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The Usage of Methylsilicones in Radiation-Chemical Protection of Concrete

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Summary: An influence of the atmosphere components on composite material such as concrete leads to the reduction of its strength and changes in its structure.Having excluded water from a concrete body it is possible to slow down the processes of its corrosion essentially. Traditional waterproofing means have various components with different viscosity in their structure. When applying them on a porous structure of a cement stone chromotropic separation of a hydrophobisator with the loss of its efficiency occurs.The impregnation of concrete by unsaturated organosiloxanes of low viscosity and their blends with dimethylsilyl and methylhydridesilyl oligomers followed by their irradiation induced curing have been studied.Samples of modified cement stone and determination of their physical-mechanical properties, namely compressive strength, waterproofness and frost resistance as well as an influence of impregnation on hydrophobisity of cement stone surface were obtained. Positive effect of the modification proposed on service properties and on durability of radiation-chemically modified concrete was observed.

Keywords: concrete; crosslinking; irradiation by accelerated electrons; polysiloxane

Introduction

Concrete, known to the mankind for ages, is a universal building material. However, an exploitation of energetic, transport and industrial constructions makes increased demands to concrete and ferroconcrete concerning their reliability and durability. The repair of ferroconcrete constructions affected by corrosion requires significant material resources. According to USA and UK specialists' data approximately 40% of all the appropriations to building industry are spent for repairing. The 42% of 578,000 state ferroconcrete highway bridges were recognized as having the defects of corrosion nature in the USA.[1] The cost of their renovation makes up US$ 78 billion. Moreover, secondary economic expenditures appear. In 2005 the annual fuel and downtime costs, connected to the poor condition of ferroconcrete bridges, were estimated at US$ 50 billion.

The essence of the problem is that due to the influence on concrete of atmospheric conditions (water, carbon dioxide, acid gases, chlorides and sulfates of metals and so on) a reduction of its strength, changes of the structure and crippling are observed. The intensity of atmospheric influence on concrete and ferroconcrete is often so high that ready-built constructions require major repairs in 2–4 years after the commencement of operation. The main reason for the loss of performance characteristics of ferroconcrete building constructions is mostly atmospheric corrosion of cement concrete protective layer followed by the corrosion of metal mountings. Therefore, the worldwide problem is the enhancement of the durability of constructions from concrete

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and ferroconcrete and reduction of the costs for running and capital repair. Chemical modification of concrete is used since the first half of the previous century. At the beginning the polymer compositions were introduced into concrete pores at high temperatures or using solvents followed by evaporation of the latter. Later the polymers were replaced by liquid monomers and oligomers that penetrate easier into concrete pores. More frequently, the acrylates, methacrylates, styrene, acrylonitrile are used.[2,3] Traditionally such monomers and their oligomers are cured by chemical method, mostly using radical initiators such as organic peroxides. However, the most promising direction of improvement of concrete technology production and properties is the radiation-chemical modification, which is also profitable from an economical point of view: it demands twice less energy compared to the chemical approach. The occurrence of new techniques of radiation exposure has stimulated intensive developments in this field. Concrete specimens modified by radiation-induced polymerization of reactive monomers were used for construction of bridges, tunnels, blocks. However, along with monomer (oligomer) polymerization in the internal concrete space it is also possible to carry out radiation-chemical grafting of organic material onto mineral substrate. It is known[4] that organopolysiloxanes functionalized with vinyl ethers can be cured using radiation process. Recently[5–12] we have started the research of radiation-chemical modification of concrete using silicone compounds. First results have shown that indeed this approach can help to improve physical-chemical properties of concrete. The objective of this work was to study the effect of silicone structure on physical-chemical properties of radiation-chemically modified concrete.

Materials and Methods

As initial organosiloxanes for impregnating compositions industrial cyclic monomers: vinylheptamethylcyclotetrasiloxane (VCS) and octamethylcyclotetrasiloxane (D4 product) were used. VCS and D4 are radiation polymerizable low-viscosity fluids. Besides these monomers the radiation transformable oligomers polymethylsiloxane (PMS-100), and oligomethylhydridsiloxane (136–157 M product), known as a highperformance waterproofing agent named GKJ-94M,[11] were used. The basic characteristics of the initial compounds are presented in Table 1

The composition of concrete impregnated with monomers was as follows, per 1 m3: cement PC/II-A-SH-400R – 300 kg, sand – 1479.17 kg/m^3, break stone fractions 5-10/10-20–300/930 kg, water – 150 l.

