An overview of nitrates-induced corrosion of reinforced concrete structures: case studies, laboratory investigations and corrosion mechanisms

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Abstract. The paper presents the results of the research on the long-term corrosion behaviour in service of the reinforced concrete structures located in nitrates-based industrial environments. Two representative types of reinforced concrete structures were investigated: industrial multi-storied buildings of fabrication and granulation towers of nitrates-based products. The case studies revealed the existence of severe nitrates-induced corrosion damage affecting the resistance, stability and durability of structures in these aggressive environments. Laboratory investigations performed on a large number of concrete and steel reinforcement samples, which were extracted from the corrosion affected elements, underlined the complexity of the corrosion process of reinforced concrete in nitrates-based environments affecting concrete and steel reinforcement by different mechanisms. The degradation of concrete consists in some decalcification and expansion phenomena which lead to cracking and, finally, to a rapid concrete destruction. The stress corrosion cracking represents the specific type of reinforcement corrosion in such aggressive environments. This phenomenon, similar with those observed at some steel tendons for prestressed concrete structures, is characterized by the cracking and brittle fracture of the steel reinforcement, without loss of steel cross-section and without visible loss of metal. The generalized and localized corrosion of steel were also identified. The possibility of apparition and development of stress corrosion cracking phenomenon of steel reinforcements, associated with the non-controlled reduction of the physical and mechanical characteristics of concrete by corrosion, lead, in the end, to a significant reduction or even to a loss of bearing capacity and sudden collapse of reinforced concrete structures, with no apparent premonitory signals.

1 Introduction

Encountered mainly in the industry of chemical fertilizers, the nitrates-based environments have various damage effects upon reinforced concrete structures, regarding the nature and the intensity of damages and also the mechanism of corrosion processes of construction materials. In comparison with other aggressive industrial environments, the nitrates-based environments from the industry of chemical fertilizers present a specific and complex aggressiveness upon reinforced concrete structures, affecting both the concrete and its steel reinforcement [1].

The corrosion processes of reinforced concrete structures in nitrates-based environments have not been widely studied due their complexity. Data and information are presented in the specialized literature, some of them contradictory, especially regarding the steel and concrete corrosion in ammonium nitrate solutions [2], [3], [4]. On the other hand, there is little information regarding the service behaviour of reinforced concrete structures in nitrates-based industrial environments, the nature and the intensity of damages and the mechanisms of the corrosion processes of concrete and its reinforcement in such aggressive environments.

The contribution that this paper aims to bring in this field is related to the results of the research on the long-term corrosion behaviour of the reinforced concrete structures located in nitrates-based industrial environments (case studies), laboratory investigations and corrosion mechanisms of concrete and steel in these specific environments.

2 Case studies

2.1 Structures

Two representative types of reinforced concrete structures were investigated, in which technological fabrication processes of chemical fertilizers occur. The investigations were done both from the point of view of the bearing structure as well as from the point of view of the aggressive agents which result from these technological processes [5]:

- Industrial multi-storied buildings of fabrication, with the bearing structure made of reinforced concrete frames (columns and beams or arches) and intermediate technological reinforced concrete floors disposed on several levels; within the buildings, the fabrication processes of raw materials and of the final products of

ammonium nitrate, calcium ammonium nitrate and complex fertilizers NPK, NP or NK types occur;
- Granulation towers, with cylindrical, tubular reinforced concrete structures and technological reinforced concrete floors disposed on several levels; within the towers, the granulation of ammonium nitrate, calcium ammonium nitrate and complex fertilizers NPK, NP or NK types takes place.

2.2 Aggressive agents

The reinforced concrete structural elements were subjected to a long term action of a strongly aggressive environment, made from various aggressive agents, gaseous, liquid or solid, used or resulting from the technological fabrication installations.

