New Radiation-Protective Binder for Special-Purpose Composites

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Abstract. The present work is devoted to the examination of new radiation-protective binder for special-purpose composite materials. The mixture for such advanced binder is developed. The mixture includes portland cement together with special component – barium hydrosilicates. The latter are micro-sized mineral admixtures which are synthesized by means of low-temperature sol-gel process. The parameters of early structure forming process (including normal density and setting time) are studied. Mechanical properties of the developed binders are determined. It has been shown that admixture of barium hydrosilicates leads to an increase of normal density. Both low and high setting times are reducing for composite binder with barium hydrosilicates. Values of compressive strength are significantly higher (up to 75%) if compared with binder which is made without micro-sized mineral admixtures. It is also revealed during examination of protective properties that for X-ray photons with energy $E\gamma = 0.1$ MeV linear coefficient of attenuation increases by 80%.

Introduction

Atomic industry is in active development now in several countries – France, United Kingdom, United States, China, Russia and others. Currently, there are more than 400 nuclear power reactors of power 370 GW and higher; there are also numerous analytical reports predicting that there will be from 17 to 94% increase of nuclear power in 2030 [1]. Because of this, research works directed to design of new protective materials for atomic industry are of immense importance.

Traditional method of improvement the protective properties of special-purpose building materials (radiation-protective or hydrated concrete) consists in adding a dispersed phase with desired chemical composition, state and structural parameters. It was shown that by means of using radiation-protective binder the effectiveness of special-purpose concretes can be significantly improved [2]. Some results concerning production of special-purpose binders (barium binder, lead-barium binder, iron-lead-barium binder and others) are summarized in [3-5]. However, actual production and use of special radiation-protective binders are still rare. This is due to the impossibility of manufacturing these binders directly on the construction site. Therefore, the primary binder even for special-purpose concrete is yet portland cement. To improve the efficiency of binders based on portland cement it is possible to use special mineral and chemical additives that regulate the chemical composition and structure formation process of cement stone.

Theoretical bases

The efficiency of binder is reflected mainly by increased density of structure of the material (for the purpose of improving the radiation-protective properties) and depends on several parameters [3]:

$$\left\{\begin{aligned} \mu &= c\rho\frac{z^{m-1}}{E_{\gamma}^{n}}\left(\frac{z}{A}\right)N_A \\ \Delta E &= 0{,}6\rho\left(\frac{z}{A}\right)\left(\frac{h}{\beta^2}\right) \end{aligned}\right. \to \max, \tag{1}$$

where μ – macroscopic cross-section of electromagnetic photon; *c* – light speed; *z* – atomic number of chemical element; *E*γ – energy of photon; *n*, *m* – constants equal to 1…3 and 4…5, respectively, *A* – mass number of chemical element; *E* – kinetic energy of incoming electron; ρ – density of material; *h* – thickness of protective layer; β = υ/c, υ – speed of incoming electron; N_A – Avogadro constant.

From the system (1), obtained by the analysis of the works [3, 4], immediately follows that all else being equal (equal energy spectrum of the incident radiation and chemical composition of material) the effectiveness of attenuation of electromagnetic radiation increases when density of the material grow. This is particularly important for building materials, which contain a considerable amount of the air phase in form of pores and voids. Such phase is formed in the material during manufacturing process as a result of trapping the air, and also during structure formation process (contraction phenomena).

We consider this in more detail. The *z*/*A* ratio which can be used to assess the effectiveness of the chemical composition is equal to

$$\frac{z}{A} = \frac{Np}{Np + Nn},$$

where indices *p* and *n* correspond to proton and neutron.

