



Chromate Ion Transfer Through Mortar by Accelerated Migration Method

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ABSTRACT: Chromium (VI) is a highly toxic heavy metal which may be present in cementitious materials (CM) within its constituting elements or external sources and could alter the structure of CM and reduce its compressive strength. Therefore penetration of chromium is an important consideration in environmental engineering concrete structures. For estimating diffusivity of chromium (chromate ion) in cementitious materials, this paper presents an accelerated migration test method for determining the non-steady-state migration coefficient following the simplified Nernst-Planck equation. Likewise, the influence of water-to-cement ratio (w/c), the applied voltage the chromium binding capacity of cement mortar specimen (CMS) and the realistic concentration profile was investigated. For calculation of migration coefficient, the color reagent diphenylamine sulfonate was identified to determine the penetration depth of chromium into the CMS visually. The concentration of chromium was estimated to be about 0.025 percent (wt of CMS) at the discolored border region, and a drop of potential about 3.4 volts was derived. The changes in the microstructure of the CMS due to chromium migration testing were studied. The migration coefficient of CMS obtained between 1.06×10^{-12} m²/s to 3.25×10^{-12} m²/s. The w/c of about 0.50 has the highest migration coefficient. The realistic chromium concentration profile in the migration test has a gradual front, and a quadratic curve obeys.

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1- Introduction

Chromium is a highly toxic and hazardous heavy metal which may be entered in cementitious materials (CM) either as part of its constituent materials (e.g. aggregate, cement or water) during mixing or due to exposure to chromate-containing external sources during service. In addition to environmental hazards, chromium could alter the structure of CM and reduce its compressive strength. Therefore penetration of chromium in CM is an essential consideration in environmental engineering concrete structures.

Chromium classified as toxic heavy metal. It can take various chemical valences the most stable of which are chromium III, and chromium VI [1]. Chromium VI due to its high solubility and mobility in water is considered about 500 times more toxic than chromium III [2, 3]. It is supposed to be highly hazardous to human health and is thought to be carcinogenic. It, therefore recommended that its release to the environment should be closely monitored and restricted [4]. Chromium can convert between forms III and VI and vice versa under various environmental conditions. It is contained in wastewater and solid forms by various human activities

such as in metallurgical, chemical, refractory industries [5], the leather industry and metal plating processes [6]. Chromium can be present within the constituents of CM [7, 8] or through the use of industrial sludge and ashes in the CM (solidification and stabilization of chromium) [9]. Furthermore, chromium may be introduced as corrosion inhibitor admixture in the form of potassium chromate to protect the reinforcement in the concrete [10, 11].

In an alkaline environment with a pH higher than about 11 (e. g. CM), chromium VI compounds are in the form of highly soluble CrO_4^{2-} anion [12, 13]. While Cr (III) is known to substitute Al (III) in calcium aluminates hydrates, as well as in ettringite and monosulfate [14, 15], binding mechanism for the mobile chromate ion (CrO_4^{2-}) is more complicated. In the highly alkaline environment adsorption of this ion is low. Results from leaching experiments have shown that CrO_4^{2-} leaching concentrations are affected by ettringite and monosulfate [16-18].

Chromium VI is present in cement phases as aluminates compounds of Ca-Cr, $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{CrO}_4$, and in as $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_5$ [14]. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} + 26\text{H}_2\text{O}$) phase could also participate in the stabilization of chromium through replacement of CrO_4^{2-} with SO_4^{2-} [19, 20].

Chromium ions can penetrate the environmental concrete

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structures from external sources (such as industrial wastewater and mining slurry wastes, etc.). Significant chromium content in CM could alter its structure and reduce its compressive strength [21, 22]. Therefore existence and penetration of chromium in CM are essential in environmental engineering concrete structures for containment of hazardous materials (for conveying, storing, or treating of industrial wastewater, and for the secondary containment of hazardous liquids and concrete barriers used in mining and industrial waste disposal, etc.).

Also leaking from environmental concrete structures (sewage containing chromium), maybe occur by diffusion phenomenon. Other routes of the release of chromium into the environment are from de-chlorination procedures [23, 24] and cathodic protection systems in reinforced concrete, where, by applying voltage, in addition to migration of chloride ions, the chromate ions also migrate and pollute the environment.

Transport of chromium in CM is controlled by diffusion [8, 25]. Historically, leaching methods such as tank-testing have been used for environmental monitoring of chromium levels in monolithic materials, e.g., EA NEN7375, 2004 [26], EPA1315, 2013 [27]. Then, for modeling the contaminants release rate from monolithic materials, the observed-diffusion-coefficient (D_{obs}) could be derived. The above methods are based on leaching of ions from the monolithic samples and cannot be used for the penetration or ingress of ions, i.e., from external contaminants to the CM. Also these tests, which were expensive, time-consuming and involved chemical analysis of the leachate. To investigate the depth of chromium diffusion and leakages in environmental concrete structures, we need to obtain the diffusion coefficient. Standard diffusion into the CM is very low (several months or years) making such tests quite costly.

In this study, an accelerated and low-cost method of estimating the migration coefficient for chromate ion (CrO_4^{2-}) within the CM developed and tested. The method was adapted from the simplified Nernst-Planck equation (by inspiration of Rapid Chloride Migration test (NT BUILD 492, 1999) [28]. Others have applied the migration method for calculation of the sulfate [29] and chloride migration coefficient for modeling the life cycle of concrete structures [30-36]. Migration tests can be carried out under steady-state or transient (non-steady-state) conditions. The steady-state method is still quite a time consuming and requires chemical analysis of the anolyte ions.

