

REZISTENȚA LA COROZIUNE NITRICĂ A UNOR MORTARE SPECIALE CU CONȚINUT RIDICAT DE ZGURĂ NITRIC CORROSION RESISTANCE OF SPECIAL MORTARS WITH HIGH SLAG CONTENT

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Constructions composed of mortars and cement concretes are exposed to advanced nitrate ion corrosion processes if they are used in aggressive mediums, specific to nitrogen fertilizer industry. The paper aims at tracking down the behavior of cement mortars with a high content of slag (75%) exposed to nitrate ion corrosion as well as carrying out a analysis that might reveal the time evolution of mechanical strength of the standard mortar samples or of those containing slag, when they are submerged in various aggressive solutions. Corrosive agents, acting on the above mentioned items are in particular nitrogen oxides and ammonia gas. These compounds are found in considerable amounts in the atmospheric feature of this type of industry and their effect is intensified by an accidental increase of humidity, temperature, or steam, or unexhausted corrosive gases accompanied, possibly, by inadequate ventilation. The analysis of complex chemical processes enables the highlighting of the influence of different corrosive agents on the strength of these special mortars.

Construcțiile alcătuite din mortare și betoane de ciment sunt expuse unor procese avansate de coroziune cu ionul azotat, fiind procese specifice industriei îngrășămintelor cu azot. Scopul lucrării este de a urmări comportarea mortarelor de ciment cu un conținut ridicat de zgură (75%), expus la coroziune cu ioni azotați și analiza evoluției în timp a rezistenței mecanice a probelor de mortar standard sau cu un anumit conținut de zgură, scufundate în diverse soluții agresive. Agenții corozivi, care acționează asupra elementelor enumerate sunt în special oxizi de azot și amoniac gazos, compuși care se găsesc în cantități apreciabile în atmosfera caracteristică a acestui tip de industrie. Efectul lor este potențat de creșterea accidentală a umidității, temperaturii sau de aburul și gazele corozive neevacuate eventual prin folosirea unor instalații de ventilație neadecvate. Analiza proceselor chimice complexe care au loc permite evidențierea influenței diferiților agenți corozivi asupra rezistenței acestor mortare speciale.

Keywords: acid nitric corrosion, slag mortar, compressive and flexural strengths

1. Introduction

Cement mortars, without additives, are not resistant to such aggressive agents as nitric acid and ammonium nitrate. The presence of basic granulated blast furnace slag in concretes and mortars subjected to this type of corrosion agents improves their behavior in such media.

Samples made from mortar containing cement with 75% slag and lime (10%) were subjected to nitrate ion corrosion. To highlight the different behavior of the binder without slag there were made, in parallel, samples with Portland cement only. The samples were placed in the corrosive medium consisting of ammonium nitrate solution with a concentration of 3% and nitric acid. These solutions represent the most widespread aggressive agents inside the chemical fertilizers complex. The compressive strength was determined on prismatic samples and graphs showing the time evolution of strength were drawn. Binders with more than 75% of blast furnace slag required the introduction of a basic activator (lime).

The statistical analysis [1, 2] shows the time evolution of mechanical strength.

Intensive studies have been carried out worldwide on the effect of different kinds of media on the cement components. To illustrate the studies in the field, one can mention the contribution of Jin Wu, Hongming Li, Zhe Wang, and Jingjing Liu who studied the transport of chloride ions in concrete [1]. This notion included a variety of mechanisms, which basically refers to: the diffusion due to the action of concentration gradient, the diffusion due to pressure, and capillary suction under the action of humidity gradient. Regarding the action of the chlorine ion one may refer to the studies of Xingji Zhu, Goangseup Zi, Zhifeng Cao, Xudong Cheng [2,3].

