Corrosion Mechanism of Cemented Soil in $MgCl_2$ Solution

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Mechanical properties of the cemented soil will be reduced when cemented soils are applied in the $MgCl_2$ corrosive environment to conduct seepage control in hydraulic engineering. The corrosive conditions will inevitably cause serious damage to the cement-soil composite, and further reduce stablity of the whole structure. Therefore, this cementation technique could be commonly used to stabilize infrastructures. More engineering practices regarding the reduction in mechanical properties of cemented soil in the $MgCl_2$ environment are required. To simulate and study the corrosion process, a series of tests including photographing, unconfined compression tests, and measuring Mg^{2+} and Cl^- concentrations of solution were conducted on cured cemented soil blocks with different concentrations of $MgCl_2$ solutions. Results show that the surface corrosion of the sample increases while the compression strength decreases with the increase in solution concentration given the same curing time of the concrete block. Chemical analysis of the corrosive environment indicates that the volumes of new products such as $CaCl_2 \cdot 6\,H_2O$ and $Mg_2(OH)_3Cl \cdot 4\,H_2O$ amount to seven times that of $Ca(OH)_2$ after reaction. The corrosion of cemented soil is a sort of crystallizing corrosion. The $Mg(OH)_2$ takes chemical reactions with $3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O$ and forms new products such as $MgO \cdot SiO_2 \cdot H_2O$, which is a sort of dissolving corrosion. In addition, the authors analysed the relationships between the unconfined compressive strength of cemented soils cured for 28 days and the initial concentrations of Mg^{2+} and Cl^-. Finally, the regression equations of the strength were established.

Key words: *Cemented soil, compressive strength, modified coefficient, corrosion*

Introduction

The cemented soil technique is defined as a method of improving soil properties by mixing cements with *in-situ* soils. Cemented soils can be used in structure retaining and seepage control of small-scale irrigation in hydraulic engineering by using a form of cushion material on large channels, roads and compound pile foundation of dam slope and other projects. They can be applied in unpolluted and polluted conditions, such as industrial land and seawater. $MgCl_2$ is one of the commonest causes resulting in pollution of cemented soils. The corrosive environment may cause the change in mechanical and engineering properties of cemented soils. Much research attention has been focused on the influence of corrosive environment on cemented soil. *Iorliam*[1] and *Moses*[2] recommended using CKD as a modifier for stabilizing BCS with cement or other additives. *Kolias* studied the effectiveness of high calcium fly ash and cement in stabilizing fine-grained clayey soils in the laboratory and the results obviously presented the technical benefits of stabilizing clayey soils using fly ash and cement.[3] *Ning et al.* investigated the behaviour of cemented soil under various environmental conditions and concluded that the environmental corrosion had little effect on the fracture process in contrast to the evident influence on mechanical strength.[4] *Xing et al.* showed that Mg^{2+}, Cl^- and SO_4^{2-} not only caused a change in the microstructure of salt-rich soil-cements, but also reduced the strength of the soil-cement composite.[5–7] To evaluate this adverse effect on the behaviour of soil-cement composite, *Yang* analysed the factors contributing to cement-based solidification/stabilization of the polluted soil and the optimum parameters.[8] Bai and Dong tested mechanical properties and electrical resistivity of cement-soil polluted by H_2SO_4.[9–10] *Yang et al.* studied the strength of soil stabilized by cement in the corrosive environment of seawater and measured the strength distribution by using micro cone-penetration tests.[11] *Liu* and *Qu* studied the durability of cemented soil under brine corrosion.[12] However, the studies of the influence of $MgCl_2$ on properties of cemented soil are limited. To understand $MgCl_2$ corrosion, a series of laboratory tests were conducted in this study on the cemented-soil blocks cured in $MgCl_2$ solutions of different concentrations.

Experimental

Preparations for cemented soil blocks

The air-dried soil with plasticity index (I_p) of 8.1 was taken from a building site in Taiyuan, China. The cement used was ordinary Portland cement (OPC), brand 32.5#, produced in Taiyuan Shitou Cement Co. Ltd. Soil, cement, and water were mixed in a certain proportion as shown in Table 1 by a HJW-30 blender at a rotating speed of 48 rounds per minute. After mixing well, the mixture was put into a steel

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mould to form a cemented soil block of 10 × 10 × 10 cm^3. After 24 hours, the blocks were taken out of the moulds, cured in a standard conservation box for seven days. The cemented soil blocks were then soaked in $MgCl_2$ solutions of various concentration prepared in advance. The main chemical composition of the cemented soil is given in Table 2.

