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INVESTIGATION AND MODELLING OF CORROSION PROCESSES OF CONCRETE BY ATTACK OF AGGRESSIVE AGENTS

AGRESĪVO VIELU IZRAISĪTĀS BETONA KOROZIJAS PROCESA IZPĒTE UN MODELĒŠANA

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Introduction

Polluted urban environment could be regarded as one of the causes of gradual deterioration and damage of concrete structures. The main harmful pollutants are acids and salts formed from SO_2, which emerge from car's exhaust gases and emissions of industrial processes and chloride salts - from de-icing agent used during winter. Freeze-thaw cycles and attack of chloride affect each other. In cold climate regions, the combined effects of fatigue loading, freezing and thawing cycles and corrosion can significantly reduce the life span of concrete structures /1-4/.

The degree of exposure can range from the intermittent exposure to sulphate and de-icing salts in the case of a concrete bridge to direct exposure to concentrated brines in industrial processing plants.

The deterioration of concrete structural components exposed to soil and groundwater contaminated with sulphate and chloride salts is a serious problem in durability of concrete, specially reinforced one.

In order to prevent decay of concrete due to the influence of aggressive agents various methods were suggested modifying concrete by addition of plasticizers and mineral admixtures as well as using different coatings. Often the application of a protective coating is proposed as a solution to an existing deterioration problem /5/. The hydrophobic silicone coating and high alkaline coating applied for the surface of concrete is one of the optional measures preventing concrete under atmospheric conditions for many years /6/.

The main aim of given research was to clarify the processes of corrosion both for the matrix of concrete and it's surface as well as to study the influence of different aggressive agents: sulphate solutions with different pH; chloride ions containing solutions – 3% NaCl and mixture of chloride salts (NaCl, KCl, $CaCl_2$, $MgCl_2$) were studied.

Materials and methods of investigation

Three series of concrete samples, were used in the experimental tests: reference or series I - concrete samples without admixture or coating; series II – concrete samples with acrylic-based admixture (A); series III - concrete samples covered with high alkaline coating Xypex .

Concrete cubes (50x50x50 mm) were prepared from Portlandcement CEM I 42,5N (PLC) and filler containing mixture of sand and gravel coarse aggregate in ratio 1:4, Table 1.

Table 1.

Compositions of model samples

Series	W/C %	PLC, kg/m^3	Water, kg/m^3	Aggregate (8-16mm) kg/m^3	Additives, %	Compr. strength, MPa
I	0,62	350	217	1876	-	32,8
II	0,55	319	175	1916	A – 5,0%	37,4
III	0,62	350	217	1876	coating	33,5

All samples were matured for 28 days at the temperature of 20^{0}C and humidity of 90%, after that each side of the cubes of series III were covered with high alkaline coating and dried for 7 days at room's temperature and then subjected for further testing.

Three different types of solutions were used for absorption measurements /8/:

1) water;

2) solutions containing chlorides – 3% NaCl and mixture of 0,5; 1; 3% solution of chloride salts (M) (KCl, $CaCl_2$, $MgCl_2$);

3) Sulphate solutions with different pH – sodium sulphate solution and sulphuric acid solution, where constant content of $SO_4^{2-} = 0.25$ mol/l.

The cubes of concrete were immersed in solution so that the solution level was 10 mm above the surface of specimens. The water uptake was measured by successive mass weighing, at regular intervals of 5 minutes in the first 30 min of testing and later at every 10 minutes up to

2 hours and at every 30 minutes up to 5 hours of measurements. Investigation was performed according to literature /8/, where the following parameters are calculated: 1)WAC (water or solution absorption capacity); 2) porosity.

After absorption measurements, the samples were immersed both in water and solution of salts for 1-12 months under static conditions. pH of solutions after definite period – every day of immersion was measured by Laboratory Jonmeters WTW pH-340. Amount of Ca^{2+} in solution after the expose of specimens was determined by chemical analysis using complexonometric titration (with trilon B) method. Amount of chloride was determined in different depth of specimen by chemical analysis using the argentometric method.

The mineralogical composition of concrete specimens, before and after immersion in solutions, were analysed by X- Ray Diffraction in different depth.

