glass fracture, feldspar concentrate) - 10...30, bentonite – 3. To improve the fluidity of the slag during grinding, the following are added to the mass, %: soda ash – 0.1...0.5; liquid glass – 0.1...0.6; sodium tripolyphosphate – 0.05...0.1. Clays are suitable as light-firing refractory and refractory clays, as well as certain types of low-melting red-firing clays. Earthenware facing tiles are made from press powders produced by wet (slip) or dry methods. The most widely used method is the grinding of raw materials. The slurry is prepared in two ways: by grinding of thinning materials with addition of clay and separate dissolution of clay and kaolin; and by grinding of thinning materials and all clay substances together. The tiles are pressed from dried slag, the pressed

products are dried, glazed, decorated and fired. Both single and double firing is used.

The floor tiles can be used both indoors and outdoors. The main raw materials used are refractory and refractory clays. Fluxing additives and their combinations are also used in the production of floor tiles to reduce the sintering temperature of tile masses and, consequently, the firing temperature of products. Such additives include nepheline concentrate, talc, pegmatite, perlite, and glass fracture. Approximate composition of the mass: clay – 77...65 %, nepheline concentrate – 20...30 %, chalk, slag waste or other calcium-containing materials – 3...5 %. The two methods of preparing press powders discussed above are used: semi-dry or slagging. The dried press powder is pressed in two stages with a specific pressure of 4...8 MPa at stage I and 20...30 MPa at stage II. The density of the semi-finished product strongly influences the subsequent sintering processes during firing and the quality of fired products, so compliance with the pressing regimes is one of the most important conditions for obtaining high quality products. After drying, the tiles are glazed or decorated. The applied layer needs to be dried, after which the tiles are fired in kilns of various designs.

The technologies which main feature is *homogenisation of dried raw materials*. Modified dry building mixtures (MDBMs) are the multicomponent products obtained by homogenisation of dry raw mineral and organic materials in a factory for a certain type of construction work, among which finishing works occupy a significant place. Mixtures for finishing mortars are in the general classification of MDBMs, that is reflected in DSTU B V.2.7-126:2011 “Modified dry building mixtures. General specifications”. The basic features for classification are: conditions of use (class of MDBM); type of binder (type of MDBM); purpose (group of MDBM). Application conditions divide MDBMs by their resistance to ambient humidity and provide for two classes: for outdoor use and interior work in rooms with a relative humidity (R.H.) of R.H.≥ 60 %; for interior work in dry rooms with a R.H.≤ 60 %. The type of binder determines the possibility of producing MDBM: cement (C); gypsum (G); lime (L); polymer (P); complex, which combine different types of binders or new types, such as composite or natural clay-based. The technology of MDBMs includes the following operational blocks: preparation of raw materials; their accumulation in intermediate silos; dosing of mixture components; forced mixing; packaging; packing; cube pallet formation;

storage. It is advisable to highlight the following features of the technological process. Preparation of raw materials involves additional technological operations. First of all, this applies to the preparation of sand (drying and fractionation), screening and aeration of cement. The high-speed forced mixing of MDBM's ingredients is carried out in mixers. Storage of products should be provided in a closed room of the calculated area and volume under regulated temperature and humidity regime.

The technologies which main feature is *the preparation of water dispersions*. Water dispersion materials (WDMs) are classified in DSTU B V.2.7-233:2010 "Modified liquid building mixtures. General specifications". WDMs can be considered as key products for painting, which are used as finishing products, as well as in external thermal insulation systems.

Deformation stresses that occur in façade systems during heating in summer or cooling in winter are largely dampened by the elastic polymer film formed during the polymerisation of the film-forming agent. The possibility of using a much larger number of colours and shades is one of the advantages of WDM (except for products based on silicate binders) over mineral solutions, which, due to their alkaline properties, limit the number of pigments for tinting. The main raw materials for WDMs are aqueous polymer dispersions, fillers, pigments, and other functional additives. The technological process of producing WDM involves the sequential performance of the following main operations: preparation of raw materials and materials, dosing of WDM components; dispersion of components in an aqueous medium; and packaging of finished products.

24.2. Selectivity of finishing materials for wall construction – external and internal application

Generally, finishing materials include mortars and concretes, natural and artificial stone materials, finishing ceramics, paints and varnishes, materials and products based on wood, paper, glass, plastics, and metals.

Depending on the conditions of use, finishing materials are divided into those used for *interior decoration* (wallpaper, wood fibre boards, etc.), *exterior decoration* (crushed natural materials, ceramic tiles, etc.), and *flooring* (polyvinyl chloride tiles, special ceramic tiles, etc.). Each of the materials has a number of special requirements: low abrasion, high impact

strength, low porosity, etc. Some of these materials are used for both interior and exterior decoration, such as natural decorative stone, ceramic materials, architectural and construction glass, etc. In turn, the destruction of the structure (corrosion) of the finishing material can be caused by: *internal factors* – mismatch of the specified material composition, thermodynamic fatigue, the condition of the material surface and its structure; *external factors* – chemical nature of the aggressive medium, the ratio between the volume of the aggressive medium and the surface of the material, the temperature of the medium, the temperature difference in the system, the flow rate and its dynamic nature.

According to regulatory documents, the construction of external walls must prevent moisture accumulation. The rate of moisture evaporation from the structure depends on the vapour permeability of the finishing layers. Therefore, it is prohibited, for example, for panels made of perlite concrete and lightweight concrete on swollen perlite sand to use ceramic or glass tiles with low vapour permeability as finishing layers. It is advisable to finish panels made of such concrete with other materials.

Special finishing materials are widely used to protect building structures and process equipment from the damaging chemical effects of the environment. The main functional property of such materials is corrosion (chemical) resistance, i.e. the ability to withstand external aggressive influences without losing performance. Corrosion-resistant finishing materials are divided into two groups: alkali-resistant and acid-resistant.

Questions for the self-control

1. What are the main requirements for interior and exterior wall materials?
2. What is the peculiarity of the processes in the chemical production of facing tiles and their difference from the processes in the production of ceramic bricks?
3. What processes form the basis for production of dry building mixtures intended for finishing the wall structure?
4. What is the essence of chemical and technological processes for the production of water-dispersed materials?

Lecture 25

CHEMICAL PROCESSES IN THE PRODUCTION OF CERAMIC FACING TILES

Plan

25.1. Features and disadvantages of the plastic method of obtaining tiles.

25.2. Chemical processes during preparation of powdered mass by the semi-dry method in tile production.

25.3. High-temperature processes in the firing of ceramic facing tiles.

25.4. Angobation and glazing.

25.1. Features and disadvantages of the plastic method of obtaining tiles

When preparing the raw materials by *the plastic means*, clay and non-plastic materials are dosed in regulated proportions mixed and moistened to a mouldable state with moisture content of 15...25 %. For moulding, screw belt, vacuum and vertical (pipe) presses are used with a pressure of 1.0...1.5 MPa. The method is used when the clay raw material is moist, loose, and soaks well in water, forming a homogeneous mass. For this purpose, the fusible medium- and moderately plastic clays are used, which are marked with sand. This method of clay mass preparation does not require high-quality processing of raw materials and mass preparation, and is used at old enterprises that are subject to reconstruction. A variation of the plastic method is hard moulding, which reduces the moulding moisture content of the ceramic mass to 13...18 %. Presses are used to mould products at a pressure of 8...10 MPa and to obtain raw materials of increased strength (0.2...0.4 MPa), which makes it possible to carry out drying and firing operations in one unit.

25.2. Chemical processes during preparation of powdered mass by the semi-dry method in tile production

By *the semi-dry method* the clay is crushed and dried, then grinded in disintegrators, sieved, moistend in the powder form with steam to the required moisture content and mixed it thoroughly in a clay mixer. A powdered mass is prepared by dosing the starting materials and moistening them. The moisture content of the powders is 5...12 %, depending on the type of product

and pressing equipment. Prior to moulding, the press powder is dried to a moisture content of 7...8 %. The tiles are pressed at a primary specific pressure of 3...5 MPa and a secondary – 27...32 MPa. This method has a number of advantages over plastic moulding: it makes it possible to use low-plastic clays and a larger number of binding additives (ash, slag, etc.); moulded products have more accurate dimensions and correct geometric shape; and the drying time before firing is reduced.The disadvantage of semi-dry pressing is the need to use more sophisticated pressing equipment and an increased firing temperature for the tiles.

25.3. High-temperature processes in the firing of ceramic facing tiles

In general, ceramic materials are formed as a result of high-temperature processes during the firing of various mineral materials that are sinterable. Sinterability refers to the ability of substances to compact during firing to form dense bodies similar to stone. Along with the formation of crystalline phases, sintering also involves partial melting, which results in the formation of a vitreous phase. The ratio of the crystalline and glassy phases largely determines the physical and mechanical properties of materials.

Sintering is carried out at a temperature, as a rule, not lower than 0.6...0.7 of the absolute melting point of the material. A number of complex physical and chemical processes occur in raw materials depending on the temperature.

