Quantitative Measurement of the Influence of Degree of Saturation on Ion Penetration in Cement Paste by Using X-ray Imaging

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Abstract

The external penetration of ions into concrete plays an important role in long-term durability of concrete structures. In addition, the degree of saturation (DoS) of the paste has a large impact on rate and mechanisms of fluid penetration into concrete. There is little knowledge of the dynamic process of fluid penetration into these materials because few experimental techniques are able to give quantitative spatial measurements of the fluid movement without damaging the sample. This paper uses laboratory transmission X-ray microscopy (TXM) to investigate the in-situ penetration of an iodide based tracer into cement paste with water-to-cement ratio of 0.40 conditioned at four different relative humidities (RH). This technique can non-destructively image the distribution of the dissolved ions at 8.8 μm resolution in minutes. In addition, micro X-ray fluorescence (μXRF) imaging and conventional gravimetric measurements were used to compare I and Cl penetration rate and validate the results from TXM. Mathematical models have been proposed to account for ion penetration in partially-saturated samples. The results show that samples that were ponded for two days after being conditioned in 35% and 70% RHs (DoS of 40.8% ($\pm 0.1\%$) and 68.8% ($\pm 0.5\%$) respectively) show a 40x and 10x increase respectively in the penetration coefficient over the saturated sample. Furthermore, important insights about combined ion transport mechanisms have been observed from concentration profiles by TXM.

Keywords: X-ray microscopy; Iodide; Chloride; Diffusion; Capillary absorption; Service life; Durability; Corrosion.

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1. Introduction

Concrete structures face many threats to their service life. A number of durability problems are caused by external fluids penetrating into cement-based materials [1-4]. These fluids can contain potentially harmful ionic species, can lead to damage from corrosion, sulfate attack, alkali silica reaction, bulk freeze thaw, and salt scaling [5-6]. Therefore, the ion transport properties of cement-based materials play an important role in the durability performance of concrete structures [7-8].

Concrete that is partially saturated has a more rapid and more complicated method of ion transport [9-13]. For concrete with very low relative humidity (RH) or low degree of saturation (DoS), many pores are empty and these empty pores will draw in outside fluid from capillary action when wetted. However, more work is needed to understand how materials conditioned at different RH or different DoS impact this process.

The most widely used method to investigate fluid ingress into partially-saturated samples is through gravimetric measurements according to ASTM C 1585 and CEN EN 1925. This test method determines the one-dimensional rate of fluid penetration in cement-based materials by measuring the increase in the weight of a specimen as a function of time. However, this method only measures the total cumulative fluid uptake into the material and does not provide information about the spatial distribution of the fluid in the specimen [12,14-15]. This test makes assumptions about the geometry of the concrete pore network to estimate a depth of penetration [9-10,14]. Furthermore, this method does not account for the porosity, initial DoS of the sample, and the effect of the fluid viscosity and surface tension on penetration [11].

Recently, neutron and X-ray imaging techniques have been used to visualize fluid penetration in cement-based materials [8,12,14-17]. Both of these methods are based on the same

principle of radiation attenuation when passing through matter. However, X-rays interact with the electron shell of the atom while neutrons interact with the nucleus. One drawback of neutron imaging is that it requires a high energy source that is typically only available at synchrotron beamlines. This reduces the availability of the method. Neutron imaging is also sensitive to hydrogen atoms and is not able to measure specific ions. This may or may not be important depending on the information needed.

Transmission X-ray microscopy (TXM) has been used to learn more about moisture movement in cement-based materials [7-8, 12,16,18-19]. Previous studies using this method have tried to image water penetration into the paste and mortar samples [8,12,19]. Unfortunately, X-rays have a weak interaction with light atoms such as hydrogen. This limits the detection sensitivity of water in the method [8,20]. Furthermore, experiments that use TXM to investigate water ingress cannot provide spatial information about the ions and these publications have not been validated by other experimental techniques.

In this work, the moisture penetration is imaged with the aid of using potassium iodide (KI) as a tracer. Iodine is strongly X-ray attenuating because of its high atomic number. Furthermore, iodide and chloride ions are similar in size (iodide radius is 206 pm versus a chloride radius of 167 pm). This property makes iodide an excellent tracer for fluid transport study in concrete [21-24]. As the tracer penetrates into the cement paste it is possible to see the corresponding changes in X-ray absorption or gray value of the material in the radiograph. These images can be captured in less than a minute. This allows time resolved images to be taken and a rate of ion penetration can be calculated. Since this technique is non-destructive, the same sample can be monitored over time or in different conditions. The method requires minimal

sample preparation and the technique can image at a spatial resolution of 200 nm to 20 μm with laboratory equipment.

