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## INFLUENCE OF SULFATE ION ENVIRONMENT ON THE CEMENT MATRIX MODIFIED BY REDISPERSIBLE POLYMERS

*Injection of sulfate ions into the cement matrix with water by wet spraying due to high moist in the environment is the reason of the deterioration acceleration and durability decrease with time. The effects of introduction of redispersible polymers (RP) and calcium formate on the increasing of the durability and decreasing of the deterioration effect caused by sulfate ions on the cement matrix were studied. Vinyl-acetate/versatate, vinyl-acrylic copolymer and calcium formate were mixed into nine separate cement mixtures at a concentration of additives 1 %, 3 % and 5 % respectively. Three different sulfate ion environment were sprayed through the fog environment at high moist concentration using a salt spray device "Salt Fog Chamber". Test results showed that different additive in different sulfate environment has various effects both on the deceleration of the structure deterioration and the reduction of the strength of cement matrix. Vinyl-acetate/versatate and calcium formate in concentrations of 1% and 3% have high stability while maintaining strength at the level of exploitational properties of the matrix. While, vinyl-acrylic copolymer at 5 % has more resistance to strength loss after 168 days of withholding in an aggressive environment compared to 1 % and 3 %. Detailed observation of the structure formation of the cement matrix at 168 days shows formation that relate both to the hydrated cement minerals and complexes of organic salts. This formation allowed at the late age of the experiment to decrease the strength loss under intensive impact of  $SO_4^{2-}$  migration through the matrix due to the encapsulating of cement minerals at early ages of hydration in polymer films with RP and active early formation of  $Ca(OH)_2$  for formate. This allowed the cement matrix to retain its shape for a long periods, become more stable, reduce the washing out of soluble cement components at early ages, and reduce the content of active Ca by bonding it into semisoluble compositions that cause the decreasing of the negative effect on cement matrix by  $SO_4^{2-}$ .*

*Key words: portland cement, dry ready-mixes, redispersable powders, calcium formate, corrosion resistance*

КОВАЛЕНКО ЮРІЙ, ТОКАРЧУК ВОЛОДИМИР

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## ВПЛИВ СУЛЬФАТ-ІОННОГО СЕРЕДОВИЩА НА МОДИФІКОВАНУ ЦЕМЕНТНУ МАТРИЦЮ РЕДИСПЕРГОВАНИМИ ПОЛІМЕРАМИ

*Введення сульфат-іонів у цементну матрицю з водою шляхом вологого розпилення через високу вологість навколишнього середовища є причиною прискорення зносу та зниження довговічності з часом. Досліджено вплив введення редиспергованих полімерів (РП) і форміату кальцію на підвищення довговічності та зменшення впливу сульфат-іонів на цементну матрицю. Вінілацетат/версатат, вініл-акриловий сополімер і форміат кальцію змішували в дев'ять окремих цементних сумішей з концентрацією добавок 1%, 3% і 5% відповідно. Три різні середовища сульфатних іонів розпорошували через туманне середовище при високій концентрації вологи за допомогою пристрою для розпилення солі «Камера соляного туману». Результати випробувань показали, що різні добавки в різних сульфатних середовищах по-різному впливають як на уповільнення руйнування структури, так і на зниження міцності цементної матриці. Вінілацетат/версатат і форміат кальцію в концентраціях 1% і 3% мають високу стабільність при збереженні міцності на рівні експлуатаційних властивостей матриці. При цьому вініл-акриловий сополімер при 5% має більшу стійкість до втрати міцності після 168 днів витримки в агресивному середовищі порівняно з 1% і 3%. Детальне спостереження за формуванням структури цементної матриці через 168 днів показує утворення, які стосуються як гідратованих мінералів цементу, так і комплексів органічних солей. Таке утворення дозволило на пізньому терміні експерименту зменшити втрату міцності під інтенсивним впливом міграції  $SO_4^{2-}$  через матрицю за рахунок інкапсуляції цементних мінералів на ранніх термінах гідратації в полімерних плівках з РП та активного раннього утворення  $Ca(OH)_2$  для форміату. Це дозволило цементній матриці тривалий час зберігати форму, стати більш стабільною, зменшити вимивання розчинних компонентів цементу на ранніх термінах, а також знизити вміст активного Ca шляхом зв'язування його в напіррозчинні композиції, що спричиняє зниження негативних впливів  $SO_4^{2-}$  на цементну матрицю.*

*Ключові слова: портландцемент, сухі будівельні суміші, редисперговані порошки, форміат кальцію, корозійна стійкість.*

### Literature review and problem statement

General development of dry building ready mix (DBRM) is based on the basics of main components such as binder (cement, lime, gypsum), filler (microsilica or etc.) and additives such as redispersible polymers (RP) or other organic or inorganic dry powders to achieve the desired properties for project mix. Mainly DBRM are

presented as stucco, tiles glue, ready concrete mixes, and others. In Ukraine, the development of DBRM has its own market and high demand amongst consumers.

