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Relationship between Chloride Migration, Bulk Electrical Conductivity and Formation Factor of Blended Cement Pastes



Maxime Ranger, MSc
Industrial PhD student
Technical University of Denmark
Department of Environmental and Resource Engineering
Brovej, Building 118, DK-2800 Kgs. Lyngby, Denmark
and
Danish Road Directorate
Guldalderen 12, DK-2640 Hedehusene, Denmark
maug@dtu.dk



Marianne Tange Hasholt, PhD
Special consultant
Danish Road Directorate
Carsten Niebuhrs Gade 43, DK-1577 Copenhagen, Denmark
math@vd.dk

ABSTRACT

This study investigates the links between the non-steady-state chloride migration coefficient, the bulk electrical conductivity and the formation factor of blended cement paste specimens. 18 different binders were tested: two Portland cements (low- and high-alkali) in combination with limestone filler, fly ash, calcined clay, two biomass ashes, sewage sludge ash and crushed brick, as well as two Portland composite cements. In addition, the latter and the low-alkali Portland cement were tested in concrete as well for comparison.

Mixes with high-alkali cement showed better resistance to chloride transport, and the effect of supplementary cementitious materials was found to be strongly linked with their reactivity. Moreover, the results showed a clear correlation of the migration coefficient with the bulk

electrical conductivity and, to a lesser extent, with the formation factor. However, these relationships are strongly influenced by the methods used to determine conductivities and they need to be validated for higher maturities. Finally, the results suggested a fairly good correspondence between the results obtained on paste and concrete.

Key words: chloride migration, electrical conductivity, formation factor, supplementary cementitious materials (SCMs), transport properties.

1. INTRODUCTION

Supplementary cementitious materials (SCMs) have significant effects on the phase assemblage [1], the pore structure [2] and the pore solution composition [3] of blended cement pastes. Consequently, moisture and ion transport properties are affected [4], which has implications for most durability issues.

The formation factor FF was proposed as a measure of transport properties in concrete [5]. It is defined as the ratio between the electrical conductivity of the pore solution σ_{ps} and the bulk electrical conductivity σ_b , as shown in Equation (1) [6]. The formation factor is also linked with the porosity Φ and a pore connectivity parameter β [7].

$$FF = \frac{\sigma_{ps}}{\sigma_b} = \frac{1}{\Phi\beta} \quad (1)$$

Huang et al. [8] showed a proportionality between the non-steady-state chloride migration coefficient D_{nssm} and the reciprocal of FF for paste samples, as per Equation (2). The coefficient of proportionality D_{ps} matched with the chloride migration coefficient in the bulk pore solution ($D_{ps} = 2.03 \cdot 10^{-9} \text{ m}^2/\text{s}$). However, different trends were reported by other authors. Baroghel-Bouny et al. [9] found a correlation between the steady-state migration coefficient D_{ssm} and $1/FF$ (on concrete), while Wilson et al. [10] reported a relationship between D_{ssm} and σ_b (on paste).

$$D_{nssm} = \frac{D_{ps}}{FF} \quad (2)$$

The present work was carried out as part of a study related to the effects of SCMs on the alkali-silica reaction (ASR). Transport properties play a large role in accelerated ASR testing, whether it is in immersion tests like accelerated mortar bar tests (transport of water and ions) or in high relative humidity (RH) tests like concrete prism tests (transport of vapour and leaching of alkali metals). Chopperla and Ideker [11] found a relationship between the expansion in the miniature concrete prism test and the hydroxide ion concentration divided by FF . Additionally, the measurements performed by Lindgård et al. [12] on ASR concrete prisms (75 x 75 x 250 mm and 100 x 100 x 450 mm) showed that the internal RH was usually above 80% after 4 weeks of storage at 38°C and 100% RH , even for low water-to-cement ratios ($w/c = 0.30$) or for binders containing fly ash. For this range of RH , Huang et al. [4] noticed that the vapour diffusion coefficient was also linearly linked to $1/FF$, with a relationship similar to Equation (2).

Based on Equation (2) and the dependencies mentioned in the previous paragraph, the influence of a binder on ions and moisture transport properties may, to some extent, be documented via chloride migration. However, the diverging conclusions from the literature create some uncertainty as to which parameter correlates best with chloride migration results. Thus, the present paper aims to explore these relationships further when the binder composition varies, i.e. the type

of SCM and the alkali content of Portland cement (PC). In addition, it is intended to evaluate the sensitivity of the pore solution and bulk electrical conductivity results when different approaches are used. The study is primarily based on paste samples, however some results on concrete specimens are also presented for comparison. Experimental work includes non-steady-state chloride migration according to NT BUILD 492 adapted for paste and bulk conductivity measurements. The conductivity of the pore solution was calculated based on pore solution compositions published previously [13,14].

This paper intends to deal with ion and moisture transport in a generic way, i.e. as independent of the species type as possible. Equations (1) and (2) are related to the pore system via the porosity and the connectivity, but do not account for chemical interactions. However, the latter may have a significant influence on transport, depending on the species. As a common example, chloride transport is significantly affected by chloride binding, which is strongly influenced by Al-rich SCMs [15]. These effects are not within the scope of the present paper.

