



Article

Impact of Temperature and Radiation Factors on Special Concretes Used for NPP Construction

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Abstract: The core catcher is arranged in an unattended, unventilated sub-reactor space. It is designed to receive molten corium in emergencies, and thus the concrete used in the core catcher must be resistant to high temperatures without significant loss of strength. During nuclear power plant (NPP) operation, these concretes are subjected to considerable radiation exposure, which may also affect their physical–chemical properties. Concrete mixes based on Portland cement and alumina cement with iron and corundum aggregate were investigated. Model samples of concrete were subjected to temperature exposure in the temperature range of 100 to 1000 °C and to radiation exposure in the field of mixed and neutron irradiation in the reactor cell at a load of at least 1×10^7 Gy. Concrete heating over 200 °C leads to a decrease in strength characteristics from 25.1 MPa to 2.6 MPa in Portland cement-based concretes and from 40 MPa to 12 MPa in alumina cement-based concretes. The decrease in concrete strength at high temperatures is due to dehydration of hardening phases, polymorphic transitions of aggregate and chemical interaction between concrete components. Radiation exposure of Portland cement-based concrete samples leads to an increase in their strength. Alumina cement-based concretes are less resistant to radiation exposure, and their strength decreases as a result of radiation exposure-induced processes.

Keywords: concrete; core catcher; density; nuclear power plant; temperature and radiation exposure



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1. Introduction

The modern international and Russian regulatory requirements for designing NPPs with VVER-type reactors stipulate the necessity for a core catcher in order to ensure corium melt retention and cooling and to maintain subcriticality in case of severe accidents with RPV melt-through [1]. The core catcher is arranged in an unattended room of the sub-reactor space. An additional structure, called the lower plate, is provided to ensure controlled receipt of the corium melt into the core catcher. The concrete structure of the lower plate shall withstand high temperature loads. Within a certain period of time, the structural material shall not melt and shall retain its strength properties without significant loss of bearing capacity. In the core catcher (similarly to the lower plate), special concretes of types HACK, HACKf, PCf and PCfm are to be used as protective and sacrificial material. The special concretes differ from the general-purpose concretes used for the main civil structures by composition. The need for special concretes is defined by the purpose of this equipment as well as its location in the nuclear power plant.

Therefore, the changes in physical and chemical properties of special purpose concretes under NPP operation conditions assuming the design period to be 60 years have not been studied earlier. Changes in strength characteristics of the applied concretes are critical for management of beyond-design-basis accidents and severe accidents at the NPP.

Throughout the reactor's lifetime, its components included either into the internal or external circuit are significantly affected by gamma and neutron radiation. The action of gamma radiation on concretes is comparable to heating and drying [2,3]. Heating of

hardened concrete and associated drying are related to the colloid and porous structure of the cement matrix and microcrack formation in the aggregate contact area when there is a difference in volumetric expansion of cement stone and of aggregate [2]. Extended exposure to gamma radiation can result in concrete damage due to partial dewatering of hardened cement rock and formation of shrinkage cracks [3,4] associated with release of the heat caused by gamma radiation [3,5,6]. The phenomenon of radiolysis of the water contained in the porous space of cement matrix leads to formation of gaseous hydrogen and hydrogen peroxide, resulting in concrete chipping and microcracks [7,8]. In the presence of CO₂, the radiolysis products react with calcium hydroxide, yielding an increased amount of calcite CaCO₃ [9].

There is also evidence of significant impact of the types of concrete aggregates used for nuclear facilities. One of the causes for concrete degradation is metamictization of minerals and associated widening of aggregate grains, which results in formation of cracks around the aggregate and decrease in concrete strength [2]. The studies [10–12] have confirmed that ionic bonds are resistant to neutron radiation; on the other hand, covalent bonds are strongly affected by the radiation, with changes in bond valence angles. The aggregates based on natural and artificial materials have low resistance to neutron radiation due to covalent bonding of the minerals (in most cases). This observation is confirmed by experimental data [13–15] for neutron radiation's effect on quartz, one of the common concrete aggregates. When affected by neutron radiation [16], the size of quartz increases by 16–18% in width and by 5–6% in length. This change is accompanied by transition of the initial quartz structure to the metamictic one with significant amorphization. The same changes are observed in quartz exposed to gamma radiation [17]. In this case, metamictization of the covalent bonding structure is caused by radiolysis and by ballistic impact.

When exposed to neutron and gamma radiation, destructive phenomena decreasing strength of concretes can be associated either with changes in the cement matrix structure or with metamictic changes in fine and coarse aggregates [2,3,18–20]. However, these phenomena do not result in total collapse of concrete structures, particularly if proper aggregates and cement matrix were provided [21–23].

During the lifetime, special concretes used in the core catcher are affected by high temperatures associated with accidents and heat from the hot part of the reactor plant. When combined with radiation exposure, the impact of high temperatures can lead to a decrease in structural strength and mechanical failure [24–26]. The processes leading to formation of internal stresses in concrete when exposed to high temperatures and associated chipping and strength decrease can be described as follows. The free water evaporates when the temperature reaches 105 °C; crystalline hydrates decompose with release of crystallization water at 80–200 °C. Dehydration of ettringite occurs at 300–800 °C, while dehydration of crystalline hydrates of calcium hydrosilicates hydroaluminates occurs at a temperature of 450–600 °C [27–29]. The aggregate grains are also susceptible to high temperature action to a variable extent; different values of coefficient of thermal expansion for the cement matrix and for aggregates and modification temperature changes in aggregate minerals can result in formation of cracks and collapse of concrete material. For concretes intended for radiation facilities, natural or artificial aggregates with increased density and heat resistance are used in most cases: magnetite, baryte, corundum and basalt aggregates [19,20,30,31].

This work contains investigations of the effect of high temperatures and radiation on changes in strength and deformation properties, phase composition and structure of special concretes used in the design of the core catcher on the basis of the matrix made of Portland cement and high-aluminate cement with various aggregates. Within the framework of NPP construction projects with VVER-type reactors, compliance with international requirements and standards, including IAEA requirements, shall be ensured since changes in material properties can result in changes in design characteristics. One important IAEA requirement is the requirement related to ageing management for equipment and for materials provided for in the design and used for construction of NPPs throughout the service life.

The data on changes in strength characteristics of concretes during NPP operation obtained as a result of research will allow for correction of the design of the nuclear power plant in the scope of use and application of special purpose concretes including their protection. The results of the research will also be used in exercising scenarios of beyond-design-basis and severe accidents with melting of nuclear fuel and the reactor vessel and, in general, will influence management of the above accidents. Forecast of the changes in concrete properties will allow for using the given properties of concretes in the design bases and will reduce excessive conservatism in justification of the NPP safety.

2. Materials and Methods

High-aluminate cement VGC 70 (as per GOST 969-2019) was used as the base for fire-resistant corundum–aluminate mix (HACK), including the modernized option (HACKf), and concrete. This is a high-strength quick-hardening hydraulic binding agent consisting mostly of calcium mono- and dialuminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$). It is made by fine grinding of source components of furnace mixture, its subsequent firing in rotating furnace at a temperature of 1450 °C and fine grinding of the obtained clinker.

The X-ray phase analysis was carried out using XRD 7000, plant manufactured by Shimadzu (Kyoto, Japan). The surveys were made in 10–90° diffraction angles. The results were processed with the use of ICDD PDF 2 database.

The phase composition of the high-aluminate cement used (Figure 1) is defined by the following phases: Fe_3O_4 , CaAl_2O_4 , CaAl_4O_7 as well as well-crystallized chromoferrite phase (Fe, Cr) (PDF card 000-41-1466) that could get into the cement from the furnace fire-resistant lining during firing.

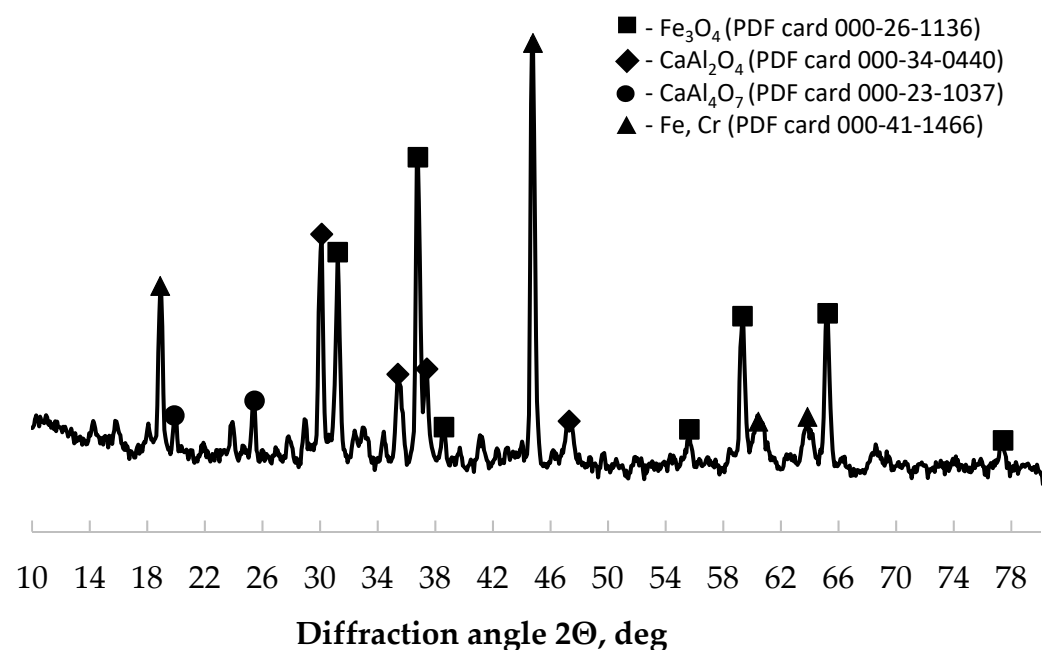


Figure 1. X-ray diffraction pattern of the high-aluminate cement.