In this study, for calculation of the migration coefficient (D_{MC}), using the non-steady-state method, the sample is placed between the catholyte and anolyte cells, and a DC voltage is applied. Then D_{MC} is calculated using the simplified Nernst-Planck equations. D_{MC} calculated at different applied voltages, and the effect of varying w/c ratio on the penetration of chromate ion in CMS was studied.

2- Theoretical Background

The process of migration in a non-steady-state condition described by a simplified form of the Nernst-Planck equation. Considering, therefore the one-dimensional penetration of ions under chemical and electrical potentials, and assuming that the flux of ions through the porous matrix (cement mortar) to be the sum of the two processes of diffusion and migration, the modified Fick's law can be written as [37, 38]:

$$J = -D(\partial c / \partial x - zFU / RTL c) \quad (1)$$

$$\partial c / \partial t = -\partial J / \partial x = D((\partial^2 c) / (\partial x^2) - zFU / RTL \cdot \partial c / \partial x) \quad (2)$$

For a semi-infinite boundary condition, the analytical solution is:

$$c = \frac{c_0}{2} \left[e^{\alpha x} \operatorname{erfc} \left(\frac{x + aDt}{2\sqrt{Dt}} \right) + \operatorname{erfc} \left(\frac{x - aDt}{2\sqrt{Dt}} \right) \right] \quad (3)$$

Where:

c: ion concentration (kgm^{-3})

D: diffusion coefficient (m^2s^{-1})

F: Faraday constant, 9.648×10^4 ($JV^{-1} mol^{-1}$)

J: Total flux of ions ($kgm^{-2} s$)

L: specimen thickness (m)

R: gas constant, 8.314 ($JK^{-1} mol^{-1}$)

T: solution temperature (K)

z: absolute value of ion valence; for chromate ion $z = 2$

x: distance from the surface exposed to the source solution of ions (m)

U: absolute value of potential difference (V)

c_0 : concentration of chromate in the bulk solution,

t: diffusion duration (s)

$a = zFU / RTL$;

erfc: is the complement to the error function (erf), $\operatorname{erfc} = (1 - \operatorname{erf})$.

Solving and simplifying Equation 3 gives D and it can then be used to arrive at the diffusion coefficient for the non-steady-state process, D_{MC} (see section 3.2.1) [31]:

$$D = D_{MC} = D_{app} = \frac{D_0}{1 + \frac{\partial C_b}{\partial c}} = \frac{D_{eff}}{\phi \left(1 + \frac{\partial C_b}{\partial c} \right)} = \text{constant} \quad (4)$$

Where D_{app} is the apparent diffusion coefficient, D_{eff} is the effective diffusion coefficient, ϕ is the porosity of the CMS, C_b is bound chromium content and $\partial C_b / \partial c$ is the ion binding capacity. It may be assumed that the binding capacity of $\partial C_b / \partial c$ in Equation 4 is constant. However, in this study, chromates' binding may be assumed to follow the linear isotherm such that $C_b = A.c$, where A is a binding constant in the instantaneous or quasi-equilibrium state. Chemical binding of chromates is a complex process. Although different phases of hydrated cement can bind at varying rates and through changing chemical or physical effects depending on the chromate concentration, a constant binding capacity [39] also assumed in this study.

Under the analytical solution in the Nernst-Planck equation (Equation 3), the concentration profiles have a sharp front moving through the specimen. Although this conventional method confirmed as the most suitable rapid migration test [37], many researchers have found the concentration profile predicted by it is different from the realistic one [36, 40-42]. The realistic profile may have linear [36], or non-linear gradual slope [43].

3- Materials and Methods

3- 1- Materials and Mixture Proportions

Cement mortar was used instead of concrete to achieve greater homogeneity within the CM to enable more precise measurement of the penetration depth; water to cement ratios (w/c) of 0.40, 0.45, 0.50, 0.55 and 0.60 were investigated and the sand to the cement ratio was retained at 2.75. The silica

sand used in the tests was in compliance with the ASTM C778 (2013) [44] standard and cement Type-I used throughout.

The polycarboxylate-based super-plasticizer used for CMS had w/c less than 0.50 and distilled water used for all mixes. The mixing method used was according to the ASTM C305 (2014) [45] standard. The casts were made in (polyethylene) cylindrical molds of about 56.5 mm diameter and 150 mm height. The CMS were placed in a humidity chamber for 24 hours to control the curing environment. The samples were then placed in the humidity chamber with >95% humidity and at 21 °C and cured for 90 days post casting. Potassium chromate (K₂CrO₄) salts were used to make the catholyte solution and potassium hydroxide (KOH) used for making the anolyte solution.

3- 2- Accelerated Migration Test (AMT)

For calculation of the D_{MC}, the samples placed between the catholyte and anolyte cells, and a DC voltage was applied. After a set time of about 24 hours, the samples split through the middle and by spray of a color indicator reagent on to the freshly split section, the surface color of the CMS changed. Then, the penetration depths of the ions were measured by spraying of a color indicator reagent. The value of D_{MC} then calculated. Three saturated CMS were used to complete a test. The thickness of individual samples was about 25mm. The samples placed in the AMT set-up; (Figure 1).