Table 1 – *General composition of cemented soil*
Tablica 1 – *Opći sastav cementiranog tla*

m(air-dried soil)/g *m*(tlo osušeno na zraku)/g	*m*(cement)/g *m*(cement)/g	*m*(tap water)/g *m*(vodovodna voda)/g
100	15	50

Preparation of $MgCl_2$ solution

The concentrations of the $MgCl_2$ solution used in this experiment were selected as 1.5 g l^{-1}, 4.5 g l^{-1}, 9.0 g l^{-1}, 18.0 g l^{-1}, and 22.5 g l^{-1} respectively, based on the *Code for Investigation of Geotechnical Engineering (GB 50021–2001, 2009)* and the *Code for Anticorrosion Design of Industrial Constructions (GB 50046–2008, 2008)*.[13,14] For $MgCl_2$ solution, the Mg^{2+} and Cl^- concentrations were measured and the corrosion degrees evaluated (Table 3) according to the *Code for Investigation of Geotechnical Engineering*. The $MgCl_2$ solutions were graded as B.

Testing procedure

In order to simulate the corrosion process and study the corrosion mechanism, the following test procedures were performed:

Step 1: Preparing the 72 blocks following the requirements given above.

Step 2: Soaking the blocks in $MgCl_2$ solutions of concentrations 0, 1.5, 4.5, 9.0, 18.0 and 22.5 g l^{-1}, respectively.

Step 3: To observe the changes in appearance during corrosion, photographing the blocks after soaking in $MgCl_2$ solutions for 3, 7, 14 and 28 days.

Step 4: Carrying out unconfined compression tests on the blocks soaked for 3, 7, 14, and 28 days, respectively. The unconfined compression strength was measured by universal testing machine (Model-5105A) with maximum load capacity of 100 kN, and loading rate 5 mm per minute. At each curing time, three blocks were tested in parallel with the one concentration of the solution. The average value of the three test results is used as the block strength.

Step 5: Measuring of Mg^{2+} and Cl^- solution concentrations immediately after the blocks were taken out.

Results and discussion

Visual observations

Figs. 1 and 2 shows the photos of the cemented soil blocks after soaking for 28 days in $MgCl_2$ solutions of various concentrations. It can be seen that the crystallization is found on the surface of the cement-soil block in the $MgCl_2$ condition. The influence of $MgCl_2$ on the blocks is more obvious with the increase in the concentration of $MgCl_2$ and curing time.

Table 2 – *Main chemical composition of cemented soil*
Tablica 2 – *Osnovni kemijski sastav cementiranog tla*

pH	$w(Ca^{2+})$ / mg kg^{-1}	$w(Mg^{2+})$ / mg kg^{-1}	$w(SO_4^{2-})$ / mg kg^{-1}	$w(NH_4^+)$ / mg kg^{-1}	$w(Cl^-)$ / mg kg^{-1}	$w(CO_3^{2-})$ / mg kg^{-1}	$w(OH^-)$ / mg kg^{-1}
9.80	427.84	354.17	2879.10	1.29	282.32	1090.8	496.64

Table 3 – *Chemical ingredients of solutions and corrosion evaluation*
Tablica 3 – *Kemijski sastav otopina i ocjena korozije*

γ/mg l^{-1}	Mg^{2+}		Cl^-	
	γ/mg l^{-1}	Corrosion evaluation Ocjena korozije	γ/mg l^{-1}	Corrosion evaluation Ocjena korozije
tap water vodovodna voda	19.37	no ne	43.06	no ne
1 500	93.90	weak slabo	227.10	no ne
4 500	278.42	weak slabo	584.21	no ne
9 000	317.81	weak slabo	795.77	no ne
18 000	402.40	weak slabo	1100.84	no ne
22 500	471.60	weak slabo	1881.69	no ne

(a) 1.5 g l^{-1} (b) 4.5 g l^{-1} (c) 9.0 g l^{-1} (d) 18.0 g l^{-1} (e) 22.5 g l^{-1}

Fig. 1 – *Photos of the cemented soil blocks soaked in $MgCl_2$ solution of different concentrations for 28 days*
Slika 1 – *Fotografije uzoraka cementiranog tla močenih 28 dana u otopinama $MgCl_2$ različitih koncentracija*