The other kind of concrete mixes (PCf and PCfm) is based in Portland cement CEM I 42.5 N. According to the XRD data (Figure 2), the Portland cement is composed of the following phases: tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$, larnite (bicalcium silicate) $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ and anhydrite phase CaSO_4 (Portland cement additive required to control setting times). Apart from the main crystalline phases, the Portland cement also includes a so-called intermediate substance, which is composed of calcium aluminates and aluminoferrites: $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. These compounds do not diffract X-rays since they are present in the clinker vitreous part; however, they provide a significant contribution to cement stone strength.

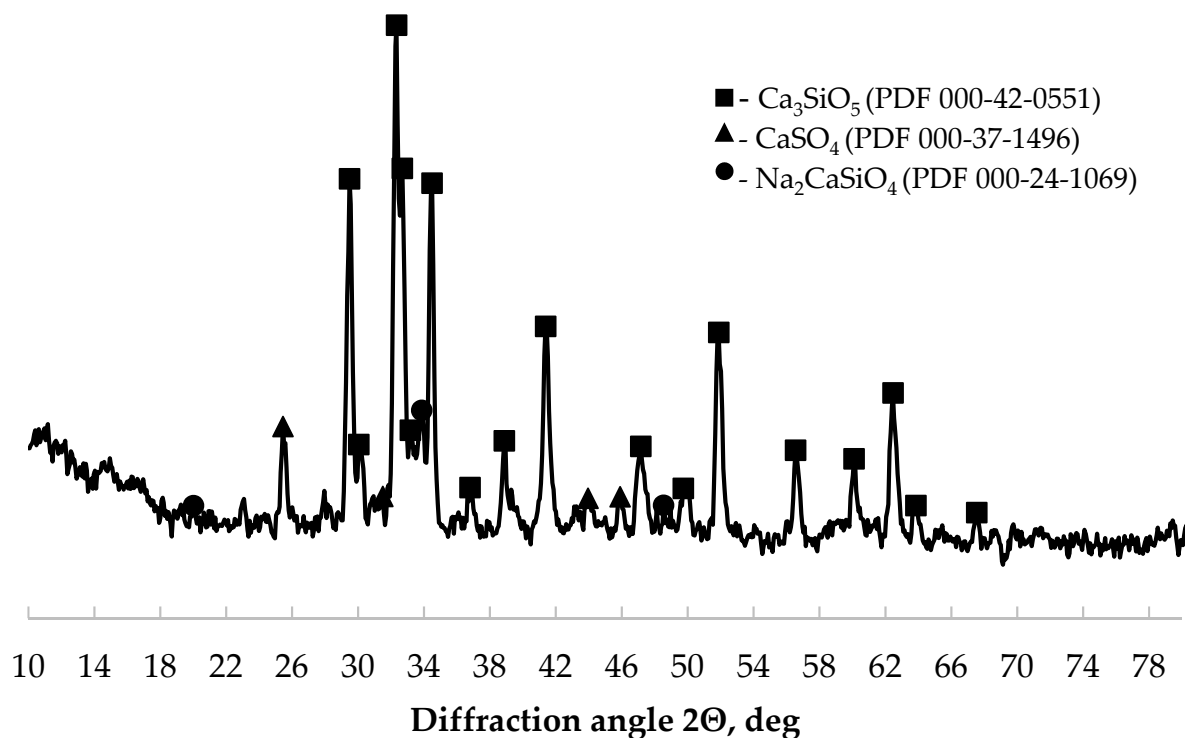


Figure 2. X-ray diffraction pattern of Portland cement CEM I 42.5 N.

The following materials were used as fine and coarse aggregates in accordance with the regulatory documents:

- iron oxide powder: based on the XRD data (Figure 3a), it is composed of a single phase of iron oxide (Fe_2O_3) in the form of hematite (PDF card 000-33-0664);
- manganese oxide powder is composed of two phases (Figure 3b): the main phase is MnO_2 in the form of pyrolusite (PDF card 000-24-0735) and a small amount of silica oxide SiO_2 in the form of quartz (PDF card 000-46-1045);
- iron ore pellets are composed of two phases (Figure 3c): iron oxide (Fe_2O_3) in the form of hematite (PDF card 000-33-0664) and silica oxide SiO_2 in the form of quartz (PDF card 000-46-1045);
- alundum is composed of corundum phases Al_2O_3 (PDF card 000-42-1468) with a small amount of silica oxide SiO_2 in the form of quartz (PDF card 000-46-1045) (Figure 3d).

Photos of the research samples are shown in Figure 4.

Component composition of the concrete compositions is given in Table 1.

Solid mixtures were prepared for experiments; the water–solid ratios of these mixtures are given in Table 1. The mixtures were used to make the specimens: cubes with a leg of 70 mm were used for determination of high temperature impact, and prisms with the size of $40 \times 40 \times 60$ mm were used for determination of the radiation load. The formed specimens were cured for the rated time period of 28 days in the ambient air humidity conditions.

After curing, the cube specimens were exposed to high temperatures in a muffle furnace. The temperature was increased in the range of 100 to 1000 °C with increment of 200 °C. After heat treatment, the specimens were subjected to visual examination, bending strength determination and investigations on changes in the phase composition associated with heat treatment by means of X-ray phase analysis.

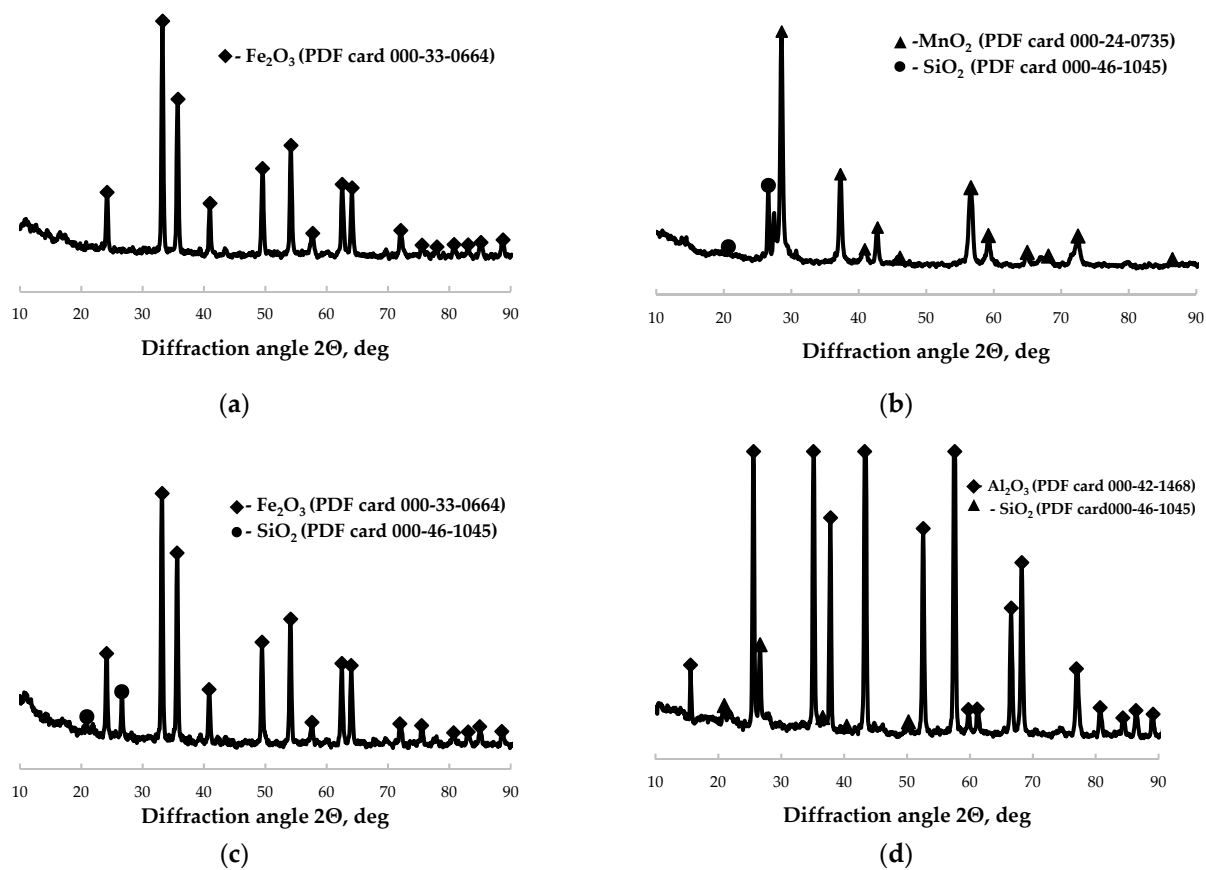


Figure 3. X-ray diffraction pattern of fine and coarse aggregates of concrete compositions: (a) = iron oxide powder; (b) = manganese oxide powder; (c) = iron ore pellets; (d) = alundum.

