

High Reaction Activity of Nano-Size Phase of Silica Composite Binder

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ABSTRACT

The article covers the study of the influence of quartziferous additives on composition, structure of neo-crystallization and hydration of clinker minerals. It has been proven that adding chalk into composite binder composition creates conditions for the formation of a cement stone at the micro- and nanoscale and shows some activity (hydraulic or pozzolanic) increasing the total content of new formations in the hardening binder.

KEYWORDS

cement stone, structure crystallization, screenings of crushing, composite binder, chalk, clinker minerals

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Introduction

Since the development of cement stone crystallization starts from the surface of the section "fine-grained filler – particles of cement", the qualitative and quantitative changes of such surface section cause change in the structure of the material, especially on the early stages of its formation. Nature of nucleation and crystallization of a new phase during binder solidifying is determined by the surface area of the section of phases, specific surface material (Chernyshov & Korotkyh, 2008). The ratio in time between the two components of a cement stone depends mainly on the brand of cement and its fineness (Kamaliyev, Korneev & Brykov, 2009). The finer the cement grinding, the faster the growth of solid crystalline part. The latter is also due to the fact that the concentration of defects on the surface of cement particles exponentially increases with decreasing of a crystal size, therefore high speed of hydration of thin cement fractions is associated not only with their high surface area, but with a higher concentration of defects on the surface (Dagotto & Moreo, 2001; Beandvin, 1976; Hobbs, 1981; Guimond, 1989; Ming, Hengjing & Ying, 2003). Hence it is clear that the most important characteristic of a binder is the value of specific surface area related to particle size composition (Sulimenko & Ukhanova, 2006).

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In this regard, especially at an early stage of hardening during the transition from coagulation to crystallization structure of a cement stone the role of filler is evident through change of the parameters of the forming structure (Klassen, Shuravlev & Klassen, 2000; Shmitko, Krylova & Shatalova, 2006; Paschenko, 1991).

Methodological framework

The influence of quartziferous additives on the composition, structure of new formations and hydration of clinker minerals has been being researched using XRF on powder x-ray diffractometer ARLX'TRA. The degree of binder hydration has been estimated based on reduction of the intensity of the reflections of basic minerals 1.76 Å (C3S); 2.74 and 2.76 Å (C3S, C2S) and increase of intensity of portlandit reflection lines (4.92; 2.63 Å) as a product of hydration (fig. 1).

Results and Discussion

Among the analyzed quartziferous additives the crushing screenings of quartzite sandstone is of the greatest interest, as well as chalk advancing hydration of aluminates and forming various compounds with them on early stages of hardening advancing the increase of early strength.

From this point of view, it makes sense to use quartziferous additive in complex: crushing screenings of quartzite sandstone and chalk.

Strength of composite binder is mainly created by an active component: clinker component. The adding of chalk to composite binder composition creates conditions for formation of a cement stone at the micro- and nanoscale and shows some activity (hydraulic or pozzolanic), increasing the total content of new formations in the hardening binder.

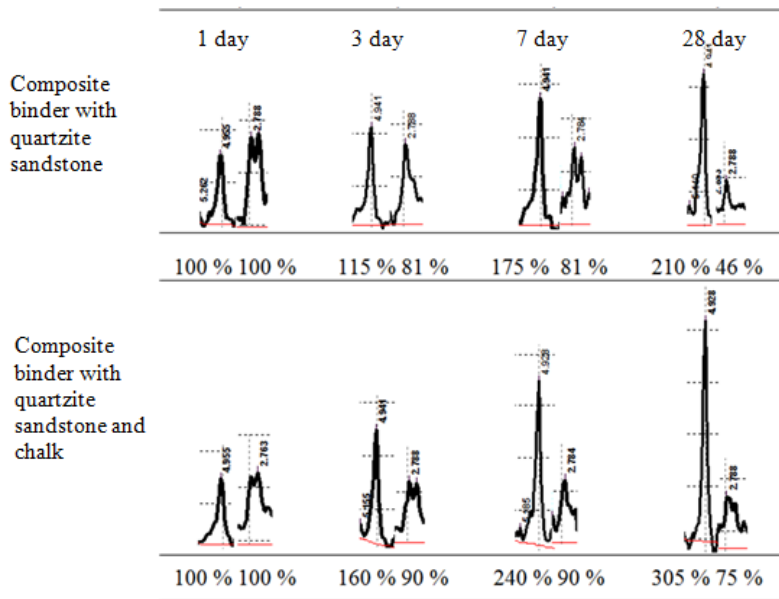


Figure 1. Diffraction profiles of alita and belita reflections (2.76Å and 2.78Å) and portlandit (4.94Å) in composite binder using chalk

By the 3d day of hardening the intensity of portlandit reflections of a composite binder using chalk exceeded the intensity of portlandit reflections of a composite

binder without chalk. By the 28th day of hardening the increase of reflection of a binder with quartzite sandstone equaled 210%, while the composite binder with quartzite sandstone and chalk equaled 305% (fig. 1).