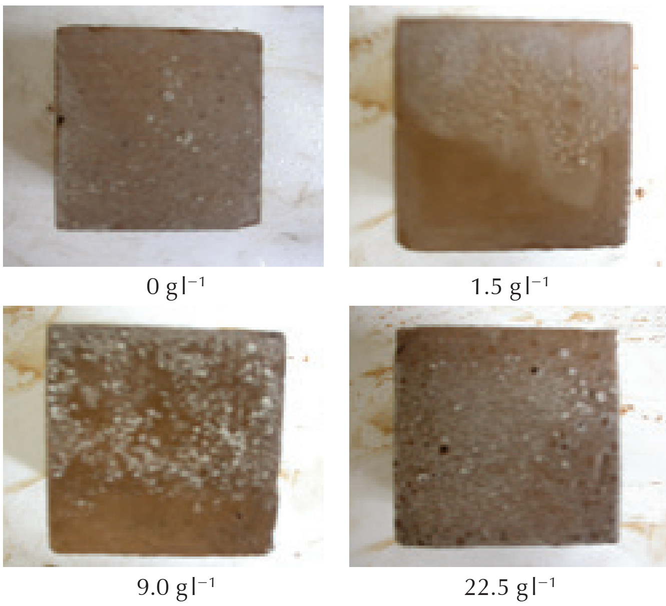


Fig. 2 – *Photos of the cemented soil blocks surfaces after soaking in $MgCl_2$ solution of different concentrations for 28 days*
Slika 2 – *Fotografije površina uzoraka cementiranog tla nakon 28 dana močenja u otopinama $MgCl_2$ različitih koncentracija*

Unconfined compressive strength test

The unconfined compressive strengths of the cemented soil blocks are summarized in Table 4. The compressive strength of cemented soil decreases with the increase in corrosive solution concentration during the same corrosion time, and the corrosion degree increases with the corrosion time (Fig. 3). The cemented soil modified coefficient, α, is defined as follows:

$$f_{cu}' = \alpha f_{cu}, \quad (1)$$

where f_{cu}' is compressive strength of the block cured in $MgCl_2$ solution; α is a modified coefficient expressing degree of blocks corrosion; f_{cu} is compressive strength of the block cured in pure water.

Table 4 presents the corresponding α to different corrosion times and concentrations. All coefficients are greater than 1 in $MgCl_2$ solution with concentration of 1.5 g l^{-1}. This result implies that the low concentration of $MgCl_2$ may be beneficial to improving strength of cemented soil. In addition, the strength modified coefficients in other environments in this study are less than 1, indicating that $MgCl_2$ solutions can induce obvious corrosion and greatly reduce the strength of cemented soils when its concentration is greater than 1.5 g l^{-1}. Therefore, to ensure safety, optimize design, cost-efficiency and suitable measurement, the environmental condition of the in-service cemented soils should be taken into account in the design and calculation of the bearing capacity and the settlement of a foundation.

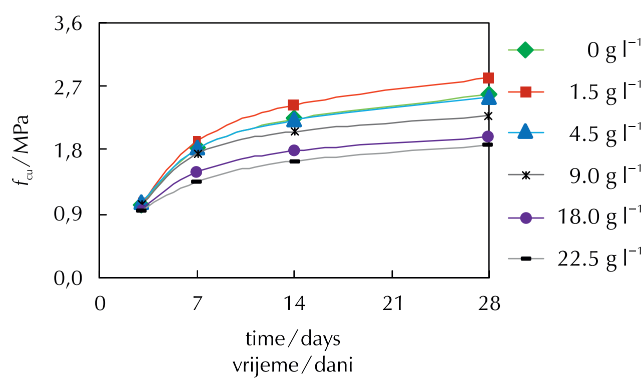


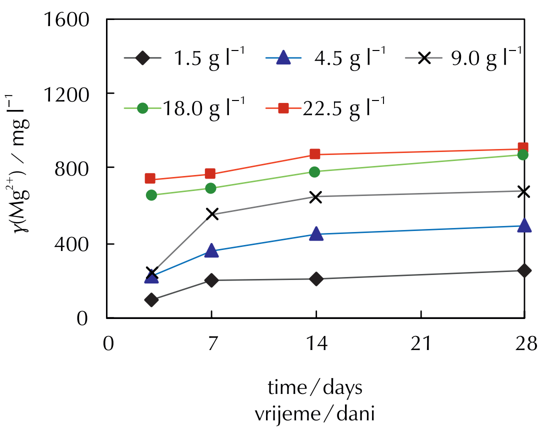
Fig. 3 – *Relationship between the compressive strength of soils and time*
Slika 4 – *Veza između tlačne čvrstoće tla i vremena*

