Radiation resistance evaluation of HCP with superplasticizers using DSC

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Abstract. Today, when constructing new nuclear power plants, they most often start from the data of studies conducted more than 50 years ago. At the same time, the modern achievements of construction science, such as high-tech concrete compositions using highly effective admixtures, are applied either without preliminary studies with irradiation, or are not applied at all. In this paper, we consider the mechanism of radiation-thermal changes in concrete under the influence of neutron irradiation, as the most dangerous factor in the external impact on the design of modern nuclear power plants. The methodology for assessing the radiation resistance of concrete developed by domestic specialists, as well as the possibility of using the differential scanning calorimetry method as part of a comprehensive assessment of the effect of modern admixtures (using the example of superplasticizers) on the radiation resistance of concrete, is considered. It was proved that when analyzing the effect of admixtures on the radiation resistance of concrete, it is sufficient to conduct studies on the HCP rather than using concrete. To analytically establish the effect of superplasticizers on the radiation resistance of HCP, polycarboxylate superplasticizers of well-known brands with short side chains and insignificant steric effect, as well as long side chains and high steric effect. The general behavior of HCP with superplasticizers was observed using DSC.

1. Introduction
Radiation changes in concrete structures of nuclear power plants are one of the main reasons for shortening their life. Research in the field of structural changes in concrete under the influence of radiation exposure is a long process both in terms of testing and further analysis. Today, when constructing new nuclear power plants, they most often start from the data of studies conducted more than 50 years ago. At the same time, the modern achievements of construction science, such as high-tech concrete compositions using highly effective admixtures, are applied either without preliminary studies with irradiation, or are not applied at all. Most of the available data on the use of various admixtures in the construction of concrete structures of nuclear power plants refers to the mid-end of the last century and needs to be significantly updated.

According to the studies of a number of domestic and foreign researchers, there is a certain pattern between thermal and radiation changes in concrete as a result of its irradiation [1-10]. Under the radiation changes of materials should be understood a change in the composition, properties, state parameters or structure of the material when exposed to or after exposure to ionizing radiation. When exposed to radiation, concrete changes in its linear dimensions and physical and mechanical characteristics.
In this paper, we consider the mechanism of radiation-thermal changes in concrete under the influence of neutron irradiation, as the most dangerous factor in the external impact on the design of modern nuclear power plants. The methodology for assessing the radiation resistance of concrete developed by domestic specialists, as well as the possibility of using the differential scanning calorimetry method as part of a comprehensive assessment of the effect of modern admixtures (using the example of superplasticizers) on the radiation resistance of concrete, is considered.

2. Method
According to numerous studies [1-7, 9-11, 17-19], the most important process occurring in concrete under the action of radiation is the process of local heating of the substance at thermal points. Such points represent micro and nano sections of matter in which a short-term temperature increase of several tens or even hundreds of degrees occurs as a result of the process of atomic displacement. Due to this thermal effect, local thermal changes occur in the concrete structure.

Radiation-thermal changes in concrete directly depend on the fluence and energy of neutrons, i.e. with increasing fluence, the magnitude of the changes also increases. It should be noted that such thermal effects to a much lesser extent affect aggregates than cement concrete. Naturally, with increasing temperature at thermal points, radiation changes in the structure of concrete increase.

A decrease in the strength characteristics of concrete is usually observed with an increase in the radiation-thermal load. This is primarily due to a change in the linear dimensions of the samples due to thermal deformation. At low temperatures and weak radiation exposure, the strength characteristics of concrete increase due to the acceleration of the hydration process. With a further increase in the linear strain of concrete during irradiation, the strength characteristics significantly decrease.

The dynamics of the thermophysical characteristics of concrete are inversely proportional to the radiation load. So at neutron fluences, at which there is an increase in volume on concrete by within 20%, the coefficient of thermal expansion decreases by 80-90%, and the coefficient of thermal conductivity - by 35-55%. In such a situation, the nature of the effect of irradiation on concrete is similar to the thermal effect.

According to research by Russian scientists, the mechanism of radiation-induced changes in the hardened cement paste (HCP) of concrete is practically not associated with the formation of radiation-induced defects in the crystal structure of minerals as a result of atomic displacement, as is the case with irradiation of rocks and ceramics [1,4,10]. This statement allows us to conclude that using heat treatment in laboratory conditions it is possible to simulate the radiation aging process of concrete structures of nuclear power plants. In [4], it was proved that when analyzing the effect of admixtures on the radiation resistance of concrete, it is sufficient to conduct studies on the HCP of concrete. This is justified by the fact that it is HCP that is most susceptible to changes due to the introduction of admixtures. The radiation changes in most aggregates used today are well understood. Carrying out such tests on full-sized concrete samples is fraught with a number of difficulties, therefore, in [2], it was decided to analyze the changes in the radiation resistance of concrete according to the results of physical and mechanical tests of HCP samples with admixtures.

In [1], according to the results of a study of HCP using various admixtures, the following values of neutron fluences and the corresponding temperatures:

| Neutron fluence, neutron/m² | Corresponding temperatures, °C |
|---------------------------|-------------------------------|
| \(1 \times 10^{23}\)      | 80                            |
| \(3 \times 10^{23}\)      | 100                           |
| \(6 \times 10^{23}\)      | 150                           |
| \(1 \times 10^{24}\)      | 180                           |
| \(1,4 \times 10^{24}\)    | 250                           |
Moreover, accelerated thermal tests themselves are carried out according to the regime in accordance with [2]. This is justified by similar changes in the structure of HCP during thermal heating to the indicated temperature values and upon irradiation with the corresponding neutron fluences [1,2,4].

