HEAT DISSIPATION AT CEMENT HARDENING

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ABSTRACT

During the construction of concrete structures of small cross-sections, the release of heat during cement hardening has no harmful effects. With the increasing temperature of the hardening cement mass, the rate of cement hydration increases. This increases the rate of release of its heat of hydration of cement. The consequence of the accelerated process of hydration of the binder is a more intensive increase in the strength of cement stone than in the case of hardening under normal conditions. This fact is widely used in practice for the intensification of the hardening of concrete. When structures with small cross-sections are being built, the heat released during hardening is relatively quickly transferred to the surrounding space and does not cause a significant increase in temperature. In structures made of massive concrete (with a large cross-section), this heat is stored in the interior of the array for a long time, which causes a rather large rise in temperature and its slow drop. This is due to the fact that heat transfer to the external environment is hampered here by the considerable thickness of the massif and the rapid rate of concreting, mechanized laying of large masses of concrete. As a result, a temperature difference is created between the internal and external parts of the structure and harmful internal stresses arise that can cause cracking in the hardened concrete. This leads to a violation of its solidity. The faster cement hydrates, the sooner and more heat is released. The types of cements with a high content of tricalcium silicate and aluminate emit more heat and rather than types of cement with a high content of dicalcium silicate and tetra-calcium aluminoferrite. However, the latter has a lower strength. The increase in strength resulting from the hydration process is inevitably associated with the release of heat into the environment.

Keywords: concrete, hydration, minerals, temperature, strength.

1. INTRODUCTION

It is known that the hydration reactions of cement minerals are exothermic, and the interaction of cement with water is accompanied by the release of heat.

According to S.D.Okorokov (Volzhensky, 1986), clinker minerals are characterized by heat release indicators at different hardening periods. According to D. Verbeck and C. Foster (Bazhenov, 2002), the heat release of three calcium silicate (C3S) and two calcium silicate (C2S) is much lower, and three calcium aluminate (C3A) and four calcium aluminoferrite (C4AF) more.

The heat release of various portland types of cements varies widely depending on their mineral composition and fineness of grinding. The presence in their composition of an increased amount of C3S glass and especially C3A, determines the intense heat release during the hardening of such types of cements, mainly in the first terms, due to the rapid interaction of these minerals with water. Cements characterized by a high content of C4AF and most of all β-C2S are characterized by a reduced heat release. Heat generation can also be reduced by introducing active mineral additives into Portland cement, in particular, finely ground granulated blast furnace slags (Volzhensky, 1986).

2. MATERIALS AND METHODS

Heat release during hardening of cements is of great practical importance. In particular, in
the process of concreting conventional structures at low temperatures, increased heat generation plays a positive role. On the contrary, the construction of massive structures, for example, hydraulic structures (especially in summer), from concrete on cements with increased heat generation leads to their heating to 50 °C and more. Subsequent cooling of concrete masses at the outer surfaces causes significant temperature differences in the outer and inner zones, the occurrence of tensile stresses in the surface layers, and the formation of cracks in them. This reduces the bearing capacity and durability of structures, therefore, when erecting massive concrete structures, low-heat types of cements are used, for example, with heat release after three days no more than 168–188 and after seven days 210–230 J/g.

The experiments of many researchers have shown that heat from a mixture of Portland cement and water is released stepwise during the first days of hardening.

Based on their data, as well as the data of V. Lerch, T. Powers, and others (Mikulsky, 2002), the time of initial hardening of the cement test can be divided into four periods according to the intensity of heat release. The first period of 30-40 min can be attributed to the first period of the interaction of cement with water, when there is a strong heat release in the test (especially during the first 5-8 min) with its subsequent decrease to small values.

The second period - the period of low heat, sometimes called induction, occurs during the second to fourth hours. Its duration depends on the properties of cement and gypsum content.

The third period, starting 3-5 hours after the moment of cement mixing with water, is characterized by the beginning of setting and a gradual increase in heat generation, reaching a maximum after 6-10 hours. At this point, the setting of the dough is usually marked.