The morphology of concrete was characterised by optical microscope (Leica M420).

Results and discussion

Absorption of water, SO_4^{2-}or Cl^- containing solutions

There is the correlation between the porosity of concrete and transport of aggressive agents causing corrosion. Due to the porosity, liquids are able to soak into the exposed surfaces of the concrete and carry contaminants such as sulphate or chloride ions with them. Therefore the alteration of porosity could be an efficient way to improve the durability of concrete.

Recently there is a common practice of employing additions as acrylic-based admixtures to cement or covering surface of concrete with high alkaline coating, allowing to obtain concrete with pores of smaller dimensions and, consequently of larger durability.

According to origin and characteristics the pores can be classified as macro pores, capillary pores and gas pores. Pores with dimensions larger than 0,1 μm contribute to the mass transport by diffusion, ionic migration, capillarity and permeability, while the smaller pores only influence the process of gaseous diffusion and sorption as well as ionic diffusion and migration. Since capillary pores and macro pores are particularly relevant with regard to quality of concrete, distribution of these two types are considered to be depending on W/C.

The porosity of concrete, in this work expressed as absorption of solution, is related to its performance as a barrier against the transport of aggressive agents that cause corrosion of concrete /9/.

During experiments it was determined that the porosity of specimens and the penetration of water, Cl^- and SO_4^{2-} containing solutions are in straight proportion versus the time of exposure and applied admixture of specimens, Fig. 1.

In all cases the weight of specimens increases for first 20 minutes of immersion in water or Cl^- and SO_4^{2-} containing solutions, Table 2.

Table 2

Average weight increase of specimens after immersion for 20 min.

	Water, %	3% NaCl solution	Solutions of chloride salts			10% Na_2SO_4 solution
			0.5%	1.0%	3.0%	
Series I	1.77±0.05	1.78±0.05	1,95±0.05	2.80±0.05	3.40±0.05	4.8±0.05
Series II	1.80	1.85	1.40	2.10	3.40	3.6
Series III	1.17	1.30	2.30	2.80	2.80	3.0

The acrylic-based admixtures and treatment of concrete surface with high alkaline coating decrease the amount of larger pores and absorption of water and chloride solutions.

Sulphate and chloride ions may be transported into concrete by one or by a combination of various transport mechanisms. In most practical applications, diffusion is assumed to be the mechanism of capillary transport. The fraction of larger pores was appearing to contribute directly to the penetration of ions.

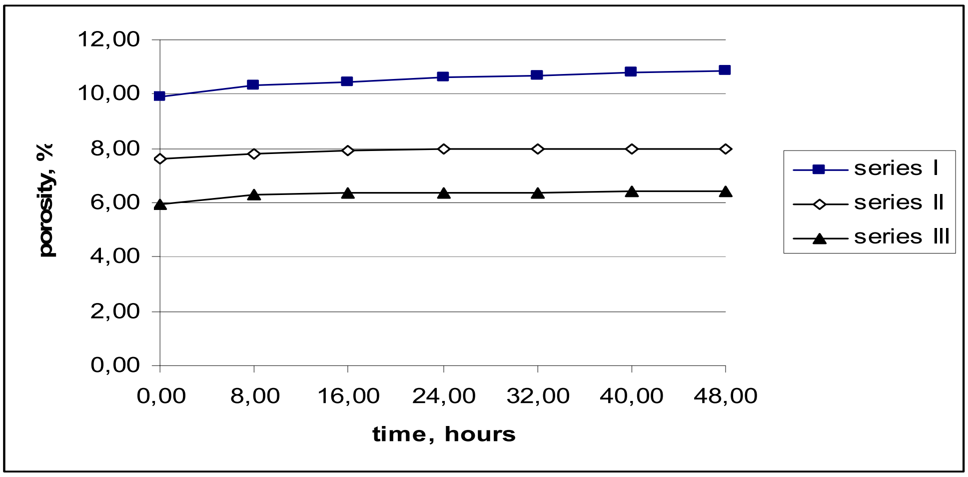


Fig. 1. Porosity of concrete after exposure in chloride containing solutions (M).