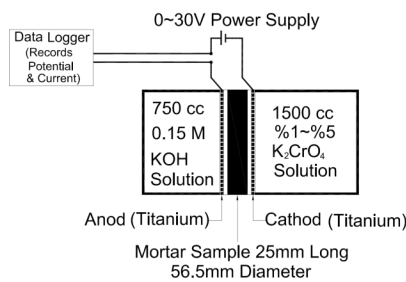


Figure 1. AMT test set-up

3- 2- 1- Calculation of Migration Coefficient in the non-steady state (D_{MC})

By solving and simplifying Equation 3, the D_{MC} of chromate ions calculated for the non-steady state using the Equation 5 [31]:

$$D_{MC} = RT/zFE \cdot x_{(d-\beta\sqrt{xd})}/t \quad (5)$$

Where:

$$E = (U - U_m)/L \quad (6)$$

U_m is drop of potential (V).

The laboratory constant β was calculated using Equation 7:

$$\beta = 2\sqrt{(RT/zFE)} \cdot \text{erf}^{-1} (1 - (2c_d)/c_0) \quad (7)$$

In this study, the following parameters determined:

The chromate penetration depth (x_d), the minimum free-chromium concentration at which the colorimetric indicator changes the color (c_d), and the correcting potential (or drop of potential) (U_m) were empirically determined.

3- 2- 2- Determination of Chromate Penetration Depth in the Mortar (x_d)

Once the sample testing time had lapsed, the CMS was split diametrically into two and then again for the half cylinder, the chromate ion penetration depth (x_d) was revealed by spraying sodium diphenylamine sulfonate and manually measured.

3- 2- 3- Determination of Chromium Concentration at the Penetration Depth (c_d)

After the laboratory tests completed, profiling grinding performed on the samples with thicknesses of about 1 mm for each grinding layer. The powder resulting from each grinding also collected in plastic bags and its chromate ion percentage was measured [46]. To determine the percentage of chromium in the powder yielded during profiling, one gram of dried powder of each layer added to 0.1 M sodium carbonate solution, and then boiled for 10 minutes. Filtration then performed, and the yielded solution was made up to 100 cc; the chromium concentration of each sample determined by using atomic absorption spectrometry. For each layer, the chromium percentage calculated and the variation of chromium percentage and the penetration depth plotted. The chromium percentage at the region of discoloration (c_d) was estimated as shown diagrammatically in Figure 3.

3- 2- 4- Estimated Correcting Potential or Drop of Potential (U_m)

Ohm's law was used to estimate the value of U_m by measuring the current at different applied voltages of 5, 10, 15 and 20 V across the samples and extrapolation to zero current. The potential drop was assumed to correspond to the potential required to overcome the summed resistances of the electrodes, the solution, and the sample.

3- 3- Bound Chromium Content

Approximately 2.5, 6.25 and 10 g of tested CMS (with various w/c of 0.40, 0.50 and 0.60) introduced into 50 ml of solution of various concentrations of Cr (VI) (80, 185 and 290 mg/L) made up of potassium chromate (K₂CrO₄) (Response Surface Method). These mixtures were placed in polyethylene bottles and agitated for 24 hours in a temperature maintained to within 20 °C and 25 °C. After this period, solution samples were filtered and acidified with HNO₃ for analyses (Cr) with an Atomic Absorption Spectrophotometer (AAS). The amount of bound chromium calculated according to Equation 8.

$$C_b = ((C_0 - C_1) * V) / m_0 \quad (8)$$

Where C_b was the bound chromium content (mg Cr/g mortar sample), C₀ and C₁ were initial and equilibrium chromium concentration (mg/L), V was the volume (L) of the chromium solution, and m₀ was the sample weight (g).

3- 4- Realistic Chromium Profiles

To obtain the realistic chloride profile curve, Huang and Yang [43] using regression analysis, fitted exponential model to the experimental data from the rapid chloride permeability test (RCPT)[43] :

$$C = C_s \cdot \exp(-ax^2) \quad (9)$$

Where C is the chloride content, x is the depth, C_{sa} is the chloride content at the surface (in $x = 0$), and a is the experimental constant. The profiles predicted by this model matched the realistic one. Equation 9 used to obtain realistic chromium profiles. However, a second-order equation for modeling the chromium profile used as follows:

$$c_x = ax^2 + bx + C_{sa} \quad (10)$$

Where a and b are experimental constants, C_{sa} is surface chromium percentage, c_x : The percentage of chromium that is obtained by profiling at a depth of x .

3- 5- Additional Tests

The following additional tests also carried out: (i) density and porosity measurements (ASTM C642 2013) [47]; (ii) measurement of the changes in the pH of the catholyte and anolyte (ASTM D1293-2012) [48]; (iii) Scanning Electron Microscope (SEM/EDS) evaluation of the CMS microstructure.

4- Results

4- 1- Accelerated Migration Test (AMT)

4- 1- 1- Determination of Chromate Penetration Depth in Mortar (x_d)

Sodium diphenylamine sulfonate was used as the color reagent to determine the x_d within the cement mortar. The reagent normally is colorless but turns green and violet in the presence of chromium III and chromium VI, respectively. The chromate ion penetration depth (x_d) revealed by spraying reagent and manually measured (Figure 2).

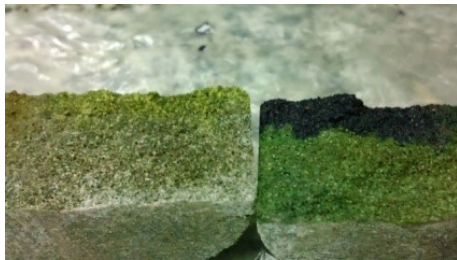


Figure 2. Color change on the CMS surface using sodium diphenylamine sulfonate indicator reagent for measurement of x_d

4- 1- 2- Determination of c_d

Figure 3 shows the results of the variation of chromium content in the different layers of specimens after migration test. Measurement indicated that the initial chromium content in CMS is negligible compared to the migrated chromium and can ignore. The penetration depth (x_d) of chromium was found to be about 5.5 mm for all samples.

c_d value of about 0.02 – 0.03 wt. Percent of CM obtained for these samples. Table 1 shows the derived D_{MC} values using the Nernst-Planck equation. Reduction of only 1% in the D_{MC} resulted for samples with a w/c ratio of 0.50 and 0.55 and when c_d increased from 0.02 to 0.03, showing the insensitivity of D_{MC} values to change in c_d ; the concentration of chromium at the region of discoloration was therefore assumed to be constant at 0.025 percent.