For example, in clay materials, free and hygroscopic water is removed at t= 100...200 °C, and at t= 600...800 °C, the bulk of chemically bound or hydrated water is removed to form metakaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O$). At t= 850...1000 °C, traces of OH^--ions are removed and the lattice of clay minerals is restructured, and the formation of mullite ($2Al_2O_3 \cdot 3SiO_2$) begins. At t= 950...1200 °C, mullite formation intensifies. The melting point of mullite (without its decomposition) is t= 1850 °C.

Clays are classified into three groups depending on their sintering temperature: low-temperature clays – t< 1100 °C, medium-temperature clays – $1100 \leq t \leq 1300$ °C, and high-temperature clays - t> 1300 °C.

The most important component of ceramic masses is crystalline silica, which can be present as an impurity (quartz sand) or introduced as an additive. When exposed to temperature, silica undergoes modification

transformations. At t= 575 °C, the transition of β-quartz to α-quartz is observed with a volume increase of 2.8 %. At t= 1000 °C, an irreversible transformation of α-quartz to α- cristobalite with a very significant (15.4 %) increase in volume is observed. The crystalline α- cristobalite is stable up to t= 1400 °C. However, when cooled to t= 240...180 °C, this form transforms into β-cristobalite. Modification transformations of silica can have a decisive impact on the physical and mechanical properties of fired products. The structure of the finished products is usually characterised by a bulk of fine-grained mullite and glass with grains of other impurities.

Single and double firing is used to produce ceramic facing tiles. *The single firing* is a modern method of producing glazed ceramic tiles, which are fired at t= 1200 °C only after the glaze is applied. It differs from double-fired tiles in its greater strength due to the use of a more powerful press and a higher firing temperature, and, accordingly, in its low water absorption (< 3 %), greater frost resistance, wear resistance and chemical resistance. *The double firing* is an ancient method of tile production. The first firing at t= 1040 °C is carried out after the tiles are formed by pressing, and the second firing is carried out after the glaze is applied at a lower temperatures (t= 700...900 °C). The disadvantage is that the products are characterised by a high water absorption rate of tiles (up to 10 %). For this reason, for example, glazed facade tiles are mainly produced by single firing. Double firing is recommended when using clays that contain a significant amount of gas-forming substances (organic matter, carbonates, iron oxides). Single firing with such clays does not allow to produce tiles with a high-quality glaze coating, because at the temperatures of softening and pouring the glaze, gases continue to be released from the tile, which disrupts the integrity of the glaze. This means that one-time firing requires more careful selection and preparation of raw materials.

The technology for producing *clinker tiles* (using plastic moulding or semi-dry pressing) is characterised by an even higher single firing temperature (up to t= 1360 °C).

Porcelain stoneware ('gres') is characterised by the highest strength, wear resistance, frost resistance, corrosion resistance and heat resistance compared to other types of ceramic tiles. The peculiarities lie both in the raw materials (clays rich in illite and kaolinite minerals, very pure quartz sand, feldspar and colouring pigments in the form of metal oxides) and in the pressing under pressure of over 50 MPa and in the rather high firing temperature (up to t= 1300 °C).

25.4. Angobation and glazing

Angobation is the application of a special ceramic coating to tiles with a thickness of 0.1...0.4 mm, which acquires a matte colour after firing; it is used to mask the colour of the tile shards and to level the surface of the tile before applying glaze. It is prepared as a finely dispersed suspension consisting of white or coloured clays. Angob does not melt during firing.

Glazing is the application of a special vitreous coating 0.1...0.5 mm thick to the angoba layer, which only acquires its main characteristics (hardness, decorativeness, chemical resistance, water resistance, etc.) after firing. When glazing tiles, fritted glazes are used to ensure their durability in weather conditions. The main components of the glaze are quartz, feldspar, kaolin or bentonite, and salts of alkaline or alkaline earth metals.

In addition, the so-called 'frit', a glassy material in the form of granules, can be used to make the glaze. The composition of frits can include borax, chalk, pegmatite, quartz sand, perlite, boric acid, zircon, zinc oxide, soda, potash, barium carbonate, ceramic dyes and other materials. The melting point of the fritters is t= 1280 °C.

The glaze containing frit has a high viscosity at dehydration and carbon burnout temperatures, pours well at temperatures within t= 1100 °C, and after cooling has increased strength and reduced abrasion loss (especially important for floor tiles).

Questions for the self-control

1. What properties of raw materials determine their suitability for plastic and semi-dry methods of producing ceramic tiles?
2. Name the disadvantages and advantages of methods of producing ceramic tiles, taking into account chemical processes.
3. What are the recipe and technological factors that affect the purpose and durability of ceramic tiles?
4. How does the quality of clay raw materials affect the process of firing ceramic tiles?
5. What are the features of the choice of raw materials for the production of angoba and glaze?
6. What is the role of frit in the glaze composition?

Lecture 26

CHEMICAL PRODUCTION OF DRY BUILDING MIXTURES

Plan

26.1. Advantages of dry mix technology over existing methods of wall construction finishing.

26.2. Processes in the implementation of preparatory operations.

26.3. Recommended zones of grain size distribution of sands, dispersion of fillers.

26.4. Portland cements and air binders in the dry mix technology, the special requirements.

26.5. Chemical nature and functionality of admixtures.

26.6. The use of high molecular weight chemical compounds.

26.1. Advantages of dry mix technology over existing methods of wall construction finishing

There are a number of reasons for the rapid development of this segment of finishing materials. The main ones are as follows: reduced time for finishing works, significant improvement in the quality of finishing works, the ability to produce materials of an extremely wide range of products and different functional purposes on one production line without re-equipping it, the efficiency of transferring responsible and labour-intensive mortar mix preparation operations from the construction site to factory high-performance equipment with a high level of automation of the production process and stable quality of the finished product, and increased productivity by 1.5...3 times due to the manufacturability of the mixtures themselves, and especially the machine application of finishing materials.

Certainly, modern modified dry building mixtures (MDBMs) are more expensive than basic cement-sand mortars and grouts, which are rightly considered their ancestors, but the use of machine application, and especially in combination with silo transportation of mixtures, allows to reduce the cost of finishing works in combination with high quality and ultra-high rates of their implementation, which can reach 800 % compared to manual application of similar materials.

26.2. Processes in the implementation of preparatory operations

Preparation of raw materials involves technological operations that can be carried out both off-site and on-site. This primarily applies to sand preparation, which includes *drying* and *fractionation*.

Quartz sand is dried in single- or double-circuit rotary drying drums using natural gas or diesel fuel.

The general requirement for sand is stability in terms of fractional composition, which is controlled by sieve analysis. The quartz aggregate is fractionated immediately after drying in horizontal circular or rectangular inclined vibrating screening plants, which are equipped with a set of interchangeable sieves and allow not only to remove dirt and impurities, but also to produce several sand fractions with a given size.

The mineralogical composition of the sand must be controlled, as it can also affect the development of the mortar structure, especially if it contains silica in an amorphous or amorphous state, causing unexpected expansion of the hardened material.

Preparatory operations include *screening of cement* before it is fed to the production line to avoid unnecessary inclusions and debris entering the MDBM. The aeration of storage silos is envisaged to avoid cement particles sticking together.

26.3. Recommended zones of grain size distribution of sands, dispersion of fillers

The mezo-level in structure formation of mortars based on MDBMs is determined by the participation of *aggregates* of various origins and *fine fillers* with different structure, chemical and mineralogical nature.

The most commonly used aggregate is quartz sand, mainly river sand due to the low level of foreign inclusions and dusty particles, and less often ravine sand with a particle size of up to 2.5 mm, although some decorative mixtures involve the use of aggregate with a particle size of 10 mm. By genesis, sands can be mountain, river, lake, and gully sands. Requirements for sand are regulated by DSTU B V.2.7-32-95 “Sand dence natural for building materials, articles, structures and construction works. Specifications”. The

silicon oxide content in sands used for the production of MDBM should be at least 90 %.

The periodicity (polyfractionation) of the aggregate particle size (filler) is of great importance for the structure formation of the solution, which makes the material as dense as possible. That is why the MDBM recipe simultaneously uses quartz sands from fine to coarse with a grain size of up to 2.5 mm. To get the grain composition into the recommended zone, the sand is sieved through sieves with a mesh size of 1.4, 1.0, 0.8, 0.5, 0.355, 0.25, 0.18, 0.125, 0.1, 0.063 mm.

To characterise the sands, it is advisable to use *the coarseness modulus*, which is defined as the sum of the total residues on the control sieves in percentage terms to 100. Accordingly, the sands are assessed as: coarse (M_c > 2.5), medium (M_c= 2.5...2.0), fine (M_c= 2.0...1.5), very fine (M_c= 1.5...1.0). The strength of the hardened mortar based on MDBM increases with an increase in the sand particle size modulus, and this dependence becomes more pronounced with an increase in the cement content.

