УДК 544.32 **doi: 10.20998/2079-0821.2024.02.12**

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SOME PHYSICAL-CHEMICAL FEATURES THE SOLID PHASES HYDRAULICITY

The most widely used in composite materials industry are concrete installations bonded with different binders. Higher energy consumption and several ecological problems make their manufacture to become more and more expensive. The growing market of construction works and constant extension of real estate property increases the demand for cheap and new materials with desired features. As a result of many years intensive scientific researches there is now a practical possibility to offer an alternative and unique products technology of manufacture based on binding suspension (bricks, wall, heat insulating and refractory materials and other) – all of them of desired size and shape. The experience of the composite materials technology development shows that in comparison with traditional the microhardness of materials with an ultradispersive structure increases several times and the specific surface increases by an order contributing to a decrease in the sintering temperature. The longevity of similar material is essentially increasing provided structure is forming under conditions of the service site. Thus, building industry will obtain improved service life and performance from binding suspensions as field installations will continue to move toward adopting and utilizing practices based on technology described herein, rather than on cement technology. Relative to conventional composite materials products with mechano-chemical binders will continue to gain in popularity because of the following advantages: low energy consumption and low prices for the products; ecological safety of the manufacture process and of the ready-made products; good mechanical and design properties; moisture and cold proofness; surface need not be fired; no shrinkage of the products after drying; simple to manufacture a variety of different products; ready availability and flexibility in design; absence of manufacture wastes.

Key words: composite materials, binding properties, colloidal suspension phase, mechano-chemical binder, mechanical-strength properties.

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ДЕЯКІ ФІЗИКО-ХІМІЧНІ ОСОБЛИВОСТІ ГІДРАВЛІЧНОЇ АКТИВНОСТІ ТВЕРДИХ ФАЗ

Індустрія композиційних матеріалів найбільш широко використовує бетонні конструкції на різноманітних в’яжучих матеріалах. Високе енергоспоживання та деякі екологічні проблеми роблять їх виробництво все дорожчим. Зростаючий ринок будівельних робіт і постійне розширення об’єктів нерухомості збільшує попит на дешеві та нові матеріали з бажаними характеристиками. В результаті багаторічних інтенсивних наукових досліджень з’явилася практична можливість запропонувати альтернативну і унікальну технологію виробництва продуктів на основі в’яжучих суспензій (цегла, стінові, теплоізоляційні та вогнетривкі матеріали тощо) – усі вони бажаного розміру та форми. Досвід розвитку технології композиційних матеріалів свідчить про те, що у порівнянні з традиційними, у матеріалів з ультрадисперсною структурою у декілька разів збільшується мікротвердість, а питома поверхня на порядок, що сприяє зниженню температури спікання порошків. Довговічність такого матеріалу суттєво зростає, якщо його структура формується в умовах експлуатації. Запропонована технологія виробництва матеріалів широкого призначення відкриває один з перспективних напрямків у розвитку нанотехнологій – створення надтвердих і надміцних матеріалів для індустрії композитів. Порівняно зі звичайними композиційними матеріалами вироби на механохімічному в’яжучому продовжуватимуть набирати популярність завдяки таким перевагам: низьке енергоспоживання та низька ціна на вироби; екологічна безпека процесу виробництва і готової продукції; хороші механічні та конструктивні властивості; вологостійкість і морозостійкість; відсутність необхідності випалу виробів; відсутність усадки виробів після сушіння; простота у виготовленні різноманітних виробів; доступність і гнучкість дизайну; відсутність відходів виробництва.

Ключові слова: композиційні матеріали, в’яжучі властивості, колоїдна фаза суспензії, механохімічне в’яжуче, міцностні характеристики.

Introduction. The limited raw materials deposits have a sequential effect on the expenditures for composite materials production. It is concerned of enrichment, conditioning, heat processing, ecologically save technology developing and other. The longevity of any constructional material is essentially increasing provided structure is forming under conditions and at the service site. That is why developing of new composite materials must be carried out by means of its structure design. These principles have been realizing in the refractory concretes technology under the limited conditions of heatup, hardening time, drying and other [1; 2].