The main aggressive agents which affect the elements are, on the one hand, ammonium and calcium nitrates and the complex fertilizers NPK, NP and NK types (ammonium nitrate, ammonium sulphate, ammonium dihydrogenorthophosphate, diammonium hydrogenorthophosphate, calcium hydrogenorthophosphate, potassium sulphate, calcium carbonate, potassium chloride) , and on the other hand, acid agents (nitric acid, phosphoric acid), in the form of solutions, melts and pastes (powders + humidity), of various concentrations and temperatures [5].

2.3. Corrosion damages

The research of the reinforced concrete elements' damage state due to corrosion, after 30-50 years of service, based on specific investigation techniques [6], pointed out severe damages mainly generated by the strongly corrosive action of the ammonium and calcium nitrates and nitrates-based compounds (NPK, NP or NK). These results are concisely presented as it follows.

2.3.1 Beams and arches

The reinforced concrete beams and arches presented severe local damages due to corrosion, which led in the end to a significant reduction or loss of bearing capacity of some elements (figures 1 and 2). Mainly, these damages consist in:

➢ concrete cracking by corrosion under the action of nitrates, especially at the bottom of the beams/arches, followed by spalling and corrosion destruction of the concrete cover and by uncovering of the reinforcements; local reduction of the elements cross-section due to corrosion of the concrete in its depth;

Fig. 1. Beam: corrosion destruction of concrete cover; fragile fractures of the longitudinal and transversal steel reinforcements by stress corrosion cracking.

➢ fragile fractures, without reduction of the cross-section, of the longitudinal and transversal steel reinforcements, in some areas, caused by nitrates-induced stress corrosion cracking; localized (pitting) and generalized corrosion phenomena of the reinforcement steel were also observed;

(a) (b)

Fig. 2. Arch: corrosion of the concrete cover (a); fragile fractures of the longitudinal steel reinforcements by stress corrosion cracking (b).

➢ failures of some beams due to fracture of the reinforcements by stress corrosion cracking [1].

2.3.2 Columns

The reinforced concrete columns presented visible damages by corrosion (fig. 3), which mainly consisted in the following:

Fig. 3. Column: corrosion of concrete cover; fragile fractures of the steel stirrups by stress corrosion cracking.

➢ concrete cracking along the longitudinal steel reinforcements, more accentuated in the marginal area, due to the corrosion by expansion of the concrete under the action of nitrates; in a further phase, spalling of the concrete cover occurred and afterwards the in depth corrosion of the concrete;

- fragile fractures, without reduction of the cross-section, of the transversal steel reinforcements (stirrups), in some areas, caused by nitrates-induced stress corrosion cracking;
- superficial corrosion of the longitudinal steel reinforcements, without a visible sign of their fractures.

2.3.3 Slabs

The reinforced concrete slabs presented severe local damages by corrosion, mainly in the perforated areas and in the areas where the anticorrosive floor was damaged. The corrosion damages are similar to the ones described at the beams and, in certain areas, they led to an important reduction and loss of bearing capacity of slabs.

2.3.4 Walls

The reinforced concrete walls of the granulation towers presented advanced damages by corrosion, visible on the exterior of the towers, in areas disposed on their entire heights, in the shape of swellings, cracks and local spallings of concrete, with reinforcements uncovering and fragile fractures of the steel reinforcements by nitrates-induced stress corrosion cracking (figure 4).

Fig. 4. Wall: local spalling of concrete cover; fragile fractures of the steel reinforcements by stress corrosion cracking.

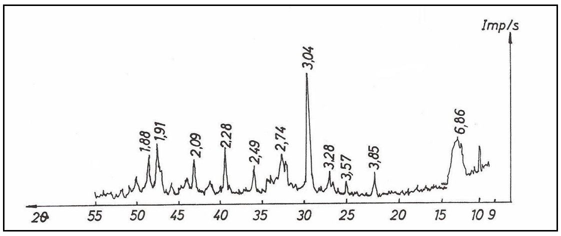
Considering the advanced corrosion damage state of some structural elements, which affects the resistance and stability of the investigated structures, intervention measures regarding the repair, strengthening or replacement of the damaged elements were proposed [5].