2. MATERIALS AND METHODS

2.1 Raw materials

Two types of Portland cement (PC) and two types of Portland composite cement (PCC) were used in the study. Each row starts with their designation in the present paper:

- PC-LA – CEM I low alkali (0.58 Na₂O_{eq} wt.%).
- PC-HA – CEM I high alkali (1.23 Na₂O_{eq} wt.%).
- PCC35 – CEM II/B-M (35 wt.% clinker replacement, calcined clay and limestone).
- PCC50 – CEM II/C-M (50 wt.% clinker replacement, calcined clay and limestone).

The clinker compositions determined by quantitative X-ray diffraction are the following:

- For PC-LA: 65 wt.% alite, 10 wt.% belite, 4 wt.% aluminate, 11 wt.% ferrite.
- For PC-HA: 64 wt.% alite, 8 wt.% belite, 7 wt.% aluminate, 10 wt.% ferrite.

PC-LA, PCC35 and PCC50 were all manufactured with the same clinker. In addition, seven different SCMs were tested in combination with the two PC: limestone filler (LL), fly ash (FA), calcined clay (CC), two biomass ashes (BA1 and BA2), sewage sludge ash (SSA) and crushed brick (CB). The chemical compositions were measured by X-ray fluorescence (XRF) on powders sieved below 63 µm (Malvern Panalytical Zetium spectrometer). The particle size distribution was measured with a laser diffractometer (Malvern Mastersize 2000). Moreover, it was assumed that PCC50 had the same density as PCC35. The values are presented in Table 1 for cements, and in Table 2 for SCMs. Reference [13] contains more information about the mineralogical composition of the cementitious materials, as well as the reactivity of the SCMs. The reactivity was investigated with the R³ method, explained in [16]. The R³ bound water values measured at 7 days are also reported in Table 2.

The aggregates in concrete consisted of a Danish 0-2 mm sand (Storebælt) and two fractions of granite (Blå Rønne), 4-8 and 11-16 mm. When necessary, a superplasticiser (SP) was added to the mixes (MasterGlenium SKY 851, active substance: polycarboxylates).

Table 1 – Chemical composition (in wt.%) of the cements measured by XRF.

Oxide	Portland cement		Composite cement	
	PC-LA	PC-HA	PCC35	PCC50
SiO ₂	19.2	19.2	22.1	26.6
Al ₂ O ₃	5.2	5.1	6.4	8.5
Fe ₂ O ₃	3.67	2.99	3.95	4.94
MgO	1.0	2.4	1.1	1.4
CaO	63.4	60.6	54.2	45.7
Na ₂ O	0.33	0.45	0.38	0.45
K ₂ O	0.38	1.18	0.69	1.09
SO ₃	3.14	3.81	2.73	2.47
Na ₂ O _{eq}	0.58	1.23	0.83	1.17
LOI	3.21	3.56	7.86	7.88
Density [kg/m ³]	3150	3130	3020	3020
d ₅₀ [μm]	14.0	10.7	17.4	14.0

Table 2 – Chemical composition (in wt.%) of the SCMs measured by XRF and reactivity measured by the R³ bound water test at 7 days [13].

Oxide	Limestone	Fly ash	Calcined clay	Biomass ash		Sewage sludge ash	Crushed brick
	LL	FA	CC	BA1	BA2	SSA	CB
SiO ₂	2.0	56.2	49.0	25.5	23.2	56.8	63.4
Al ₂ O ₃	0.4	23.8	17.3	4.8	4.3	8.4	11.2
Fe ₂ O ₃	0.12	6.90	9.74	1.80	1.93	19.57	4.32
MgO	0.3	1.8	2.5	3.5	4.0	0.9	1.2
CaO	54.2	3.9	10.1	34.1	30.9	1.4	9.0
Na ₂ O	0.03	0.49	0.81	0.87	0.71	1.03	2.81
K ₂ O	0.06	1.64	2.66	4.93	7.35	2.43	0.43
SO ₃	0.08	0.79	0.98	4.58	12.66	0.38	0.63
Na ₂ O _{eq}	0.07	1.57	2.55	4.12	5.55	2.63	2.91
LOI	42.52	1.57	4.94	15.83	10.26	3.77	5.37
d ₅₀ [μm]	3.8	18.0	39.4	15.5	70.2	11.1	42.8
R ³ bound water [g/100 g dry paste]	2.08	5.90	8.28	3.24	2.63	5.15	3.89

2.2 Preparation of samples

Paste

Paste samples were produced by mixing 300 g of dry cementitious materials and 150 g of deionised water ($w/b = 0.5$) with a high-shear laboratory mixer (capacity of 1.2 ℓ, unloaded speed announced at 22 000 rpm). For blended mixes, 35 wt.% of the PC was replaced by SCMs. The constituents were added into the mixing bowl in the following order: water, cement and SCM. The blend was mixed two times 30 s, with a resting time of 90 s in between. The specimens were cast in hollow polyoxymethylene (POM) cylinders sealed with rubber bungs. The cylinders were

approx. 120 mm long, diameter 22 mm for migration tests and diameter 25 mm for conductivity and pore solution analysis. The specimens were rotated along their longitudinal axis for 24 ± 2 h until demoulding, and then cured at 20°C in sealed pouches of aluminium-plastic composite foil (“coffee-bag foil”).

