Study of the kinetics of hardening in “activated cement-water” system

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Abstract. The paper considers alternative methods of activation of cement systems based on the use of internal properties of cement. Their peculiarity is the use of activated cement and changing the sequence of mixing of cement mortar. Mixing of the main volume of Portland cement with cement slurry and its prior curing for 15 minutes allowed increasing the strength characteristics of hardened cement paste. As shown by experimental studies, the strength of the samples increases by 10–30% depending on the method of preparation and curing time of the cement slurry. Further experiments will be aimed at researching “activated cement–activated water” system.

1. Introduction
Cement compositions (hardened cement paste, building mortars, concretes, dry mixtures, etc.) represent the most typical building materials widely applied in construction. Improvement of the main properties of cement compositions include qualitative selection of their compositions based on various components and modification of the technology of their production. Initially, the increase of strength parameters was provided due to appropriate selection of concrete and mortar composition by adding chemical admixtures, whereas in recent times their properties are improved by modifying the technology of producing building materials based on Portland cement, including activation of their components.

The previous studies [1, 2] show that activation of mixing water for cement compositions using combined material and field research methods is the most available and economically feasible method for improving strength and other operational characteristics of hardened cement paste.

Activation of Portland cement is usually aimed at increasing its reactivity to water. This task can be performed in different ways [3, 4]; however they are not always successful.

The study of V. Solomatov [5] demonstrates the principal possibility of the so-called intense separate technology of concrete mixtures production. It provides separation of producing concrete and mortar mixtures and transition from their slow mixing in concrete mixers to brief intensification of this process.

At the same time, it is known that size distribution of Portland cement particles has the shape of a classical Gaussian curve, according to which circa 50–55% of particles are 8–20 µm, 25–30% are less than 8 µm, and 15–20% are larger than 20 µm. When using mechanical activation by dispersing Portland cement, the number of smaller particles grows, which leads to increase of its hydraulic activity. However, Portland cement where smaller particles prevail is unable to develop increased long-time strength, as obviously the most part of it is hydrated at early age.
Activation of all Portland cement required for producing mortar and concrete mixtures is also economically inefficient.

The purpose of this study is development of economically and technically feasible technology for activation of Portland cement due to actualization of its inner properties.

The following key tasks were set to achieve the above purpose:
1. develop alternative technology for cement systems activation;
2. perform physical and chemical study of curing products;
3. define physico-mechanical characteristics of hardened cement paste.

To perform the listed tasks the study offers several options of preparing cement mortar with the use of activated cement:

Option 1 – reference samples (traditional technology of samples production) are prepared both with M500 Portland cement and with admixture of activated cement with larger specific surface;

Option 2 – part of Portland cement (10% of total volume) is subjected to mechanical activation, mixed with the total amount of water, right after which the obtained suspension is added to the rest part of non-activated cement;

Option 3 – part of Portland cement (10% of total volume) is subjected to mechanical activation, mixed with the total amount of water, cured for 15 minutes, and then the obtained suspension is added to rest part of non-activated Portland cement.

Options 2 and 3 were repeated in both M500 Portland cement and in cement with activated Portland cement admixture.

2. Experiment

The following equipment was used while doing the research:
– Planetary mill MP 4/1, in which Portland cement was activated;
– PSH 10 setup for defining specific surface of Portland cement;
– PSU-10 hydraulic press for defining strength of the samples;
– Instron 3382 setup for testing for compression and/or tension;
– DRON-6 setup for X-ray diffraction analysis.

In order to define compressive strength of samples cubes with the size (2×2×2)×10⁻² m were prepared from M500 Portland cement mortar according to the 3 offered options. Water-cement ratio in all variants was permanent and equal to 0.34. The samples were produced in metal molds, cured in moist cabinet and tested for compressive strength within the settled period and in compliance with the standard methods.

3. Results

After 15 minutes of mechanical activation in a planetary mill the specific surface of Portland cement increased from 4,422 cm²/g to 4,976 cm²/g, which makes about 13%.

Compressive strength of the samples was defined with the use of PSU -10 hydraulic press and Instron 3382 setup.