In the last ten years, DBRM found their application as repairing mixes for reconstruction and repairing damaged structures due to prolonged exposure under the influence of aggressive environment. Mostly this environment included sulfate ( $\text{SO}_4^{2-}$ ) ion that is mostly widespread due to its presence in soils, marine environment, underground water, products of combustion, etc. Even though sulfates attack the cement paste matrix, the value of their impact varies depending on the type of cement used in DBRM [1]. Moreover, in this consideration, pH levels of the environment were also noticed, due to the fact that the lower pH, the more deteriorative damage would be [2].

The main question of recent studies on the matter of these problems was considered mostly to the impact on cement mineral itself [3-5]. Moreover, recent examinations of the hydration behavior of cement pastes modified by RP [6-8] concluded that interactions between the environment and modifiers (RP and formates) are not possible. Such conclusions are made on the basis that with time, after 28 days of curing, any remains of polymer structures are decomposed [8, 9]. Yet by Kardon [10], it is stated that polymer formation in an alkaline environment may interact with cement components resulting in creating organic salts similar in structure to the hydrated cement minerals at late stages.

In the similar study [11] influence of sulfate ion environment on the cement matrix modified only with methyl hydroxyethyl cellulose ethers, the question of influence was limited only by the strength coparesment. Moreover, most studies [7, 11-13] emphasise the influence of RP and formates only on the stated characteristics such as work (setting) time, viscosity, water retention, adhesion activity and hydration mechanism [14].

Film formation of RP described by Kim [8], shows that injected in to the mix polymers form early structure that respond to lowering the strength of the cement matrix. Therefore, at early and later ages of curing, samples with RP gain much lower strength than the control one. Yet for formates such tendency is a bit different [7], the early curing time of the matrix shows an increase in strength because of the early formation of  $\text{Ca}(\text{OH})_2$ . Structurally, such difference is described by the process of filling of the voids in the cement matrix by calcium hydrate at the period of early hidratation. Therefore, developing early strength of samples and compacting the matrix occur. Including the information from Kardon [10], it can be assumed that every development and reaction that occurred along the hidratation processes in the cement matrix potentially can play role in the development of mixtures with improved resistance to the sulfate impact.

In this paper, redispersible powders (RP) of vinyl acetate/versatate, vinyl-acrylic copolymer and calcium formate were selected as widely spread organic additives in the production of repaired building ready mixes (RBRM). Sulfate environments with close to real impact were introduced through the "Salt Fog Chamber" (SFC) to prevent a high negative impact on the truthfulness of the results. Chambers were used to conduct the corrosion durability test under the action of sulfate spraying in fog environment on both cement and mixes with additives samples to prevent any deviation while compression strength tests. After compression strength, samples were observed with the electrical microscope to study changes in structure. The studies were conducted only to examine the impact of sulfate ion environment on the modified cement matrix with additives. Such a decision was made due to the lack of studies in this field and to provide a detailed analysis over the chemical reactions that may occur with components of the matrix with the application of chemical additives of organic derivation. This work will provide information on the possible solutions in the development of RBRM for environments with high impact of aggressive ions.

#### **The aim and objectives of the study**

The aim of this work is to identify the nature of the action of the three most common in the production of cement building mixtures of redispersed powders on the corrosion resistance application for DBRM. The data to be obtained will make it possible to conclude about not only the physical and mechanical nature of the effect on the cement matrix but also confirm or deny the presence of chemical transformations. The would-be results can be applied in practice in the production process to create new formulations of building mixtures, as well as in the production of new concrete compositions.

To accomplish the aim, the following tasks have been set:

- to investigate the effect of the amount of additive on the control strength at 28 days;
- to investigate the effect of the amount of additive in the mixtures under the influence of sulfate ion environment on the compressive strength after 168 days;
- to analyze the chemical interaction of additives with cement particles in a cement matrix in the sulfate medium based on the obtained data and photographs of structure formation.

#### **The study materials and methods**

##### **Examined materials and equipment used in experiments**

Standardized Portland cement of the PC I 500N brand were used for control samples and mixes. The object of the study was dry building ready mixes with redispersible additives, such as: copolymers of vinyl acetate/versatate (Neolith 4400) and vinyl-acrylic (Neolith 6700). Calcium formate (FormateCa) was chosen because of its widespread use in dry building mixes together with redispersible polymers.

The compressive strength indicators, were determined by methods represented in DSTU EN 196-1: 2007 (EN 196-1: 2005, IDT). The electron microscope (REM 106-I) with XDR was used to acquire the results of the interaction of additives on the structure formation of the cement matrix.

**Compressive Strength of Cement Mixes.**

According to the standards for cement and cement-based ready mix durability testing (EN 196-1 and EN 1015-11), the mixes were cured for 28 days before control measurement of the compressive strength test. For the test, the size of the samples were accepted accordingly to the method for “Determination of The Impact of Aggressive Environment” by Kind [14]. Each group of four 20 x 20 x 20 mm specimens were cured in a controlled environment accordingly for 28 days and later for 168 days, a total of 196 days

**Structural analysis of sulfate impact on the modified cement matrix**

Samples 2 x 4 mm (size depends on the observing surface of microscope) are previously dried before taking photos in full vacuum on the REM to ensure the absence of any possible remaining molecular water in structure. Such presence can be negatively reflected on the structural photograph of the sample by including the migration of dust particles which are disruptive to the receiving sensors.