In this paper, an analytical comparison of the results obtained in [2] with the results of DSC.

3. Results

The Portland cement of the Volsky plant of the M500 grade “PC 500 D0 Volsky” with the content of the main minerals: C3S - 64.8%; C2S - 11.1%; C3A - 4.4%; C4AF - 15.5%; Bassanite-2.3%; Gypsum-1.9% (control sample labeled “0”), corresponding to that used in [2].

To analytically establish the effect of superplasticizers on the radiation resistance of HCP, polycarboxylate superplasticizers of well-known brands with short side chains and insignificant steric effect (sample “1.X”), as well as long side chains and high steric effect (sample “2.X”). To draw an analogy with physical and mechanical tests for these samples, we selected the minimum (sample “X.1”) and maximum (sample “X.2”) concentrations of these additives. Samples of HCP were made in accordance with [1,2].

DSC was performed using a standard instrument for conducting thermal analysis with open-type corundum crucibles. Test conditions: constant air flow, preheating to 50°C to stabilize the heat flux, heating rate of 10°C / min., sample preparation - grinding the sample to a powder state, sample - 50±3 mg.

Test results are shown in Figure 1-3:

![Figure 1. DSC result for control sample](image1.png)

![Figure 2. DSC results for HCP samples](image2.png)

**Figure 1.** DSC result for control sample

**Figure 2.** DSC results for HCP samples

a – sample 1.1; b – sample 1.2
4. Discussion

According to the results of the analysis, it was revealed that the introduction of superplasticizers into the composition of HCPs, the changes occurring in their phase composition are insignificant. As can be seen from Figures 1-5, almost no new phases are formed. It should be noted a number of characteristic changes inherent in all samples:

- in the range of 120–130°C, a characteristic weight loss of the sample indicates the removal of chemically bound water;
- at 150-160°C an endothermic effect is observed, which is characteristic for dehydration of ettringite. Ettringite, formed in the early stages of HCP hydration, after dehydration as a result of thermal exposure becomes heat-resistant.
- loss of sample mass in the range of 50-1000°C indicates the decomposition of calcium hydrosilicates and aluminate phases.
- the endothermic effect in the temperature range of 550-580°C indicates the decomposition of portlandite and is accompanied by a characteristic weight loss.
- the endothermic effect at 720-900°C characterizes the process of decomposition of calcite with a corresponding weight loss. It should be noted that in this temperature range, decomposition of other components can also be observed, which are difficult to identify unambiguously.
- the phase transition of the dehydration product of the C-S-H gel to wollastonite is characterized by an exothermic effect at 830-860°C.
- It should also be noted that in the graphs presented, the exothermic effect in the range of 290-330°C can be attributed to the decomposition of organic additives.

A summary of the results of the DSC are shown in table 2:

| Sample | Mass loss in the temperature range, % | Estimated initial quantity, % |
|--------|-------------------------------------|------------------------------|
|        | 50-900                             | 50-150                       |
| 0      | 17,416                             | 3,832                        |
| 1.1    | 19,935                             | 4,720                        |
| 1.2    | 23,315                             | 5,383                        |
| 2.1    | 24,184                             | 5,507                        |
| 2.2    | 13,909                             | 2,382                        |
|        | Ca(OH)₂                            | Ca(OH)₂                      |
| 0      | 10,70                              | 7,96                         |
| 1.1    | 14,84                              | 5,43                         |
| 1.2    | 13,93                              | 7,34                         |
| 2.1    | 15,92                              | 7,39                         |
| 2.2    | 9,51                               | 7,01                         |

Based on the data obtained, it follows that there is greater resistance to thermal effects in a HCP sample with the addition of a maximum dosage of polycarboxylate with long side chains and a high
steric effect. This effect is due to the reduced content of free and interlayer water, which also affects the total mass loss.

A sample with a maximum concentration of the additive with long side chains and a high steric effect is characterized by a decrease in the content of portlandite by 10-45% compared with the control sample. Along with this, the remaining compounds show an increase in the content of portlandite (Figures 4 and 5).

**Figure 4.** Mass loss comparison of samples 1.1 and 1.2 with the control sample

**Figure 5.** Mass loss comparison of samples 2.1 and 2.2 with the control sample

5. **Conclusions**

In general, the results of the analysis confirm the data obtained in [2]. The analysis confirmed that the use of a polycarboxylate-based superplasticizer with long side chains and a high steric effect helps to increase the thermal stability of HCP. This additive has a negligible effect on the change in strength
characteristics and the content of free and interlayer water in HCP. This can be explained by a higher dispersion effect.

According to the technique specified in [1, 2, 4], for the construction of structures subject to irradiation with neutron fluences up to $3 \times 10^{23}$ neutrons/m$^2$, it is possible to use all the additives studied, since insignificant deformations are predicted during irradiation. This conclusion can be made based on the similarity of the phase composition of HCP samples with additives and the control sample.

At high neutron fluences ($6 \times 10^{23} - 1 \times 10^{24}$ neutron/m$^2$), the use of additives based on polycarboxylate esters with short side chains and weak steric effect can cause excessive radiation gas emission due to the increased content of capillary and interlayer moisture.

The provision of increased radiation resistance for concrete structures of nuclear power plants operating in conditions of increased neutron fluences ($1 \times 10^{24}$ neutrons/m$^2$) is predicted for compositions using superplasticizers based on polycarboxylate esters with long side chains and high steric effect.

The study showed that the application of the method of accelerated thermal aging and DSC can provide enough information for an analytical assessment of the radiation resistance of HCPs with additives.

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