

Investigation of the influence of magnesium chloride to sulfate corrosion of concrete

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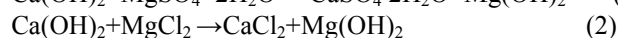
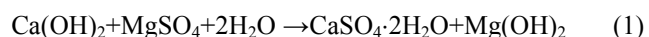
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Abstract: The paper research subject is to examine whether chlorides of magnesium chloride block the affect of sulphate of magnesium sulfate to the concrete, that is, whether they block the sulfate corrosion of concrete. The cylindrical samples of cement paste measuring 80 × 40 mm of varying water-cement ratio 0.5 and 0.7 (kg H₂O / kg of cement) were prepared for implementation of planned research. The samples were immersed and treated for nine months in following solutions: 1% MgCl₂, 1% MgSO₄, 1% MgCl₂ + 1% MgSO₄, 5% MgCl₂, 5% MgSO₄, 5% MgCl₂ + 5% MgSO₄. In order to study concrete corrosion, the samples were dried, grounded and analyzed by X-ray diffraction analysis (XRD), after being removed from the solutions. Treated cement paste samples in solutions of MgSO₄, the concentration of 1% MgSO₄ and 5% MgSO₄, at both water-cement ratios form ettringite formula 3CaO·Al₂O₃·3CaSO₄·31H₂O. Ettringite occurs in reactions of sulfate and aluminate hydrate and could lead concrete structure to a state of destruction. The reaction is also known as sulphate corrosion of concrete. In joint solutions of magnesium salt of concentration of 1% MgCl₂ + 1% MgSO₄ and 5% MgCl₂ + 5% MgSO₄, at both water-cement ratios, chlorides with aluminate hydrate form monochloroaluminate hydrate formula 3CaO·Al₂O₃·CaCl₂·10H₂O, while sulfates react with calcium hydroxide to gypsum without forming expansive ettringite on samples of the cement paste. Blocking the formation of expansive ettringite verifies the blocking of sulfate corrosion of concrete by chloride from magnesium chloride.

INTRODUCTION

A great threat towards concrete and reinforced concrete structures represent magnesium salts, mainly sulphates and chlorides. The basic processes that take place in cement stone in the presence of magnesium salt solution are based on their reaction with calcium hydroxide, known in the chemistry of cement as "portlandit" (Mladenović, 2008):



The product reaction of (1) and (2) is magnesium hydroxide, whose solubility is small, 18.2 mgdm⁻³ at room temperature, and as such precipitates from the solution. Binding of OH⁻ ions in the magnesium hydroxide is accompanied by reduction of pH value of the solution in the pores of the cement stone to pH = 10 (Mladenović, 2008). Reduction of pH of concrete leads to increased corrosion intensity of concrete and steel reinforcement. Otherwise, the pH of the solid concrete pores is in the interval from 12.5 to 13.5, thanks to the calcium hydroxide

generated through the process of cement hydration (Angst, 2011; Đureković, 1996). In addition to the basic reactions, reaction 1 and 2 in the concrete exposed to a solution of a magnesium salt lead to other reactions that occur between the mineral cement hydrate, chloride and sulfate, and magnesium ions. Among the most dominant reactions, as the research results show, are the reactions between the aluminate hydrate and chloride as well as sulphate of magnesium. Chlorides that penetrate to concrete from the environment enter into reaction with aluminate hydrate. The most common product of the reaction of chloride and aluminate hydrate is monochloroaluminate hydrate formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$, known as the Friedel's salt. (Hirao et al. 2005; Sumranwanich et al. 2004; Hewlett, 1998; Bikić et al. 2009).