When *Nn* and *Np* are approximately equal (this holds for most chemical elements except hydrogen), latter relation is near 0.5. Intensity of influences of density and *z*/*A* ratio as well as the prevalence of factors can be estimated by relation

$$\frac{d\mu}{d\rho}\Bigg/\frac{d\mu}{d(z/A)} = (z/A)/(\rho\cdot m).$$

Taking into account values of density and *m* we get:

$$\frac{d\mu}{d\rho}\Bigg/\frac{d\mu}{d(z/A)} < 1.$$

Thus, to change the value of μ it is preferable to vary chemical composition. However, it is clear that the variation interval of *z*/*A* ratio is much smaller than range of variation of the density; Δμ ratio at constant chemical composition $[\Delta\mu]_{(z/A)}$ and constant density $[\Delta\mu]_{\rho}$ is equal to

$$\frac{[\Delta\mu]_{(z/A)}}{[\Delta\mu]_{\rho}} = \frac{\delta\rho}{[1+\delta(z/A)]^m - 1},$$

where δρ – relative variation of density, δ(*z*/*A*) – relative variation of *z*/*A* ratio. It follows from the last relation, that

$$\delta\rho = [1+\delta(z/A)]^m - 1 \text{ or } \delta(z/A) = \sqrt[m]{1+\delta\rho} - 1.$$

Results of modeling the δρ = f(δ(z/A)) variation (values of m are 4 and 5) are summarized in table 1.

Relative variation of density of material depends not only on chemical composition, but also on porosity Π. The dependencies for the latter are

$$\delta\rho = 1 - \frac{1-\Pi_i}{1-\Pi_o} \text{ or } \delta\rho = \frac{\Delta\Pi}{1-\Pi_o},$$

where Π_o – initial porosity of material.

The variation of porosity ΔΠ with respect of δρ was also modeled. In the Table 2 we have summarized the results.

Table 1. Results of modeling the δρ = f(δ(*z*/*A*)) variation.

Parameter		Value				
$\delta(z/A)$		0.02	0.04	0.06	0.08	0.10
δρ	m=4	0.082	0.170	0.262	0.360	0.464
	m=5	0.104	0.217	0.338	0.469	0.610

Table 2. Results of ΔΠ = *f*(δρ) calculation

Variation of porosity	Value of δρ				
	0.104	0.217	0.338	0.469	0.610
ΔΠ, [%] (for Πo = 20 %)	8.3	17.4	–	–	–
ΔΠ, [%] (for Πo = 30 %)	7.3	15.2	23.7	–	–

Analysis of tables 1 and 2 shows that controlling porosity of the material is equivalent to a change in its peculiar chemical composition:

$$\delta(z/A) = \sqrt[m]{1 + \frac{\Delta\Pi}{1-\Pi_o}} - 1.$$

For example, changing the porosity of the material by 15% (for Π_o = 30%) is equivalent to relative change of δ(*z*/*A*)=4% ratio (or, for $z/A \cong 0{,}5$, Δ(z/A) = 0.02). Therefore, reducing the porosity of the material is of important technical and economical significance.

Under otherwise equal conditions it is possible to change the average density and porosity of the cement stone by means of use of additives which are regulating the pore structure of the material. The other method consists in addition of mineral supplements containing elements with high atomic mass. Such additives should be divided into chemically active and chemically inert. Obviously, the reactive additives are advantageous because they can interact with the hydration products of portland cement, resulting compaction of the final composite structure. Such additives include barium hydrosilicates [6]. Their preparation is possible with low-temperature synthesis from sodium hydrosilicates (water glass) and precipitants (water-soluble barium salts) [7]. This can significantly reduce their cost. When combined with cement hydrosilicates, barium hydrosilicates form composite binder. Depending on the synthesis procedure, composition of and additive based on barium hydrosilicates also varies [8]. Therefore, properties of the composite binder will also be changed. Because of this, it is necessary to establish the basic operational characteristics of the composite binder which are required for the preparation and processing of concrete mixture: normal consistency, setting time, strength of the resulting composite artificial stone, along with radiation-protective properties.

Experimental results and discussion

Examination of normal density (determined according to relevant RO GOST) of the developed composite binder (Table 3) show that variation of the amount of barium hydrosilicates leads to complex character of normal density. This can be explained as follows. It is known [8] that decrease in the amount of precipitant in the additive induces increase of the amount of silicic acid. Thus, it is obvious that by using barium hydrosilicates produced with 100% of precipitant, the mixing water is consumed by wetting of layered structure [9, 10] of barium hydrosilicates and under identical experimental conditions causes the increase of normal density. With a decrease in the content of the precipitant silicic acid prevents the penetration of water between the layers of barium hydrosilicates. Accordingly, water-cement ratio is reduced. However, further reduction of amount of precipitant leads to increase of silicic acid content. It is known [11] that silicic acid is able to bind and retain water. Naturally, that the normal density of the composite binder is increased.