3 Laboratory investigations

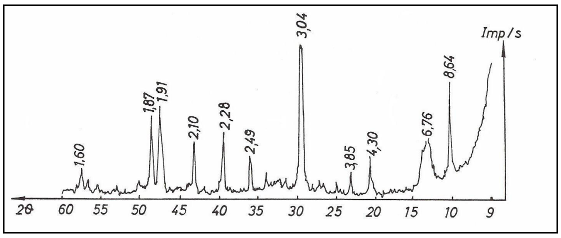
3.1. Concrete samples

The laboratory investigation results performed on a large number of concrete samples extracted from the corrosion affected construction elements and cement paste and concrete (reinforced and prestressed concrete) specimens exposed to the action of the ammonium nitrate solutions of different concentrations, are presented as it follows.

- The pH of aqueous suspension of the concrete samples damaged by corrosion varied between 5.5...8.5, values showing a total or partial removal of alkalinity in the concrete cover, under the action of aggressive agents, respectively the loss of the concrete capacity to ensure the protection of the reinforcement by passivation phenomenon.
- The concentration of water soluble nitrate (NO_3^-) and ammonium (NH_4^+) ions in the concrete samples damaged by corrosion varied, depending on the construction element type and on the extraction depth, between 0.70...9.02 % NO_3^- and respectively between 0.15...2.15 % NH_4^+ (by weight of concrete); these values of NO_3^- and NH_4^+ ions concentration have induced corrosion of the concrete and corrosion of the steel reinforcement.
- The analysis of the cement paste/concrete specimens damaged by corrosion, by X-ray diffraction, pointed out structural and compositional changes, produced in the cement paste under the action of the ammonium nitrate. As shown in figure 5, besides the peaks corresponding to the values of 3.04, 2.50, 2.29, 2.10, 1.91 and 1.87 Å, characteristic to the unattacked cement paste compounds, new peaks appear at values of 8.64, 4.30 and 1.60 Å, characteristic to new crystalline compounds based on calcium nitrates-aluminates hydrated, resulted by the corrosive attack of the ammonium nitrate solution. These new compounds, such as $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$, are responsible for the damage by expansion (increasing volume) of the concrete.



(a)



(b)

Fig. 5. X-ray diffraction patterns of cement paste hydrated: a) unattacked cement paste; b) cement paste attacked by 5 % ammonium nitrate solution, after 6 months exposure.

- The compressive strength of apparently undamaged concrete samples varied between 16.3 and 29.5 MPa, while the compressive strength of the damaged concrete was diminished to zero. This significant difference is explained by the fact that in the first phase of the corrosion process, the mechanical characteristics of the concrete do not change significantly, sometimes even temporarily increasing, while in the second phase, the mechanical characteristics gradually decrease, as an effect of corrosion by expansion, until the complete destruction of the concrete.

3.2 Steel reinforcement samples

The laboratory investigation results performed on a large number of steel reinforcement samples extracted from the corrosion affected elements are presented as it follows.

➢ The steel reinforcements presented three main types of corrosion: (i) and (ii) - generalized and localized corrosion, types of common corrosion in the case of mild carbon steels for reinforced concrete; (iii) - stress corrosion cracking, the specific type of corrosion in case of high strength steel used as tendons in prestressed concrete structures [7].

➢ The examination of the samples surface revealed, in some samples, the existence of thin cracks, perpendicularly to the samples axes, some of them inducing incomplete fracture of the reinforcements (figure 6).