Concrete

Concrete batches of 20 ℓ were prepared in a 50 ℓ pan mixer. The dry constituents were mixed for 1 min, then water was added ($w/b = 0.50$), and the concrete was mixed for 2 min. If the slump measured according to EN 12350-2 [17] was below 80 mm, the concrete was mixed again for 1 min with the addition of superplasticiser. The air content was measured as per EN 12350-7 [18]. The concrete compositions and the fresh properties are given in Table 3.

Table 3 – Concrete compositions (in kg/m³) and fresh properties.

	Cement	Water	Aggregates			SP	Slump [mm]	Air content [vol.%]
			0-2 mm	4-8 mm	11-16 mm			
Density [kg/m ³]	See Table 1	1000	2620	2720	2640	1050	-	-
PC-LA	440	220	586	489	598	0.0	80	1.4
PCC35	440	220	580	485	593	1.3	120	1.1
PCC50	440	220	580	485	593	2.6	100	1.2

For each batch, three cylinders (diameter 100 mm x height 200 mm) were cast on a vibrating table (filled in two layers) and demoulded after 24 ± 2 h. The specimens were sealed cured in aluminium-plastic bags stored at 20°C until 28 days after casting.

2.3 Chloride migration

Chloride migration was performed according to NT BUILD 492 [19] on both concrete and paste specimens. After 28 days of curing, 50 mm long pieces were cut and vacuum saturated with a saturated $\text{Ca}(\text{OH})_2$ solution for 18 ± 1 h. The specimens were then placed in the migration setup (anolyte: 0.3 mol/ℓ NaOH, catholyte: 10 wt.% NaCl) with 30 V applied to determine the initial current.

For concrete samples, the test settings (voltage, current and duration) were determined according to Appendix 2 in NT BUILD 492 [19]. At the end of the test, the specimens were split into two parts, and the broken surfaces were sprayed with AgNO_3 . The penetration depth of chlorides was measured with a calliper in seven different locations, evenly distributed along the penetration front. The outer 10 mm on each side was avoided. All tests were duplicated in a setup where the two specimens shared the same catholyte solution (12 ℓ in total).

A similar procedure was used for paste specimens, but several adjustments were made to deal with the smaller sample size and the difference in transport properties. Some illustrations of the setup are shown in Figure 1. First, the volume of anolyte and catholyte were reduced, respectively, to 20 ml and 3.5 ℓ per sample. Second, Appendix 2 in NT BUILD 492 [19] could not be used to choose the voltage and the test duration. For practical reasons, the test duration was chosen to be 24 h. A series of trial-and-error tests were then performed to determine appropriate voltages as a function of the initial current, where the objective was to obtain a penetration depth of around

25 mm. Finally, only two measurements of the chloride front were taken (omitting the outer 5 mm on each side).

For both paste and concrete, the non-steady-state chloride migration coefficient was calculated according to Equation (3) [19].

$$D_{nssm} = \frac{0.0239 \cdot (273 + T) \cdot L}{(U - 2) \cdot t} \left(x_d - 0.0238 \sqrt{\frac{(273 + T) \cdot L \cdot x_d}{U - 2}} \right) \quad (3)$$

Where:

- D_{nssm} : non-steady-state chloride migration coefficient [$10^{-12} \text{ m}^2/\text{s}$].
- U : absolute value of the applied voltage [V].
- T : average value of the initial and final temperatures in the anolyte solution [$^{\circ}\text{C}$].
- L : Thickness of the test specimen [mm].
- x_d : average value of the penetration depths [mm].
- t : test duration [h].

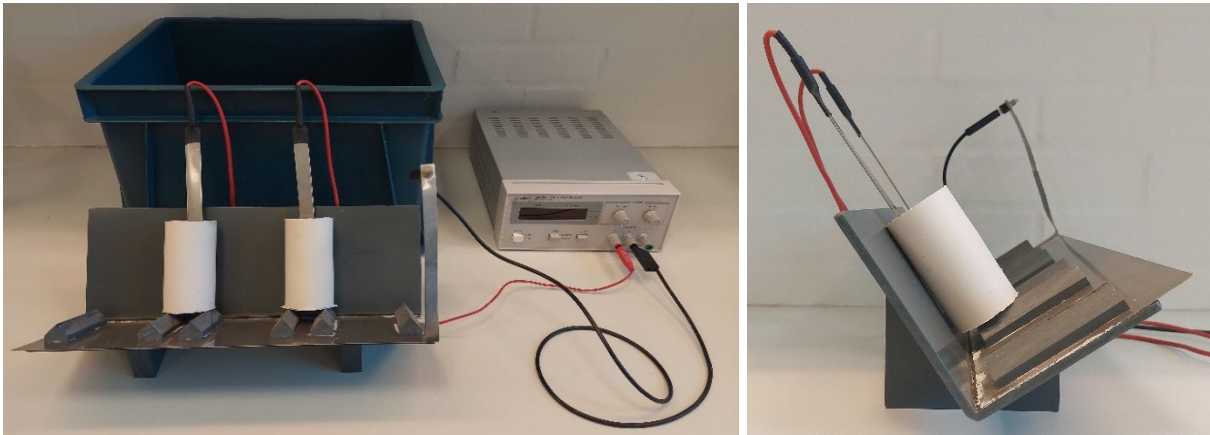


Figure 1 – Chloride migration setup for paste samples. The plastic support where the sleeves are resting is normally placed in the box, which is filled with 10 wt.% NaCl solution.