Impregnation of concrete by organosiloxane compositions and irradiation The impregnated initial individual organosiloxane monomers and their mixtures were subjected to irradiation by accelerate electrons in electron accelerator at Institute of Nuclear Research of the National Academy of Sciences of Ukraine. with the following parameters: energy of accelerated electrons - 4,0 MeV, current density of electrons - 200–400 mA/cm^2, dose range - 25–300 kGy.[8]

Hydrophobicity of surface of cement stone samples, impregnated with organosiloxanes and irradiated with electrons, was estimated by measuring wetting angle.[14] Wetting degree of cement stone with water

Table 1.
Characteristics of organosiloxane monomers and oligomers.

Composition/Symbol (chemical name)	Viscosity (20°C) cSt	Molecular weight, g/mol	Density (20°C) g/cm^3
[(CH2 = CH)(CH3)SiO][(CH3)2SiO]3/ VCS (vinylheptamethylcyclotetrasiloxane)	1.2	308	0.96
[(CH3)2SiO]4/D4 (octamethylcyclotetrasiloxane)	1.1	296	0.95
PMS/PMS-100 (polymethylsiloxane)	98	5000	0.98
∼CH3(H)SiO∼/GKJ-94M (oligomethylhydridsiloxane)	84	2000	0.991

was determined by the correlation between adhesion of liquid to solid and cohesion of the liquid itself. This relationship is characterized by interfacial wetting angle (θ) formed by the water drop surface with the surface of cement stone. For the controlled cement samples the value was 53°. Electron microscopy of surface splits of concrete samples, sputtered with gold in order to relieve a dielectric stress, was carried out using scanning electron microscope ZEISS EVO 50XVP (ZEISS production), equipped with energy-dispersing analyzer of X-ray spectra INCA450, detector NCAPentaFETx3 and with HKL CHANNEL-5 system (OXFORD) for diffraction of the reflected beams. FTIR spectra were recorded using Nicollet Nexus 470 with KBr tablets. Probe analysis of chemical elements was done according to the method described in.[13] Water absorption and average density of samples was measured on concrete cubes of a size 100 × 100 × 100 mm according to SSTU B.V.2.7–170: 2008 (Concrete. Methods for determination of average density, moisture, water absorption, porosity and water resistance) and ISO 1920-5 (Testing of concrete – Part 5: Properties of hardened concrete other than strength). Compressive strength was measured on concrete cubes of a size 100 × 100 × 100 mm according to SSTU B.V.2.7-214: 2009 (Building Materials. Concrete. Methods for determination of strength on control samples), EN 12390-2 (Testing hardened concrete – Part2: Making and curing specimens for strength tests) and EN 12390-3 (Testing hardened concrete – Part3: Compressive strength of test specimens).[14–15]

Results and Discussion

Figure 1 represents the dependence of filling of free volume of pores of cement stone with experimental mixtures of silicone compounds for 24h at 25°C. One can see that D4 has the highest penetrating ability (70,4% of open porosity), VCS penetrates slightly less (61.8%). PMS-100 has much higher viscosity (see Table 1) compared to D4 and VCS monomers, but it fills pores (apparently of the largest diameter) up to 48,7%. GKJ-94M product has viscosity close to PMS-100, but it fills pores of cement stone only up to 7,8%, that is 6.2 times lower than PMS-100.

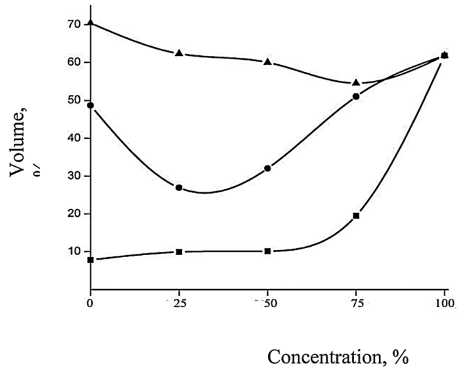


Figure 1.
Dependence of degree of pore free volume filling (V) of cement stone on concentration (C) of vinylheptamethylcyclotetrasiloxane (VCS) in mixtures with: octamethylcyclotetrasiloxane (D4) (▲), polydimethylsiloxane (PMS-100) (●),oligomethylhydridsiloxane (GKJ-94M) (■).

