Assessment of concrete strength development in winter

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Abstract. The study attempts to demonstrate that it is possible to apply classical equations of chemical reactions for assessing the strength of concrete, cured in winter. This assumption differs from the existing classical theories of strength development in concrete, based on physical approaches. The graphs of the known normal temperature dependences of the chemical reaction rate and the increase in substance concentration in time allowed us to confirm the possibility for further research of strength development in concrete from the standpoint of chemical theories. For these purposes, the Van’t Hoff and Arrhenius equations were considered. To compare the results of theoretical studies with real constructions, we conducted an extensive experiment that involved a testing machine and a temperature chamber to assess the actual development of concrete strength in time at different temperatures (5, 20, 40, and 60°C). The temperature graphs of hardening of B40 concrete were plotted. Both equations showed identical results in calculating the increase in the reaction rate with the increase in concrete temperature. The research results allowed us to conclude that classical chemical theories used to assess the dependence of the reaction rate on temperature can be applied for calculating the concrete strength in winter.

1. Introduction
The correct determination of concrete strength is fundamental for ensuring the quality of cast-in-place structures. This is particularly relevant for winter cast-in-place construction, when incorrect assessment of concrete strength may lead to its early freezing and, thus, to its incomplete design strength [1-6]. There is a set of empirical dependences obtained from the studies of concrete and based on the approximation of exponential graphs of concrete strength development in time at a given temperature [7-13].

Most of these dependences are accurate enough for practical purposes. At the same time, it is noteworthy that the authors have followed almost the same course of scientific research, due to their identical views on hardening of concrete, which has been considered as a physical phenomenon.

2. Experimental data
Let us consider the issue from the other side. The hardening of concrete is caused by the hydration of cement (with the formation of crystalline hydrates), which is a classical chemical reaction. For most chemical reactions it is true that when the temperature rises, the reaction rate increases [14-16]. This type of temperature dependence of chemical reaction rate is normal (Figure 1).
Figure 1. Normal temperature dependence of chemical reaction rate and increase in substance concentration.

To plot the temperature dependences of concrete strength, we conducted an experiment on standard sample cubes with an edge of 100 mm. Six samples were prepared in each set. Sets of concrete samples were stored at 5, 20, 40, and 60 °C before the test. The first 24 hours, the samples were stored in forms until the time of formwork removal. The samples stored at 40 and 60 °C were covered with polyfilm to prevent excessive evaporation of moisture.

The samples cured at 20 °C were stored in a curing tank type KPU-1M at relative humidity of 95%. The other samples were stored in an environmental test chamber Nyte 0800 (produced in China). The distance between individual samples was at least 5 mm.

The concrete samples were tested on the Matest Cyber-Tronic press (produced in Italy). The limiting compression force of the press is 1500 kN.

The test results were processed according to [17]; the strength of concrete in a set of 6 samples was determined as the arithmetical mean value of the strength of 4 samples with the greatest strength. The scale factor was taken as 0.95. The obtained results are shown in a graph (Figure 2).

The experiment results showed that the coefficient of variation in strength of each set did not exceed 15%, while the actual class of concrete was B40.

When compared, the curve outlines in Figure 1 and Figure 2 indicate the possibility of applying classical theories of chemical reactions to concrete.

3. Analytical solution of the problem
The dependence of the reaction rate on temperature can be expressed by the empirical rule of Van’t Hoff (1884). According to this rule, the rate of most reactions increases 2...4-fold with every 10° C rise in temperature, and is determined by the temperature coefficient of reaction rate $\gamma$. This coefficient is determined empirically and shows how many times the chemical reaction rate has increased with a change in temperature. In general, the Van’t Hoff rule can be written as follows:

$$k_t = k_i \cdot \gamma^{\frac{t_i-t}{10}}$$  \hspace{1cm} (1)

here $k_t$ is the reaction rate at the temperature $t$. 
Let us consider a graph of strength development in concrete (class B40) at different curing temperatures (Figure 2) obtained during the experiment. Let us choose three isotherms at 20, 40, and 60 °C. It is evident that in order to achieve the same strength (70%), different curing time is necessary (84 hours for 60 °C ($k_{60} = 20 \% / 24$ h), 110.4 hours for 40 °C ($k_{40} = 15.2 \% / 24$ h) and 146.4 for 20 °C ($k_{20} = 11.5 \% / 24$ h)). Then the temperature coefficient of the reaction rate from (1) is:

$$\gamma = \frac{k_{60}}{k_{40}} = \frac{24}{11.5} = 2.09 \approx 1.15$$

Figure 2. Graph of concrete strength development.

Now, knowing the temperature coefficient of the reaction rate, it can be calculated how many times the reaction rate will increase if the temperature rises from 20 to 50 °C:

$$\frac{k_{50}}{k_{20}} = \gamma^{50-20} = 1.15^3 = 1.52 \text{ times}$$

The Swedish scientist Svante-August Arrhenius obtained in 1889 a more precise equation that defines the dependence of the reaction rate on temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

where $k$ is the reaction rate constant; $A$ is the pre-exponential factor that is temperature-independent (its dimension coincides with that of the rate constant); $R$ is the universal gas constant (8.3143 J/Mole.K); $t$ is the absolute temperature; $E_a$ is the activation energy of the reaction, i.e. the minimum energy that is required for the reaction and that is temperature-independent (J/Mole).

It follows from the Arrhenius equation that, since $t$ forms part of the exponent, the chemical reaction rate is very sensitive to temperature change (Figure 1). At low temperatures, there are
practically no chemical reactions \((k \to 0)\), and at very high temperatures, the rate constant tends to the limiting value \((k \to A)\).

Solving equation (2) for two temperatures, we obtain:

\[
E_a = \frac{R \cdot \ln \left( \frac{t_2}{t_1} \cdot \frac{k_2}{k_1} \right)}{t_2 - t_1} \tag{3}
\]

Let us consider two isotherms 20 and 40 °C from the previous example. Then, according to (3), the activation energy of the chemical reaction is:

\[
E_a = \frac{8.3143 \cdot 293.15 \cdot 313.15}{313.15 - 293.15} \ln \left( \frac{15.2}{11.5} \right) = 10645 \text{ J/Mole}
\]

Let us determine how many times the reaction rate will increase if the temperature rises from 20 to 50 °C:

\[
\frac{k_{50}}{k_{20}} = A \cdot e^{-\frac{E_a}{R_50}} = e^{\frac{E_a}{R_20} \left( \frac{1}{t_2} - \frac{1}{t_50} \right)} = e^{\frac{10645}{8.3143} \left( \frac{1}{293.15} - \frac{1}{323.15} \right)} = 1.5 \text{ times}
\]

Evidently, the results of calculations according to the Van’t Hoff and Arrhenius equations were almost identical. These results allow us to consider the possible application of classical chemical theories of assessing the dependence of reaction rate on temperature to calculating the strength of concrete in winter.

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