The fourth period begins after the heat release indicator passes through a maximum and is characterized by a decrease in the amount of heat by the daily time to approximately 4.19 J/h per 1 g of cement. At this time, an intensive increase in the strength of the system is observed, and the heat release in ordinary cements after a day of hardening reaches 15-20% of the total (Volzhensky, 1986; Bazhenov 2002). At the same time, according to the data of Yu. S. Malinin and others, there is a stepwise change in the concentration of calcium hydroxide and silica in an aqueous solution of cement paste. A curve with sharp kinks is also characteristic, illustrating the growth of the ultimate shear stress measured by a conical plastometer. Here, the moments of decrease in the indices of the ultimate shear stress coincide in time with the onset of strong drops in the concentration of calcium hydroxide in the liquid phase of the test (Mikulsky, 2002; Dvorkin, 1991; Solomatov, 1989).

The presence of an induction period with low heat generation is explained by the formation of clinker particles of helium shells of hydrated compounds, which almost cease water access to unreacted inner zones of binder grains. But the presence of a saturated solution of Ca(OH)₂ and other compounds in the gel formed, and on the unreacted surface of the cement, particles create the conditions for the diffusion influx of water from the intergranular space with a low concentration of the solution. As a result, the osmotic pressure gradually increases in the gel shells, leading to rupture at certain values. In this case, there is the possibility of direct access to water to exposed fresh surfaces and its reaction with cement. This moment is the end of the induction period of low activity and the beginning of the third period with increasing heat dissipation (Krivenko, 1989; Neville, 1972; Reichel, 1979).

The data obtained by M.I. Strelkov (Reichel, 1979), during observations under a microscope, confirm the possibility of rupture of the gel shells that arise on the surface of cement grains. He also believes that the phenomenon of rupture of the shells on individual particles contributes to their movement into the grain space, which, due to this, is filled with cementing neoplasms.

The rate of heat release and the formation of particles of a new solid phase during the hydration of binders has a great influence on the formation of a bound structure with the formation of a "hardened stone". For example, the formation of calcium hydroxide from oxide usually proceeds very quickly with the release of a new substance. Theoretically, they are able to increase its temperature by 878:1.17 = 750 °C (here 1.17 J/g °C is the heat capacity of the hydrate) (Artyukhovich, 2011).

Hydration (α-semi-aquatic gypsum comes with the release of 112 J/g. In this case, with stoichiometric ratios of the reacting components, the resulting two hydrates can theoretically heat up only by 112:1.09 = 103 °C. It is important to note that hydration of calcium oxide or gypsum proceeds practically within 1-2 hours with the...
release of all the heat.

Of the clinker minerals, only C₃A can be compared to some extent with CaO and semi-aquatic gypsum. With its full hydration, 1082 J/g is released, or in terms of C₃AH₁₂ 600 J/g. If we allow the possibility of a fairly rapid interaction of this substance with water even in half, then in the absence of heat loss, the temperature of the reaction product can reach approximately 300: 1.26 = 237 °C.

Hydration of semi-aquatic gypsum with relatively small heat release proceeds quietly only with a moderate increase in the external volume, while hydration of three calcium aluminates, according to some researchers, causes an insignificant strength of the formed stone, and according to others its zero strength.

It is characteristic that the presence of 3CaO·A1₂O₃ in clinkers in an amount of 5-10% is useful, while its higher content already leads to a temporary decrease in the strength of types of cements. This phenomenon can be partially explained by the peculiarity of hydration C₃A (Shevchenko, 2004).

Of the other clinker minerals, C₃S - 500 J/g, according to V. Lerch and R. Bogg (Puliaev, 2011), is distinguished by high heat release during full hydration. However, this process, it is relatively slow, and even under favorable conditions at ordinary temperature during the first 12 hours, the degree of hydration barely exceeds 15-20%. In this case, heat generation can reach 100-126 J per 1 g of the starting substance, and even less per 1 g of neoplasms. These heat dissipation indicators are close to those characteristics of semi-aquatic gypsum, which interacts with water for 1-2 hours. Thus, one can not be afraid of significant heating of C₃S hydration products and deformations inherent in C₃A.

The two calcium silicate C₂S, as well as the four calcium aluminoferite C₄AF in terms of heat during the initial hydration periods, cannot have a significant effect on the heating of the system, in which dangerous deformations can occur.

Thus, it is necessary to evaluate the true astringent properties of certain substances with due regard for the factor of heat release, which from a certain threshold exerts a sharply negative effect on the hardening effect of the system. It should be emphasized that the above applies to stoichiometric mixtures of binders with water. The hardening of concrete and mortar mixtures is less affected by the factor of the intensity of heat generation due to the presence of aggregates and excessive amounts of water preventing the system from overheating (in the absence of artificial heating).