This fact can be associated with chemical adsorption of hydridsiloxane molecules onto cement stone surface through reaction of ≡SiH active groups, leading to sealing of the surface pores and to reducing oligomer mobility in the pore volume. Such behavior of GKJ-94M leads to very low ability of its mixtures with VCS to penetrate inside free pore volume of cement stone even at high excess of VCS in the mixture (Fig. 2, curve c). VCS and D4 are close in chemical structure, therefore the behavior of their mixtures (Fig. 2, curve a) has mainly additive character. Properties of the mixtures of PMS-100 with VCS (Fig. 2, curve b) is described by eutectic dependence with a minimum at25–50% of VCS that is apparently caused by decreasing surface tension of the mixtures compared to the individual compounds. It is known[16] that decreasing surface tension of impregnating compositions impairs wettability of cement stone and consequently impairs the degree of filling of pore free volume.

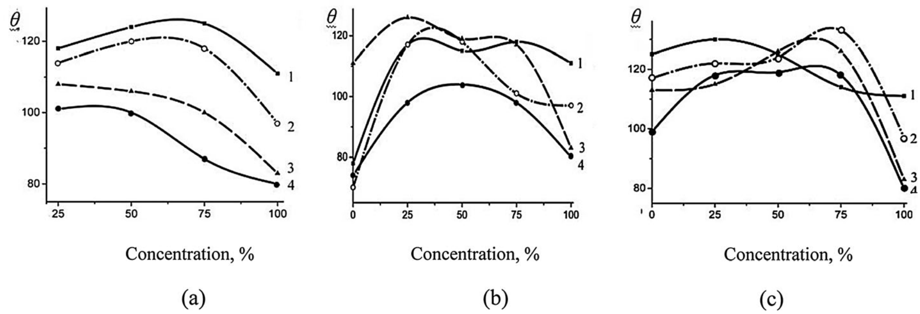


Figure 2.
Dependence of limiting wetting angle (θ) on concentration (C) of vinylheptamethylcyclotetrasiloxane (VCS) in the mixtures with: octamethylcyclosiloxane (D4) (a), polymethylsiloxane (PMS-100) (b), oligomethylhydridsiloxane (GKJ-94M) (c), irradiated with the following doses, Gy: 25 (1), 50 (2), 100 (3), 200 (4).

Initial individual organosilicone monomers and their mixtures were subjected to irradiation in electron accelerator[16] with the following parameters: energy of accelerated electrons – 4,0 MeV, current density of electrons – 200–400 mA/cm^2, dose range – 25–300 kGy. Hydrophobicity of surface of cement stone samples impregnated with organosiloxanes and irradiated with electrons, was estimated by wetting angle measurement. This relationship is characterized by interfacial wetting angle (θ), formed by the water drop surface with the surface of cement stone. For the controlled cement samples the value was 53°. The individual octamethylcyclotetrasiloxane (D4) under model conditions at irradiation dose equal to 300 kGy does not form polymeric products. At low irradiation doses (25–50 kGy) the mixtures of VCS and D4 monomers form a hydrophobic coating on the cement stone surface (Fig. 2a). Within the indicated irradiation doses some eutectic concentration dependence of wetting angle with a maximum at 50–75% of VCS in composition is observed. Increase of irradiation dose up to 100–200 kGy leads to reduction in hydrophobic properties of the surface layer of cement stone. Regularity of θ decrease with increasing irradiation dose is common to all compositions (Fig. 2a). This fact can be explained by radiation degradation of the polymer obtained at increasing irradiation dose. Extraction was carried out using Soxhlet's apparatus and gel fraction content was determined as a part that was insoluble in oxylene for 16 h. Obviously, the extraction affects not only reconstruction of molecular chains due to recombination, but is also accompanied by the loss of methyl groups.[17] Taking into account that the brush of methyl groups provides water-repellent film on the surface of solids, one can assume that substantial destructive processes of polymers occurred on a surface of cement stone are reflected in decreasing θ value. Study of chemistry of interaction of silicone compounds with concrete using methods of FTIR spectroscopy and Scanning Electron Microscopy From microphotographs of split surface of cement stone (impregnated with VCS/D4 mixture and irradiated with accelerated electrons with irradiation dose of 50 kGy) made by scanning electron microscopy (SEM) one can see crystals of calcium hydroxide with fuzzy edges (see Fig. 3). This fact may testify to the presence of chemical interaction between the components of cement stone and chemical components of the impregnating composition. Such behavior is not typical for other samples. Analyzing the chemical compositions for impregnation, one can admit that D4 interacts with $Ca(OH)_2$. This assumption is in a good agreement with the literature data. It is known[18] that in the presence of alkali decomposition of siloxane bond of D4 cycle takes place (see Scheme 1).

