Early Structure Formation in Concrete with Water-to-Cement Ratio 0.2

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**Synopsis:** Concrete with w/c ratio of 0.2 and lower is indeed material of a new generation. Its properties significantly surpass such of regular concrete grades in large due to the absence of mixing water not actively involved in the physical-chemical processes of cement hydration. In a sense, w/c ratio of 0.2 signifies a threshold in the material science of concrete that no research did reach before 1990s. To move this realm even further, we have been aiming at producing UHPC that crosses this threshold we felt a necessity to define a basic phenomenology of such concrete hardening, especially on the early stages. Our analysis of the kinetics of the strength gain provides that this concrete gains its main physical-mechanical properties after 7 days, and its compressive strength exceeds 100 MPa (14 500 psi) already after 24 hours in normal conditions. At last, this type of UHPC is economically viable due to a relatively low content of cement (500kg/m$^3$ (31.2 pcf)), the use of ordinary fine aggregate, and a possibility of using standard batching equipment in the production.

**Keywords:** durability, ultra-high-performance concrete, water-cement ratio, early stage hardening, cement stone, ettringite, cement hydration
INTRODUCTION

It was only after the invention of superplasticizers based on naphthalene sulfonate and polycarboxylate ether that production of UHPC became possible. However, at the first instance, this admixture was designed to provide high flowability for the technical purpose of concrete pumping. As it was specified by the producers at that time, the amount of the admixture should not have exceeded approx. 0.8% of the mass of cement. While these conditions had fully provided the necessary rheology, it soon has been revealed that the admixture can be used to produce good workability of concrete mixtures with reduced content of water, and therefore physical-mechanical properties of concrete can be improved. These findings have served as a point of departure towards the UHPC, followed by the attempt to densify microstructure of concrete with finely dispersed fillers, such as silica fume, or to improve its tensile strength with steel or glass fibers. However, we should not disregard the fact that the key-factor of concrete durability is the strength of cement stone. Therefore, in this research work, our main effort was to explore the nature of cement alone and to identify the limits of its performance. The results of our experimental work show that it is possible to achieve an ultra-high performance with standard cements and ordinary aggregate, through a reduction of water content and a use of superplasticizer. Concerning concrete designs produced with use of advanced ingredients, such as finely dispersed and fiber fillers, it is reasonable to give such a composite material a different name, precisely UHPFRC - Ultra-High-Performance Fiber Reinforced Concrete - that is a specific class of materials that shouldn’t be directly compared to UHPC as such.

From the practical side, affordability is often the main factor of choice in the realm of construction materials. Hence economy and convenience define demand of a material on the market. It has to be said that contemporary cements and superplasticizers ubiquitously used in construction are by themselves high performance materials if compared with their recent predecessors. Therefore, in our research we were intending to develop a type of UHPC using only standard materials and basic equipment. Therefore, in the process of designing an affordable UHPC we’ve declined the use of silica fume and fiber reinforcement not solely upon economic reasons, but also due to convenience of production. Firstly, finely dispersed fillers have a huge surface area per a mass unit that is they absorb large amounts of water. Secondly, fiber reinforcement also deteriorates rheology and increases the yield stress. Both factors reduce work- and mouldability of the mix and lead to an increased content of water and superplasticizer. In turn, while attempting to improve the properties of concrete, one actually runs a risk of decreasing quality and durability of the cement stone itself. In our work we are attempting to resolve this problem with a simple and economic design of UHPC through gaining full control over the process of cement hydration. For these reasons our work targets at critically low w/c ratio in concrete, while maintaining good workability of the mix. We have identified that w/c ratio of 0.2 provides almost complete absence of direct porosity in mature concrete, resulting in an extremely dense structure and outstanding durability. The advantage of this concrete design is economic efficiency and ease of production. To be more specific, its compressive strength exceeds 100 MPa (14500 psi) in a day time, providing prerequisites for integration in the most challenging fields, such as road and bridge constructions.

