On the issue of water activation for Portland cement

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Abstract. The article is devoted to the problem of Portland cement activity increase by changing its mixing water structure due to mechanical, magnetic, electromagnetic and certain other treatments. Known facts are analyzed on specific condition and behavior of cement grout liquid phase which is determined by the effect of crystalline field of the surface of cement minerals. The authors substantiated that this condition is more important for cement behavior under hardening than the consequences of eventual structural changes in its pretreated mixing water. An original method for controlling the hardening of cement paste based on measuring the hardness of cement samples is proposed. The method allows you to control the behavior of the material itself without taking into account the influence of the size and shape of the analyzed samples.

1. Introduction

The problem of cement saving due to activation of its mixing water interested from time to time many experts, beginning from the middle of past century [1, 2]. The sense of this approach lies in attempts to amend water structure and properties owing to mechanical, magnetic, electromagnetic and some other treatments performed at special appliances.

Publications devoted to the dynamics of Portland cement (PC) hardening by pretreated water may be divided into two basic groups. One of them perceives the reason of instability of positive effect after such treatment in inadequate control of structural transformation of the object of study [3]. The other one ascertains the attained advantages, including those obtained in pilot studies [4]. The existing situation is most correctly described by a phrase “The secret of water treatment has not been totally disclosed up to this day, whereas the problem itself has not been totally closed” as stated in source [1].

According to our opinion, the described situation is to a substantial degree caused by lack of sufficiently sensitive methods of PC hardening dynamics control, especially at its initial stages. Authors are not informed of any successful example of cement saving on an industrial scale due to its mixing water activation.

One of problems consists in the fact that actually all explanations of eventual positive effect from water pretreatment add up to expected changes in its structure, value of pH or other parameters which must improve activity of water interaction with PC minerals [5,6]. In this the circumstance is neglected that such increased activity is not always favorable, for example, it may disturb the established optimal pattern of PC hardening dynamics which may have negative consequences [7].
Problems in substantiation of water pretreatment effectiveness are caused by lack of due attention to terms of its transformation into cement grout liquid phase. This aspect it important, because positive effect from mixing water activation may be attained only via change in properties of hardening cement liquid phase.

It is easy to determine that under complete wetting of PC particles with specific surface 300 m\(^2\)/kg at W/C = 0.30 thickness of water films will not exceed 1 μm. In other words, cement grout liquid phase is represented by thin films located in crystalline force field of surface of PC minerals. It is well known that the structure of materials formed as thin films on the surface of objects with different crystallographic pattern may be subdued to substantial transformation under the action of its substrate properties [8,9]. It is also known that the structure and properties of liquid phase located close to the surface of PC minerals substantially differs from parameters of initial water. Thus, in the opinion was stated that “…Fixed water may be imagined as a medium under pressure of tens of thousands bar due to the effect of the surface of solid state… Even density is changed, reaching at border layers as much as 1.2-1.4 g/cm\(^3\)” [10]. This work specified that heat conductivity factor of 0.1 μm water film is 40 times higher than its value in water volume, whereas dielectric permeability grew from 5 to 16 at water layer thickness increase 0.2 to 0.5 μm, its value for water in free state is 81.

The cited results show that the bulk of cement grout liquid phase, especially located at the area of interaction with surface of cement minerals and neoformations, is a substance with basic parameters substantially different from their initial values. This is confirmed by well-known fact that water in cement grout capillaries freezes at temperatures of −25 to −78 °C. The thinner are capillaries, the lower is freezing point. This phenomenon is caused by effect of capillary walls, i.e. the surface of water-cement minerals interaction products.

Returning to change in water structure and properties under its activation, it should be noted that their subsequent spontaneous relaxation is indicative of instability of such changes. From the other side, the above-mentioned characteristics of cement grout liquid phase hint that it may be treated as a system being in pseudosolid state. Hence, the change of water initial properties under activation is not commensurable with their subsequent fundamental transformations taking place after its interaction with cement. The authors opine that these changes should be treated as marginal ones, not of any practical importance at the background of deeper structural transformations taking place in thin films of cement grout liquid phase. Such situation may explain the lack of reproducible consequences from variegated attempts to treat cement mixing water.