This work aims to use TXM to investigate in-situ iodide penetration in paste samples with water-to-cement ratio (w/c) of 0.40. These samples were conditioned in four different RHs to examine the effect of DoS on the ion penetration progress. The penetration of Cl and I in paste samples was also determined gravimetrically and with micro X-ray fluorescence (μXRF) at these same conditions and then compared with the TXM results. μXRF provides individual compositional maps which can be combined into a single map that simultaneously provides unique compositions and location [25-29]. Furthermore, μXRF imaging was used to compare I and Cl penetration concentration profiles in paste samples.

2. Experimental Methods

2.1 Mixture Proportion and Sample Preparation

The cement is an ASTM C 150, Type I. The chemical composition of cement with bulk XRF is provided in **Table 1**. The paste mixture had a w/c of 0.40 and the mixture proportion is given in **Table 2**. Cylindrical micro vials with inside dimension of 9.5 $\times$ 46 mm were used to cast the samples. A lid was used to seal each vial. The vials were partially filled up to 30 $\pm$ 1 mm. Twelve samples were made for each RH condition (three samples to measure KI penetration with TXM, six samples for gravimetric measurement of KI and NaCl penetration, and three samples for measuring porosity and DoS). All samples were cured for 35 d in a sealed condition at 23°C to remove the impacts of early hydration on the measurements. Based on previous publications by other researchers these samples would be expected to have a 70% degree of hydration [30-31].

Table 1. Chemical composition of cement with bulk XRF

Oxide content (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	L.O.I
Type I	20.40	5.03	2.95	62.89	2.08	0.35	0.35	0.28	3.05	2.09

Table 2. Cement paste mixture proportion

Mixture	water (g)	cement (g)	w/c
P-40	340	850	0.40

After 35 d curing, the samples were demolded and conditioned at four different RHs ($\approx$ 0%, 35%, 70%, and 100%). The 35% and 70% RH samples were stored in sealed containers above saturated MgCl₂ and KI salt solutions at 23 °C according to ASTM E 104 to reach mass equilibrium, respectively. An RH sensor was used for each container to monitor and verify the RH. The samples were placed in the container and their mass was measured daily until there was less than 0.03% change in mass loss over a 24 h period. It was then assumed that the moisture in the pore networks had sufficiently equilibrated with the environment. The 35% and 70% RH samples reached mass equilibrium after 50 d and 30 d, respectively.

The 100% RH samples were submerged in tap water inside a sealed container. The tap water was first boiled and allowed to cool to ambient temperature according to ASTM C 1202. These samples were then measured every 24 h until there was less than 0.03% mass change. This was reached after 5 d. The $\approx$ 0% RH samples were stored in a sealed container above saturated MgCl₂ solution (35% RH) at 23 °C for 40 d and then dried in an oven at 50 °C for 7 d until there was no measurable change in mass. For these samples they were assumed to be at approximately 0% RH and consequently a DoS of 0%. Because there may still be some moisture in the pores these samples are labeled as RH $\approx$ 0% and DoS $\approx$ 0%.

Since the 35% RH samples required 50 d to reach mass equilibrium, all samples were kept in a sealed container at 23 °C until 50 d in order to test all samples at the same age. The mass of the samples was monitored during the storage before testing and the mass change was found to be negligible.

2.2 Determining DoS

The samples for porosity and DoS were left in their respective environments and the 100% RH sample was kept in a sealed container within an environmental chamber at 97 ± 1 % RH at 23 °C until they were tested. The porosity and DoS of the samples were determined according to ASTM C 642. Three samples from each RH condition were submerged in water and weighed after achieving mass equilibrium. Next, the weight of the saturated samples immersed in water was measured and then the samples were dried in an oven at 50 °C and weighed again. In all measurements, it was assumed that the sample had reached mass equilibrium when the mass change was less than 0.03% during a 24 h period. The porosity and DoS for each sample at different RH is summarized in **Table 3**.

Table 3. Porosity and DoS of paste samples at different RH

RH	Porosity (%)	DoS (%)	D_i (%) [*]
$\approx 0\%$	39.8 ± 0.6	0 ^{**}	0
35%	42.8 ± 0.6	40.8 ± 0.1	17.5 ± 0.3
70%	40.2 ± 0.1	68.8 ± 0.5	27.7 ± 0.4
100%	38.5 ± 0.2	100	38.5 ± 0.2

^{*} D_i is the initial DoS of the sample in volume fraction.

^{**} It has been assumed that an approximate DoS of 0% achieved in this condition.

2.3 In-Situ Ion Penetration Using TXM

The samples that were investigated for ion ingress were sealed with wax on all sides but the finished surface 50 d after curing. After sealing, the samples were placed inside a cylindrical

plastic vial with a 25 mm diameter and 65 mm height. A hole with diameter of 10 mm was drilled in the lid of the vial to hold the sample. Next, water resistant epoxy was used to align the sample vertically and to seal the area between the sample and hole. A small piece of aluminum wire of 0.6 mm diameter was attached to the side of the vial to help align the images. The setup is shown in **Fig. 1**.