2.4 Porosity and degree of saturation

The porosity was measured according to the PF method [20] on paste specimens cast with PC-LA, PCC35 and PCC50. After 23 days of sealed curing (mass m_1), the specimens were immersed in the simulated pore solutions for 5 days (m_2), and then dried at 105°C until reaching constant mass (m_3). The porosity (Φ) and the degree of saturation (S) were determined according to Equations (4a) and (4b), respectively, where v is the volume of the specimen calculated from its dimensions and ρ_w the density of water (1000 kg/m^3).

$$\Phi = \frac{m_2 - m_3}{\rho_w \cdot v} \quad (4a)$$

$$S = \frac{m_1 - m_3}{m_2 - m_3} \quad (4b)$$

2.5 Formation factor

As shown in Equation (1), the formation factor can be calculated from the bulk conductivity and the pore solution conductivity. The procedure to determine these two values is detailed below.

Bulk conductivity

The bulk conductivity for paste specimens was measured with a procedure similar to the volumetric method in EN 12390-19 [21]. On each end of a cylindrical specimen the following items were placed: a sponge soaked in deionised water, an electrode, and a non-conductive POM plate, 1 cm thick. The specimen stood vertically, and a steel mass of 500 g was placed on the top POM plate. Two conductive rings with 40 mm spacing were clamped onto the specimen, with a sponge between the specimen surface and the ring. A picture of the setup is shown in Figure 2. An alternative voltage (amplitude 5 V, frequency 50 Hz) was applied to the outer electrodes. Two parameters were measured: the current passing through the outer electrodes, and the voltage between the inner electrodes. The bulk conductivity σ_b (in S/m) was then calculated according to Equation (5).

$$\sigma_b = \frac{I}{U_e} \cdot \frac{L_e}{A} \quad (5)$$

Where:

- I : amplitude of the current applied on the outer electrodes [A].
- U_e : amplitude of the voltage between the inner electrodes [V].
- L_e : distance between the inner electrodes [m].
- A : cross-sectional area of the specimen [m²].

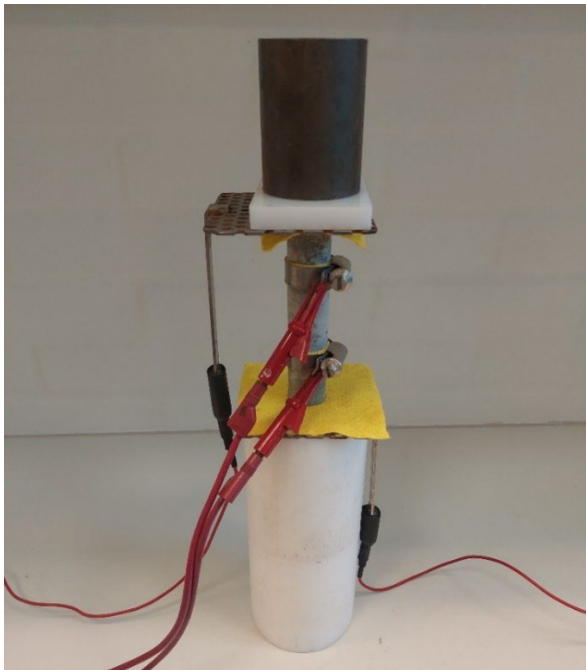


Figure 2 – Bulk electrical conductivity setup for paste samples. The measurements are made between the inner rings (voltage) and through the outer electrodes (current).

Most measurements were conducted on sealed cured samples which were not saturated before the test. This is because the same paste samples were also used for Cold Water Extraction, where it

was desired not to disturb the pore solution. To evaluate the influence of such conditioning, companion specimens made of plain PC-LA, PCC35 and PCC50 (both paste and concrete) were cured in simplified pore solutions at 20°C. The simplified pore solutions were prepared by dissolving NaOH and KOH pellets in deionised water. The concentrations were based on previous studies on the same materials [14,22] and are summarised in Table 4. Ca(OH)₂ was then added to the solutions until saturation. The intention was to (1) avoid leaching of alkalis in order not to alter the conductivity of the pore solution and (2) avoid leaching of calcium hydroxide in order not to increase the porosity [5].

Table 4 – Concentrations of alkali hydroxides in the simplified pore solutions used for curing some of the specimens.

Mix	NaOH [mol/ℓ]	KOH [mol/ℓ]
PC-LA	0.25	0.23
PCC35	0.18	0.17
PCC50	0.17	0.15

For comparison, the bulk resistivity was also determined on concrete specimens for PC-LA, PCC35 and PCC50. Both curing regimes were implemented. The bulk conductivity was calculated as the reciprocal of the resistivity, which was measured according to the Wenner probe method with a Proceq Resipod instrument [21]. Measurements were taken at four locations around the cylinders (90° between each) and averaged.

Pore solution conductivity

The pore solution composition was determined by Cold Water Extraction (CWE) on paste specimens sealed cured for 28 days. CWE was performed by crushing paste to obtain 20 g of the 0.5-1 mm fraction, which was then mixed with 20 g of deionised water and stirred for 5 min. The slurry was vacuum filtered, and the filtrate was analysed with ICP-OES (Varian 720-ES) [22] to determine the concentrations of Na and K. The volume of pore solution was estimated by drying pieces of paste of approximately 30 g in a desiccator containing silica gel, stored at 40°C. The results were published in previous publications [14,22]. For PC-LA, PCC35 and PCC50, the pore solution was also studied by Pore Water Extraction (PWE, high-pressure extraction).

