Properties of Concrete Modified by Ultrafine Cement Admixture

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Abstract. This article describes possibility using hydrated cement as additions for batching new concrete. Time of cement hydration was 2, 4 and 6 hours. Quantity of pre-hydrated cement for batching admixture was equal 5, 10, 15, 30% dry matter content in relation to cement for control mixture. Influence of addition on normal consistency, concrete unit weight and compression resistance was determined. Cement particles distributions of control and pre-hydrated specimens was studied. The article shown need for increasing water quantity to getting normal consistency which led to decreasing unit weight. As a result of adding hydrated cement particles an early strength increased with amount of admixture less than 10%. Received results were discussed according to cement hydrations mechanism.

1. Introduction
One of the main directions of modern building material industry is developing ecology-friendly materials [1]. It can be achieved by using special material which is not hazardous on every stage of life circle (obtaining, exploitation and utilization). Another way is integration technologies of recycling in industrial plant [2]. Recycling technologies suppose using industrial waste to obtaining a new building material. Those technologies help neutralize hazardous waste. Hereby building material industry would be more compare to sustainable development concept [3].

A lot of modern concrete mixing machine have same mistake connected with unavailable to become total empty. It’s caused by thixotropic character of mixture and specific character of mixing machine. To achieve total empty of mixing machine some type of washing are used. But washed out concrete wastes must be disposed according to directives of ecological security. Using this kind of material as secondary material obtained by recycling system is more sustainable and correct.

Current recycling technologies suppose using fine and coarse aggregate obtained by concrete mixer washing for batching new concrete mixture with possibility non-adverse effect to concrete [4-6]. Cement or correctly hydrated cement suspension obtained by concrete mixer washing may effect on properties of new concrete mixture and consequently on concrete [7].

2. Materials and methods
Straight cement (CEM I 42,5 H) from AO «Podolsk-Cement» was used for this study. Chemical and mineral composition showed in table 1 and 2. Hydrated cement was used as mineral admixture and named pre-hydrated admixture (PHA).
PHA was obtained by pre-hydrated cement during 2, 4 and 6 hours. After hydration these additions were mixed with water and batched with cement. Water/cement ratio for obtaining these additions was 0.7. Water for obtaining additions was considered in water for batching. Cement quantity for admixture was equal 5%, 10%, 15%, and 30% of cement for obtaining control mixture.

In this way mixture designed as “control” was control mixture for this research and contained no admixture. Other mixtures designed as “PHAX Y”, where “X” – time of pre-hydration (2, 4 or 6 hours) and “Y” – quantity of dry content in relation to cement for control mixture (5%, 10%, 15% or 30%).

For unit weight and strength research lightweight-aggregate concrete with proportion 1:1:1:2.6 (cement : lightweight aggregate : fine aggregate) PHA6 10% was designed. Also control concrete was designed with same proportion but without admixture. As lightweight aggregate claydite gravel with particle size 5…10 mm was used. As fine aggregate quartz sand with fineness modulus equal 2.43 was used. Quantity of water was near 220 liter for 1 m$^3$ for each mix with adjustment by normal consistency.

### Table 1. Chemical composition of cement from AO «Podolsk-Cement».

| Components | CaO | SiO2 | Al2O3 | Fe2O3 | MgO | SO3 | R2O |
|------------|-----|------|-------|-------|-----|-----|-----|
| Content, % | 62.75 | 20.10 | 4.56 | 8.72 | 1.99 | 0.57 | 1.58 |

### Table 2. Mineral composition of cement from AO «Podolsk-Cement».

| Mineral content, % | C3S | C2S | C3A | C4AF |
|--------------------|-----|-----|-----|------|
| 60.00              | 12.00 | 3.00 | 21.00 |

Influences of hydrated cement on normal consistence of cement paste, unit weight and strength of concrete specimen are determined in current work. Also granulometric analysis of hydrated cement particles was accomplished.

Normal Consistency study was according to GOST 310.3-76 for each mixture.

Hydrated cement particles size changing was determined by the laser diffraction analysis according to GOST R 8.777-2011 for all types of designed mixture.

Unit weight and strength research of concrete specimens was according to GOST 10180-2012 after 7 days of normal hardening.

3. Results and discussion

Result of normal consistency and Mixture unit weight study of cement paste showed on Fig. 1.