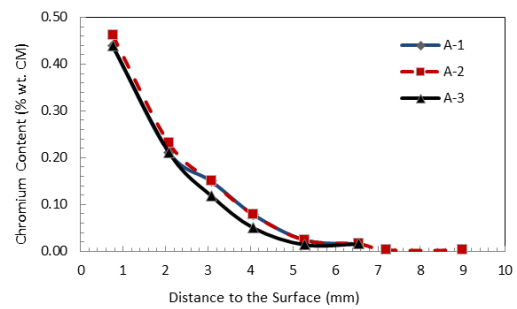


Figure 3. Chromium content profiles in CMS after migration test (three similar samples A-1, A-2 and A-3 tested); the applied potential was 20V and w/c of 0.50

4- 1- 3- Estimation of Correcting Potential (U_m)

Figure 4 shows the variation of the current with applied voltage. From which the correcting potential was found to be about 3.4 V. The correcting potential for the NT Build 492 (1999) [28] standard using the same method, was estimated to be about 2.1 V which is close to the recommended value of this standard (2V).

Table 1. The effect of varying the amount of c_d in the amount of D_{MC}

w/c	x_d (mm)	$D_{MC} (m^2s^{-1}) \times 10^{-12}$	
		$c_d = 0.02$ (wt. of CM)	$c_d = 0.03$ (wt. of CM)
0.50	13.0	2.78	2.82
0.50	14.0	3.04	3.08
0.55	14.5	3.15	3.19
0.55	15.5	3.36	3.41

4- 1- 4- Calculation of the Migration Coefficient (D_{MC}) of Chromate Ion

The effects of the testing time, w/c, concentrations of chromium in catholyte and applied voltage on the penetration depth and D_{MC} investigated... Figure 5 shows the effect of the testing time on the penetration depth and D_{MC} . By Increasing the testing time from 12 hours to 24 hours and up to 36 hours, the average penetration depth increased by about 18.3% and 25.5%, respectively and the D_{MC} decreased by about 8% and 17%, respectively.

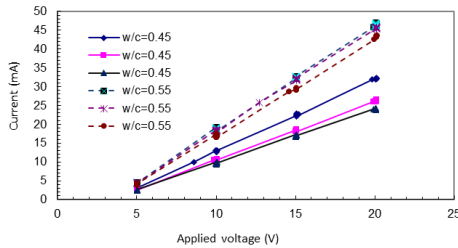


Figure 4. Variation of the current passing through the CMS under applied voltages (5, 10, 15, 20V)

Table 2 shows the effect of the changing w/c ratio, the applied voltage and the catholyte concentration on the D_{MC} . It found that the D_{MC} of chromium increased, with increasing w/c ratio from 0.40 to 0.50 regardless of the concentration of chromium in the catholyte or the applied voltage. This finding attributed to increased porosity and the increased permeability of the CMS. Increasing the w/c ratio from 0.50 to 0.60 caused a decrease in the D_{MC} of chromium which could be due to the increased solubility of other ions such as calcium ions and their reaction with chromate ions [49]. Although increasing w/c from 0.50 to 0.55 did not affect the D_{MC} significantly.

At the higher w/c ratio (0.60), the level of porosity and therefore the internal contact surface were greater and could cause higher adsorption and reaction of ions on the interior surfaces of the CMS.

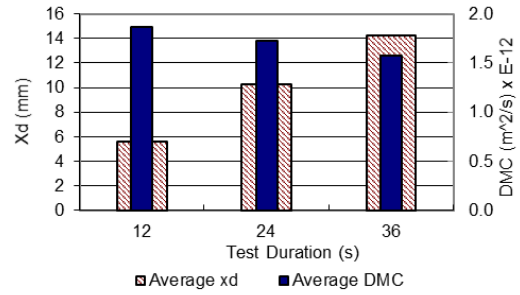


Figure 5. Effect of the testing time on the penetration depth (x_d) and DMC; (w/c of 0.45, catholyte 1% K_2CrO_4 and applied voltage of 25 V)

Chen and Wu, (2013) [50] have investigated the effect of a change in the w/c ratio on the CMS pores volume with different diameters. They have shown that increasing the w/c ratio from 0.40 to 0.50 and 0.60 lead to an increased volume of pores with the diameters of less than 0.1 microns. For higher w/c ratios, the volume of pores with diameters smaller than 0.01 microns increases and probability of their blocking (clogging) during the migration test is more elevated. It is probable that the decrease in the D_{MC} of chromium at the higher w/c ratios is due to the capillary pores blocking by reaction and precipitation of ions, especially by chromate ions. Measurement of bounded chromium content on CMS and Scanning electron microscopy (SEM/EDS) was carried out to investigate these effects, see sections 4.2 and 4-4-3.

