Degradation of composites containing alkali-resistant glass fibres by ammonium nitrate solutions

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Abstract. The aim of the research program was a degradation of composites containing alkali-resistant glass fibres (ARGF) by ammonium nitrate solutions. The effect of 3 and 5% ammonium nitrate solutions and storage long time on physical properties and structure of cement composites is presented. Application of glass fibre had a positive effect on the properties of cement pastes, most notably, this was reflected on the compressive strength and transverse tensile strength. Despite the positive effects but also the application of fiberglass there was a significant loss of strength cement mortars exposed to prolonged exposure to ammonium nitrate solutions.

1. Introductions

History of fiberglass applications is relatively young. In the past were not available suitable sources of alkali-resistant glass fibers appropriate to the concrete. Glass fibers that were used initially in cement composites were disturbed with alkalis in pore solution of cement stone. Durability of cement stone and composites decreased as a result of degradation of fibers.

Electrical grade glass (E-Glass) was originally developed for standoff insulators for electrical wiring. It was later found to have excellent fiber forming capabilities and was used as the reinforcing phase in the material commonly known as fiberglass. With further research proved to be unsuitable for use in fiber reinforced concrete. Fiber E-glass has a low resistance to acids and alkalis contained in the cement stone. It is characterized by high electrical resistance and good deformation characteristics.

Glass fibers currently used to produce reinforcing bar are made of glass resistant to the effects of alkali. They were developed from the 1960th in England and Spain. It was found that the content of zirconia in the glass fiber has a positive impact on the resistance against alkali. Fibers initially contained 16% ZrO₂; gradually increasing doses up to 20%. The alkali-resistant fibers are suitable to produce diverse types of cement composites with wide application in the construction industry [1,2].

Glass fibers Cem-FIL are produced from molten glass with temperature up to 1 560°C flowing through perforated plate. Diameter of glass fibers that are produced by this method is 14 µm. The resulting monofilament cool quickly, and the surface lubrication is directly sprayed onto and connects them to the springs. Lubrication must ensure resistance to high fiber co-alkaline environment of cement paste (pH 12 to 14). In addition, it provides a straight-line basis stirring fiber composite in the shape, which is most appropriate for the reinforcement. In the production of continuous glass fibers, it is used a variety of sizing according to technological requirements specified for use springs. When applied to concrete, strands of fiberglass must withstand the friction when mixed with aggregate and friction in the production of dry mixtures. If there was a breakage of spring during mixing, may produce clusters of broken fibers, which reinforcement ability is virtually nil. Lubrication shall allow the flexibility of springs, to avoid breaking of springs during mixing [3].
The object of the research was to verify the impact of alkali-resistant glass fibers Cem-FIL AntiCrak and the properties of cement pastes exposed to aggressive action of ammonium nitrate solutions. This medium can cause intense leaching of cement composites, under certain circumstances and expansion processes of concrete corrosion (rust Moskvin by type III [4]).

2. Materials and methods

Samples were made of cement CEM I 42.5 R and potable mains water. Samples were blended with alkali-resistant glass fibres Cem-FIL AntiCrak (ARGF) up to 6mm at 2.5wt.% and 5wt.%.

As aggressive media were used ammonium nitrate solutions with concentration at 3% and 5%. In the production of samples, it was important to determine the optimal water cement ratio. Based on tests of consistency of cement slurries was elected a single factor for all water produced composites 0.33. With this factor it reached a generally good workability and mixing water was not separating.

Cylindrical samples with a diameter and height of 30mm were made of cement paste blended with fibers and as a comparative sample without fibers additives. Samples were prepared by a standard manner in a standard mixer used to make a standard cement mortar according to EN 196-1 [5]. Samples were treated 24 hours in a humid environment, and for another 27 days were stored in water. Then they were treated with water or were placed in a solution of ammonium nitrate.

Aggressive media volume was ten times the volume of samples. NH₄NO₃ solution was exchanged with decreasing concentration of the aggressive component of 10%. Water was exchanged at regular 28-day intervals.