A fine aggregate for a MDBM is a material of granular or fibrous structure, if its particle size does not exceed 0.16 mm and it has no chemical activity in relation to other components of the mixture. However, the chemical nature of some aggregates implies the presence of activity to the extent that it is necessary to determine experimentally and calculate the consumption in the formulation accordingly (e.g. fly ash, finely ground silica, etc.). The moisture content of aggregates must be brought to 0.5 wt. % for roduction of MDBMs.

By the chemical nature, aggregates can be *calcium* and *magnesium* (marble flour, chalk, limestone, dolomite), silica (marshmallow, white soot, silicate dust), and aluminosilicate (natural and burnt clays, fly ash).

Fibrous and lamellar aggregates differ from granular aggregates in terms of particle shape. Among them, dispersed natural mica and hydromica, as well as products of their heat treatment, and perlite swollen during firing are commonly used. Fibrous fillers are mainly represented by organic substances of artificial origin, among which the most commonly used in the production of MDBMs are polypropylene, acrylonitrile and cellulose fibres.

26.4. Portland cements and air binders in the dry mix technology, the special requirements

Dry mixes, as the basis for mortars, are very sensitive to the type of mineral binder used, given the importance of early strength and frost resistance.

In this regard, when choosing Portland cement, both the characteristics of the clinker and the content and nature of the mineral additive are important. DSTU B EN 197-1:2015 "Cement. Part 1: Composition, specifications and conformity criteria for common cements" offers 27 types of conventional cements, of which only CEM I does not contain mineral additives. In contrast to the initial period of development of the MDBMs formulations, when only CEM I was used, modern receptures are not limited to this type of cement and do not preclude the use of, for example, CEM II/A cements with additives such as slag, pozzolans, fly ash and limestone. To ensure that a mortar gains intensive early strength, it is advisable to use cements of strength classes 42.5R and 52.5R. Ukraine has Portland cement producers in all regions.

White Portland cement is a significant part of the formulations of finishing SBSMs, but it is not produced by domestic cement plants. Its suppliers are powerful companies from Denmark (Alborg Portland), Slovenia (Holcim), Turkey (Chimsa), and Bulgaria (Devna Cement).

Among the air hardening binders used in MDBN technology, construction gypsum and lime are the most widely used.

Building gypsum (DSTU B V.2.7-82:2010 "Gypsum binders. Specification") is a part of a large group of products and is effective as a binder that provides short curing times and high enough plasticity of the mortar mixture. Depending on the presence of the appropriate phase in the product, the firing product can be ordinary and high-strength, characterised by grades G5...G25, which is determined after 2 hours of hardening under the conditions regulated by the standard.

Building lime (DSTU B V.2.7-90:2011 "Building lime. Specifications"), i.e. $Ca(OH)_2$ is used in MDBMs formulations. Quicklime CaO can be also used in some products in very small quantities. The quality of lime is assessed by several indicators, including its activity, which is assessed by the content of active CaO and MgO: 67 % – 1st grade, 60 % – 2nd grade. To avoid the negative impact of unexpected unquenched particles,

lime should be finely dispersed: residue on 0.2 mm sieve should not exceed 2 wt. %.

26.5. Chemical nature and functionality of admixtures

Two types of organic additives by their chemical nature are those whose use determines the principal distinction of MDBMs – cellulose ethers (CEs) and polymerisation and copolymerisation products capable of redispersion in the aqueous medium –redispersed polymer powders (RPPs).

It is *water-soluble CEs* that determine long-term water retention in a thin layer of mortar mixture and provide optimal conditions for further hydration of the mineral binder, which is a prerequisite for strength formation. In addition, the modification of dry mixes with CE admixtures (dosage of 0.05...0.5 wt. %) allows you to regulate the plasticity and consistency of the mortar mixture.

However, even mortar mixtures modified with cellulose ethers do not solve a number of technical problems, such as increased adhesion to dense materials, withstanding temperature deformations, and adhesion between different layers of finishing materials, so the range of mortars modified only with CEs can be limited to plaster and masonry mortars.

The use of RPP in MDBM provides a higher level of modification. In the presence of RPP, the compressive strength of the cement matrix in a thin layer, elasticity and tensile strength, and adhesion to the base are increased. If mineral binders provide the required compressive strength of the mortar, but do not always work satisfactorily in tension and bending, they have insufficient adhesion, especially to materials such as glazed ceramics, plastics, metals, polystyrene foam, etc. When using RPP admixtures in the range of 0.5...5 wt. %, the workability of mortar mixtures, adhesion to the base, flexural strength, water and frost resistance are significantly improved. At a dosage of 5...7 wt. %, such polymers begin to work as independent polymeric binders. Modified materials begin to exhibit elastic properties, withstand high deformation loads, and increase abrasion resistance.

A number of other high-molecular-weight chemical compounds provide mortars based on MDBMs an increased thixotropy, have a thinning effect, regulate the setting time, accelerate curing, etc.

The most effective diluents are superplasticisers, for example, represented by polycondensation products of naphthalene or melamine

formaldehyde, polycarboxylates, polyethylene glycol. Such compounds are added to the composition of MDBM in the amount of 0.05...1.5 % by weight of the binder to increase the fluidity of mortar mixtures, reduce water consumption and, as a result, increase the strength, density and uniformity of the hardened artificial stone. Such admixtures are especially necessary in the formulation of self-leveling mixtures, where they act as diluents, plasticisers, dispersants, and reduce shrinkage.

Questions for the self-control

1. What are the advantages of MDBMs technology over the existing methods of wall structure finishing?
2. What is the essence of the processes during preparatory operations in the technology of MDBMs?
3. What justifies the possibility of using certain aggregates and fillers in the composition of MDBMs?
4. What are the principles for adjustment of the binders in the technology of MDBMs?
5. What are the roles of chemical admixtures in MDBMs?

Lecture 27

CHEMICAL PROCESSES DURING STRUCTURE FORMATION OF CEMENT-POLYMER FINISHING MIXTURES IN A THIN LAYER

Plan

27.1. Hydration of portland cement in the presence of water-dispersible polymers.

27.2. Efficiency of pozzolanic cement and blast furnace cement.

27.3. The role of alumina cement in structure formation.

27.4. Regulation of deformation processes during hardening.

27.5. Participation of fine aggregates in the formation of material properties.

27.6. The role of dry mixes in the formation of a wall structure insulation systems.

27.1. Hydration of portland cement in the presence of water-dispersible polymers

Among hydraulic binders, portland cements remain the most widely used. The concept of hydration includes a number of chemical, physical and physicochemical processes, among which the most important are dissolution, hydrolysis, hydrate synthesis, colloidation, gel formation, crystallisation and recrystallisation.

The problem of curing mortar in a thin layer is that the intensive movement of water into the base and its evaporation by the surface of the curing layer determines the uneven phase formation in the hydrate product system over the layer volume. In time, the hydration process of portland cement follows classical laws. The priority of hydrate formation is influenced primarily by clinker mineralogy, gypsum content and temperature and humidity conditions.

However, there are peculiarities of physicochemical processes in a thin layer of cement matrix compressed by materials with different porosity. For example, there is an increased concentration of calcite on the surface of the layer, which is explained by the availability of carbon dioxide from the air and corresponds to the complete carbonation of lime. Reduced cement hydration at the surface compared to the depth is associated with intensive water evaporation. The lower concentration of C_3A and C_4AF hydration products at depth compared to the surface is explained by the fact that these minerals hydrate at a higher rate than silicates. The increased content of calcium hydrosilicates in the deep zone of the layer is explained by more favourable conditions for hydration of C_3S and C_2S in confined conditions.

Differences in the morphological features of hydrates in the thin layer:

- hexagonal products (hydroaluminates, AFt, AFm, calcite, portlandite) and gel-like hydrosilicate masses are formed, while in the thin plate – mostly fibrous formations;

- the transition of gel-like phases to submicrocrystalline and crystalline phases is more intensive; at the same time, the recrystallisation of portlandite into calcite and the transition of the AFt phase to AFm in the compressed conditions of the surrounded thin layer is much slower than under standard conditions.

The main groups of chemical admixtures that modify the properties of mortars include water-soluble cellulose ethers (CE) and polymer water

dispersion powders (redispersed polymer powders, hereinafter referred as RPP). Such admixtures provide the ability to implement the work of mortars in a thin layer, including with a sharp disproportion between the thickness and area of the layer, as well as the presence of substrates of different density and structure, including those that limit the solution on both sides (e.g. masonry, floor layers). This feature, in turn, determines the development of portland cement hydration process.

Thus, at the very initial period, the growth rate of plastic strength of fresh mortars with the addition of EC and RPP is at the same level as the reference without admixrures. However, after overcoming the plastic strength value, the strength growth rate of the system with the addition of methyl cellulose and carboxymethyl cellulose slows down. The addition of RPP contributes to an intensive increase in the plastic strength of the cement batter, especially at an increased polymer concentration. In the presence of RPP, the strength of the cement stone is slightly higher than the control strength throughout the entire period.