To assess the impact of quantitative ratios of calcium silicate hydrate (C-S-H) on strength properties of composite binder a modified (within standard) XRF method on the basis of H.M. Rietveld (1967; 1969) (full-profile) settlement procedures has been applied.

Figure 2 shows the Rietveld diagram of the hydrated composite binder based on clinker.

Quantitative concentration parameters based on the foregoing approach allowed building graphical representation of changes in the concentration of portlandit in the hydrated composite binder (fig. 3).

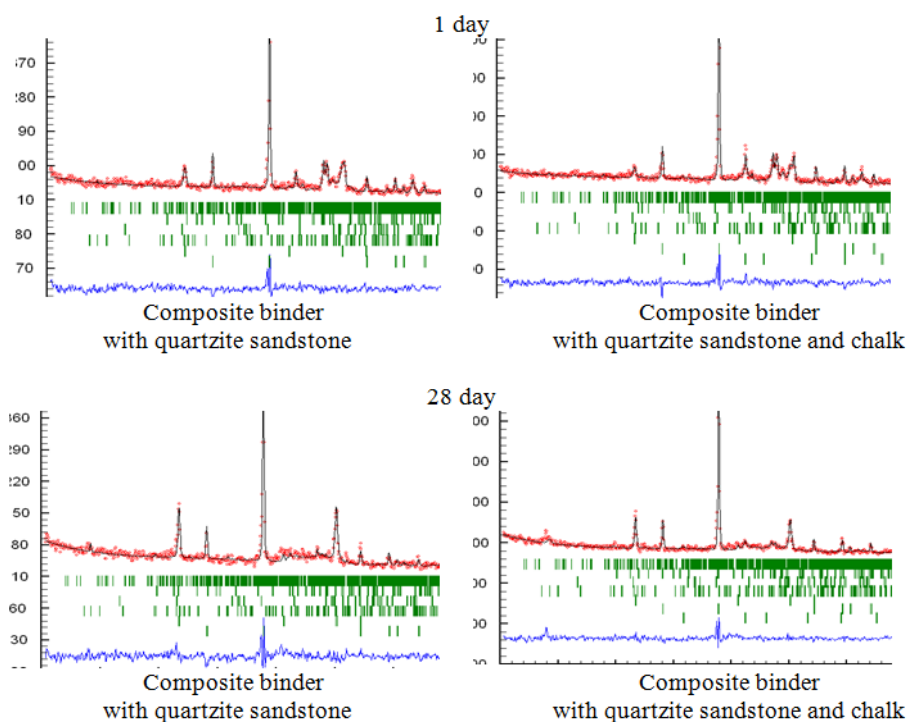


Figure 2. Rietveld diagram of the hydrated composite binder

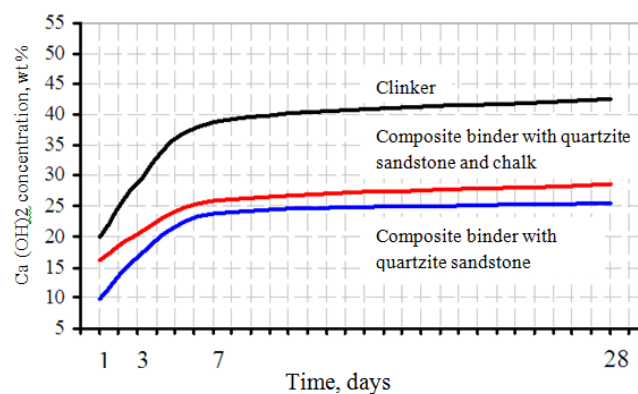




Figure 3. Change of the portlandit concentration in composite binder in the process of hydration based on the results of the full-profile XRF

For a meaningful comparison of portlandit concentration in composite binder with quartzite sandstone and in composite binder with quartzite sandstone and chalk normalized to a concentration of portlandit in hydrated clinker.

For Rietveld (full-profile) diagram construction internal etalon (standard) was introduced into composite binder in the amount of 10 wt. % of binder – titanium dioxide (TiO₂).

Concentration of portlandit in composite binders with quartzite sandstone and quartzite sandstone and chalk is less than in straight clinker. It can be argued that a significant reduction in the concentration of portlandit is due to linking of crushing screenings by its active siliceous component and formation of additional low-basic calcium silicate hydrates, which leads to increased strength characteristics of composite binder.