Bilan Lin, Yuye Xu [4] have studied the corrosion behavior of fine-grain high-strength reinforcement in simulated concrete pore (SCP) solutions with various $[\text{NO}_2^-]/[\text{Cl}^-]$ ratios. This parameter was investigated using polarization and electrochemical impedance spectroscopy (EIS) techniques. The conclusion is interesting because

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Fig.1 -The trials during corrosion process / Probele pe durata procesului de coroziune.

they established that a higher concentration of chloride ions (0.598 mol/L NaCl) leads to a serious cracking of the passivation film and a poor corrosion resistance of concrete reinforcement. In the presence of nitrite inhibitor, the corrosion resistance of concrete reinforcement improves. With an increase in $[\text{NO}_2^-]/[\text{Cl}^-]$ ratio, the electrochemical indexes first quickly increase and then become nearly stable.

Industrial wastes such as furnace slag, fly ash or metallic waste are a major source of pollution and its storage requires additional protection surfaces and measures, it is much more useful to recycle recovery and reintroduce it into the industrial circuit. Fly ash was successfully used as a raw material in sintering and preparing Calcium Sulpho-Aluminate (CSA) cement in the laboratory, where its compressive strength, durability and microstructure were studied [5]. There are other studies [6-11] that highlight the importance of using industrial waste in the context of primary resources diminishing and global economy. Thus, in the present study, it was considered useful to put the slag into the mix formula.

The penetration of ions into concrete is a complex phenomenon, due to the fact that concrete is a kind of non-homogeneous material, and the micro defects or damage are produced during the service period.

2. Experimental. Materials and methods

The experimental program was designed in such a way as to reveal the physical-mechanical characteristics of the samples of mortar, with or without admixtures. According to European Normative SR EN 196-1:2016 [12] forty-five prismatic samples, 40×40×160 mm in size, were manufactured from plastic mortars, through vibration, and they were introduced into corrosive environments, after a previous curing for 28 days maturation in tap water, taking into account the slower reactions of the slag compared to those of the cement. The notations are as follows: P₁ - standard samples; P₂ - samples with slag; P₃ - slag samples with lime paste.

The binder used to make the mortar prismatic samples subjected to corrosion and mechanical tests is made of 75% granulated blast

Binder with slag physical-mechanical characteristics / *Caracteristicile fizico-mecanice ale liantului cu zgură*

Specific surface cm ² /g	Density g/cm ³	Paste of normal consistency (% water)	Setting		Hydration heat Cal/g		Mechanical resistance (28 days)	
			beginning	end	3 days	7 days	Compressive strength (Rc)	Flexural tensile strength (Rti)
4300	2.7	34	3h30min	7h	27	30	21.7	6.43

Table 1

The chemical composition of Portland cement / slag / gypsum
Compoziția chimică a cimentului portland / zgură / gips

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	TiO ₂	Na ₂ O	K ₂ O	Insoluble	CaSO ₄ ·2H ₂ O
Slag	41.3	7.43	0.07	43.3	4.4	1.0	0.3	0.4	0.5	1.3	-
Portland Cement	21.7	7.3	3.4	64.1	1.7	-	0.2	0.5	0.8	0.3	-
Gypsum	0.07	0.08	0.1	2.24	0.09	-	-	0.04	0.02	-	97.36

Table 2

The mineralogical composition of Portland cement / activity modules
Compoziția mineralogică a cimentului portland / module de activitate

C ₃ S	C ₂ S	C ₃ A	C ₄ AF	M _{Si}	M _{Al}
57.19	1.9	10	10.7	2.34	1.87

Table 3

furnace slag (basic), 20% Portland clinker and 5% gypsum. The physical – mechanical characteristics of the slag - Portland clinker binder are shown in Table 1.

The chemical composition of Portland cement, slag and gypsum are shown in Table 2. In Table 3 are shown the mineralogical composition of Portland cement and its modules.

The binder has been ground to a considerable grinding fineness (specific surface area of 4300 cm²/g), which can positively influence the mechanical strength, even if the slag used has low hydraulic capacity. The hardening of the binder is slow, the values of the initial and the final of setting time being between the ordinary limits for the cements with admixtures. The hydration heat for 3 days and respectively 7 days has low values due to the low exothermal characteristic of the slag.