The conductivity of the pore solution was then derived from the concentrations of Na⁺, K⁺ and OH⁻, as proposed in [23]. Since [OH⁻] was not measured, it was assumed that [OH⁻] ≈ [Na⁺] + [K⁺]. The calculated conductivity is given by Equations (6a)-(6c) [23].

$$\sigma_{ps} = \sum_i z_i \cdot c_i \cdot \lambda_i \quad (6a)$$

$$\lambda_i = \frac{\lambda_i^0}{1 + G_i \cdot \sqrt{I_M}} \quad (6b)$$

$$I_M = \frac{1}{2} \sum_i z_i^2 \cdot c_i \quad (6c)$$

Where:

- σ_{ps} : calculated conductivity [S/m].
- z : valence of [-].
- c : concentration [mol/ℓ].

- λ : equivalent conductivity [$\text{cm}^2 \cdot \text{S/mol}$].
- λ^0 : equivalent conductivity at infinite dilution [$\text{cm}^2 \cdot \text{S/mol}$].
- G : empirical conductivity coefficient [$(\text{mol}/\ell)^{-1/2}$].
- I_M : ionic strength of the solution [mol/ℓ].

The values of λ^0 and G used in the calculations were taken from [23] and are shown in Table 5.

Table 5 – Equivalent conductivity at infinite dilution and conductivity coefficient at 25°C [23].

Species	λ^0 [$\text{cm}^2 \cdot \text{S/mol}$]	G [$(\text{mol}/\ell)^{-1/2}$]
OH^-	198.0	0.353
K^+	73.5	0.548
Na^+	50.1	0.733

3. RESULTS AND DISCUSSION

The results and the associated raw data presented in this section are available online, see reference [24]. All tests were carried out 28 days after casting. As a preliminary remark, the authors would like to highlight that some graphs contain a limited number of data points. Even though some elaboration will be made on the visible trends, one must remain cautious with respect to the validity of these observations.

3.1 Comparison of properties measured on paste and concrete

Non-steady-state migration coefficient

Figure 3 displays the non-steady-state migration coefficient (D_{nssm}) determined on paste and concrete samples cast with the same binders.

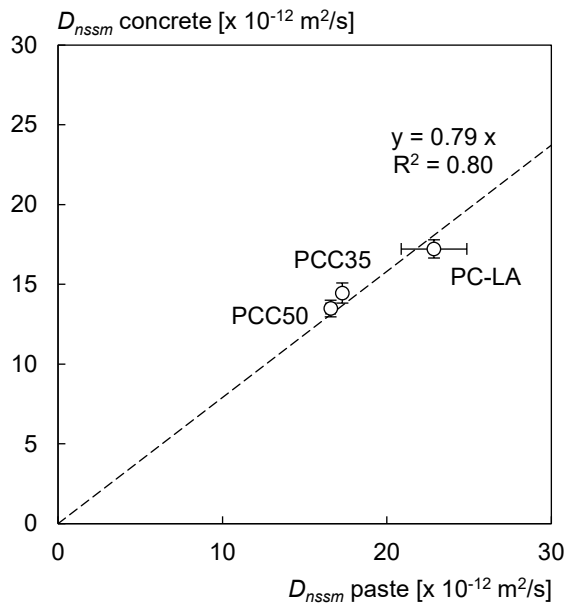


Figure 3 – Non-steady-state migration coefficient (in $10^{-12} \text{ m}^2/\text{s}$) at 28 days for paste and concrete samples cast with the same binders and w/b. The trend line was forced to pass through (0,0) for physical reasons.

The value for concrete cast with PC-LA is in agreement with Hasholt and Jensen [25], who used the same cement and w/c , and a similar paste content. Moreover, PCC35 and PCC50 perform better than PC against chloride ingress, which was already observed by other authors for limestone calcined clay cements [2]. Based on the three data points, the relationship between concrete and paste can be reasonably well described by a linear fit.

Previous work by Delagrave et al. [26] and Yang and Su [27] investigated the changes in steady-state chloride migration coefficient (D_{ssm}) induced by the presence of aggregates. Both studies were conducted on mortar samples, where the sand volume fraction was increased from 0 to 40 [27] or 57% [26]. It was concluded that increasing the aggregate content leads to:

- On the one hand, a decrease of D_{ssm} due to paste dilution and increased tortuosity.
- On the other hand, an increase of D_{ssm} due to enhanced transport properties in the interfacial transition zone (ITZ).

The studies also showed that increased tortuosity and modified transport properties in the paste (increased in the ITZ, hampered otherwise) roughly compensate each other, so that accounting for paste dilution only gives a reasonably accurate estimate. Jensen et al. [28] conducted diffusion tests and highlighted this fact as well. Moreover, it was shown that similar chloride profiles were obtained on paste and corresponding mortar exposed to the same conditions [29].