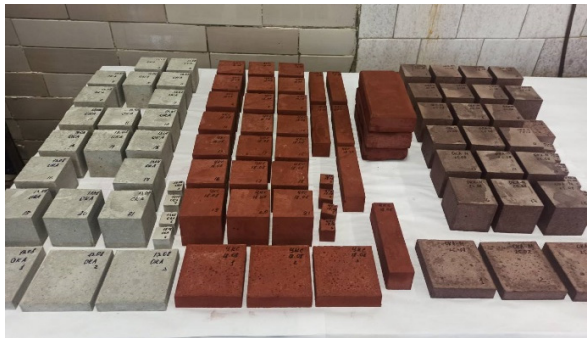


Figure 4. Photos of concrete samples made for research.

Table 1. Composition of concrete.

Series	Mix	Water–Solid Ratio, W/S	Cement, %	Iron Oxide Powder, %	Manganese Oxide Powder, %	Alundum, %	Iron Ore Pellets, %
PC	PCf	0.4–0.5	50.0 ± 5.0	50.0 ± 5.0			
	PCfm	0.4–0.5	50.0 ± 5.0	40.0 ± 5.0	10.0 ± 5.0		
HAC	HACk	0.10–0.13	30.0 ± 5.0			70.0 ± 5.0	
	HACkf	0.10–0.15	30.0 ± 5.0			25.0 ± 5.0	45.0 ± 5.0

The prism specimens were exposed to radiation in a channel of the IR-T research reactor. The radiation load value (absorbed dose) was no less than 1×10^{-7} Gy corresponding

to 60 years of NPP operation at normal conditions. The exposure was arranged in the field combining gamma and neutron radiation of the reactor. The heat component of the neutron spectrum was excluded due to structural features of the experiment channel.

After irradiation, the specimens were subjected to compressive strength tests and investigations on changes in the phase composition by means of X-ray phase and thermal analysis.

The characteristic values of the concrete specimens after the tests were compared with similar characteristics of the initial specimens, which were not subjected to heat and radiation exposure.

The thermal analysis was carried out using STA 449 F3 Jupiter plant manufactured by NETZSCH (Netzschkau, Germany). The analysis was carried out in corundum crucibles in air conditions with the temperature up to 1000 °C and temperature increment of 10 °C/min.

Specimens made of a cement mix were prepared for the determination of concrete strength characteristics. Six specimens were made for each of the determined testing periods.

For mix compaction, a mold with head tip is fixed in the center of the vibrating plate by pressing it firmly to the plate. After manufacturing, the specimens were stored inside the molds for (24 ± 1) hours in a bath with a hydraulic gate ensuring the relative air humidity of at least 90%. After this storage period, the specimens were carefully removed from the molds.

Strength was determined using beam-shape specimens with the size of $40 \times 40 \times 160$ mm.

The first test was the determination of transverse bending strength; for this purpose, a specimen was clamped between three roller supports. The distance between the lower supports (between their axes) was 100 mm; the upper support was used to transfer the bending force. The average load increment value was (0.05 ± 0.01) kN/s. The ultimate bending strength R_{bend} , MPa (kgf/cm²) was determined using the formula:

$$R_{bend} = \frac{3Pl}{2bh^2}$$

where P is the maximum load identified during the test, kgf;

l is the distance between support axes, cm;

b is the specimen width, cm;

h is the specimen height in the middle of the span, cm.

After this, halves of these beams were used for the determination of compressive strength. The specimen together with plates was installed in the center of the press supporting plate. The average rate of load increment during the test was (2.0 ± 0.5) MPa/s. The ultimate compressive strength of an individual specimen was calculated as the quotient of division of the destructive load on the working area of the specimen. The ultimate compressive strength was calculated as the arithmetic mean value of the four highest test results of six specimens.

The phase composition of the components of concrete mixes and hardened concrete specimens before and after thermal and radiation treatments were investigated using X-ray phase analysis as well as scanning and electron microscopy. Scanning electron microscopy was carried out using electron microscope JSM 6000 Neoscop manufactured by JEOL (Tokyo, Japan).

3. Results and Discussion

3.1. Thermal Treatment of Concrete Compositions

Specimens of all mixes were exposed to thermal treatment after 28 days of curing. For convenience, they were divided into two groups: the first group includes specimens based on Portland cement (PCf and PCfm), and the second group includes specimens based on high-aluminate cement (HACK and HACKf).

3.1.1. PCf and PCfm Concrete Compositions

As a result of heat treatment, various physical–chemical processes occur in concretes, which determine the concrete behavior.

During heat treatment of concretes based on PCf and PCfm mixes, the density of the specimens decreases as the treatment temperature increases (Figure 5); the decrease in density is gradual in the temperature range from room temperature to 400 °C; then, in the 400–600 °C temperature range, there is some slowdown of density decrease; after 600 °C, density decreases again. Curves characterizing the compressive strength for these specimens behave similarly (Figure 6).

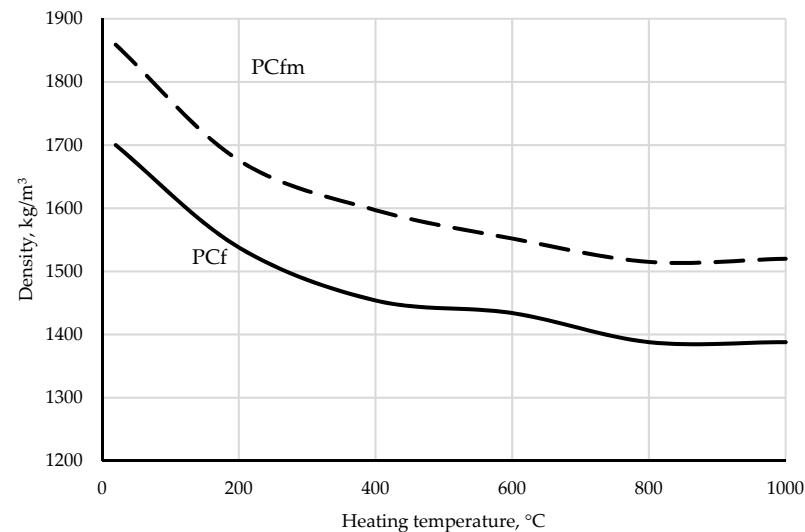


Figure 5. Change in density of PCf and PCfm concretes.

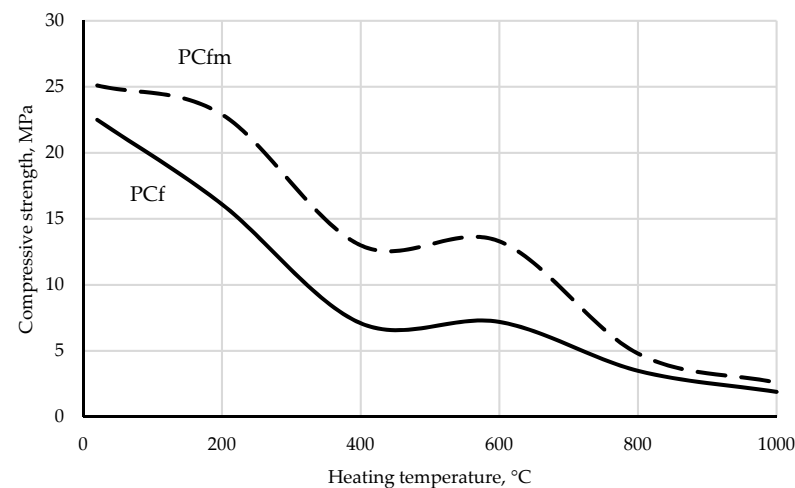


Figure 6. Change in compressive strength of PCf and PCfm concretes.

The results of changes in the phase composition of concrete specimens during heat treatment are shown in Figures 7 and 8. The X-ray diffraction pattern (Figure 7) clearly show the evolution of the phase composition of concrete based on the PCf mix. The main reflections of concrete based on the PCf mix at 28 days are due to the iron oxide (Fe_2O_3) aggregate phase as the most well-crystallized one. The cement hydration product phases include $\text{Ca}(\text{OH})_2$; the intensity of the hydration product phases is much lower since they are in a finely crystallized state. Further, as the treatment temperature increases (200–600 °C), the decomposition of phase $\text{Ca}(\text{OH})_2$ occurs; gradually, the intensity of reflection $\text{Ca}(\text{OH})_2$ decreases, and, at 600 °C, it disappears.

