Plasticizer Type Influence on HCP Radiation Resistance

Vyacheslav Medvedev

Abstract In recent years, the variety of such additives with different functional effects has reached an unprecedented amount. Of greatest interest is the use of functional additives in the construction of modern nuclear power plants, since this directly affects the quality and timing of construction. However, exposure to radiation is a unique environment, and radiation-induced changes in concrete have only been little studied. Each type of plasticizing additives has its own chemical structure and mechanism of action, therefore their influence on concrete composition will be different. Judging by the existing experimental data on various additive research, it can be concluded that the study of the effect of the chemical structure or type of the plasticizer on radiation resistance is of significant practical interest for modern construction. In the current work, the analysis method using DSC is adopted as a research technique. Since the study of plasticizing additives based on polycarboxylate ethers was carried out in the recent work, to analyze the effect of the type of the plasticizing additive, in the current work the plasticizing additives based on naphthalene formaldehyde, melamine formaldehyde and lignosulfonates were chosen as the object of study.

Keywords Plasticizers · Chemical additives · Concrete · HCP · Radiation resistance

1 Introduction

The use of various mineral and chemical additives in the construction of modern buildings and structures is not uncommon. In recent years, the variety of such additives with different functional effects has reached an unprecedented amount. Of greatest interest is the use of functional additives in the construction of modern nuclear power plants, since this directly affects the quality and timing of construction. However, exposure to radiation is a unique environment, and radiation-induced changes in concrete have only been little studied. The use of various additives directly

V. Medvedev (✉)
Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow 129337, Russia
e-mail: MedvedevVV@mgsu.ru

P. Akimov and N. Vatin (eds.), *Proceedings of FORM 2021*, Lecture Notes in Civil Engineering 170, https://doi.org/10.1007/978-3-030-79983-0_7

affects the chemical and mineral composition of concrete, which creates an even greater variety of data for study.

Plasticizing additives are among the most common and in demand in the industry. One of the most developing directions in the field of improving the technology of concrete work is the use of concrete mixtures with additives for concreting monolithic structures, as well as highly mobile and cast concrete mixtures obtained by introducing plasticizing additives. The use of such additives makes it possible to simplify the technology of molding products and structures, to abandon energy-consuming equipment for vibration compaction of concrete mixtures and to achieve the required quality of concrete structures. However, plasticizing additives slow down the hydration of alite, which reduces the durability of hardened cement paste (HCP) and concrete in the early stages and is a serious drawback of this line of research, because a decrease in the time for placing the concrete mixture in the formwork will be accompanied by an increase in the time for the concrete to reach the estimated durability [1]. At the same time, the positive effect of the use of this type of additives is expressed in a significant decrease in the water-cement ratio, an increase in the mobility of the concrete mixture, an increase in the physical-mechanical and operational properties of concrete, which leads to an acceleration of the construction process and a decrease in construction costs.

In terms of technical effects, plasticizers are dispersants—stabilizers of the cement system, forming a structured film as a result of adsorption on the interface between the solid and liquid phases [2, 3].

The experience in the production of plasticized concrete is closely related to the preliminary assessment of the following main indicators: the rheological efficiency of the plasticizing additive in cement concretes, the early hydraulic activity of the cements in the presence of the plasticizing additive, the mineralogical composition and fineness of the selected cement [4–6].

Ensuring the workability of the mixture is one of the key factors for accelerating the production of concrete works and creating a homogeneous structure of concrete structures, providing the design characteristics and the estimated life of the final product [6–8]. For the construction of critical structures of nuclear power plants (such as, for example, dry containment of the nuclear reactor), the workability of the mixture and the uniformity of the structure directly affect the efficiency and safety of the entire project. The use of plasticizers for concrete of such structures can significantly improve the quality of work. However, it is not known how such concretes will behave when irradiated. At the same time, the composition or the type of the plasticizer itself plays a significant role in the formation of the structure of the HCP, which requires special attention when conducting experiments in the study of the radiation resistance of concrete.

2 State of the Issue and Research Methods

To date, there is a lot of data on the study of the effect of various additives on the radiation resistance of concrete. However, most of the experimental data were obtained in the 80s and 90s of the last century. At the same time, today the variety of additives used cannot be compared with what was at that time [9–11].