Fig. 1. Schematic diagram of the penetration test setup to measure penetration (a) and for scanning (b).

Next, the surface of the sample was ponded with 0.6 mol/L KI up to a level of 3 ± 1 mm for 14 d. This KI concentration was selected based on preliminary experiments to attain suitable contrast between the KI solution and the paste. As shown in **Fig. 1a**, the samples were stored where the fluid penetration and gravity effects are in the same direction. This simulates fluid penetration in flat surfaces such as bridge decks, an important application for the findings of this work. The KI solution level above the surface of samples was kept constant for all paste samples (3 ± 1 mm). The KI solution was refreshed every 5 d to maintain a constant KI concentration. Samples were stored inside a sealed container at 23°C during the penetration testing.

A laboratory Skyscan 1172 μ CT was used to conduct the experiments. A radiograph was taken from the paste samples before ponding with KI solution. This was used as a reference radiograph. Radiographs were also taken over time to track the fluid penetration into the sample. The time intervals for taking radiographs were selected according to ASTM C 1585 recommendations for gravimetric measurements. This allowed a comparison to be made between the moisture penetration into the sample and the mass change. The vial was inverted to stop the fluid penetration during the imaging as shown in **Fig. 1b**. Each radiograph took less than 1 min and so this should not disturb the test. Radiographs were also taken with no samples on the stage to be used to subtract the background attenuation. This also helped correct for variations in X-ray transmission between images. The radiograph used a pixel size of 8.8 μ m (2096 $\times$ 2096 pixels) and tube voltage and current of 100 KeV and 100 μ A. A 0.5 mm Al and 0.5 mm Cu filter was used to absorb lower energy X-rays and allow high energy X-rays to interact with the sample. Acquisition time of 8 s per frame was used to collect each radiograph. **Table 4** summarizes the TXM settings.

2.4 Cl and I Penetration Test Using the Gravimetric Method

The same experimental setup as TXM was used to gravimetrically measure ion penetration in paste samples, but instead of radiographs, the mass of the sample was measured. The paste samples were ponded with either 0.6 mol/L KI or 0.6 mol/L NaCl solutions for 14 d to compare I and Cl ion penetration. Three samples were tested for each salt solution. The sample was taken out of the vial for the weight measurement and excess solution at the surface and sides of the sample was removed with a damp paper towel before weighing. An empty vial was used on the scale to place the sample and avoid the contact between wet surface of the sample and scale pan. The sample was immediately returned back to solution after measurement. A scale

with 0.002% accuracy was used for the gravimetric measurements. The sample was polished and then analyzed with μ XRF after the ponding period to compare the results.

2.5 Comparing Cl and I Penetration Using μ XRF

As explained earlier, the paste samples were ponded with either 0.6 mol/L KI or 0.6 mol/L NaCl solutions for 14 d to compare I and Cl penetration rate. After the ponding period, the investigated samples from TXM and mass change were polished for analysis with μ XRF to compare the results. Each sample was polished on a sanding belt for 2 min with 120 grit sandpaper to create a flat surface for further analysis with μ XRF. Ethanol was used to remove dirt and residue from the polished surface.

The μ XRF analysis was conducted using the Orbis by EDAX. The instrument uses an 80 mm² Silicon Drift Detector Energy Dispersive Spectrometer (SDD-EDS) and a capillary optic that produces a 50 μ m diameter beam. Images are created by moving the sample under the stationary X-ray beam. The X-ray beam causes characteristic fluorescence X-rays to be emitted at each spot. **Table 4** summarizes the settings used by the μ XRF in this work. More details can be found in other publications [25-26].

Table 4. Summary of TXM and μ XRF settings used

Parameter	TXM	μ XRF
voltage (keV)	100	40
current (μ A)	100	1000
filter	0.5 mm Al + 0.5 mm Cu	25 μ m Al
pixel size (μ m)	8.8	50
acquisition time	8 s	400 ms/pixel (dwell time)
chamber condition	air	vacuum
dead time	-	maximum of 20%

2.6 TXM Data Analysis

First, the radiographs of the air were subtracted from sample scans to remove the background attenuation effects. Next, an average gray value profile was calculated through the sample depth. Ten scan lines were randomly used that were perpendicular to the surface of the sample. Each line was located at the middle 40% (4 mm) of the sample to avoid beam hardening and to keep the analyzed region at an almost constant depth. The effect of inconsistent thickness of cylindrical sample on TXM results was investigated in previous publications [32] and it was not found to be significant in this region of the sample. Next, each time series radiograph was subtracted from the radiograph before solution was added to the sample. This allowed the change in the gray value to be easily observed and the spatial changes due to absorption from I to be mapped. The Beer-Lambert Law (**Eq. 1**) [22-23] was used to calculate a change in attenuation due to I ($\Delta\mu$) at different depths of sample.

$$(\Delta\mu)_x = \ln(I_{\text{ref}})_x - \ln(I_t)_x \quad (1)$$

Where $(I_{\text{ref}})_x$ is the transmitted X-ray intensity (gray value) at depth x on the reference profile and $(I_t)_x$ is the transmitted X-ray intensity at the same location at a future time. The fluid accessible porosity and the sample thickness are not included in **Eq. (1)** since these parameters are constant for each sample. More details can be found in other publications [32-33].