For calculation of the total porosity the following equation was used /8/:

$P = (1-\rho_r / \rho_a)$. 100%, were ρ_r – real density, ρ_a – apparent density.

where $\rho_r = M_1/(M_1-M_2)$, g/cm^3

$\rho_a = M_1/(M_3-M_2)$, g/cm^3 , where M_1 – weight of dry specimen, M_2 – weight of waterlogged specimen in water, M_3 - weight of waterlogged specimen in air.

The porosity of all specimens depends on the type of concrete and concentration of chloride or sulphate ions in the solution, Figure 2.

The admixture A (series II) and coating (series III) reduce the porosity of concrete.

The porosity of samples of series I after exposure in 3% NaCl solution is 15 – 17%, while exposure of concrete (series II, III) to solution of chloride salts reduces the porosity for ~5 % due to precipitation of salts in capillary pores. Similar processes occur in solutions containing sulphate.

Solution in pores of concrete is a concentrated electrolyte; there is a chemical equilibrium of its chemical and ionic species, that takes into account the ion-ion and the ion-solvent interactions; i. e., ionic activities instead concentrations. A change in concrete mineralogy can lead to a change in composition of pore solution, as the equilibrium is changed.

For samples of IIIrd series the formation of a dense superficial layer controls the kinetics of the deterioration process and hinders the penetration of solution of salts.

Alteration of content of calcium ions.

The processes during immersion in solution of chloride salts could be divided into two steps:

1) initial period of immersion with significant fluctuation in the pH of the solution and dissolution of $Ca(OH)_2$. It should be noted, that low or no influence of admixture to the durability of concrete exposed to chloride containing solution was observed. High

concentrations of calcium in solution were detected that is evidence of the de-calcification of the specimens;

2) carbon dioxide (CO_2) reacts with $Ca(OH)_2$ forming carbonates, and following decarbonisation of carbonates in liquid phase. After exposure the considerable proportion forms a dense superficial layer of carbonates on surface of concrete what possibly further influences the kinetics of the deterioration process.

Due to the crystallisation and precipitation of carbonate on concrete surface the amount of dissolved Ca ion in mixture *of chloride salts* solutions decreases. The high alkaline coating provides good protection on surface – eluted amount of Ca ion is 4 mg/l and it remains constant with increasing concentration of solution. The interaction between cement hydrates and solution, i.e., the calcination of all types of concrete specimens (content of Ca ion in solution reaches 26 mg/l) in *NaCl solution* demonstrate high activities.

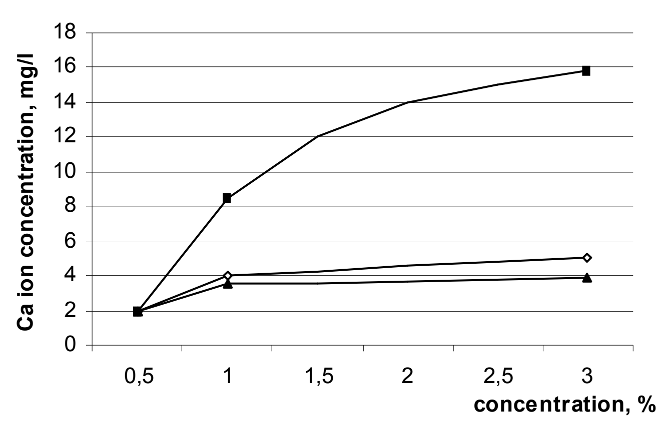


Fig. 2. *Calcium ion concentration in chloride solution M after exposure 12 months.*
■- series I, ◊ - series II, ▲- series III

The next step of investigation was to consider the action of sulphate containing solution with different pH (sodium sulphate solution and sulphuric acid solution, where $SO_4^{2-} = 0,25$ mol/l) on concrete specimens (series I-III). Immersion in distilled water can cause a leaching of portlandite, sulphuric acid produces a dissolution of CSH and portlandite, and which in turn leads to the formation of a dense superficial layer of gypsum which controls the kinetics of deterioration process.