In works [12–15], a study of the influence of most of the most popular mineral and chemical additives used in the construction of existing nuclear power plants was carried out: fly ash, finely ground quartz, a number of anti-freeze additives, granulometric slag, high and low calcium ash, tripoli, amorphous silica, a number of set retarders, a number of plasticizing additives, etc. All these data were obtained during the actual irradiation of cement stones and concretes with additives with various neutron fluences and are of great interest to the scientific community.

At the same time, the authors of works [3, 7, 9, 12, 16] note that in the case of using most of the studied chemical additives in the manufacture of HCP, the radiation resistance of the HCP practically does not change or increases, since the values of radiation-thermal shrinkage and decrease in mechanical properties practically do not change or decrease.

It should be noted that conducting such a full-scale test is fraught with enormous difficulties and costs in terms of time and resources.

In continuation of these works, methods were developed for conducting accelerated tests to determine the radiation resistance of cement stones and concrete. In works [1, 16, 17] one of such techniques is described and its efficiency is proved. In this case, the main emphasis is placed on the similarity of thermal and radiation-thermal changes in concretes, which makes it possible to reduce tests to determine the radiation resistance of concrete to the study of the thermal behavior of samples [16]. This significantly reduces the cost of testing and allows you to obtain data that correlate with the actual tests of concrete under irradiation as shown in [1, 16, 17].

According to the classification of the British Association for Concrete Additives [18], depending on the chemical composition, plasticizing additives are divided into the following types:

1. Based on sulfonated melamine-formaldehyde polycondensates
2. Based on sulfonated naphthalene-formaldehyde polycondensates
3. Based on lignosulfonates refined from sugars
4. Based on polyacrylates and polycarboxylates.

Each type of plasticizing additives has its own chemical structure and mechanism of action, therefore their influence on concrete composition will be different. The first three types of plasticizers are also called “traditional”. Plasticizers based on polyacrylates and polycarboxylates, which have become widespread in the last decade, are more effective than other types of plasticizing additives. Many experts associate the advantage of the latter with the structure of molecules: other types of plasticizing additives are characterized by a linear form of the polymer chain; for additives based on polyacrylates and polycarboxylates, the spatial form of polymer value with cross links is characteristic [19, 20].

In [1, 12, 16, 17], the effect of polycarboxylates on the radiation resistance of HCP is considered, but the authors of [12] say that the most significant increase in radiation resistance is provided by plasticizing additives based on formaldehyde. At the same time, all authors agree that it is the plasticizers that have the greatest impact on the radiation resistance of concrete.

Based on these data, it can be concluded that the study of the effect of the chemical structure or type of the plasticizer on radiation resistance is of significant practical interest for modern construction. In this work, the method described in [17] is adopted as a research technique. Since the study of plasticizing additives based on polycarboxylate ethers was carried out in [17], in this work, to analyze the effect of the type of the plasticizing additive, plasticizing additives based on naphthalene formaldehyde, melamine formaldehyde and lignosulfonates were chosen as the object of study.

3 Results

As a part of the experiment the plasticizing additives, which are currently used in the construction of the structures of the Voronezh, Leningrad and Rostov nuclear power plants were selected. At the same time, the key requirement for those additives was that the selected additives should not delay the hardening of concrete and have a stable effect for cements of different phase composition.

As it was shown in [17], the current studies were carried out on HCP made in accordance with the method described in mentioned work. For the subsequent correlation of the obtained data with the results of work [17], a similar Portland cement with the following content of the main minerals was chosen: C3S—64.8%; C2S—11.1%; C3A—4.4%; C4AF—15.5%; Bassanite—2.3%; Gypsum—1.9%. For each experimental composition, the dosage of the additive, which made it possible to obtain the cement pastes closest in rheology at the same W/C was selected (Table 1).

