Destruction of cement stone modified with a plasticizer and a nanoscale aluminum oxide

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Destruction of cement stone modified with a plasticizer and a nanoscale aluminum oxide

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Abstract. It is well known that hydration and hardening of Portland cement are associated with complicated physical and chemical processes, in particular the interaction of clinker minerals with water to form new hydrate phases of different composition. Sometimes the presence of various substances can affect these processes leading to self-destruction of the hydrated cement stone. The morphology and composition of damaged cement stone modified with an additive and with a nanoscale aluminum oxide were studied. It is shown that in the presence of the 'Linamix PC' plasticizer and a nanoscale aluminum oxide, well-crystallized $Ca(OH)_2$ plates with an average thickness of 1.5 microns and a length and width equal to 300–400 microns are formed. Also, a network of thread-like ettringite with a diameter of less than 1 micron on the surface of microcracks of cement stone is formed. Most likely the cement stone sample could be damaged by the forces of crystallization pressure during the growth of both $Ca(OH)_2$ and ettringite crystals.

1. Introduction

Hydration and hardening of Portland cement is a complex of physical and chemical processes that is accompanied by the formation of hydrate phases when clinker minerals interact with water. Crystals of calcium hydrosilicates, hydroaluminates and hydroalumoferrites, their solid solutions and complex compounds which differ by composition and structure are formed during hydration of the clinker minerals. A large variety of crystallohydrates in cement stone greatly complicates its study [1]. Also, the hydration and hardening processes are strongly affected by the presence of various plasticizers and other substances (nanoscale additives) [2–3]. Ettringite is the first stable hydration product that is formed by the reaction of C_3A, calcium sulfate (gypsum) and water [1, 4]. It is reported in [2, 4–7] that plasticizer molecules are usually adsorbed primarily on the surface of both C_3A and new formed ettringite. This leads to a change in its morphology. It was found in [8] that the composition and type of chemical functional additives affect the shape and size of ettringite. It is also known that as a result of the ettringite crystals growth under an increased content of gypsum destructive processes can occur in the cement stone leading to a decrease in strength [9].

The aim is to study the morphology and composition of damaged cement stone modified with an additive based on polyoxyethylene derivatives of unsaturated carboxylic acids and with nanoscale aluminum oxide.

2. Raw materials and mix preparation

The following materials were used in the work:

- Portland cement of CEM I 42.5 B type produced by JSC 'Sukholozhskcement' (Sverdlovsk region);

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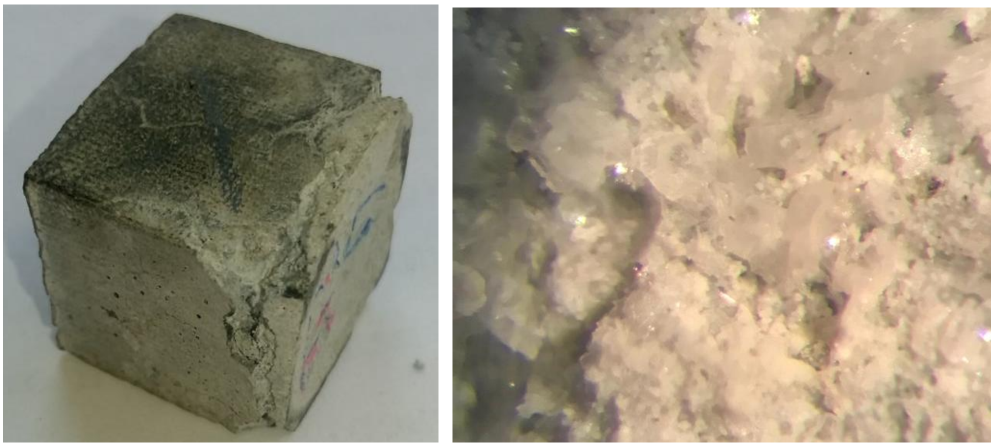
- aluminum nanooxide ‘TG’ which is obtained by thermal hydrolysis method developed at the Institute of chemistry of solid state of the Ural branch of the Russian Academy of Sciences (Ekaterinburg) [10];
- plasticizer ‘Linamix PC’ based on polyoxyethylene derivatives of unsaturated carboxylic acids produced by JSC ‘Polyplast-URALSIB’ (Pervouralsk).

The basis of the method for preparing the cement mix was taken from [11]. 0.3 % of Portland cement was introduced into 30 ml of water with addition of 0.5 % of nanooxide. The suspension obtained was treated with ultrasound for 30 minutes at a temperature of 30 °C in an ‘Elmsonic S30N’ ultrasonic bath. The suspension treated was then mixed with 1.0 % plasticizer and then injected into the remaining part of cement (99.7 %). Nanooxide and plasticizer were introduced in excess of 100 % of the cement mass. After combining all components, the mix was thoroughly mixed in a ‘SL-1500’ high-speed mixer for two minutes.

