# Polymer reagent in construction practice

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**Abstract.** This article is devoted to the use in concrete of the polymeric reagent POLY-ANS, developed based on the production waste of polyacrylonitrile fibers. The results of the effect of the reagent on the capillary absorption of concrete, which contributes to the provision of high resistance of cement concrete in saline environments, are given.

## 1 Introduction

The most urgent problems in the republic requiring an early resolution include the problem of protecting the buried concrete structures of buildings and structures from sulfate aggression.

Corrosion processes occurring in concrete in a sulfate environment lead to the formation of gypsum and hydrosulfoaluminates in the concrete structure with an increase in the volume of solid phases, which causes the appearance of internal stresses exceeding the strength of concrete and destroying concrete [1].

An increase in the resistance of concrete to corrosion processes and inhibition of destructive processes in cement stone and concrete are achieved by several technological measures. The most significant measures are limited $C_2S$ content to reduce the Ca(OH) content in the cement stone; introduction of amorphous silica additives into cement for chemical binding of calcium hydroxide; increasing the density with the help of surfactants, water repellents, etc. [2].

## 2 Method of testing concrete for capillary permeability. Comparative experiments.

To modify the structure of a cement stone, the most relevant from the point of view of protection against crystallization corrosion and exposure to a hot and dry climate at the moment are the additives of water-soluble polymers - polymer gels (gel polymers). In Uzbekistan, reagents - polymer stabilizers based on nitron and acrylonitrile fiber production waste - K-9, POLY-ANS have been developed.

In particular hydrolyzed stabilizing polyacrylonitrile was obtained by hydrolysis in a silk medium using cross-linking agents (polymerizers) and modifiers [3]. Waste polyacrylonitrile fibers are used as polyacrylonitrile raw materials for the agent's preparation.

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The POLY-ANS reagent is intended for use as a stabilizer of drilling fluids in drilling oil and gas wells and in agriculture as a soil structure former and in other sectors of the national economy.

The reagent is an effective stabilizer of drilling fluids, salt-resistant (up to full saturation with NaCl). Brand - POLY-ANS Tsh 64-22165670-001: 2012. Appearance viscous yellow liquid. Mass fraction of dry residue, % not less than 10. Nominal viscosity of a 1% aqueous solution according to a viscometer at a temperature of 20+ 0.50C within 30-60. The index of hydrogen ions Ph is in the range of 10-12. Density in g/cm$^3$ - not less than 1.050. The guaranteed shelf life is 3 months. At normal temperatures, the reagent does not emit harmful substances. The reagent is fire and explosion-proof.

## 3 Results

The polymer reagent is used to develop corrosion-resistant concrete intended for operation under conditions of sulfate aggression.

The development of corrosion-resistant concrete was carried out based on local materials: alite Portland cement of the Kuvasay cement plant; aggregates (large and small) of the Akbarabad and Beshalysh quarries; fillers - acid ashes of dry extraction TPP of Fergana TPP; chemical additive - polymer reagent POLY-ANS; corrosive environments - saline groundwater.

For the research, the compositions of the concrete mixture were used for three classes of concrete B15, B25, B30, and their compositions were determined ((C:P:Sh) - (1: 2.31: 4.57); (1: 1.72: 3.42 ); (1: 1.26: 2.50) respectively.

The sulfate resistance of cements was assessed according to the coefficient of resistance, determined by the method of V.V. Kind. At the same time, such cement is considered to be sulfate-resistant, in which the resistance coefficient after 6 months is at least 0.8.

The strength of samples with POLY-ANS additives is: from 3x to 180 days hardening in a solution of 1% $MgSO_4$ - 43-106MPa; in a solution of 5% Na2SO4 varies from 41 MPa to 110 MPa, i.e., strength in solutions of 1% $MgSO_4$ increases by 92%, in 5% $Na_2SO_4$ by 130%.

