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Research paper

Effect of Heat Treatment on the Formation Cement Stone Microstructure

Viktor Sopov[1]*, Tatyana Kugaevska[2], Vladimir Shulgin[3], Heorhii Durachenko[4]

[1]Kharkiv National University of Civil Engineering and Architecture, Ukraine
[2]Poltava National Technical Yuri Kondratyuk University, Ukraine
[3]Poltava National Technical Yuri Kondratyuk University, Ukraine
[4]Poltava National Technical Yuri Kondratyuk University, Ukraine
**Corresponding author E-mail: vsopov@ukr.net*

Abstract

The influence of temperature on the cement stone structure formation of was investigated. The role of gel and capillary porosity of cement stone in the formation of basic properties of concrete is shown. The regularities of pore structure formation under the influence of the temperature factor are established. The advantage of "soft" heat treatment of modes of hardening concrete is shown for the optimal pore structure formation of cement stone that provides specified properties.

Keywords: *capillary pores; cement stone; gel pores; heat treatment; porosity; scanning calorimetry; thermoporometry.*

1. Introduction

Cement stone - as the main structural element of concrete, determines its most important properties. The formation of the structure of cement stone occurs as a result of the interaction of cement with water due to the formation of hydration products, the type, size and ratio of which change in accordance with the conditions and technological factors of hardening.

The main products of Portland cement hydration are calcium hydro-silicates, calcium hydroxide, hydroaluminate, and calcium hydrosulphoaluminates, which have various forms in the form of leaflets, plates, needles, etc. The complexity and morphological diversity of new growths of cement stone contribute to the formation of a discrete pore system of very bizarre forms.

Cement stone porosity is represented by a widely developed network of pores of various shapes with sizes ranging from a few angstroms to a few millimeters [1-2]. At the same time, the concept of a separate pore is conditional. In most cases, the division of pore space into elementary pores is quite arbitrary and sometimes simply impossible. The main characteristic of pores is their size, the concept of which is also arbitrary and ambiguous. In the pores of complex shape, several characteristic sizes can be distinguished - the size of the cavity a not the size of the "throat" of the pores. Therefore, the most fruitful way is when the pore size is associated with measured physical quantities. One of such methods is the thermoporometry method [3], in which the pore size is related to the experimentally determined temperature of crystallization of pore water.

The formation of the structure and properties of concrete is a complex multistage process, the beginning of which is determined by the moment of cement mixing with water. In general, it can be represented as a diagram (Fig. 1).

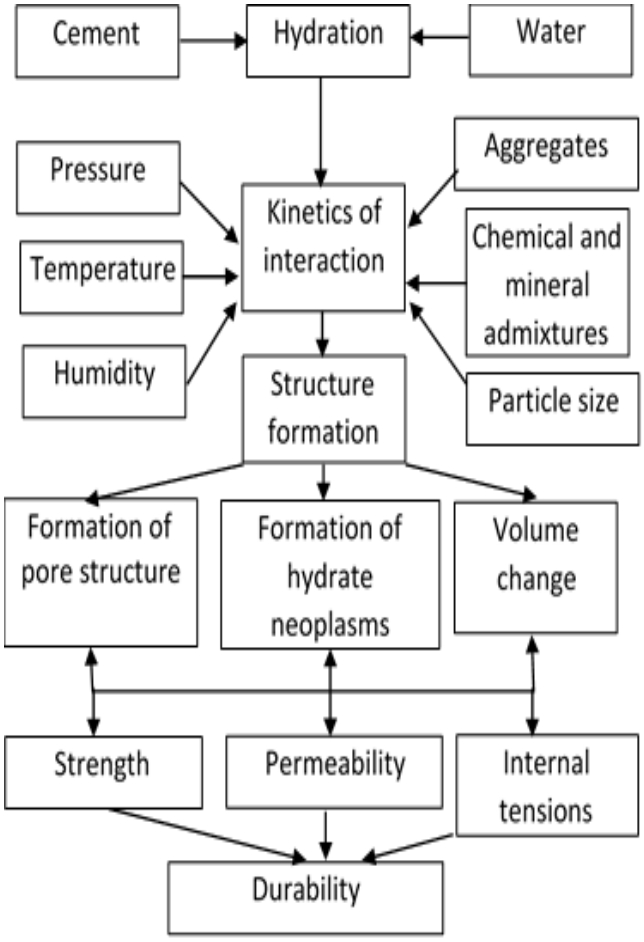


Fig. 1: Formation of the structure and properties of concrete.