Prismatic samples of mortar with Portland cement and 75% slag were made, with the binder/sand ratio of 1/1.5, given the slow hardening of this binder. Samples of Portland cement and slag binder were made, without activator as well as with basic activator – lime, in the same ratio: 1:1.5. The samples were then subjected to corrosion with nitrogen compounds.

The lime was introduced into the mortar as a paste of 12 cm consistency in an amount of 10% (in relation to the cement). In all these cases, the water/cement ratio, experimentally determined, ensured a weak plastic consistency, with a penetration of the standard cone of 5 to 5.5 cm. In order to highlight the different behavior of the mortar with the high slag content binder, there were also made specimens of cement without admixture, considered to be non-resistant to corrosion with nitrogen compounds.

The aggregate used was poly-granular quartz sand with four fractions, according to European Normative SR EN 12620:2003 [13] relating to concrete aggregate. As corrosive media were used ammonium nitrate solution of 3% concentration and nitric acid of 0,2n concentration (the choice was based on the fact that these solutions are the most common aggressive agents in the nitrogen fertilizers factories and their storage warehouses). The sample/aggressive solution ratio (in volume) was ¼, the solutions being periodically replaced.

The method of total immersion of the samples in corrosive media was employed since these binders can be used for underground construction elements that are in permanent contact with a wet environment: foundations, drains or sewers, tanks, etc.

Before being introduced into the aggressive solutions and before the mechanical tests, the samples were weighed and measured in order to determine the possible weight losses and size changes. In the meantime, benchmark specimens

were tested, having the same composition, but kept in tap water. The trials were made at different times, ranging between one month and two years (as shown in the following tables and diagrams).

3. Results and discussions

3.1. Corrosion behavior investigation

The parameters identified as important for this analysis were selected by the authors: type of aggressive agent and mortar composition. Certainly there are other parameters that can have influence on these results, such as: the presence of activator (lime) and the duration of keeping samples in solution. In this study were limited to a first analysis of the above mentioned parameters. For the future are considering expanding number of factors using advanced experimental method - Design of experiments [14-17].

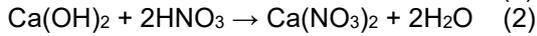
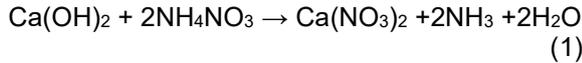
The graphs in figures 5-7 show the evolution in time of the mechanical strengths of the standard cement mortar samples and of the samples of mortar with slag addition, immersed into aggressive solutions in relation to the reference specimens made of the same mortars kept in tap water. After the analysis of these graphs and the periodical visual observations on the samples, it has to be noticed that the standard cement mortar samples are greatly corroded by the nitric acid solution that actually destroys the binder (it attacks it chemically in a quite aggressive way). The mortar becomes crumbly, while the aggregate which is visible on the surface is easily displaceable.

In section, the exterior attacked area that has a reddish hue is visibly differentiated from the central unattached area. These samples are actually destroyed after 2 years of kept in nitric acid.

For the samples made of cement with slag, even though the initial strengths are lower, the beginning of the corrosion phenomena is delayed. There is a slower forming of some white jelly-like precipitates as a result of chemical interactions of some basic components of the binder with the corrosive agent. The exterior aspect of the samples does not change significantly. After two years of immersion in nitric acid solution, the mechanical strengths are still considerable (14.8 N/mm² – compressive strength of the samples with slag addition without the lime activator).

It has to be noticed that, in all cases, the flexural tensile strengths are more affected by the corrosion of the nitrogen compounds than the compressive strengths. This behavior is explained by the increase of the jelly component of the binder with slag due to the corrosion phenomena, and by the change in the structure of the calcium silicate hydrates gels through the dissolving and leaching of the calcium hydroxide by the corrosive agent.

The reactions (1, 2) which occur between calcium hydroxide and nitric solution result in the formation of calcium nitrate (soluble) and the release of ammonia:



The reaction products are easily dissolved in water and displaced by "washing". Furthermore, the dissolution of calcium hydroxide (by chemical reaction) in the ammonium nitrate solution is higher than that in tap water. Therefore, that the ammonium nitrate decalcifies the hardened cement paste due to removal of calcium hydroxide.