THEORETICAL INVESTIGATION

It is well known that the theory of concrete durability is based on the law of water-to-cement ratio. Thereof, until the properties of cement and sand remain constant, and while the quality of sample moulding and the overall conditions during hardening remain unchanged, the durability of concrete can be expressed as the w/c function:

\[ R_c = f \left( \frac{W}{C} \right) \]  \hspace{1cm} (1)

This law has been defined in an empirical equation by Belyaev [1] and later developed in the work of Skramtaev [2] and Bolomey [3]:

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\[ R_{28} = AR_{Ca} \left( \frac{c}{w} - 0.5 \right) \]  

(2)

where

- \( R_{28} \) – the compressive strength at the age of 28 days (MPa or psi)
- \( A \) – coefficient of the aggregate quality (for ordinary sand is equal to 0.6)
- \( R_{Ca} \) – cement activity (MPa or psi)
- \( c/w \) – cement-to-water ratio.

Therefore, we can withdraw from (2) that the ratio of concrete strength to the cement activity is linearly depended to the c/w ratio:

\[ \frac{R_{28}}{R_{Ca}} = 0.6 \left( \frac{c}{w} - 0.5 \right) \]  

(3)

However, the early studies were considering that the linear relation described in (3) applies merely to concretes with c/w between 1.0 \ldots 2.5 (1.0 \ldots 0.4 of w/c ratio respectively). For concrete with c/w between 2.5 \ldots 5.0 (0.4 \ldots 0.2 of w/c ratio respectively) a different equation was proposed (4).

\[ \frac{R_{28}}{R_{Ca}} = 0.4 \left( \frac{c}{w} + 0.5 \right) \]  

(4)

Obviously, the adjusted coefficients in equation (4) lessen the estimation of durability. For example, for concrete with w/c = 0.2 the modified formula (4) reduces the compressive strength by 23% compared to the one calculated with the original equation (3) (Fig.1). However, our numerous tests of strength gain of concrete with w/c ratio between 0.2 and 0.4 provided that the actual strength gain precisely matches the behavior of the original function (3) (Fig.1). That is strength fully corresponds to the original function (2) and doesn’t require any modifications of coefficients. Note, that good workability of the mix was not anyhow affected with the reduced w/c due to applied superplasticizer.

Therefore, with the use of superplasticizers it is possible to achieve ultimately low w/c ratios in workable concrete mixes and produce concrete with compressive strength of 130MPa (18 850 psi). Though these properties don’t exceed such of UHPC produced with advanced additives, here we’d like to draw attention to a different aspect. Particularly, our research addresses the fact that on the early stages of hardening (approx. 14 days) one can find identical kinetics of strength gain in concrete made with ordinary raw materials and UHPC produced with advanced additives and compounds.

**EXPERIMENTAL INVESTIGATION**

**Materials**

Our UHPC design is based on white portland cement M500 (CEM I 42.5), free of mineral additives (tab. 1). As an aggregate we’ve used ordinary construction sand with fineness modulus from 2.5 to 3.0. The dust presence in the sand did not exceed 1% of its mass. All the aggregate was dried prior to mixing at room temperature and normal humidity.

In our work we have also used a superplasticizer based on polycarboxylate produced in Russia.

**Specimens**

Due to the type of aggregate we’ve been using, it was possible to conduct all experiments and to identify compressive and tensile strengths using 40mm*40mm*160mm (1.57in.*1.57in.*6.30in.) concrete specimens. While in our work we are attempting to develop a simple and economical solution for production of UHPC in conditions typical for a precast factory, all of our samples were produced at constant temperature of 23°C (73.4°F). The specimens were immediately covered with plastic foil to prevent the loss of water during hardening.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Early Stage Strength Gain**

After conducting a series of tests on various mixes we have identified that in 7 days our samples approach their maximal compressive strength (Fig. 2) and the increment during the following period from 7th to 28th day did not exceed 5% of the total. At the same time, the increase of the tensile strength at bending was more substantial during the whole period of four weeks (Fig. 3). Still, the strength obtained during 2nd, 3rd and 4th week was estimated at the level of merely 16% from the total. Worth noting is that increased amount of superplasticizer has
a positive influence on tensile performance: specimens containing 3.5% of superplasticizer showed approx. 55% improvement in comparison to ones with only 1.5% (Fig. 3). Interestingly, no change in the compressive strength could be identified.

