Curing kinetics in the activated cement-water system

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Abstract. The paper deals with the strength improvement in the cement-water system that generally leads to the improved performance of hydrated cement and concrete. After many years of experiments conducted by Russian and foreign experts, many ways to improve the strength of cement systems have been developed. The most efficient are various activation methods of either cement or water, which is then used as water of mixing for cements. This work studies the structure formation processes in the activated cement-water system, which are still less investigated. Cement is activated through its dispersion in a planetary mill, and water is activated by a constant magnetic field with 0.1 T flux density. It is found that the strength of the cement-water system increases by 38% in comparison with the untreated test samples.

1. Introduction

According to the developing paradigm of the modern science of construction materials [1], any construction material for engineering purposes as well as of any artificial nature, must meet the following basic criteria: technological efficiency and availability, energy and resource saving, environmental safety, natural balance, biocompatibility and bioethics, economic feasibility, aesthetic significance, practical ethical acceptability and social orientation. These are also achievable in full respect for Portland cement-based systems.

Cement compositions (hydrated cement, mortars, concretes, dry mix mortars, etc.) are the most common types of building materials, which are widely used in construction. The improvement of their basic properties is carried out through the qualitative selection of material composition and changes in the production process. Unlike the early stage, when the strength properties were improved by the proper selection of concrete and mortar compositions and the introduction of chemical additives, in recent years the strength improvement is provided by changing the manufacturing technology of Portland cement-based materials, including activation of their components.

In our early research [2–7], we show that the most affordable and economically feasible way to increase the strength and other operational properties of hydrated cement, is the activation of mixing water in cement compositions using a combination of physical and chemical methods.

Activation of Portland cement is usually performed to increase its reactivity relative to water. This can be implemented by different methods [8-13], which, however, not always will contribute significantly to achievement of the desired goals.

At the same time, it is known that the Portland cement particle distribution can be represented by the most common distribution function, viz. the Gauss curve. According to this curve, the amount of 8–20 µm particles is about 50–55 %, 8 µm particles range between 25 and 30 %, and 20 µm and coarser particles vary from 15 to 20 %. Mechanical activation via the Portland cement dispersion
increases the number of fine particles and improves its hydraulic activity. However, Portland cement containing the predominant number of fine particles does not provide the higher strength at last stages of curing. This is probably because its most part hydrates at early stages of the curing process.

It is not appropriate therefore to activate the whole cement. On the contrary, it is advisable to mix a portion of the activated Portland cement with the rest portion of non-activated.

The purpose of this work is to develop the economically and technologically affordable activation technique for individual components of the cement-water system through the realization of their internal properties. The object of this study is the activated cement-water system.

2. Materials and methods
A planetary mill MP 4/1 (Russia) was used for Portland cement activation. The specific surface of Portland cement was measured on a PSKh-10 device (Russia). A hydraulic press PSU-10 (Russia) was used to determine the strength of the cement samples. In this experiment, we utilized the test machine Instron 3382 (USA) to measure tensile and/or flexural strengths. The X-ray diffraction (XRD) analysis was carried out by a DRON-6 diffractometer (Russia). An ultraviolet (UV) spectrometer (Shimadzu, Japan) was used to study the water spectra before and after the activation process.

Activation of the type CEM I 42.5H (M500) Portland cement was performed by its dispersion in a planetary mill for 15 minutes, in the amount of 10 % of the total cement mass required to produce the samples. Activation of water was carried out by the cyclic magnetic treatment, i.e. water flows through the gap between the magnetic poles at a 0.1 T magnetic flux density.

The cement composition consisting of 10% activated and 90% non-activated Portland cement was mixed with activated water. The water-cement ratio of the resulting mixture was 0.34. The test samples were prepared from non-activated cement of the same type. The obtained samples were mixed with non-activated water at the water-cement ratio of 0.34.

The (2×2×2)‧10⁻² m cement samples were prepared from the cement mortar (M500 Portland cement) for the compressive strength tests. The test samples were fabricated using metal molds and then subjected to normal curing in a chamber. Compressive tests were conducted in accordance with the standard procedures.

3. Results and discussion
Table 1 contains the compressive strength values of cement samples of the activated cement-water system. According to this table, the compressive strength of the cement samples increases by 38% after 28-day curing and by 33 % after shorter-term curing. The specific surface increases from 3650 to 5250 cm²/g, which is about 44 %.

| Table 1. Compressive strength of cement samples. |
|-----------------------------------------------|
| Compressive strength, MPa                      |
| Curing time, days                              |
| 1     | 3     | 7     | 28    |
| Test system                                   |
| 37.5  | 42.5  | 47.0  | 52.5  |
| Activated cement and water                     |
| 49.3  | 57.0  | 62.5  | 72.5  |

The observed changes can be explained by several factors. The most important of them are as follows.

1. Dispersion of cement particles. The increase in the specific surface undoubtedly intensifies the hydration processes of the cement components. The XRD pattern in figure 1 supports this
factor. According to the XRD analysis, the peak intensity of portlandite \((\text{Ca(OH)}_2)\) increases by 30 \%, that indicates to the enhanced cement hydration.

![Figure 1. XRD pattern of hydrated cement after 28-day curing.](image)

As is known, the formation of \(\text{Ca(OH)}_2\) occurs during alite hydrolysis by the heat release reaction:

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2; \quad \Delta H = 502 \text{ J/g.}
\]

On the one hand, the more intense \(\text{Ca(OH)}_2\) release contributes to its interaction with aluminates and the ettringite formation, which forms films on the reaction products during the first minutes of the hydration process. The system volume increases, and the silicate structure gradually displaces the primary aluminate phase due to which the cement curing occurs. At the same time, the excess of \(\text{Ca(OH)}_2\) can lead to the so-called leaching corrosion, when portlandite leaks out from hydrated cement. In order to eliminate this deficiency, we propose to introduce silica fume in the system, which promotes not only binding of the \(\text{Ca(OH)}_2\) excess, but also the formation of low-basic calcium silicates, and, ultimately, higher strength. It should be also noted that without a sufficient amount of \(\text{Ca(OH)}_2\), further strengthening of the structure is impossible as well as the ability of hydrated cement to harden for decades.

![Figure 2. UV spectra of water before and after cyclic magnetic treatment.](image)
2. Modification of physicochemical properties of water via its activation by a magnetic field. Figure 2 shows the UV spectra of non-activated and activated water. As can be seen from this figure, the optical density of water increases by 1.5 times. Since the chemical composition of water remains constant, the observed experimental fact can be stipulated by changes in the polarization degree of water molecules after interaction weakening between the individual dipoles. This leads to more intensive hydration of the cement particles and, consequently, an increase in the portlandite amount.

Today, it is impossible to assess the extent to which the first or second factor affects the strength of hydrated cement. Thus, the obtained effect in the activated cement-water system can be considered as an effective method of increasing the strength and other properties of the cement compositions.

4. Conclusions
Based on the results, it can be concluded that the proposed activation technique of the cement-water system is in full compliance with the above-mentioned basic criteria for the development of building materials with the specified properties.

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