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The scientific basis for the creation of a composite binders class, characterized of the low heat conductivity and low sorption activity of cement stone

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Abstract

The physical-chemical and heat-physical basis of macro- and microstructures formation, phase content of "cement stone" of low-clinker composite binders for particularly lightweight concrete of heat-insulation designation are presented. The results of corresponding studies on the influence of chemical, mineralogical and phase compositions of the composite binders, their components and formed from them "cement stone" on the activity of the composite binder and its heat-physical characteristics of such cement stone are presented. Submitted work accomplished in the development of the European standard EN 197-1:2000 Cement. Part I. Composition, specification and conformity criteria for common cements.

Keywords: Composite binders; Cement stone; Chemical-mineralogical composition; Phase content; Macro - and microstructure; Activity of the binder; Heat-conductivity; Sorption humidity; Lightweight aggregate concrete

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1. Introduction

Owing to the upgrading of regulatory requirements to buildings’ thermal protection level, the demand for lightweight aggregate concretes (LAC) with high thermal characteristics is increasing, particularly, for superlightweight heat insulating concretes (up to D500 mass specific gravity grades).

The research results and application experience show that heat insulating LAC are essentially more reliable in service as compared with conventional insulation (polystyrene foam and mineral wool plates) currently used in sandwich envelopes structures.

There is the urgent necessity to improve indicators of heat-technical quality of these concretes for upgrading thermal-protective properties of envelope structures where they are used. There are technological opportunities to achieve this aim by using in them the composite low-clinker binders (LCB) with the appreciably reduced heat conductivity values and sorption activity of the cement stone to those of conventional cement binders. Such binders hereinafter are conditionally called as “low heat-conductive” LCB, i.e. LH-LCB.

Development of the new binder class – LH-LCB – was commenced under scientific management of the present paper authors about 20 years ago for structural-heat-insulating concretes (expanded clay concrete, slag pumice concrete, etc.) widely used at that time in single-layer envelope structures. Basing on the fact that the cement stone constituting 25-40% from the total volume of the moderately pore forming (air entrainment volume – 10-12%) structural-heat-insulating concrete, it is most heat-conducting component of LAC. According to summarized data of various researchers the heat conduction coefficient \( \lambda \) of the hardened Portland cement paste matrix (cement stone) is from 0.56 to 0.72 W/moC, whereas \( \lambda \) of the grain of porous aggregates of having various types and densities of LAC is from 0.15 to 0.3 W/moC.

The use of LH-LCB is most cost-effective in structural-heat-insulating LAC used for non-reinforced building elements (specifically for wall blocks) and particularly in heat-insulating concretes used both for precast elements (e.g. in heat-insulating boards) and for cast-in-situ heat insulation of layer envelope structures. For such concretes and building elements the Portland cement clinker content is not regulated from the viewpoint of ensuring the concrete passivating action in relation to steel reinforcement, namely: the necessary maintenance of alkaline conditions in concrete pores (pH≥11, 8) is not regulated. Evidently the use of Portland cement in these concretes in no case is rational either economically or from the viewpoint of ensuring the required indicators of heat-technical quality taking into account the above mentioned relatively high heat conductance of hardened cement clinker (paste matrix).

Here the most efficient will be low energy-consuming and low-clinker binders of LCB type (calcination of the admixture-free Portland cement clinker with 50 MPa activity requires on the average 220 kg of equivalent fuel for 1 ton of clinker, while calcinations of LH-LCB of the same activity requires not more than 110 kg of equivalent fuel for 1 ton of clinker).

2. Scientific conception. Working hypotheses

When developing LH-LCB to be manufactured mainly on the basis of chemically mutually compatible large-scale industrial by-products and its recycling, one should proceed from the following basic prerequisites:

2.1. Improvement of LCB heat-physical properties is really and most efficiently possible owing to incorporation the products of recycling of blast furnace or ferroalloy slag smelt (silicomanganese or ferromanganese) into the material constitution of LCB such a relatively low-heat-conductive and low- sorption-active component; the same applies to electrothermophosphorus slag smelt as the product of recycling under high-power cooling conditions (in particular by water under pressure) that ensure the predominant content of the amorphized phase in granulated slag.