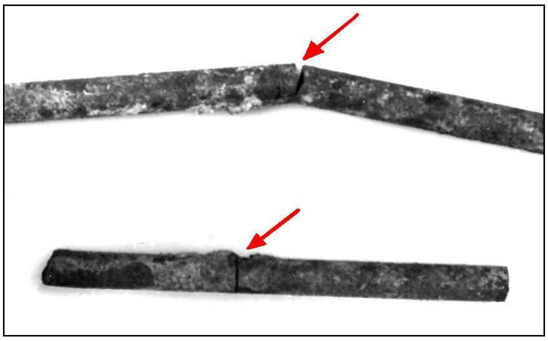


Fig. 6. Steel reinforcement samples: incomplete fracture by stress corrosion cracking.

➢ The fracture aspect of samples affected by stress corrosion cracking has a fragile character, due to the presence of typical corrosion-induced crack (figure 7)

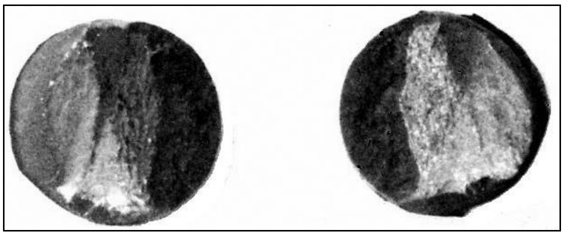


Fig. 7. Steel reinforcement sample: macroscopic appearance of the fracture surfaces by stress corrosion cracking.

After the traction test, more or less developed cracks (as width and depth) appeared on the samples surface, with the same origin as the main crack which caused the samples fracture. The fracture of steel samples occurred in a perpendicularly or inclined plane towards the samples' axes and had a fragile character (without reduction of the cross-section).

➢ The propagation of the cracks has an intergranular aspect (figure 8), some samples showing a corrosive attack at the grain boundaries, especially in the superficially decarburized areas [5].

➢ The analysis by X-ray diffraction of the corrosive products from the corrosion crack surface has revealed the presence of magnetite (Fe_3O_4) [5].

➢ The values of the mechanical characteristics of samples unaffected by stress corrosion cracking are generally between the limits prescribed in the Romanian standard for mild carbon steel reinforcements, while the values of the mechanical characteristics of samples affected by this specific corrosion type are sensitively diminished; the reduction of those characteristics is correlated with the depth of the corrosion- induced crack.

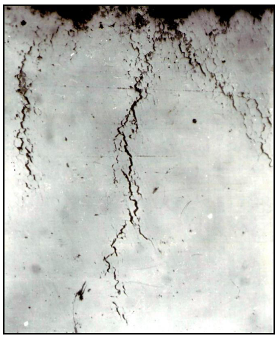


Fig. 8. Steel reinforcement sample: intergranular cracks caused by stress corrosion cracking (200:1).

4 Corrosion mechanisms

4.1 Concrete degradation

The degradation of concrete in ammonium nitrate-based aggressive environments consists in two successive stages, characterized by:

➢ decalcification phenomena, resulting from ammonium nitrate reaction with calcium hydroxide in the cement paste, with formation of hydrated calcium nitrate and emission of gaseous ammonia (NH_3) which leaves the system, having as effect the removal of alkalinity of the concrete:

$$2\ NH_4NO_3 + Ca(OH)_2 + 2\ H_2O \rightarrow Ca(NO_3)_2{\cdot}4H_2O + 2\ NH_3\uparrow \qquad (1)$$

➢ expansion phenomena, resulting from hydrated calcium nitrate reaction with calcium hydroaluminate in the cement paste, with formation of some new complex crystalline compounds and with important volume increase:

$$Ca(NO_3)_2{\cdot}4H_2O + 3CaO{\cdot}Al_2O_3{\cdot}6H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}Ca(NO_3)_2{\cdot}10H_2O \qquad (2)$$

These decalcification and expansion phenomena lead to removal of alkalinity, cracking and finally to a rapid concrete destruction by corrosion (figure 9).

(a) (b)

Fig. 9. Reinforced concrete specimens: concrete cracking due to corrosion by expansion (a); concrete corrosion (b).