**Test Results and Discussion**

**Compressive strength before and after sulfate impact**

Table 1 shows the resulting influence of the additives on the grade strength and strength of samples at the 168 days of durability test in aggressive environment. It is shown that plain cement has undeniably high strength value compared to modified mixes. Yet, the rapid decrease of the final date in the aggressive environment shows that plain cement is more influenced by the direct impact of sulfate ions rather than project mix. Moreover, it can be seen that along the 168 days of curing, most of the samples that remained in the water environment gained more strength. For mixes with calcium formate this increase is true for 3 % and 5 %, while for Neolith 4400 is 3 % and for Neolith 6700 is 3 % and 5 % of additive respectively.

**Table 2**  
**Change in strength (unit: MPa) of samples with and without additives at 28 days before and 168 days after sulfate impact**

Name of mixes	28 days before sulfate impact	Control strength in water after 168 days	168 days after sulfate impact		
			Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	CaSO <sub>4</sub>
Plain cement	52	54.5	33.5	32.5	37
FormateCa 1 %	47.5	45	35.5	39	36.5
FormateCa 3 %	35	46	36.25	32.75	27
FormateCa 5 %	40	43.5	38	33.5	14
Neolith 4400 1 %	45.25	44.75	40	34	28.75
Neolith 4400 3 %	40	51.25	37.5	31	39.75
Neolith 4400 5 %	38.75	38.25	35	31.25	31.25
Neolith 6700 1 %	44	33.75	29.75	30	25
Neolith 6700 3 %	38	39.25	27.25	29	27.25
Neolith 6700 5 %	29.5	40.75	34.5	27.5	34.5

**Influence of calcium formate on the sulfate durability of cement matrix.**

Figure 1 graphically shows changes in the strength of the mixes that have in their compound Calcium Formate. Rapid strength fall for plain cement is seen at 168 days in all sulfate ion solutions. From Figure 3, the following can be seen:

- (1) Strength of cement mixes modified by Formate Ca with 1 % are higher for both sodium and magnesium sulfate environments. Strength value of 1 % mix in both sulfate environments is higher compared to cement. For CaSO<sub>4</sub> solution, the strength value of 1 % mix is close to plain cement. Such difference can be explained by the amount of active calcium in the structure of the cement matrix.
- (2) In general, with a calcium formate content of up to 1 wt. % loss of strength of the samples makes up from 6 to 10 MPa and 9 to 12 MPa, respectively, in sodium and magnesium sulfate solution compared to the initial values. Moreover, comparing the loss of strength with the plain cement, where the loss of strength is from 17 to 22 MPa in sulfate environments, it can be stated that calcium formate in general exhibits the character of an anticorrosion additive. This statement is confirmed by low indicators of loss of strength and for mixtures with an additive content of up to 3 wt. %
- (3) Absence of calcium ions in sodium and magnesium sulfate solutions except the ones in the cement mix, do not quicken the processes of formation of nonsoluble calcium sulfate that are destructive for the cement matrix. Exceeding the amount of CaSO<sub>4</sub> of the third solution consisted of, quickens the formation of non-soluble crystals that are the reason of the decreasing of strength because of the character of the dissociation of formate.
- (3) Free Calcium ions from formate group, calcium hydroxide, and the presence of dissociated sulfate ions are the reason of the active formation of the calcium sulfate that partially washes out. That is the main reason why 3 % and 5 % mix of CaSO<sub>4</sub> solution have lower strength.
- (4) Moreover, the strength values for mixes with 1 % - 5 % of additive at sodium and Magnesium Sulfate environment and 1 % at Calcium Sulfate environment, respectively, indicate that Calcium Formate can be potentially used as an anticorrosion agent as well as its established antifreeze properties.

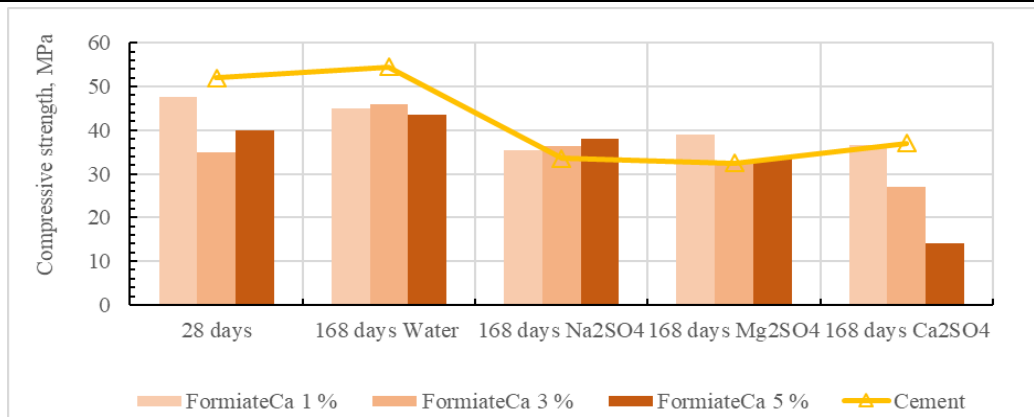


Figure 1: Comparison of the compressive strength of initial samples (28 days), nonimpacted samples (after 168 days), and impacted (after 168) by sulfate environment samples for FormiateCa mixes.