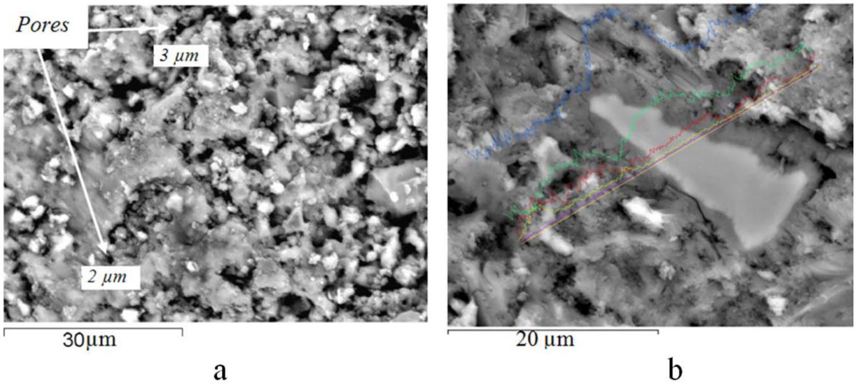
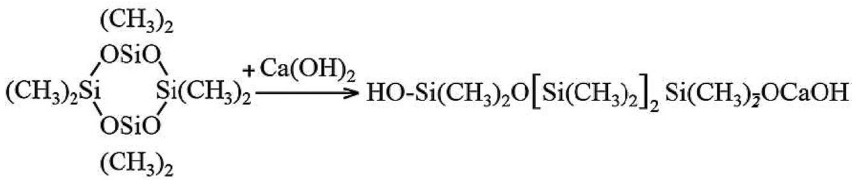


Figure 3.
Photos of microstructure of cement samples: a – controlled sample, b – sample impregnated with mixture of VCS/D4 and irradiated with 50 kGy.

Such chemical reaction is confirmed by FTIR spectra. In a spectrum of the sample of initial cement stone (see Fig. 4) the bands of valence vibrations corresponding to OH groups of calcium hydroxide and crystalline hydrates at 3643 cm^{-1}, and narrow bands at 875 and 713 cm^{-1} relating to valence vibrations of Ca-O bond are observed.



Scheme 1.

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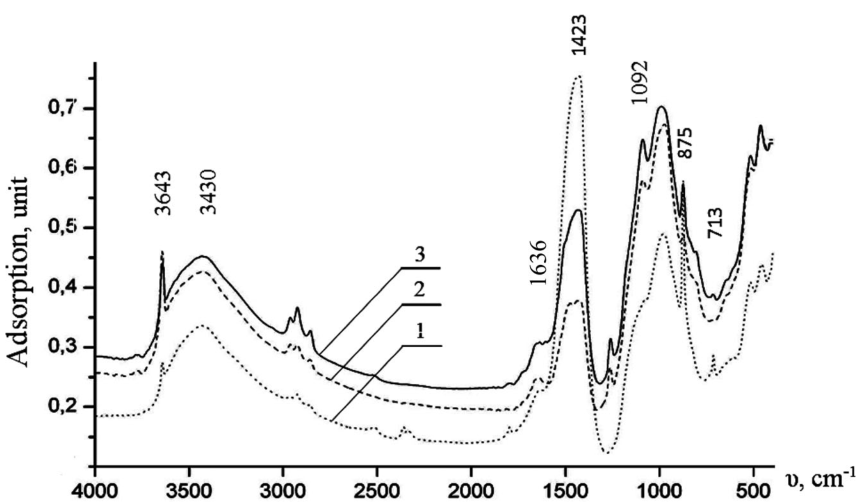

Figure 4.
Infrared absorption spectra of samples of cement stone: controlled (1), and impregnated with VCS/D4 mixture after irradiation, kGy: (2) 100, (3) 200.