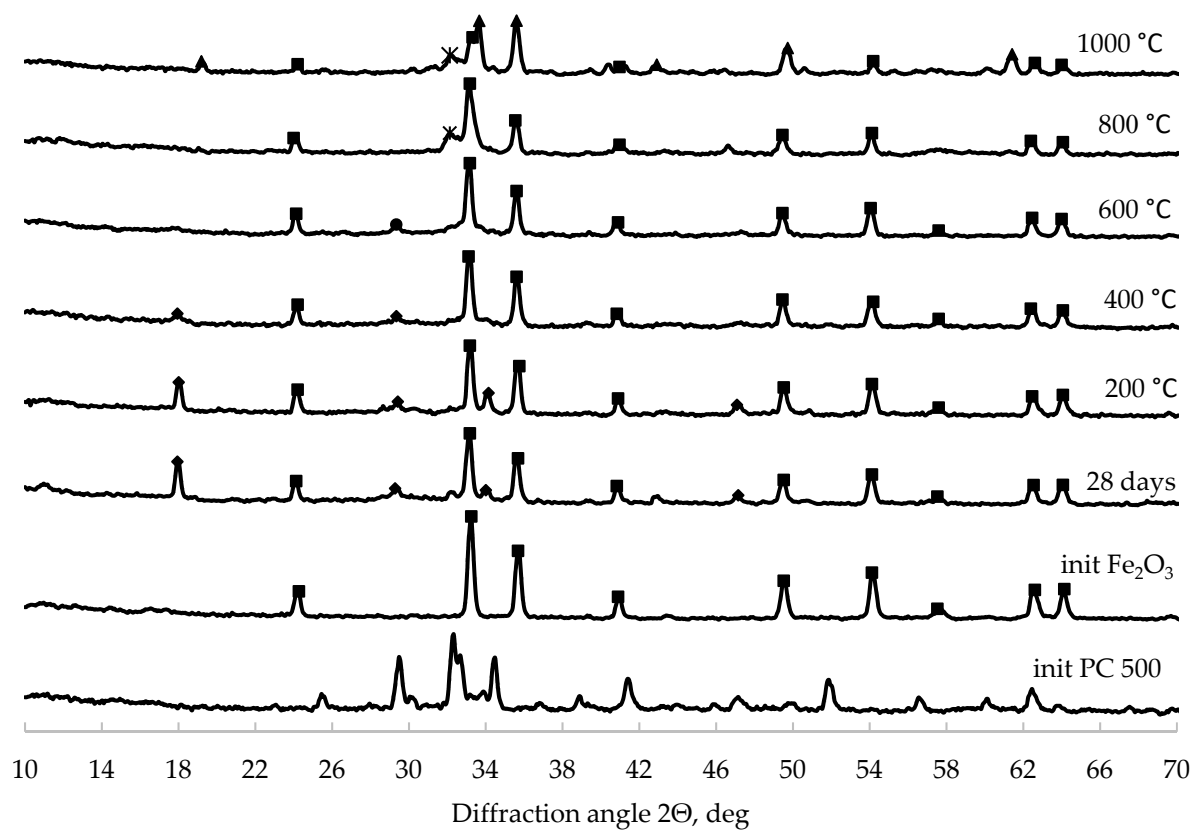


Figure 7. X-ray diffraction pattern of concrete specimens based on PCf mix after heat treatment: ■ = Fe₂O₃; ◆ = Ca(OH)₂; ▲ = CaFe₂O₄; ✱ = Ca₂SiO₄.

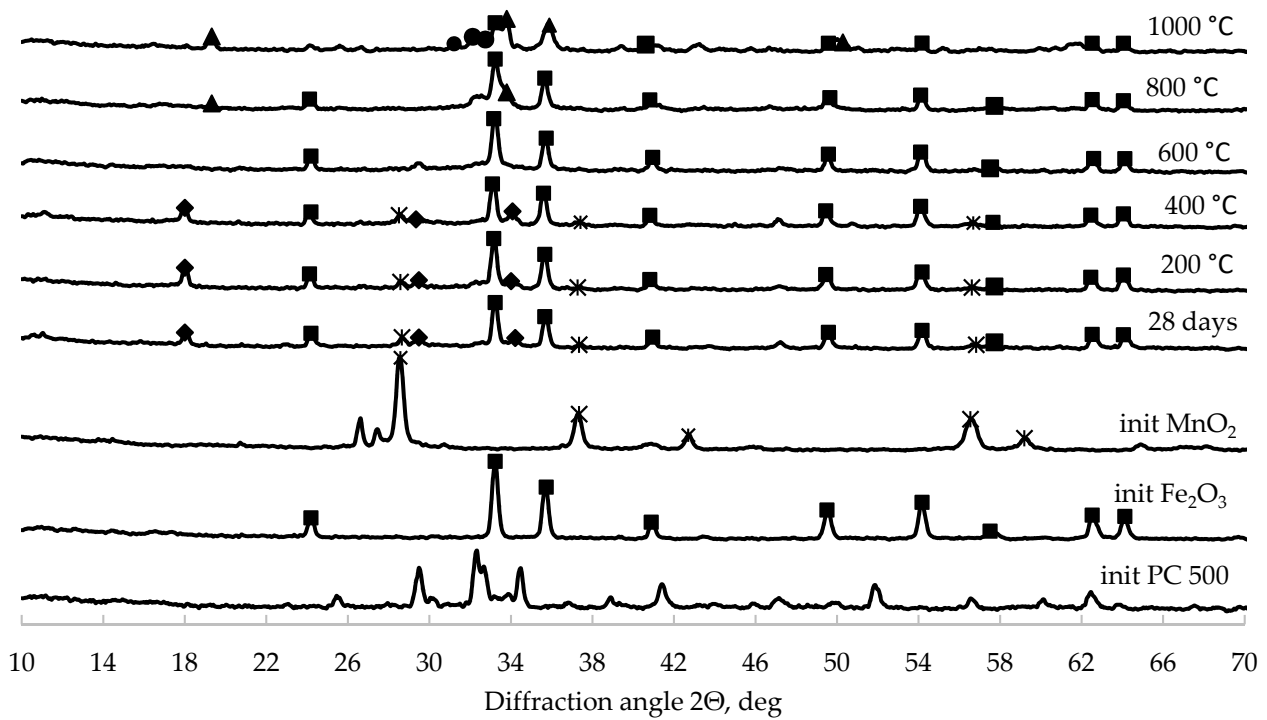


Figure 8. X-ray diffraction pattern of concrete specimens based on PCfm mix after heat treatment: ■ = Fe₂O₃; ◆ = Ca(OH)₂; ● = Ca₂SiO₄; ▲ = CaFe₂O₄; ✱ = MnO₂.

At high treatment temperatures, due to the decomposition of Ca(OH)_2 , CaO is released, which begins to interact with the concrete components with the formation of phase Ca_2SiO_4 as well as with the iron aggregate to form CaFe_2O_4 .

The behavior of concrete based on the PCfm mix is similar. As the temperature increases, there is a decrease in strength of specimens; in the temperature range from 400 to 600 °C, the drop in strength slows down; after 600 °C, it resumes again.

This behavior of this concrete is indicative of the processes that occur in it:

- at 200–400 °C, water removal from the calcium hydrosilicates (dehydration) is observed;
- at 400–600 °C, calcium hydroxide decomposes;
- at 600–800 °C, complete dehydration of calcium hydrosilicates and hydroaluminates occurs;
- at 1000 °C, polymorphic transition of calcium silicate takes place (C_2S to $\beta\text{-C}_2\text{S}$).

A significant decrease in strength properties of Portland cement-based concrete specimens when exposed to high temperatures is mainly due to the process of dehydration of crystalline hydrates. In addition, at high temperatures, polymorphic transformations occur in both the aggregate, i.e., iron oxide powder, and dehydrated calcium silicates and aluminates.

3.1.2. HACK and HACKf Concrete Specimens

Figures 9 and 10 show data on change in density and strength of concrete specimens based on HACK and HACKf, as well as strength and density of concretes based on HACK and HACKf with increasing temperature.

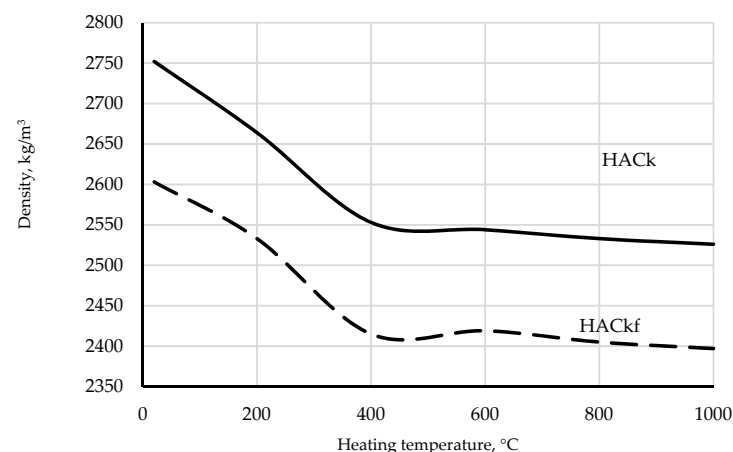


Figure 9. Change in density of HACK and HACKf concretes.

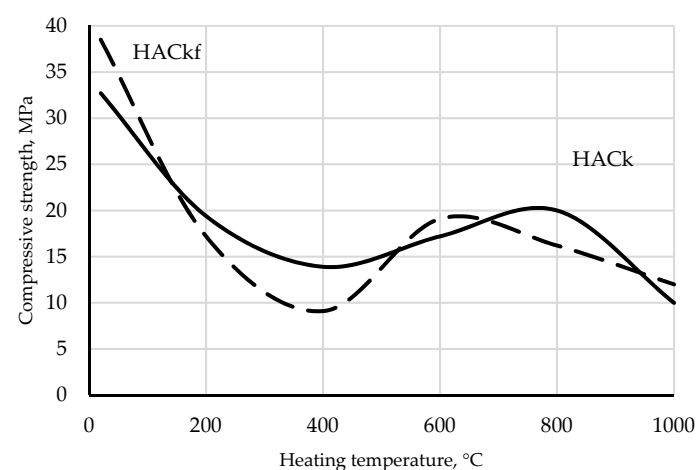
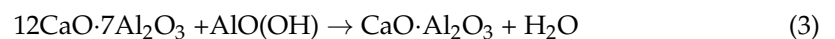
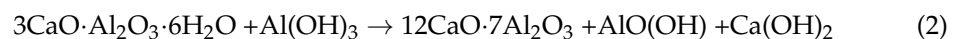
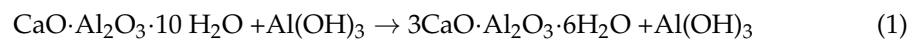


Figure 10. Change in compressive strength of HACK and HACKf concretes.

A change in the phase composition and structure of HACK and HACKf concrete specimens when exposed to high temperature results in a decrease in strength properties but to a lesser extent compared with Portland cement-based concretes. Additionally, after heat treatment at high temperatures of 800 and 1000 °C, no significant external damage only is observed; only small shrinkage cracks can be seen.