In explaining the different reaction activity of siliceous components of a composite binder a number of researchers (Zhernovsky, Strokova & Fomenko, 2007; Zhernovsky, Strokova & Lesovik, 2008; Murtazaev et al., 2015a; 2015b) brought their "degree of crystallinity" data. It should be noted that this value is a very abstract, essentially qualitative characteristic of crystalline materials and has no quantitative information on the structural condition of the object of study.

Currently complex quantitative parameters of phase and dimensional heterogeneity are increasingly applied in construction sciences instead of this characteristic. These parameters include the concentration of X-ray amorphous (cryptocrystalline) phase of material, its quantitative phase composition and the size of the fields of coherent X-ray scattering, which is interpreted as the size of the crystallites.

To obtain quantitative information on the degree of crystallinity of siliceous component of a composite binder a quantitative X-ray phase identification of the concentration of amorphous component in quartzite sandstone was done (fig. 4).

The method of identifying the concentration of amorphous phase is based on the introduction of a certain concentration of the well-crystallized substance with known crystal structure (Zhernovsky, 2010) into the investigated sample. In this case natural fluorite was used as an etalon.

After conducting quantitative XRF using Rietveld method identification of the concentration of X-ray amorphous phase is done on the basis of true and estimated concentration of internal etalon:

$$C_{amorph} = \left\{ 100 \cdot \left(c_{etalon}^{estim} - c_{etalon}^{true} \right) \cdot \frac{100 \cdot \left(c_{etalon}^{estim} - c_{etalon}^{true} \right)}{c_{etalon}^{estim} \cdot \left(100 - c_{etalon}^{true} \right) / 100} \right\}$$

For dispersed in the CPCA to $S_{sp} = 500 \text{ m}^2/\text{kg}$ crushing screenings of quartzite sandstone the concentration of amorphous phase equals to 45 wt. %.

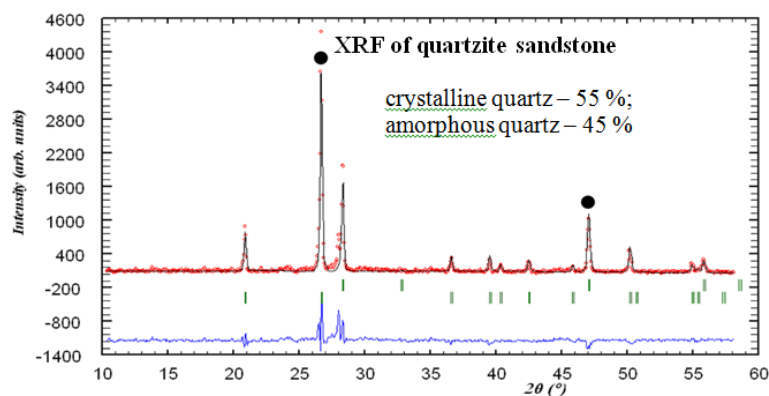


Figure 4. Rietveld diagram of quartzite sandstone: ○ - experimental diffraction curve; - estimated curve; - difference curve of experimental and calculated diffraction spectrum; | - Bragg reflection markers for all phases; ● - fluorite reflection

Parameters of phase-dimensional heterogeneity of crystalline components of quartzite sandstone defined by the X-ray-graphical full-profile quantitative microstructural analysis are presented in table 1.

Table 1. Parameters of phase-dimensional heterogeneity of quartzite sandstone

Polymorphic modifications	Concentration, weight %	Size of the crystallites, Nm
α-quartz	75	70
β-quartz	25	30

The obtained results are correlated with similar data, as described in work (Lesovik & Zhernovsky, 2008; Zhernovsky & Shamshurov, 2012; Suleymanova, Lesovik & Suleymanov, 2010; Lesovik, Suleymanov & Kara, 2010; Kara, 2011; Suleymanova & Kara, 2012a; 2012b).

Thus, composite binder composition in the original (non-hydrated) state with 70% clinker + 20% of crushing screenings of quartzite sandstone + 10% chalk + 1% superplasticizer contains about 9 wt. % amorphous silica.

Conclusion

The content of X-ray amorphous phase in cretaceous component of a composite binder has not been specified separately. However, on the basis of quantitative XRF, the concentration of calcite in this composite binder is about 7 wt. %. Consequently, the amorphous phase in the calcareous component of a composite binder equals to 3 wt. %. Thus, the total content of amorphous phases in composite binder is 12 wt. %, which provides its high reaction activity.

Therefore, quantitative parameters of phase-dimensional heterogeneity of cretaceous component (crushing screenings of quartzite sandstone) of a composite binder by means of concentrations of polymorphic modifications of quartz, the size of their crystallites, as well as the concentration of amorphous Nano-size silica phase providing its high reaction activity.

Disclosure statement

No potential conflict of interest was reported by the authors.



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