Meanwhile refractory concretes bonded with the different hydraulically setting cements at the temperature range defined have the strength losses as the ceramic processes and chemical conversions (dehydration, bonds disruption, easy-melting compositions forming) occur. The last ones are accompanied by the volume changes. It emphasizes the necessity for developing binders to obtain optimum concrete performance and to avoid structural defects relating to the transition of hydrated phases and gels. Permeable crystalline phases are then developed that maximize structural stability and ensure safe heating of large cross sections.

As for our opinion similar binders must have a high binding properties; the soundness through the whole range of service temperatures; to be matched by nature or to approximate to the utmost of refractory constitution; to be technological (to have a good distribution between the grains during a mixing) and resistant to preaging [3, 4].

Experimental. The solid phases hydraulicity can be influenced on some factors. They are caused by atom structure, chemical bonds nature, anion and cation properties. Four main of them are presented herein [5].

Central atom of EO_4^{n-} anions is in the sp^3-hybridization state and each anion has one vacant 3-d orbital but different number of unpaired electrons that influences on the internal hybridization possibility while the vacant orbitals number in outer level is decreasing. A presence of vacant orbitals in outer level defines a possibility of multiple, donor-acceptor bonds forming along with the electrons transition occurs during the chemical reactions. This premise explains the phases chemical activity – this is a first factor.

Next factor determining a phase ability to interact with water is E-O chemical bond nature in anion. The initial steps of hydration are polarization and polycondensation processes with subsequent hydroxyl bonds developing result in E-O-E bonds are forming in setted stone. This factor is evaluated by chemical bond nature analysis in anions. The evaluation is carried out by ionic covalent resonance energy value ΔE according to Polling's equation. This value is a measure of deviation the chemical bond nature from covalent. The larger ΔE value the larger ionic nature of bond. The larger ΔE value (it means more ionic nature of E-O bond) the larger phase activity containing EO_4^{n-} anion. Binding properties appear when the ionic bond degree is reached not the less 25% – this is a second factor.

Within the period from SiO_4^{4-} to SiO_4^{2-} central atom sp^3-hybridization is reducing and π-bonding becomes important to stabilize of hybridization. The given transition is accompanied by the O_2 atoms number decreasing that able to form of π -bonds in following reactions. The some anions electron structure analysis carried out by means of Molecular Orbitals Method has shown the electron distribution on the molecular orbitals:

$$AlO_4^{3-} - \left[\sigma_b\right]^6 \cdot \left[\pi_{nb}\right]^{13}; PO_4^{3-} - \left[\sigma_b\right]^8 \cdot \left[\pi_b\right]^2 \cdot \left[\pi_{nb}\right]^{11}$$

$$SiO_4^{4-} - \left[\sigma_b\right]^8 \cdot \left[\pi_{nb}\right]^{12}$$ [5].

The subscripts *b* and *nb* in these distributions identify bonding and nonbonding σ and π molecular orbitals accordingly. In PO_4^{3-} anion the electrons on π-bonding orbital appear stabilizing sp^3-hybridization state. The delocalized d_π-p_{nb} bond arises due to that. Reducing of phases hydraulicity from aluminate to sulfate of calcium results in π-bonding enhancing, with E-O bond strength increases. Third factor is absence or a minimum of π-bonding in EO_4^{n-} anions.

The cation properties also have an important significance. The screening constants *S* for s-elements that define an effect degree on the internal orbitals of Me-O anion were calculated $(S_{Ca^{2+}} = 18, S_{Mg^{2+}} = 10)$). From Be^{2+} to Ba^{2+} cation effecting on oxygen ions decreases and Me-O bond strength reduces. Also the ionic field intensity (cation polarizability) value were evaluated $Ca^{2+} = 1,85; Mg^{2+} = 3,65; St^{2+} = 1,67; Ba^{2+} = 1,45$ The higher cation polarizability, the lower activity of anhydrous phases, while the binding properties appear when intensity is not the less 2 – this is a four factor [5].

In present work a specific method of binders obtaining based on the reactants implantation was used, with their enable to initiate the binding properties of materials surface. Similar method is supplying the chemical compositions formation on the particle surface during of the mechanical dispersion. The suspension should be a final product of mechano-chemical implantation. The suspensions being used for refractories manufacture have the important advantages as: a high concentration and polydispersity of solid phase and the bonded liquid a minimum also. As implantators carriers the water solution of salts, acids, bases can perform. To obtain with mechano-chemical method the suspensions on the base of corundum and zirconia as effective implanting reactant is phosphate ion.