By hydrolysis of calcium silicate and calcium aluminate hydrates, they could be finally converted into soft silica gel ($\text{SiO}_2 \cdot p\text{H}_2\text{O}$) and alumina ($\text{Al}_2\text{O}_3 \cdot p\text{H}_2\text{O}$) gels which are water soluble and are washed away.

Nitric solutions are very corrosive for this kind of materials. Strength of the specimens stored in water increased continually for 2 years, but the strength of the specimens immersed in NH_4NO_3 solution and HNO_3 solution clearly decreased.

Table 4 contains the values of flexural tensile strength of the three types of samples (P_1 - standard sample; P_2 - sample with clinker and slag; P_3 - sample with Portland cement, slag and lime paste), immersed into mentioned corrosive agents with their evolution in time up to 2 years.

For standard sample immersed in water (Fig. 2), 3% NH_4NO_3 solution and 0, 2n HNO_3 solution, a halving of tensile strength in the first six months could be noticed in the samples immersed in NH_4NO_3 solution. Then a decrease of up to 75% of initial strength, while in the samples immersed in HNO_3 there is a significant reduction of tensile strength for the next 6 months and practically its total loss could be seen after 24 months.

Regarding the samples with added slag (Fig. 3) their behavior into the two nitric solutions is much improved - there is a decrease of approximately 20% in the first 6 months following that up to two years to remain with just over 25% of flexural tensile strength samples immersed in water.

For the samples with lime paste (Fig. 4) there was noticed a sudden reduction in tensile strength since the first month for the HNO_3 solution, when it lost nearly 30% of initial strength and it continuously decreased in the following 24 months by approximately 60%, while the samples immersed in the NH_4NO_3 solution showed a 10% loss in 24 months. The strength of all these samples in normal water increased by at least 25%.

Table 5 contains the values of compressive strength of the three samples (P_1 , P_2 , P_3) immersed into mentioned corrosive media and their evolution in time up to 2 years.

Table 4

Flexural tensile strength evolution in different corrosive agent / *Evoluția rezistenței la întindere din încovoiere la diferiți agenți corozivi*

Aggressive agent Time	In water			In solution 3% NH_4NO_3			In solution HNO_3 0,2n		
	P_1	P_2	P_3	P_1	P_2	P_3	P_1	P_2	P_3
Samples									
1 month	8.7	6.4	7.7	6.1	4.8	7.1	5.8	4.7	5.2
3 months	9.3	7	8.5	5.5	4.3	7.7	5.2	4.2	4.9
6 months	10.1	7.3	9.1	5.1	4	7.0	4.9	2.3	4.0
12 months	11.8	7.6	9.4	4	3.2	6.8	4.3	1.8	4.0
24 months	12.1	8.1	9.9	3.4	2.8	6.1	3	0.7	3.7

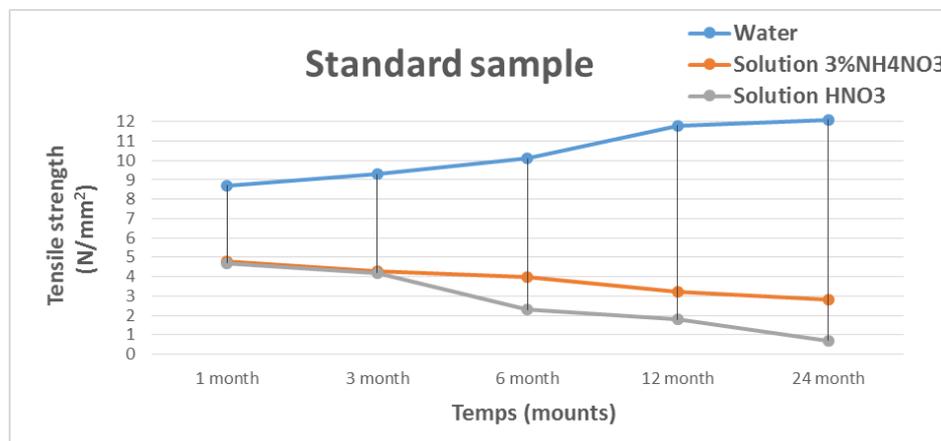


Fig. 2 - Flexural tensile strength evolution of the standard sample in different corrosive media / *Evoluția rezistenței la întindere din încovoiere a probelor standard la diferiți agenți corozivi.*