A specific attention was payed to the kinetic of strength gain during the first 24 hours of hardening. During this period our mix design gains 75% of its total strength that is approx. equal to 100 MPa (14 500 psi). It’s 10 times higher than what a regular C40 concrete shows: during the first day the latter gains only 25% of its total strength that is approx. 10 MPa (1 450 psi). Therefore, if the difference between absolute strengths of these concretes is only 3.5 times, the difference on the first day of hardening is somewhat 10 times. Though, the high strength achieved on 28th day can be explained by the law of w/c ratio, the accelerated early stage strength gain can be interpreted only through an accelerated process of hydration of cement minerals.

**Hydration of Cement Minerals**

It is known that the three minerals responsible for the final strength of cement are alite C3S, belite C2S and tricalcium aluminate C3A that are able to crystalize and form strong hydroxides calcium hydroxide Ca(OH)2. However, on the very early stages of the cement hydration, particularly in the excessive presence of water, the increase in concentration of calcium hydroxide is proceeding slowly. It’s clear that the more mixing water there is, the longer it takes for it to reach the necessary level of saturation. However, practically immediately after mixing another mineral starts to form and actively grow, namely ettringite. This mineral is suspected in negative effect on formation of cement stone, which has been studied in works of numerous authors such as Shtark [5] and Kozlov [6]. One instance of formation of prime ettringite is the reaction of cement sulfate dihydrate with tricalcium aluminate in the presence of large amount of water:

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]

(5)

We consider that prime ettringite doesn’t merely act as regulator of setting of concrete, but also as a retarder of the following hardening. The reason being is that on the early stages it blocks the cement grains from access of water, and hence delays the formation of stable hydroxides and hydroaluminates. However formation of ettringite can only occur in the alkali environment of pH 10.4 – 13.0. However, at ultimately low levels of w/c such as w/c=0.2 the total amount of water is so little that the alkali concentration of Ca(OH)2 in the capillary liquids promptly reaches the critical level. Therefore, it prevents the growth of ettringite and promotes the formation of main cement minerals through topochemical reactions. This conjecture can be supported by the fact that the formation of colloid structures of silica gel during formation of cement minerals occurs only in access of water, in solutions with concentration of CaO less than 0.08 gr/l (0.005 pcf). Therefore, by minimizing the amount of water one can achieve prolific conditions for the hydration of cement, significantly increasing the rate of strength gain, and largely avoiding the interfering influence of ettringite.

There are two other positive factors of reduced water amount that have to be mentioned. One is that lesser volume of water provides smaller spaces between the grains of cement. These smaller spaces take shorter time for merging of grains into a continuous solid structure. The other factor is the absence of unbounded water. This condition eliminates directed porosity in microstructure of concrete increasing material’s durability. In regular concretes this pores soon develop into micro cracks and lead to structural damages.

We consider that the above mentioned factors generate a synergy of effects and result in a skyrocketing strength gain on early stages of hardening of concrete with w/c<0.2.

**The Influence of Inert Fillers**

In the research of concrete durability today, a very high attention is payed to the quality of the inert fillers. In particular, natural fine aggregate that is basically sand, exist in a very broad variety and differ from one another by minerology, gradation of grain size, topology of particles and of course by strength. Fortunately, the standards established by the concrete industry for fine aggregates allow determining qualities of various types of sand and therefore estimating the resultant strength of concrete produced with them.

Since most sands consist of silica, granite, lime or other ubiquitous stones, their strength substantially exceeds such of the cement stone in ordinary concretes. Based on this assumption many scholars have stated that the discontinuity in the process of concrete destruction occurs through the interface between cement mortar and aggregate particles. And while this rule remains true for concrete with ordinary w/c ratios, we have identified that it doesn’t apply to the concrete with w/c=0.2.