Next, standards of cement paste containing different KI concentrations were used to develop a relationship between the gray value and I concentration level. The same sample size, mixtures, curing procedure, and scan setup were used to prepare and investigate these samples. The same samples were then polished and analyzed with μXRF . This again allowed the concentration and counts measurements by μXRF to be calibrated. In addition, a set of paste samples with different NaCl concentrations were also used to convert Cl counts from μXRF to

concentrations. The calibration curves are included in the supplementary section (**Figs S1 and S2**).

2.7 μ XRF Data Analysis

A Matlab code was used to analyze the spatial and compositional data. A border detection algorithm was then used to find the top surface of the sample. The sample is then separated into 0.50 mm layers of equal thickness from the surface of the sample through the entire depth. The average I and Cl counts in each layer can then be plotted for different depths. Next, the calibration curves are used to convert I and Cl counts to concentrations. Additional details can be found in previous publications [25-26].

2.8 Gravimetric Data Analysis

According to ASTM C 1585, the penetration is the change in mass divided by the product of the exposed area of the sample and density of water, as formulated in **Eq. (2)**.

$$I = \frac{\Delta m}{A \times \rho_w} \quad (2)$$

where I is the penetration; Δm is the change in sample mass; A is the exposed area of the sample; and ρ_w is the density of water.

However, this equation does not account for the porosity and initial DoS of the sample. In addition, it does not consider the effect of fluid viscosity and surface tension on penetration. Therefore, this equation is not directly applicable to salt solutions [11,34]. Farnam et al. [34] proposed a modified equation (**Eq. (3)**) to estimate the intrinsic penetration of the sample exposed to salt solution.

$$I_i = \frac{\Delta m}{A \times \rho_s \times \Phi(1 - D_i)} \times \sqrt{\frac{\gamma_w \times \eta_s}{\gamma_s \times \eta_w}} \quad (3)$$

where I_i is the intrinsic penetration (this value is frequently interpreted as the depth of fluid penetration in the sample); ρ_s is the density of solution; Φ denotes the porosity of the sample in volume fraction; D_i is the initial degree of saturation of the sample in volume (See **Table 3**); γ_w and γ_s are the surface tensions of water and solution, respectively; and η_w and η_s represent the viscosity of water and solution, respectively. In the current study, **Eq. (3)** was used to find the depth of fluid penetration based on the gravimetric measurements and compare to the TXM measurements. The density, viscosity, and surface tension for water and NaCl was obtained from [35-36], and KI from [37]. These values are summarized in **Table 5**.

In addition, a linear model was used to find the intrinsic penetration versus square root of time with **Eq. (4)** to determine the sorptivity of the samples [9,38]. For the regression analysis, all data points from 1 min to 6 h were used.

$$I_i = S \times \sqrt{t} + B \quad (4)$$

where S is the sorptivity coefficient; t denotes the time; and B is a correction term added to account for surface effects when the sample comes in contact with the solution.

Table 5. Density, viscosity, and surface tension of solutions [35-37]

Solution	density (g/cm ³)	viscosity (μPa.s)	surface tension ×10 ⁻⁶ (N/mm)
KI	1.070	949.48	73.5
NaCl	1.023	945.74	72.8
Water	0.997	890.30	71.8

2.9 Determining I and Cl Penetration Coefficient

Fick's second law for diffusion is shown in **Eq. (5)** [39-40],

$$\frac{\partial C}{\partial t} = D_c \left(\frac{\partial^2 C}{\partial x^2} \right) \quad (5)$$

where x is distance from sample surface; t denotes time; D_c is diffusion coefficient; C_s is surface ion concentration; and $C_{(x,t)}$ represents ion concentration at the depth of x from the surface after time t .

A general solution to the equation is given in **Eq. (6)**,

$$C_{(x,t)} = C_s \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_c \times t}} \right) \right) \quad (6)$$

$$C_{(x,0)} = 0 \quad x > 0, \quad C_{(0,t)} = C_s \quad t \geq 0$$

where x is distance from sample surface; t denotes time; C_s is surface ion concentration; $C_{(x,t)}$ represents ion concentration at the depth of x from the surface after time t ; and erf is the error function and D_c is the diffusion coefficient in a fully saturated sample.