Table 2 also indicates that increasing the voltage from 15 to 20 V did not cause a significant change in the D_{MC} of chromate ion at 0.45 and 0.50 w/c ratios (about 7% and 6% decrease, respectively) and a chromium concentration of 5%. Moreover, Table 2 indicates that the D_{MC} decreased by reducing the concentration of chromium from 5% to 1%; the w/c ratios were 0.45 and 0.55 (about 10% and 16% decrease, respectively).

Table 2. The effect of w/c, applied voltage and catholyte concentration on the D_{MC}

sample No.	w/c	CO(% K_2CrO_4)	U (v)	Average $D_{MC} \times 10^{-12}$ (m^2/s)
1	0.40	5	15	1.14 ± 0.08
2	0.40	5	20	1.06 ± 0.06
3	0.45	1	20	1.56 ± 0.14
4	0.45	5	20	1.74 ± 0.18
5	0.50	5	15	3.25 ± 0.38
6	0.50	5	20	3.05 ± 0.13
7	0.55	5	20	3.18 ± 0.17
8	0.55	1	20	2.68 ± 0.22
9	0.60	5	15	1.54 ± 0.09

The migration coefficient of CMS obtained for chromate ion in this study is between $1.06 \times 10^{-12} \text{ m}^2/\text{s}$ and $3.25 \times 10^{-12} \text{ m}^2/\text{s}$. Because for the first time this method was used to calculate the chromate ion migration coefficient, did not find any reference for comparison of results. Other researchers determined the migration coefficient for chloride and sulfate ions. The migration coefficient of chloride determined by Spiesz and Brouwers [30] is between 3.84×10^{-12} and $16.45 \times 10^{-12} \text{ m}^2/\text{s}$. Also, the migration coefficient of sulfate determined by Karkar [51] is between 0.06×10^{-12} and $0.69 \times 10^{-12} \text{ m}^2/\text{s}$ and the migration coefficient of chloride is between 2.70×10^{-12} - $21.4 \times 10^{-12} \text{ m}^2/\text{s}$ in the various cementitious materials.

4- 2- Bounded Chromium Content

Figure 6 presents the experimental results of bounded chromium content on CMS. Figure 6 shows that by comparing samples with a w/c of 0.40 to 0.60, at low chromium concentrations, a sample with a w/c of 0.50 has the least bounded chromium content.

This finding suggests that one of the reasons for changes in chromate migration coefficient with the change in the w/c is the difference in chromium adsorption capacity in these specimens. The migration coefficient decrease could be a result of reduction in porosity in the w/c less than 0.5 and the presence of super-plasticizer (adsorption of chromium ions on organic materials) in CMS. In the CMS with w/c greater than 0.5, increased internal porosity can increase the bounded chromium content and therefore decrease the migration coefficient in these types of samples.

4- 3- Chromium Profile Obtained After AMT

The amount of chromium in various mortar samples was measured up to a depth of x_d by profiling. The tests results showed that the amount of chromium in the surface layer of the samples differs from the concentration of chromium in the solution of catholyte. The results also showed that the chromium profile in the samples decreases with a gradual slope. This point indicates that the realistic profile is different from the profile obtained by the Nernst-Planck method.

To obtain the realistic profile curve, the experimental data are fitted using linear and non-linear exponential regression analysis, as described by some researchers [36, 43] and derived semi-empirical models. In this study, both methods for matching these models with the realistic chromium profiles have investigated. The linear model did not match the realistic profile; however, the non-linear exponential regression did. Figure 7 shows that the determination coefficients (adj. R-square) are almost between 0.95 and 0.98 judging from this, the exponential semi-empirical model has a reasonably good match with the realistic profile.

Figure 8 shows the chromium profiles modeling with the second-order polynomial equations. Figure 8 indicates that the determination coefficients (adj. R-square) are almost higher than 0.97. Judging from this, the use of a second-order equation shows a good fit with the realistic profile. The test results obey a quadratic curve.

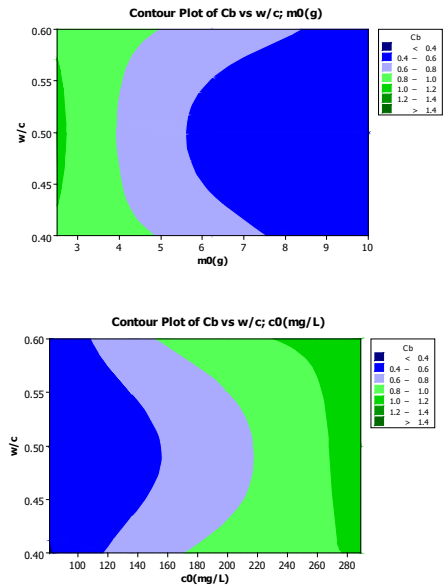


Figure 6. Contour plot of the bounded chromium content (C_b); a) effect of w/c and m_0 b) effect of w/c and C_0

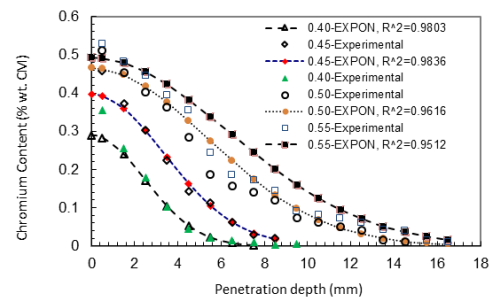


Figure 7. The chromium profiles in the CM after AMT –Fitting with the exponential semi-empirical model

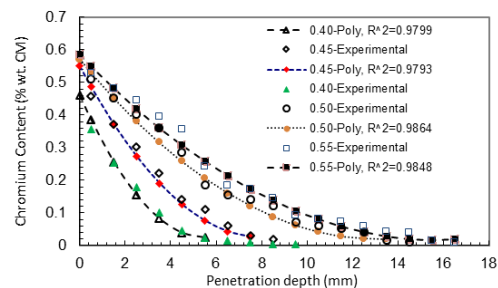


Figure 8. The chromium profiles in the CM after AMT – Fitting with the second-order polynomial equations.