Table 3

Evolution of the pH of water and sulphate solutions during immersion

		Time of immersion, h								
s.	initial medium	24	48	72	96	120	144	192	240	288
I	water pH=6	9.2	9.4	9.6	9.7	9.9	10,0	10.2	10.4	10.6
	Na_2SO_4 pH=7	9.5	9.6	9.8	10.1	10.2	10,4	10.8	11.0	11.0
	H_2SO_4 pH=0,21	0.47	0.80	0.90	1.03	1.05	1,10	1.20	1.30	1.40
II	water pH=6	7.8	7.9	8.0	8.0	8.1	8,1	8.2	8.2	8.2
	Na_2SO_4 pH=7	8.4	8.5	8.6	8.7	9.0	9,3	9.6	9.8	10.0
	H_2SO_4 pH=0,21	0.46	0.60	0.60	0.66	0.70	0,80	1.10	1.20	1.36
III	water pH=6	10.0	10.1	10.1	10.2	10.2	10,2	10.3	10.5	10.6
	Na_2SO_4 pH=7	10.1	10.1	10.2	10.2	10.3	10,3	10.5	10.4	10.5
	H_2SO_4 pH=0,21	0.30	0.44	0.45	0.46	0.55	0,55	1.04	1.0	1.15

Calcium ion concentration in 10% sodium sulphate solution after immersion for 240 hours is following: for concrete series I – 8.9 mg/l, series II – 7.1 mg/l, series III – 6.2 mg/l.
High concentration of calcium - as far as 2000 mg/l in sulphuric acid solution was detected what is evidence of the de-calcification of the concrete.

Simulation of attack of sulphate and chloride containing solutions.
After exposure of the specimens in solution a visual evaluation was carried out. The specimens immersed in water exhibit no visible signs of surface deterioration or formation of surface deposits. The surface deterioration was observed only after immersion in sulphate or chloride containing solutions.
The sulphate or chloride concentration within the concrete tends to equalize with the concentration of salts at surface of specimens over the time. Concentration curves show typical distribution of sulphate or chloride ions at different depth of specimens. The concentration of ions within the concrete is greater near the surface of specimens, and at any point x within the concrete it increases within the time.
In relation to corrosion of concrete, especially reinforced concrete is an electrochemical process whereby both chemical reactions and the movement of electrons and ions are occurring simultaneously. The locations where corrosion reactions are occurring are referred to as anodic sites. Cathode areas are protected by the corrosion, which occurs at anodic sites.
On a localized basis, corrosion cells can be formed due to differences in the chloride concentration at various locations along a single bar. Macro-cell corrosion can be very aggressive, and is responsible for the major part of the severe structural damage.
Patching a chloride-contaminated structure will create additional incompatibilities between the new chloride free patches and the surrounding chloride contaminated concrete. As a result, patching can create additional corrosion cells between the patches and surrounding concrete /10/.
The content of sulphate and chloride was measured in various depths of specimen.

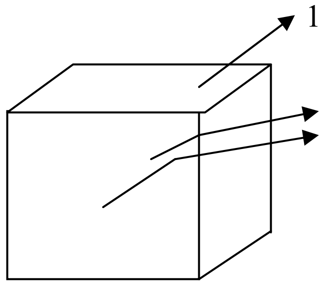


Fig. 3. *Pattern of investigation.*
1. – surface of specimens,
2. – depth 12.5 ± 0.2 mm,
3. – depth 25 ± 0.2 mm

Remarkable progressive surface deterioration underwent the concrete of series I after immersion in solutions of salts.

Table 4

Amount of chloride in specimens after exposure in M solutions for 12 months

Series	Depth, mm	Na^+, wt.%	Ca^{2+}, wt.%	SO^{2-}_4, wt.%	Na_2SO_4, wt.%
I	0 ± 0.2	0.34 ± 0.1	0.24 ± 0.1	1.97 ± 0.1	2.32 ± 0.1
	12.5	0.23	0.56	1.74	1.67
	25	0.15	1.35	1.36	1.23
II	0	0.38	0.91	0.98	1.05
	12.5	0.31	0.99	0.83	0.71
	25	0.14	1.47	0.79	0.43
III	0	1.20	-	0.92	0.45
	12.5	0.11	1.40	0.43	0.30
	25	0.00	1.53	0.00	0.00

The concentration of sulphate and chloride in pores of samples with acrylic-based admixtures (series II) and samples covered with high alkaline coating (series III) is much lower than that in specimens of serie I.