Both **Eq. (5)** and **(6)** assume that the porous material is fully saturated; the ion concentration at the exposure surface is constant; and there is no impact of co-existing ions. In addition, this equation does not take into account the effect of other ion penetration mechanisms such as capillary absorption. Although these assumptions do not apply to all of the conditions in this study, this equation may still be useful where diffusion plays a significant role in the penetration of outside ions and so these models will be used for comparative purposes.

In the case of $\approx 0\%$, 35% , 70% , 100% RH samples, a nonlinear regression was conducted on I and Cl profiles from TXM and μ XRF with a modified version of **Eq. (6)** that is shown in **Eq. (7)**. First, the diffusion coefficient (D_c) was replaced with a term called the penetration

coefficient (P_c). This term primarily controls the slope of the line describing the concentration versus depth into the sample. This term has been renamed because the penetration of the outside ions is controlled by a combination of mechanisms and not just diffusion. Next, a constant value, known as the absorption coefficient (A_c), was added that can account for the initial uptake or absorption of the fluid into the samples. The absorption coefficient was zero for all samples except for the $\approx 0\%$ RH sample. Because the $\approx 0\%$ RH samples required a combination of both the absorption coefficient (a constant value) and the penetration coefficient (value that controls the slope) the P_c for the $\approx 0\%$ RH sample is not able to be compared with the P_c of the other samples. This is likely caused by the vastly different mode of ion transport in this sample. This will be an area of future research.

$$C_{(x,t)} = C_s \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{P_c t}} \right) \right) + A_c \quad (7)$$

3. Results and Discussion

3.1 Comparison of TXM Results with μ XRF

Figure 2 shows a comparison between concentration profiles from μ XRF and TXM for paste samples with different DoS after 14 d of ponding with 0.6 M KI solution. In addition, the calculated P_c for I and percent difference from both methods based on **Eq. (7)** are summarized in **Table 6**. Based on **Fig. 2**, the two techniques show a good correlation. The difference between the P_c for I from TXM and μ XRF was on average 4% for paste samples conditioned in different RHs. This shows that there is good agreement between μ XRF and TXM for the investigated samples and conditions. In addition, a two tail t-test with the assumption of unequal variances was conducted to compare the mean P_c of the two methods. Based on this analysis, the

difference between means was not significant ($p\text{-value} = 0.93 \gg 0.05$). This suggests that these two methods provide statistically comparable results. Therefore, this suggests that TXM method based on the established procedure and spatial resolution provides reliable results for ion penetration in cement-based materials for these time scales and materials.

Fig. 2. Comparison of TXM results (lines) with results from μ XRF (data points) for paste samples with w/c of 0.40 conditioned in: (a) $\approx 0\%$ and 35% RHs (b) 70% and 100% RHs.

Table 6. Comparison between I penetration coefficients from TXM and μ XRF

Sample	TXM Pen Coef $\times 10^{-11}$ (m^2/sec)	R^2	μ XRF Pen Coef $\times 10^{-11}$ (m^2/sec)	R^2	% Difference $\frac{(\text{TXM} - \mu\text{XRF})}{\mu\text{XRF} \times 0.01}$
$\approx 0\%$	6.62	0.95	6.56	0.99	0.9
35%	16.13	0.98	17.92	0.99	-10
70%	5.86	0.99	5.89	0.99	-0.5
100%	1.41	0.98	1.47	0.98	-4

3.2 Comparison of the I and Cl Penetration

Figure 3 shows a comparison between KI and NaCl intrinsic penetration by gravimetric measurements for samples conditioned at different RH and ponded with 0.6 M KI and 0.6 M NaCl solutions for 14 d. In addition, the calculated sorptivity coefficients from the initial penetration versus square root of time by using **Eq. (4)** are summarized in **Table 7**. Based on

Fig. 3, there is a similar penetration for both the KI and NaCl samples with matching DoS. The average difference between the calculated KI and NaCl sorptivity coefficients of different samples is about 15%. KI showed higher sorptivity in samples with lower DoS compared to NaCl. However, the initial penetration of KI is lower than NaCl in the case of paste samples with higher DoS (e.g. 70% and 100% RH samples). This can be attributed to the differences in fluid properties such as surface tension.

In addition, the I and Cl concentration profiles of samples from μ XRF after 14 d ponding with 0.6 M KI and 0.6 M NaCl solutions are shown in **Fig. 4**. The calculated I and Cl penetration coefficients from concentration profiles by using **Eq. (7)** are summarized in **Table 8**. The average difference between the calculated I and Cl penetration coefficients of different samples is about 6%. Because of the differences in fluid properties, size and ionic mobility we would not expect the penetration rate to be the same for these two different ions. Overall, I shows a similar penetration performance to Cl in paste samples with different DoS and serves as a satisfactory substitute to understand ion penetration.

Fig. 3. Time-dependent KI and NaCl intrinsic penetration in paste samples with w/c of 0.40 conditioned in different RHs by gravimetric method.

