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APPLICABILITY OF ALKALI-ACTIVATED CEMENT FOR IMMOBILIZATION OF LOW-LEVEL RADIOACTIVE WASTE IN ION-EXCHANGE RESINS

P. Kryvenko
Doctor of Technical Science, Professor*
E-mail: pavlo.kryvenko@gmail.com
H. Cao
PhD, Professor**
E-mail: caohl@hit.edu.cn
O. Petropavlovskyi
PhD, Senior researcher*
E-mail: petropavlovskii@mail.ru
L. Weng
PhD, Professor**
E-mail: leeweng@126.com
O. Kovalchuk
PhD, Senior researcher*
E-mail: kovalchuk.oyu@gmail.com
*V. D. Glukhovskii Scientific Research
Institute for Binders and Materials
Kyiv National University of Construction and Architecture
Povitroflotskyi ave., 37, Kyiv, Ukraine, 03037
**Shenzhen Academy of Aerospace Technology
Advanced Materials Research Institute
The Tenth Kejinan Road, High-tech Zone,
Nanshan District, Shenzhen, PR. China, 518057

Розглянуто два типи радіоактивних іонообмінних смол із низьким рівнем активності: суміш катіонної та аніонної смол у пропорції 2:1 та аніонообнінну смолу. Наведено результати розробки компаундів відповідно до вимог стандартів КНР GB 7023 та GB 14569. Доведено високу ефективність використання шлаколужних систем для імобілізації рідоактивних відходів

Ключові слова: лужно-активовані цементи, геополімери, імобілізація, радіоактивні відходи низького рівня активності

Рассмотрены два типа радиоактивных ионообменных смол с низким уровнем радиоактивности: смесь катионной и анионной смол в пропорции 2:1 и анионообменная смола. Представлены результаты разработки компаундов в соответствии с требованиями стандартов КНР GB 7023 и GB 14569. Показана высокая эффективность использования шлакощелочных систем для иммобилизации радиоактивных отходов

Ключевые слова: щелоче-активированные цементы, геополимеры, иммобилизация, радиоактивные отходы низкого уровня радиации

1. Introduction

The basic method used for immobilization of low- and intermediate radioactive wastes is to incorporate them into a cement matrix in order to provide their safety for human health and environment for a long period of time [1].

There exist a great variety of radioactive wastes that are difficult to process by cementation and, therefore, require an individual approach to their processing. That is why a priority task is to develop new formulations of cements that would enhance immobilization of these wastes. Ion-exchange resins are the most difficult to process among all varieties of wastes such as liquid organic wastes, salt solutions containing large quantities of surfactants, filtrating materials, bottom precipitants or soils, and ash residues. Due to their nature, ion-exchange wastes are incompatible to cement stone hydration products; therefore, radioactive nuclides are retained in a cement matrix only due to physical or adsorption binding. These wastes are difficult to incorporate in final products, and only small quantities of these wastes can be incorporated.

2. Analysis of the scientific references and formulation of the problem

The most advantageous cements for immobilization of radioactive wastes are the alkali-activated cements (for example, geocements) [2–4], which are themselves a combination of aluminosilicates and alkali-metal compounds [5]. In case of natural aluminosilicate minerals such as kaolinite and montmorillonite, hydration products are analogs to naturally occurring zeolites of the Me_2O Al_2O_3 (2–4) SiO_2 $2H_2O$ type (where M is an alkali metal). These are: hydronepheline, natrolite, kaliophilite, analcime, etc. [6]. In case of metallurgical slags (alkali-activated slag cement), hydration products also contain tobermorite-like basic calcium silicate hydrates, hydrogarnets, as well as alkaline-earth and alkali-earth aluminosilicate hydrates [7].

When these cements are used for immobilization of radionuclides represented by alkaline-earth and alkali-earth elements, these elements are safely incorporated in the solidified waste structure (final products) as its constituents.

Synthesis of zeolite-like hydration products in the alkali-activated cement matrix, which are known for their excellent sorption property, is an additional factor to provide physical binding of radioactive elements. Thus, hazardous elements not only form a structure of the final product but turn out to be locked in a three-fold lattice of the zeolite matrix, which has many energy-unsaturated cavities [8].

The mentioned mineral-like hydration products exhibit high durability, water resistance, and high strength [9, 10]. Similar compounds were discovered in the structures made of ancient concretes, which explains the substantial durability of these concrete structures that have remained undamaged until now.