2.2. In addition to the effect of such a favorable factor as the appropriate phase composition, the reduced heat-conductivity of the composite binder with hydraulically active ground metallurgical or electrothermophosphorus granulated slag shall ensure the relatively higher content of hydration products – fine-crystalline low-base calcium hydroxides of CSH (B) type, as well as low-base hydroaluminates of C2AH8 type.
2.3. Evidently, the advantage of the relatively reduced heat-conductivity of fine-crystalline structures in hardened binders as well as basically amorphized structures can be explained by “the effect of short range order phonon path”, well known in heat physics. To that end it is recommended to proceed from T. Pierles’ formula of heat conductivity [1]:

\[ \lambda = \frac{1}{3} \lambda_{\text{av}} \cdot U \cdot C \]

where \( \lambda_{\text{av}} \) - mean average path of phonons (quasi-particles of energy of solid body lattice site coupled thermal vibrations); \( U \) - phonon propagation velocity, \( C \) - volumetric heat capacity.

Value \( \lambda_{\text{av}} \) depends on the phonon scattering process in the solid body lattice arrangement: the higher is scattering intensity, the lower is the phonon path length and the higher is the crystal heat resistance. The phonon scattering intensity is higher and hence the heat conductivity is lower in the amorphized or glass-like materials, as in much less organized structures when compared to the crystalline ones having the short range atom arrangement. The less is the crystal size, the more is their quantity in the solid body unit volume, the more intensive shall be phonon scattering and, consequently, the less shall be heat conductivity.

3. Research results with regard to scientific conception

3.1. First of all, it is advisable to note the research results on effects of metallurgical slag LH-LCB component chemical composition on their phase content and heat conductivity. The studies conducted by L.R. Zyatkova, I. Ya. Chernyavsky and S.N. Miller [2] at UralNIItromproyekt on heat conductivity of semi-synthetic SiO2-Al2O3-CaO-MgO slag glasses. Their results are presented in Fig. 1.

![Fig. 1. Influence of the chemical composition of semi-synthetic CaO-Al2O3-MgO slag glasses on the values of: a) density \( \gamma_0 \), g/cm3 b) coefficient of heat conductivity \( \lambda_0 \), W/ (m °C)](image)

The analysis of these results shows: if the slag glass density (\( \gamma_0 \)) varies rather insignificantly depending on their mineralogical composition (from 2.54 to 2.76 t/m³, i.e. only by 8.7%), then variation of their coefficients of heat conductivity (\( \lambda_0 \)) is rather essential – from 0.50 to 1.50 W/ (m 0°C). At that it should be noted that the minimum
coefficient of heat conductivity values are observed on Al2O3- CaO line, while the maximum ones – under partial substitution of CaO and SiO2 for MgO.

In regard to the influence of the cement stone mineralogical and phase composition on its heat conductivity, the mechanism of this effect may be presented as follows.

It is known that the hardened cement clinker silicate phase has a negative surface charge, while the aluminate and alufoferrite phases – positive. If supposedly the phonon path energy has an electrical nature, i.e. the negative charge, then one can expect that when getting into the cement stone silicate phase, it does not only lose its power, but increases (therefore the silicate phase conducts heat flow well). When meeting the aluminate and alufoferrite phases, the phonon charges are compensated (i.e. diminish depending on the volume and morphology of the positively charged aluminate structure).

If the silicate phase is morphologically presented mainly in the form of needle and fibrous crystals and tubes, the aluminate and alufoferrite phases – in the form hexagonal plates and polygons, the size of which 2-3 orders less than the silicate phase particle size. Most probably this explains a significantly greater extent of phonon scattering in the lattice arrangement of the cement stone aluminate and alufoferrite phases as compared with its silicate phase; the higher is the scattering intensity, the less is the phonon path length, and accordingly, the higher is the crystal heat resistance.

3.2. This hypothesis is confirmed by the results of experimental studies conducted in 2007-2009 by Siberian Road Institute with participation of Research Institute of Building Physics (NIISF) [3] regarding the effect of the cement stone basic minerals relative content on its heat conductivity ($\lambda_{cs}$). Indeed, the analysis of the results obtained has shown that relative increase of C2S alite content leads to $\lambda_{cs}$ increase. With decreasing of C3S content and similar increasing of C2S, calcium aluminate C3A and calcium alufoferrite C4AF the cement stone its value of $\lambda_{cs}$ decreases. The most significant effect on $\lambda_{cs}$ is exercised by calcium aluminate C3A content.

3.3. As a result of the studies in effects of cement basic minerals relative content on the value $\lambda_{cs}$, the regression equations have been obtained; they establish the dependence of $\lambda_{cs}$ value on the relative content of basic minerals C3S, C2S, C3A, C4AF in Portland cement. The analysis of the results has shown that C3S alite content really leads to the increase of $\lambda_{cs}$. With decreasing of C3S content and the appropriate increase of C2S content, C3A calcium aluminate and C4AF calcium alufoferrite the value of $\lambda_{cs}$ decreases. The most significant effect on it is exercised by C3A calcium aluminate content.

