Identification of a materials destruction nature with simultaneous exposure to freeze / thaw cycles and chloride environment

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Abstract. The article is the first to consider the simultaneous impact on concrete structures of two destructive factors: low temperatures and aggressive environments, which are chloride-deicing agents (CDA). Then the results of experimental data obtained are presented. Finally, it is concluded that that with the simultaneous action of two factors on concrete, instantaneous destruction of concrete occurs due to the action of the Rebinder's effect, and not to the process of chemical corrosion, as it was thought earlier. **Key words:** simultaneous action of two factors on concretes, chloride anti-icing agents, Rebinder effect.

1 Introduction

The winter of 2020 was warm record-breaking on almost the whole territory of Russian Federation. At the same time, the number of frosty nights and the amount of relatively warm days were significant. The media began to complain that such weather contributes to the destruction of various technical facilities. However, until now we believed that the influence of climatic conditions on the techno sphere state and the destruction is greatly exaggerated. When analyzing accidents that took place in the railway transport in Russia in the past, there are indications that the causes of the accident are unknown [1]. However, when studying the factors affecting the strength, wear resistance and the rate of concrete destruction, Stepanova V.F. noted that the combined effect of an aggressive medium and processes (cycles) of freezing / thawing has not been investigated yet [2]. Scientific staff of the Chemistry and Environmental Engineering department of Russian University of Transport carried out the tests in which they studied the result of simultaneous exposure of chloride environments and freeze / thaw cycles on concrete structures.

There are many concrete structures in railway transport. Objects of passenger infrastructures (passenger platforms, high and low, pedestrian passenger bridges, ground passenger crossings over railway tracks), elements of a contact network for electrification of railways (supports, foundations of supports) are among them. To combat icy roads and prevent people injuries at objects of passenger rail infrastructure, it is recommended to use deicing agents. Usually they choose hloride-deicing agents

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(CDA). They are considered safe for people as well as for the environment and for the objects of the techno sphere consisting of a concrete [3]. In order to confirm or to refute these statements, the above studies were carried out.

Ehe effect of chlorides on concrete was studied in the past. In the 19-th century, L.Zh. Wick identified the negative effects of chloride environments on concrete structures [4]. In the 20-th century, such studies were carried out by A.R. Shulyachenko , V.I. Charnomsky , A.A. Baikov, N.K. Lakhtin, V.M. Moskvin, N.A. Moshchanskiy , A.F. Polak , V.B. Ratinov, T.V. Rubetskaya , V.G. Bartashevich , V.G. Batrakov, F.M. Ivanov, V.V. Kinda , A.I. Minas , O.P. Mchedlov- Petrosyan, S.N. Alekseev and V.I. Babushkin, A.V. Volzhensky [5]. In the 21st century, the most significant contribution to research on the destruction of concrete in aggressive environments, including chloride ones, was made by N.K. Rosenthal [6].

O.A. Shvagireva also carried out a study of the effect of de-icing agents on an asphalt concrete. However, in her work, a number of de-icing agents have been investigated, not only chloride ones, and the asphalt concrete was the only object for her study, but it's physical, chemical, physicochemical, mechanical, and other properties differ from concrete [7].

All the authors believe that when concrete structures exposed to aggressive environments, the destruction will proceed as a corrosion, i.e., there will be a gradual destruction that takes place at a certain speed. Corrosion, of course, is a dangerous phenomenon, but it is not a spontaneous process that occurs suddenly and immediately. Corrosion is considered as a gradual process in which it is possible to notice changes occurring with the material and to take measures for slowing down or for destruction preventing. However, there are such destructions that occur instantly. They are extremely dangerous. They cannot be prevented. They just happen suddenly and immediately, at the background of seemingly complete well-being in the appearance of the tested material. The material, it would seem, does not contain any external damage, but when exposed to any substance and mechanical action, it suddenly completely disintegrates. We write "seemingly external well-being" because any solid body has minor external damage.

But with any efforts applied (namely: aggressive medium -chemical exposure, mechanical effects - stretching / impact / compression, moistening / drying, etc. – the magnitude of external defects (pores) increase (according to the Griffiths criterion) and the body collapses.