3. RESULTS AND DISCUSSION:

The most significant influence on the rate of hardening of concrete is exerted by the mineralogical composition of cement. According to the intensity of the increase in concrete strength at normal temperature, modern types of cements are divided into four types (Table 1).

At the same time, type I and type II types of cements, which provide a faster increase in concrete strength, at an early age, sharply slow down the increase in strength during long hardening periods, while type III and type IV cements, slowly hardening at the beginning, show a noticeable increase in strength over a long time. Under favorable conditions, the strength of concrete on these types of cements by the half-year age increases by 1.5 to 1.8 times compared with the strength at the age of 28 days, and there is also an increase in strength over the next several years, although at a slower pace.

A noticeable effect on the rate of hardening of concrete is exerted even by relatively small fluctuations in air temperature.

To determine the temperature of cement hydration during hardening of concrete, thermometers of the TM-1288/1 type are installed in the structure. Thermometer readings were recorded in an eight-channel TM-5103. The arrangement of thermometers in the structure is shown in Figure 1.

From Figure 1, it is seen that on the first and second foundations, thermometers No.1 and No.6 in the center are installed, respectively, thermometers No.2, No.3 and No.7, and No.5 are installed along the edge of the formwork at different levels. Thermometers No.4 and No.8 are installed to control the outside temperature or air temperature.

Figure 2 and Table 2 show the change in temperature of concrete over time in various places of structures. Therefore, when concreting massive structures, especially in the spring-autumn period, it is necessary, if possible, to take into account temperature fluctuations and its effect on the hardening of concrete.

Analysis of the results of changes in concrete temperature shows that 5 hours after
Pouring, the temperature of concrete began to rise markedly and amounted to 37.1-38.3 °C (Table 2). Such a relatively slow rise in temperature is due to the regular process of cement hydration.

This process is very intense. Since, at this stage, the number of hydrated phases is relatively small, in the space between the cement particles, there is free growth of thin plates of calcium hydroxide and calcium hydrosilicates and ettringite in the form of long fibers that form simultaneously.

In the process of intensive hydration of clinker minerals $C_3A$, $C_4AF$, and $C_3S$, after 22 hours and 30 minutes, thermometers No.1 and No.3 (structures No.1) respectively reached a maximum temperature of 76.3 and 69.1 °C (2017/08/12, at 08:30 h).

In construction No.1, the maximum temperature was recorded by thermometers:

- No.1 - after 22 hours 30 minutes - 76.2 °C;
- No.3 - after 22 hours 30 minutes - 69.1 °C;
- No.2 - after 29 hours - 49.6 °C.

In construction No.2, the maximum temperature was recorded by thermometers:

- No.7 - after 23 hours 30 minutes - 68.8 °C;
- No.5 - after 24 hours - 60.7 °C;
- No.6 - after 26 hours 30 minutes - 79.0 °C.

The preservation of the reached maximum temperature of concrete can be observed from 4 to 9 hours, depending on the location of the thermometers. This fact confirms that the third stage of the hydration process, occurring after 5 hours 30 minutes, lasts up to 27 hours.

After 27-30 hours, a uniform, and a slight decrease in temperature is observed at all studied points of concrete structures (Figure 2). This confirms the completion of intensive hydration of $C_3A$ and $C_4AF$, as well as the end of the crystallization of calcium hydroxide through the liquid phase.

The degree of hydration depends on the water-cement ratio, and reaches its maximum value only after 1-5 years (Evlanov, 2002; Krasnovsky, 2004; Shifrin, 1985; Sychev, 1974; Lukyanov, 1972; Velichko, 1972).

The degree of hydration (Figure-3) is determined in various ways: by the amount of Ca (OH)$_2$, by heat, by the specific gravity of the cement paste, by the amount of chemically bound water, by the amount of non-hydrated cement (18,19), or indirectly by the strength of cement stone (Shifrin, 1985; Sychev, 1974; Lukyanov, 1972; Velichko, 1972; Solovyanchik, 1985; Shifrin, 2007).

Hydration products vary in strength. The main carriers of strength are calcium hydrosilicates (Krivenko, 1989). In the process of hydration of clinkers $C_3S$ and $C_2S$, in addition to calcium hydrosilicates, hydrated lime Ca (OH)$_2$ is formed, which is stored in the cement stone and prevents corrosion of steel inside the cement stone (Solovyanchik, 2015).