Table 7. Comparison between KI and NaCl sorptivity coefficients from gravimetric method

RH	parameter	KI	NaCl	% difference (KI-NaCl) /NaCl×0.01
≈ 0%	S (mm/√s)	0.123	0.1096	12.23
	B (mm)	2.835	2.501	13.35
	R ²	0.99	0.98	
35%	S (mm/√s)	0.0902	0.0742	21.56
	B (mm)	2.686	2.66	0.98
	R ²	0.98	0.99	
70%	S (mm/√s)	0.0392	0.0469	-16.42
	B (mm)	1.593	1.256	26.83
	R ²	0.99	0.99	
100%	S (mm/√s)	0.0325	0.0369	-11.92
	B (mm)	1.129	1.227	-7.99
	R ²	0.97	0.97

Fig. 4. Comparison of I and Cl concentration profiles in paste samples with w/c of 0.40 conditioned in: (a) $\approx 0\%$ RH (b) 35% RH (c) 70% RH (d) 100% RH from μ XRF after 14 d of ponding with 0.6 M solution.

Table 8. Comparison between I and Cl penetration coefficients from μ XRF after 14 d of ponding with 0.6 M solution.

Sample	I		Cl		% Difference $\frac{(I - Cl)}{Cl \times 0.01}$
	Pen Coef $\times 10^{-11}$ (m^2/sec)	R^2	Pen Coef $\times 10^{-11}$ (m^2/sec)	R^2	
$\approx 0\%$	6.56	0.99	7.72	0.99	-15
35%	17.92	0.99	17.76	0.98	0.9
70%	5.89	0.99	6.13	0.98	-3.9
100%	1.47	0.98	1.55	0.97	-5

3.3 Time Resolved I Penetration with TXM

Figs 5 to 13 compare the I penetration and concentration profiles of the paste samples after 5 min, 30 min, 1 h, 2 h, 6 h, 1 d, 5 d, 8 d and 14 d of ponding with the KI solution. The depth of penetration was estimated by reporting where the I concentration was greater than 0.10 % weight of the paste (≈ 0.14 % weight of the cement). This value was chosen so that it was statistically greater than background I concentration found at inner depths of the samples where the solution had not penetrated. This data shows that TXM is capable of providing time-series penetration depths and concentration profiles with high spatial resolution. Because of the high resolution of the data, the I profile can be measured within minutes of adding the material to the surface.

Based on **Figs 5 to 13**, all paste samples showed initial absorption within 2 mm to 4 mm of the surface after 5 min of ponding. However, the rate of I penetration in samples with lower DoS ($\approx 0\%$ and 35% RH) is much higher than samples with higher DoS with time. The $\approx 0\%$ and 35% RH samples showed 3.5x more penetration than the 100% RH samples after 1 h of ponding. The I penetrated for the $\approx 0\%$ and 35% RH samples was observed over the entire scan depth (≈ 20 mm) after only 6 h of ponding. After 14 d of ponding the I penetration of the 100% RH sample reached ≈ 11.5 mm. This highlights the change in ion transport with different saturation levels. The low DoS samples will have a higher number of empty pores. These empty pores will create greater capillary forces that draw the fluid into the sample. Modeling efforts are underway and will be presented in future publications.

In addition, the non-destructive nature of TXM enables us to visualize and quantify the combined transport mechanisms at early ages. Based on **Figs 5 to 13**, the concentration profiles can be categorized into three different types of transport: diffusion-based profiles (e.g. profiles of 100% RH sample); absorption-based profiles (e.g. profiles of $\approx 0\%$ RH samples at early ages;

Fig. 5); and profiles from combined transport mechanisms (e.g. profiles of 35% RH and 75% RH samples).

Figure 14 provides an overview of the ion penetration for the $\approx 0\%$ RH sample. There is a constant I concentration following the ion penetration front. The initial ion penetration is likely caused by capillary absorption. This occurs at the onset of ion penetration into the sample and is described by a front progressing through the sample. Following this region the concentration profile seems to change so that there are two modes of ion penetration. It is interesting that the $\approx 0\%$ RH and the 35% RH samples have almost the same ion concentration from the sample surface until 4 mm from the surface for all of the time periods investigated. This can be due to higher capillary forces at the surface of these samples resulting from the lower DoS.

The 35% RH and 70% RH samples show an almost linear slope over the depth of penetration. This shape is different from pure ionic diffusion and could be caused by a mixed mode of ion transport from diffusion and capillary absorption. The 100% RH sample shows a more typical diffusion shaped curve. A comparison between the calculated P_c of samples with different DoS will be discussed later in the paper.

Fig. 5. TXM comparison of I penetration in different RH after 5 min ponding.

Fig. 6. TXM comparison of I penetration in different RH after 30 min ponding.

Fig. 7. TXM comparison of I penetration in different RH after 1 h ponding.

