

1. Classification of fillers Production of most varieties of artificial construction compositional materials (ACCM) is accompanied by the introduction of mineral and organic components of natural and anthropogenic origin as powdered fillers [1-3]. Fillers, depending on the type of ACCM, are applied to the specific surface within a ranging of $2 \cdot 10^{-4}$ to $2 \cdot 10^{-9}$ m²/kg. The introduction of fillers is one of the most effective way of control economic performance, structure and the physico-technical and technological properties of ACCMs. It is common to classify mineral admixtures on inert and active. The definition of fillers that do not form hardening products with binding properties as “inert”, limits their significance and accordingly, limits the research of their role in the structure and properties formation processes of ACCMs. In addition this distinction is obviously relative because all types of mineral powders have some degree of effect on the structure and properties of the mixed binders, and therefore they are not only active but multifunctionally active, differing only in the mechanism of influence on the binder gel composition, structure and properties of the filled binders. Therefore it seems reasonable to divide mineral filling materials not on whether they are “inert” – or “active”, but rather on whether they are “chemically active” – that is they form hydration products with binding properties, “physically active” – that is they do not forming hydration products, but they do affect the physical structure and properties of mixed binders, or “physically active and reactive” supplementary materials. The group of “physically active” blending materials includes mineral supplements of crystalline structure and(or) chemically inert admixtures. When mixed with PC for example they: - promote the hydration of the cement particles in blended cements by heterogeneous nucleation and dilution effects [4,5], - form transitional zones between the mineral matrix and admixture particles which has a different composition and properties than that of the bulk matrix [6], - have an effect on the pore structure of the hardened cement paste [7,8]. All these result in changes in the physical structure and properties of the hardened cement paste. The nature of the binder gel of blended cements at the introduction of “physically active” SCM is virtually unchangeable. It is worth noting nevertheless, especially given the trend towards the use of finer mineral admixtures, that the described changes significantly depend on the specific surface area of the blending materials [9-14]. Grinding can cause the surface amorphisation of inert crystals. In the case of quartz, a decrease in size from 50 to 3 μm increases its solubility 80-fold at room temperature [15]. Benezet [11] supposed that if the particle size of a quartz powder is smaller than 5 μm the quartz powder can have the pozzolanic activity. Quyen [13] found the pozzolanic reaction effect, the nucleation effect, the effect of the physical interaction between hydrating cement particles and micronised sand, and the effect of the actual water-cement ratio in the hydration of blended cements with micronised sands (5–50 μm). Hereby quartz powder at a high specific surface area can demonstrate weak “chemical” activity. It is important to keep in mind that chemically active fillers have physical activity as well. The definition of fillers that do not form hardening products

with cementing properties as “inert”, limits their significance and the research of their role in formation of the structure and properties of ACCMs. In determination of the effectiveness of the influence of fillers on the properties of the hardened binder pastes, consideration of their influence on the structure is important. It is expedient to describe the mechanism of the influence of the fillers on the properties of ACCMs by modelling their structure and structural elements formation. There are numerous examples of the modelling of ACCM structures and structural elements based on various types of binders and mineral admixtures [16-21]. Modern perspectives of ACCM development technology are based on the materials science and methodological and information resources that allow the development of so-called virtual cements and concretes [22]. The design of generalized models of the structure and structural elements of ACCMs, depending on filler size, particle size distribution, density and physical and chemical activity is reasonable for this development and some models, based on the analysis of well-known research and the research by the authors of the present paper [16-25], are presented below.

2. Topological models

2.1. Enlarged models

The models of structure are classified as porphyritic, contact and over-contact types (Fig. 1). I II III

Fig. 1 - Enlarged models of ACCM structure: porphyritic (I), contact (II) and over-contact (III): 1 – filler particle, 2 – binder, 3 – hollow space