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The structure formation of cement stone is significantly complicated due to the presence and interaction of two parallel developing structures - crystalline hydroaluminate and hydrosulfoaluminate and amorphous hydrosilicate. Cement stone, therefore, is a bidisperse structure, which is a combination of spongy (hydrosilicate gel) and particulate structures. This leads to cement stone pores separation into two groups which differ sharply in size - gel and capillary pores.

Many properties of concrete are determined by the microstructure of the cement stone. The microstructure depends on the nature of both the solid and non-solid phases, i.e. pore space. The formation of the microstructure is influenced by many factors, such as the physical and chemical nature of the cement, the type and amount of additives added, the temperature, the hydration time and the initial water-cement ratio.

2. Materials and Methods

Cements of three plants were studied, the mineral composition of which is given in Table 1.

Table 1: The mineral composition of cements

Cement	Mineral content, %			
	C_3S	C_2S	C_3A	C_4AF
1 Euro Cement Group	58,7	18,8	9	12
2 Heidelberg Cement	61,5	17,2	6	11
3 Dyckerhoff Cement	59	14	7	13

Samples of cement paste hardened at temperatures of 20, 50 and 80 °C.

Thermoporometry was used to analyze the pore structure, which is based on the thermodynamic pore fluid crystallization temperature dependence on the pore size [4-5]:

$$\frac{1}{R} = \frac{1}{2\gamma}\int_{T_0}^{T}\frac{\Delta S dT}{V}, \quad (1)$$

where R is the pore radius; γ is the free surface energy at the solid-liquid interface; V is the volume of the liquid phase; ΔS is the change in entropy during crystallization; T is the crystallization temperature; T_0 = 273 K.

The experimental basis of the method is differential scanning calorimetry. A differential scanning microcalorimeter DSM-2M was used in the work (Fig. 2).

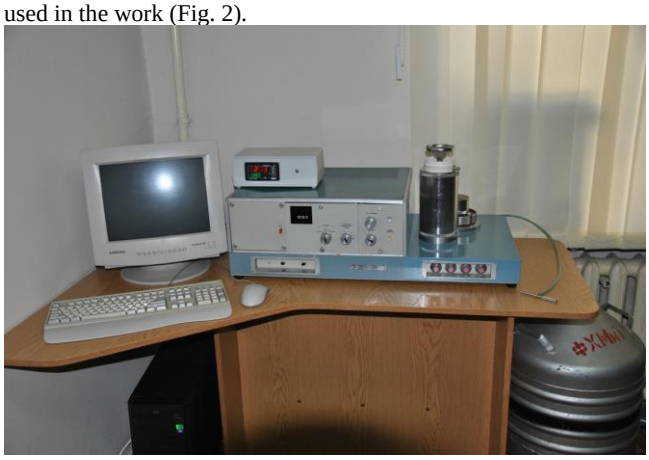


Fig. 2: The differential scanning microcalorimeter DSM-2M

Cement samples were mixed with water with a water-cement ratio of 0.5 and were hardened in normal conditions in the absence of moisture exchange with the environment.

Then the samples were placed in a differential scanning calorimeter and subjected to freezing. When it was recorded, the crystallization temperature of the pore fluid. The experimental curve is the temperature dependence of the difference in heat flow between two calorimetric cells (Fig. 3).

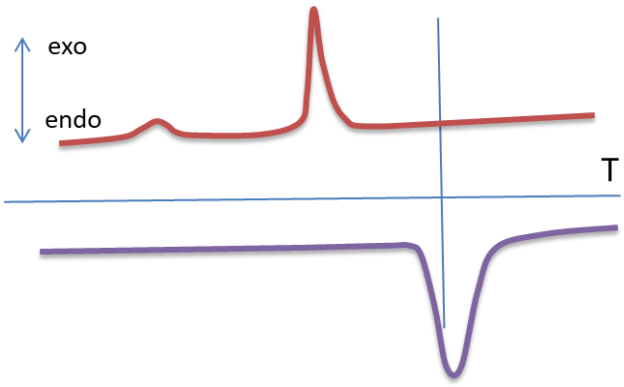


Fig. 3: The experimental curves

From the experimental curves, it is possible to calculate the temperatures and the heats of the water-ice phase transitions with high accuracy, which allows us to estimate, respectively, the size and volume of pores.