The samples were determined by the following properties: appearance and weight change, porosity, water absorption, density, compressive strength, splitting tensile strength. The microstructure and the interaction between the fibers and the cementitious stone were examined on selected samples using a scanning electron microscope (SEM), specifically TESCAN VEGA3 (SEM HV: 30.0kV, SEM MAG: 2.40kx, View field: 100μm).

Properties of the samples treated in water were tested at 28, 56, 308 and 1488 days. Properties of the samples stored in the aggressive solutions were tested at 1, 28, 280 and 1460 days of storage in aggressive solutions (the prior 28-day storage in water).

3. Results and discussion

3.1. Appearance and weight change subsection

Samples of hardened cement composites stored in water showed almost no change in appearance during the reporting periods.

The samples appearance in 3% and 5% solutions NH₄NO₃ has changed over time. The first 28 days samples without fibers and samples with 2.5wt.% glass fibers were no changes. Continuing storage samples in solutions started to emerge cracks on the surface of the samples, which incurred due to the ongoing corrosion processes. After 280-days storage in solution, samples have already been cracked. After 1460 days of storage in solution, it led to destruction of the surface structure of samples (figure 1).

Samples with addition of 5wt.% fiberglass at all concentrations throughout the period showed no change in appearance.

Weight of test samples hardening cement composites stored in water during treatment increased. The increase has caused ongoing cement hydration and absorbed water pore structure of the samples. After the 308-day and 1488-day storage in water, there were no major difference in weight between the samples without additives and samples blended with glass fibers.

Weight of the samples stored in cement composites aggressive NH₄NO₃ solutions (due to the ongoing corrosive processes in the cement stone) decreased with storage time of the samples and with increasing concentration of the solution. This is consistent with literature data [4]. For samples without additives fiberglass was the decline after 1460 days of storage at 3% solution of NH₄NO₃ 20%, in 5% to 27% nominal. Samples blended with 5% glass fibres had a lower decline in the 3% - a solution of
9.5% and 5% - 19% of nominal, which can be attributed to the positive impact of the presence of glass fibres.

Figure 1. Appearance of samples of cement composites after 1460 days of storage at 5% solution ammonium nitrate without additives (X5) with admixture of 2.5wt.% (L5), and 5wt.% (M5) glass fibers.

3.2. Porosity
Porosity of the samples of cement composites stored in water treatment decreased with time because of progressive hydration structure and compacting samples. In the samples, stored in 3% and 5% NH₄NO₃ solutions, had gone in due course of corrosion II. type with storage time to porosity increased. A higher concentration of the solution generally means higher porosity of cement stone. The porosity was reflected positively by the impact of fiberglass. With increasing dose glass fibers are generally decreasing porosity (table 1).

3.3. Bulk density, compressive strength and splitting tensile strength
Bulk density, compressive strength and splitting tensile strength of samples of cement composites stored in water and aggressive solutions NH₄NO₃ in terms of the test set out in table. 1

Bulk density samples stored in water without additives and with addition of glass fibres with time of treatment grew larger. This corresponds with an increase in weight and a decrease in porosity. For samples stored at 3% and 5% NH₄NO₃ solutions out there was a reduction of their density with time saving, while for samples stored in aggressive environment was more pronounced decline.

The compressive strength of samples without additives blended with glass fibers deposited in water treatment has risen over time (figure 2) [6,7]. Compressive strength of the samples stored in the out of 3% and 5% solutions of NH₄NO₃-out with time and storage generally decreasing concentration of the solution.

Application of glass fibers has generally positive impact on reducing the strength of cement slurry stored in aggressive solutions. Strength loss was mitigated mainly by prolonged storage in aggressive solutions. For example, in the case of cement paste without fibers decreased compressive strength after 1460 days of storage at 3% solution of NH₄NO₃ from about 79 MPa to 13.5 MPa, while in the case of slurries containing 2.5% glass fibers was about the decline of 80 MPa to 34.6 MPa. Increasing doses of fiberglass from 2.5% to 5%-lo contributed to an increase in strength during prolonged storage in solution.