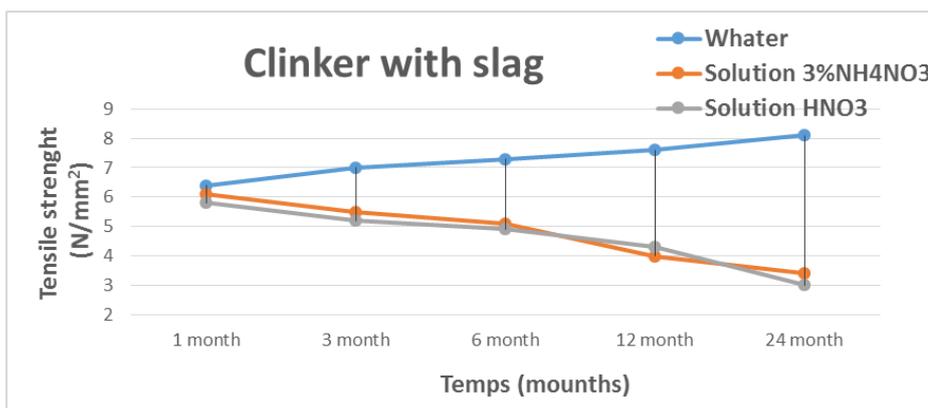


Fig. 3 - Flexural tensile strength evolution in different corrosive media of samples with slag cement / Evoluția rezistenței la întindere din încovoiere a probelor cu adaos de zgură la diferiți agenți corozivi

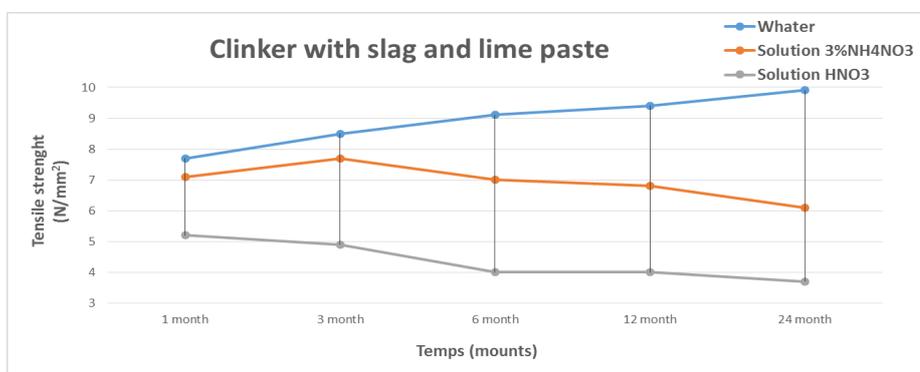


Fig. 4 - Flexural tensile strength evolution in different corrosive media of samples with lime paste / Evoluția rezistenței la întindere din încovoiere a probelor cu adaos de pastă de var în diferite medii corozive.

Table 5

Compressive strength evolution in different corrosive agent / Evoluția rezistenței la compresiune a probelor la diferiți agenți corozivi

Aggressive agent Time	In water			In solution 3%NH ₄ NO ₃			In solution HNO ₃ 0,2n		
	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃
1 month	37	21.5	26.1	33.1	20.2	22.5	22.9	16.8	22.7
3 months	41.2	22.3	28.4	31.9	19.1	24.2	21.7	15.5	22.5
6 months	42	22.7	30.3	30.7	17.7	22.9	18.8	15.2	21.9
12 months	42.3	24.3	30.7	30.1	17.0	22.3	15.1	15	20.2
24 months	41.8	25.8	30.8	29.8	17.0	22.0	10.4	14.8	18.7