Table 1 Compositions of HCP accepted for the current research

No.	Additive marking	Type of plasticizing additive	Recommended dosage, %	Dosage used, %	W/C, l/kg
0	Control	–	–	–	0.26
1	MF	Based on sulfonated melamine-formaldehyde polycondensates	0.3–1.0	0.41	0.24
2	NF	Based on sulfonated naphthalene-formaldehyde polycondensates	0.4–0.8	0.44	0.24
3	LS	Based on lignosulfonates refined from sugars	No data	0.42	0.24

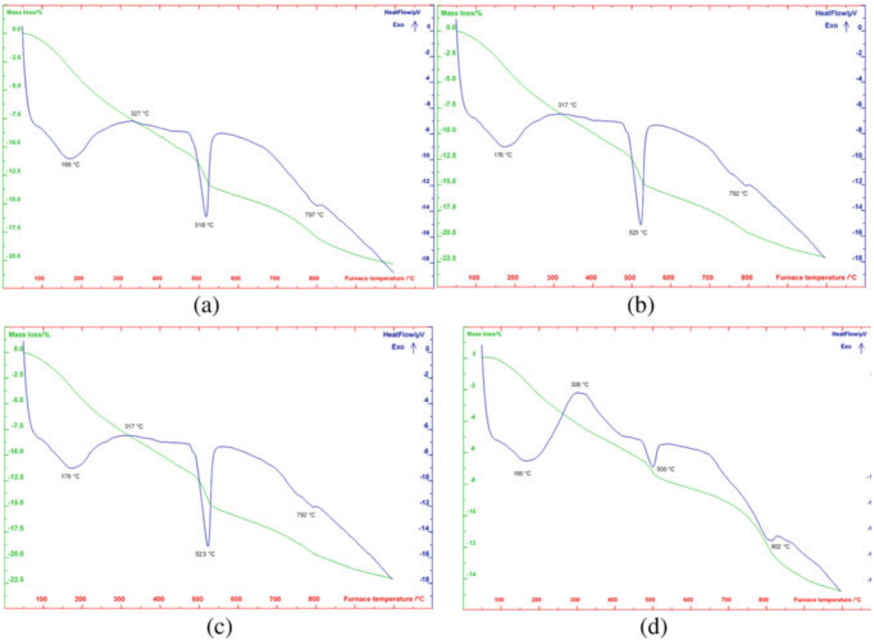

Fig. 1 DSC graphs obtained for samples of HCP: **a** sample 0 (Control sample); **b** sample 1 (MF); **c** sample 2 (NF); **d** sample 3 (LS)

It should be noted that the selected additives can be used both in the form of a powder and in the form of a suspension, therefore, the dosage data are indicated in terms of the dry residue.

DSC was carried out using a specialized thermal analysis apparatus, using open corundum crucibles. The test conditions were also chosen corresponding to the work [17]: constant air flow, preheating to 50 °C to stabilize the heat flow, heating rate 10 °C/min, the samples were preliminarily milled to a homogeneous powdery state, the mass of each test sample was 50 ± 3 mg.

The results of the experiments performed are presented in the Fig. 1.

4 Discussion

In general, all studied samples of HCP exhibit a similar thermal behavior. Throughout the experiment, a stable weight loss is observed, which may be associated with the decomposition of aluminate phases and calcium hydrosilicate compounds.

At the early stage of the experiment (up to 130–140 °C), the process of removing chemically bound water is observed. Significant endothermal effects at 500–530 °C and 780–810 °C, accompanied by weight loss, are characteristical for cement

Table 2 Estimated content of base components

No.	Additive marking	Estimated content of base components, %	
		$Ca(OH)_2$	$CaCO_3$
0	Control	9.04	7.80
1	MF	12.74	6.27
2	NF	14.55	5.77
3	LS	6.87	9.64

systems and indicate the decomposition of portlandite and calcite, respectively. The exothermal effect at 810–840 °C indicates the formation of wollastonite as a result of the phase transition of the dehydrated C–S–H gel under thermal exposure.

In general, the differences in the thermal behavior of samples 0, 1, and 2 are of a similar nature. The effect of the plasticizing additive is expressed in an increased content of portlandite and a decrease in the amount of calcite in the HCP sample in comparison with the control sample (Table 2).

At the same time, in the case of a sample with a plasticizing additive based on lignosulfonate, a significant decrease in the initial amount of portlandite and an increased content of calcite are observed. Also, the graph of this sample shows the presence of an exotermal effect at 300–310 °C without a sharp change in the dynamics of weight loss, which may indicate the formation of new phases upon the additive usage.