Upon contact with water in the mortar mixture, the particles of RPP are redispersed, distributed among the particles of the mineral binder and aggregate, and then, as hydrate formation proceeds, polymer domains are formed and polymer films are formed in the cracks and micro-void spaces of the hardened mortar, which significantly affects the quality of the resulting material.

In presence of EC, the initial hydration of cement is slowed down, weakening the intensity of strength synthesis. However, over time, the development of hydration is promoted by the water retention function of EC, the process of polymer chains formation and compaction of the system in the presence of RPP. At the same time, a positive collimating effect of the RPP is observed.

The structure formation of modified portland cement in a thin layer of mortar can be divided into the following stages: initial hydration with the formation of portlandite $Ca(OH)_2$; blocking the active centres of cement particles by a polymer film formed with the ‘packing’ of water in the cement-water system; intensive formation of calcium hydroaluminates and ettringite against the background with slow hydration of calcium silicates; formation of reinforcing polymer network and intensification of hydration of the silicate component of the cement.

27.2. Efficiency of pozzolanic cement and blast furnace cement

Guided by economic and environmental aspects, it is relevant to use cements with a partial replacement of the clinker with wastes and industrial by-products in the composition of MDBMs. The most interesting in this regard are pozzolanic cement (CEM IV) and blast furnace cement (CEM III). According to DSTU B EN 197-1:2015, the clinker content in CEM IV can be 45...89 % when using natural or artificial pozzolana (fly ash). In CEM III, the clinker content can be reduced to 5 % when the particle size of granulated blast furnace slag is increased up to 95 %. Despite the possible loss of activity of these types of cements, DSTU B EN 197-1:2015 regulates their compliance with strength classes 32.5, 42.5 and 52.5. The only peculiarity is that blast furnace cements with low early strength (designation L) are allowed.

Pozzolanic cement or blast furnace cement have a positive effect on the water retention capacity of mortar mixtures, cause higher strength of mortars at later stages of hardening, maintain their corrosion resistance, eliminates efflorescence, and reduce shrinkage deformations.

Given the need to ensure the stability of the perfomances of MDBMs, the use of fuel fly ash and slag in cement requires stabilisation of their charecteristics. In addition, it is difficult to ensure early strength and frost resistance of mortars, which requires additional chemical modification.

27.3. The role of alumina cement in structure formation

The use of MDBMs is mainly determined by the need to ensure high early strength (for example, for cast-in-place mortars when installing floor coverings of 5...18 MPa), limiting deformations while maintaining the working properties of the mortar mixture for a long time. At the same time, the use of traditional binders does not allow to provide the whole range of stable indicators of these properties if only aluminate cement, in the world terminology – aluminate cement, is used to accelerate structure formation.

During the hydration of the system “portland cement – alumina cement”, the Portland cement component serves as a supplier of portlandite, which immediately determines the conditions of hydration of alumina cement, its tendency to form a highly basic phase C_3AH_6. In fact, it is this reaction that explains the instant setting of the binder and the rather low strength of the material. In the case of gypsum, this process is superimposed by the formation

of eryngite. The role of ground granulated blast furnace slag (further, slag) in the system “portland cement - alumina cement - slag” is primarily as a carrier of active silica. Several ways of chemical reactions are possible, the advantage of which cannot be stated unequivocally. The following main transition schemes are valid: slag silica performs pozzolanic functions and partially binds portlandite; a decrease in the concentration of the latter creates favourable conditions for the formation of the most stable hydrate – C_2AH_8. Further process deepends on the slag glass destruction and is accompanied by additional gel formation with subsequent crystallisation of hydrogenelite C_2ASH_8 on its basis; the stable state of the C_2AH_8 phase under such conditions ensures the transition of amorphous alumina hydrate into crystalline gibbsite $Al(OH)_3$. As a result, the transition of hydroaluminates to the highly basic form of C_3AH_6 at the initial stage does not occur due to additional gelation, but eventually due to the crystallisation of a stable hydrogenelite C_2ASH_8.

Thus, the use of alumina cement in combination with portland cement can provide high stable strength of artificial stone, but only in the presence of slag as a component of the binder. The presence of slag blocks the recrystallisation of the hydroaluminate phase due to additional formation of the hydroaluminosilicate phase in the form of hydrogenelite, which doesn’t cause decrease in early strength.

27.4. Regulation of deformation processes during hardening

Conventional cements are characterized by high shrinkage deformations during curing due to drying and compaction of colloidal products of their hydration that can cause cracks in the hardened mortars. Reducing shrinkage can be achieved by a number of design measures, such as the installation of temperature-shrinkage joints and the use of non-shrinkage and expanded cements. Such cements should not only compensate for shrinkage during hardening, but also achieve such expansion that the mortar will obtain the required stress state over a long period of operation. Cements of this group provide, when curing in water and air-wet conditions, an increase in volume and compaction of the cementitious matrix of mortars.

Expanded and stress cements are produced on the basis of portland cement, alumina cement, and their compositions with the use of expanding components and additives. Alumina cement is a well-known binder for the

production of expansion cements. Such cement is a fast-setting binder, its hardening rate is determined by the predominant content of low-base calcium aluminates.

One of the areas of application of alumina cement is the production of special multicomponent expanding binders, which are widely used in repair mortars.

The oxide and hydrosulfoaluminate mechanisms of expansion of binders are known, which occur due to the crystallization pressure of hydrates at the initial stages of hardening.

27.5. Participation of fine aggregates in the formation of material properties

As *a fine aggregate* in MDBMs is considered to be a material of granular or fibrous structure if its particle size does not exceed 0.16 mm and it has no chemical activity in relation to other components of the mixture.

However, the chemical nature of some aggregates implies the presence of such activity to the extent that it is necessary to experimentally determine and calculate the dosage in the formulations (for example, fly ash, finely ground silica, etc.).

Fillers allow to replace a part of the binder without affecting the working (rheological) properties of the mortar mixture (consistency, delamination, plasticity, water retention capacity, water demand) and construction and technical properties of mortars (strength, deformability).

By their chemical nature, aggregates can be calcium and magnesium (marble flour, chalk, limestone, dolomite), silica (marshmallow, white soot, silicate dust), and aluminosilicate (natural and fired clays, fly ash).

Typically, *granular aggregates* are used in the amount from 3...5 % up to 10...20 %, depending on their nature and product design properties.

In addition to granular, *fibrous aggregates* of natural and artificial origin, as well as *plastic (flaky) aggregates* are used as fillers. Fibrous fillers are mainly represented by organic substances of artificial origin, among which the most widely used in the production of MDBMs are polypropylene, acrylonitrile and cellulose fibers. Common plate fillers are dispersed natural mica and hydromica, as well as products of their heat treatment, and perlite swollen during firing.

27.6. The role of dry mixes in the formation of a wall structure insulation systems

Thermal insulation mortars based on MDBMs are one of the types of special-purpose plaster mortars and are relevant due to the regulated requirements for thermal protection of wall structures. The plaster layer is involved in the formation of barriers to heat loss. The defining indicator is the thermal conductivity coefficient.

Thus, the national standard DSTU B V.2.7-126:2011 "Modified dry building mixtures. General specifications" provides MDBMs for various purposes (groups) with a limited value of the thermal conductivity of mortars (λ): arrangement of heat-saving enclosing structures – $\lambda \leq 0.35$ W/(m·K); plastering of cellular concrete – $\lambda \leq 0.3$ W/(m·K); plastering with heat-insulating solutions – $\lambda \leq 0.2$ W/(m·K). In addition, the mentioned standard sets out requirements for mortars for fixing elements of thermal insulation systems, and for decorative plastering and thermal insulation systems – the groups of MDBMs for which the value of thermal conductivity is not directly limited, taking into account high thermal insulation properties of the finishing material.

The standard DSTU EN 998-1:2023 "Specification for mortar for masonry. Part 1. Rendering and plastering mortar" stipulates that the thermal conductivity of plaster mortars in dry state should not exceed $\lambda \leq 0.2$ W/(m·K). Such values can be achieved due to high porosity and low average density of the mortars.

By increasing the porosity, it is possible to reduce the density and to raise the volume of air in the material with a decrease in the thermal conductivity of mortars based on MDBMs to $\lambda \leq 0.02$ W/(m.K). This method is realized through the use of air-entraining admixtures and highly porous aggregates. Most often, inorganic aggregates are used to obtain the "warm" mortars – swollen perlite (25...150 kg/m^3), swollen vermiculite (25...600 kg/m^3), and pumice stone (300...600 kg/m^3). It is also known the aggregates of organic nature, for example, polystyrene foam granules. The proportion of lightweight aggregates in the thermal insulation mortars is 5...10 % by weight, the content of functional chemical admixtures is up to 3 %. Mortars with an average density of less than 1300 kg/m^3 are lightweight, characterized by low compressive strength: not less than 2.5 MPa and not more than 5.0 MPa at design age.