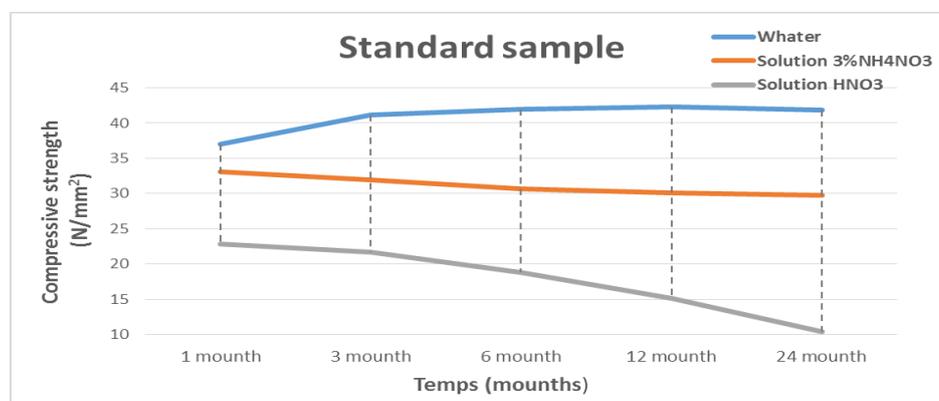


Fig. 5 - Compressive strength evolution in different corrosive media for standard samples / Evoluția rezistenței la compresiune a probelor standard în diferite medii corozive.

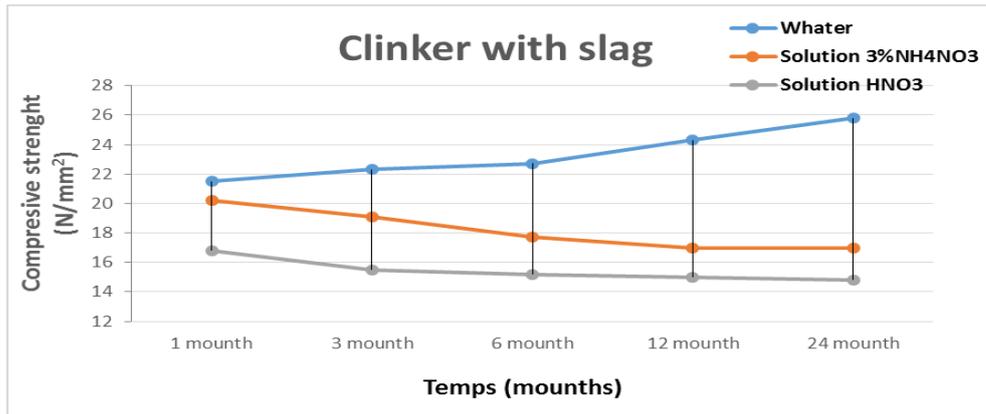


Fig. 6 - Compressive strength evolution in different corrosive media for samples with slag / *Evoluția rezistenței la compresiune a probelor cu zgură la diferiți agenți corozivi.*

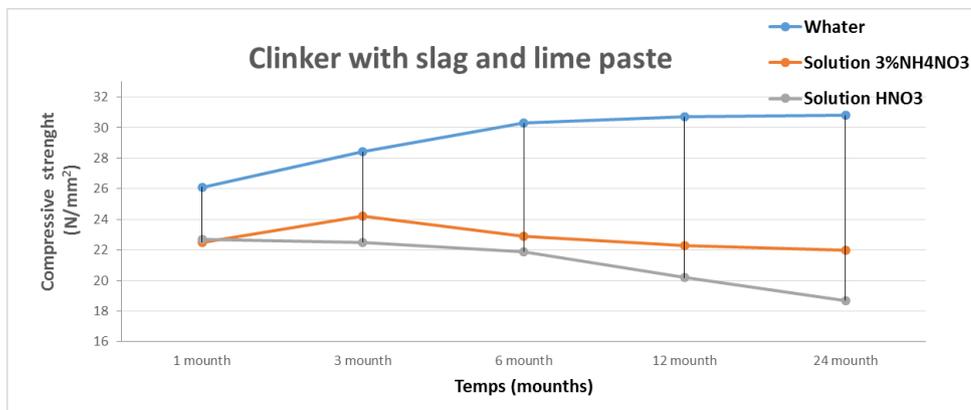


Fig. 7 - Compressive strength evolution in different corrosive media for samples with slag and lime paste / *Evoluția rezistenței la compresiune a probelor cu zgură și pastă de var la diferiți agenți corozivi.*

Compressive strength is less steep for all three samples (Fig. 5). It should be noted that in the sample immersed in NH_4NO_3 the decrease of strength is slow.