An implantator solution-carrier optimum concentration selection is determined by following requirements: suspensions must have a good flowability with humidity a minimum, ensure the proper strength and density and also soundness of casting. Typical suspensions with mechano-chemical method obtained are given in Table 1 [6].

Results and discussion. An important technological task of mechano-chemical method to suspensions obtaining is maximum developed active interphase surface conditions creating that be able to interact with implanting ion. Similar topochemical interaction is accompanied by appearance of complicated content colloid phases that give the specific properties set to suspensions enabling to combine a cementitious ability required with soundness during a heating.

The phosphate-ion chemical interaction technological product on the ZrO_2 particles surface is gel $ZrO_2 \cdot P_2O_5 \cdot 5H_2O$. On carrying out sequentially first raw materials dry grinding with particles size 2–0.5 mm to particles size less 60 μm and then their chemical interaction with H_3PO_4 water solution about 1.3% gel is forming into suspension, when the both processes gathering – 3.7%. At the ZrO_2 grains mechanical grinding into the water environment (wet grinding) the gel-shaped substances are not forming into suspension [6].

The influence of suspensions preconditioning and implantator (H_3PO_4) concentration on the castings properties are shown in Figures 1 and 2. Optimum castings strength and density with their shrinkage a minimum develop in the 1.40–1.55 PH range. Meantime topochemical interaction during the wet grinding into the water environment for materials with the higher ionic

Table 1. Characteristics of suspensions obtained with mechano-chemical method.

Characteristics of suspensions						Properties of castings		
Solid phase content	Ion-implantator	Solid phase volume part	Density, g/cm^3	PH	Specific viscosity, ^{0}E	Density, g/cm^3	Opened porosity, %	Bending strength, MPa
Fused ZrO_2	PO_4^{3-}	0.45-0.50	3.10	1.2	18	3.40	34.0	14.0
Sintered corundum	PO_4^{3-}	0.45	2.48	1.4	40	2.52	27.0	18.0

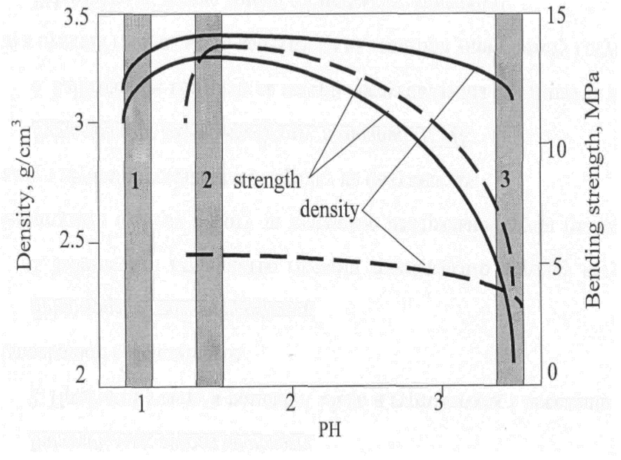

Figure 1 – Influence of zirconia (–) and corundum (--) suspensions preconditioning on bending strength and density of castings dried 300 ^{0}C: 1 – dry grinding with sequential powder suspending into H_3PO_4 water solution; 2 – wet grinding into H_3PO_4 water solution; 3 – same as 2, but with gel substitution by water.

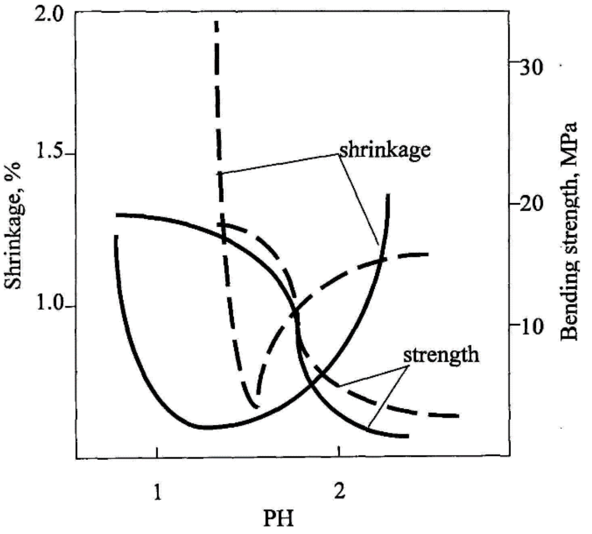

Figure 2 – Influence of zirconia (–) and corundum (--) suspensions PH on properties of castings dried at 300 ^{0}C.

potential than ZrO_2 and Al_2O_3, for example β-quartz and chamot, occurs [6, 12].