By XRD analyses of samples after treatment in Na_2SO_4 solutions – quartz, calcite and Na_2SO_4 were detected, but after treatment in H_2SO_4 solution - quartz, calcite and gypsum, see Table 5. The formation of gypsum can lead to further deleterious reactions in the cement matrix. Gypsum may react also with other cement phases forming $3CaO.Al_2O_3.3CaSO_4.32H_2O$ (ettringite) or $Ca_6[Si(OH)_6]_2.CO_3.(SO_4)_2.12H_2O$ (thaumasite) /11,12/.

Quartz, calcite and chloride salts after treatment in chloride containing solutions were detected. A low amount of chloride as $CaCl_2$ on surface and at the depth of 12.5 mm of concrete of series I was determined. It can be explain with overlapping of diffraction lines of quartz and chloride salts of XRD patterns.

Table 5

Crystalline phases after immersion into sulphate solutions

Series	Depth, mm	Na_2SO_4	H_2SO_4
I	0 12.5 25	quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4	quartz, gypsum quartz, calcite and gypsum quartz, calcite and gypsum
II	0 12.5 25	quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4	quartz, calcite and gypsum quartz, calcite and gypsum quartz, calcite
III	0 12.5 25	quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4 quartz, calcite and Na_2SO_4	quartz, calcite and gypsum quartz, calcite quartz, calcite

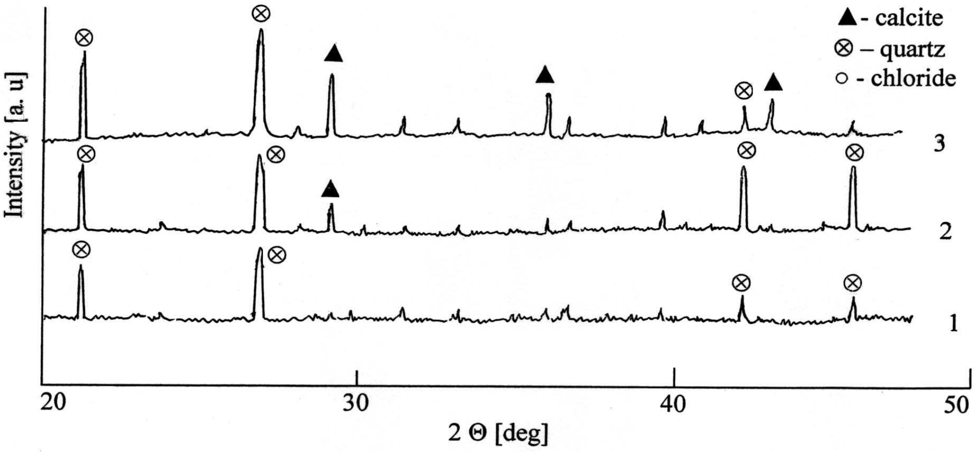


Fig. 4. *XRD patterns of concrete at the depth of 12.5 mm after exposure in solution of chloride salts. 1 – series I, 2– series II, 3 - series III.*