Figure 2 shows the difference between the structure of nonimpacted (a) at 28 days of curing and impacted (b) FormiateCa 3 % samples in sulfate environment after 168 days:

- (1) Figure 2 (a) shows an exceeding amount of C-S-H gel formation among the variety of  $\text{Ca}(\text{OH})_2$  crystallisation structures on the 28-th day of curing. Such amount of formation confirms the reason of increasing the strength value in non-aggressive environment and at the same time confirms the reason of strength decreasing in sulfate environment.
- (2) Figure 2 (b) shows fully formed  $\text{CaSO}_4$  crystal that are vertically oriented between the presence of vast formation of newly formed C-S-H gel. This are an indication that most of the previously formed  $\text{Ca}(\text{OH})_2$  were washed out and currently forming spikes of  $\text{CaSO}_4$  are now replacing it causing the decrease in strength.

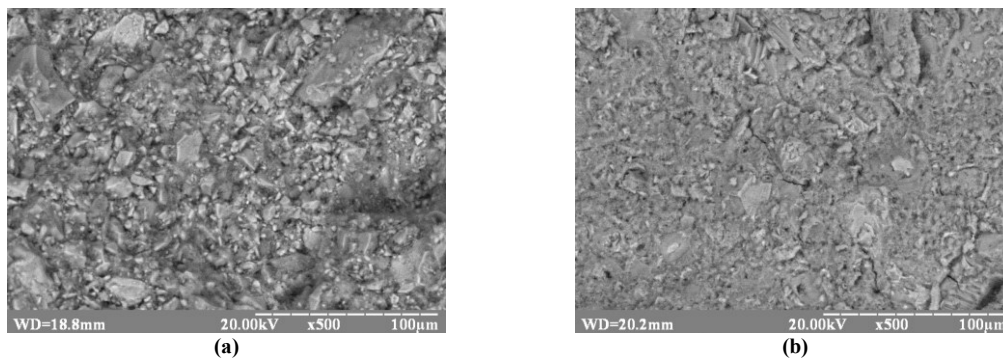


Figure 2: structure of non-impacted (a) at 28 days of curing and impacted (b) FormiateCa 3 % samples in sulfate environment after 168 days

#### 4.3. Influence of Neolith 4400 on the sulfate durability of cement matrix.

Figure 3 graphically shows changes in the strength of the mixes that have in their compound vinyl acetate/versatate (Neolith 4400) additive. From Figure 3, the following can be seen:

- (1) Strength of cement mixes modified by Neolith 4400 with 1 % and 3 % have similar aspects as for FormiateCa mixes for both sodium and magnesium sulfate environments. Exceptions are only for 3 % and 5 % in magnesium sulfate environment where the strength is a bit lower compared to plain cement. Strength value of 1 % mix in both sulfate environments is higher compared to cement.
- (2) For  $\text{CaSO}_4$  solution, the strength value of 2 % mix is a bit higher compared to plain cement. Possible explanation for such anomalous behaviour of the strength jump for Neolith 4400 3 % mix may be explained by the hydrophobic behaviour of the versatate component of the additive itself.
- (3) In total, the differences between non-impacted and impacted strength values of samples vary between 1-7 MPa for the initial values of the strength of control samples in water and 6-9 MPa for plain cement in solution of  $\text{CaSO}_4$ . This may be considered as the positive result to assume the possibility of using vinyl acetate/versatate as a sulfate retention agent in concentrations of 3 % and 5 % in RBRM.

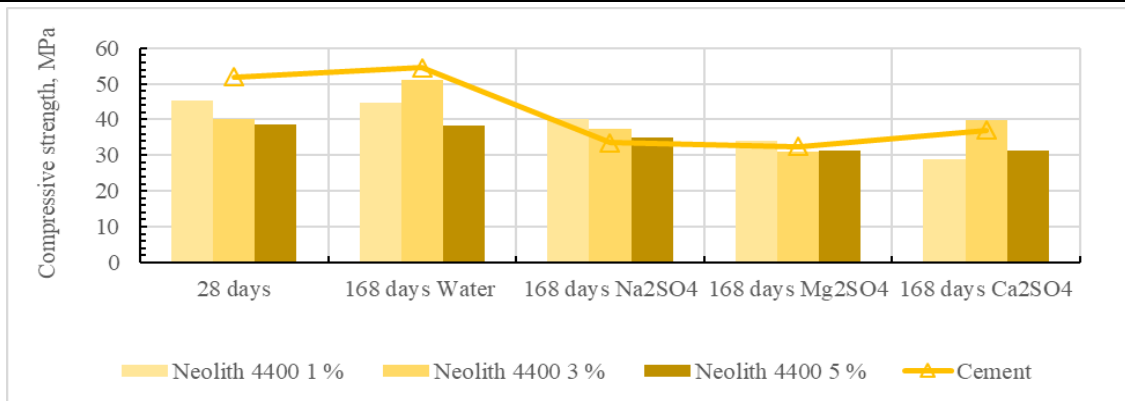


Figure 3: Comparison of the compressive strength of initial samples (28 days), nonimpacted samples (after 168 days) and impacted (after 168) by sulfate environment samples for Neolith 4400 mix

Figure 4 shows the difference between the structure of nonimpacted (a) at 28 days of curing and impacted (b) Neolith 4400 5 % samples in sulfate environment after 168 days:

- (1) Figure 4 (a) shows the stable formation of polymer film of Neolith 4400 additive on the surface of the cement minerals can be observed in the porous part of the cement matrix. Formation of both C-S-H gel and Ca(OH)<sub>2</sub> can be observed on the edges of the pore structure of the matrix. Such formation on the 28-th day of curing shows that even after standard curing time, the cement matrix maintained its hydrophobic character applied by the versatate group of additives.
- (2) Figure 4 (b) shows fully formed CaSO<sub>4</sub> crystal that are both vertically and horizontally oriented in the porous part of the cement matrix structure the same as in the structure itself. Amount of such formations not only presented in the voids of the cement matrix but also spread through all the volume of sample. Which is indicative of the presented cracks on the surface of samples with high inner pressure due to the high amount of nonsoluble formation which CaSO<sub>4</sub> are. This explains the low strength values for samples that were in CaSO<sub>4</sub> solution.

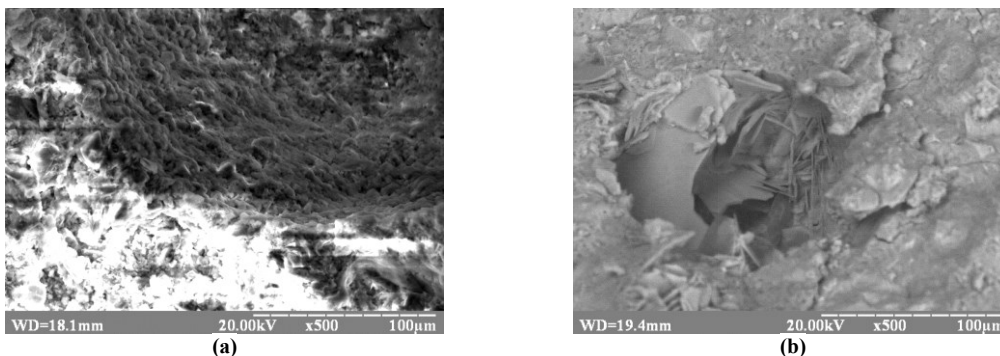


Figure 4: structure of nonimpacted (a) at 28 days of curing and impacted (b) Neolith 4400 5 % samples in sulfate environment after 168 days

#### 4.4. Influence of Neolith 6700 on the sulfate durability of cement matrix.

Figure 5 graphically shows changes in the strength of the mixes that have in their compound vinyl-acrylic copolymer (Neolith 6700) additive. From Figure 5, the following can be seen:

- (1) Vinyl-acrylic copolymer (Neolith 6700) affects the stability of cement samples similarly compared to the other two additives (Neolith 4400 and FormateCa). Despite the fact that the overall strength of the samples at 28 days (after curing) decreases with increased concentration of the additive, Neolith 6700 itself shows significant stability at 5 wt. % of additives in the mixture at 168 days of durability test in aggressive environments.
- (2) It is also worth noting that the samples Neolith 6700 3 % and 5 %, after 28 days in the water environment continued to gain strength, which generally corresponds to the nature of the water-retaining agent.
- (3) Neolith 6700 has the most stable values in terms of the difference in strength over the entire range of the studied mix durability under the influence of sulfate ion environments. This is reflected in the difference in the values of 1-5 MPa with the control values of the tested samples. This difference indicates that Neolith 6700 has a more pronounced characteristic of hydrophobicity, which is manifested during the curing of the cement matrix for 28 days. This, in turn, is reflected in the control values of the strength of the mixture with the additive at 168 days with 3 % and 5 % of additive where strength increases have had occurred. This indicates the possibility of the use of the additive as an anticorrosion agent.



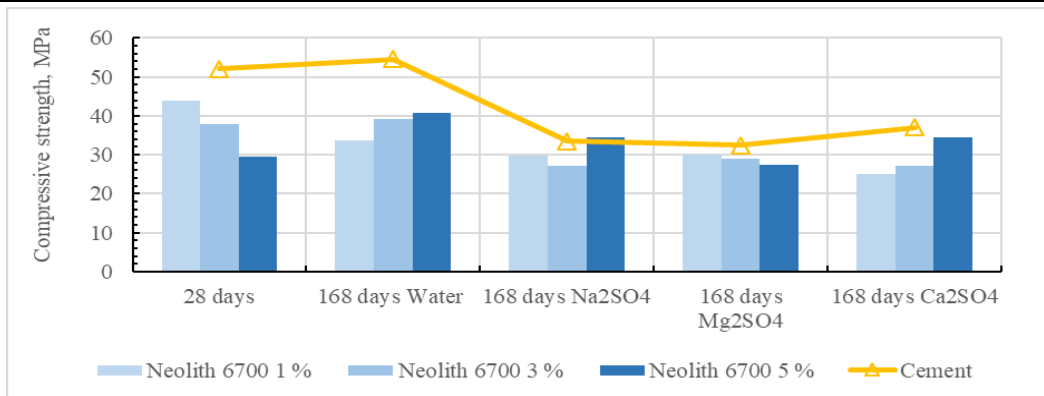


Figure 5: Comparison of the compressive strength of initial samples (28 days), non-impacted samples (after 168 days) and impacted (after 168) by sulfate environment samples for Neolith 6700 mix