Table 3. Normal density of composite binder

Amount of barium hydrosilicates, [%]	Amount of precipitant, [%]				
	60	70	80	90	100
5	0.30	0.30	0.29	0.29	0.28
10	0.31	0.33	0.31	0.30	0.29
20	0.32	0.32	0.32	0.31	0.31
30	0.33	0.32	0.32	0.31	0.33
40	0.34	0.34	0.33	0.32	0.34

Setting time of the binder determines the possibility of its use for the manufacture of building materials. For the processing of concrete low setting time of the cement paste with normal density should not be earlier than 45 minutes, and high setting time (end of the setting) should not be later than 10 hours after mixing. Thus, the time of use of the cement mixture must be sufficient for its molding, but not be too long, since the latter reduces productivity. The experimentally obtained values of setting time are shown in Table 4.

Table 4. Setting time of the composite binder (low/high, [min])

Amount of barium hydrosilicates, [%]	Amount of precipitant, [%]				
	60	70	80	90	100
5	155/230	170/245	190/255	230/280	255/300
10	140/160	120/175	150/200	190/240	210/270
20	75/120	70/105	90/120	170/210	80/150
30	35/65	45/75	75/95	95/115	30/50
40	25/35	35/60	55/75	75/95	25/40

Analysis of Table 4 shows that for 5% amount of barium hydrosilicates which are obtained by precipitation with 100% of precipitant, there are only small reduction of setting time. Setting of the binder accelerates together with an increase of the mentioned amount. This can be explained as follows. Barium hydrosilicates are artificially synthesized analogues of hydration products of cement stone. Increased amount of barium hydrosilicates corresponds to reduced average distance between particles. The synthesized products of hydration of cement stone interact with silicic acid, which is part of the additive, and form numerous centers of crystallization. Under such conditions, increased the amount of hydration products formed as a result of accelerated cement hydration. This leads both to acceleration of crystallization of calcium hydrosilicates and to shift of low and high settings times. It the barium hydrosilicates were synthesized with low amount of precipitant, then silica acid content in additive increases. However, for composition comprising of 20% barium hydrosilicates produced with 60% precipitant, retarding of setting is observed. This may indicate an excess of silicic acid, which is able to block surface of hydration products and to slow down the setting [12].

Inherent features of structure formation influence the compressive strength of the final structure of composite binder. The compressive strength is an important operation characteristic even for special-purpose binder because such binder can later be used for concrete constructions. There are local maxima on cross-sections of the response surface representing the dependence between amount of admixture, precipitant in admixture, and compressive strength (Figure 1). Protective properties of the developed composite binder are summarized in Table 5.

The response surface presented on Fig. 1 indicates the occurrence of two processes during structure formation and curing; one process is “constructive” and another is “destructive”. Maximal strength is achieved for the binder with 10% of barium hydrosilicates synthesized with 90% of precipitant.

Studies of radiation-protective properties of the developed binder (Table 5) shows that linear adsorption of gamma-rays has nonlinear character and strongly depends on amount of micro-scale barium hydrosilicates. This is determined both by chemical composition and density of the hardened composite binder. The efficiency of attenuation of X-ray and gamma radiation depends on the operating conditions: for $E\gamma$ = 0,1 MeV application of micro-scaled admixture improves the efficiency of attenuation by 80%. However, for high-energy particles (Eγ = 0,5 ... 1,0 MeV) using of composite binder is inappropriate.