For the samples with slag (Fig. 6) the evolution of strength in normal water has an increase tendency by 20%, while for the samples immersed in nitric solutions the trend is of decrease by 12% in comparison with those for the first month.

For the samples containing lime paste was (Fig. 7), the trend is the same as in the case of the first two types of compositions - increase of up to 18% for the sample immersed in water. The third sample showed a very slow variation of strength, reaching 72% of the initial one, within a period ranging from one year to 24 months.

The weakening of the mechanical characteristics is obvious even starting from the first six months of keeping the cement samples in aggressive solutions, while in the case of the cement with slag samples, this weakening is noticeable after 12 months only. The lime-paste activator introduced into the mortar of cement with slag, even though it triggers an initial increase of the strengths, it does not alter significantly its

behavior in the case of nitric acid solution. However, one can notice a slight increase of the compressive strength of the specimens immersed in ammonium nitrate during the first six months, which is not the case of the samples without activator.

During these experiments there were considered for statistical analysis groups of 3 samples (P_1 , P_2 , P_3) with 5 levels of evaluation in time of compressive strength and flexural tensile strength (one month, 3 months, 6 months 1 year and 2 years). In total, 15 samples were evaluated for each aggressive media and each kind of mechanical test. For statistical analysis the utility Excel in Microsoft Office 2013 package was used.

Different parameters were used for the purpose of statistical analysis of the compressive or flexural tensile strength data. The standard deviation, simple variance, standard error, range and arithmetic mean or average values were calculated for the purpose of analysis (Tables 6, 7).

Thus the statistical analysis for samples immersed in water shows a decrease in strength influenced by the addition of slag and a decrease in the range which signifies a small difference

Table 6

Descriptive statistics of flexural tensile strength / *Indicatori statistici ai rezistenței la întindere din încovoiere*

Aggressive agent Statistics	In water			In solution 3%NH ₄ NO ₃			In solution HNO ₃ 0,2n		
	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃
Samples									
Mean	10.40	7.28	8.92	4.82	3.82	6.94	4.64	2.74	4.36
Standard Error	0.67	0.29	0.38	0.49	0.36	0.26	0.48	0.75	0.29
Median	10.10	7.30	9.10	5.10	4.00	7.00	4.90	2.30	4.00
Standard Deviation	1.50	0.64	0.85	1.10	0.81	0.58	1.06	1.67	0.65
Sample Variance	2.26	0.41	0.72	1.22	0.66	0.33	1.13	2.80	0.42
Range	3.40	1.70	2.20	2.70	2.00	1.60	2.80	4.00	1.50
Minimum	8.70	6.40	7.70	3.40	2.80	6.10	3.00	0.70	3.70
Maximum	12.10	8.10	9.90	6.10	4.80	7.70	5.80	4.70	5.20

Table 7

Descriptive statistics of compressive strength / *Indicatori statistici ai rezistenței la compresiune*

Aggressive agent Statistics	In water			In solution 3%NH ₄ NO ₃			In solution HNO ₃ 0,2n		
	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃	P ₁	P ₂	P ₃
Mean	40.86	23.32	29.26	31.12	18.20	22.78	17.78	15.46	21.20
Standard Error	0.98	0.77	0.90	0.61	0.63	0.38	2.28	0.35	0.76
Median	41.80	22.70	30.30	30.70	17.70	22.50	18.80	15.20	21.90
Standard Deviation	2.19	1.72	2.02	1.37	1.41	0.86	5.11	0.79	1.71
Sample Variance	4.82	2.96	4.06	1.87	1.99	0.74	26.07	0.63	2.92
Range	5.30	4.30	4.70	3.30	3.20	2.20	12.50	2.00	4.00
Minimum	37.00	21.50	26.10	29.80	17.00	22.00	10.40	14.80	18.70
Maximum	42.30	25.80	30.80	33.10	20.20	24.20	22.90	16.80	22.70

between the minimum and maximum strength. This is explained by the negative influence of the slag addition. (Tables 6, 7).