As can be seen on the fig. 4, the split took place through all the grains of sand disregarding of their size. The grains of yellowish colors are particles of silica, the darker reddish are such of granite. This effect should be explained not merely due to the high strength of cement stone, but also due to a very strong adhesion between new hydrates of cement minerals and the particles of inert aggregate. It can be explained by the fact that while the volume of new formations in the process of hydration exceeds such of the initial components, the absence of free water
facilitates densification of the structure of concrete. On this basis it can be said that, while cement itself is a finely dispersed powder, it can form extremely dense and durable microstructures at the usage rate of 500 – 1000 kg/m³ (31.2 – 63.4 pcf), if the water amount doesn’t exceed 20% of its mass. Important is that the aggregate should be dry. In this case it absorbs a predictable amount of batching water and preserves it during hydration of cement, promoting a deep integration of cement minerals into pores of the aggregate particles, and provides formation of concrete of critical performance.

SUMMARY AND CONCLUSION
On the basis of experimentally assessed physical-mechanical properties of concrete with w/c=0.2 on early stages of hardening, we can withdraw the following fact:

1. The main factor of early strength gain in concrete with w/c ratio of 0.2 is the rapid increase of concentration of Ca(OH)₂ in the mixing water that immediately provides high alkali level (pH=13.0) and promotes formation of durable minerals of cement.
2. The addition of silica fume and fiber reinforcement does not affect the early strength gain. While maintaining same amounts of mixing water and mixture workability, concretes produced solely on fine aggregates had the same dynamics of strength gain during the first week of hardening as the one made with more complex composition.
3. Concrete with w/c=0.2 and without finely dispersed fillers generates an extremely dense material structure already during the first day of hardening, and therefore provides a durable and frost-resistant material.

NOTATION
w/c = water to cement ratio
c/w = cement to water ratio
UHPC = ultra-high performance concrete
UHPFRC = ultra-high performance fiber reinforced concrete

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TABLES AND FIGURES
Table 1 – Mineralogical composition of clinker

| Component | Percentage by mass |
|-----------|--------------------|
| C3S       | 63.1               |
| C2S       | 12.8               |
| C3A       | 13.9               |
| C4AF      | 1.3                |
| CaO       | 2.5                |

Table 2 – Fine aggregate grading

| ACI 318M Units | ASTM E 11 | Percentage passing by mass |
|----------------|-----------|-----------------------------|
| 9.5 mm         | 3/8 in.   | 99                          |
| 4.75 mm        | No. 4     | 95 to 100                   |
| 600 µm         | No. 30    | 35 to 55                    |
| 150 µm         | No. 100   | 0 to 5                      |
**Table 3 – Mineralogical and petrological content of sand**

| Mineral    | Percentage by mass |
|------------|--------------------|
| Quartz     | 54.1 to 68.5       |
| Granite    | 10.3 to 13.8       |
| Feldspars  | 7.0 to 8.0         |
| Limestone  | 6.1 to 7.9         |
| Dolomite   | 0 to 2.9           |
| Silica     | 1.2 to 2.0         |
| Quartzite  | 0.2 to 0.4         |
| Mica       | 0 to 0.6           |
| Sandstone  | 0 to 1             |

**Fig. 1** – Linear relation between c/w (w/c) ratio and the ratio of concrete strength after 28 days to cement activity ($R_{c28}/R_{CA}$) according to the equations with original (3) and modified (4) coefficients. Red marks (+) map experimental results of compressive strength tests of blends with specific c/w ratios.
Fig. 2 – Compressive strength gain of our UHPC (red) in comparison to UHPC design used by Graybeal [4] (blue)

Fig. 3 – Tensile strength gain in relation to amount of superplasticizer (red = 1.5%; blue = 3.5%)
Fig. 4 – A photo of the cleavage surface of our specimen exposed to a critical bending stress. It illustrates that the fracture takes place through the particles of the fine aggregate.