The results of compressive strength testing of the sample using a hydraulic press are given in Tables 1 and 2.

| Type of production | Samples strength, MPa / %R₂₈, during the hardening process, days |
|--------------------|---------------------------------------------------------------|
|                    | 1     | 3     | 7     | 28             |
| Option 1           | 34.2/56 | 43.0/71 | 49.3/81 | 60.8/100 |
| Option 2           | 38.1/63 | 50.3/83 | 56.3/93 | 61.3/101 |
| Option 3           | 45.1/74 | 55.3/91 | 62.3/102 | 66.8/110 |
Table 2. Strength of hardened cement paste with the addition of activated cement.

| Type of production | Samples strength, MPa / %R<sub>28</sub>, during the hardening process, days |
|--------------------|----------------------------------------------------------------------------------|
|                    | 1   | 3   | 7   | 28  |
| Option 1           | 39.5/57 | 51.1/74 | 64.5/92 | 69.5/100 |
| Option 2           | 41.8/60 | 52.5/75 | 66.5/95 | 77.5/112 |
| Option 3           | 45.4/65 | 56.8/82 | 65.1/94 | 91.3/131 |

It is seen from the Tables that adding 10% of activated Portland cement results in the increase of compressive strength in samples by 15–30% depending on the curing time. One might suggest that highly dispersed Portland cement particles more actively react with water forming the coalescence contacts of colloid and crystal nature, which leads to strength increase in cement samples.

When mixing Portland cement with suspension strength of hardened cement paste grows by 10–15% with Portland cement and by 5–10% with activated cement admixture. Additional curing of cement suspension for 15 minutes and subsequent mixing it with Portland cement results in the average increase of samples strength by 10–30% depending on the curing time.

The results of a set of tests with samples using Instron 3382 setup after 7 days' curing are presented in Figure 1.

The obtained data confirm the test results for PSU-10 hydraulic press. Also, the graphs analysis shows that variation of sequence of mixing the cement samples causes both increase of strength compared to the reference samples and improvement of their mechanical properties. The difference of strains in reference samples and the ones produced according to the offered options makes 30–50%, which indicates a more integrated structure of hardened cement paste and a less amount of pores. Besides, the limit of elastic strain was increased, which demonstrated the ability of structures to adapt to variation of operation loads. The average increase of elastic modulus by 20–25% is observed.

The results of X-ray diffraction analysis are given in Figure 2.

X-ray diffraction analysis of hardened cement paste showed that the intensity of diffraction peaks in portlandite Ca(OH)<sub>2</sub> prepared according to the Option 3 increased by 25–30%, it may indicate a higher cement hydration degree.

It is known that hydrated lime Ca(OH)<sub>2</sub> is formed due to alite hydrolysis in the following reaction

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

which proceeds with heat generation. One the one hand, more intense production of hydrated lime Ca(OH)<sub>2</sub> enables production of ettringite which forms films on reaction products within first minutes of hydration; the system grows in volume and silicate structure gradually replaces initial aluminum phase, due to which hardening of cement paste occurs. At the same time, excess of hydrated lime may lead to the so-called leaching corrosion, i.e. lime washout from the hardened cement paste. However, further structure solidification and the ability of hardened cement paste to grow hard for a long period of time within decades are impossible without the sufficient amount of Ca(OH)<sub>2</sub>. In this regard, the effect obtained after cement composition activation can be considered an efficient method of increasing strength and other operational characteristics of cement compositions.
Figure 1. Results of testing hardened cement paste samples produced according to Option 1 (a), 2 (b), 3 (c)
Figure 2. X-ray diffraction analysis of hardened cement paste produced according to Option 1 (a) and 3 (b) with activated cement admixture

The next stage of the research includes studying the behavior of “activated cement – water” system in concrete samples.

4. Conclusion.
The research outcomes include techniques of preparation of cement compositions with improved strength parameters. Mixing of Portland cement with suspension increases strength of the hardened cement paste by 5–15 %. Besides, additional curing of cement suspension for 15 minutes with further mixing it with Portland cement results in 10-30% growth of strength depending on the curing time. It is found that due to adding 10% of activated Portland cement strength of hardened cement paste increases by 15–30 % depending on the curing time.
Further research will include studies on cement compositions in “activated cement – activated water” system.

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References
[1] Allahverdi A, Maleki F, Mahinroosta M 2018 Chemical activation of slag-blended Portland cement *Journal of Building Engineering* vol 18, pp 76–83
[2] Rubanov A, Gorlenko N, Vergasov V 2018 Material and Field Impacts on Cement Compositions MATEC Web 4th International Young Researchers Conference “Youth, Science, Solutions: Ideas and Prospects” p 143
[3] Zhou W, Li L., Liu S-H, Vinh T N D, Liu X-H 2017 Hydration properties and thermal analysis of cement-based materials containing limestone powder *Journal of Central South University* 24 (12) pp 2932–39
[4] Liu S-H, Kong Y-N, Wang L 2014 Hydration mechanism of low quality fly ash in cement-based materials *Journal of Central South University*, 21 (11), pp 4360–67
[5] Solomatov V 1989 Problems intensive separate technology *Concrete and reinforced concrete* 7 p 4