However, in real conditions, at least two factors simultaneously act on the body: for example, humidification / drying plus vibration (in other words, precipitation / drought after that plus vibration from any mechanical impact); aggressive environment & shock loads (acid rain & mechanical impact); as well as cycles of freezing / thawing & chloride reagents impact considered in this article. Unfortunately, such sets (pairs) of impacts are still understudied.

You should also not forget about such a serious aspect of the impact as the Rebinder effect. It should be reminded that in 1928 the Soviet physical chemist Peter Rebinder, a very young scientist at that time, discovered the effect of adsorption reduction of solids strength named the Rebinder effect in his honor. The essence of this phenomenon lies in the fact that when a solid is simultaneously exposed to a liquid substance, which is a surfactant for this particular body, i.e., a substance capable of reducing the surface tension and wetting of this body with a specific liquid for this particular solid. If after wetting of the solid with such liquid any physical effect is applied to the body, then the body under study will completely collapse. For example, the following phenomena can be considered:

1. Ammonia causes cracking of brass parts.
2. Gaseous products forming during the combustion of fuel cause the process of destruction of turbine blades.
3. Molten magnesium chloride has a destructive effect on high-strength stainless steels.
4. When the bearings melt, cracks appear in the axles of railway cars.

5. The destruction of a lump of sugar moistened with water (with a small drop).
6. Destruction of brass products by wetting them with liquid mercury, and much more.

In the examples given, there are no surfactants in the sense in which we are used to define them.

The effect is almost instantaneous. And for many solids, such effect can pose a serious danger.

It should be noted that all above authors did not consider the destruction of concrete structures from the point of view of the possibility of the Rebinder effect occurring in these structures. A.Y. Davydenko considered the appearance in concrete structures of the effect of absorption decrease in strength, namely the Rebinder effect. Her work was aimed at investigating the effect of classical surfactants on the properties of concrete when a uniaxial load is applied [8]. But no studies have been conducted to identify the mechanism of concrete destruction from the effects of chlorides under conditions of freezing / thawing processes.

The authors conducted their testing in the laboratories of "Chemistry and Environmental Engineering" department of RUT MIIT. As mentioned above, the combined effect of freeze / thaw cycles and chloride environments on concrete samples was studied. Concrete samples were taken at one of the railway platforms near Moscow. The samples were placed in a solution of deicing reagents of the calculated concentration (the concentration of the reagent solution was calculated in accordance with the instructions (manuals) for the reagent usage) [9]. Test conditions chosen according to the climate and conditions of the middle band of RUSSIA (with the continental climate). The test regimes tried to bring them closer to the natural climatic conditions under which both the deicing agents themselves and their "residues" (that remain in various environmental objects after the end of the cold season) usually "work". On average, in a temperate climate, the cold period is considered from October up to April inclusive. Freezing temperatures can last from one month to three months. Thaws can take place even in the middle of winter. Salts of anti-icing reagents, having got into the soil, on the surface of the objects under study (on the concrete and metal coatings of platforms, bridges, crossings, elements of the electrification contact network), and remain there until spring. And in spring, cyclical temperature changes are very frequent: subzero temperatures prevail at night, plus temperatures do during the day. Both in winter and in spring, both negative and positive temperatures can be kept for some time. To reproduce such climatic features, cyclic temperature changes were also modeled in this work. Studies were carried out on the CDA effect on environmental objects at positive temperatures, because, as mentioned above, reagents that got into the environment do not disappear from there, but continue to affect its objects in other climatic periods.

In accordance with the above-mentioned features of the climate of central Russia, the studies were carried out at different temperature conditiones.

Mode 1 - (corresponds to Experiment 1 in all tests) - tests were carried out at positive temperatures corresponding to the ambient temperature, in the range from 0 to 25 ˚C.

Mode 2 - (corresponds to Experiment 2 in all tests) - tests were carried out at negative temperatures, corresponding to the temperature in the freezer, in the range from -12 to -18 ˚C.