3. Results

Changes in the mineral composition of cement (Table. 1) leads to a substantial change in the character of the porosity (Fig. 4).

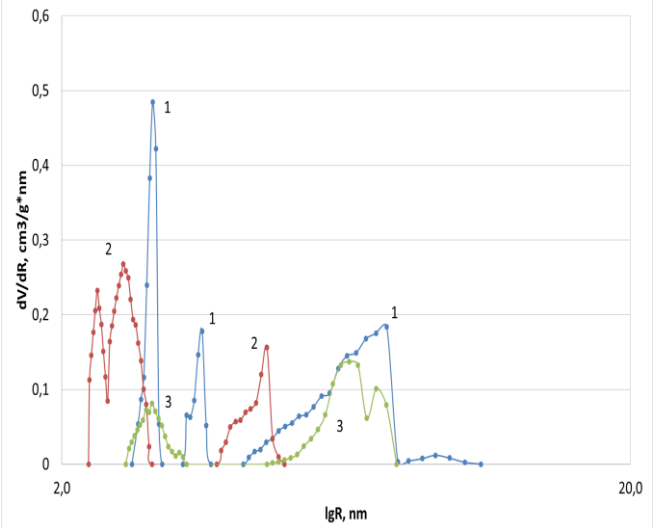


Fig. 4: The influence of the mineral composition of cements on the pore size distribution (symbols correspond to table 1).

From Fig. 4 it follows that a change in the mineral composition of the cement, even within 2-3%, leads to differences in the nature of the porosity of the cement stone. The increase in the content of the alumina ferrite phase of the cement contributes to the formation of larger pores located in one area. The width of this area and the maximum distribution of pore size will also depend on the percentage of minerals. The decrease in the content of aluminate phases leads to the appearance of pores with a smaller size of 2.2 ... 2.9 nm (curve 2), which are a result of the interaction of the silicate phases with water. The decrease in pore volume is observed in the following sequence 1- (0.48 cm^3/g); 3 - (0.24 cm^3/g); 2 - (0.18 cm^3/g), which coincides with the change in the ratio of aluminate phases of cement (Fig. 5).

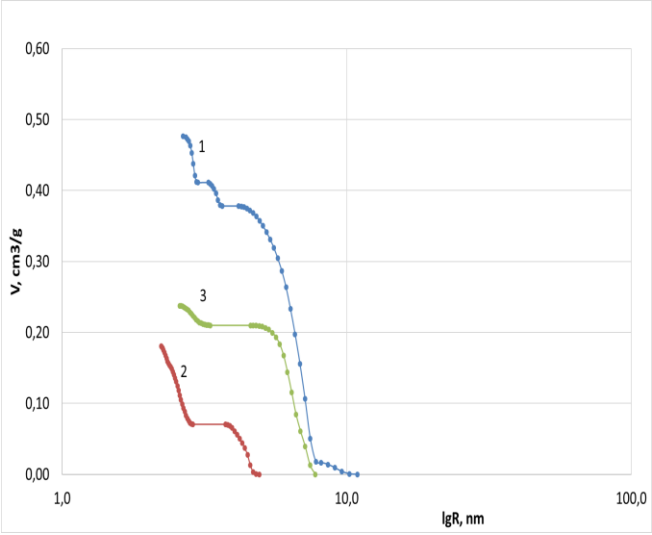
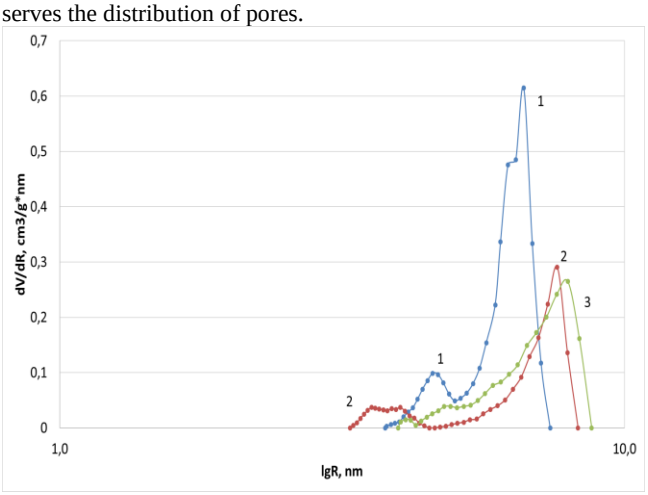
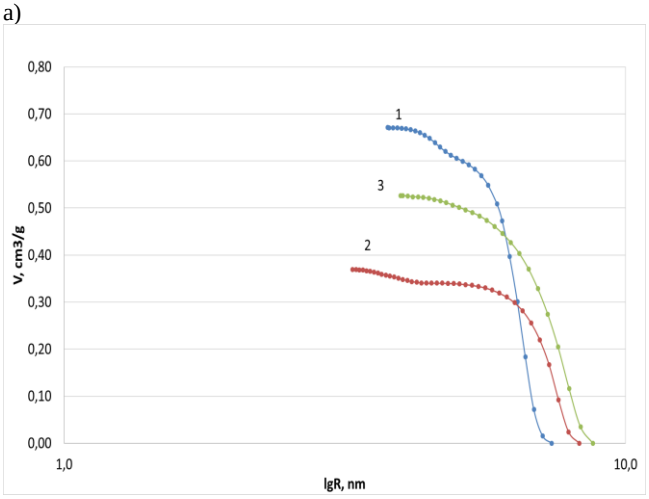