4.1 Reinforcement corrosion

4.1.1 Generalized corrosion

The high oxidation capacity of NO_3^- ions and the complexing action of ferrous ions (Fe^{2+}) by the NH_4^+ ions cause the generalized corrosion of steel in ammonium nitrate environments.
The corrosion process of steel in NH_4NO_3-NH_3-H_2O system is complex, as a result of electrochemical conjugated reactions [5]:
- anodic reactions:

$$Fe \rightarrow Fe^{2+} + 2\ e^- \quad (3)$$

$$Fe + 6\ NH_3 \rightarrow Fe(NH_3)_6^{2+} + 2\ e^- \quad (4)$$

(depending on the ammonia concentration in the system);
- cathodic reactions:

$$NO_3^- + H_2O + 2\ e^- \rightarrow NO_2^- + 2\ OH^- \quad (5)$$

$$NO_3^- + 6\ H_2O + 8\ e^- \rightarrow NH_3 + 9\ OH^- \quad (6)$$

$$2\ NO_3^- + 6\ H_2O + 10\ e^- \rightarrow N_2 + 12\ OH^- \quad (7)$$

$$NO_3^- + NH_4^+ + 2\ e^- \rightarrow NO_2^- + OH^- + NH_3 \quad (8)$$

$$NO_2^- + 5\ NH_4^+ + 6\ e^- \rightarrow 6\ NH_3 + 2\ OH^- \quad (9)$$

(depending on the electrode potential value and on the NH_4^+ ions amount in solution).
The global corrosion reaction can be written as follows:

$$9\ NH_4NO_3 + 14\ NH_3 + 4\ Fe \rightarrow 4\ [Fe(NH_3)_6)].(NO_3)_2 + 3\ H_2O \quad (10)$$

The steel corrosion products in these environments are composed from a mix of $[Fe(NH_3)_6)].(NO_3)_2$ and Fe_3O_4, unadherent and unprotective products towards steel.

4.1.2 Localized corrosion

The localized corrosion of the steel in nitrates-based environments is caused by the depassivating action of NO_3^- ions similar to that caused by chloride ions (Cl^-), with formation of corrosion pits (pitting). Local destruction of the passivation film, formed at the steel reinforcement surface in the concrete pores electrolyte, is produced by a mechanism based on anionic penetration reactions [8].

4.1.3 Stress corrosion cracking

The stress corrosion cracking is a specific corrosion type of steel in nitrates-based environments, characterized by the cracking and brittle fracture of the steel reinforcements, without reduction of the cross-section and without visible loss of metal. It is produced by electrochemical selective dissolution of the anodic areas (active path corrosion), the crack is progressing by an anodic mechanism, with an intergranular aspect [7].

5 Conclusions

The results of the research on the long-term corrosion behaviour in service of reinforced concrete structures located in nitrates-based industrial environments has pointed out the existence of a severe corrosion-induced damage, which affected the resistance, stability and durability of these structures.

The corrosive action of nitrates-based environments against reinforced concrete structures acts in a complex and specific manner, by different mechanisms, both upon the concrete as well as its steel reinforcement. The degradation of concrete consists in some decalcification and expansion phenomena (similar to sulphate corrosion). These corrosion phenomena lead to cracking and, finally, to a rapid concrete destruction. The stress corrosion cracking of mild carbon steel reinforcements is a specific corrosion type in these aggressive environments, characterized by the cracking and brittle fracture of the steel reinforcements, similar to those observed at some steel tendons for prestressed concrete structures.

The possibility of apparition and development of stress corrosion cracking phenomenon of steel reinforcements in such aggressive environments, associated with the non-controlled reduction of the physical and mechanical characteristics of concrete by corrosion, lead, in the end, to significant reduction or even to a loss of bearing capacity and sudden collapse of reinforced concrete structures, with no apparent premonitory signals.

In order to assure normal service conditions of structures located in nitrates-based industrial environments, intervention measures to remedy existing damages and systematic monitoring of the service behaviour of reinforced concrete structures are required.

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