Small samples–cubes (2×2×2 cm) were formed from the mix obtained, at the age of 24 hours they were removed from the forms and then stored in high humidity conditions.

3. Results and discussion

After 28 days of storing the destruction and formation of crystals were observed in cement samples of the composition mentioned above. Figure 1 shows an image of one of the samples that were damaged. It can be seen that one side of the sample was exfoliated, macro- and microcracks appeared and small crystals were found on the surface of the rift and the sample itself. Some of the crystals were visible even at low magnification (figure 1, b).



a b

Figure 1. Sample of cement stone with destruction signs: a – general view of the sample; b – new formations on the sample surface at 25X magnification.

For a more detailed study micrographs of cement stone were made with the determination of the chemical composition at some points. The morphology of the samples and their chemical composition were studied using a JEOL JSM-6390LA scanning electron microscope equipped with an 'EDS Inca Enegy 250’ X-ray spectrometer (figure 2–3).

Figure 2 shows well-crystallized plates arranged in order and parallel to each other. The thickness of formed plates on a cement stone sample with signs of destruction from 0.6 to 2 microns, on average – 1.5 microns. The length and width of the plates are approximately 300–400 microns.

The forming spherical particle that can be observed in figure 3 has a diameter of 30 microns. Smaller spherical particles attached to a large sphere have an average diameter of 2–5 microns. Thin fibers with a diameter of less than 1 micron were also detected; they are uniformly distributed on the cement stone sample surface and also in micro cracks (figure 3).

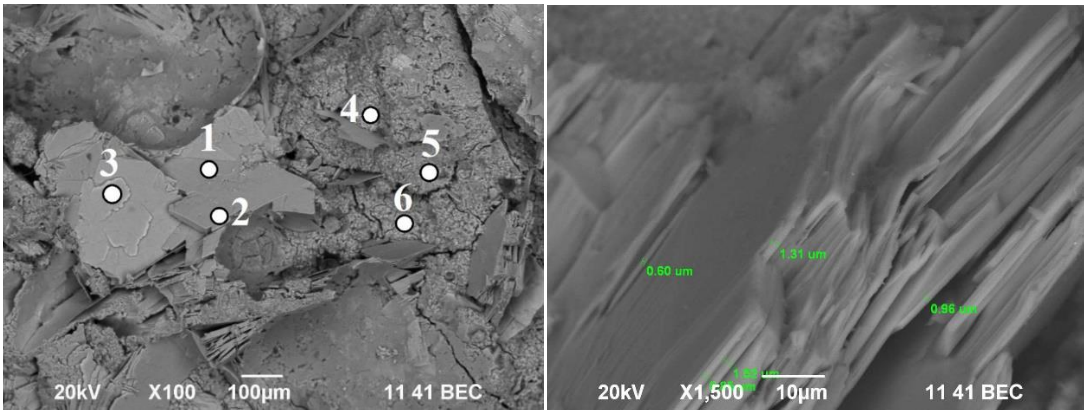


Figure 2. Structure of cement stone at different magnification.

The quantity of basic oxides obtained from microanalysis of points shown in the figures 2–3 is presented in table 1. It can be assumed that the distinct plates at the image (figure 2, points 1, 2 and 3) are $Ca(OH)_2$ which formed as a result of the hydration reaction of alite and belite [1]. The sphere (figure 3) can be formed by the main products of alite (C_3S) hydration which are calcium hydrosilicates (the ratio of CaO/SiO_2 is equal 3/1 according to table 1, points 13 and 14). The fibres on image (figure 3) are most likely ettringite.