Fig. 5: Formation of the cement stone pore structure at a temperature of 20 °C (symbols correspond to table 1).

The nature of the pore structure varies considerably depending on hardening conditions. Samples of cement stone, solidified at a temperature of 80 °C, are characterized by a higher total porosity with simultaneous absolute and relative decrease in mesopores due to a corresponding increase in microporosity (Fig. 6). This preserves the distribution of pores.



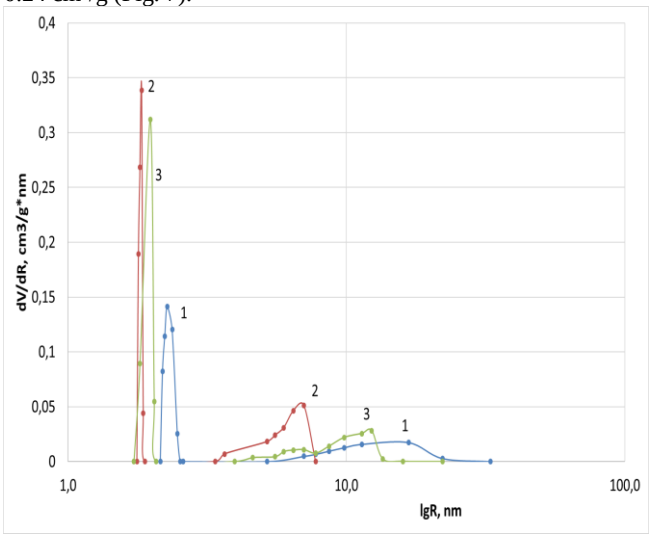
a)



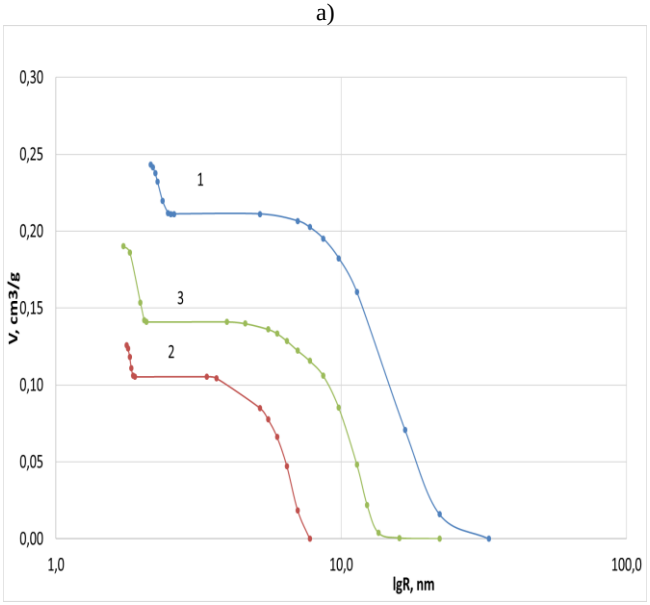
b)