Non-steady-state migration experiments are based on measuring the chloride penetration depth, not the chloride flux through the entire cross-section. Thus, the pure paste dilution effect caused by aggregates is expected to have a smaller influence on non-steady-state results compared to steady-state ones. This was experimentally observed by Luping and Nilsson [30], who found that D_{nssm} for mortar was about 70% of that in a corresponding paste, with $w/c = 0.4$ and a sand volume fraction of 51% in the mortar. This is in line with the trend stemming from the data in Figure 3.

Bulk conductivity

The bulk conductivity correspondence between paste and concrete is shown in Figure 4 for PC-LA, PCC35 and PCC50. For each curing regime, a linear relationship exists independently of the binder type. The data published by Princigallo et al. [31] show that a concrete containing 60 vol.% of aggregates has approximately 35% of the bulk conductivity of a corresponding paste after 2 days of sealed curing. This ratio for sealed cured specimens in Figure 4 varies between 20 and 40%, which is a similar order of size. Higher values are obtained with specimens cured in solution, which will be discussed in detail in Section 3.2.

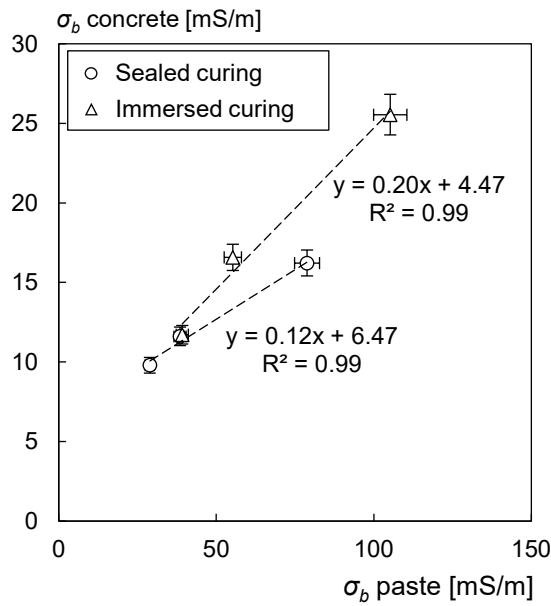


Figure 4 – Bulk conductivity at 28 days measured on paste and concrete, for specimens sealed cured or cured in simplified pore solution (PC-LA, PCC35 and PCC50).

3.2 Influence of specimen conditioning and measuring methods on conductivities

Bulk conductivity

The influence of the curing regime on σ_b is presented in Figure 5, which shows the same data as in Figure 4 but plotted in a different way. As observed by Weiss et al. [32], samples cured in solutions have a higher σ_b than sealed cured specimens. However, a linear relationship with a very good fit ($R^2 = 0.99$) seems valid for both paste and concrete.

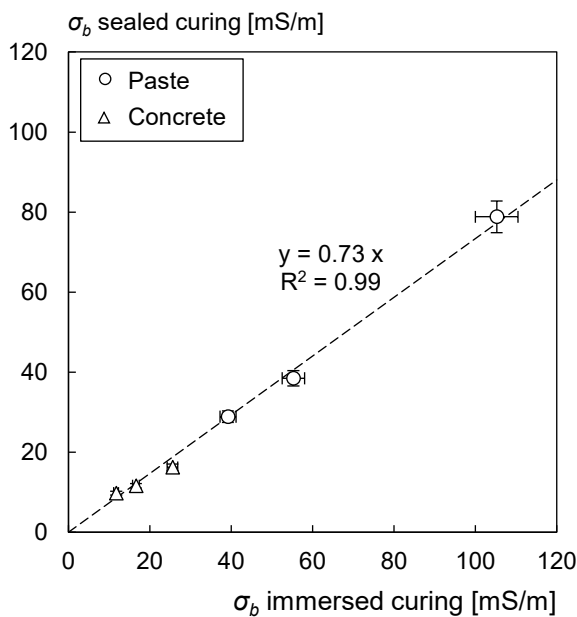


Figure 5 – Bulk conductivity at 28 days measured on specimens cured under two different regimes: sealed curing and immersed curing (in simplified pore solution).

According to Bentz and Stutzman [33], sealed curing creates a more disconnected pore network. Hydration products in sealed cured specimens tend to concentrate in the smallest pores between unhydrated cement particles, contrary to saturated curing where hydration products are more evenly distributed. Another significant difference is the degree of saturation of the specimens. The work of Weiss et al. [32] suggests that the ratio between the bulk conductivity of a non-saturated sample and that of a saturated sample is equal to $S^{n-l+\delta}$, where S is the degree of saturation, n is an empirical coefficient typically between 4 and 5 for cementitious materials and δ is a correction term accounting for the increased ionic strength of the pore solution in non-saturated samples, which varies between 0.1 and 0.3.

The porosity and the degree of saturation of the sealed cured samples are shown in Table 6, together with the factor $S^{n-l+\delta}$ calculated with $n = 5$ and $\delta = 0.15$. These values were taken from reference [32], for an ionic strength around 0.3-0.4 mol/l.

Table 6 – Porosity and degree of saturation measured on sealed cured specimens. The term $S^{n-l+\delta}$ was calculated with $n = 5$ and $\delta = 0.15$.