Value of $\lambda_{cs}$ for alite cement is equal to 0.435 W/(m$\cdot$C), for belit cement – 0.368 W/(m$\cdot$C), for aluminate cement – 0.351 W/(m$\cdot$C), for alufoferrite cement – 0.397 W/(m$\cdot$C).

The formula has been obtained to calculate the effective coefficient of heat conductivity $\lambda_{ef}$ of aerated heat insulating lightweight concrete depending on the basic mineral content in cement and concrete porosity.

$$
\lambda_{ef} = [0,427 + (0,15 \cdot C_{3S} – 0,12 \cdot C_{2S} – 0,45 \cdot C_{3A} – 0,38 \cdot C_{4AF} \cdot 10^{-2}] \cdot (1 – Vc) + (\lambda_\gamma + \varepsilon \cdot C_0 \cdot \theta \cdot d) \cdot Vc
$$

(2)

where $\lambda_{ef}$ – coefficient of effective heat conductivity of concrete, W/(m$\cdot$C); $\lambda_\gamma$ – coefficient of heat conductivity of still air in closed pores at temperature 200C; $Vc$ – heat flow conducting pore volume in LAC, part of unit (1); $\varepsilon = 0,91$ – given the degree of blackness of concrete; $C_0 = 5.77$ W/(m2 $\cdot$C) – concrete emissivity coefficient ; $\theta = 1$ – temperature coefficient at 200C; $d$ – mean average pore diameter in concrete structure, mm.

3.4. Possible activity reduction of a composite binder at the expense of Portland cement clinker substitution with a less hydraulically active slag or any component of the same activity from industrial by-products (IBP) is compensated here by incorporation of another component into the binder composition together with the ground blast furnace granulated slag (substituting a part of cement clinker); chemical interaction of this component with the slag results in formation of new growths, which will ensure the required (with reduction of cement clinker consumption) increase of the cement stone structural strength without deterioration of its heat-transfer properties. As the studies conducted by the Pavlodar Technical University together with NIISF [4] have shown that this component can be a bauxite sludge (BS) – the aluminous industry by-products represented mineralogically mainly by belit C2S and tricalcium aluminate C3A with considerable content of basic alumina (up to 7-10%). The latter facilitated development of BS alkali reaction with blast furnace granulated slag minerals (as a slag-alkali binder) and,
consequently, the required increase of structural strength of the hardened mixed binder. Preservation and even improvement of this sort of binder its indicators of heat-technical quality values was enhanced by high intergranular BS porosity and fine-pored structure of resultants of BS alkalis reaction with blast furnace granulated slag as another component of LH-LCB.

Low-clinker (cement clinker consumption from 10% to 30% by binder mass) composite polymerized slag binders (LH-LCB) of M300-M400 grades have been developed. In the tests as raw components we used Portland cement clinker of the Lipetsk cement plant, blast furnace granulated slag of the Novolipetsk’ metallurgical plant with the glass phase content 85-90% and C-3 superplasticizer in the powdered state.

The optimum LH-LCB compositions were determined as a result of the test conducted by the mathematical planning approach. Its results are given in the nomographic chart (see Fig. 2).

Fig. 2. Nomographic chart of the dependence of compression strength (R28) at the age of 28 days under normal humidity curing, coefficient of heat conductivity in the dry state (λ₀) and coefficient of heat conductivity increment by 1% of humidity (Δλ) of LH-LCB on cement clinker (CC) consumption and superplasticizer C-3 consumption at the raw mix grinding fineness S = 3250 cm²/g.

The chart data analysis shows that LH-LCB with activity, e.g. 40 MPa, has the following advantages in heat-physical properties over the equal grade admixture-free Portland cement:

- reduced by 28-32% heat conductivity coefficients in dry conditions;
- reduced by 27-41% increments of heat conductivity coefficient per 1% of humidity;
- reduced values of sorption humidity at φa=80% - by 62%, and at φa=97% - by 68%.