Table 4 – *Compressive strength modified coefficients of cemented soil in $MgCl_2$ solution*
Tablica 4 – *Koeficijent promjene tlačne čvrstoće cementiranog tla u otopini $MgCl_2$*

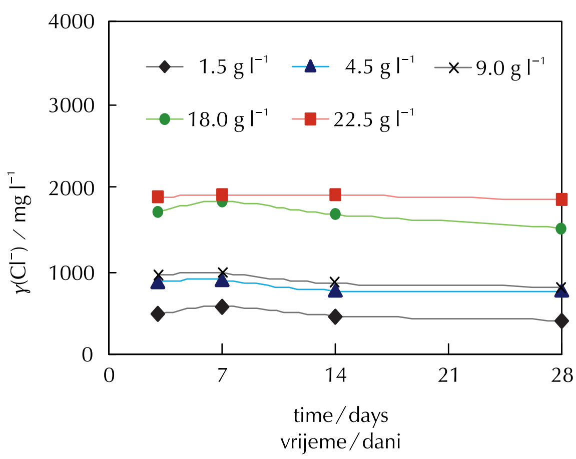
$\gamma(MgCl_2)$ / g l^{-1}	Corrosion time Trajanje korozije			
	3 days 3 dana	7 days 7 dana	14 days 14 dana	28 days 28 dana
	α			
0	1.000	1.000	1.000	1.000
1.5	1.029	1.060	1.089	1.089
4.5	1.039	1.000	0.991	0.981
9.0	1.010	0.962	0.920	0.880
18.0	0.942	0.819	0.799	0.768
22.5	0.922	0.742	0.732	0.718

Changes of Mg^{2+} and Cl^- concentration with corrosion time and regression analysis

Figs. 4 and 5 shows the relationships between the Mg^{2+} or Cl^- concentration and the corrosion time with various $MgCl_2$ concentrations. The concentration of Mg^{2+} in the solutions increases with curing time. The curve of Mg^{2+} concentration versus corrosion time can be divided into two parts: when the corrosion time is less than seven days, the Mg^{2+} concentration in the solutions rapidly increases and then tends to stabilize (Fig. 4). The Mg^{2+} concentration increases with the increase in $MgCl_2$ solution. Tables 1 and 2 show that the Mg^{2+} concentration was 354.17 mg l^{-1} in the cemented soil, and greater than that of the $MgCl_2$ solution (concentration: 1.5 g l^{-1}, 4.5 g l^{-1}, and 9.0 g l^{-1}). To reach the chemical equilibrium state, Mg^{2+} is likely to leach from cemented soils. By contrast, the Cl^- concentration of the solution almost keeps steady when the corrosion time increases with the given concentration of $MgCl_2$ solution, and it increases with the concentration of $MgCl_2$ solution at the same corrosion time.



F i g. 4 – *Plot of Mg^{2+} concentration versus time*
S l i k a 4 – *Koncentracija Mg^{2+} u odnosu na vrijeme*



F i g. 5 – *Plot of Cl^- concentration versus time*
S l i k a 5 – *Koncentracija Cl^- u odnosu na vrijeme*

The corrosion mechanism

The relationships between unconfined compressive strengths of the cemented soil cured for 28 days and initial concentrations of Mg^{2+} and Cl^- ions are analysed by regression procedure. Regression equations are established in Table 5. The results of regression shows that the unconfined compressive strength of the cemented soil decreases with increase in concentration of Mg^{2+} or Cl^- for the same corrosion time. This means that the compressive strength of cemented soils is closely related to the concentrations of Mg^{2+} and Cl^- ions in an $MgCl_2$ corrosive environment.

T a b l e 5 – *Strength formulae of cemented soil in dependance of Mg^{2+} concentration, $\gamma(Mg^{2+})$, and Cl^- concentration, $\gamma(Cl^-)$, at cured time of 28 days*

T a b l i c a 5 – *Čvrstoća cementiranog tla kao funkcija koncentracije iona Mg^{2+}, $\gamma(Mg^{2+})$, i Cl^-, $\gamma(Cl^-)$, nakon izloženosti otopini $MgCl_2$ tijekom 28 dana*

Cemented soil strength Čvrstoća cementiranog tla	
Mg^{2+}	Cl^-
$f_{cu} = 8.80\ [\gamma(Mg^{2+})/\text{mg l}^{-1}]^{-0.241}$; $R^2 = 0.80$	$f_{cu} = 9.06\ [\gamma(Cl^-)/\text{mg l}^{-1}]$ $C^{-0.210}$ $R^2 = 0.93$