Mix	Φ [vol.%]	S [-]	$S^{n-l+\delta}$ [-]
PC-LA	45.5	0.925	0.723
PCC35	48.3	0.930	0.740
PCC50	49.4	0.926	0.728

The values for $S^{n-l+\delta}$ presented in Table 6 fit well with the slope in Figure 5, which suggests that the degree of saturation is the main reason for the deviation from the 1:1 line. The degree of hydration may also play a role [32]. However, the degree of hydration was found to be relatively high for a sealed cured paste specimen with PC-LA at 28 days (0.89) [13]. Thus, no significant increase is expected with immersed curing.

Pore solution conductivity

Figure 6 shows the pore solution conductivity calculated from Equations (6a)-(6c), using two different datasets obtained on paste samples with PWE and CWE [13,14]. The calculations with CWE lead to higher conductivities, which is a direct consequence of CWE giving systematically larger alkali metal concentrations in the pore solution compared to PWE [13,14].

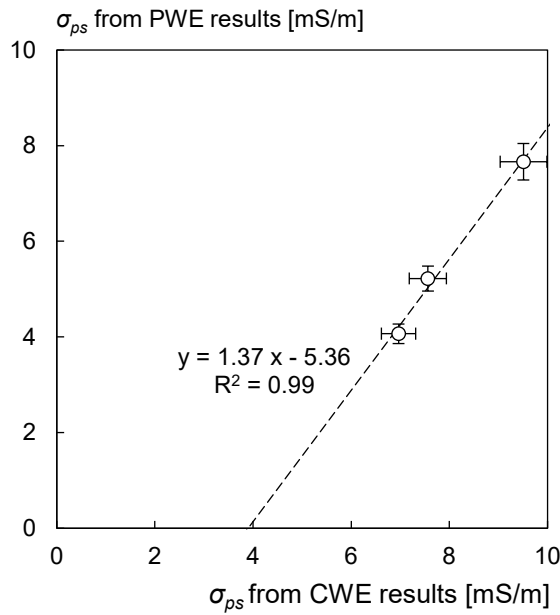


Figure 6 – Pore solution conductivity for PC-LA, PCC35 and PCC50 calculated from CWE and PWE results at 28 days.

Huang et al. [4] already underlined the influence of the method to determine the conductivity of the pore solution. The authors argued that squeezing out the pore solution may not extract ions present in the diffusion layer of the electrical double layer, which would underestimate the conductivity of the pore solution. This explanation was put forward to explain the difference between their results and those of Wilson et al. [10]. As mentioned in a previous study [22], it is suspected that alkali metals initially present in the electrical double layer may be released during CWE. This might partly compensate for the pitfall mentioned above, but a quantitative analysis is necessary to evaluate the magnitude of the change.

Formation factor

The results from the previous sections can be combined to evaluate the sensitivity of the formation factor to the different methods used to determine conductivities. Figure 7 shows $1/FF$ for PC-LA, PCC35 and PCC50 for the four combinations: bulk conductivity measured on sealed cured specimens or specimens cured in their pore solution, and pore solution conductivity determined from CWE results or PWE results. One can see that $1/FF$ may vary by a factor >2 between the two extreme combinations. Even though it is not intended to discuss here which approaches are the most appropriate ones, it must be highlighted that the choice significantly influences the results. A more in-depth discussion on the topic can be found in Weiss et al. [32], where it is emphasised that FF depends on both the saturation state and hydration.

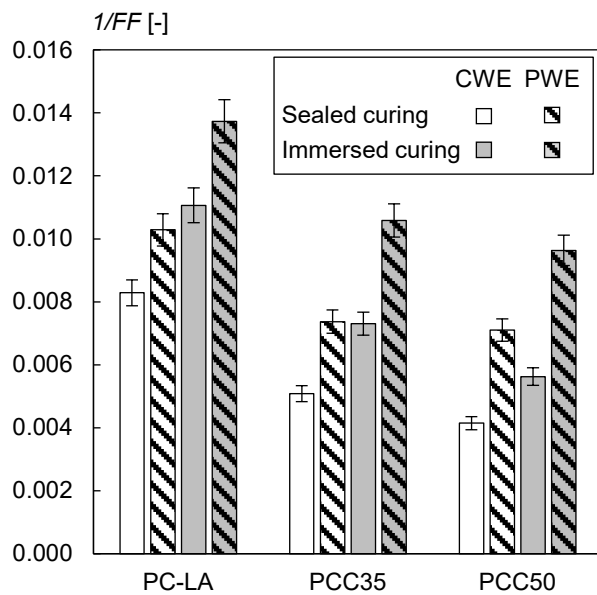


Figure 7 – Sensitivity of the formation factor reciprocal ($1/FF$) for paste specimens. The bulk conductivity was measured on specimens either sealed cured or cured in solution, and the pore solution conductivity was calculated from CWE or PWE results.

3.3 Influence of the binder composition on the migration coefficient

Table 7 presents the parameters used in the migration test with paste samples: initial current at 30 V, adjusted voltage and subsequent intensity. In addition, the chloride penetration depth at the end of the test (average of two samples) is also given.