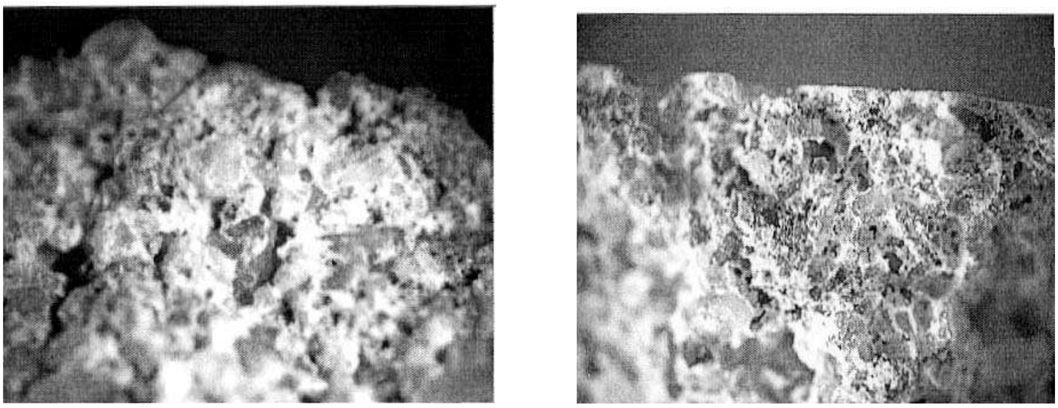
The quality of concrete after exposure in salts solution can be characterized as content of crystalline phases. Due to the decalcination of structure, amount of calcite in concrete decreases. The amount of calcite depends on depth of specimens – the highest content of calcite is on surface. Better protection of concrete provides high alkaline coating, high concentration of calcite at the depth of 12.5 mm, could be observed, see Figure 4.

Investigation by optical microscope shows that concrete in the fully cured state has heterogeneous structure consisting of a cement matrix and other components and with pores of varying size, Fig. 5.

The cross-section of concrete of series I and III after exposure in solution of chloride salts demonstrate hindered penetration of chloride salts in concrete specimens, Fig. 5, 6.

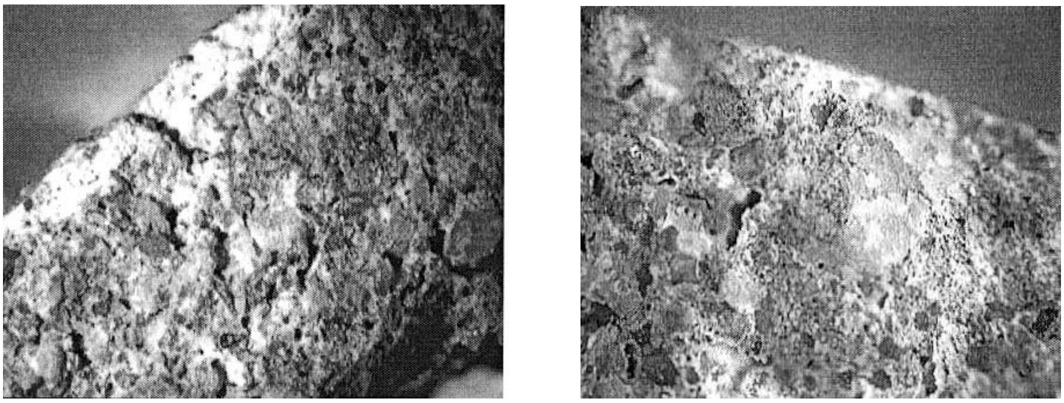
Different processes take place in the specimens immersed in the solution of sulphuric acid. Calcium ions have been reacted with sulphate ions to produce gypsum in pores.

High alkaline coating on the surface provides high protection of concrete against solutions containing aggressive ions.



a) b)

Fig. 5. *The cross-section of concrete of series I after exposure: a – in water, b – in solution of chloride salts (M). (Magnification 40×).*



a) b)

Fig. 6. *The cross-section of concrete of series III after exposure: a – in water, b – in solution of chloride salts (M). (Magnification 40×).*

Conclusions

1. The processes in the chloride and sulphate containing solutions after immersion of concrete samples could be divided into two steps:
   - dissolution of $Ca(OH)_2$;
   - carbonization of $Ca(OH)_2$ in liquid phase and precipitation of carbonate on concrete surface.
2. The porosity of samples after exposure in solution of chloride and sulphate containing solutions depends on the type of salt and concrete.
3. The processes of penetration of aggressive ions and deterioration of concrete samples are most active in following cases:
4. chloride ion containing solutions – from NaCl solution;

5. sulphate ion containing solutions - from sulphuric acid solution.
6. By XRD analyses after exposure of concrete in different solutions quartz, calcite and accordingly chloride salts (NaCl, mixture of chloride salts) or gypsum (Na_2SO_4, H_2SO_4 solutions) were detected. Lower content of crystalline phases due to decalcination of structure was detected in samples of concrete without admixture.
7. The high alkaline coating decreases the penetration of aggressive ions into concrete samples and decalcination of structure.