5 Conclusions

The results of the analysis and their comparison with the data obtained in [17] showed that the use of plasticizing additives based on naphthalene formaldehyde and melamine formaldehyde can potentially lead to a slight decrease in the thermal stability of the HCP, since their usage increases the amount of chemically bound water in the samples, but at a slight decrease in strength is predicted due to a decrease in the amount of calcite. This may be due to the greater dispersion effect of these additives.

It should be noted that the increased content of portlandite and chemically bound water in the HCP as a whole has a positive effect on the radiation resistance of concrete, as it slows the irradiation effect.

The additive based on lignosulfonate, in general, provided an increase in the thermal stability of the test sample, as evidenced by the lower overall weight loss compared to the rest of the samples and the presence of a larger amount of calcite, which also indicates the potentially higher strength of such a cement stone.

According to the technique indicated in [1, 16, 17], the investigated additives can be used in the manufacture of concrete structures exposed to neutron fluences up to 3×10^{23} neutron/m^2.

However, a comparison of the data with those obtained in [17] testifies to the greater efficiency of plasticizing additives based on polycarboxylate esters in comparison with other groups of additives, presumably due to the steric effect of action and the special effect of binding cement paste molecules using side polymer chains.

All tests were carried out using research equipment of The Head Regional Shared Research Facilities of the Moscow State University of Civil Engineering.

References

1. Ershov VYu (1992) Radiation resistance of Portland cement stone with chemical and mineral additives. The dissertation for the degree of candidate of technical sciences, Moscow
2. Batrakov VG (1998) Constr Mater Prod, 768
3. Batrakov VG, Shanov FM, Silina BS, Falikman VR (1988) Constr Mater Prod 1.2(7):59
4. Ramachandran VS, Feldman RF, Beaudoin JJ (1981) Concr Sci 427
5. Nithya R, Barathan S, Govindarajan D, Raghu K, Anandhan N (2010) Int J Chem 2(1):121–127
6. Hilsdorf HK, Kropp J, Koch HJ (2014) International Committee on Irradiated Concrete (ICIC) Information Exchange Framework Meeting, vol 1, pp 223–251
7. Thomas DR (1965) Nucl Struct Eng 1:368–384
8. Nowak-Michta A (2015) Procedia Eng 108:262–269
9. Denisov A (2017) Civ Eng J 5:70–87
10. Nkinamubanzi PC, Mantellato S, Flatt RJ (2016) Science and technology of concrete admixtures, pp 353–377
11. Field KG, Remec I, Le Pape Y (2015) Nucl Eng Des 282:126–143
12. Dubrovsky VB, Korenevsky VV, Muzalevsky LL, Pergametsik BK, Sugak EB (1980) Radiation safety and protection of nuclear power plants, 4:240
13. Dubrovsky VB, Korenevsky VV, Pospelov VP, Sugak EB (1985) Investigation of a binder for protective concretes with increased plasticizing properties (in Russian). In: Proceedings of the third all-union scientific conference on protection against ionizing radiation of nuclear engineering installations, vol 5, 27–29 October, 1985, Tbilisi, Georgia, pp 62–69
14. Sugak EB, Denisov AV, Korenevsky VV, Muzalevsky LL, Pergametsik BK (1978) Energy Constr 9:11–13
15. Ershov VYu, Dubrovsky VB, Muzalevsky LL, Kolesnikov NA (1988) Questions of atomic science and technology (Design and construction series), vol 2, pp 120–129
16. Medvedev V, Pustovgar A (2015) Appl Mech Mater 725–726:337–382
17. Medvedev V (2020) IOP Conf Ser Mater Sci Eng 869:032033
18. Vavrzhin F, Krchma R (1964) Stroyizdat 18
19. Jeknavorian A, Roberts J, Jardine L et al (1997) Condensed polyacrilic acid-aminated poly ether polymers as supciplasticizers for concrete. In: Proceedings of the fifth CANMET ACI international conference, Rome, Italy, vol 173, p 52
20. Ohta A, Sugiyama T, Tanaka Y (1997) Fluidizing mechanism and application of polycarboxylate-based superplasticizers. In: Proceedings of the fifth CANMET ACI international conference, Rome, Italy, vol 173, p 359