Questions for the self-control

1. Describe the features of portland cement hydration in the presence of water-dispersible polymers.
2. What are the prospects for the use of pozzolanic cement and blast furnace cement in MDBMs?
3. Under what conditions is it advisable to use alumina cement in MDBMs?
4. Name the ways to regulate deformation processes during hardening of mortars in a thin layer.
5. Justify the role of fine fillers in the formation of material properties based on MDBMs.
6. What roles MDBMs can play in insulation of a wall?

Lecture 28
WATER DISPERSIBLE MATERIALS

Plan

28.1. The role of the chemical nature of film formers in the production of paints and varnishes.

28.2. Participation of pigments and fillers in chemical technology.

28.3. The use of functional admixtures: rheological, coalescing, biocidal and anti-foaming admixtures.

28.4. Chemical technology of paints and varnishes based on acrylic and vinyl polymers.

28.5. The main characteristics of polymer dispersion when used on wall.

28.1. The role of the chemical nature of film formers in the production of paints and varnishes

According to standard DSTU ISO 4618:2013 “Paints and varnishes. Terms and definitions”, paints and varnishes are natural or artificial materials that are applied in a viscous-liquid state in a thin layer (60...500 microns) to the surface of building materials and structures (concrete, wood, metal, etc.)

to form a coating with the required properties – protective, decorative, and special.

Film forming agents are mineral or polymeric substances that provide or promote film formation. The main function of a film-forming agent is to combine all the components of the system that make up the finishing material into a single matrix with specified properties and ensure its adhesion to the substrate. *The mineral film formers* are, for example, sodium and potassium silicates. *The polymeric film formers* include chlorinated rubber, alkyd resin, polyester-polyisocyanate mixtures (two-component resins), and oligoether acrylates (radiation-curable), aqueous dispersions of acrylic copolymers (pure acrylates), styrene-acrylic copolymers, as well as vinyl acetate homo- and copolymers (with ethylene, vinyl chloride, acrylic or methacrylic acid esters).

Styrene-acrylic polymer dispersions are considered to be the basic ones, which are obtained by copolymerising acrylic resin with non-acrylic monomers such as styrene. Such products are referred to as synthetic film formers. Styrene-acrylic dispersions have a high curing rate and form a decorative film characterised by high elasticity, adhesion to various materials, water resistance, vapour permeability and low toxicity.

Acrylic polymers are hard, elastic, soft or sticky at normal temperature, transparent products. They are thermoplastic and can be easily processed using various technological methods.

Polyacrylates are characterised by high weather resistance, UV resistance, water resistance and yellowing resistance of coatings based on them, and the ability to easily produce copolymers with the required stiffness, flexibility and hardness. The high gloss of the coatings and its preservation under prolonged weathering combined with the resistance of the coatings to alkalis, acids and water makes this class of copolymers effective in the formulation of paints for outdoor use.

28.2. Participation of pigments and fillers in chemical technology

Pigment is a substance consisting of particles that are practically insoluble in the environment of their use and is used as a colouring agent or corrosion inhibitor. The use of pigments and dyes in the production and application of water dispersible materials (WDMs) is widespread, as the ability to obtain the required colour or shade is one of the advantages of such

materials over mineral systems. Examples of pigments include titanium dioxide, carbon black, pearlescent pigments, zinc phosphate, etc.

The most widely used pigment today is titanium dioxide (TiO_2), which is mainly represented by rutile (α-TiO_2) and anatase (β-TiO_2) forms. TiO_2 is produced from the natural mineral ilmenite $FeTiO_3$ or from tetrachloride titanium $TiCl_4$, which is obtained by treating ilmenite with chlorine in presence of carbon at t= 900 °C:

$$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$$

Fillers are finely ground powdered natural materials (calcite, dolomite, talc, kaolin, mica) that are insoluble in water and impart or improve certain technological properties of WDMs and increase the volume of the finishing material.

One of the peculiarities of fillers for production of WDMs is the high requirements for their whiteness. For example, high-quality plaster and paint require aggregates with a whiteness factor of at least 85 % (by $BaSO_4$ etalon). This requirement is related to the need for further tinting of the material, so whiteness is especially important for formulating light-coloured tinting formulations. High whiteness values are typical of carbonate ($CaCO_3$), which includes calcite and chalk, and dolomite ($CaCO_3 \cdot MgCO_3$) sedimentary rocks. The properties of dolomites are almost identical to those of carbonates, but unlike carbonates, dolomites have a higher degree of hardness and are less sensitive to acids. Calcites and dolomites are widely used due to their low binder dispersion requirements, fairly high weather resistance and compatibility with pigments.

Silicate fillers include talc (magnesium silicate hydrate $Mg_3[Si_4O_{10}(OH)_2]$), kaolin (aluminium silicate hydrate $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and natural mica (muscovite) (potassium aluminosilicate hydrate $K_2O \cdot 2Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$).

The filler fractions range from 0.8 μm to 160 μm, depending on the type of finishing material. The domestic industry can only partially meet the demand for fillers such as kaolin and highly conditioned hydromica, so the main supplier countries are Turkey, Greece, and the Czech Republic. The quality of such materials is regulated by the requirements set out in the regulatory documents of the origin country.

28.3. The use of functional admixtures: rheological, coalescing, biocidal and anti-foaming admixtures

Functional admixtures include rheological ones, coalescents, biocides, anti-foaming agents, admixtures to improve frost resistance, neutralising admixtures, admixtures to improve wetting of substrates, admixtures to improve lightfastness of coatings, etc.

Rheological admixtures are primarily intended to provide the required viscosity level of paints, as water-dispersion film-forming systems are usually low-viscosity liquids. At the same time, such additives improve the processability of the product during application. By mechanism of thickening action, rheological admixtures are divided into three types: classical thickeners that thicken the aqueous phase; admixtures that increase viscosity by structuring the system as a whole (associative thickeners); admixtures that combine both mechanisms.

Water-phase thickeners are predominantly water-soluble polymers whose molecules contain a large number of polar hydrophilic groups *(OH¯, COOH¯)*. The most common thickeners of this type used in waterborne paints are water-soluble cellulose derivatives – Na-salt of carboxymethyl cellulose, oxyethyl cellulose, and methyl cellulose.

Associative thickeners are alkali-soluble dispersions (latexes) of highly carboxylated acrylate copolymers with a significant content of methacrylic acid. The advantages of associative thickeners include rapid thickening, unlike cellulose derivatives, which take much longer to dissolve in water. In addition, they are more efficient due to the fact that less is needed to achieve the same viscosity level, and the paints in which they are used have a better balance in the ‘high viscosity – acceptable pourability – no splashing’ property system.

Combined action thickeners thicken the aqueous phase and form associations through hydrophobic interaction. They are hydroxyethyl cellulose hydrophobically modified with urethane fragments.

Coalescing admixtures promote the coalescence (adhesion) of polymer particles during the formation of coatings from water-dispersed film-forming systems. Low-volatile organic liquids with certain solubility in the aqueous

and polymer phases are used as admixtures of this type. They are various glycol ether derivatives, and some solvents (e.g. white spirit).

Biocidal admixtures are essential components of WDMs, as the water environment favours the development of aerobic and anaerobic bacteria and fungi. At the same time, contamination of paints with microorganisms is irreversible, they are introduced with natural raw materials (fillers), penetrate from the walls of pipelines, etc. Paint and varnish coatings, as well as paints, are subject to various types of biodegradation under certain conditions – fungal and mould growth, algae growth, and loss of appearance. Depending on the effect on microorganisms, there are three types of biocidal admixtures: *bactericides* – to prevent the development of bacteria; *fungicides* – to prevent the development of fungi; *algaecides* – to prevent the development of algae. Biocidal admixtures are based on combinations of acyclic and heterocyclic nitrogen-containing compounds, which include halogens and sulphur.

Antifoaming admixtures reduce foaming of waterborne paints. Antifoaming agents, which are liquids with low surface tension, include aqueous emulsions of silicone liquids, silicone, mineral, vegetable oils, and water-insoluble surfactants. To enhance the foaming effect, hydrophobised silica particles are added to the composition of anti-foaming additives.

Admixtures to increase frost resistance are used in paint formulations to avoid loss of their technological properties at low temperatures. By action, these admixtures can be divided into antifreeze and water-retaining admixtures. Antifreeze admixtures reduce the freezing point of water. Glycols, in particular ethylene glycol, are admixtures of this type.

Water-retaining admixtures (organic water-soluble substances that are concentrated in the inter-particle spaces of polymer particles) reduce the freezing point of water locally in the interfacial layers, which helps to preserve liquid layers inside the frozen ice-like paint, so that it returns to its original state during defrosting. This type of admixtures includes urea.

Admixtures to increase the lightfastness of coatings inhibit the photochemical degradation of polymers by intercepting radicals that appear in the coating at the initial stages of photodegradation. This ability is possessed by amino-cyclic compounds and ultraviolet absorbers. Derivatives of benzophenone and benzotriazole (e.g. oxanilide) are used as light stabilisers.