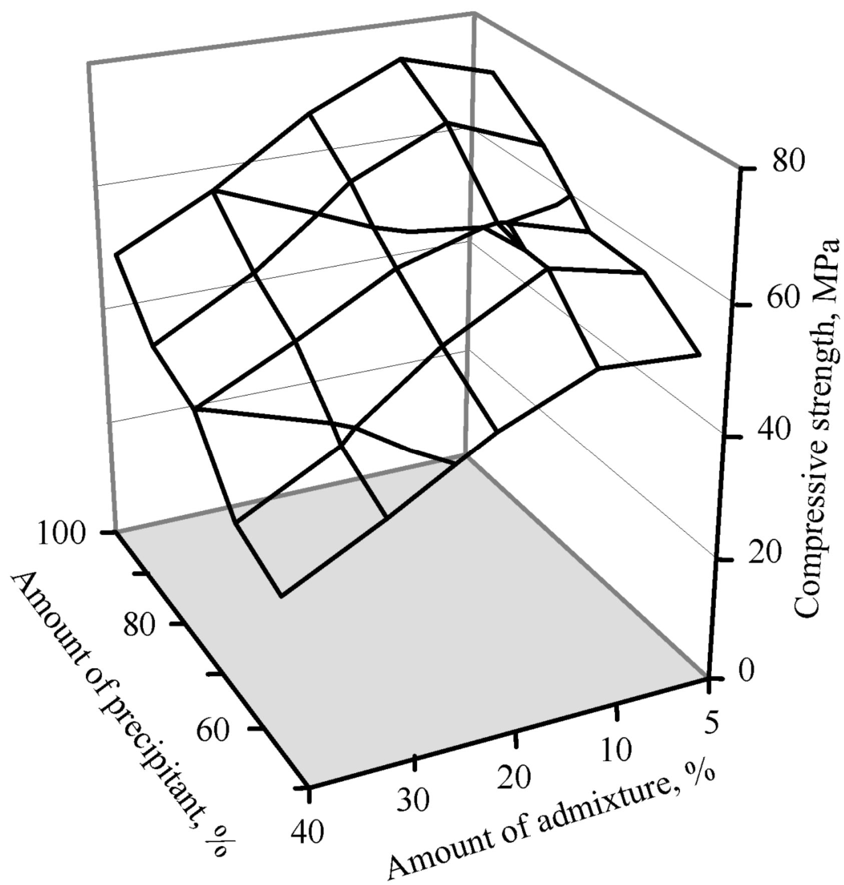

Figure 1. Compressive strength of cement stone based on composite binder

Table 5. Protective properties (cm^{-1}) of the developed composite binder

Amount of barium hydrosilicates, [%]	Amount of precipitant, [%]				
	60	70	80	90	100
E_γ = 0.1 [MeV]					
0	0.380				
5	0.404	0.414	0.421	0.430	0.437
10	0.434	0.462	0.484	0.493	0.483
20	0.486	0.527	0.544	0.573	0.565
30	0.531	0.558	0.600	0.638	0.628
40	0.571	0.604	0.635	0.677	0.685
E_γ = 0.5 [MeV]					
0	0.172				
5	0.168	0.169	0.170	0.171	0.172
10	0.167	0.174	0.177	0.176	0.170
20	0.165	0.172	0.171	0.174	0.167
30	0.163	0.163	0.169	0.172	0.164
40	0.161	0.162	0.163	0.167	0.163
E_γ = 1.0 [MeV]					
0	0.126				
5	0.122	0.123	0.123	0.124	0.127
10	0.121	0.126	0.128	0.126	0.121
20	0.119	0.124	0.123	0.125	0.120
30	0.117	0.117	0.121	0.123	0.117
40	0.116	0.116	0.117	0.119	0.116

Conclusion

We have developed new composite binder consisting of portland cement and barium hydrosilicates. The primary operational properties of the developed binder are determined. It has been shown that admixture of barium hydrosilicates leads to an increase of normal density. Both low and high setting times are reducing for composite binder with barium hydrosilicates. Values of compressive strength are significantly higher (up to 75%) if compared with binder which is made without micro-sized mineral admixtures. It is also revealed during examination of protective properties that for X-ray photons with energy $E\gamma$ = 0.1 MeV linear coefficient of attenuation increases by 80%.

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