In the presence of magnesium sulfate in the surface layers of concrete, a magnesium hydroxide forms, while hydrated calcium aluminum sulfate hydroxide forms in the inner layers $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$, known in the chemistry of cement as "ettringite" (Mladenović, 2008; Đureković, 1996). Ettringite is the phase that occurs in concrete, in reactions of sulfate and aluminate hydrate and could lead concrete to a state of destruction. The reaction is known as sulphate corrosion of concrete. In some studies dealing with the test of concrete exposed to seawater, it was found that chlorides slow down the affect of sulphate ions to concrete. Without the presence of chloride, ettringite may form in the concrete in the presence of sulphate, while gypsum forms in the presence of chloride (Mladenović, 2008). However, a more detailed literature review about chloride role at the impact of sulfate on concrete point to the three scholar thoughts: (a) in the presence of chloride the sulfate intensity affect on the concrete increases, (b) in the presence of chloride the sulfate intensity affect on the concrete decreases, (c) there no significant impact of chloride at the affect of sulfates on concrete (Hossain et al. 2005). The paper research subject is to examine whether chlorides block the affect of sulphate on the concrete, that is, whether they block the sulfate corrosion of concrete.

EXPERIMENTAL

The cylindrical samples of cement paste measuring 80×40 mm were prepared for implementation of planned research. For sample preparation the Portland cement class PC 42.5 with following clinker mineralogical composition was used: alit, tricalcium silicate (C_3S) - 66.37%; belit, dicalcium silicate (C_2S) - 8.32%; tricalcium aluminate (C_3A) - 9.62%, celite, and tetracalcium alumoferit (C_4AF) - 10.77%. The samples were prepared in varying water-cement ratio 0.5 and 0.7 (kg H_2O / kg of cement). After preparation, the samples were placed in molds in a heated space with relative humidity of at least 90%. The molds were held in such state for 24 hours. After demolding, the samples were immersed in the following solutions: 1% MgCl_2 , 1% MgSO_4 , 1% MgCl_2 + 1% MgSO_4 , 5% MgCl_2 , 5% MgSO_4 , 5% MgCl_2 + 5% MgSO_4 . In the above

mentioned solutions, the samples were treated at room temperature for the next 9 months. After 9 months, the cement paste samples were extracted from the above solution, dried in an oven at 105°C to constant weight, cooled in a desiccator and then grounded. In order to study the corrosion of concrete, the samples were analyzed after grinding using X-ray diffraction analysis (XRD). In addition, certain phases of importance were followed in assessing the corrosion of concrete. In this paper, three phases were followed, namely portlandite, ettringite and monochloroaluminate hydrate. Diffraction lines of highest intensity of portlandite are located at the following angles: 2Θ : $11,2^\circ$ ($I/I_0 = 100\%$), $22,6^\circ$ ($I/I_0 = 60\%$), $30,9^\circ$ ($I/I_0 = 50\%$). Diffraction lines of highest intensity of ettringite are located at the following angles: 2Θ : $9,65^\circ$ ($I/I_0 = 100\%$), $5,58^\circ$ ($I/I_0 = 80\%$), $3,21^\circ$ ($I/I_0 = 60\%$). Diffraction lines of highest intensity of monochloroaluminate hydrate are located at the following angles: 2Θ : $11,2^\circ$ ($I/I_0 = 100\%$), $22,6^\circ$ ($I/I_0 = 60\%$), $30,9^\circ$ ($I/I_0 = 50\%$) (Bikić et al. 2009; Perkins, 2000; ARL X'TRA, 2008). Mineralogical analysis of cement clinker and x-ray diffraction analysis of the cement paste samples (XRD) were carried out on "X-Ray Diffractometer SIEMENS D 5000" device.

RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show diffraction patterns of the cement paste treated in solutions of 1% MgCl_2 and 5% MgCl_2 of varying water-cement ratio.

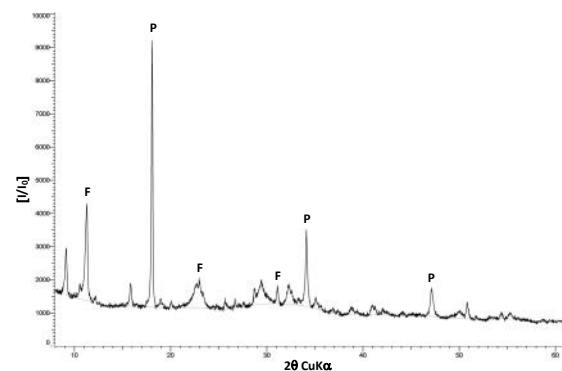


Figure 1. X-ray diffractogram of a sample treated in a solution of 1% MgCl_2 $v/c=0,5$