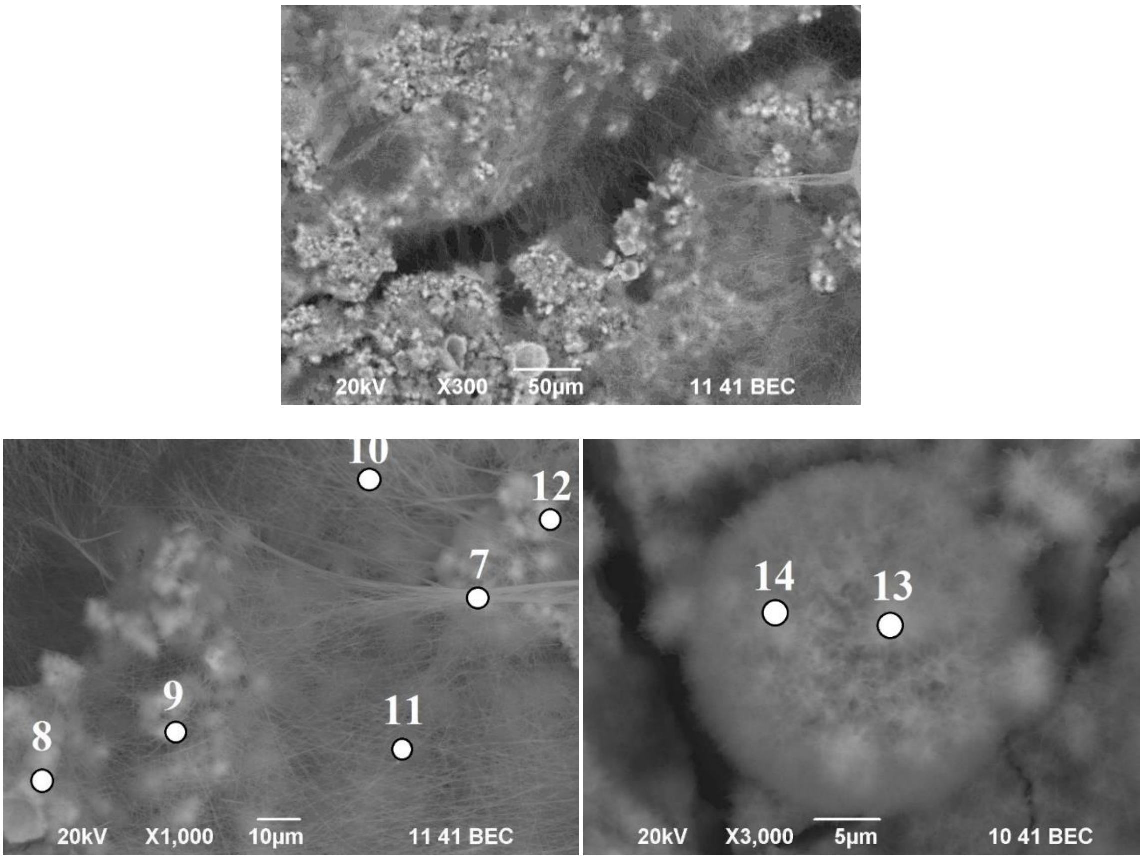


Figure 3. Fibres and sphere in the structure of cement stone at different magnification.

Chernyshov and Korotkikh reported in [12] about the effect of nano-self-reinforcement of the cement stone structure in which needle-fiber reinforcing elements (filamentous new formations of ettringite) are formed directly during the physical and chemical processes of hydration and hardening of the binder. The sizes of hydrate crystals formed in cement stone do not exceed several tens, less often hundreds of nanometers across [13]. However the situation is not so simple since the crystallization of long hydrates is accompanied by an increase in the crystallization pressure as a result of which the positive effects of nano-reinforcement of cement stone are ‘superimposed’ by the negative effects of its possible self-destruction from the action of such pressure [14]. Most likely the signs of such processes were encountered and recorded during the hardening of the cement stone containing the plasticizer ‘Linamix PC’ and aluminum nanoxide.

Table 1. Microanalysis results of cement stone at individual points.

Point number (at figures 2 and 3)	Quantity of basic oxides (%)						
	$Ca(OH)_2$	CaO	SiO_2	Al_2O_3	SO_3	FeO	MgO
1	100.00	–	–	–	–	–	–
2	97.10	–	2.90	–	–	–	–
3	100.00	–	–	–	–	–	–
4	–	85.07	6.85	1.44	1.14	5.50	–
5	–	69.32	23.27	2.30	–	5.11	–
6	–	76.21	3.51	6.02	3.16	11.10	–
7	–	61.66	13.86	8.68	14.73	2.88	–
8	–	59.51	27.36	2.54	1.42	3.61	–
9	–	60.06	14.61	8.50	14.30	2.53	–
10	–	60.91	22.81	6.00	7.13	3.14	–
11	–	59.19	25.49	5.08	5.47	3.92	0.85
12	–	59.68	19.93	6.84	8.69	3.41	1.44
13	–	60.19	23.19	5.32	5.95	4.37	0.98
14	–	56.35	27.11	6.46	6.69	3.39	–

4. Conclusions

The morphology and composition of damaged cement stone modified with an additive and with a nanoscale aluminum oxide were studied. It is shown that in the presence of ‘Linamix PC’ plasticizer and a nanoscale aluminum oxide, well-crystallized $Ca(OH)_2$ plates with an average thickness of 1.5 microns and a length and width equal to 300–400 microns are formed. Also, on the surface of microcracks of cement stone a network of thread-like ettringite is formed with a diameter of less than 1 micron. Most likely the cement stone sample could be damaged by the forces of crystallization pressure during the growth of both $Ca(OH)_2$ and ettringite crystals.

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