Figure 6 shows the difference between the structure of non-impacted (a) at 28 days of curing and impacted (b) Neolith 6700 5 % samples in magnesium sulfate environment after 168 days:

- (1) Figure 6 (a) shows the formation of polymer film of Neolith 6700 similarly to Neolith 4400; the additive has high viscosity due to the hydrophilic character of acrylate group. Because of the high viscosity of the additive structures we have high porous content. Formed films of polymer can be observed on partially covered formations of both the C-S-H gel and  $\text{Ca}(\text{OH})_2$ . Such porous formation on the 28-th day of curing explains the low strength values of the control samples.
- (2) Figure 6 (a) shows the heterogeneous formation of the film that can be observed by the presence of clump formation over the structure of the cement components. This indicates that such formation of the structure of cement matrix will potentially cause a negative influence on the strength of the matrix by causing inner stresses over all matrix structures allowing the creation of a vast amount of nonsoluble components and intensive washing out of soluble minerals during which are not connected to samples that were in water for 168 days after curing.
- (3) Figure 6 (b) shows the fully formed  $\text{CaSO}_4$  structure in mix with  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ ; the high activity of chemical reaction between Magnesium Sulfate and Calcium Hydroxide explains such amount of Calcium Sulfate structures in the pores.
- (4) Figure 6 (b) shows the complete absence of any kind of remaining organic composition. This shows that the durability of the modified cement matrix by RP is influenced by chemical-mechanical character due to the formation of structures that cause the inner stress of the cement matrix. This explains the negative impact of using RP additives as an anticorrosion agent for cements in the magnesium sulfate environment.

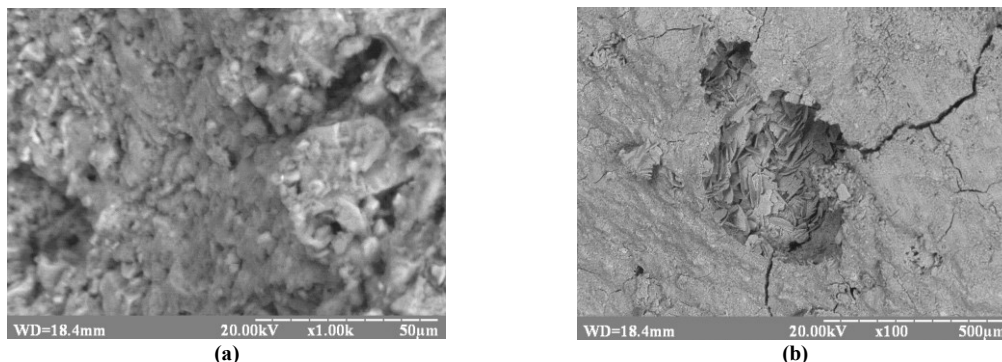


Figure 6: structure of nonimpacted (a) at 28 days of curing and impacted (b) Neolith 6700 5 % samples in sulfate environment after 168 days

### 3.5. Chemical explanation of similarity between Neolith 4400 and Neolith 6700.

Both RP additives are copolymers and have similar basic vinyl acetate basis according to the production passport of RP presented by manufacturer. Thus explains such variability in strength values after sulfate ion impact on the modified cement matrix with these RPs. In these study, Calcium Formate were used as a comparative agent because of its antifreeze and potential anticorrosive characteristics that were proposed by Chen et al. [14], the second of which were confirmed during this study. As for RP Neolith 4400 and 6700 such statement somewhat inconsistent because of the chemical properties that have a place to occur after the observed structure formation of the mixes.

Because of Vinyl-Acetate basis present in both 6700 and 4400, during 28-day during test, three chemical reactions in the alkali environment of the cement matrix occurred. First reaction is presented in Figure 7.

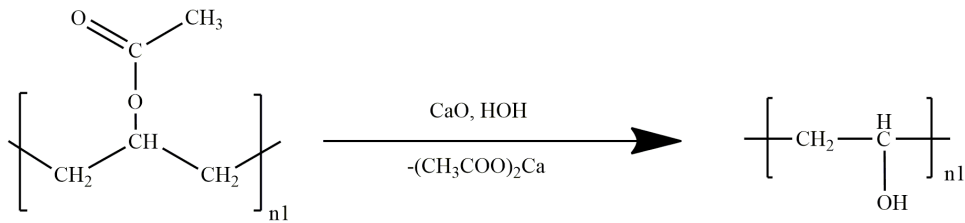


Figure 7: reaction of transformation of Vinyl-acetate group of copolymer in alkali environment

The formed fragment of polyvinyl alcohol as shown in Figure 7, is in nature good hydrophobic. It has the form of semitransparent gel as can be seen on Figure 8 (a) and fragments on Figure 7 (a). Because of this, it injects himself in a polymer film structure that gives additional hydrophobic characteristics for the matrix and simultaneously plays the role of water retention agent for Neolith 6700. As for Neolith 4400, this change begins later because of the big size of the versatate radical group that plays the role of hydrophobic agent. High compressive strength values are indicative of this.