Analysis of the research findings lets us anticipate high efficiency of using alkali-activated cements for immobilization of radioactive wastes because of higher durability of the new formation phases in comparison with traditional analogues.

3. The purpose and objectives of the study

The purpose of the study is to optimize compositions of the alkali-activated cements for immobilization of low-level radioactive ion-exchange resins and study the properties of the resulting final products.

In accordance with the set goal, the study objectives are as follows:

– to provide a grout design using two types of ion-exchange resin;

– to study the effect of the quality of raw components (alkaline component, clay component, and Ca-containing component) on properties of the final product;

– to study service properties of the developed final products.

4. Materials and testing methods

The radioactive waste for immobilization includes: a mixture of cation and anion-exchange resins (taken as 2:1 with 50 % water content by mass), $CsNO_3$ – 7.5 g/l, $Sr(NO_3)_2$ – 12 g/l, boron acid – 74.8 g/l, and NaOH – 80 g/l. Density of the resulting pulp was 1180 kg/m^3, and pH=12.

The requirements to the grouts are as follows: waste (pulp) loading-not less than 60 % by volume, flow ≥180 mm, the initial setting time ≥2 hours, and the final setting time <36 hours. The alkali-activated cement-based grouts have been prepared in a mixer of the “Hobart” type.

First the pulp was properly mixed in a plastic container where it was kept for good distribution of the resin particles. The properly homogenized ion-exchange resin pulp was brought into a mixer bowl, then the alkali-activated cement components were added and a final mixing took place (for 7 min).

The flowability of the alkali-activated cement-based grouts was measured by two methods: (1) the Vicat cone and (2) with the help of a special testing equipment (a paddle with openings). Testing by the latter method showed that in case the flow value =180 mm, “cleansing” of the openings took place 1–2 seconds after the paddle was lifted from the mixer bowl (Fig. 1).

Fig. 1. Determination of flowability (VISUAL ASSESSMENT) with a special testing equipment (a paddle with openings)

This value (1–2 sec) means and guarantees that the paddle will be capable of “self-cleansing” and no any grout will remain on the mixing tool (paddle). In this case, no any cleansing of the mixing tool is required before the next charge of grout constituents.

Beam (40×40×160 mm) and cylinder specimens (d=h==50 mm) were made of the developed alkali-activated cement-based grouts. 1–2 days after demoulding, the specimens were placed in a laboratory climatic chamber or exicator for further curing during the following 28 days.

Stability of the alkali-activated cement-based grouts to water (free liquid) was determined with the help of cylinder specimens (d=120 mm; h=800 mm).

5. Results and discussions

5. 1. Mix design of the solidified waste forms (final products)

The known data [12] on the role of each alkali-activated cement constituent in formation of the above properties served as a basis for studying the effect of the amounts of clay components-bentonite and Ca-containing components (OPC or $Ca(OH)_2$), as well as types and quantity of alkaline activator ($Na_2O{\cdot}SiO_25H_2O$ or Na_2CO_3). Test results are given in Table 1.

Analysis of the data presented in Table 1 reveals the influence of each constituent on the above listed properties.

The effect of alkaline activator

The alkaline activator content in the alkali-activated cements should be calculated to provide the initial setting-not earlier than after 2 hours, and the final setting-not later than after 36 hours. As it follows from Tables 1 and 2, the final products containing Type I and Type II ion-exchange resins met the target requirements (with the exception of composition 4C). In addition, alkaline component was found to affect strength gain of the final product, especially at early stages of hardening. Therefore, for example, the final product containing Type I ion-exchange resin in case of $Na_2O{\cdot}SiO_25H_2O$ after 1 day of hardening had a compressive strength of 6.9–8.0 MPa (compositions 4C and 5C), after 6 days – 15.2 MPa (composition 5CM-1), in case of Na_2CO_3 the compressive strength of similar formations was 6.25–7.4 MPa (compositions 9C and 9CM), after 6 days – 8.2 MPa (composition 9CM).

However, at the later stages of hardening this difference in strength development tended to become closer.

Evidently, the final choice in favor of this or that alkaline component can be made after completion of all scheduled testing of the final products such as leachability, pore structure, resistance to elevated and subzero temperatures, free liquid, and fire resistance.

The effect of the clay component

The clay component in the composition of the final product plays a double role: at the stage of grout preparation, it acts as a regulator of rheological properties, whereas at the stage of properties formation, it gives rise to adsorption properties of the alkali-activated cement matrix with regard to radionuclides. In addition, in the presence of alkali it can serve as a formation source for alkaline and alkaline-earth aluminosilicate hydrates that are known to affect favorably both adsorption properties and durability of the final product.

