Study of natural self-healing of materials based on inorganic binders

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Abstract. The study of natural self-healing of materials based on inorganic binders has been carried out. The age of the study was one month after loading with cracking. Microscopic analysis of samples with cracks based on Portland cement, oxychloride cement and gypsum showed that all studied materials are capable of filling cracks on their own. The filler, such as calcium carbonate or gypsum dihydrate, can have a sufficiently high strength so that a self-healing effect is present. A filling agent such as magnesium hydroxide cannot have strength, and then only the crack is filled without restoring strength. Filling of cracks at the age of up to one month is insignificant and does not exceed 0.5 microns. This is not enough to fill large cracks. For modern building structures, natural self-healing is ineffective. This requires the use of artificial methods of self-healing in modern building structures.

1. Introduction

It is known that many materials are prone to natural self-healing. This is especially true for materials such mineral binders with high chemical activity. The hardening process of mineral binders is very long. During this process, the system is able to independently form new substances. They can participate in the self-healing process. Neoplasms can fill cracks and defects formed during the life cycle and restore the strength of constructions [1].

There are also techniques for artificial self-healing. The methods of artificial self-healing include the introduction into a construction of objects that can be activated in the event of damage of the construction. For example, this is the introduction of specific bacteria with a nutrient medium for them. Such bacteria are capable of producing substances for filling cracks and defects and restoring the strength of a product or structure [2-6]. These techniques are quite effective, but so far they are not widely used in construction practice.

The aim of the work was to study of natural self-healing of various building materials and to assess the effectiveness of natural self-healing.

2. Methods and materials

The structure of the materials was studied using a Jeol scanning electron microscope. Compositions based on Portland cement, magnesium oxychloride cement and gypsum were used in the work. All samples were prepared from normal consistency dough. All samples hardened for 28 days. The
dimensions of the samples were 2x2x12 cm. After removal from the form, gypsum and oxychloride samples hardened in air, while Portland cement samples hardened in water. After 28 days, some of the samples were loaded to 95% of the breaking-bending load, then the load was immediately removed. After loading, all the samples retained their shape, but they had a significant number of nano- and microcracks in the stretched zone. Then all samples were again placed under the same hardening conditions for 28 days. Then, within 7 days, the samples were dried and prepared for analysis under a microscope. After that, the structure of the stretched zone was examined under a microscope, and comparative tests of the samples were carried out to determine the breaking load.

3. Results and discussion
It has been established that all studied materials are more or less susceptible to the self-healing process.

In samples based on portland cement, a large number of new crystallites are present in cracks (Figure 1, 2).

Emersion analysis showed that the neoplasms consist mainly of calcium hydroxide. Such crystals have a hexagonal crystal structure. The samples were exposed to air during drying. Therefore, in the most permeable areas, calcium hydroxide began to carbonize and turn into calcium carbonate. These observations indicate that the cement samples are undergoing a self-healing process. The cracks are filled with calcium hydroxide and calcium carbonate. This process is rather slow. At 28 days, cracks with a width of 5 microns were filled by 10-15%. It is worth noting that the final filling material, calcium carbonate, is a tough, low solubility and low permeability mineral. Calcium carbonate is a good option for self-healing. However, this self-healing option is not suitable for highly hydrated cements. This means that the formation of additional calcium hydroxide requires the decomposition of highly basic hydrosilicates of calcium into low-basic hydrosilicates and a portion of calcium hydroxide. This process leads to a general weakening of the cement matrix. Thus, the natural self-healing process of cementitious materials is not efficient enough. It does not provide fast filling of cracks and gives only partial restoration of properties. Comparative tests of a batch of specimens subjected to loading at intermediate age and control ones showed only 10% recovery of strength (Table 1).

| Table 1. Strength of samples based on Portland cement. |
Control batch of samples | Batch of samples loaded at intermediate age
---|---
Terms and conditions of hardening | 1 day in sample form, 55 days in water | 1 day in sample form, 55 days in water
Loading up to 95% bending breaking load | Not loaded | The load was 4.9 MPa at the age of 28 days
Flexural strength at the age of 56 days, MPa | 6.7 | 0.7

<sup>1</sup>Flexural strength at the age of 28 days was 5.2 MPa

Samples based on magnesia oxychloride cement have similar results. Cracks in the samples were filled with magnesium hydroxide (Figure 3, 4).

![Figure 3](image1.png)
**Figure 3.** Micrograph of cracks in samples based on magnesium oxychloride cement.

![Figure 4](image2.png)
**Figure 4.** Micrograph of cracks in samples based on magnesium oxychloride cement.

However, magnesium hydroxide carbonizes much more slowly than calcium hydroxide. Therefore, even during long-term storage, cracks in the samples of magnesium oxychloride cement are filled with weakly crystallized low-strength crystallites of magnesium hydroxide. This does not give any self-healing effect for strength (Table 2).

| Terms and conditions of hardening | Control batch of samples | Batch of samples loaded at intermediate age |
|---|---|---|
| 1 day in the form for samples, 55 days in air (relative humidity 60 ± 5%, temperature 20 ± 5 °C) | Not loaded | The load was 6.0 MPa at the age of 28 days |

<sup>1</sup>Flexural strength at the age of 28 days was 6.3 MPa

In the cracks of gypsum samples, crystallites of gypsum dihydrate grow over time (Figure 5, 6).
However, it should be noted that this effect is only present in samples that were stored at a relative humidity of at least 60%. It is likely that the formation of secondary gypsum dihydrate requires water and some unreacted gypsum hemihydrate. Filling cracks with gypsum dihydrate is good for strength. Self-healing of the sample at the selected age occurred in at least 30% (Table 3).

**Table 3.** Strength of gypsum-based samples.

|                        | Control batch of samples | Batch 1 of samples loaded at intermediate age | Batch 2 of samples loaded at intermediate age |
|------------------------|--------------------------|---------------------------------------------|---------------------------------------------|
| Terms and conditions of hardening | 1 day in the form for samples, 55 days in air (relative humidity 30±5%, temperature 20±5°C) | 1 day in the form for samples, 55 days in air (relative humidity 30±5%, temperature 20±5°C) | 1 day in the form for samples, 55 days in air (relative humidity 60±5%, temperature 20±5°C) |
| Loading up to 95% bending breaking load | Not loaded | The load was 6.6 MPa at the age of 28 days | The load was 6.6 MPa at the age of 28 days |
| Flexural strength at the age of 56 days, MPa | 7.6 | 0.5 | 2.3 |

*Flexural strength at the age of 28 days was 7.0 MPa*

4. **Conclusions**

Natural self-healing of materials based on Portland cement, magnesium oxychloride cement and gypsum occurs to a greater or lesser extent in all materials. Artificially created cracks are filled with a substance of the corresponding nature. In samples based on Portland cement, cracks are filled with calcium hydroxide, which can eventually transform into calcium carbonate. In oxychloride samples, cracks are filled with magnesium hydroxide, and in gypsum samples, the cracks are filled with gypsum dihydrate. The filling substances such calcium carbonate or gypsum dihydrate can have a sufficiently high strength and then the effect of self-healing is present. The filling substance such magnesium hydroxide may not have the strength and then only the crack is filled without returning strength. In addition, for all studied materials, the crack filling process was found to be very long. This circumstance dictates the need to use artificial methods of self-healing.

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