The porphyritic structure of an ACCM is formed when the volume of the matrix of the binder V_b is much higher than the volume of the filler V_f . Therefore, not all V_b is modified as a result of interaction with the filler in the interfacial transition zone (filler particles float in the binding). A contact (“restricted”) structure is formed when V_f/V_b is higher. The filler particles that are in contact with each other through a thin layer of the binder creates a hard skeleton. Each piece of the filler is covered with a layer of binder and interparticle voids are filled with the binder. An over-contact structure is formed at high V_f/V_b , where the rigid framework of the fillers is bound by the binder in the point contacts between them. The particles of the filler are not covered by a continuous film of the binder and interparticle voids are not filled with the binder. Varying of the binder content in ACCMs of the structure of model III allows control its heat engineering and acoustic properties. The varying of the content of the filler, the thickness and the structure of the interfacial layer allows control the strength, deformation and other properties of filled structural ACCMs with the structure of models I and II. The properties of ACCMs with the structure of models I and II are predetermined to a large extent by the properties, structure and thickness of the interfacial layer. These depend on the composition and structure of the binder and the filler and on the mechanism, duration and conditions of their interaction. The structure of ACCMs of model I can be transformed into a structure of model II when at the increase of temperature, the pressure and curing duration increasing thickness of the interfacial layer on the surface of the filler, leads to the formation of a rigid frame of contiguous filler with developed interfacial transitional zones. In ACCMs with the structure of model II, as a result of processes similar to those described above, when the growing volume of

interfacial layer leads to an increase in internal stress, the physic-mechanical properties with the formation of micro-and macro-cracks can be reduced up to a spontaneous breaking.

2.2. Structure models of the hardened materials with physically active fillers

The following do not form hardening products with cementing properties but influence the structure, properties and kinetics of hydration. They are mostly mineral and organic fillers in the gypsum-based hardened pastes, organic fillers, graphite and metal fillers in the lime- and cement-based hardened pastes. The surface of the filler material does not undergo a change of chemical composition. The structure of the dense fillers surface area also does not undergo the changes. The density of the surface area of the porous filler is changed by introducing the components of the binder into the pores. However, depending on the surface energy, the fillers affect the structure of the interfacial layer (Fig.2).

a b Fig. 2 - Structure models of filled materials with dense (a) and porous (b) physically active admixtures: 1 – particles of the dense (a) and porous (b) physically active fillers, respectively; 2 – mineral matrix, 3 – modified layer of binder; 4 – compacted by penetration of the binder surface layer of the porous filler

The thickness, structure and properties of the interfacial layer depend on the type of the binder and the filler. The thickness and properties of the compacted surface layer of porous filler depends on the porosity character and the type and rheological properties of the binder.

2.3. Structure models of the hardened pastes with “physically active and reactive” fillers

Practically all types of mineral fillers in one way or another chemically interact with lime and PC bindings via the formation of a interfacial layer of reaction products with binding properties [26,27]. To some extent, mineral binders with fillers can be considered as blended cement depending on the process of hydrate formation, which appears in the following form [28]: $Cl + W \rightarrow RP1$, (1) $RP1 + F + W \rightarrow RP2$, (2) where Cl is the clinker component, F is the mineral microfiller, RP1 is the reaction products of the clinker, RP2 is the reaction products of microfiller. An exception is the interaction of fillers with gypsum binders, occurring without the formation of reaction products with binding properties but affecting the structure, properties and kinetics of their hydration [29,30]. The structure and composition of an interfacial layer depends on the type of the binder, degree of fineness and hydraulic activity of the filler. Fig.3 shows the model of an interfacial layer as an example in the paste of lime-silica binder.

Fig. 3 - Structure of interfacial layer in the paste of the blended sand-lime binder: 1 – particles of siliceous fillers; 2 – interfacial layer, decreasing in density and concentration from filler to reaction products with cementing properties, including low-basic CSH; 3 – volumetric $Ca(OH)_2$ at hardening in medium of CO_2 and long-term hardening crystallises in succession $Ca(OH)_2 \rightarrow Ca(OH)_2 + CaCO_3 \rightarrow CaCO_3$