Fig. 8. TXM comparison of I penetration in different RH after 2 h ponding.

Fig. 9. TXM comparison of I penetration in different RH after 6 h ponding. *The ion penetrated through the entire scan depth.

Fig. 10. TXM comparison of I penetration in different RH after 1 d ponding.

Fig. 11. TXM comparison of I penetration in different RH after 5 d ponding.

Fig. 12. TXM comparison of I penetration in different RH after 8 d ponding.

Fig. 13. TXM comparison of I penetration in different RH after 14 d ponding.

Fig. 14. An example of two modes I penetration in $\approx 0\%$ RH sample.

3.4 Comparison of TXM Results with Gravimetric Method

Figure 15 compares the I penetration depths from TXM with calculated penetration depths from gravimetric measurements based on **Eq. (3)** over the first 6 h of ponding. In addition, the calculated sorptivity coefficients from both techniques based on **Eq. (4)** are summarized in **Table 9**. Based on **Fig. 15**, **Eq. (3)** underestimates the estimated penetration depth when compared to the measured penetration depths from TXM. These differences show an even wider variation over time. This difference is about 23% on average for samples with different DoS after 6 h of ponding. In addition, the average difference between the calculated sorptivity coefficients and the correction constants (B) of different samples from TXM and gravimetric method is about 25%. Again, the gravimetric method underestimates the sorptivity coefficient in all of the samples conditioned in different RHs compared to TXM results. Consequently, the use of these equations would overestimate the service life of concrete structures. This difference can be attributed to the generalized assumption of the simplified capillary pore structure made in **Eq. (3)**.

Fig. 15. Comparison between I penetration depths from TXM and gravimetric method.

Table 9. Comparison between I sorptivity values from TXM and gravimetric method

RH	parameter	gravimetric	TXM	% difference (GV-TXM) /(TXM×0.01)
≈ 0%	S (mm/√s)	0.123	0.1653	-25.59
	B (mm)	2.835	1.672	69.56
	R ²	0.99	0.99	
35%	S (mm/√s)	0.0902	0.1229	-26.61
	B (mm)	2.686	2.431	10.49
	R ²	0.98	0.97	
70%	S (mm/√s)	0.0392	0.0645	-39.22
	B (mm)	1.593	1.467	8.59
	R ²	0.99	0.99	
100%	S (mm/√s)	0.0325	0.0369	-11.92
	B (mm)	1.129	1.253	-9.89
	R ²	0.97	0.99	

3.5 Time-dependent I Penetration Coefficient

Figure 16 displays time-dependent I penetration coefficient based on **Eq. (7)** for cement paste samples conditioned at 35%, 70%, and 100% RH from TXM. As explained earlier, the calculated P_c considers the combined effect from capillary absorption and diffusion in partially-saturated samples. The calculated P_c and A_c of the $\approx 0\%$ RH sample based on **Eq. (7)** is shown in **Fig. 17** over time. Based on **Fig. 16**, the P_c of 35% RH sample is about 40x the sample conditioned in 100% RH at 2 d of ponding. This ratio decreases over time and reaches 11x after 14 d of ponding. The 70% RH sample also has a higher P_c when compared to 100% RH sample ($P_{c,(70\%)} / P_{c,(100\%)} = 10$ at 2 d of ponding). This can be caused by the early age combined transport mechanisms in partially-saturated samples. This highlights the importance of DoS in ion transport into cement-based materials.

As shown in **Fig. 17**, the ratio of P_c of $\approx 0\%$ RH to P_c of 100% RH is about 12 at 2 d of ponding. This ratio decreases to 4 after 14 d of ponding. As mentioned earlier, the calculated P_c of $\approx 0\%$ RH sample based on **Eq. (7)** does not take into account the effect of capillary absorption. Therefore, the calculated P_c for $\approx 0\%$ RH sample is not directly comparable with P_c of other partially-saturated samples. Furthermore, the calculated P_c of $\approx 0\%$ RH sample shows a decreasing rate until 7 d of ponding, then it starts to slightly increase from 7 d to 14 d of ponding. The A_c constant, which accounts for the effect of capillary absorption, also decreases from 7 d to 14 d of ponding. This could be caused by a change from capillary absorption to diffusion in the $\approx 0\%$ RH samples after 7 d of ponding. It has been reported that capillary forces decrease after 24 h from ponding resulting from the increasing DoS and further penetration of ions occurs as a result of diffusion process [38].

Fig. 16. Time-dependent I penetration coefficients of 35%, 70%, and 100% RH samples by TXM.

Fig. 17. Time-dependent P_c and A_c for $\approx 0\%$ RH samples by TXM; estimated by using **Eq. (7)**. P_c is penetration coefficient and A_c is the capillary absorption constant.