After impregnation of cement stone with VCS/D4 mixture and irradiation treatment an intensity of absorption of hydroxyl groups changes. Shift and extension of absorption band of hydroxides with maximum at 3430 cm^{-1} occur that indicates the presence of OH groups with different energy in the system. Moreover, shift by 812 cm^{-1} of valence bands of Ca-O bonds to low-frequency region is observed.

Similar transformations at the conditions used are not observed for the individual VCS, probably due to degree of stress of its cycle and redistribution of electron density in the molecule. Using probe microanalysis the chemical elements distribution on a surface of crystal of calcium hydroxide with fuzzy edges was determined (see Fig. 5). The analysis of the results shows that in transition (fuzzy on photos) layer of crystalline formation (zone B) the content of calcium is higher than in surrounding cement mass (zone C), but lower than in central part of the split of crystal (zone A). At that, concentration of silicon in transition zone (B) is minimal. The unsteady distribution of silica on the probe surface may be caused not only by filling of pores with impregnating VCS/D4 composition, but also by chromatographic separation of the latter along the thickness of cement stone. Due to different adsorbing capacity and, therefore, to various speeds of penetration of compounds of impregnating mixture on an active layer of cement stone an accumulation of D4 near the surface of Ca(OH)2 crystals and the reaction (1) are expected that, consequently, leads to the formation of the transition zone B. Average chemical elemental analysis of the surface splits of the impregnated cement samples (see Table 2) shows that oxygen content increases compared to the controlled sample, apparently due to the presence of this element in the molecules of silicones. Saturation of cement stone with silicone leads to logical decrease of magnesium and potassium content in the samples (Table 2).

Properties of the Modified Concrete

Durability of concrete is characterized by a complex of characteristics including compression strength, frost resistance, water impermeability and water absorption, abrasion. Efficiency of chemical compositions used in concrete impregnation is determined by porosity of concrete. Therefore, the selection of concrete type was

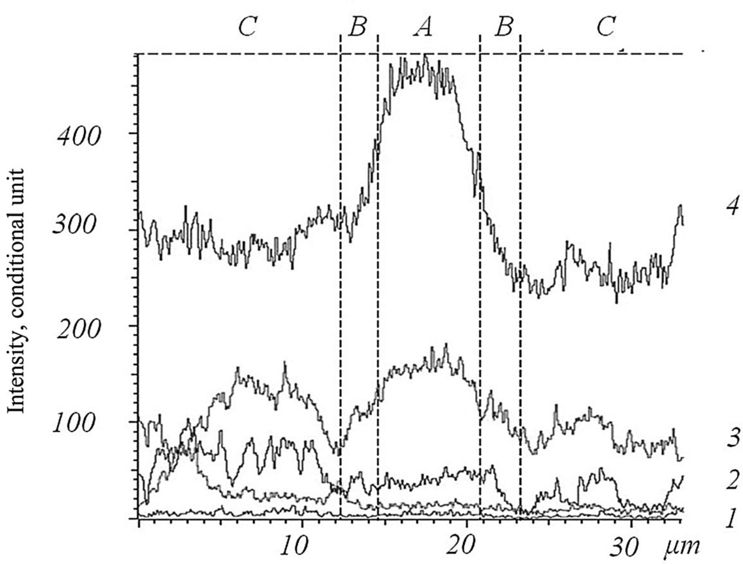

Figure 5.
Distribution of chemical elements on the split surface of crystal: 1–calcium,2–silicon.

Table 2.
Average chemical elemental analysis of surface split of the cement samples.