The strength of cement samples with the addition of finely ground TPP ash at 3-180 days of age has the following results: in a solution of 1% $MgSO_4$ -33-96MPa; in a solution of 5% Na2SO4 3 5-102 MPa, i.e., the increase in strength by 180 days in 1% $MgSO_4$ is 88%, in a solution of 5% $Na_2SO_4$ - 122%.

**Table 1.** Strength of a multicomponent binder with a polymer additive

| № | Introduced additive | Aggressive Wednesday | Compressive strength of samples, MPa, days | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 3 | 7 | 14 | 28 | 90 | 180 | 360 |
| 1 | POLY– ANS | 1% $MgSO_4$ | 43 | 48 | 54 | 63 | 79 | 98 | 106 |
| 2 | Ash TPP | 1% $MgSO_4$ | 33 | 36 | 40 | 54 | 78 | 96 | 102 |
| 3 | - | 1% $MgSO_4$ | 33 | 41 | 50 | 53 | 50 | 51 | 48 |
| 4 | POLY– ANS | 5% $Na_2SO_4$ | 41 | 50 | 54 | 62 | 85 | 106 | 110 |
| 5 | Ash TPP | 5% $Na_2SO_4$ | 35 | 40 | 48 | 66 | 84 | 102 | 109 |
| 6 | - | 5% $Na_2SO_4$ | 26 | 28 | 35 | 41 | 45 | 46 | 47 |

Non-additive Portland cement has a resistance coefficient in the water of 1.00 by 28 days of hardening; in 1% $MgSO_4$ -1.43, in 5% $Na_2SO_4$ -0.95. With the addition of POLY-ANS additives and finely ground TPP ash, the samples' resistance coefficients in water and saline solutions increase and have maximum values in water, solutions of 1% $MgSO_4$ and 5% $Na_2SO_4$ (Table 2).

**Table 2.** Resistance coefficients of cements with additives

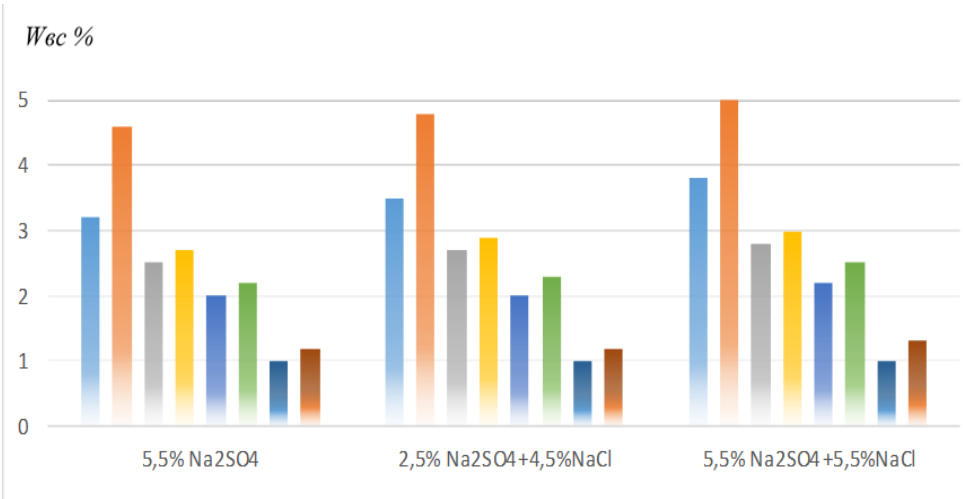
| № | Introduced additive | Resistance coefficient, Ks, day | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $H_2O$ | | | 1% $MgSO_4$ | | | 5% $Na_2SO_4$ | | |
| | | 90 | 180 | 360 | 90 | 180 | 360 | 90 | 180 | 360 |
| | Portland cement (alite Kuvasay) | | | | | | | | | |
| 1 | POLY– ANS | 1.73 | 2.13 | 2.20 | 1.52 | 1.53 | 1.58 | 1.63 | 1.66 | 1.67 |
| 2 | Ash TPP | 1.00 | 1.14 | 1.07 | 1.35 | 1.33 | 1.33 | 1.45 | 1.42 | 1.42 |
| 3 | - | 1.05 | 1.00 | 1.02 | 1.17 | 1.14 | 1.04 | 1.05 | 1.05 | 1.02 |

The increase in the sulfate resistance of cements due to the addition of POLY-ANS additives and finely ground TPP ash is explained by the binding of calcium hydroxide released during hydration.