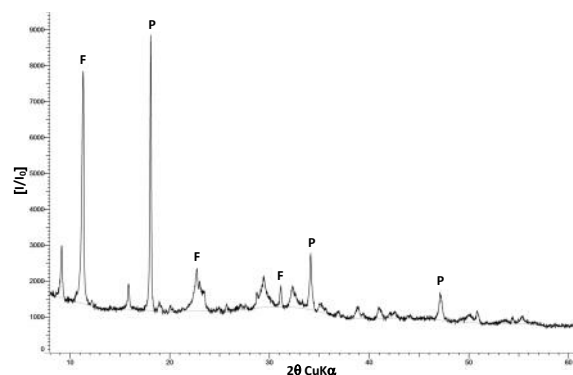


Figure 2. X-ray diffractogram of a sample treated in a solution of 1% MgCl_2 $v/c=0,7$

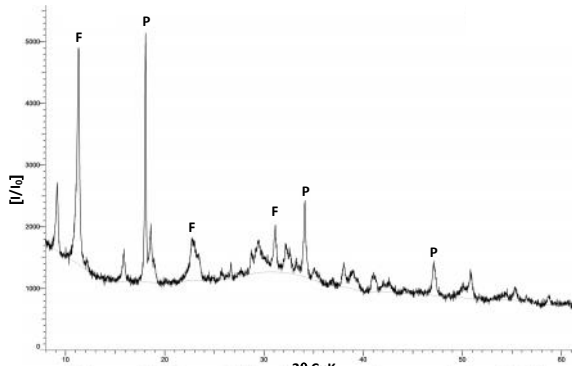


Figure 3. X-ray diffractogram of a sample treated in a solution of 5% MgCl₂ v/c=0,5

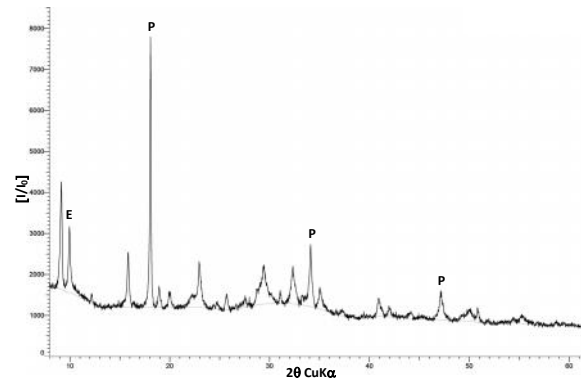


Figure 6. X-ray diffractogram of a sample treated in a solution of 1% MgSO₄ v/c=0,7

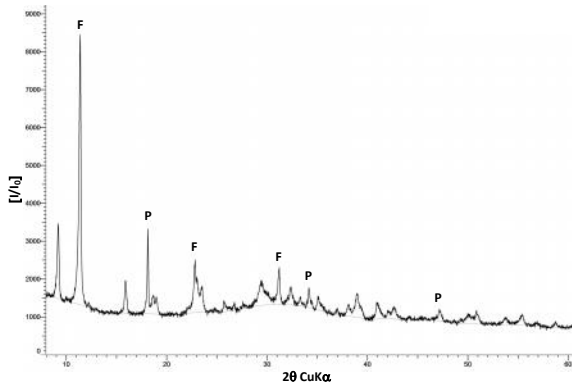


Figure 4. X-ray diffractogram of a sample treated in a solution of 5% MgCl₂ v/c=0,7