28.4. Chemical technology of paints and varnishes based on acrylic and vinyl polymers

The incoming quality control of materials is based on their testing when they arrive at the plant in accordance with the requirements of the relevant regulatory documents and should exclude the possibility of mixing and haphazard storage, as well as the use of materials in production without prior testing. Incoming inspection establishes that the quality of the source materials meets the requirements of regulatory documents. It is carried out by the plant's laboratory on the basis of passports or quality certificates for the supplied materials. The type and frequency of tests are set by the company's standards or national standards. The standard methodology determines the following indicators: grinding fineness, bulk density, pH, and density of liquid materials, grain composition, and binding capacity.

Dosing (weighing) of components, depending on their aggregate state, is mainly carried out using platform scales with load cells installed under the tanks. In some cases, volumetric dosing can be used.

A homogeneous mixture is prepared in a mixer-dissolver during the dispersion process. As a rule, the components are loaded using manual labour. Such equipment is typical for small-scale production facilities or facilities that manufacture specific and low-tonnage products. In some cases, dissolver tanks are fitted with weight strain gauges that allow components to be dosed directly into the working tank.

Operational control of technological processes is performed during operations or after they are completed. It is characterised by operations to determine stratification, mixing time, and component content.

28.5. The main characteristics of polymer dispersion when used on wall

The main characteristics of the polymer dispersion, which are fundamentally important when used on a wall structure, include the following: appearance, particle size, minimum film formation temperature, dispersion density, surface tension, dry residue, pH value, viscosity, glass transition temperature, strength, tensile strength, elongation at break, water absorption.

Accordingly, the following are monitored during the final inspection (quality control of finished products): mobility, viscosity, pH, mass fraction of non-volatile substances, plasticity, hiding power, whiteness, resistance to wet abrasion, and dry film thickness. Based on the results of this control, a decision is made on the product's readiness.

WDM-based coatings are environmentally safe, non-toxic, explosion and fireproof, relatively low cost, processable (easily diluted with water) and easy to apply to surfaces (including wet ones) by spraying, pouring, roller, or brush. Such coatings dry at normal temperatures, forming matte, porous, vapour- and air-permeable films.

Coatings based on polymer dispersions are characterised by high adhesion to almost all substrates. The disadvantage is their relatively low mechanical strength, water and frost resistance, which causes seasonality of production and use. Special preparation of metal surfaces for coating is also required due to the high surface tension of the polymer dispersion.

Questions for the self-control

1. Describe the group of water-dispersible polymers that affect the development of structure formation processes in the finishing layer.
2. Describe the role of the chemical nature of film formers in production of paint and varnish finishing materials.
3. Explain the functions of pigments and fillers in chemical technology, the rationale for their choice.
4. What are the functional additives used for in coatings based on waterborne materials?
5. What are the features of the chemical technology of paints and varnishes based on acrylic and vinyl polymers?
6. What are the main characteristics of polymer dispersions for finishing materials?

Lecture 29

FUNDAMENTALS FOR WOOD PROCESSING INTO FINISHING MATERIALS

Plan

29.1. Modern types of wood finishing.
29.2. Materials for finishing from partially processed wood.
29.3. The technologies with deep processing of raw wood.

29.1. Modern types of wood finishing

Wood-chipboards and *wood-fibreboards*, which recently were popular finishing materials in the 20th century, are now being replaced by new wood-based materials such as *OSB (Oriented Strand Board)* and *MDF (Medium Density Fiberboard)*. Due to their high strength and moisture resistance along with low cost, OSB boards have become a versatile general construction finishing material. Improvements in fibreboard production technology have resulted in the production of MDF boards, a material that is more environmentally friendly and more reliable due to its high performance properties.

Substandard wood of various coniferous or deciduous species is used to make the mentioned above finishing materials. Its composition and structure largely determine the conditions for processing and obtaining materials with the specified properties.

Wood is composed of cellulose, lignin, hemicellulose, which form a cell membrane and contain tannins and colouring substances, resins, essential oils, etc. in the cell cavities. *Cellulose* is a type of polysaccharide, a chemically stable crystalline substance that is insoluble in water and hydrates under the influence of t= 180 °C and steam pressure 1...1.5 MPa. Its structure is represented by stick-shaped crystallites-micelles. Associating into fibres, they form fibrous cells, which are called tracheids in conifers and libroforms in deciduous species. *Hemicellulose* is similar in composition to cellulose. *Lignin* is an amorphous substance that has no constant chemical composition, is not chemically bound to cellulose, interacts with alkalis and acids, but is not hydrated.

Wood-based finishing materials are divided into: a) unprocessed (lumber) – lining; false beams; block house; mouldings; b) with partial

processing of raw materials based on veneer – plywood, laminated plywood, chip-based – laminated particle board, sanded particle board, oriented strand board (OSB); c) with deep processing into fibres – fibreboard with an average density of 650…850 kg/m^3 (MDF).

Lining is a cladding material in the form of a board with a groove and a tenon with a smooth and even surface made of wood. For the production of euro lining, mainly more valuable tree species are used. This implies that there is no loss of appearance and deformation both during installation and further operation. At the same time, modern lining does not rot, does not change its colour, smoothness and surface texture. Raw materials for the production of lining are divided into 4 grades:

'Extra' – is a material with a smooth, even surface characterised by the absence of defects; elite wood species with a beautiful structure and pattern are used to produce this type of lining;

'A' – the presence of small cracks up to 5 mm, but no more than 2 per product, as well as one knot up to 3 mm long with a product length of 1.5 m or more is allowed;

'B' – cracks, knots, small depressions and holes; defects are repaired with putty.

'C'– is the lowest grade of wood used for lining, characterised by larger defects than in the previous grades.

At the first stage of lining production, edged boards are made from the material on a band sawmill. The edged boards are then dried in a drying chamber at a temperature of up to t= 65 °C to a moisture content of 10...15 % to prevent deformation or cracking of the board and to disinfect it. After drying, the edged boards are fed to a four-sided machine, where a number of operations are performed sequentially: planing the front side; cutting connecting grooves on the side surfaces; and making longitudinal notches on the front side. The process is completed by sorting the products. Thus, in fact, most products are made from partially prepared raw materials in the form of semi-finished products.

29.2. Materials for finishing from partially processed wood

Partial processing of raw materials involves the production of veneer during wood processing to produce thin strips (sheets) with a thickness of 0.1 to 10 mm, which are usually glued to wood or fibreboard panels. The main

advantage of the material is that it preserves the natural wood grain. Other advantages of veneer are its durability and the ability not to dry out or delaminate.

Plywood is a sheet material in the form of a layered wood product consisting of three or more sheets of peeled veneer glued together with a mutually perpendicular arrangement of wood fibres in adjacent layers. Plywood is made from birch, poplar, and coniferous species; depending on the type of adhesive and moisture resistance, it can be moisture-resistant, which is ensured by the use of adhesives based on urea resins; and high moisture-resistant, which is bonded with adhesives based on phenol-formaldehyde resins; bakelite plywood, in which each layer of veneer is impregnated with bakelite varnish and then bonded with glue based on phenol-formaldehyde resins; laminated plywood, lined with a film coating on one or both sides. By the number of layers, it can be three-layer, five-layer, or multilayer.

A type of plywood is *laminated plywood*. The essence of lamination is to cover a plywood sheet with a paper resin film, which makes it highly durable and moisture resistant. Laminated plywood is one of the forming materials used in monolithic concrete construction and is used as formwork. Materials in this group also include chipboards, where partial wood processing involves the production of chips.

Wood-chipboards are produced by coating and gluing together chip particles with a synthetic polymer. Antiseptics are added to the raw material to make the products biostable, and flame retardants are added to increase fire and heat resistance. Phenol-formaldehyde and urea resins are used as synthetic polymers for coating and gluing wood chips. The polymers must be waterproof, non-toxic, fire and explosion-proof, firmly bond wood particles (high adhesion), harden during heat treatment of the mass, and have a light colour and no pungent odour. Wood-chipboards are available in solid single-layer, two-layer, three-layer or multi-hollow, as well as combined boards, which are produced by gluing two or more boards together. In this case, such products are made with deep processing of raw materials. The boards are manufactured using extrusion or flat pressing methods. Depending on the surface finish, they can be lined or unlined. Preparation of raw materials involves hydrothermal treatment at an overpressure of 0.15...0.2 MPa or boiling in water with subsequent bark removal. Wood-chipboards are characterised by a number of disadvantages: low strength, low water

resistance, and high binder consumption. The non-competitiveness of such boards in the construction market was particularly pronounced with the emergence of Oriented Strand Board (OSB), which is free of these disadvantages. Due to their high performance properties, OSBs have almost completely replaced plywood and wood-chipboards as materials for finishing.