Composition	Dose, kGy	Elemental composition, mass. %					
		O	Mg	Al	Si	K	Ca
Control nonimpregnated concrete samples	50	44.9	0.49	1.35	6.85	0.88	39.2
VCS: D4	50	47.3	0.39	1.44	9.36	0.51	35.3
GKJ-94M	50	47.0	0.42	1.27	10.1	0.55	32.3

determined by its permeability: the higher permeability of concrete, the better its impregnation with monomer. Permeability of concrete is defined by water impermeability and indirectly by water absorption. According to the guidelines the composition of concrete with presumably low water impermeability marked as W2 was selected for research. After impregnation of concrete samples with monomers during optimal time of impregnation and their irradiation with accelerated electrons the concrete samples were tested for compression strength, frost resistance, water impermeability, water absorption and abrasion. Similar tests were made on non-impregnated and nonirradiated controlled concrete samples. Determination of average density of the concrete samples impregnated with silicone monomers has not shown a significant difference compared to the nonimpregnated concrete. The results of evaluation of water absorption and compression strength of the impregnated and irradiated concrete samples are given in Table 3. Analysis of the data presented in Table 3 shows that impregnation of concrete with silicone monomers and their mixtures, followed by radiation treatment of the impregnated concrete increases its strength (almost by 1,5 times) that can be explained by formation of polymer inside concrete pores and formation of complex organosilicone bonds as a result of chemical interaction of silicones with cement stone. Impregnation of concrete samples with GKJ-94 and their subsequent irradiation does not affect durability of the material.

Impregnation of concrete with silicones followed by radiation treatment reduces water absorption of concrete (see Table 3). This effect is explained by pore colmatage by organic compounds (silicones), and in a case of GKJ-94M it is explained by its waterproofing effect. Table 4 presents the results of determination of water impermeability of concrete. The analysis of the data presented in Table 4 shows that impregnation of concrete samples with silicone monomers and their subsequent radiation treatment allow significant improvement of water impermeability from W2 grade to W6 grade (grades of concrete according to their water impermeability[19]) for the compositions based on VCS, however for concrete impregnated with GKJ-94M the water impermeability grade increases even to W8, that may be explained by hydrophobic effect of this organic compound.

Table 5 represents the results of frost resistance measurements of concrete pre-impregnated with silicone compositions and irradiated with accelerated electrons using accelerated technique.[8] The controlled

Table 3.
Compressive strength and water absorption of concrete samples impregnated with silicone compositions.

Composition	Water absorption of concrete, %	Compressive strength of concrete samples, MP
Control nonimpregnated concrete samples	1.60	23
VCS/D4 = 75/25	0.28	30
GKJ-94M	0.05	23

Table 4.
Impermeability of concrete impregnated with silicone compounds.

Samples (sample height, cm)	Plan grade on impermeability	Actual grade on impermeability
Control nonimpregnated concrete samples	W2	W2
Concrete impregnated with VCS:D4 composition and irradiated	W2	W6
Concrete impregnated with GKJ-94M	W2	W8

Table 5.
Results of determination of changes in the strength values of concrete, impregnated with silicones, after 200 cycles of alternate freezing and defrosting (frost resistance).

Compression strength	Concrete samples impregnated with the following silicones and irradiated	
	VCS:D4	GKJ-94M
Before tests, MPa	34.5	31.0
After tests, MPa	33.4	35.75
Change of strength, %	−3.2	+15.3

samples of the nonimpregnated concrete do not correspond to the frost grade F 150, because after 150 cycles of alternate freezing and defrosting they got destroyed and were withdrawn from further testing. On the contrary, impregnation of concrete with silicone compositions with following irradiation provides increase in frost resistance corresponding to the frost grade not less than F 200.

Conclusion

1. The concrete modified with radiation curable silicone compounds was obtained by surface impregnation of concrete samples by low-viscosity silicone compositions followed by irradiation by accelerated electron bunch.
2. The method of irradiation of silicone monomers/oligomers with accelerated electrons was adapted for radiation curing of silicone compositions in concrete (cement stone).
3. The physical-chemical and mechanical properties such as compression strength, impermeability, chemical and frost resistance of cement stone surface were determined. Positive effect of the radiation-chemical modification on performance characteristics and durability of concrete was observed. Impregnation of cement with silicone monomers and their mixtures with further radiation treatment allows increasing compression strength of standard concrete samples by 1.5 times, their grade on water impermeability by 2–3 times, frost resistance by 2 times.
4. Using FTIR spectroscopy, SEM and probe chemical analysis, chemical grafting of siloxane monomer D4 onto the cement stone surface through interactions of methyl groups of D4 with hydroxyl groups of calcium hydroxide as a part of cement stone was detected.

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