LH-LCB efficiency was verified in the Laboratory of resource- and energy-saving light-weight concretes and structures NIISF, when using in heat insulating polystyrene concrete (PC) of D400 density grade in comparison with an analogue – polystyrene concrete based on Portland cement. Heat conductivity coefficient of PC made on the basis of LH-LCB with 40 MPa activity and 25% cement clinker content happened to be lower by 22% than a similar Portland cement PC characteristic for the concrete dry state (λ₀), and for the equilibrium humidity state λ – by 37%, thereat the concrete sorption humidity (oc) at φa= 97% was lower by 47%.
The effect of improving PC-concrete heat-technical quality according to values $\lambda$ and $\alpha$, when Portland cement is replaced by LH-LCB, is governed not only by better values of similar characteristics of the composite binder cement stone (see Fig.1), but also by modifying of the concrete mortar fraction structure. Here when using LH-LCB characterized by the lower normal consistency of the cement past matrix (19.2% versus 25.5%, when using Portland cement). The latter was ensured by introduction into the LH-LCB raw charge of the polymerizing and water-reducing chemical admixture, namely – the powdered superplasticizer C-3.

Owing to the latter factor the PC-concrete water-cement ratio required to ensure workability of polystyrene concrete mix has decreased when Portland cement was replaced by polymerized LH-LCB with $W/C=0.41$ to $W/C=0.33$. This resulted in transformation of the mortar fraction pore structure of concrete towards essential reduction in the relative volume (Voc) and the average size (value $\lambda_{ocp}$) of open capillary pores (see Table 1).

This implies the reduced values of concrete sorption humidity determined by its capillary porosity as well as reduction of its coefficient of heat conductivity governed (according to the above T. Pierles’ formula) by the relatively fine-pored structure of the concrete mortar fraction. The latter predetermines the decrease of the phonon average path length, intensification of their scattering effect on structure defects (particularly, small pores, see formula 1).

<table>
<thead>
<tr>
<th>Binder type with 50 MPa activity</th>
<th>Polystyrene concrete density $\rho_\text{c}$, kg/m$^3$</th>
<th>Polystyrene concrete structure characteristics</th>
<th>$W_\text{am}$, %</th>
<th>$V_{tp}$, %</th>
<th>$V_{oc}$= $W_\text{av}$, %</th>
<th>$V_{igv}$, %</th>
<th>$V_{cp}$, %</th>
<th>$\lambda_{ocp}$</th>
<th>$\alpha_{ocp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH-LCB</td>
<td>374</td>
<td></td>
<td>19.3</td>
<td>84.8</td>
<td>7.3</td>
<td>4.1</td>
<td>73.4</td>
<td>0.071</td>
<td>0.21</td>
</tr>
<tr>
<td>PC</td>
<td>381</td>
<td></td>
<td>22.3</td>
<td>83.3</td>
<td>8.7</td>
<td>5.3</td>
<td>69.3</td>
<td>0.096</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Notation: $\rho_\text{c}$ - dry concrete density; $W_\text{am}$ - water absorption by mass; $W_\text{av}$ - water absorption by volume; $V_{tp}$ - total pore volume; $V_{oc}$ - open capillary pore volume; $V_{igv}$ - intergranular void volume; $V_{cp}$ - conditionally closed pore volume; $\lambda_{ocp}$ - open capillary pore average size value; $\alpha_{ocp}$ - open capillary pore size uniformity value.

There are other examples of the NIISF and Moscow State University of Civil Engineering joint developments in efficient use of chemical mutually compatible by-products of metallurgy and of by-products of other industries, in particular, chemical industry, or their recycling products.

Their chemical interaction has allowed making quite a wide range of low-clinker composite binders with reduced heat conductivity and sorption activity of the hardened cement paste matrix as compared with conventional cement binders.

4. Conclusions

A fundamentally new class of a rather wide range of low-clinker composite binders (LH-LCB) has been developed. They are manufactured on the basis of chemically mutually compatible by-products of various kinds, the hardened cement paste matrix (cement stone) of which differs from the Portland cement matrix by essentially reduced heat conductivity and sorption humidity.

With significant saving of Portland cement clinker (from 30 to 60%) such binders have activity (40-50 MPa) sufficient for structural-heat-insulating and heat-insulating concretes and are characterized by essentially improved indicators of heat-technical quality (namely, reduced heat conductivity and sorption humidity of hardened paste matrix, while preserving its strength as compared with the Portland cement matrix).

The research results for superlightweight heat-insulating concretes produced on the basis of binders type LH-LCB as compared with admixture-free Portland cement with 40-50 MPa activity have shown the decided advantage in the fine-pored structure of the concrete hardened paste matrix (mortar part) with the reduced capillary pore content. Accordingly such structure of hardened mortar part, there is an advantages in heat-physical properties of concrete...
based on this binder, i.e. the scientific conception of really obtaining low-energy composite low-clinker binders characterized by significantly improved heat-physical properties of cement stone was proved.

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**References**