OSB is a multilayer (3 layers) sheet composite product consisting of wood chips bonded with an organic binder with the addition of synthetic wax. The chips in the board layers have a different orientation: longitudinal in the outer layers and transverse in the inner (middle) layer. This creates high mechanical strength due to the very structure of the material. OSB is a very popular product due to its advantages. First and foremost, it is an improved raw material that is stronger and more elastic. The properties are ensured by the nature of chip stacking – during operation, when loaded, the chips transmit stresses through each other, thus creating a single structural element devoid of stress concentrators, combining high strength with elasticity.The specially treated surface of the chips ensures water and fire resistance of the boards, which significantly exceed the similar characteristics of solid wood, and the physical and mechanical properties of the board are 2.5 times better than those of wood-chipboard. The low binder content ensures not only environmental safety but also all other useful operational and production properties of wood, such as lightness (board density is 550...650 kg/m^3), low thermal conductivity, good sound insulation, and aesthetic appearance.

The processing of raw materials involves *debarking*. After the bark is removed, *the chips are removed* in a chip machine and *separated*. Three types of chip machines are used: traditional ones for short logs; disc machines that chop whole logs; and rotary (ring) machines that differ from disc machines in the design of the cutting tool. The resulting chips are 75...150 mm long, 10...50 mm wide, and 0.6...1.5 mm thick.

After the chip-splitting machine, the raw chips are accumulated in special hoppers, from where they are fed to drying drum for *the drying*. Single-pass or three-pass drum dryers, as well as a combination of both, are used in the production of OSBs. Modern three-pass conveyor dryers have a number of advantages over traditional drum dryers: they allow drying longer chips without damaging them.

The chips are *impregnated* with an organic binder in mixers. Paraffin, resin, etc. are fed into the drum through separate pipelines. Paraffin is introduced before the resin in its raw or emulsified form. Resins with a

minimum content of phenol formaldehyde, such as isocyanate or polyurethane, are used as binders.

The three-layer carpet is formed in several stages. The layers with orientated chips are fed onto the conveyor and laid out in sequence: first the outer layer (longitudinal coarse chips), then the inner layer (short transverse chips), and then the outer layer again. Each layer is formed and laid out by a separate forming machine. The upper and lower outer layers account for 25 % of thickness, and the inner middle layer for 50 %.

The pressing. The carefully prepared carpet is fed under a hot press, which, through pressure, turns the loose chip mass into a slab, where the binder contained in it polymerises under the influence of temperature. The pressing temperature is t= 180...220 °C.

After pressing, the boards are unloaded from the press and *cut* to the required dimensions. The finished boards are then sent for further *finishing*: grinding, facing with finishing materials, coating with paints and varnishes, etc.

29.3. The technologies with deep processing of raw wood

Large-sized sheet products made by moulding wood into a fibrous pulp and then heat-treating it are called *wood-fibreboards*. *Medium-density fibreboards (MDFs)* are commonly used as wood-based finishing materials, produced by dry and wet methods. Dry-processed fibreboards are called MDF because of their compliance with the European standard adopted as the national DSTU EN 622-1:2006 “Fibreboards. Specifications. Part I. General requirements”. Wood-fibreboards with an average density of 650...850 kg/m^3, depending on the conditions of use (dry conditions, wet conditions, under load) and thickness, are characterised by a bending strength of 15...34 MPa, tensile strength of 0.5...0.7 MPa, thickness swelling in 24 hours of 6...45 %, and bending elastic modulus of 1700...3000 MPa.

Wood, stems of certain plants, antiseptics, and adhesives are used as raw materials for the production of wood-fibreboard. The feasibility of using a particular type of raw material is determined by economic considerations (availability of raw materials, transportation distances, and quality of finished products). Wood chips are used, while coniferous wood is more appropriate for the manufacture of fibreboards.

Deep processing of raw materials involves grinding and processing of wood chips, followed by the formation of boards. The grinding process is carried out using a thermomechanical method, which involves heating the wood with hot water ($t \geq 70$ °C) or high-pressure steam, followed by grinding it between two rotating corrugated discs. The heating of the mass causes the lignin of the wood to soften, hydrolyse carbohydrates and facilitates shredding. The wood fibres formed during grinding are characterised by an undisturbed structure and have the most favourable properties for the formation of high-quality carpets.

The moulding mass can be produced in two ways – wet and dry.

The wet method is based on the ability of wood fibres to form a carpet when their water slurry is dehydrated by creating a framework as a result of the interweaving of these fibres. Short fibres give up water quickly, so a carpet with a small number of contacts is formed on the moulding machine grid. Such boards are characterised by low density and strength. Long fibres have a lower water release rate, so in this case, the carpet will be formed with a significant number of contacts between the fibres as a result of their interweaving. To produce semi-hard and hard boards, the carpet is hot-pressed, during which the fibres are brought closer together and form stronger contacts. In addition, the pressing process involves physical and chemical processes caused by the hydrolysis of hemicellulose and the formation of resinous products that glue the fibres together and create a strong backbone. After hot pressing, to improve the quality, the boards are soaked for 30 seconds in a bath of hot oil (tung, linseed, tallow) at $t = 110...120$ °C. Water absorption is reduced and the strength of the plates is increased by quenching with hot air at $t = 150...170$ °C in quenching chambers for 2...3 hours. After quenching, to eliminate warping, the slabs are passed through humidification chambers for 6...8 hours, where their moisture content is increased to equilibrium values (6...10 %) as a result of sorption humidification.

The dry method allows producing a material that is more in line with modern requirements, i.e. MDF boards. In MDF, unlike wood-fibreboard made by wet process, finely dispersed wood fibres are glued together with the help of natural glue, lignin, and a small amount of organic binders (urea resins modified with melamine). This ensures formaldehyde emissions are comparable to those of natural wood. The first stages (debarking, chip production, fractionation) of the production of boards produced by dry and wet methods are almost identical. The resulting fibrous mass treated with a

binder is dried to a moisture content of 10 %. Next, cyclones remove air from the mass, after which it enters the forming machine, where, depending on the thickness, the carpet is formed. The carpet, moving along the conveyor, undergoes preliminary cold pressing by a continuous roller press. The carpet then goes to a hot press where it is pressed at temperatures up to 280 °C. After pressing, the continuous board is cut to the required dimensions and cooled for 20...25 minutes. For the final polymerisation of the adhesive, the MDF board must be kept for three days in a room equipped for a regulated temperature regime. To eliminate unevenness of the MDF board after pressing, it is passed through a grinder and can be further laminated.

Questions for the self-control

1. What is the difference between the raw materials used to produce lining of different quality?
2. What is veneer?
3. What indicators determine the quality of plywood?
4. Why are orientated strand boards (OSBs) popular?
5. What technological operations does deep processing of wood raw materials involve?

Lecture 30
PROSPECTS FOR THE NANOTECHNOLOGY IN THE CHEMICAL PRODUCTION OF BUILDING MATERIALS

Plan

30.1. The directions for the use of nanomaterials.

30.2. High-strength concrete using composite nanopowder additives.

30.3. Structural composites based on a polymer, metal or ceramic matrixes.

30.4. Nanocoatings and nanogels with heat-, sound-insulating, sterilising, self-cleaning, and energy-saving properties.

30.1. The directions for the use of nanomaterials

An analysis of current trends in the introduction of new building materials and technologies in economically developed countries suggests that materials and technologies based on advances and developments in nanotechnology will become the basis for dynamic implementation in the coming decades. The interest in nanomaterials is primarily driven by their properties, which sometimes exceed those of already known materials by several times.

The use of nanomaterials to improve the functional properties of construction materials and products is a new promising area in science and knowledge-intensive manufacturing, which will reduce material and labour costs, increase service life and, accordingly, improve the ergonomics and environmental friendliness of construction products.

At the same time, the use of nanomaterials in the construction industry in Ukraine has not yet become as widespread as it is abroad due to a lack of financial and investment resources for their development, certification and marketing promotion, and insufficient readiness and interest of construction organisations in introducing innovative methods of work using nanotechnology and nanomaterials.

Modern technologies make it possible to produce materials with a particle size of less than 100 nm (nanomaterials) in a production cycle of up to several tonnes per year. Among the nanomaterials synthesised, researched and introduced into production in recent decades are graphene, fullerene, nanocrystalline oxides of titanium, silicon, aluminium, carbon nanotubes, etc. Nanomaterials demonstrate high mechanical properties (hardness, strength), tribotechnical properties (wear resistance, friction coefficient), electrical and a number of other properties, which allows them to be successfully used to solve problems related to durability and aesthetics (repelling dampness, dust, bacteria); improve energy storage systems, electrical conductors and semiconductors, water purification, etc.

Nanomaterials are of great interest to architects, engineers, developers and builders, who can use them in the construction of structures such as roofs, mezzanines, walls, columns, grilles, double-glazed windows, finishes, smart home technologies, etc. Areas of effective use of nanomaterials include facade paints, water repellents (to protect marble, granite, stone, porous

building materials, wood), deep penetrating primers to fix worn building surfaces, fungicides, nanofilms, nanocoatings, etc.

According to Zion Market Research, the global nanomaterials market is expected to expand steadily, with revenues growing by around 15.5 % annually.