When HACK concrete specimens are heated to a temperature of 200 °C, strength drops by 40%. The loss of strength is due to the phase transition of hexagonal phase CAH_{10} into cubic form C_3AH_6 (reaction 1); the occurring reactions are presented below. During further heat treatment up to 400 °C, the process of decomposition of C_2AH_6 and dewatering of $\text{Al}(\text{OH})_3$ occurs. Boehmite $\text{AlO}(\text{OH})$, $\text{Ca}(\text{OH})_2$ and C_{12}A_7 (reaction 2) appear in HACK concrete. In the same temperature range, a significant amount of crystallization water is removed, and strength is decreased by 57.5%. The further increase in temperature to 600–800 °C is due to the formation of C_{12}A_7 . At the same time, the interaction of this compound with boehmite yields calcium monoaluminate (CA) (reaction 3). In this section, the specimen thickens as a result of the developing sintering process, which slows down the rate of strength loss. At 1000 °C, the amount of C_{12}A_7 decreases, and the amount of CA increases, which leads to a sharp drop in strength.



Figures 11 and 12 show XRD data for HACK and HACKf concrete specimens after heat treatment.

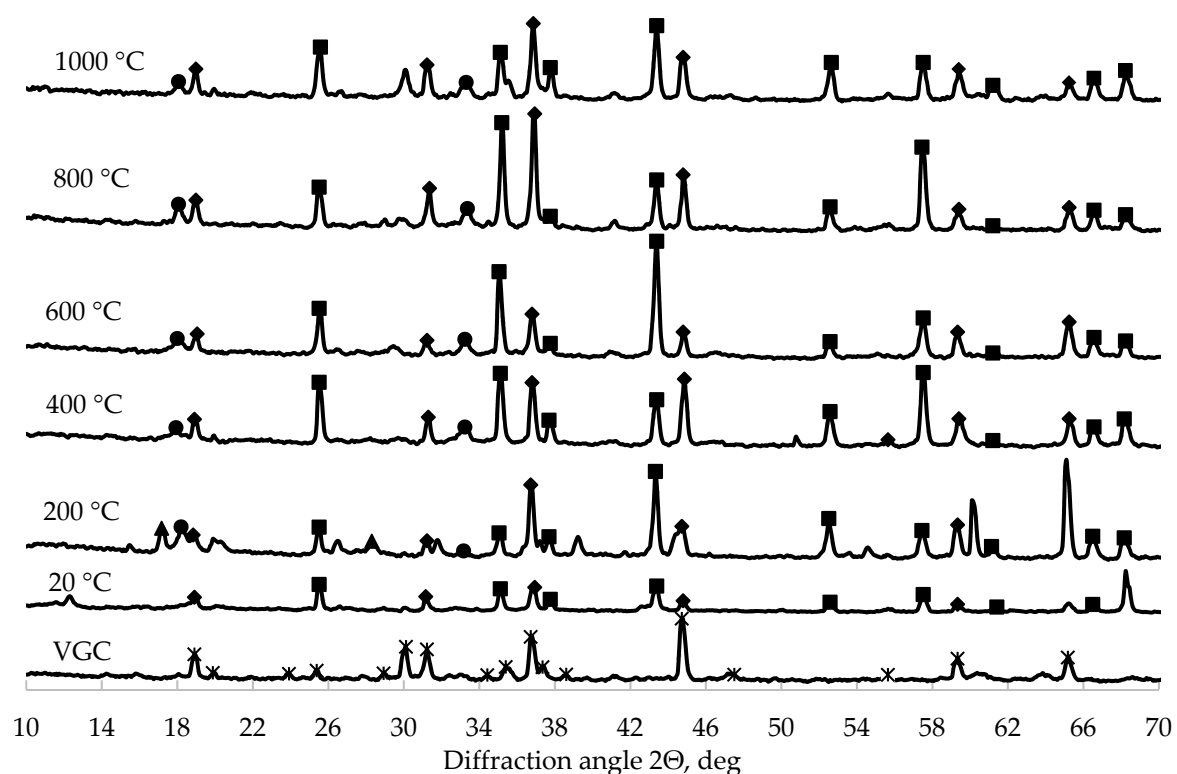


Figure 11. X-ray diffraction pattern of HACK concrete specimens before and after heat treatment: ■ = Al_2O_3 ; ◆ = spinel; ● = $\text{Ca}(\text{OH})_2$; ▲ = CaAl_2O_4 ; ✕ = VGC.

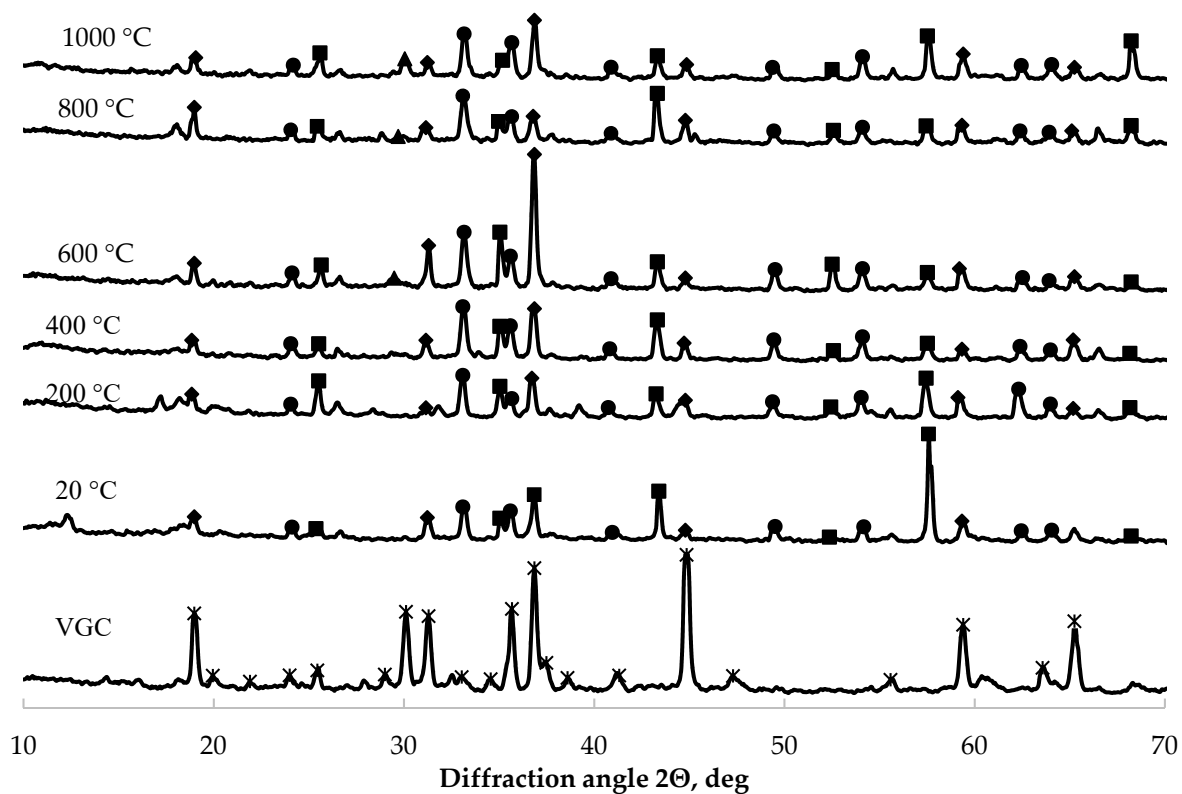


Figure 12. X-ray diffraction pattern of HACKf concrete specimens before and after heat treatment: ■ = Al_2O_3 ; ◆ = spinel; ● = Fe_2O_3 ; ▲ = CaAl_2O_4 ; ✕ = VGC.

Thus, the heating of concretes at all temperatures above 200 °C results in a decrease in strength characteristics. The change in strength vs. heating temperature curves for all concretes is similar. Three strength decrease sections with different strength decrease rates can be identified in the curves. The strength decrease is due to the physical–chemical processes taking place in the concretes. These are processes of dehydration of hardening phases, processes of polymorphic transitions of aggregate and dehydrated phases as well as processes of chemical interaction between concrete components at high temperatures.

3.2. Change in Concrete Properties upon Irradiation

During the service life, concrete structures of the NPP reactor cavity are exposed to considerable radiation loads. This is especially true for devices in close proximity to the reactor. For example, the lower plate and the core catcher are located directly under the reactor.

The concrete mixes for the core catcher are presented in Table 1. Neutron radiation has the greatest radiation effect, but, in this work, the effect of neutrons during irradiation was prevented by the design of the cell, so the main effect was caused by gamma radiation.

According to literature data, natural and artificial minerals predominantly with covalent bonds are subjected to the destructive effect of gamma radiation [2,13–16,32–37] to a greater extent and those with ionic bonds to a lesser extent. Alundum Al_2O_3 is used as aggregate in HACK and HACKf concretes, and powder of iron oxide Fe_2O_3 in the form of hematite mineral is used as aggregate in PCf and PCfm concretes. These substances have ionic bonds with a small fraction of the covalent component. The radiolysis resulting from exposure to gamma radiation will have less effect on the ionic bond and will not lead to a decrease in structural strength. However, when exposed to gamma radiation, structural rearrangement of iron oxide can occur, which results in order–disorder transformations in the structure elements, i.e., amorphization. Hematite can be transformed into magnetite and maghemite.

After irradiation in the vertical channel of the IR-T research reactor, the specimens were tested for bending strength and compressive strength. The data obtained were compared with the initial values before irradiation.