By that, the reaction presented in Figure 7 may occur later after the process of deterioration of the versatate group for Neolith 4400. Thus, Neolith 4400 is more suitable for the role of anticorrosive agent. And yet, because of formation Calcium Acetate ((CH<sub>3</sub>COO)<sub>2</sub>Ca) that has similar dissociative character as Calcium Formate ((CHCOO)<sub>2</sub>Ca) during the hidratation. Increase in strength of Neolith 6700 samples in water after 168 days for 3 % and 5 % mixes are indicatives of this statement. Moreover, the acetate radical, due to the nature of chemical bounds between acetate and alcohols, forms again vinyl acetate component. This reaction continues until the amount of vinyl acetate would be a bit lower than the acrylic component. After that, for Neolith 6700 comes the next two parallel reactions presented in Figure 8.

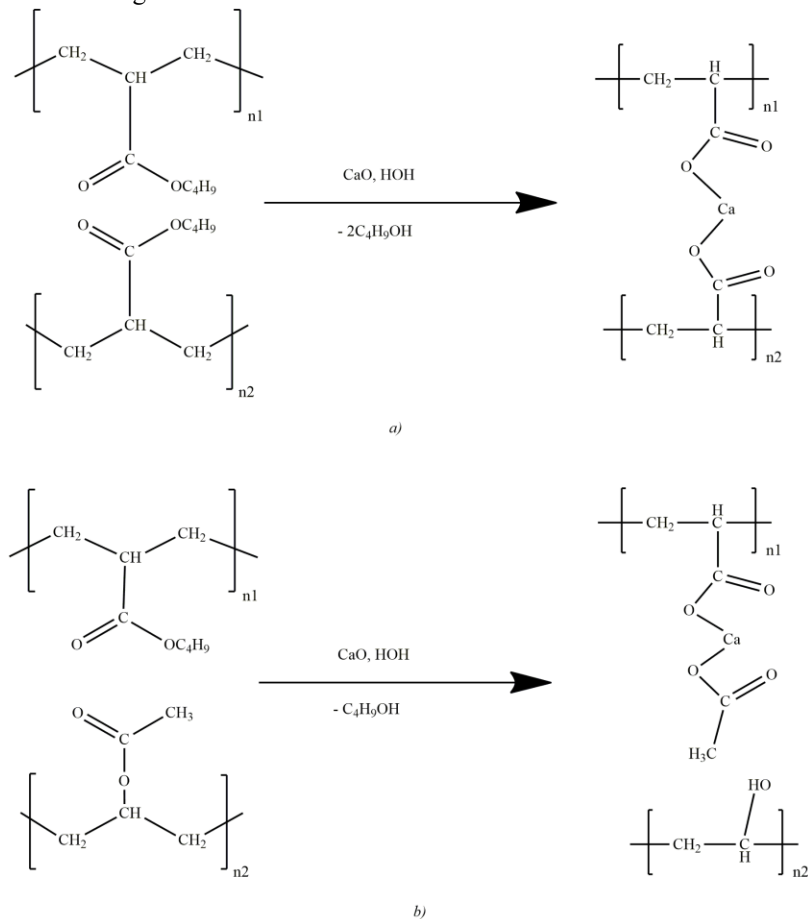


Figure 8: reaction of transformation of butyl-acrylic copolymer (a) and butyl-acrylic copolymer with remains of vinyl acetate copolymer (b) in alkali environment

Figure 8 (a) shows the reaction of the formation of two organic solutions: hard organic-based calcium salt and butanol alcohol. Figure 8 (b) shows the reaction of formation of two organic solutions: hard organic-based Calcium-acetate salt, polyvinyl alcohol and butanol alcohol. Possibility of formation of the similar salts described by Kardon [10]. The amount of butanol is so low that in the sulfates environment with remaining acetate groups forming the butyl acetate witch is washed by water from opened seams and pores of the cement matrix. Thus, the formed organic calcium salts collected in the seams and pores were polymer films were presented. Their number and size are thinner and sometimes smaller than CaSO<sub>4</sub>, so their impact on the inner tension of cement matrix could be misinterpreted.

## Conclusions

1. The 28 days compressive strength test shows that the usage of RP lowers the grade strength with the increasing of the amount of additives, respectively. Calcium Formate has similar effect yet due to the difference in grade strength results for 3 and 5 % values are 35 MPa and 40 MPa, respectively, and its decreasing effect is questionable.
2. Further curing of samples in water environment after 168 days showed an increase in strength values for 3 % and 5 % for each additive, respectively. This indicates that all additive has water retention characteristics.
3. Durability test of the impact of sulfate ion environment on the modified cement matrix with additives is different for each additive.
4. Calcium Formate shows more stable strength values to the impact of sodium and magnesium sulfate environment which resulted in lower difference between control values and project. Yet, for Calcium Sulfate the environment values were critically low. Structural analysis and strength results confirmed the possibility of using Calcium Formate as an anticorrosive agent. All studied concentrations are optimal for sodium and magnesium sulfate environment.
5. Potential of usage of Neolith 4400 additive is high enough due to the stable values of strength during the durability test. Moreover, structural analysis showed that polymer film formation occurs mostly on all cement components. Taking into account that Neolith 4400 has versatate radical in the polymer group, it gives the matrix hydrophobic properties. Such statement has its confirmation by the results of the durability test under the impact of sulfate ion environment in all environments.
6. Optimal concentration of Neolith 4400 as a corrosive resistant agent is 3 %.
7. Neolith 6700 has the most rapid decrease in grade strength with increasing the amount of additive in mixture, respectively. After 168 days of prolonged curing in water environment for concentrations 3 and 5 % growth of strength occurred.
8. Values of control strength and project strength after durability test show the potential usage of the additive due to its hydrophobic application because of the formation of polyvinyl alcohol during the chemical reactions that occur in the curing period.
9. During curing, there is possible formation of organic salt compounds that similar in form to  $\text{CaSO}_4$ . Yet the amount of such formation is low and they mostly have minimal effect on the inner pressure strength of cement matrix.
10. The possibility of using Neolith 6700 spread on each concentration. Yet the mixture with vinyl-acrylic copolymer must not be used in Magnesium Sulfate environment due to its decreasing strength character with increasing of the concentration, respectively.