High-strength structural composite materials in the presence of nanofibre and powder particles have been used in the construction industry, which acquire the necessary plasticity and have reduced shrinkage and creep. The combination of traditional materials such as cement, concrete, aerated concrete, foam concrete, gypsum with nanomaterials (carbon nanofibres, nanotubes, silica nanoparticles) in ultra-low amounts (0.1...0.05 wt. %) or colloidal mineral nanosubstances (zeolite gels) can increase the final bending strength by 10...20 %, compressive strength by 20...40 %, and water resistance by 50...150 %. Reinforcement with nanofibres reduces shrinkage and increases crack resistance and wear resistance of the finished product. Along with this, the use of nanomaterials allows for improved performance and aesthetic properties.

Thus, the scope of possible applications of nanomaterials and nanotechnology in the construction and building materials industry is very diverse. Next, we will consider the most promising areas of their use in terms of commercial attractiveness.

30.2. High-strength concrete using composite nanopowder additives

One of the most relevant areas in which research has been intensively conducted recently and there are prospects for implementation in production is the creation of high-strength concrete using composite nanopowder additives. According to calculations such concrete can function for 300...500 years without destruction.

To create the high-strength concrete, nanoinitiators are used as plasticisers, which are microscopic hollow tubes in several atomic layers of carbon polymers. The diameter of these nanotubes is only a few microns, but their strength is more than 100 GPa. When nanoinitiators interact with cement, they activate the growth of crystals in the mineral substance, intertwining their needle-like branches with each other to give the material greater strength, changing its structure at the molecular level (the process of

dispersed self-reinforcement). Nano-initiators also increase the adhesion of concrete to metal, while they interact at the molecular level even with the upper layers of corroded metal. Internal molecular reinforcement reduces the need to reinforce the concrete structure with metal reinforcement without losing strength.

Changes in the structure of "nanoconcrete" dramatically reduce the need for binder in water, which can reduce the weight of concrete structures and the likelihood of cracks by six times. Due to its dense, lightweight, homogeneous structure, nanocrete does not require waterproofing, and its high strength allows for a 30% reduction in material consumption. As nanocrete buildings are lighter in weight than those made of conventional concrete, they do not require a strong foundation, which will reduce construction costs and material consumption. In addition to increased strength (up to 150 %), frost resistance (up to 50 %), and resistance to high temperatures (the material retains its characteristics at temperatures up to t= 800 °C), such concrete also demonstrates increased resistance to alkalis and acids, and biological contamination (bacteria and fungi). Promising areas for the use of high-strength concrete as a wall material include the construction of facilities with increased requirements for durability, fire safety and earthquake resistance, e.g. for skyscrapers. As a protective material, nanoconcrete is promising, for example, for the containment of nuclear reactors.

30.3. Structural composites based on a polymer, metal or ceramic matrixes

Another promising area for the use of nanotechnology in construction is the manufacture of structural composites based on a polymer, metal or ceramic matrix (base). *The advantage of composites* is the possibility of forming a new material based on natural or artificial raw materials, which retains the primary properties inherent in the base (raw materials). The effects achieved are usually multifunctional. The main task of improving composite materials using nanomaterials is, first of all, to reduce the high costs of construction and maintenance of buildings and structures, their elements (roof structures, facades), which, due to their high weight and low strength, constantly require repair and reconstruction during their service life; secondly, to speed up construction time by reducing the complexity of installation, providing the desired characteristics for the project on the basis of innovative

ultralight construction systems, which are distinguished by their high For example, nanocomposite pipes designed for water supply, heating and gas supply systems, which are cheaper, lighter and more resistant to corrosion than cast iron pipes, have been actively used abroad.

30.4. Nanocoatings and nanogels with heat-, sound-insulating, sterilising, self-cleaning, and energy-saving properties

Nanocoatings and nanogels with heat- and sound-insulating, sterilising, self-cleaning and energy-saving properties are being actively introduced in construction practice in Europe.

For example, the introduction of nanostructured titanium dioxide *(TiO_2)* into cement has made it possible to obtain a snow-white material with *the self-cleaning properties* (imitating the effect of lotus petals). The titanium dioxide added to the cement works as a photocatalyst under the influence of sunlight, in the presence of which contaminants of various kinds – bacteria, fungal spores, mould, which usually cover the walls of buildings – simply decompose into water, oxygen and salts. The self-cleaning properties of such cement with nanoparticles are due to the hydrophobicity of its components, in particular titanium dioxide. It is known that almost any hard surface repels water. Typically, the wetting angle is around 80°. After the sun's rays hit the material containing TiO_2, this angle decreases to 0°. The surface containing TiO_2 nanoparticles (or covered with a film of TiO_2 nanoparticles) becomes susceptible to wetting (hydrophilic), i.e. instead of forming droplets, water spreads evenly over it. For a long time (about 4 months), the hydrophilicity remains, and then the wetting angle begins to gradually increase until it reaches 80° again. The surface becomes hydrophobic, and the water that has accumulated during this time rolls off the surface, taking dirt particles with it.

Using the revealed photocatalytic activity of titanium dioxide of anatase modification, a technology for the production of self-cleaning glass, called Pilkington Aktiv, was developed. When applied to the surface of float glass directly during its manufacture, a thin layer of metal oxides $In\text{-}SnO_2$ (by pyrolysis), its heat transfer coefficient is reduced by 70...80 %, and the thermal conductivity of a double-glazed window with its use is reduced by 2...2.5 times. The thermal conductivity of a double-glazed unit is further reduced when using float glass with vacuum coating of three or more layers of alternating silver and dielectrics *(BiO, AlN, TiO_2, etc.)* on its surface. A

special compound with TiO_2 nanoparticles is sprayed onto the surface of the still-cooled float glass, which forms a single unit with the glass after it has cooled. As in the case of facing ceramics, this coating ensures the neutralisation of organic compounds on the glass surface and its complete hydrophilisation, which helps water to drain off the glass along with contaminants.

The unique properties of nanomaterials make it possible to use new heat-insulating materials, paints, enamels, varnishes, etc. in construction. For example, *nanogels (aerogels)* –transparent nanomaterials with *high sound* and *heat insulation characteristics*, are now being used in energy-saving roofing systems and finishes.

Aerogel (also called *frozen smoke* or *solid air*) is a gel whose liquid phase has been replaced by a gaseous phase. An aerogel looks like foam or hard foam. While having an impressively low density, it also has many important properties, such as hardness, heat resistance, transparency, etc. An aerogel can withstand loads thousands of times its weight. Nanogel-based materials can be used for thermal insulation of buildings, structures, and equipment. Such heaters have a wide temperature range (-)270 °C $\leq t \leq$ (+)385 °C. The aerogel is an absolutely safe material for the environment (including its disposal) and for humans, and is also durable in operation.

Nanocoatings can replace conventional thermal insulation materials by simply applying *water-based thermal insulation acrylic paints* (instead of installing insulation fasteners and profiles). Such paints contain special nano- and micro-sized thermal protection components that reflect thermal radiation (94 % reflectivity in the infrared spectrum), prevent heat transfer (thermal conductivity is 0.1 W/(m·K)), provide significant energy savings in winter and summer, and have good performance properties (wear-resistant, suitable for hardware application, high adhesion and flexibility of the coating, antifungal effect, moisture resistance).

The use of nanomaterials is also promising due to their *energy-saving properties*, in particular through *the accumulation of solar energy*. When applied to windows and walls of buildings, nanofilms will give the facades a stylish look and at the same time can work as solar panels, significantly reducing electricity consumption. Innovative films based on nanomaterials designed to protect coloured plastic windows from infrared (thermal) radiation have special pigments that allow them to reflect up to 80% of infrared rays and prevent structures from overheating. As a result, this film

protects both the windows and the room itself from overheating, thus extending the service life of structures and reducing air conditioning costs. At the same time, the innovative coloured film applied to the profile during lamination is able to give the frame a visual 3D effect due to the use of a special film component −diamond inks. These inks also create micropores on the film surface, which make the coating look like shagreen. During lamination, the innovative nanofilm is able to completely cover geometrically complex PVC-profiles and exactly repeat their shapes.

A unique system has been developed, which is an optical fibre with a large number of sensors. This fibre is installed in various construction projects and allows for continuous monitoring of the state of building structures. The sensors enable measurement and monitoring of deformation values during construction and operation. Further development prospects include building foundations with self-regulating soil compensation systems, load-bearing structures that monitor their own stress-strain state, solar panels with built-in photovoltaic cells and batteries, coatings that respond to the psychophysical state of people, energy-efficient windows with heat-generating double-glazed windows − all of which should form the basis of a new generation of modern smart homes.

Questions for the self-control

1. What determines the prospects for the development of chemical nanomaterials technology?
2. Describe the properties of nanomodified concrete as a wall and protective material.
3. What are the promising areas of application of structural composites?
4. What are the functions of nanocoatings and nanogels?

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Конспект лекцій
У двох частинах
Частина 2

«Хімічні виробництва матеріалів для тепло- і гідроізоляції та оздоблення стінової конструкції»
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