The test results are presented in Table 2.

Table 2. Strength characteristics of initial and irradiated concrete specimens.

Concrete	Initial Specimens		Specimens after Irradiation		Change in Compressive Strength Values, %
	Ultimate Bending Strength, MPa	Ultimate Compressive Strength, MPa	Ultimate Bending Strength, MPa	Ultimate Compressive Strength, MPa	
PCf	2.3	30.7	2.5	35.9	16.9
PCfm	4.3	32.4	3.8	32.7	0.9
HACK	7.0	59.5	6.9	59.0	−0.8
HACKf	8.6	65.5	6.4	45.0	−31.3

Studies of changes in strength properties of concrete specimens exposed to gamma radiation (Table 2) show various changes in both compressive strength and bending strength depending on concrete composition.

3.2.1. PCf and PCfm Concretes

After the exposure, the strength of PCf and PCfm concretes does not decrease but, on the contrary, increases (Table 2). The increase in strength is due to the ongoing transformations in the concrete caused by exposure to radiation and a slight heating. When high-quality Portland cement is used in the composition, the products of hydration and hardening are hydrosilicates, calcium hydroaluminates and calcium hydroxide (Figure 2). When exposed to gamma radiation, the material is heated insignificantly to a temperature of about 70–80 °C. This is accompanied by the process of concrete drying with removal of weakly bound water and dehydration of low-base gel-like calcium hydrosilicates. The released water vapor, as well as the free water present, may undergo radiolysis, which leads to formation of hydrogen gas and H₂O₂. Water vapors and products of radiolysis interact with unreacted Portland cement grains, resulting in additional amounts of low-base calcium hydrosilicates and Ca(OH)₂, which fill the free pore space. These processes compensate for the formation of cracks after drying as well as for destructive changes in the aggregate grains, and the concrete strength is not decreased but, on the contrary, increased.

The suggested stability mechanism of strength properties is confirmed by studies of changes in phase composition. It was found that there is no change in the qualitative phase composition of the cement matrix and aggregates of PCf and PCfm concretes, but there is an increase in hydrate products of hydration, i.e., crystalline hydrates of calcium hydrosilicates and calcium hydroxide (Figures 13 and 14, Table 3).

Table 3. Thermal effects and mass losses during heating of PCf and PCfm concretes.

Stage	Process	PCf		PCfm	
		Temperature Effect, °C	Mass Loss, %	Temperature Effect, °C	Mass Loss, %
1	Removal of free water Dehydration of low-base calcium hydrosilicates	50.0–200.0 50.0–330.0 *	4.69 4.22	50.0–200.0 50.0–345.0	4.45 5.13
2	Dehydration of Ca(OH) ₂ (Dehydroxylation)	420.0–490.0 435.9–467.7	1.99 2.30	420.0–510.0 437.7–465.3	1.97 2.4
3	Decarbonization	610.0–690.0 599.0–685.2	3.31 3.15	590.0–730.0 601.4–670.9	3.59 2.83

* The temperature and mass loss values of concrete specimens before irradiation are shown above the line and those after irradiation below the line.

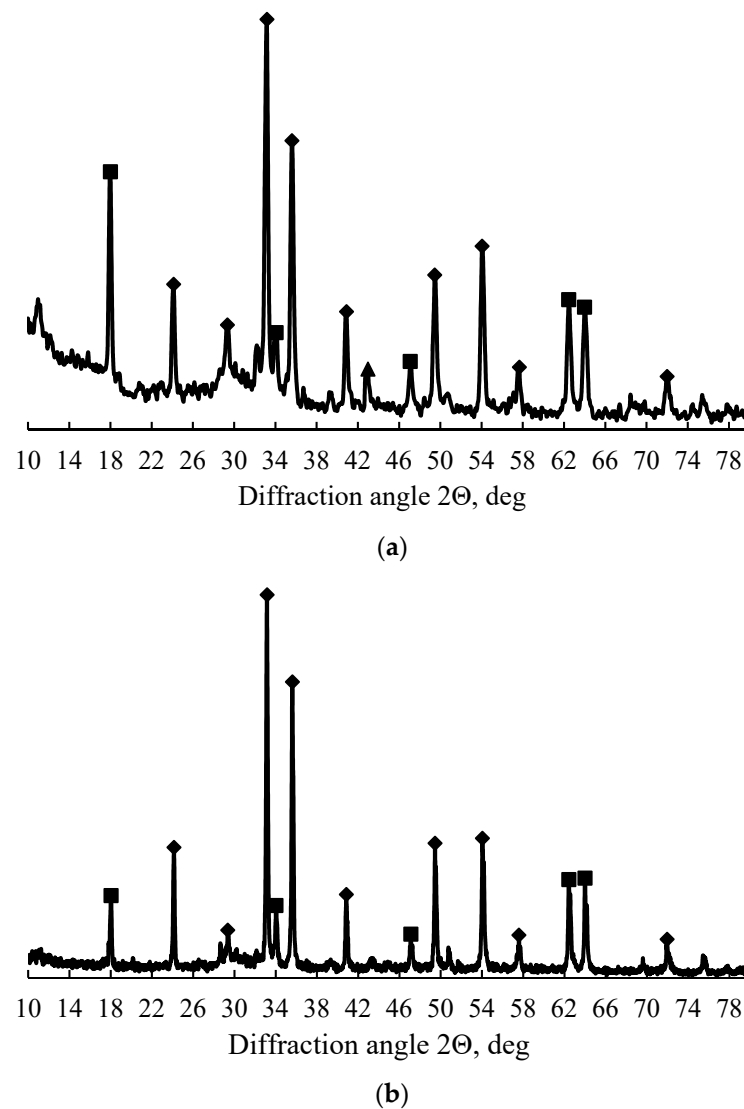


Figure 13. X-ray diffraction pattern of PCf concretes in the initial state (a) and after irradiation (b): ■ = Ca(OH)_2 (000-04-0733); ♦ = Fe_2O_3 (PDF card 000-33-0664); ▲ = Ca_2SiO_4 (PDF card 000-14-0693).

The main crystalline phases after irradiation according to XRD analysis (Figures 13b and 14b) are: manganese oxide MnO_2 ; hematite Fe_2O_3 (for it, a slight increase in reflection intensity is observed); calcium hydroxide Ca(OH)_2 (for this phase, increased crystallinity and intensity is observed). It is also observed that the reflections corresponding to the original non-hydrated cement grains disappear, which is indicative of the hydration of these particles during irradiation. The hydration products themselves are not displayed in the diffractogram as they are in a weakly-crystallized gel-like X-ray amorphous state.

Thermal analysis of PCf and PCfm concrete specimens (Figure 15, Table 3) confirms the data of X-ray phase analysis. The thermograms (Figure 15) of concrete specimens before and after irradiation show the presence of characteristic thermal effects:

- 50–300 °C: removal of free water, dehydration of low-base calcium hydrosilicates;
- 420–490 °C: dehydration of Ca(OH)_2 ;
- 599–690 °C: decarbonization of calcite.

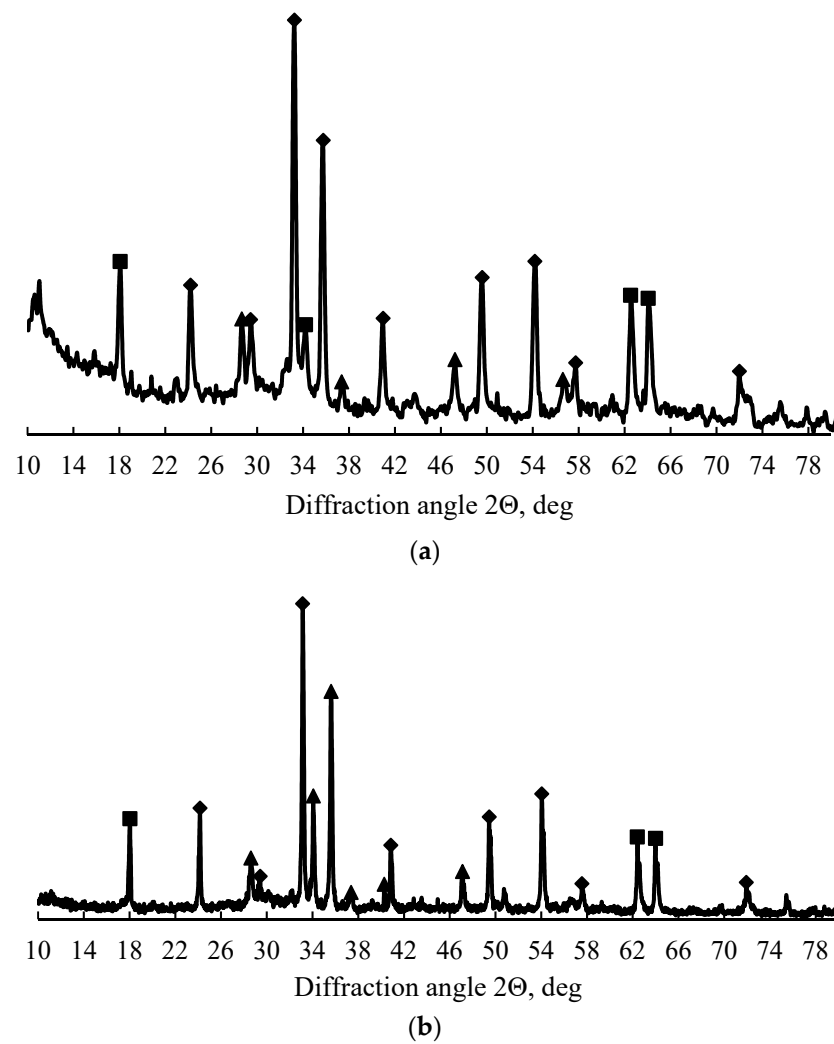


Figure 14. X-ray diffraction pattern of PCfm concretes in the initial state (a) and after irradiation (b): ■ = Ca(OH)_2 (PDF card 000-04-0733); ♦ = Fe_2O_3 (PDF card 000-33-0664); ▲ = MnO_2 (PDF card 000-24-0735).