The study of rheological properties of the alkali-activated cement-based grouts showed that at the stage of grout preparation the bentonite additive is more preferable (acts better) than the kaolin one.

The research findings show that flowability of the alkali-activated cement-based grouts depends on the amount of the bentonite additive. Thus, composition 1C without bentonite had a flow value of 235 mm, whereas with 8.2 % bentonite by mass the flow value lowered down to 127 mm (composition 2C).

Table 1

Constituents, compositions and properties of the final products containing Type I ion-exchange resin

Composition number		1C	2C	3C	4C	5C	5CM–1	5CM	6C	6CM	7C	8C	9C	9CM	10C
Constituents		% by mass													
S–1 (slag, ggbs)		38.4	32.7	34.6	38.6	40.0	40.8	39.4	35.2	35.4	35.6	36.8	35.2	34.3	40.2
$Na_2SiO_35H_2O$		6.6	5.6	5.9	5.9	6.6	6.7	6.5	–	–	–	–	–	–	–
Na_2CO_3		–	–	–	–	–	–	–	2.5	3.0	1.6	2.4	2.2	3.0	2.5
OPC		9.9	8.4	8.9	–	–	–	–	8.8	8.8	8.8	–	–	–	–
Bentonite		–	8.2	5.5	5.5	2.8	3.7	3.6	5.2	4.5	5.1	4.9	4.7	4.0	2.5
$Ca(OH)_2$		–	–	–	4.9	5.5	5.6	5.4	–	–	–	4.7	4.5	4.0	4.9
Ion-resin pulp (mixture of cation and anion exchange resin)		45.1	45.1	45.1	45.1	45.1	43.2	45.1	42.4	42.4	41.9	40.1	43.7	45.0	41.3
H_2O		–	–	–	–	–	–	–	5.9	5.9	7.0	11.1	9.7	9.7	8.6
Flow, mm		235	127	180	135	170	200	210	150	183	160	155	170	187	160.0
Waste (pulp) loading, % by volume		63.2	63.3	63.2	62.4	62.2	60.4	62.5	60.2	60.3	59.2	54.2	58.3	60.0	57.0
Initial setting time, hr-min		Over 2 hours			1–30	Over 2 hours									
Final setting time, hr-min		Shorter than 22 hours													
Compressive strength, MPa	1 day	3.9	5.1	4.0	4.7	4.4	5.1	3.9	4.8	4.2	3.6	–	–	–	–
	3 days	6.3	6.0	6.6	8.0	6.9	–	–	–	–	–	7.1	6.25	–	7.4
	4 days	–	–	–	–	–	–	–	7.2	–	4.7	–	–	–	–
	5 days	–	–	–	–	–	14.1 10.2 8.5	–	–	–	–	–	–	8.3	–
	6 days	–	–	–	–	–	15.2	–	–	–	–	–	–	8.2	–
	7 days	5.0	5.25	5.4	8.8	6.1	–	11.4	–	7.1	–	–	–	–	–
	8 days	–	–	–	–	–	13.7 16.1	–	–	10.9	–	–	–	–	–
	11 days	–	–	–	–	–	–	–	12.5	–	9.3	13.2	8.4	–	13.1
	14 days	6.4	10.0	8.8	12.6	9.25	–	–	–	–	–	–	–	–	–

A proper choice of the required bentonite additive amount (5.5 % by mass) resulted in obtaining the alkali-activated cement-based grout with the required flowability – at least 180 mm (composition 3C).

The effect of the Ca-containing component

The Ca-containing component plays a double role in the final product formulation. Firstly, being present in the ion-exchange resins containing boric acid, it enters into interaction with this acid to bind the boron into insoluble compounds of the $CaO \cdot B_2O_3 \cdot 6H_2O$ type and in this way neutralize a negative action of boron on the processes of hydration and hardening of the alkali-activated cement. Secondly, the OPC or $Ca(OH)_2$ in the alkali-activated cement composition accelerates structure-forming processes in the cement matrix, thus intensifying strength gain, especially in the initial phase of hardening.