As the reactors enabling to obtain the suspensions with mechano-chemical method the 7 m^3 volume ball and tube mills were used [7].

Mechano-chemical implantation results in the solid phase concentration increasing to 0.5 with the suspension humidity 14–15%. Such conditions provide growing of the colloid component content, while compressive strength of zirconia and corundum suspensions castings is increasing. When sufficiently high degree of solid phase volume concentration is reached, growing together of particles due to polycondensation processes is beginning in despersive system on the phosphate base. With original coagulative structures appear, that are followed by the phase crystalline contacts forming.

At this step slower compressive strength in comparison with crystalline structures having the same degree of volume filling occurs. Colloid phase provides a thixotropy (a capability of colloid "setted" structures to decay reversible result from mechanical action), cementitious ability of hydrosuspensions by the mechanism: sol–gel–xerogel [8].

A presence into suspension of colloid component with the high specific surface of particles (250–270 m^2/g), while its content into suspension solid phase reaches 1 (mass) %, increases the active centers amount to reactants implanting. It is characteristic for silica and alumina the Lewis acid centers forming results in the vacant orbitals presence with the high cohesive energy.

Corundum suspension colloid phase IR-spectrum after the wet grinding at the range of frequencies 460-650 and 785–800 cm^{-1} shown in Fig. 3 is typical for O-P-O bonds deformation oscillations of phosphate-anion. IR-spectrum range of frequencies 2900–3500 cm^{-1} is very important. If 1630 cm^{-1} frequency belongs the free water oscillations, then 2945, 3000, 3450 cm^{-1} frequencies correspond with the occurrence of hydroxyl vicinal groups adjacent to “cristobaphite” (aluminum orthophosphate) tetrahedron structure defects [8].

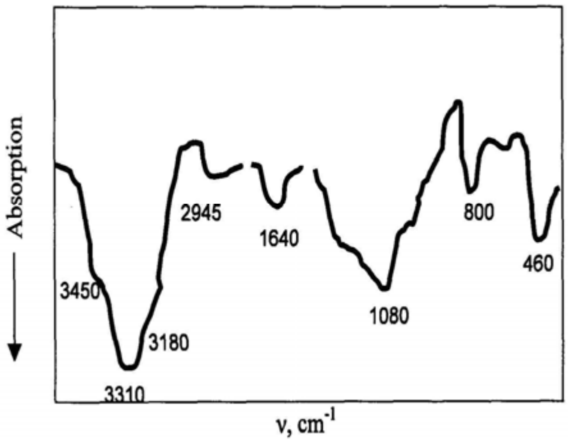

Figure 3 – Corundum suspension colloid phase IR-spectrum after the wet grinding.

Beside 785–800 cm^{-1} oscillations clarify the interaction product as $AlPO_4$ (orthophosphate phase). $AlPO_4$ phase elementary cell geometrical parameters are similar to the same of quartz, but in comparison with the close-packed quartz lattice, the structure voids occur as the result of larger distances between the tetragonal complexes of $AlPO_4$ [6, 8].

These voids enable to accept the different ionic groups as during the P–O and P–OH bonds polymerization with O–P–O bonds forming into “branching” structures of phosphate binder and at the solid phase interaction during heating as well. Thus, active absorption at the range of spectrum involved may be explained by the reactant implanting (PO_4^{3-}–groups) on particles surface after the mechanical activation [9].