4- 4- Further Tests

4- 4- 1- Porosity and Density Variations

Table 3 indicates that the porosity and density under SSD conditions increased as the w/c ratio increased. However, the dry density did not follow the same trend.

Table 3. Density and porosity variations at CMS with different w/c ratios

Sample No.	w/c	Porosity ϕ	Dry Density (gcm^{-3})	SSD Density (gcm^{-3})
1	0.40	0.166	1.886	2.051
2	0.50	0.258	1.914	2172
3	0.60	0.290	1.848	2138

4- 4- 2- Changes in the pH of the Catholyte and the Anolyte

Investigation of several CMSs indicated that the pH of the anolyte changed over the migration testing period. Ion movement towards the oppositely charged electrodes causes polarization in the catholyte and the anolyte and may cause pH changes. The pH of the anolyte remained almost constant during the migration test. This point meant that collection of OH^- ions at the anode balanced with the release of ions from the samples into the anolyte. The pH of the catholyte increased from about 10 to about 12 over the test duration. The OH^- concentration showed an increase by a factor of

higher than two over the 24 hour period. This result indicates that, at the end of the test, a larger fraction of the current was carried by the OH^- ions than by the CrO_4^{2-} ions, compared to the initial conditions when the concentration of OH^- was very low. These results were consistent with the reported outcomes from chloride ion migration studies [31].

4- 4- 3- Scanning Electron Microscope (SEM) Results

After migration tests, a mortar sample split into halves, and SEM analysis was carried out in the region close to the cathode. It was not possible to prepare thinner sections, due to restructuring and the weakness of the sample affected by penetration of chromate ion.

Figure 9 shows the SEM images and the EDS results. Outcomes showed high accumulation of calcium crystals in the regions near to the cathode; aluminum, silicon, iron, and chromium also detected. The calcium ion migration towards the cathode and their reactions with chromate (and other) ions would have led to the precipitation of calcium compounds in the sample near the catholyte. This point could then have led to a reduction in the conductive pore solution and a decrease of CMS permeability in this region.

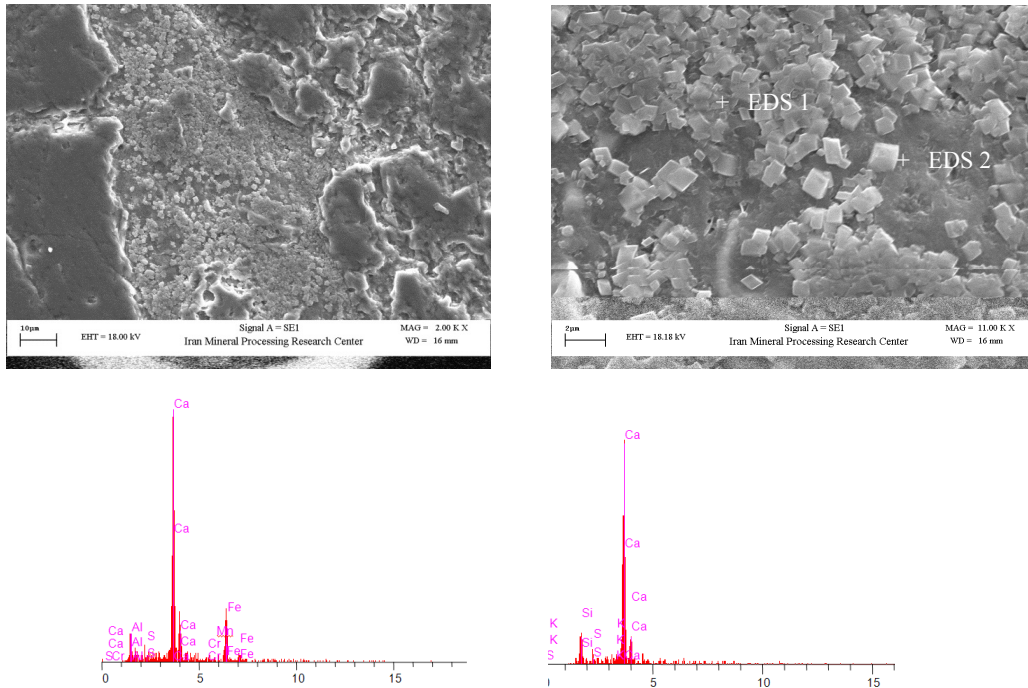


Figure 9. SEM/EDS image of the sample CMS near the cathode (cell containing chromium)

5- Conclusions

A simple method of deriving the D_{MC} of chromate ion has been presented using the simplified Nernst-Planck equation.

1. For the calculation of D_{MC} of chromate ion, the color reagent diphenylamine sulfonate was identified and successfully used to visualize and to determine the penetration depth of chromium in the cement mortar.
2. The c_d and U_m were estimated about 0.025 percent (wt. of CMS) and 3.4 V for use in calculation of D_{MC} .
3. Increasing the applied voltage from 15 V to 20 V caused a little effect on the D_{MC} .