The same downward trend strength is confirmed also in the case of testing transverse tensile strength (table 1). For samples stored in aggressive solutions NH₄NO₃ there was a reduction in
transverse tensile strength with time in storage solutions, and this decrease is highlighted with increasing concentration of aggressive media.

Table 1. Bulk density, porosity, compressive strength and splitting tensile strength.

| Dose glass fiber | Medium | Age of samples /time saving in solution (days) | Bulk density (kg/m³) | Porosity (%) | Splitting tensile strength f<sub>sp</sub> (MPa) | Compressive strength f<sub>c</sub> (MPa) | f<sub>c</sub>/f<sub>28</sub>/100 (%) |
|------------------|--------|---------------------------------------------|-----------------------|--------------|---------------------------------|-----------------------|-------------------|
| (wt.% )          |        |                                             |                       |              | f<sub>c</sub>/f<sub>28</sub>/100 |
| 0                |        |                                             |                       |              |                                 |                       |                   |
| water            | 28/0   | 2120                                         | 31.3                  | 7.1          | 77.7                            | 100.0                 |                   |
|                  | 56/0   | 2130                                         | 31.0                  | 7.9          | 85.0                            | 109.4                 |                   |
|                  | 308/0  | 2140                                         | 28.6                  | 8.4          | 93.8                            | 120.7                 |                   |
|                  | 1488/0 | 2180                                         | 28.4                  | 9.1          | 94.9                            | 122.1                 |                   |
|                  | 29/1   | 2100                                         | 32.1                  | 6.6          | 78.7                            | 100.0                 |                   |
| 3% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 2020                                         | 37.1                  | 5.6          | 68.3                            | 86.8                  |                   |
|                  | 308/280| 1950                                         | 40.8                  | 3.8          | 48.7                            | 61.9                  |                   |
|                  | 1488/1460 | 1550                       | 57.0                  | 0.5          | 13.5                            | 17.2                  |                   |
|                  | 29/1   | 2150                                         | 34.5                  | 7.0          | 78.1                            | 100.0                 |                   |
| 5% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 1930                                         | 41.6                  | 5.3          | 50.6                            | 64.8                  |                   |
|                  | 308/280| 1850                                         | 49.2                  | 2.9          | 38.0                            | 48.7                  |                   |
|                  | 1488/1460 | 1460                     | 65.4                  | 0.04         | 5.0                             | 6.4                   |                   |
| 2.5              |        |                                             |                       |              |                                 |                       |                   |
| water            | 28/0   | 2150                                         | 31.7                  | 12.4         | 80.9                            | 100.0                 |                   |
|                  | 56/0   | 2160                                         | 29.1                  | 13.3         | 88.8                            | 109.5                 |                   |
|                  | 308/0  | 2160                                         | 26.8                  | 10.6         | 96.2                            | 118.9                 |                   |
|                  | 1488/0 | 2170                                         | 26.5                  | 7.4          | 97.8                            | 120.9                 |                   |
|                  | 29/1   | 2150                                         | 31.1                  | 11.9         | 80.8                            | 100.0                 |                   |
| 3% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 2060                                         | 35.3                  | 10.6         | 74.8                            | 92.6                  |                   |
|                  | 308/280| 2000                                         | 37.6                  | 8.4          | 67.1                            | 83.1                  |                   |
|                  | 1488/1460 | 1730                       | 47.7                  | 4.6          | 34.6                            | 42.8                  |                   |
|                  | 29/1   | 2150                                         | 29.6                  | 12.5         | 77.0                            | 100.0                 |                   |
| 5% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 2030                                         | 37.1                  | 10.4         | 57.1                            | 74.2                  |                   |
|                  | 308/280| 1960                                         | 41.1                  | 7.5          | 40.0                            | 51.9                  |                   |
|                  | 1488/1460 | 1560                     | 62.0                  | 3.1          | 15.6                            | 20.3                  |                   |
| 5                |        |                                             |                       |              |                                 |                       |                   |
| water            | 28/0   | 2120                                         | 29.1                  | 9.6          | 67.7                            | 100.0                 |                   |
|                  | 56/0   | 2130                                         | 28.6                  | 10.5         | 78.4                            | 115.8                 |                   |
|                  | 308/0  | 2150                                         | 27.5                  | 8.9          | 95.8                            | 141.5                 |                   |
|                  | 1488/0 | 2170                                         | 26.1                  | 6.4          | 97.4                            | 143.9                 |                   |
|                  | 29/1   | 2130                                         | 29.3                  | 9.6          | 71.4                            | 100.0                 |                   |
| 3% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 2080                                         | 33.2                  | 8.6          | 68.7                            | 96.2                  |                   |
|                  | 308/280| 2010                                         | 34.0                  | 7.3          | 64.2                            | 89.9                  |                   |
|                  | 1488/1460 | 1920                       | 42.8                  | 5.5          | 37.4                            | 52.4                  |                   |
|                  | 29/1   | 2120                                         | 31.2                  | 10.5         | 75.2                            | 100.0                 |                   |
| 5% NH<sub>4</sub>NO<sub>3</sub> | 56/28  | 2020                                         | 39.0                  | 9.3          | 59.9                            | 79.7                  |                   |
|                  | 308/280| 1920                                         | 43.8                  | 7.0          | 44.6                            | 59.3                  |                   |
|                  | 1488/1460 | 1680                     | 58.8                  | 4.6          | 29.0                            | 38.6                  |                   |