In the $MgCl_2$ solution environment, the main chemical reaction of the soil and $MgCl_2$ can be described as:

$$MgCl_2 + Ca(OH)_2 + 6\,H_2O \rightarrow CaCl_2 \cdot 6\,H_2O + Mg(OH)_2 \quad (2)$$

$$3\,Mg(OH)_2 + MgCl_2 + 8\,H_2O \rightarrow 2\,Mg_2(OH)_3Cl \cdot 4\,H_2O \quad (3)$$

It is well known that the volumes of the resultant are seven times that of $Ca(OH)_2$. When the amount of the $MgCl_2$ in the solution is suitable, the increased volume produced by $CaCl_2 \cdot 6\,H_2O$ and $Mg_2(OH)_3Cl \cdot 4\,H_2O$ may fill the void in the cemented soil, and result in the increase in compressive strength of the cemented soil. However, when the amount of $MgCl_2$ in the solution is large enough, the increased volume caused by formation of $CaCl_2 \cdot 6\,H_2O$ and $Mg_2(OH)_3Cl \cdot 4\,H_2O$ will not only fill the voids, but inflate the cemented soil, crack and even break. This could explain why the unconfined compressive strength of cemented soil blocks soaked in pure water is less than that of blocks soaked in low concentration solutions and greater than that of blocks soaked in high concentration solutions.

As defined in Eq. 3, $Mg(OH)_2$ is the product of the reaction between cemented soil and $MgCl_2$. In the cemented soil with high level of $Mg(OH)_2$, the following chemical reaction is presented:

$$2\,Mg(OH)_2 + 3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O \rightarrow 2\,(MgO \cdot SiO_2 \cdot H_2O) + 3\,Ca(OH)_2 \quad (4)$$

In the soil, $3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O$ is a sticking material which can increase the strength of cemented soils by sticking the soil particles together. The product, $MgO \cdot SiO_2 \cdot H_2O$ (MSH) of chemical reaction (4), is not a sticking material, and produces an unsteady structure that reduces the strength of the soil.

In summary, the cemented soils undergo $MgCl_2$ corrosion during the crystallization and dissolution process.

Conclusions

(1) The unconfined compressive strength of the cemented soil decreases with increase in concentration of the $MgCl_2$ solution and corrosion time.

(2) Based on the relationships between the unconfined compressive strength of cemented soils cured for 28 days and the initial concentration of Mg^{2+} and Cl^{-} in laboratory tests, regression equations of strength have been established.

(3) The chemical mechanism of the $MgCl_2$ corrosive solution on cemented soils is discussed and analysed. The $MgCl_2$ corrosion is a combinative corrosion during the crystallization and dissolution process.

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List of symbols and abbreviations
Popis simbola i kratica

f_{cu} – compressive strength of the material cured in pure water, MPa
– posmična čvrstoća materijala obrađenog čistom vodom, MPa

f_{cu}' – compressive strength of the material cured in $MgCl_2$ solution, MPa
– posmična čvrstoća materijala obrađenog otopinom $MgCl_2$, MPa

I_p – plasticity index
– indeks plastičnosti

R^2 – coefficient of determination
– koeficijent determinacije

m – mass, g
– masa, g

w – mass fraction, $mg\,kg^{-1}$
– maseni udjel, $mg\,kg^{-1}$

α – soil modified coefficient
– koeficijent promjene svojstava tla

γ – mass concentration, $mg\,l^{-1}$, $g\,l^{-1}$
– masena koncentracija, $mg\,l^{-1}$, $g\,l^{-1}$