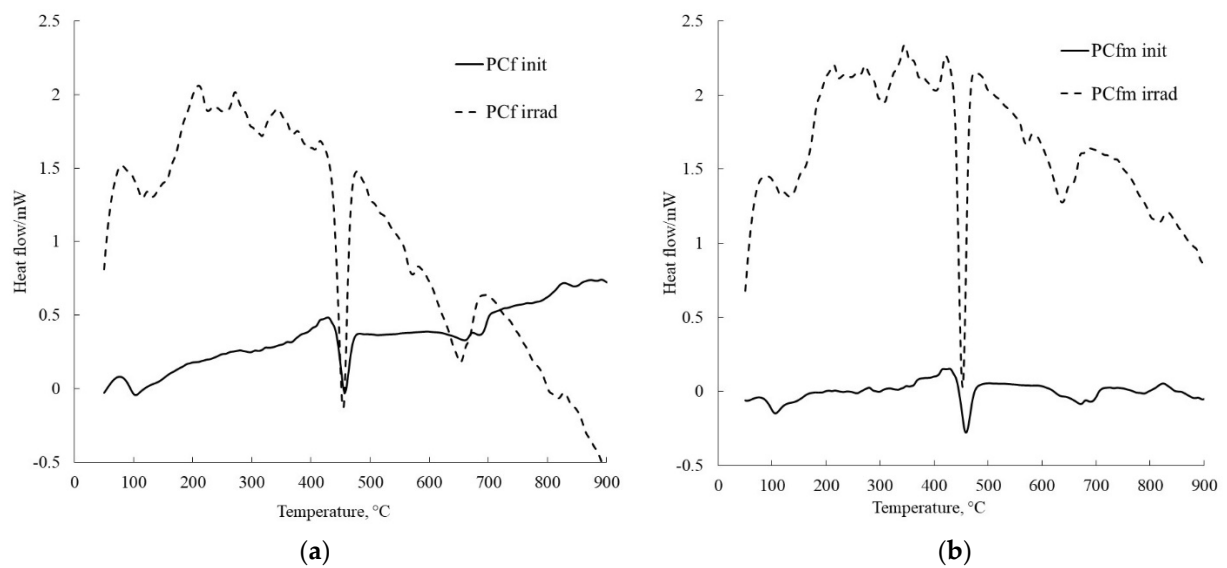


Figure 15. Thermograms of initial and irradiated PCf (a) and PCfm (b) concretes.

These effects are accompanied by loss of mass, which can be used to judge the peculiarities of hardening processes and the effect of gamma radiation on concrete. Upon gamma exposure of the studied PCf concrete, decrease in weight losses during the first temperature period is observed, which is indicative of decrease in free water content in concrete. At the same time, there is a significant increase in mass loss at 420–490 °C, which is indicative of the increase in the number of new hydrate formations, including calcium hydroxide. However, the amount of calcium carbonates in the irradiated PCf concrete decreases since no calcite particles are formed from the resulting Ca(OH)_2 due to limited interaction with the ambient air during irradiation. Thermal analysis of irradiated PCfm concrete specimens shows an increase in mass loss in the temperature range of removal of free and weakly bound water, i.e., 50–300 °C; at the same time, an increase in thermal effects of dehydration of low-base calcium hydrosilicates can be observed in the thermogram. This is also indicative of an additional process of hydration in PCfm concrete under irradiation.

Thus, the occurrence of these processes during irradiation is confirmed by study data. The strength increase value in PCf concretes is larger than in PCfm ones since PCfm concretes contain a larger amount of fine aggregate that consumes water during hardening, and this water is not spent on the formation of hydration phases during further irradiation. It was found that aggregate particles, i.e., iron and manganese oxide powder, remain unchanged, which is confirmed by X-ray phase analysis data.

3.2.2. HACK and HACKf Concretes

HACK and HACKf concretes, which are based on high-aluminate cement, behave differently under irradiation as compared to PCf and PCfm concretes. Strength characteristics of HACK concrete (Table 4) when exposed to gamma radiation remain virtually unchanged. However, there is a decrease in strength after irradiation of HACKf concrete (Table 4), which is due to an abnormal change in the structure and phase composition of the high-aluminate cement matrix initiated by the iron aggregate.

Table 4. Thermal effects and mass losses during heating of HACK and HACKf concretes.

Stage	Process	HACK		HACKf	
		Temperature Effect, °C	Mass Loss, %	Temperature Effect, °C	Mass Loss, %
1	Removal of free waterDehydration of calcium hydroaluminates	50.0–190.0 50.0–190.0 *	4.44 1.81	50.0–190.0 50.0–190.0	3.49 0.69
2	Dehydration of gibbsite Al(OH)_3 , bayerite $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, dehydration of calcium hydroaluminates	196.6–342.9 240.8–336.2	5.34 7.44	190.0–342.0 213.3–301.9	4.14 8.03
3	Decarbonization	640.3–714.5 646.2–692.0	1.28 0.68	600.0–730.0 652.2–710.1	0.72 1.12

* The temperature and mass loss values of concrete specimens before irradiation are shown above the line and those after irradiation below the line.

X-ray phase (Figures 16 and 17) and thermal analyses (Figure 18, Table 4) show a change in the phase composition of HACK concrete. According to the X-ray phase analysis, the main crystalline phases of HACK concrete (Figure 16a) before irradiation are: corundum Al_2O_3 spinel MgAl_2O_4 (aggregate grains) and calcium hydroaluminates $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (base substance of the hardened high-aluminate cement matrix). Due to this mineralogical composition, the concrete has high strength and fire resistance.

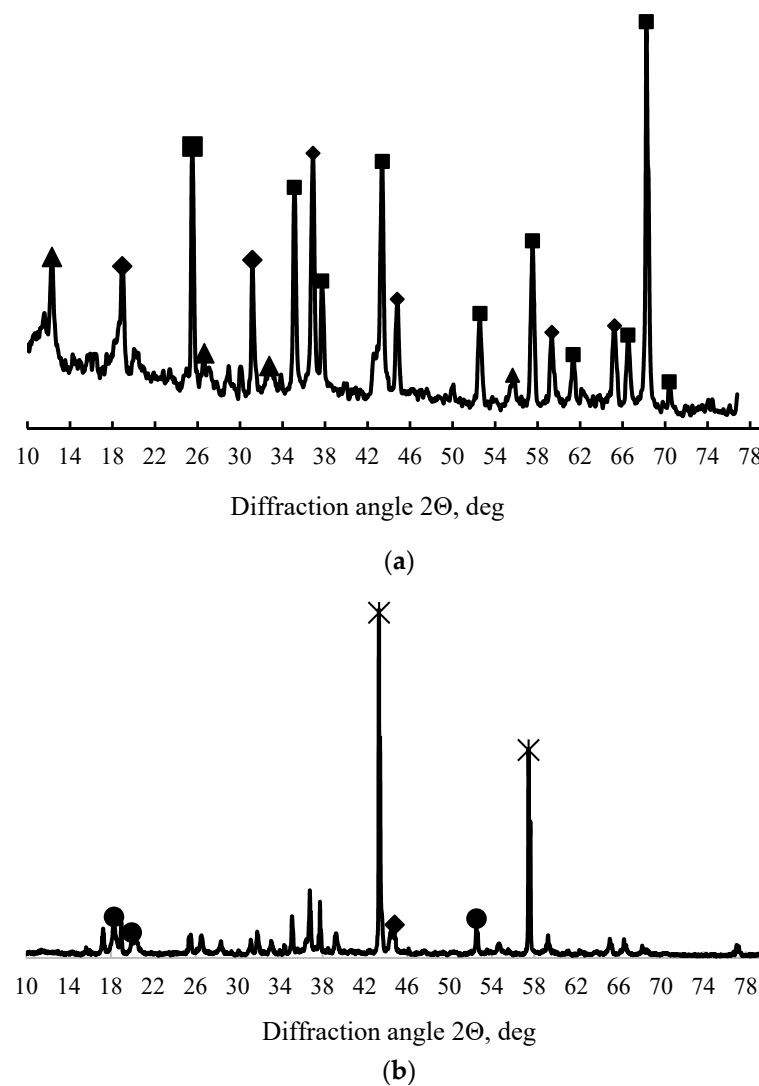
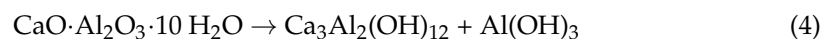


Figure 16. X-ray diffraction pattern of HACK concretes in the initial state (a) and after irradiation (b): Δ = Fe_2O_3 (PDF card 000-33-0664); $\blacksquare$ = Al_2O_3 (PDF card 000-42-1468); $\blacklozenge$ = MgAl_2O_4 (PDF card 000-21-1152); $\blacktriangle$ = $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (PDF card 000-11-0204); $\bullet$ = $\text{Al}(\text{OH})_3$ (PDF card 000-12-0460); $\times$ = $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ katoite (PDF card 000-24-0217).