Fig. 6: Formation of the cement stone pore structure at a temperature of 80 °C: a) pore size distribution; b) pore volume (symbols correspond to table 1)

Cements that hardened at 50 °C are characterized by a shift in the maximum distribution of mesopores towards decreasing sizes with a simultaneous decrease in the total porosity for samples 1 - from 0.67 to 0.47 cm^3/g, 2 - from 0.37 to 0.18 cm^3/g, 3 - from 0.53 to 0.24 cm^3/g (Fig. 7).



a)



b)

Fig. 7: Formation of the cement stone pore structure at a temperature of 50 °C: a) pore size distribution; b) pore volume (symbols correspond to table 1)

The effect of relative air humidity on the pore formation in the cement stone is due to the change in the condensation processes of the liquid phase and, accordingly, the degree of pore filling with water [6]. The nature of the formation of the pore structure of cement stone in different humidity conditions for all types of cement has the same tendency shown in Fig. 8 for Heidelberg Cement samples.

The ratio of gel and capillary pores in the cement stone is a criterion for the strength of concrete, since the amount of calcium hydrosilicates determines the final strength. The ratio of gel and capillary pores at different temperatures and humidity are given in Table. 2.

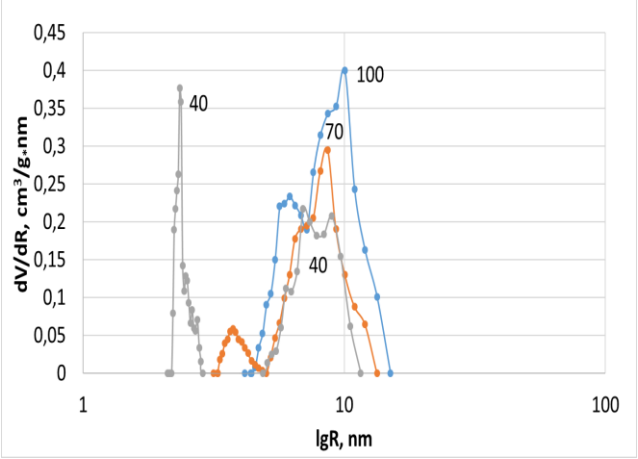
As can be seen from the Table. 2, almost all cements are characterized by a decrease in the number of gel pores with increasing temperature, up to their complete absence.

The increase in humidity also leads to a decrease in the number of gel pores in the structure of cement stone.

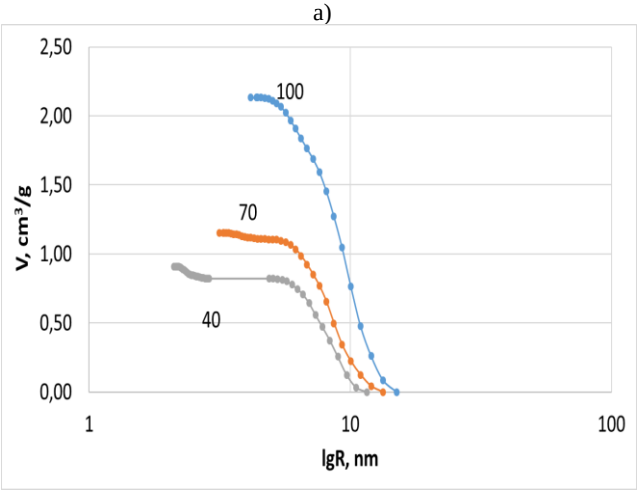
Table 2: The ratio of gel and capillary pores

Parameters	The ratio of gel and capillary pores for cements		
	1 Euro Cement Group	2 Heidelberg Cement	3 Dyckerhoff Cement

Temperature			
20	0,62	1,43	0,12
50	0,14	0,18	0,36
80	0	0,06	0
Humidity			
40		0,098	
70		0,018	
100		0	



a)



b)

Fig. 8: The formation of the cement stone pore structure, hardened in various humidity conditions: a) pore size distribution; b) pore volume

4. Discussion

In accordance with the rule of Van't Hoff, a temperature increase of 10 °C leads to an increase in the rate of chemical reactions by 2-4 times. The interaction of cement with water is a complex multistage process consisting of several elementary acts that take place simultaneously and overlap each other. These include chemical reactions, nucleation, crystallization, adsorption, dissolution, etc. Acceleration of at least one of these elementary processes will lead to a general change in the nature of structure formation.