The effect of the type and dosage of POLY-ANS additives (0.01.0.02.0.04%) on capillary absorption in working highly concentrated saline solutions was studied: 5.5% $Na_2SO_4$; 2.5% $Na_2SO_4$ + 5.5% NaCl ; 5.5% $Na_2SO_4$ + 5.5% NaCl.

Capillary absorption of concrete was studied by assessing the ability of concrete to absorb a saline solution in direct contact with the surface of an aggressive liquid medium after cyclic temperature exposure. The amount of aggressive solution absorbed by the concrete sample for a certain period ($W_{suc}$,%) is taken as the indicator of capillary absorption.

It was found that the capillary absorption of concrete naturally increases as the composition of the saline solution becomes more complex.




1, 2 are reference concrete; 3, 4, 5, 6, 7, 8 are concrete with additives, respectively POLY-ANS1; POLY– ANS2; POLY– ANS 3; -normal hardening; -after preliminary cycle. temperature effect

**Fig. 1.** Diagram of the effect of POLY-ANS additives on capillary absorption

Capillary absorption of concrete naturally increases as the composition of the saline solution becomes more complex. This can be explained by a higher concentration of ions in sulfate-chloride solutions and a relatively large accumulation of salts in the pores of the concrete. POLY-ANS additives reduce $W_{suc}$, to the extent that they affect the decrease in the water demand of the concrete mixture, the parameters of the pore structure, and the water impermeability of the concrete. According to the degree of reduction of $W_{suc}$, of concrete, the additives are arranged in the following row: POLY – ANS3> POLY– ANS2>

POLY– ANS 1; the relative decrease in $W_{suc}$, of concrete in comparison with the standard is 3.1; 1.6 and 1.4 times. It was found that the preliminary cyclic temperature effect on concrete specimens with POLY-ANS additives hardly noticeably affects the capillary absorption of the saline solution, and $W_{suc}$ changes by 1.09; 1.1, and 1.12 times (Figure-1).

Thus, the decrease in $W_{suc}$ of concrete is because under the influence of POLY-ANS additives, the density and water resistance of concrete increase, and the hydrophobization of the walls of pores and capillaries is ensured. Or in other words, the wettability of concrete decreases.

As you know, the value of $\cos\theta$ (contact angle of wetting) is taken as the measure of wettability $(M_c)$, which is associated with surface tension at the boundary of three interfaces that are in contact along the perimeter of wetting:

$$M_c = \cos\theta = \frac{\sigma_{tg-\sigma_{tj}}}{\sigma_{jt}} \quad (1)$$

Depending on the values of the contact angle, the following cases are distinguished:

Acute contact angle: $\theta < 90°$, $i.e.,$ $\cos\theta > 0$; in this case, one speaks of wetting (or "limited wetting") of the surface with a liquid.

Obtuse contact angle: $\theta > 90°$, $i.e.,$ $\cos\theta < 0$ ; then, one speaks of the non-wetting (or "poor wetting") of the surface.

The contact angle is not set, and the drop spreads into a thin film - they speak of "complete wetting", or spreading.

For assessing the hydrophobic properties of the concrete surface, this criterion is not acceptable since the assessment of hydrophobicity can be made only in limited cases when:$\theta > 90°$.

In addition, the value of the measure of wetting at the same time acquires a negative value. These factors allow one value of the criterion to evaluate the hydrophobic properties of surfaces and hence the hydrophobic properties of additives.