2. Equations and mathematics

For mechanical activation of water we applied a laboratory homogenizer with linear velocity at its activator periphery circa 40 m/s. Such value ensured cavitation processes in treated liquid, as they are known to appear already at 15-20 m/s velocities [11]. Magnetic treatment of water flow was effected by installing permanent neodymium magnets at opposite walls of homogenizer working vessel. For UV treatment we used a DRT-400 mercury-quartz lamp. Anolyte and catholyte were obtained by water electrolysis at a special unit, pH values being read from indicators.

Cement setting dynamics was controlled using a conical plastometer modified by authors [12, 13]. Changes in physical-mechanical properties of cement grout were determined with a special hardness gauge. The method enables direct reading of information on physical mechanical changes taking place in hardening cement grout, suppressing the effect on test samples of sample shape instability factor under nondestructive control methods.

In order to measure physical mechanical parameters of tested material it was mixed with water at water-cement relation W/C = 0.27. Continuous stirring of the obtained mixture lasted for about 300 s. For plastometric measurement the grout was poured into a stainless steel form. After measurement the samples were sealed to favor subsequent hardening at 100% humidity. After 24 hrs the samples were extracted from form and put into water. Hardening samples were compared within the first 72 hrs of cement-water interaction. Tested samples were of dry process cement grades PC 400 and PC 500.
3. Main part
To estimate water activation effect on cement grout process dynamics, test samples were prepared on PC 400 basis mixed with water subdued to such treatments: 1 – no treatment, 2 – cavitation for 5 minutes, 3 – cavitation for 5 minutes and UV irradiation for 20 minutes, 4 – cavitation for 5 minutes together with magnetic treatment, 5 – melt water, 6 – water with addition of 0.02% C-3 plasticizer, 8 – water after electrolysis at pH = 5 (anolyte); 9 – water after electrolysis at pH = 9 (catholyte); 10 – PC 500 mixed with water at zero treatment.

The hardening results of obtained samples within 72 hrs are presented in Figure 1. Curves are numbered in accordance with the list above.

![Figure 1. Cement grout hardness alteration dynamics.](image)

Curve 10 is shown for scale comparison of behavior of cement whose activity (strength) is 10 MPa higher than that of tested samples.

As seen from Figure 1, the applied method of physical mechanical transformation control in cement grout did not show any practical effect of specified water activation techniques on PC hardening dynamics. This is especially obvious from lack of any substantial difference among Curves 1-9 at the background of PC 500 hardening dynamics (Curve 10).

Plastometric measurement of setting dynamics in Samples 1-9 also did not show any difference of relevance.

With due consideration of the circumstance that in our case structural transformation of activated water was not actually controlled, the authors specified curves characterizing PC behavior when mixed with water possessing controllable signs of change in its properties, namely, anolyte and catholyte with pH values of 5 and 9, respectively (Figures 2 and 3).

![Figure 2. Hardening dynamics of PC mixed with water possessing acidic (Curve 1) and alkaline (Curve 2) properties.](image)
In Figure 2 it is evident that in spite of substantial differences in properties of tested waters, difference between durations of structuring of tested system does not actually exist (not more than 10 minutes). Curves in the next Figure 3 show that formation dynamics of physical mechanical properties in both systems is also identical.

![Figure 3. Change in physical mechanical properties of hardening PC mixed with water possessing acidic (Curve 1) and alkaline (Curve 2) properties.](image)

In order to explain the obtained result it will suffice to remember that PC is a source of Ca\(^{+2}\) ions and its content in cement grout is 2-3 times higher than that of water. This circumstance leads to the condition when immediately after PC mixing the value of its hydrogen exponent instantly returns to its usual alkaline level about pH = 12.4, and this takes place irrespective of its initial value for applied mixing water. The described process in cement-water system runs due to manifestation of its basic alkaline properties which are determined by mineralogical composition of Portland cement.

4. Conclusion
Based on the properties of thin films under the influence of the crystal field of their substrate, the authors substantiated that such manifestation of PC basic properties takes place under water structure transformation on the surface of its particles, irrespective of water initial conditions, including its post-activation state. The achievable result of this transformation depends on crystalline force field value of the surface of cement minerals whose parameters have been specified in design of binder chemical-mineralogical composition, their formation and milling [14, 15]. On this basis we conclude that:
- the terms of liquid phase formation are more important for Portland cement behavior under hardening than the consequences of eventual structural changes from pre-activation of applied water;
- positive results from cement grout liquid phase properties should be sought for not in the line of applied mixing water pretreatment, but in attempts to act on crystalline field parameters of the surface of Portland cement minerals in the course of its manufacture.

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