Cements are multicomponent substances, which include at least four major minerals: C_3S, C_2S, C_4AF, C_3A. Each of them interacts differently with water in the process of hydration. The ratio of minerals determines the nature of the structure formation of the cement stone and the final formation of the properties of concrete. An increase in temperature changes the nature of the interaction of minerals with water and leads to a change in the type and properties of hydrated.

A.V. Usherov-Marshak classified cementitious clinker binders and minerals by heat evolution and effects on properties [7]. The composition and dispersion of hydrates formed during cement hardening change with increasing temperature, which naturally affects the nature of the pore structure. CSH gel is not only the most common cement hydration product, occupying about 50% of the paste volume, but it is also responsible for most of the engineering properties of concrete. All other cement hydration products are formed as discrete crystals that do not form strong bonds between themselves and the CSH gel.

The structure of the CSH gel is represented by a solid phase and gel pores filled with water, which has unique properties: it does not participate in the further hydration of cement, does not freeze up to -90 ° C, etc. [8].

The formation of capillary pores due to the presence of excess mixing water and mass transfer processes in hardening cement paste.

When the temperature rises above 65 °C, intensive evaporation of moisture from capillary and gel pores begins. Dehydration leads to the destruction of the structure of a hydrosilicate gel and an increase in pore volume [9-10]. The increase in porosity at 80 °C M. C. R. Farage explains the collapse of the structure of the C-S-H-gel [11].

H. Kasami showed that the degradation of concrete due to elevated temperatures is due to an increase in the size and volume of pores, which leads to a decrease in strength, the appearance of shrinkage cracks in the cement stone and in the transit zone around the aggregates [12].

An increase in temperature leads to the occurrence of mass transfer processes in the capillary pores of the cement stone, which also contributes to a change in its pore structure.

The results obtained by us are in good agreement with the data obtained by V.I. Solovyov with employees [13], who also observed an increase in the total pore volume and a decrease in the number of gel pores.

The hardening of cement paste at 80 °C significantly speeds up the formation of cement stone, however, a large-pore structure is formed, contributing to a decrease in strength and performance characteristics.

During cement hardening at a relative humidity of φ = 40%, three micropore areas are formed in the range of 1.97 ... 2.9 nm; 4.8 ... 8.3 nm and 8.3 ... 11.6 nm. This suggests that at this humidity, water is retained not only by the forces of adsorption, but also due to capillary condensation. Earlier [14] it was stated that with this humidity, water is possible only in gel pores. Hardening at a relative humidity of φ = 70% is accompanied by the formation of pores in the range of 3.2 ... 4.9 nm and 4.9 ... 13.5 nm. The sample, solidified at φ = 100%, has two regions of the distribution of capillary micropores with maxima at 6.2 and 10 nm.

Thus, an increase in humidity leads to an increase in volume and the formation of larger micropores. Under conditions of low humidity, the dehydration of larger pores and the condensation of moisture in the pores occur. This is due to the fact that, at a humidity of less than 40%, water is retained only by adsorption forces, and at higher humidity due to capillary condensation.

5. Conclusions

The nature of cement stone pore formation at temperatures of 20, 50, 80 °C has been investigated. It has been established that the most favourable conditions for the formation of the optimal structure of cement stone, which is characterized by the minimum number of capillary pores, are created at a temperature of 50 °C. It is shown that pre-exposure for 2:00 at a temperature of 20 °C helps to reduce the total pore volume of samples that are hardening at 80 °C. For samples hardening at 50 °C, the previous exposure does not have a significant effect on change the characteristics of cement stone pore structure. It has been established that a cement stone structure, which is formed at a high rate of temperature rise, is characterized by a large number of open capillary pores. The obtained patterns give grounds to assert that the use of "soft" heat treatment modes contributes not only to the acceleration of hydration processes, but also to the formation of a fine-pore structure of cement stone.

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