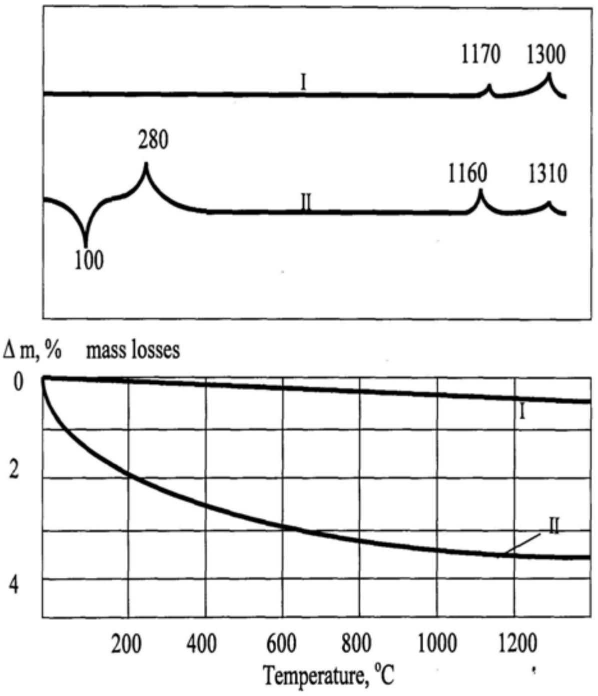

Figure 4 – Thermogram of suspension: mineral content of zirconia suspension – I and colloid component after the wet grinding – II.

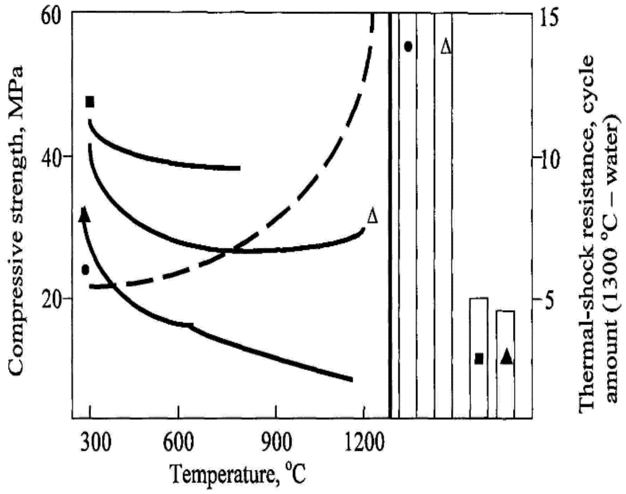

Figure 5 – Comparative mechanical-strength properties of the concretes. Concretes on the base: ■ – liquid glass; Δ – AC; ▲ – HAC; • – mechano-chemical zirconia binder.

Figure 4 shows that colloid component losses under the suspension heating achieve 4 (mass) %. This amount consist of 60–65 (mass) % – physical H_20, remaining – structural H_20 within the implanting groups and crystalline hydrates. Since the colloid component content into suspension is about 1%, great amount of implanting groups have no influence on the shrinkage and other service properties of refractory concretes, thus, at the temperature range defined the drop-off in fired strength is absent. Figure 5 supports this premise (dotted line).

The dried and fired strengths developed in refractory concretes are critically dependent on use of:

- the correct amount of tempering H_2O required by the specific method of placement to assure installation of a sound lining having minimum structural defects;
- proper curing conditions to ensure development of the desired hydrated phases to maximize structural integrity;
- controlled uniform heating schedules [10, 11].

The binders obtained by means of the raw mix mechano-chemical processing (mechanical dispersion and chemical interaction processes combination) become the most important ceramic setting binders used for bonding refractory concretes because they develop initial strength during a heatup of the units within 8–10 h, in contrast to 24 h after placement for HAC cements. This strength development enables high temperature processing units to be put back on stream with minimum turnaround time, thus providing a favored cost/performance ratio.

Relative to conventional, composite materials with mechano-chemical binders will continue to gain in popularity because of the following advantages:

- quick installation;
- possibility of fully anchored construction;
- reduced and simplified furnace maintenance;
- good thermal-shock resistance;
- monolithic (no joints);
- linings/elements of the units done need not be setted to develop initial strength;
- ready availability; and flexibility in design [12].

Conclusion. A priority of the technology developed is the specific method of the non-firing binders obtaining for concretes bonding. It is necessary that binders (suspensions) have the important advantages as: high concentration and polydispersity of solid phase and the bonded liquid a minimum also when their being used for refractory materials manufacture. We conclude that industry will obtain improved service life and performance from refractory concrete or castable lining as field installations will continue to move toward adopting and utilizing practices based on high concentrated bonding suspensions (HCBS) technology described herein, rather than on cement technology.

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