Since the thermal conductivity of concrete is relatively low, hydration leads to a significant increase in temperature inside massive concrete structures. At the same time, the outer part of the concrete massif loses a certain amount of heat, so that a sharp temperature gradient is established.

Like many chemical reactions, the hydration reaction of clinker minerals is exothermic, with cement emitting up to 120 cal/g (Solovyanchik, 2015).

Strictly speaking, the total heat release is the sum of the heat of a chemical reaction and heat as a result of the sorption of water by the surface of a gel formed during hydration. The heat of sorption is a quarter of the total heat dissipation.

Bogg's research results showed that ordinary Portland cements emit about half of the total heat in 1-3 days. The heat release depends on the chemical composition of the cement and represents the sum of the heat of hydration of all cement constituents. From this, it follows that, if the composition of cement is known, its heat release can be determined with a high degree of accuracy (Shevchenko, 2004; Neville, 1972).

Since at an early age, the hydration of the individual components proceeds at different speeds, the rate of heat release, as well as the total amount of heat, depends on the composition of the cement. From this, it follows that by reducing the percentage of the most rapidly hydrating components ($C_3A$ and $C_3S$), the rate of heat generation of concrete at an early age can be reduced.

On the other hand, heat release during cement hydration can prevent the freezing of water in the capillaries of freshly laid concrete in cold weather. Therefore, high heat release, in this case, is a positive factor. It is clear that it is desirable to know the heat release value of various cements in order to choose the most suitable type of cement for each specific case.
For many applications of concrete, moderate heat generation is a positive factor (Neville, 1972).

The initial framework of the cement stone that arose during the setting significantly affects the further structure of the hydration products, in particular, the crack resistance and strength growth rate. Therefore, it is not surprising that there is a definite relationship between the degree of hydration and strength.

Temperature changes do not occur instantly, and it depends on the temperature difference, the properties of concrete, the massiveness of the structure, the heat generation of cement, and other factors. Therefore, a jump-like change in temperature can be arbitrarily adopted, especially since the strength of concrete hardening at different temperatures is affected by the mineralogical composition of cement, water-cement ratios, and others. The normal temperature of the concrete hardening medium is conventionally considered 15 ... 20 °C.

It is known that heating accelerates chemical reactions. An increase in concrete temperature activates the interaction of water and cement and accelerates the hardening of concrete. Moreover, the phase composition of cement hydration products hardening at different temperatures remains almost the same.

The resulting neoplasms fix the expanded volume of concrete, however, concrete exhibits residual deformations, that is, its volume after heating is greater than the original.

4. CONCLUSIONS:

1. In concrete, the maximum hydration temperature - 79.0 °C was reached 26 hours 30 minutes after pouring structures No.2 and maintaining a high temperature in the range of 78.0-79.0 °C continues for 9 hours.

2. The preservation of the reached maximum temperature of concrete in thermometers can be observed from 4 to 9 hours, depending on the place of their installation. This fact confirms that the third stage of the hydration process, occurring after 5 hours 30 minutes, lasts up to 27 hours after pouring concrete.

3. It should be borne in mind that the rate of increase in the strength of concrete is gradually slowing down, and its final strength will depend on in which growth certain temperature fluctuations occur.

4. In fact, temperature changes do not occur instantly. The intensity of heating and cooling depends on the temperature difference, the properties of concrete, the massiveness of the structure, heat dissipation of cement, and other factors.

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### Table 1. Classification of cements by hardening rate

| Type of cement                                      | The mineralogical characteristics                                                                 | \( K_{28...90} \) | \( R_{28} \) | \( K_{28...180} \) | \( R_{180} \) |
|-----------------------------------------------------|--------------------------------------------------------------------------------------------------|------------------|-------------|------------------|-------------|
| I Aluminate cement (C\(_3\)A)>12%                  |                                                                                                  | 1...1,05         |             | 1...1,05         |             |
| II Alite cement (C\(_3\)S>50%, C\(_3\)A<8%)       |                                                                                                  | 1,05...1,2       | 1,1...1,3   |                  |             |
| III Cement with complex mineralogical characteristics (pozzolanic, Portland cement with content C\(_4\)AF>14%, Portland cement slag with slag content 30...40%) |                                                                                                  | 1,2...1,5        | 1,3...1,8   |                  |             |
| IV Belite Portland cement and slag Portland cement with a slag content of more than 50% |                                                                                                  | 1,6...1,7        | 1,85        |                  |             |
| For comparison                                     |                                                                                                  | \( Lg n \)       | 1,35        | \( R_28 = \ldots \) |             |
|                                                    |                                                                                                  | \( Lg_{28} \)    | 1,55        |                  |             |