Mode 3 - (corresponds to Experiment 3 in all tests) - the tests were carried out cyclically when changing temperatures from negative (corresponding to the temperature in the freezer) in the range from -12 to -18 ˚C (i.e., samples in solutions were first frozen), to positive, corresponding to the ambient temperature, in the range from 0 to 25 ˚C (the samples were taken out of the freezer). The cycles were replaced after 24 hours.

The whole testing period for all three variants was a month (30 days).

Samples measuring 20x20x20 mm (on average) were placed in a three-component 2.4% solution consisting of 0.8% NaCl, 0.8% $CaCl_2$ and 0.8% $MgCl_2$.

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The tests were conducted in accordance with ASTM C-672-76 standard, "quiz resistance to cracking when exposed concrete surfaces against sleet chemicals."

The purpose of this test is to determine the level of cracking of concrete specimens studied at different temperature conditions in different model solutions. The level of cracking according to this technique was determined visually, by external examination of the samples. Upon completion of the tests, the surface of each specimen was checked and the crack sizes were assessed using a 5-point system:

0 - no cracking
1 - Slight cracking
2 - Slight to moderate cracking
3 - Moderate cracking
4 - Moderate to strong
5 - Severe cracking

The grades were established by the observation and the size of the cracking.

Slight cracking = 1.59 mm to 4.76 mm in diameter
Large cracking = 4.76 mm to 9.53 mm in diameter
Very large cracking = more than 9.53 mm in diameter

Changes in the samples after testing were compared with the original samples. The test results are presented in Table 1.

Table 1. The degree of cracking of concrete samples after testing (For convenience, numbers with symbols "less than" (<) have been placed in the middle between the numbers. For example, "<2" would be somewhere between 1 and 2, or 1.5).

Experience number	Temperature conditions	Cracking degree	Sample appearance	Notes
1	Constant positive temperature in the range from 0 to +25 ˚C	> 1, but 2 <points, various inclusions are observed in the sediment		The beginning of corrosion processes
2	Negative temperatures, corresponding to the temperature in the freezer, in the range from -12 to -18 ˚C	5> points		A lot of homogeneous fines and fewer large pieces. Complete destruction
3	Changing temperatures from negative, corresponding to the temperature in the freezer, in the range from -12 to -18 ˚C, i.e. the samples in solutions were first frozen, at positive temperatures corresponding to ambient temperatures, in the range from 0 to 25, C, the samples were taken out of the freezer. Cycles changed after 24 hours	5>>> almost complete destruction		Homogeneous fines. Absolute destruction

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The results showed that samples that were tested at a constant low temperature and samples that were subjected to temperature cycling (from positive to negative) showed complete failure.

Initial concrete samples are shown in Figure 1.

Fig. 1. Samples of concrete taken from the Moscow Region platform.

According to table 1, it can be seen that at positive temperatures it is precisely the corrosion of concrete in chloride environments that is possible. But when two influences are applied: freezing / thawing and an aggressive environment, complete destruction of concrete occurs. Destruction proceeds according to the Rebinder effect type. It is dangerous because it arises without any prerequisites (cracking, changing the shape of the sample, changing color, the formation of any build-ups, etc.). Until now, as noted in this article, there have been no studies that have examined the simultaneous effects of freeze / thaw cycles and corrosive environments.

Thus, having received such an ambiguous result, it should be recommended to conduct research in the direction of identifying environments that cause a similar effect while simultaneously exposed to temperature cycles in order to prevent this kind of destruction.

However, in countries with a cold climate it is impossible to do without the usage of deicing reagents. If you do not use reagents, the percentage of injuries to the population will increase very much, and the number of accidents on highways will increase too. Therefore, it is necessary to develop measures to prevent the negative impact of chloride DIR on concrete structures (bridges, road surfaces, passenger railway platforms, etc.). We have repeatedly recommended and continue to recommend using sand instead of chloride reagents, and as wide as possible arranging heated road surfaces, that will pay off much faster than one might assume. Such measures make it possible to prevent emergencies.

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