4. With increasing w/c from 0.40 to 0.50, D_{MC} increased, but by further increasing w/c up to 0.60, the D_{MC} decreased.
5. The migration coefficient of chromate ion in CMS was between $1.06 \times 10^{-12} \text{ m}^2/\text{s}$ to $3.25 \times 10^{-12} \text{ m}^2/\text{s}$, and the w/c of 0.50 have the highest D_{MC} .
6. Ignoring the surface concentration, the realistic chromium concentration profile in the migration test has a gradual front, and a quadratic curve obeys.
7. SEM and EDS analyses of the CMS microstructure showed that the calcium ions (as well as some other

positive ions) migrated towards the cathode within the CMS and precipitated in regular crystals forms.

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References

- [1] T. Becquer, C. Quantin, M. Sicot, J.P. Boudot, Chromium availability in ultramafic soils from New Caledonia, *Science of The Total Environment*, 301(1) (2003) 251-261.
- [2] R. Saha, R. Nandi, B. Saha, Sources and toxicity of hexavalent chromium, *Journal of Coordination Chemistry*, 64(10) (2011) 1782-1806.
- [3] A. Husnain, I.A. Qazi, W. Khaliq, M. Arshad, Immobilization in cement mortar of chromium removed from water using titania nanoparticles, *Journal of Environmental Management*, 172 (2016) 10-17.
- [4] J. Guertin, C.P. Avakian, J.A. Jacobs, Independent Environmental Technical Evaluation Group, (IETEG), *Chromium(VI) Handbook*, CRC Press, 2004.
- [5] A.D. Dayan, A.J. Paine, Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000, *Human & experimental toxicology*, 20(9) (2001) 439-451.
- [6] P. Sharma, V. Bihari, S.K. Agarwal, C.N. Kesavachandran, B.S. Pangtey, N. Mathur, K.P. Singh, M. Srivastava, S.K. Goe, Groundwater contaminated with hexavalent chromium (Cr (VI): a health survey and clinical examination of community inhabitants (Kanpur, India), *PLOS ONE* 7(10) (2012) 3-9.
- [7] L.M. Hills, V.C. Johansen, Hexavalent Chromium in Cement Manufacturing: Literature Review, in, *Portland Cement Association, USA, 2007*, pp. 1-16.
- [8] H.A. van der Sloot, Comparison of the characteristic leaching behavior of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behavior in construction products during service life and recycling, *Cement and Concrete Research*, 30(7) (2000) 1079-1096.
- [9] P.H. Shih, J.E. Chang, H.C. Lu, L.C. Chiang, Reuse of heavy metal-containing sludges in cement production, *Cement and Concrete Research*, 35(11) (2005) 2110-2115.
- [10] J.O. Okeniyi, O.A. Omotosho, O.O. Ajayi, C.A. Loto, Effect of potassium-chromate and sodium-nitrite on concrete steel-rebar degradation in sulphate and saline media, *Construction and Building Materials*, 50 (2014) 448-456.
- [11] R. Roskovic, I. Stipanovic Oslakovic, J. Radic, M. Serdar, Effects of chromium(VI) reducing agents in cement on corrosion of reinforcing steel, *Cement and Concrete Composites*, 33(10) (2011) 1020-1025.
- [12] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environmental Pollution*, 107(3) (2000) 263-283.
- [13] D. Stephan, H. Maleki, D. Knöfel, B. Eber, R. Härdtl, Influence of Cr, Ni, and Zn on the properties of pure clinker phases: Part II. C3A and C4AF, *Cement and Concrete Research*, 29(5) (1999) 651-657.
- [14] N.D.M. Evans, Binding mechanisms of radionuclides to cement, *Cement and Concrete Research*, 38(4) (2008) 543-553.
- [15] A. Kindness, A. Macias, F.P. Glasser, Immobilization of chromium in cement matrices, *Waste Management*, 14(1) (1994) 3-11.
- [16] H.A. van der Sloot, Characterization of the leaching behaviour of concrete mortars and of cement-stabilized wastes with different waste loading for long term environmental assessment, *Waste Management*, 22(2) (2002) 181-186.
- [17] M. Zhang, Incorporation of oxyanionic B, Cr, Mo and Se into hydrocalumite and ettringite: application to cementitious systems, 2000.
- [18] J.Y. Park, W.H. Kang, I. Hwang, Hexavalent Chromium Uptake and Release in Cement Pastes, *Environmental Engineering Science*, 23(1) (2005) 133-140.
- [19] A. Macias, A. Kindness, F.P. Glasser, Impact of carbon dioxide on the immobilization potential of cemented wastes: Chromium, *Cement and Concrete Research*, 27(2) (1997) 215-225.
- [20] A. Vollpracht, W. Bramshuber, Binding and leaching of trace elements in Portland cement pastes, *Cement and Concrete Research*, 79 (2016) 76-92.
- [21] S. Wang, C. Vipulanandan, Solidification/stabilization of Cr(VI) with cement: Leachability and XRD analyses, *Cement and Concrete Research*, 30(3) (2000) 385-389.
- [22] S. Sinyoung, P. Songsiriritthigul, S. Asavapisit, P. Kajitvichyanukul, Chromium behavior during cement-production processes: A clinkerization, hydration, and leaching study, *Journal of Hazardous Materials*, 191(1) (2011) 296-305.
- [23] Q.f. Liu, J. Xia, D. Easterbrook, J. Yang, L.-y. Li, Three-phase modelling of electrochemical chloride removal from corroded steel-reinforced concrete, *Construction and Building Materials*, 70 (2014) 410-427.
- [24] J.H. Zhu, L. Wei, Z. Wang, C.K. Liang, Y. Fang, F. Xing, Application of carbon-fiber-reinforced polymer anode in electrochemical chloride extraction of steel-reinforced concrete, *Construction and Building Materials*, 120 (2016) 275-283.
- [25] H. Lu, F. Wei, J. Tang, J.P. Giesy, Leaching of metals from cement under simulated environmental conditions, *Journal of Environmental Management*, 169 (2016) 319-327.
- [26] EA NEN 7375 Determination of Leaching of Inorganic Components with the Diffusion Test -the Tank Test, in, *Netherlands Normalisation Institute Standard*, , Netherland, 2004.
- [27] E.P. Agency, EPA 1315 Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using A Semi-Dynamic Tank Leaching Procedure, in, *EPA, USA, 2013*.
- [28] Nordtest, Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-