According to study results, using of PHA leads to increasing water demand for obtaining normal consistency cement paste. Maximum changing of normal consistency was determined for 6 hours of pre-hydration. With increasing pre-hydrated particles quantity necessary water demand was increased. For PHA2 5% and PHA4 5% normal consistency almost doesn’t changed and was about 27…28%. Same effect shown PHA2 10% and PHA4 10%. Normal consistency for them was about 29%.

Increasing water demand may be explained by increasing particles quantity in batching and processes arising during hydration. Immediately after mixing cement with water, the cement particles hydrolysis occur and they dispersive capacity increased [8]. As a result the specific surface of particles is increased. As known adsorption capacity directly depend on the specific surface and affect bound water quantity.
After 4 hours of hydration cell of hydration product starts forming [9-15]. Dispersive capacity of particles is increasing and consequence physical coherent water quantity is decreased by decreasing adsorption capacity. In the result normal consistence is changing. Hydration cells may play a role of lubrication substance, which allow cement particles slide between each other. But this effect work with small amount of admixture (PHA 5%…10%). After 6 hours due to the flocculation of particles, mutual movement is hindered, which leads to increase the water demand.

![Figure 1. Normal consistency of cement paste.](image1)

These hypothesis and theory confirmed by granulometric analysis of hydrated cement particles (Fig. 2). As a result of analysis determined that hydrated cement contains more quantity of micro particles than non-hydrated cement. For better understanding is needed to examine step-by-step particles size changing charts (Fig. 3, 4, 5).

![Figure 2. Differential cement particle distributions.](image2)
During 2 hours of hydration particle amount size 30…110 μm was decreased on 4.0% and particle amount size 0.3…1 μm and 3…12 μm was increased on 2.3% (Fig. 3). This explained by hydrolysis of cement particles described earlier. After 4 hours particle amount size 0.3…10 μm was increased due to hydrolysis of cement particles size 10…90 μm and forming crystalline and gel products (Fig. 4). The little change of amount cement particles size 90…100 μm can be explained by starting forming hydration cell around cement particles. Between 4 and 6 hours cement solution became supersaturated by ions of $\text{Ca}^{2+}$, $\text{OH}^-$, $[\text{SiO}_4]^{4-}$ as a result new product started forming [12-16]. New hydrate products forming illustrated on Fig. 5, where particles amount size 20…100 μm was increased on 0.6% by decreasing particles amount size 0.6…1 μm and 1…3 μm.
From the point of recycling 6 hours of pre hydration is interest. For this reason, lightweight concrete specimens were tested. Results are shown on Fig. 6 and Fig. 7. As a result of changing water demand, unit weight with increasing amount of admixture was decreasing [17, 18]. This can be explained by the appearance of larger capillary voids after evaporation of more amount of water.

**Figure 6.** Influence of value of admixture on concrete specimen unit weight (7 days of normal hardening).

Usually decreasing unit weight accompanied by decreasing strength of concrete specimens [19]. This rule for specimens with amount of admixture more than 10% worked, but for PHA6 5% and PHA6 10% the opposite effect is observed. For PHA6 5% increasing compression strength was 4.8% while decreasing unit weight was 0.8%. For PHA6 10% slightly decreasing 1% was observed, while decreasing unit weight was 6.4%. This can be explained by different kinetics of hardening [20, 21]. Kinetic of hardening are accelerating with PHA, because it contain substance at later stage of hydration, which may works like crystallizing nucleus or some king of aggregating agent, or flocculator, or additional ions promoting early supersaturation.

**Figure 7.** Influence of value of admixture on concrete specimen compression strength (7 days of normal hardening).

**4. Conclusion**

Influence of pre-hydrated cement suspension on cement paste and concrete properties have investigated. In result of study have determined that:
1. PHA leads to increasing water demand for obtaining normal consistency cement paste and the more, the longer the pre-hydration took place and the more pre-hydrated particles. Maximum changing of normal consistency was determined for PHA6 30% (increasing was 13%). Minimum changing – PHA4 5% (increasing was 1%);
2. PHA leads to decreasing unit weight of concrete due to increased water demand;
3. PHA with amount of admixture more than 10% leads to decreasing early strength of concrete;
4. For PHA6 5% increasing compression strength and decreasing unit weight were 4.8% and 0.8% respectively. For PHA6 10% decreasing compression strength and decreasing unit weight were 1% and 6.4% respectively.

The addition of PHA at certain concentrations allows increasing the physical and mechanical properties of concrete at early age. That can solve the problem of its utilization at the enterprises of concrete mixture plants.

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