BCS – black cotton soil
– vertisol, tip humusno-akumulacijskog tla

CKD – cement kiln dust
– prašina klinkera

MSH – $MgO \cdot SiO_2 \cdot H_2O$

OPC – ordinary Portland cement
– obični portland-cement

References
Literatura

1. *A. Y. Iorliam, I. O. Agbede, M. Joel,* Effect of Cement Kiln Dust (CKD) on some geotechnical properties of Black Cotton Soil (BCS), Electron. J. Geotech. Eng. **17** (2012) 967–977.
2. *G. K. Moses, A. Saminu,* Cement Kiln Dust stabilization of compacted black cotton soil, Electron. J. Geotech. Eng. **17** (2012) 825–836.
3. *S. Kolias, V. Kasselouri-Rigopoulou, A. Karahalios*, Stabilisation of clayey soils with high calcium fly ash and cement, Cem. Concr. Compos. **27** (2005) 301–313, doi: http://dx.doi.org/10.1016/j.cemconcomp.2004.02.019.
4. *B. K. Ning, S. J. Jin, S. L. Chen,* Influence of erosive ions on mechanical properties of cemented soil, J. Shenyang Univ. Technol. **28** (2006) 178–181.
5. *H. F. Xing, X. M. Yang, C. XU, G. B. YE,* Strength characteristics and mechanisms of salt-rich soil-cement, Eng. Geol. **103** (2009) 33–38, doi: http://dx.doi.org/10.1016/j.enggeo.2008.07.011.
6. *H. F. Xing, C. Xu, G. B. Ye*, Mechanism analysis of influence of soluble salt ions on strength of salt-rich cement-soil, J. Highway Transp. **11** (2008) 26–30.
7. *H. F. Xing, X. M. Yang, C. Xu*, Strength and microstructure of salt-rich soft soil improved by cement, J. Tongji Univ. **36** (2008) 1606–1610.
8. *W. Yang, L. A. Wang, W. H. Tan*, Cement-based solidification/stabilization of high concentration chromium-contaminated soil, Adv. Mater. Res. **414** (2012) 232–237, doi: http://dx.doi.org/10.4028/www.scientific.net/AMR.414.232.
9. *X. H. Bai, Y. Q. Zhao, P. J. Han, J. Y. Qiao, Z. A. Wu*, Experimental study on mechanical property of cemented soil under environmental contaminations, Chin. J. Geotech. Eng. **29** (2007) 1260–1263.
10. *X. Q. Dong, X. H. Bai, Y. K. Lv*, The influence of pH value and SO_4^{2-} concentration on strength of cemented soil, Adv. Mater. Res. **223** (2011) 2006–2010, doi: http://dx.doi.org/10.4028/www.scientific.net/AMR.233-235.2006.
11. *J. J. Yang, T. Sun, Y. C. Zhang,* Deterioration of soil cement stabilized in corrosive site, Chin. J. Geotech. Eng. **34** (2012) 130–138.
12. *Z. P. Liu, Q. S. Qu,* Study on durability of cement soil under brine erosion, Adv. Mater. Res. **446** (2012) 1858–1863, doi: http://dx.doi.org/10.4028/www.scientific.net/AMR.446-449.1858.
13. *B. H. Gu, D. Z. Gao, Z. X. Lin, S. Z. Li*, Chinese Stand GB 50021–2009, Code for investigation of geotechnical engineering, China building industry P., Beijing, 2009, p. 122.
14. *D. E. Fan, J. Y. He, W. J. Yang, W. Xiong, X. Z. Zeng*, Chinese Stand GB/T 50046–2008, Code for anticorrosion design of industrial constructions, China project P., Beijing, 2008, p. 6.

SAŽETAK

Mehanizam korozije cementiranog tla u otopini $MgCl_2$

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Mehanička svojstva cementiranog tla slabe kada je cementacija primjenjena u hidrotehnici za kontrolu propusnosti tla u korodirajućem okruženju s $MgCl_2$. Korozija uzrokuje ozbiljnu štetu kompozitu tla i cementa te dodatno smanjuje stabilnost cijele strukture. Stoga je potrebno podrobnije istražiti mehanizme kojima opadaju mehanička svojstva cementiranog tla pod utjecajem $MgCl_2$. Kako bi se simulirali i proučavali erozijski procesi, proveden je niz ispitivanja na blokovima cementiranog tla u otopinama $MgCl_2$ različitih koncentracija, uključujući fotografiranje, ispitivanje neograničene tlačne čvrstoće i mjerenja koncentracije Mg^{2+} i Cl^-. S povećanjem koncentracije raste stupanj korozije na površini uzoraka dok se posmična čvrstoća smanjuje. Kemijska analiza korozijskog okoliša pokazuje da novonastali spojevi kao što su $CaCl_2 \cdot 6\,H_2O$ i $Mg_2(OH)_3Cl \cdot 4\,H_2O$ imaju sedam puta obujam veći od $Ca(OH)_2$. Korozija cementiranog tla vrsta je kristalne korozije i $Mg(OH)_2$ reagira s $3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O$ te nastaje $MgO \cdot SiO_2 \cdot H_2O$. Istodobno je analizirana veza između početnih koncentracija iona Mg^{2+} i Cl^- i čvrstoće te nađene regresijske funkcije čvrstoće.

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