In this regard, the concept is introduced - measures of hydrophobicity (Mg), which characterizes the hydrophobic properties of the concrete surface and is determined by the formula:

$$M_g = 1 - \cos\theta \quad or \quad M_g = 1 - \frac{\sigma_{tg-\sigma_{tj}}}{\sigma_{jt}} \quad (2)$$

There is the following relationship between the measure of hydrophobicity (Mg) and the measure of wetting $(M_c)$:

$$M_g = 1 - M_c \quad (3)$$

As applied to concrete surfaces, it is difficult to determine the measure of hydrophobicity using formula (2) since it is practically impossible to establish its components by known classical methods due to the material's porous structure.

In this regard, an analytical method is proposed for calculating the measure of the hydrophobicity of concrete by the value of capillary suction, which makes it possible to make a comparative assessment of the effect of POLY-ANS additives and other recipe-technological factors on the change in the relative measure of hydrophobicity, taken according to the formula:

$$OM_g^D = 1 - \frac{\cos\theta^D}{\cos\theta^\circ} = 1 - \frac{\tan\varphi^D \cdot r^\circ}{\tan\varphi \cdot r^D} \quad (4)$$

Where $\tan\varphi^{\circ}$ is the tangent of the angle of inclination of the straight line in coordinates $\frac{1}{\mathrm{H}}$ ; $\frac{dH}{d\tau}$ is for concrete without additives; $\tan\varphi^{\mathrm{D}}$ is the same for concrete with an additive; $r^{\circ}$ is average radius of capillaries of concrete without additive; $r^{D}$ is the same for concrete with additives.

When calculating $\tan\varphi$ according to the method of A.V.Lykov, it was taken into account that for capillary-porous bodies, the relationship between the rate of change in the height of capillary suction in time $\frac{dH}{d\tau}$ and size $\frac{1}{\mathrm{H}}$ , the inverse height of the capillary suction is close to linear. In addition, the capillary suction height is proportional to the amount of absorbed water, i.e., capillary suction of concrete ($W_{suc}$,). Having addiction $W_{suc} = f(\tau)$, it became possible to determine $\frac{d\mathrm{Wsuc}}{d\tau} / \frac{1}{\mathrm{Wsuc,}}$ both for concrete without additives and with additives. Substituting into formula (5.4) the experimentally found values $\frac{d\mathrm{Wsuc}}{d\tau} / \frac{1}{\mathrm{Wsuc,}}$ and the average radius of the capillaries of cement concrete $r_{\mathrm{cp}}$, you can calculate the value of the relative measure of the hydrophobicity of concrete. The average radius of the concrete capillaries was determined by the mercury porosimetry method. Experimental data show that a direct relationship between Wws and τ persists up to 48 hours of capillary absorption of the salt solution. In the future, the direct relationship will be violated due to moisture evaporation from the surface of concrete samples. Therefore the values $\frac{d\mathrm{Wsuc}}{d\tau} / \frac{1}{\mathrm{Wsuc,}}$ are determined precisely in this rectilinear region

## 4 Discussion

POLY-ANS additives reduce Wws to the extent that they affect the decrease in the water demand of the concrete mixture, the parameters of the pore structure, and the water impermeability of the concrete. The decrease in Wws of concrete is because under the influence of POLY-ANS additives, the density and water resistance of concrete increases, and the hydrophobization of the walls of pores and capillaries is ensured; that is, the wettability of concrete decreases.

An analytical method for calculating the measure of the hydrophobicity of concrete by the value of capillary suction is proposed, which makes it possible to make a comparative assessment of the effect of POLY-ANS additives and other recipe-technological factors on the change in the relative measure of hydrophobicity [17-22].

This technique revealed the effect of POLY-ANS additives and filler (TPP ash) on the relative measure of the hydrophobicity of concrete

The relationship between capillary permeability and the salt resistance of concrete was determined by an indirect method: by the change in the ultimate tensile strength of concrete specimens in bending, the magnitude of the relative expansion deformations of concrete, and the accumulation of SO2-4 and Cl- ions, as well as the salt resistance coefficient (Kc).

The degree of change in bending strength, relative expansion deformations, and the depth of corrosion destruction of samples when tested in saline solutions is inversely proportional to the measure of the hydrophobicity of concrete.