According to the research content of this work, the results can be further used in both manufacturing and scientific sectors. Yet, to better meet further improvements, next steps must be done:

1. This paper mostly focused on controlled environments and the resulting strength values of the durability test; in the actual test there is used more field environment (at a site) with the using of coarse fillers such as dispersed silica or other nonsoluble filler.
2. The influence of marine environment on durability must be also considered in further development and should be investigated the durability under bending load.

## References

1. Kanaan D., Soliman A. M. and Suleiman A. R. Zero-Cement Concrete Resistance to External Sulfate Attack: A Critical Review and Future Needs. *Sustainability*, 14 (4), no. 2078, 2022. <https://doi.org/10.3390/su14042078>
2. Baldermann C., Baldermann A., Furat O. et al. Mineralogical and microstructural response of hydrated cement blends to leaching. *Constr. Build. Mater.*, 229, 116902, 2019. <https://doi.org/10.1016/j.conbuildmat.2019.116902>
3. Türker F., Aköz F., Koral S. et al. Effects of magnesium sulfate concentration on the sulfate resistance of mortars with and without silica fume. *Cement and concrete research*, 27(2), pp. 205–214, 1997. [https://doi.org/10.1016/S0008-8846\(97\)00009-4](https://doi.org/10.1016/S0008-8846(97)00009-4)
4. Ma Y., Qian J. Influence of alkali sulfates in clinker on the hydration and hardening of Portland cement. *Construction and Building Materials*, 180, pp. 351–363, 2018. <https://doi.org/10.1016/j.conbuildmat.2018.05.196>
5. Huang H., Fu Y., Li F. et al. Orderly self-assembly of new ionic copolymers for efficiently protecting copper in aggressive sulfuric acid solution. *Chemical Engineering Journal*, 384, 123293, 2020. <https://doi.org/10.1016/j.cej.2019.123293>
6. Zhang Y., Jiang Z., Zhu Y. et al. Effects of redispersible polymer powders on the structural build-up of 3D printing cement paste with and without hydroxypropyl methylcellulose. *Construction and Building Materials*, 267, 120551, 2021. <https://doi.org/10.1016/j.conbuildmat.2020.120551>
7. Jo Y. K. Adhesion in tension of polymer cement mortar by curing conditions using polymer dispersions as cement modifier. *Construction and Building Materials*, 242, 118134. <https://doi.org/10.1016/j.conbuildmat.2020.118134>
8. Min Ook Kim. Influence of Polymer Types on the Mechanical Properties of Polymer-Modified Cement Mortars. *Applied Sciences*, 10, 1061, 2020. <https://doi.org/10.3390/app10031061>
9. Knapen E., Van Gemert D. Polymer film formation in cement mortars modified with water-soluble polymers. *Cement and Concrete Composites*, 58, pp. 23–28, 2015. <https://doi.org/10.1016/j.cemconcomp.2014.11.015>
10. Kardon J. B. Polymer-modified concrete. *Journal of Materials in Civil Engineering*, 9(2), pp. 85–92, 1997. [https://doi.org/10.1061/\(ASCE\)0899-1561\(1997\)9:2\(85\)](https://doi.org/10.1061/(ASCE)0899-1561(1997)9:2(85))
11. Kovalenko Y., Klymenko A., Tokarchuk V. et al. Effect of sulfate ion environment on physical and mechanical durability of cement products modified by cellulose ethers. *Technology audit and production reserves*, 6 (1), pp. 6–12, 2020. <https://doi.org/10.15587/2706-5448.2020.218410>
12. Wang R., Wang P. M. Action of redispersible vinyl acetate and versatate copolymer powder in cement mortar. *Construction and building materials*, 25(11), pp. 4210–4214, 2011. <https://doi.org/10.1016/j.conbuildmat.2011.04.060>



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13. Zhang B., Jiang W., Xu Q. Experimental feasibility study of ethylene-vinyl acetate copolymer (EVA) as cement stabilized soil curing agent. *Road Materials and Pavement Design*, 1-22, 2020. <https://doi.org/10.1080/14680629.2020.1834442>
  14. Chen L., Jiang L., Liu X. Understanding the role of calcium formate towards hydration and deformation property of light-burned magnesia cement. *Construction and Building Materials*, 289, 122995, 2021. <https://doi.org/10.1016/j.conbuildmat.2021.122995>