In this model, in the case of a dense silica filler, the milled quartz sand thickness of the interfacial layer is determined by the grinding fineness, increasing solubility of the sand, thickness of the amorphous layer on its surface, which reaches 150–400 angstroms and significantly increases at steam curing and autoclave treatment. Heat treated and milled quartz sand has a thicker

surface layer of amorphous and fractured defects, which provides high reactivity, and a thicker layer of reaction products when interacting with lime [27]. In the case of introducing fillers of porous amorphous siliceous rocks (diatomite and tripoli) into the lime binders, depending on their fineness and curing conditions, the structure formation occurs as follows. The pores of particles are filled with tobermorite-like reaction products and ultrafine particles that interact with lime are transferred completely into the reaction products [31]. Here, in the material of the matrix of the stone of the binding is a combination of the two grids:- hydrated lime and calcium hydroxide, where particles of not fully reacted silica filler and the silicate interphase layer are distributed. In the cement hardened paste, the role of the filler, depending on its dispersion and the activity, is seen in the following directions: it acts as the filler in the cement paste, as in microconcrete, forming products with cementing properties and modifying the structure and properties of a main binder, which acts as a seed crystal. Fig.4 shows an example of a model of cement-based system with polydispersed fillers.

Fig. 4 - Model of cement-based system with polydispersed fillers: 1, 2 - unreacted particles of clinker and filler, respectively; 3 - reacted part of clinker grain; 4 - interfacial layer

In this model, the isometric shape of the particles of clinker and fillers is conditionally accepted. The reacted part of the cement clinker is represented by gel, crystalline reaction products of various shapes; and submicro-, micro- and macro-pores. The structure and composition of the interfacial layer at the hydraulically active fillers are described by a model similar to that shown in Fig.3. The composition of the interfacial layer on carbonate fillers (limestone, marble, magnesite, dolomite) is represented by calcium carbonated hydrates $\text{Ca}(\text{OH})_2 \cdot \text{CaCO}_3 \cdot n\text{H}_2\text{O}$ and in the presence of clay enclosures in addition to calcium carboaluminium silicate hydrates, calcium carboaluminate hydrates and calcium or magnesium carboferrite hydrates [32]. Micro- and nanoparticles sized from $1 \cdot 10^{-7}$ up to $2 \cdot 10^{-9}$ m of the hydraulically active fillers are absorbed in the process of cement hydration with an increase in the content of low basic calcium silicate. Nanoparticles of physically active fillers, penetrating the intergranular and intracrystalline pores due to high (up to 1.25 J/m^2) surface energy, increase the adhesion strength of the particles and the density of the gel and thus, reduce shrinkage and the tendency for microcrack formation of the hardened paste. As the final properties of the cement-filled pastes to a large extent are determined by the properties of the interfacial layer and its adhesion strength with the filler, these are important results of its research. In this regard, the results of well-known studies of interfacial layers of different types of cements and selected minerals, in their hardening in pastes and mortars on the surface of various fillers with a thin layer between them, are of great interest. By considering that the microhardness determines directly the strength of the cement paste, it is important to study the microhardness of the interfacial layer. In particular, it is known that the microhardness of the contact layer of Portland cement on the border with quartz, feldspar, calcite, marble and limestone, depending on the type of mineral and rock, rises from 2 to 7

times compared with the microhardness of the binder in the volume and it also depends on the curing duration. It is noted that the maximum hardness of the contact layer is at the boundary with quartz sand and regardless of the type of the binder, the thickness of the maximum hardened layer is 20–30 μm . Modelling of the structure and study of the composition and properties of the structural elements of the filled materials, allows to control its properties and predict the properties of the filled ACCM.

Conclusion 1. A new approach to the classification of filling for ACCM is proposed. The fillers are divided according to: - “Chemically active”: which consist only of amorphous structures, form reaction products with binding properties and modify the composition of the binder. - “Physically active”: which consist only of crystalline and(or) chemically inert structures, do not modify the composition of the binder, but do affect the physical structure of the mixed binder. - “Physically active and reactive”: which are of partially crystalline structure, and combine both above effects.

2. Generalised topological models of the structure and structural elements of blended binders depending on filler size, particle size distribution, density, chemical activity, based on the analysis of well-known research and own research on the structure formation of stone based on Portland cement, lime, gypsum, sand-lime are developed by the authors. The models are intended for forecasting the structure and properties of materials based on the various binders and fillers and materials they are based on and can be used for developing the theory of strength of filled materials and computerised systems for designing the structure, properties and interactions of components.