As it follows from the analysis of resin-containing formulations, in case of solidification of Type I ion-exchange resin containing boric acid, $Ca(OH)_2$ will be the most suitable Ca-containing additive to neutralize a negative effect of boron. The experimental research findings prove this assumption. Thus, compressive strength of the final product containing resin with the OPC additive is: after 3 days of hardening – 6.0–6.6 MPa (compositions 1C, 2C, and 3C), after 7 days – 5.0–5.4 MPa, and after 14 days – 6.4–10.0 MPa. Compressive strength of the final product containing resin with the additive of $Ca(OH)_2$ is: 6.9–8.0, 6.1–8.8, and 9.25–12.6 MPa respectively.

Therefore, the results of experiments on the production of grouts with target properties (waste (pulp) loading, flowability, and setting time) and their further testing predetermined selection of the following compositions for specimens of the final products: 3C, 5CM, 6CM, and 9CM.

Cylinder and beam specimens were placed into an exicator 1 day after the preparation. The beam specimens were removed after 1 day from the moulds and placed in a chamber with normal humid conditions ($t=20 \pm 2$ °C and RH=95±3 %). The cylinder specimens for testing a free liquid content after placing into moulds were covered with a film and stored in ambient conditions ($t=22–24$ °C and RH=80–85 %) (Fig. 2).

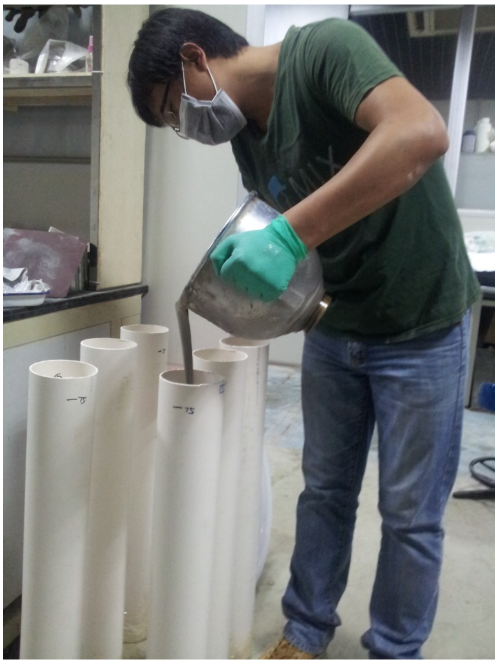

Fig. 2. Filling moulds with the grout (cylinder specimens: d=120 mm and h=800 mm)

A preliminary study of the alkali-activated cement-based grouts stability to segregation showed that the ion-exchange resin contained in the solidified waste forms (final products), despite high flowability of the grouts, turned out to be homogeneously distributed over the solidified waste forms (Fig. 3, *a*).

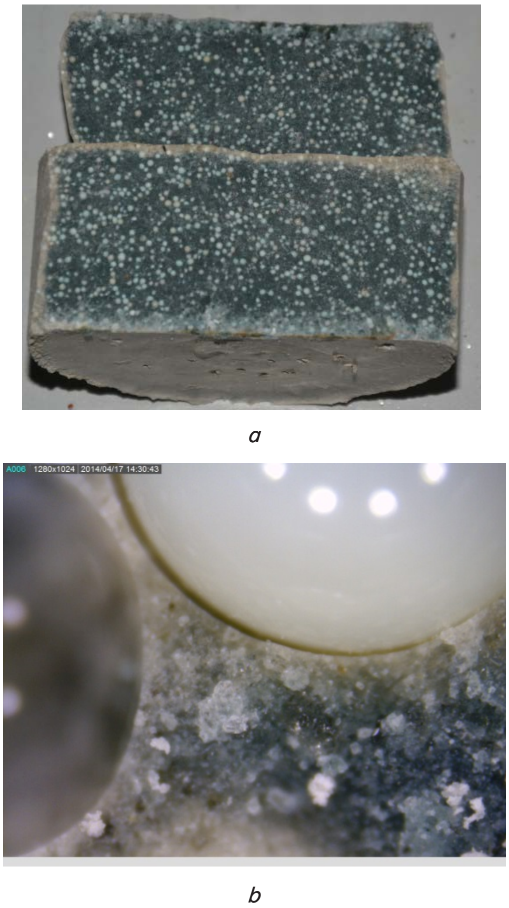

Fig. 3. Distribution of the resin particles in the solidified waste forms (final products) (composition 6-CM): *a* — general view; *b* — micro-photo of the contact zone

The results of electron microscopy showed that the final products had a uniform structure in cross-section with the ion-exchange resin particles homogeneously distributed in the alkali-activated cement matrix, whereas the interfacial transition zone was clear and without any visible cracks (Fig. 3, *b*).