When exposed to gamma radiation, the phase composition of the aggregate of HACK concrete remains virtually unchanged. However, when exposed to gamma radiation and its thermal effect, the base of the cement matrix, i.e., calcium hydroaluminates $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$, decomposes as per reaction 4, yielding katoite and large amounts of $\text{Al}(\text{OH})_3$ in the form of short-prismatic bayerite (hydrargillite) formations.



The changes experienced by HACKf concrete are almost the same. However, the formation of large amounts of bayerite in conjunction with katoite, iron aggregate and crushed iron ore pellets leads to loosening of the structure and decrease in concrete strength.

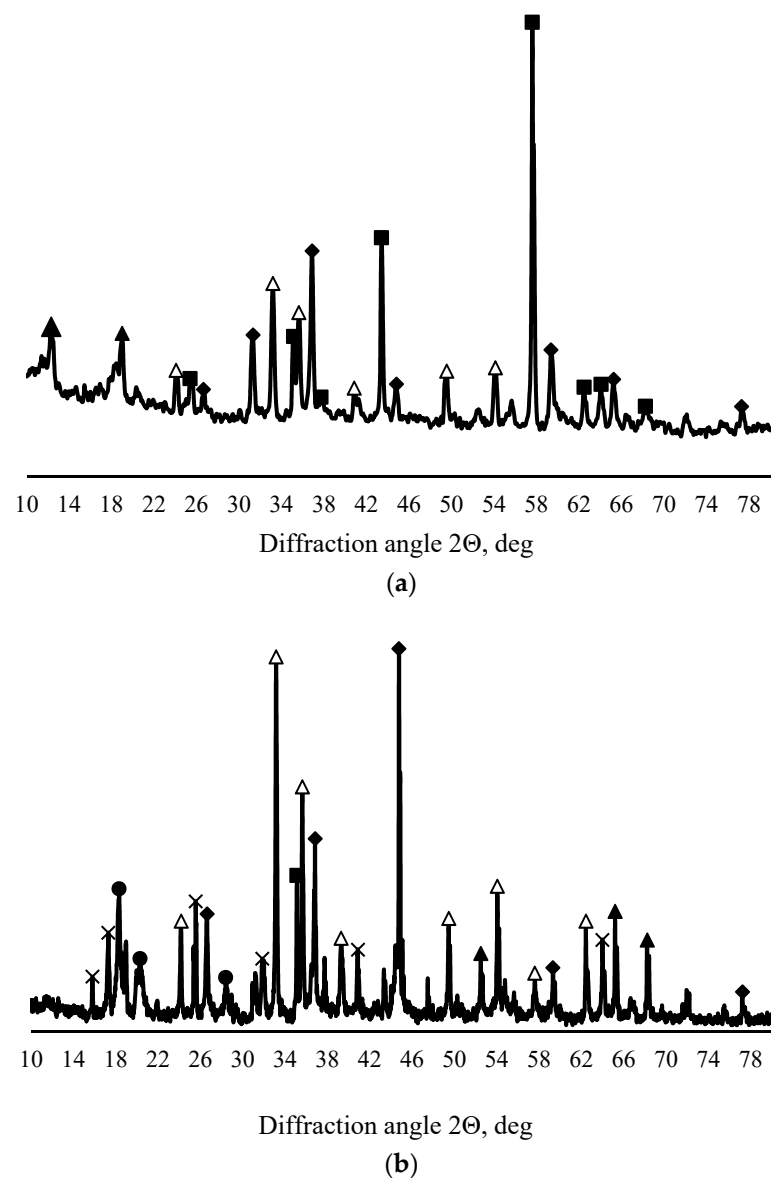


Figure 17. X-ray diffraction pattern of HACKf concretes in the initial state (a) and after irradiation (b): Δ = Fe_2O_3 (PDF card 000-33-0664); $\blacksquare$ = Al_2O_3 (PDF card 000-42-1468); $\blacklozenge$ = MgAl_2O_4 (PDF card 000-21-1152); $\blacktriangle$ = $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (PDF card 000-11-0204); $\bullet$ = $\text{Al}(\text{OH})_3$ (PDF card 000-12-0460); $\times$ = $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ katoite (PDF card 000-24-0217).

Thermal analysis of HACK and HACKf concrete specimens confirms the change in phase composition as a result of gamma exposure. This phenomenon is expressed in the change in values of mass loss of certain thermal effects (Figure 18, Table 4). For instance, the following thermal effects accompanied by mass loss are observed in the thermograms of HACK and HACKf concretes before and after irradiation:

- 50–190 °C: removal of free water, dehydration of calcium hydroaluminates;
- 190–336 °C: dehydration of gibbsite $\text{Al}(\text{OH})_3$, bayerite $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, dehydration of calcium hydroaluminates;
- 600–730 °C: decarbonization.

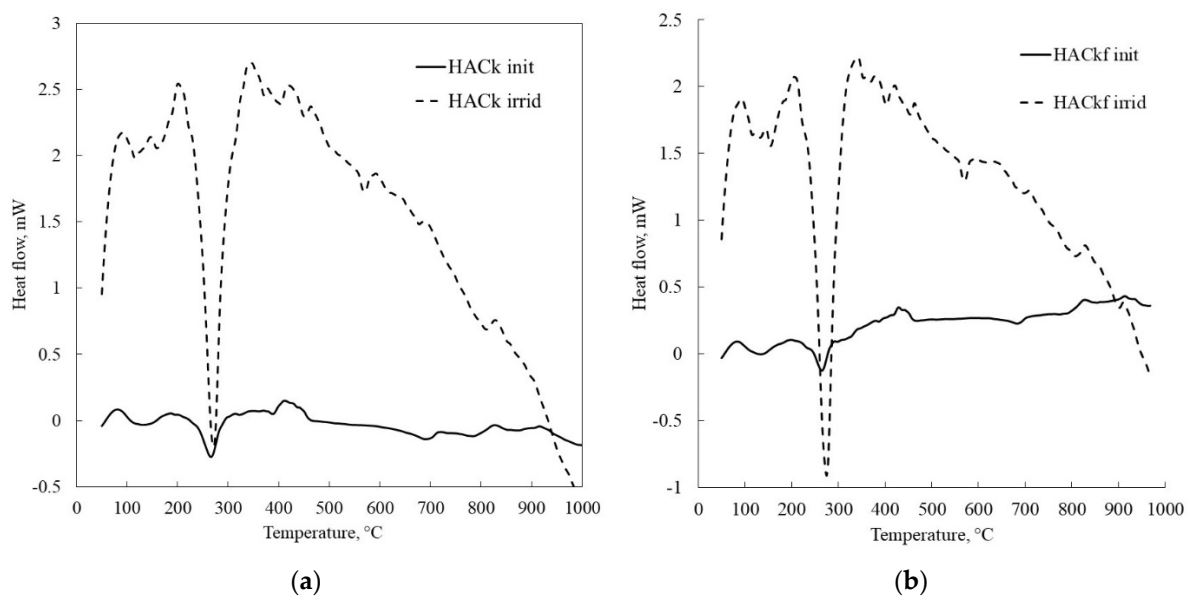


Figure 18. Thermograms of initial and irradiated HACK (a) and HACKf (b) concretes.

In addition, thermograms show exothermic effects at temperatures above 700 °C corresponding to polymorphic transformations of γ - Al_2O_3 into θ - Al_2O_3 formed during dehydration of gibbsite and bayerite. These effects are particularly pronounced in specimens of HACKf concrete after irradiation, which is indicative of an increased content of aluminum hydrate. Additionally, a significant (twofold) increase in the value of mass loss of HACKf concrete in the temperature range of 213.3–301.9 °C after exposure to gamma radiation is indicative of the formation of a critical amount of aluminum hydrate, which decreases the strength of concrete.

Thus, HACK concrete has relatively high resistance to gamma radiation. A significant decrease in the strength of HACKf concrete during irradiation is due to the formation of an increased amount of hydrates of aluminum, gibbsite, bayerite and boehmite.

4. Conclusions

The following main conclusions may be drawn:

- The patterns of changes in the properties of concretes used in the core catcher under high-temperature and radiation exposure have been established.
- Strength characteristics of PCf and PCfm concretes when heated above 200 °C are sharply decreased and have a pronounced step dependence. At 1000 °C, ultimate compressive strength of 22.5 and 25.1 MPa decreased to 1.9 and 2.6 MPa, respectively.
- The strength decrease during calcination of HACK and HACKf concretes, which are based on fire-resistant high-aluminate cement, has a similar nature. After calcination at 1000 °C, compressive strength decreases from 30 to 10 MPa for HACK concretes and from 40 to 12 MPa for HACKf concretes.
- The strength decrease is due to the physical–chemical processes taking place in the concretes during heating. These are processes of dehydration of hardening phases, processes of polymorphic transitions of aggregate and dehydrated phases as well as processes of chemical interaction between concrete components at high temperatures.
- It has been established that during gamma exposure the strength properties of concretes based on Portland cement and iron aggregate are not reduced; on the contrary, strength is increased by 0.9 and 16.9%. This is due to the additional hydration of cement clinker minerals with the participation of water vapors released during the thermal effect of radiation exposure.
- The radiation effect on HACK and HACKf concretes is of the opposite nature. Strength characteristics of HACK concrete remain virtually unchanged since a small amount

of aluminum hydroxide formed as a result of radiation exposure creates a strong structure, replacing the recrystallized particles of calcium hydroaluminates. A large percentage of the strength decrease during irradiation of HAcKf concretes is due to the formation of a large amount of aluminum hydrates, which are unable to form a hardening structure. The decrease in strength characteristics is not critical, as a high compressive strength of 45.0 MPa is maintained.

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