Loss transverse tensile strength with time saving samples in aggressive solutions was also quite significant, but more modest than the compressive strength. For example, long-term storage for the sample in a 5% solution of NH<sub>4</sub>NO<sub>3</sub> to achieve a decrease of 75.2 MPa to 29.0 MPa, a decrease to 38.6% of the original strength, the transverse tensile strength, the decrease from 10.5 MPa to 4.6 MPa, which represents 43.8% of the original strength.

In the case of transverse tensile strength more effectively showed a positive impact on reducing fiberglass tensile specimens stored in aggressive media. The achieved results are consistent with literature data [3,4,8,9].
Figure 2. The compressive strength of the samples with the addition of 0, 2.5 and 5 wt.% of the glass fibres as a function of time, represented by a logarithmic trend line.

Figure 3. SEM micrograph of the sample with cement composites admixture 2.5wt.% fibreglass stored 1460 days in 3% NH₄NO₃ solution.

Figure 4. SEM micrograph of the sample with cement composites admixture 2.5wt.% fibreglass stored 1460 days in 5% NH₄NO₃ solution.
Figure 3 and 4 are SEM micrographs of cement composites samples with 2.5wt.% alkali-resistant glass fibers stored 1460 days in 3% and 5% NH₄NO₃ solutions. The microstructure is significantly disturbed by the effect of aggressive influence of ammonium nitrate solution, which are corresponded with decreasing of the compressive strength and increasing of the porosity (table 1). Surface of the glass fibers is smooth and without damage.

4. Conclusion
The achieved results confirm the significant effect of aggressive NH₄NO₃ solutions, which appeared to pre-weight loss, increase porosity, decrease in density, compressive strength and transverse tensile strength. These results point to a leaching test samples and their corrosion II type. Application of glass fibre had a positive effect on the properties of cement pastes, most notably, this was reflected on the compressive strength and transverse tensile strength. Despite the positive effects but also the application of fiberglass there was a significant loss of strength cement mortars exposed to prolonged exposure to ammonium nitrate solutions. The obtained results are showed that the application of glass fiber can mitigate or slow down the process of corrosion of concrete leaching, respectively corrosion II type. Fiber application can extend the durability of structures exposed to such action but cannot prevent the corrosion process.

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