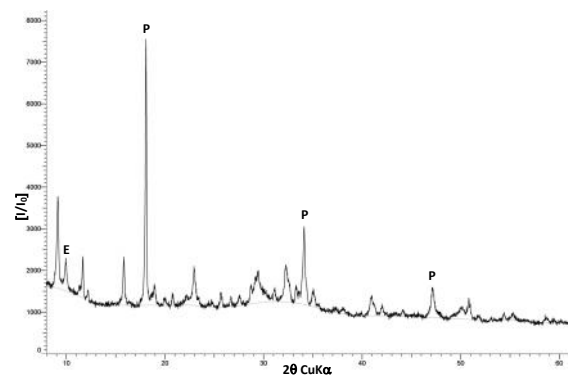


Figure 7. X-ray diffractogram of a sample treated in a solution of 5% MgSO₄ v/c=0,5

Figures 1, 2, 3 and 4 detect diffraction lines of portlandite, mark P, and monochloroaluminate hydrate, mark F. Diffraction lines of monochloroaluminate hydrate prove that there has been a reaction between chlorides that penetrate the concrete, the cement paste, and aluminate hydrate, at both concentrations of MgCl₂ and water-cement ratios. The formation of monochloroaluminate hydrates negatively impact concrete because it leads to the destruction of aluminate hydrate, one of the main constituents of concrete.

Figures 5, 6, 7 and 8 show diffractograms of cement paste treated in solutions of 1% MgSO₄ and 5% MgSO₄ of varying water-cement ratio.

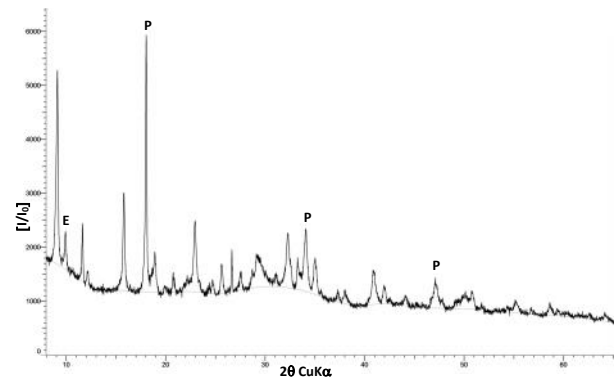


Figure 8. X-ray diffractogram of a sample treated in a 5% MgSO₄ v/c=0,7

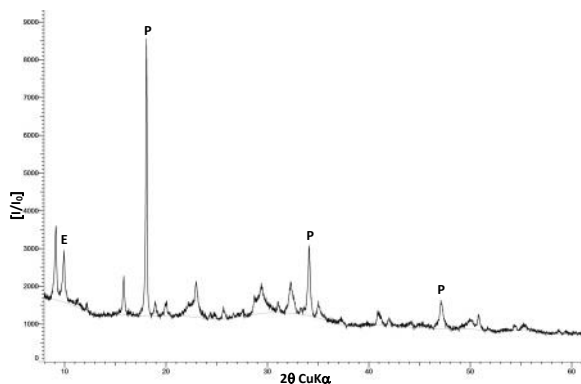


Figure 5. X-ray diffractogram of a sample treated in a Solution of 1% MgSO₄ v/c=0,5

Figures 5, 6, 7 and 8 detect diffraction lines of portlandite, mark P, and ettringite, mark E. Diffraction lines of ettringite prove that there has been a reaction between the sulfate of magnesium sulfate that penetrate the concrete and aluminate hydrate, at both concentrations of MgSO₄ and water-cement ratios. This also verifies that the samples of cement paste treated in solutions of MgSO₄ of both concentrations show sulphate corrosion of concrete. Key research carried out in this paper shown in Figures 9, 10, 11 and 12, represent the influence of magnesium chloride on the sulfate corrosion of concrete.

Figures 9, 10, 11 and 12 show comparative diffractograms of cement paste treated in joint solutions of magnesium salt 1% $MgCl_2$ + 1% $MgSO_4$, then 5% $MgCl_2$ + 5% $MgSO_4$, and concentration solutions of 1% $MgSO_4$ and 5% $MgSO_4$, while fluctuating water-cement ratio. The intensity of diffraction lines is proportional to the amount of certain mineral species in the testing sample (Petrovski, 2006).