- steady-state migration experiments (NT BUILD 492), in, NORDTEST, FINLAND, 1999.
- [29] S. Lorente, M.-P. Yssorche-Cubaynes, J. Auger, Sulfate transfer through concrete: Migration and diffusion results, *Cement and Concrete Composites*, 33(7) (2011) 735-741.
- [30] P. Spiesz, H.J.H. Brouwers, Influence of the applied voltage on the Rapid Chloride Migration (RCM) test, *Cement and Concrete Research*, 42(8) (2012) 1072-1082.
- [31] P. Spiesz, H.J.H. Brouwers, The apparent and effective chloride migration coefficients obtained in migration tests, *Cement and Concrete Research*, 48 (2013) 116-127.
- [32] V. Elfmarkova, P. Spiesz, H.J.H. Brouwers, Determination of the chloride diffusion coefficient in blended cement mortars, *Cement and Concrete Research*, 78 (2015) 190-199.
- [33] M. Aguayo, P. Yang, K. Vance, G. Sant, N. Neithalath, Electrically driven chloride ion transport in blended binder concretes: Insights from experiments and numerical simulations, *Cement and Concrete Research*, 66 (2014) 1-10.
- [34] R.A. Patel, Q.T. Phung, S.C. Seetharam, J. Perko, D. Jacques, N. Maes, G. De Schutter, G. Ye, K. Van Breugel, Diffusivity of saturated ordinary Portland cement-based materials: A critical review of experimental and analytical modelling approaches, *Cement and Concrete Research*, 90 (2016) 52-72.
- [35] B. Šavija, M. Luković, E. Schlangen, Modeling the rapid chloride migration test for concrete using the lattice model and characteristic Galerkin approach, in: N. Bicanic, H. Mang, G. Meschke, R.d. Borst (Eds.) *Computational Modelling of Concrete Structures*, Taylor & Francis Group, London, 2014.
- [36] L. Jiang, Z. Song, H. Yang, Q. Pu, Q. Zhu, Modeling the chloride concentration profile in migration test based on general Poisson Nernst Planck equations and pore structure hypothesis, *Construction and Building Materials*, 40 (2013) 596-603.
- [37] L. Tang, Electrically accelerated methods for determining chloride diffusivity in concrete—current development, *Magazine of Concrete Research*, 48(176) (1996) 173-179.
- [38] L. Tang, L.O. Nilsson, Rapid Determination of the Chloride Diffusivity in Concrete by Applying an Electrical Field, *ACI Materials Journal*, 89(1) (1992) 49-53.
- [39] G. Laforest, J. Duchesne, Immobilization of chromium (VI) evaluated by binding isotherms for ground granulated blast furnace slag and ordinary Portland cement, *Cement and Concrete Research*, 35(12) (2005) 2322-2332.
- [40] K. Stanish, R.D. Hooton, M.D.A. Thomas, A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 1. Theoretical description, *Cement and Concrete Research*, 34(1) (2004) 43-49.
- [41] E. Samson, J. Marchand, K.A. Snyder, Calculation of ionic diffusion coefficients on the basis of migration test results, *Materials and Structures*, 36(3) (2003) 156-165.
- [42] K. Krabbenhøft, J. Krabbenhøft, Application of the Poisson–Nernst–Planck equations to the migration test, *Cement and Concrete Research*, 38(1) (2008) 77-88.
- [43] K.-S. Huang, C.-C. Yang, Using RCPT determine the migration coefficient to assess the durability of concrete, *Construction and Building Materials*, 167 (2018) 822-830.
- [44] ASTM C778-13, Standard Specification for Standard Sand, in, ASTM International, West Conshohocken, 2013.
- [45] ASTM C305-14, Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency, in, ASTM International, West Conshohocken, 2014.
- [46] S.S. Potgieter, N. Panichev, J.H. Potgieter, S. Panicheva, Determination of hexavalent chromium in South African cements and cement-related materials with electrothermal atomic absorption spectrometry, *Cement and Concrete Research*, 33(10) (2003) 1589-1593.
- [47] ASTM C642-13, Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, in, ASTM International, West Conshohocken, 2013.
- [48] ASTM D1293-12, Standard Test Methods for pH of Water, in, ASTM International, West Conshohocken, 2012.
- [49] H.A. van der Sloot, Waste Materials In Construction, Putting Theory into Practice, in: J.J.J.M. Goumans, G.J. Senden, H.A. Van der Sloot (Eds.) *International Conference on the Environmental and Technical Implications of Construction with Alternative Materials*, Elsevier, The Netherlands, 1997, pp. 257.
- [50] X. Chen, S. Wu, Influence of water-to-cement ratio and curing period on pore structure of cement mortar, *Construction and Building Materials*, 38 (2013) 804-812.
- [51] E. Karkar, Developing and Evaluating Rapid Test Methods for Measuring the Sulphate Penetration Resistance of Concrete in Relation to Chloride Penetration Resistance, University of Toronto, Toronto, 2011.

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