In addition, a power model based on the experimental results is shown in **Eq. (8)** to estimate the P_c of partially-saturated paste samples with w/c of 0.40 from a fully saturated sample, as formulated in **Eq. (8)**.

$$\frac{P_h}{P_{100\%}} = a \times t^{-(1-\frac{h}{100})} \quad (8)$$

where P_h is the penetration coefficient of the sample conditioned at relative humidity of h , which accounts for the combined transport mechanisms from capillary absorption and diffusion; $P_{100\%}$ is penetration coefficient of the sample conditioned at 100% RH; t denotes the time; and a is the regression constant. The regression results for 35% and 70% RH samples are summarized in **Fig. 18**. Based on **Fig. 18**, there is good correlation between the developed model and experimental results. The regression constant, “ a ”, decreases with the increase of DoS in the sample. Additional work is needed to extend **Eq. (8)** to other RH and mixture proportions. This model could be used in computational modeling efforts to predict the service life of concrete structures in harsh environments.

Fig. 18. A power model to estimate time-dependent penetration coefficients of 35% and 70% RH samples from 100% RH results.

3.6 Practical Implications

This work provides quantitative insights into the penetration of ions into cement paste at different moisture conditions. Typically, laboratory testing is carried out at 100% RH and the results from the testing are used to predict the long-term resistance to Cl penetration. This work provides important data that makes quantitative measurements of how partially-saturated samples perform in these tests and shows that rate of penetration is higher in these situations. Furthermore, a power model has been presented that would allow testing results from saturated samples to be used to predict performance in partially-saturated materials. This is a useful contribution to the literature. Although more work is needed to extend these findings to different materials and conditions, this work is an important step to improve our predictive powers of the durability of concrete infrastructure. Furthermore, the findings from this work show that the previously suggested equation to estimate the depth of ion transport based on ASTM C 1585 is unconservative by $\approx 23\%$ for the materials and conditions investigated.

4. Conclusions

The presented work uses a non-destructive and rapid imaging method to investigate in-situ and time resolved I penetration into cement paste samples with different DoS. The sorptivity of Cl and I ions in paste samples was also determined gravimetrically and compared with the TXM results. In addition, the same samples from TXM and gravimetric methods were also examined with μ XRF in order to verify their results and compare the I and Cl penetration. Furthermore, time-series I concentration profiles and penetration depths with 8.8 μm resolution from TXM were used to obtain sorptivity and penetration coefficients at different conditions and to observe important insights about combined ion transport mechanisms in partially-saturated samples. This work also suggests a modified version of the simplified solution to Fick's second law to take into account the capillary absorption and complex penetration of outside chemicals

into cement paste. A constant value, known as the absorption coefficient (A_c), was added to the simplified solution of Fick's second law that can account for the initial uptake or absorption of the fluid into the $\approx 0\%$ RH sample.

The following conclusions can be drawn from this work:

- The samples conditioned at $\approx 0\%$ and 35% RHs showed about 3.6X more penetration of I compared to saturated samples at 1 h of ponding.
- After only 6 h of ponding for the $\approx 0\%$ and 35% RH samples the I was observed to penetrate over 20 mm.
- The initial penetration of I into the $\approx 0\%$ RH sample shows an almost constant concentration of 2% I by weight of the paste. This is likely due to capillary suction.
- Over time the concentration profile at the surface of the $\approx 0\%$ RH sample continues to increase suggesting that there are other modes of ion penetration controlling the rate of penetration.
- The 35% and 70% RH samples show a 40x and 10x increase respectively in the penetration coefficient over the fully saturated sample at early ages (2 d of ponding). However, this ratio decreases over time. This can be caused by the early age combined transport mechanisms in partially-saturated samples.
- Previously suggested equations to estimate the depth of ion transport based on gravimetric analysis were found to be unconservative by $\approx 23\%$ for the materials and conditions investigated and this may cause an overestimation of the predicted service life.
- A power model was successfully used to estimate the P_c of partially-saturated paste samples based on the P_c of fully saturated samples.

- Iodide shows a $\approx 15\%$ difference in sorptivity coefficient and $\approx 6\%$ difference in penetration coefficient compared to Cl in samples with different DoS.
- There was a 4% difference found between the calculated P_c from the μ XRF and TXM techniques and the results between the two methods were found to be statistically comparable.

The use of TXM offers advantages over conventional methods to investigate the effect of DoS for ion penetration into cement-based materials with a number of different conditions. Since TXM allows non-destructive and time-dependent concentration profiles to be measured with little sample preparation, TXM can be used to measure the evolution of the penetration over time. These findings show promise to help refine service life modeling techniques for concrete materials and to ultimately improve the predictive capabilities of the lifetime of concrete structures. This data quantifies the impacts of partial saturation on ion transport and shows that even partial drying of concrete will increase the penetration of outside ions through mixed modes of mass transport. This can help owners in dry environments better predict and maintain their concrete structures. Additional modeling efforts are underway to provide additional insights.

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