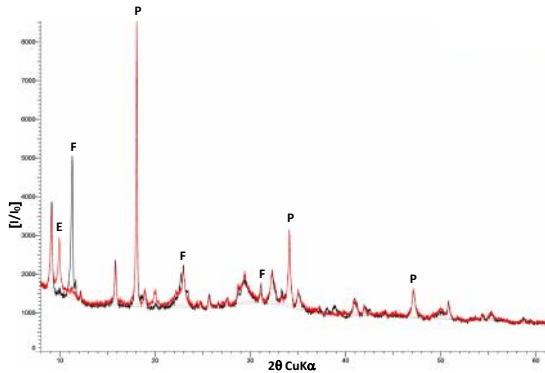


Figure 9. X-ray diffractograms of a samples treated in a solutions of: Black - 1% $MgSO_4$ + 1% $MgCl_2$ $v/c=0,5$; Red - 1% $MgSO_4$ $v/c=0,5$

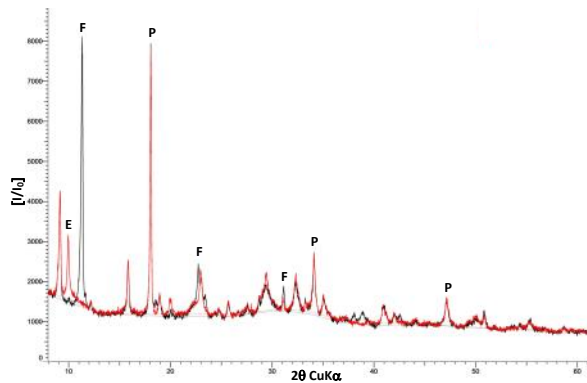


Figure 10. X-ray diffractograms of a samples treated in a solutions of: Black - 1% $MgSO_4$ + 1% $MgCl_2$ $v/c=0,7$; Red - 1% $MgSO_4$ $v/c=0,7$

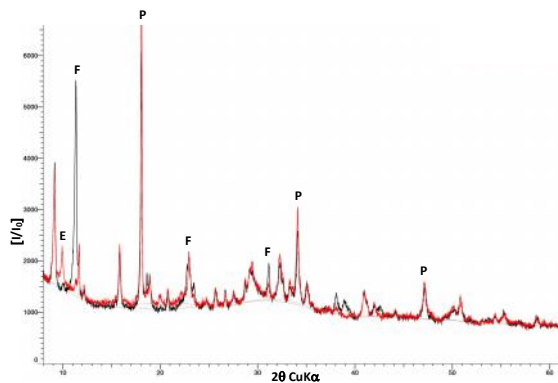


Figure 11. X-ray diffractograms of a samples treated in a solutions of: Black - 5% $MgSO_4$ + 5% $MgCl_2$ $v/c=0,5$; Red - 5% $MgSO_4$ $v/c=0,5$

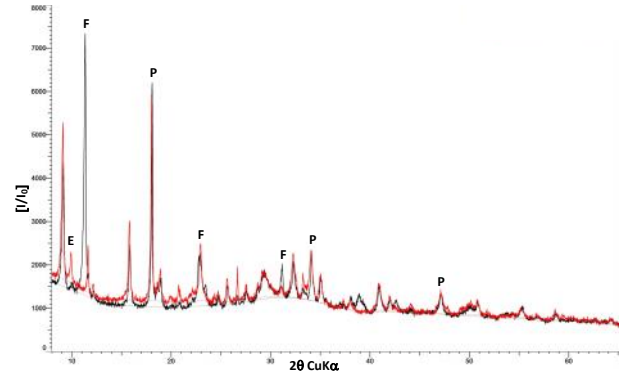


Figure 12. X-ray diffractograms of a samples treated in a solutions of: Black - 5% $MgSO_4$ + 5% $MgCl_2$ $v/c=0,7$; Red - 5% $MgSO_4$ $v/c=0,7$

Figures 9, 10, 11 and 12 depict that the addition of a solution of $MgCl_2$ to $MgSO_4$ block the formation of ettringite. As Figures 9, 10, 11 and 12 depict, diffraction lines of ettringite, mark E that appears on the samples of cement paste treated in solutions of $MgSO_4$, the concentration of 1% $MgSO_4$ and 5% $MgSO_4$, at both water-cement ratios, is disappearing in samples treated in joint solutions of magnesium salts. This proves that chlorides of $MgCl_2$ block the formation of sulfate corrosion of concrete. That means that joint solutions of magnesium salts ($MgCl_2$ + $MgSO_4$) of higher and lower concentrations of chlorides of magnesium chloride form monochloroaluminate hydrate, while sulfates of magnesium sulfate react with portlandit to gypsum without forming expansive ettringite later on.