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J. Sētiņa, I. Vītiņa, L. Krāģe, G. Šahmenko. Agresīvo vielu izraisītās betona korozijas procesa izpēte un modelēšana.

Betona korozijas procesa pētīšanai dažādos dziļumos izveidoti modeļparaugi ar koroziju kavējošām piedevām-poliakrila piedevu masā un augsti sārmainu pārklājumu virsmai. Korozijas process modelēts sulfāta jonus saturošos šķīdumos ar dažādu pH un hlorīda sāļu šķīdumos. Noteikts, ka korozijas process sāļu šķīdumos notiek

divās fāzēs: $Ca(OH)_2$ izskalošana no betona un sekojošā $Ca(OH)_2$ karbonizācija un nogulsnēšanās uz modeļparaugu virsmas. Korozijas procesa intensitāte sāļu šķīdumos un paraugu porainības izmaiņas ir atkarīgas no izmantotiem antikorozijas materiāliem. Rentgenfāžu analīzē noteiktas kristāliskās fāzes pirms un pēc eksponēšanas sāļu šķīdumos: līdzās galvenām kristāliskām fāzēm kalcītam un kvarcam pēc apstrādes hlorīdu šķīdumos konstatēti līdz 25 mm dziļumam atbilstošie hlorīdu sāļi; pēc apstrādes sulfātu šķīdumos konstatēti – kalcīts, kvarcs un ģipsis. Secināts, ka labāko aizsardzību betona modeļparaugiem agresīvās koroziju izraisošās vidēs nodrošina augsti sārmains virsmas pārklājums Xypex.

J. Setina, I. Vitina, L. Krage, G. Sahmenko. Investigation and modeling of corrosion processes of concrete by attack of aggressive agents

In order to study the processes of concrete corrosion in different depth, model samples were prepared containing corrosion preventing additives: acrylic-based admixture and high alkaline coating on the surface. The process of corrosion was simulated both in solutions containing sulphate ions with different pH as well as in solutions of chloride salts. The process of corrosion in the salt solutions could be divided into two steps: dissolution of $Ca(OH)_2$ and following carbonisation of $Ca(OH)_2$ in liquid phase and precipitation of carbonate on concrete surface. Both the intensity of corrosion processes as well as the alteration of the porosity of samples is dependent from the type preventive remedies. Crystalline phases before and after exposure in salt solutions were detected by XRD: after the exposure in chloride solutions along to the main phases of calcite and quartz the salts of chlorides were detected in samples up to the depth of 25 mm; after exposure to sulphate solution – calcite, quartz and gypsum were detected. It could be concluded that from all the protective measures, the surface treatment of concrete samples with high alkaline solution (Xypex) exhibits the best protection against aggressive environment.

Я. Сетиня, И.Витиня, Л.Краге, Г.Шахменко. Изучение и моделирование процесса корозии бетона вызванной действием агресивных веществ.

С целю изучения профиля процесса корозии бетона, приготовлены модельные образцы с различными антикорозными добавки – добавка полиакрилата в массе и обработка поверхности образцов сильно щелочным раствором. Процесс корозии моделирован в растворах солей - сульфата с различным pH а также в растворах солей хлорида. Установлено, что процесс корозии бетона в растворах солей двух стадийный: вымывание $Ca(OH)_2$ из бетона и последующий процесс карбонизации и осаждение кальцита на поверхности бетона. Интенсивность процесса корозии в растворах солей и изменение пористости образцов зависит от примененного антикорозионного средства. Рентгенно-фазовым анализом орпеделены кристаллические фазы в бетоне до и после экспонирования в растворах солей: главные кристаллические фазы - кальцит и кварц, после обработки в растворах солей добавочно, определены соответсвующие соли хлоридов или гипс. Сделан вывод, что наилучшую антикорозионную защиту модельных образцов бетона обеспечивает поверхностная обработка сильно щелочным раствором – Xypex.