5. 2. Properties of the solidified waste forms

Leaching behavior was studied as specified in the Chinese standards GB 7023 and GB 14569. According to these requirements, leach rate after 42 days should be as follows: for Cs – 137–1×10^{-3} cm/d and for Sr – 90–6×10^{-4} cm/d. Test results are given in Table 2.

As it is seen from Table 2 the final products (compositions 3CM, 6CM, and 9CM) are in conformity with the requirements of the Chinese standards.

Mechanical properties were studied in accordance with the Chinese standard GB 14569 requirements.

The specimens of the alkali-activated cement-based grouts under study were tested for flexural and compressive strength with a drop test (a prescribed height of drop =9 m). The results of drop testing with a drop height of 11 m are given in Table 3 and Fig. 4.

Table 2

Leaching from the solidified waste forms (final products). Test results

Composition number	Resin content, % by mass	Weight, g	Height, cm	Diameter, cm	Open surface (volume) of a specimen, cm^2 (cm^3)	Leaching from a specimen in deionized water after 42 days, g		Content, in a specimen, g		Leaching after 42 days (P$_{42}$), cm/d	
						Cs	Sr	Cs	Sr	Cs	Sr
3CM	42.4	157	5.5	4.6	112.66 (91.36)	0.0010	0.0048	0.43	0.69	2.6x10^{-4}	6.0x10^{-4}
5CM	45.0	165	6.0	4.6	119.88 (99.66)	0.0037	0.0040	0.47	0.75	9.3x10^{-4}	6.3x10^{-4}
6CM	44.3	140	5.1	4.6	106.88 (84.71)	0.0022	0.0015	0.38	0.61	6.5x10^{-4}	2.8x10^{-4}
9CM	41.1	128	4.8	4.6	102.55 (79.73)	0.0045	0.0021	0.36	0.57	1.3x10^{-3}	4.1x10^{-4}

Table 3

Strength characteristics. Test results

Composition number	Flexural strength, MPa	Compressive strength, MPa
3CM	3.8	18.3
5CM	2.5	15.6
6CM	3.5	14.7
9CM	2.5	9.5

After the drop testing from a drop height of 11 m there were no serious changes in shape (loss of integrity) of the cylinder specimens (d=h=50 mm).

According to the test results, the specimens of compositions 3F, 3CM, 5CM and 6CM are in compliance with the requirements for strength properties (compressive strength >7.5 MPa) and successfully passed the drop test.

Free liquid. No free liquid was reported when the cylinder specimens (d=80 mm and h=750 mm) were tested in accordance with the P. R. China standard GB 14569 after 7 days of hardening in hermetically sealed conditions.

Biological stability was studied in accordance with the Russian Federation standard GOST 27677-88 requirements with the help of beam specimens (40x40x160 mm). Test results are given in Table 4.

Table 4

Biological stability. Test results

Composition number	Compressive strength before the test, MPa	Compressive strength after the test, MPa	Flexural strength before the test, MPa	Flexural strength after the test, MPa	Coefficient of corrosion resistance
3CM	18.3	16.4	3.8	2.9	0.90
5CM	15.6	16.0	2.5	2.8	1.12
6CM	14.7	15.1	3.5	2.8	0.80
9CM	9.5	11.2	2.5	1.7	0.68

As it follows from Table 4, after 3 months of storage in a sulfuric acid solution (pH=3) the specimens of three compositions – 3CM, 5CM, and 6CM – exceeded a minimum coefficient of corrosion resistance (0.8), being in compliance with the requirements set in the standard.

Openness and penetration were assessed with a water saturation test of the specimens and calculation of the pore volume (porosity) in accordance with the Russian Federation standard GOST 12730.3-84, according to which it should not exceed 37.9 %. As it follows from Table 5, the specimens of all compositions were in compliance with these requirements.