The lowest values of strength were registered for the group of samples immersed in nitric acid, as aggressive agent but also with most value range. A drastic reduction is explained by the fact that nitric acid is a strong corrosive agent (it is even one of the strongest acids known in chemistry). Also, the highest value of Standard Deviation (1.67) is noticed in this group, which can also induce a higher probability of error.

In the case of compressive strength (Table 7) a similar behavior was noticed in the samples immersed in the nitric acid solution, whose minimal sample resistance P₂ was 14.8 and 16.8, respectively, which implies an increase of only two units in two years (range = 2).

In this context a standard deviation close in value to the control sample is also found for the samples P₂ (NH₄NO₃ solution - 1.41) and P₃ (HNO₃ solution - 1.71) which shows that even if there is a spectacular increase their strength range is above average.

For sample P₁ in HNO₃ solution, an increase more than twice of the minimum with the greatest variation (range - 12.5) and a maximum standard deviation of 5.11 were noticed, although the initial strength is strongly influenced by the corrosive agent with a drastic reduction of its exposure in the first period. In time its values are not so much reduced.

An atypical behavior is noticed for the

sample P₂ in HNO₃ solution, which has a very low strength variation during the exposure period of two years (only 2 points from a min of 14 to a max of 16.8 only), which can be explained by the very strong aggressive action of the HNO₃ on the mechanical properties.

4. Conclusions

The main conclusions derived from this investigation are summarized as follows:

- The mortars with Portland cement without admixture are not resistant to corrosive agents' action (nitric acid and ammonium nitrate) in the places where nitrogen fertilizers are manufactured or stored.
- As it was presented in the „Introduction” section, the ions penetration into mortar is a complex phenomenon. The main reason is that mortar is a kind of non-homogeneous material, and the micro defect or damage is formed during the service period and also because one of its component, Ca(OH)₂ is easily attacked by aggressive ions such as Cl⁻, SO₄²⁻ or NO₃⁻ in this case.
- Nitrate ion solutions are very corrosive to this kind of materials. The strength of the samples stored in water increased continually until 2 years, and however, the strength of the samples immersed in NH₄NO₃ solution and HNO₃ solution clearly decreased.
- The presence of basic granulated blast furnace slag in the binder used in the manufacturing of

the mortars and concretes subjected to this type of corrosion improves their behavior by reducing and delaying the corrosion phenomena and preserving the strengths for a longer time than in the case of the binder without slag. The use of the basic blast furnace slag for the construction elements subjected to corrosion leads to a lower price of the binder and, at the same time, allows the reuse of a considerable amount of this waste.

- The flexural tensile strengths are more affected by the corrosion of the nitrogen compounds than the compressive strengths. This behavior is explained by the increase of the jelly component of the binder with slag due to the corrosion phenomena, and by the change in the structure of the calcium silicate hydrates gels through the dissolving and leaching of the calcium hydroxide by the corrosive agent.
- The cement with more than 75% basic blast furnace slag requires the introduction of basic activators (such as lime, calcium chloride), especially if this kind of binder has to be used in manufacturing of the mortars or concretes resistant to the corrosion of nitrogen compounds. It should be noted that the use of activators, such as calcium chloride, has a good influence on ensuring a weak plastic consistency and accelerating hydration - hydrolysis reactions of the cement components and precipitating of the reaction products.
- This type of cement with slag addition is preferable for the manufacture of underground elements or elements in wet environments, especially if it is used to make small blocks of non-reinforced concrete. In the case of reinforced concretes, due to the low basicity of these binders, the reinforcement has to be protected by introducing of some corrosion inhibitors.

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