The higher the value of $OM_g$ of concrete, the lower the drop in Rben, the lower ε and the depth of corrosion destruction.

It has been established that the higher the value of $OM_g$ of concrete, the lower the drop in Rben, the lower ε and the depth of corrosion destruction. At the same time, sulfate resistance on ordinary Portland cement under conditions of capillary absorption and evaporation of saline groundwater can be ensured by the combined use of the POLY-ANS 2 additive and the filler (TPP ash) [7-14].

It is accepted to calculate the coefficient of concrete resistance from the ratio of the tensile strength of concrete in bending after testing the samples for capillary suction to the tensile strength of concrete in bending after holding the samples under normal conditions at 28 days of age.

**Table 3.** Values of the relative measure of the hydrophobicity of concrete with POLY-ANS additives when testing samples for capillary absorption of saline solutions

| Supplement type | Average pore radius, and for concrete with cement consumption, kg/m$^3$ | | | Values of the relative measure of concrete hydrophobicity with cement consumption, kg/m$^{3,}$ when tested in saline solutions (numerator - sulfate, denominator - sulfate-chloride | | |
|---|---|---|---|---|---|---|
| | 290 | 360 | 430 | 290 | 360 | 430 |
| No additive | 96.5 | 92.4 | 90.8 | - | - | - |
| POLY– ANS1 | 83.4 | 80.2 | 78.6 | $\frac{0.46}{0.61}$ | $\frac{0.50}{0.62}$ | $\frac{0.61}{0.65}$ |
| POLY– ANS2 | 78.3 | 76.1 | 74.2 | $\frac{0.60}{0.70}$ | $\frac{0.67}{0.73}$ | $\frac{0.76}{0.78}$ |
| POLY– ANS3 | 69.1 | 66.2 | 64.0 | $\frac{0.82}{0.89}$ | $\frac{0.87}{0.90}$ | $\frac{0.91}{0.93}$ |

It is recommended to consider concrete with a polymer additive as corrosion-resistant if Kc after one year of testing is at least 0.85. Table 4 shows the Kc data of concrete on ordinary Portland cement with a polymer additive and a micro-filler (TPP ash) after one year of testing for capillary absorption of aqueous sodium sulfate and sulfate-chloride solution.

**Table 4.** Data of the coefficient of salt resistance Kc of concrete

| Concrete class | Concrete class | Salinity coefficient in solutions | |
|---|---|---|---|
| | | 5.5 %$Na_2SO_4$ | 5.5 %$Na_2SO_4$ + 5.5% NaCl |
| B 15 | POLY– ANS1 | 0.64 | 0.58 |
| | POLY– ANS2 | 0.83 | 0.79 |
| | POLY– ANS3 | 0.85 | 0.77 |
| B 25 | POLY– ANS1 | 0.63 | 0.59 |
| | POLY– ANS2 | 0.79 | 0.69 |
| | POLY– ANS3 | 0.85 | 0.84 |
| B 30 | POLY– ANS1 | 0.65 | 0.58 |
| | POLY– ANS2 | 0.83 | 0.78 |
| | POLY– ANS3 | 0.88 | 0.85 |

## 5 Conclusions

Thus, introducing the POLY-ANS polymer reagent ensures the salt resistance of concrete. After one year of testing, the salinity coefficient is generally within the established requirement - 0.85.

For an accelerated assessment of the degree of influence of the reagent (and other additives) on the permeability of concrete, it is effective to use the criterion of the relative measure of hydrophobicity.

When developing technological methods for reducing capillary permeability with the use of additives, the determination of the relative measure of the hydrophobicity of concrete is carried out in a certain sequence; in particular, the samples are tested for capillary

absorption during evaporation of the saline solution, the average radius of capillaries is determined by the concrete method of mercury porosimetry, and more [13-22].

The conducted research has established the positive effect of the polymer reagent POLY-ANS on capillary absorption, and capillary permeability of concrete, predetermining the high resistance of cement concretes in various aggressive environments

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