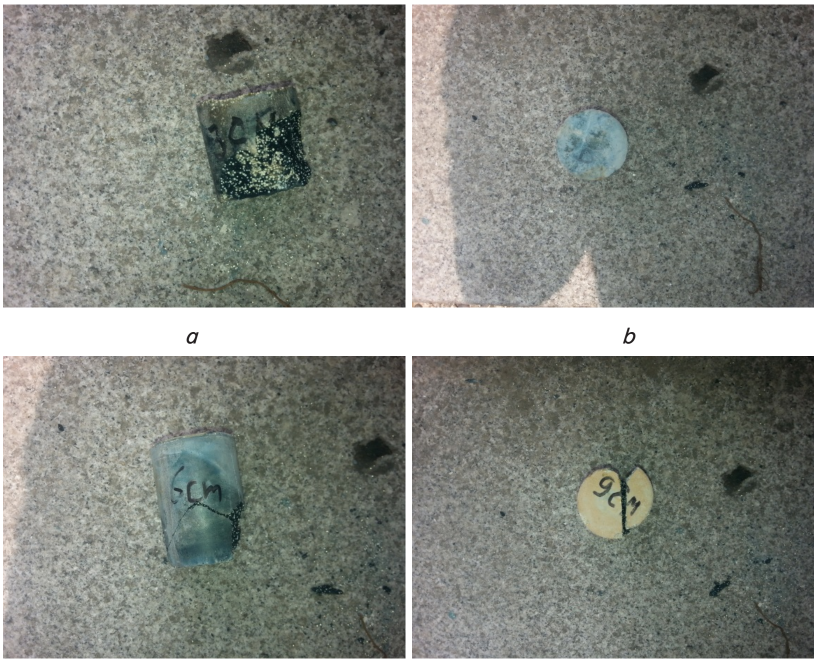
a *b*
c *d*

Fig. 4. Photos of the specimens after the drop test: *a* — composition 3CM; *b* — composition 5CM; *c* — composition 6CM; *d* — composition 9CM

Table 5

Openness. Test results

Composition number	Mass before saturation, g (not saturated specimens)	Mass after saturation, g (water saturated specimens)	Calculated openness, %
3CM	354	440	24.2
5CM	350	427	22.0
6CM	357	430	20.5
9CM	303	400	32.0

Fire resistance was tested in accordance with the Russian Federation standards GOST 30402-96, GOST 30244-94, and GOST 30444-97 with the use of beam specimens (40×40×160 mm) that were first kept in a drying chamber at t=60±5 °C for 24 hours, then heated in an oven until the temperature of 600 °C and cured at this temperature for 30 min.

The results of the tests (Table 6) show that all the compositions under study met the requirements with regard to fire resistance-there was no burning of specimens during the test and the strength losses did not exceed 50 %.

Table 6

Fire resistance. Test results

Composition number	Mass before the testing, g	Mass after the testing, g	Mass loss Δm, %
3CM	404	246	39.1
5CM	421	254	39.6
6CM	427	257	39.8
9CM	385	223	42.0

Freeze-thaw resistance was tested in accordance with the Chinese standard GB-14569 requirements using beam specimens (40×40×160 mm) that were allowed to freeze for 3 hours until the temperature of –20 °C, then allowed to thaw for 4 hours until the temperature of +20 °C.

As it follows from Table 7, after 10 freeze-thaw cycles the compressive strength was in compliance with the requirements as to frost resistance – the loss of compressive strength was less than 50 %.

Table 7

Freeze-thaw resistance. Test results

Composition number	Flexural strength, MPa	Compressive strength, MPa	Strength loss, %
3CM	1.25	15.03	17.9
5CM	0.8	12.75	22.3
6CM	2.0	11.31	23.1
9CM	0.8	9.03	4.95

Resistance in long-term storage in water was studied in accordance with the P.R. China standard GB-14569 requirements with the use of specimens after their 28-day storage in an exicator.

The results of tests after 90 days of hardening in these conditions are given in Table 8.

Table 8

Resistance in long-term storage in water. Test results

Composition number	Compressive strength before the test, MPa	Compressive strength after the test, MPa	Strength variations, %
3CM	18.3	20.8	+13.6
5CM	15.6	19.0	+21.8
6CM	14.7	13.6	–7.5
9CM	9.5	9.1	–4.2

The test results show that all the specimens met the requirements for water resistance (loss of compressive strength did not exceed 25 %).

6. Conclusions

The experimental research findings lead to the following conclusions:

– it is possible to obtain a final product with high waste loading (about 60 % by mass of the compound), meeting strength requirements of the standards (the compressive strength is higher than 7.5 MPa);

– it is shown that the most effective clay component is bentonite clay, the most effective alkaline component is sodium carbonate, and the most proper Ca-containing component is calcium hydroxide;

– all the compositions under study meet the requirements of the PRC standards for all service properties, whereas the most important characteristic – leaching of radioactive metal – is 10 times lower in comparison with standard demands.

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