CONCLUSIONS

Researching the influence of magnesium chloride to sulfate corrosion of concrete, the following was verified:

- the XRD method verifies that treated cement paste samples in solutions of $MgCl_2$ of concentration of 1% $MgCl_2$ and 5% $MgCl_2$, in both water-cement ratios ($v/c = 0.5$ and $v/c = 0.7$), form a monochloroaluminate hydrate $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$. The same occurs in reactions of chlorides and aluminate hydrate.
- the XRD method verifies that treated cement paste samples in solutions of $MgSO_4$ of concentration of 1% $MgSO_4$ and 5% $MgSO_4$, in both water-cement ratios, form ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. The same occurs in reactions of sulfate and aluminate hydrate and could lead to the state of destruction of concrete structure. The reaction is also known as sulphate corrosion of concrete.
- the joint solutions of magnesium salt of concentration of 1% $MgCl_2$ + 1% $MgSO_4$ and 5% $MgCl_2$ + 5% $MgSO_4$, in both water-cement ratios, verifies that the chlorides of magnesium chloride block the formation of sulfate corrosion of concrete on cement paste samples. Chloride with aluminate hydrate form monochloroaluminate hydrate while sulfates of magnesium sulfate react with portlandit to gypsum

without forming expansive ettringite later on. Therefore, in the joint solutions of magnesium salts ($\text{MgCl}_2 + \text{MgSO}_4$), the chlorides are inhibitors of sulfate corrosion of concrete.

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Summary/Sažetak

Predmet istraživanja provedenih u ovom radu je ispitati da li hloridi iz magnezijum hlorida blokiraju djelovanje sulfata iz magnezijum sulfata na beton, odnosno da li blokiraju sulfatnu koroziju betona. Za realizaciju planiranih istraživanja pripremljeni su cilindrični uzorci cementne paste, dimenzija (80×40) mm, varirajući vodocementni faktor, 0,5 i 0,7 (kg H₂O/kg cementa). Uzorci su potapani i tretirani 9 mjeseci u sljedećim rastvorima: 1% MgCl₂, 1% MgSO₄, 1% MgCl₂ + 1% MgSO₄, 5% MgCl₂, 5% MgSO₄, 5% MgCl₂ + 5% MgSO₄. U cilju ispitivanja korozije betona, uzorci su nakon vađenja iz navedenih rastvora, sušenja i mljevenja analizirani koristeći rendgensko difrakcionu analizu (XRD). Na uzorcima cementne paste koji su tretirani u rastvorima MgSO₄ koncentracija 1% MgSO₄ i 5% MgSO₄, kod oba vodocementna faktora, formira se etringit formule 3CaO·Al₂O₃·3CaSO₄·31H₂O. Etringit nastaje u reakcijama sulfata i hidrata aluminata i zna dovesti betonsku konstrukciju do stanja destrukcije. Reakcija je poznata i kao sulfatna korozija betona. U zajedničkim rastvorima magnezijumovih soli koncentracija 1% MgCl₂ + 1% MgSO₄ kao i 5% MgCl₂ + 5% MgSO₄, kod oba vodocementna faktora, hloridi s hidratima aluminata formiraju monohloraluminathidrat, formule 3CaO·Al₂O₃·CaCl₂·10H₂O, dok sulfati reaguju s kalcijum hidroksidom do gipsa, ne formirajući kasnije ekspanzivni etringit na uzorcima cementne paste. Blokiranje formiranja ekspanzivnog etringita dokaz je blokiranja sulfatne korozije betona od strane hlorida iz magnezijum hlorida.