### Table 2. The change in temperature of concrete over time

| Time       | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------|---|---|---|---|---|---|---|---|
| 10:00      | 29 | 30 | 30 | 25 | 31 | 30 | 30 | 29 |
| 10:30      | 30 | 31 | 30 | 26 | 31 | 29 | 31 | 28 |
| 11:00      | 30 | 31 | 31 | 27 | 31 | 31 | 31 | 29 |
| 11:30      | 30 | 31 | 31 | 27 | 31 | 31 | 31 | 29 |
| 12:00      | 31 | 31 | 31 | 28 | 31 | 31 | 31 | 30 |
| 12:30      | 32 | 32 | 32 | 29 | 31 | 31 | 31 | 31 |
| 13:00      | 33 | 33 | 33 | 30 | 32 | 32 | 32 | 33 |
| 13:30      | 33 | 33 | 33 | 30 | 33 | 33 | 33 | 31 |
| 14:00      | 34 | 34 | 34 | 31 | 34 | 34 | 34 | 31 |
| 14:30      | 36 | 35 | 36 | 31 | 35 | 35 | 36 | 32 |
| 15:00      | 38 | 37 | 38 | 32 | 37 | 38 | 38 | 32 |
| 15:30      | 40 | 39 | 41 | 33 | 39 | 40 | 40 | 31 |
| 16:00      | 43 | 42 | 43 | 34 | 42 | 43 | 43 | 32 |
| 16:30      | 45 | 44 | 46 | 34 | 43 | 46 | 45 | 32 |
| 17:00      | 48 | 46 | 49 | 34 | 46 | 49 | 48 | 32 |
| 17:30      | 52 | 49 | 53 | 34 | 48 | 52 | 51 | 32 |
| 2019/08/23 | | | | | | | | |
| 08:30      | 76 | 47 | 69 | 27 | 60 | 78 | 69 | 29 |
| 09:00      | 76 | 47 | 69 | 27 | 60 | 78 | 69 | 30 |
| 09:30      | 76 | 47 | 69 | 29 | 61 | 78 | 69 | 32 |
| 10:00      | 76 | 48 | 69 | 31 | 61 | 78 | 69 | 34 |
| 10:30      | 76 | 48 | 68 | 32 | 61 | 78 | 69 | 35 |
| 11:00      | 76 | 48 | 68 | 31 | 61 | 78 | 69 | 34 |
| 11:30      | 76 | 48 | 68 | 33 | 61 | 79 | 69 | 36 |
| 12:00      | 76 | 48 | 68 | 33 | 61 | 79 | 69 | 36 |
| 12:30      | 75 | 49 | 68 | 37 | 60 | 79 | 69 | 35 |
| 13:00      | 75 | 49 | 68 | 37 | 60 | 79 | 68 | 35 |
| 13:30      | 75 | 49 | 68 | 37 | 60 | 79 | 68 | 35 |
| 14:00      | 75 | 49 | 67 | 38 | 60 | 79 | 68 | 35 |
| 14:30      | 75 | 49 | 67 | 38 | 60 | 79 | 68 | 36 |
| 15:00      | 75 | 50 | 67 | 38 | 60 | 79 | 68 | 36 |
| 15:30      | 75 | 50 | 67 | 36 | 59 | 78 | 68 | 35 |
| 16:00      | 74 | 49 | 67 | 36 | 59 | 78 | 68 | 34 |
| 16:30      | 74 | 49 | 67 | 35 | 59 | 78 | 68 | 34 |
| 17:00      | 74 | 49 | 66 | 35 | 59 | 78 | 68 | 33 |
| 17:30      | 74 | 49 | 66 | 34 | 59 | 78 | 68 | 33 |
| 18:00      | 74 | 48 | 66 | 34 | 58 | 77 | 68 | 33 |
| 18:30      | 73 | 48 | 66 | 32 | 58 | 76 | 68 | 31 |
| 19:00      | 73 | 47 | 65 | 30 | 57 | 76 | 67 | 30 |
| 2017/08/12 | | | | | | | | |
Figure 1. The scheme of the installation of the temperature sensor

Figure 2. Concrete temperature change over time
Figure 3. The degree of hydration of minerals