The calculated D_{nssm} is shown in Figure 8A as a function of the binder composition (i.e. PC alkali content and SCM type). For all mixes, using PC-HA systematically leads to a lower migration coefficient compared to PC-LA. Bu and Weiss [34] observed the same effect of the cement alkali content on diffusion properties and related it to a densification of the microstructure. It should be mentioned that a higher alkalinity also enhances the pozzolanic reaction [35]. Therefore, it is likely that after 28 days of curing at 20°C, SCMs with PC-HA have reacted more than with PC-LA, which can also explain the higher D_{nssm} for mixes with PC-LA. However, in the long run, SCMs would likely reach similar degrees of reaction in low- and high-alkali systems. In this case, the effect of the alkali content may not be so pronounced, or even negligible. Higher maturities would be needed to verify this assumption. Figure 8B illustrates the relationship between (1) the reactivity of SCMs measured by the R^3 bound water test [13] and (2) the relative difference for D_{nssm} , where PC samples were taken as the references.

Table 7 – Settings used in the chloride migration test on paste (given for one paste specimen). The test duration was set to 24 h for practical reasons.

Mix		Initial current at 30 V [mA]	Adjusted voltage [V]	New current [mA]	Cl penetration depth [mm]
PC-LA	Ref	25	12	9	19.7
	LL	39	9	10	32.8
	FA	20	10	12	40.9
	BA1	35	10	10	28.1
	BA2	47	8	10	27.2
	CC	6	30	6	22.9
	SSA	11	20	10	34.8
	CB	35	10	10	31.7
PC-HA	Ref	20	20	13	21.0
	LL	31	11	10	25.6
	FA	11	25	9	23.4
	BA1	35	10	10	23.7
	BA2	48	8	9	22.6
	CC	3	45	5	13.1
	SSA	11	12	9	26.0
	CB	23	15	11	25.3

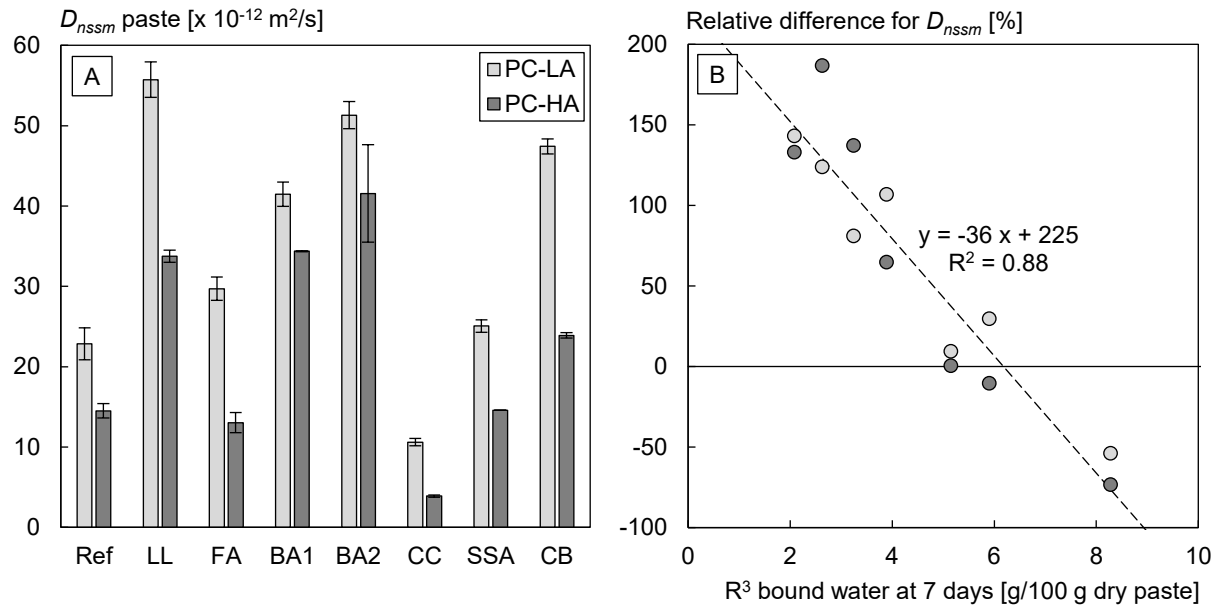


Figure 8 – A: Non-steady-state migration coefficient (in $10^{-12} \text{ m}^2/\text{s}$) at 28 days determined on paste samples. B: Relative non-steady-state migration coefficient plotted (with respect to the plain PC samples) as a function of the R^3 bound water at 7 days (in g/100 g dry paste) [13].

Figure 8B shows a strong correlation, which emphasises the dominant effect of the SCM reactivity on D_{nssm} . Such influence of the reactivity is clearly visible in long-term studies, for instance with fly ash which is known to barely affect transport properties at early age but dramatically reduce chloride ingress in the long run [36]. It is however promising to see that the SCM effect can be anticipated with a simple R^3 bound water test. For future studies, it would be interesting to test

the influence of the SCM replacement level in the mixes and expand the reactivity range to validate the linearity observed in Figure 8B, for instance by including metakaolin and silica fume.

3.4 Relationship between the migration coefficient and conductivities

Figure 9 displays D_{nssm} as a function of σ_b (9A) and $1/FF$ (9B). σ_b is the one measured on sealed cured samples, and σ_{ps} is the one calculated from CWE results. As shown in Figure 9A, a reasonable proportionality exists between D_{nssm} and σ_b . A subsequent link with $1/FF$ is also observed in Figure 9B, even though the data are more scattered and all above the straight-line representing Equation (2).

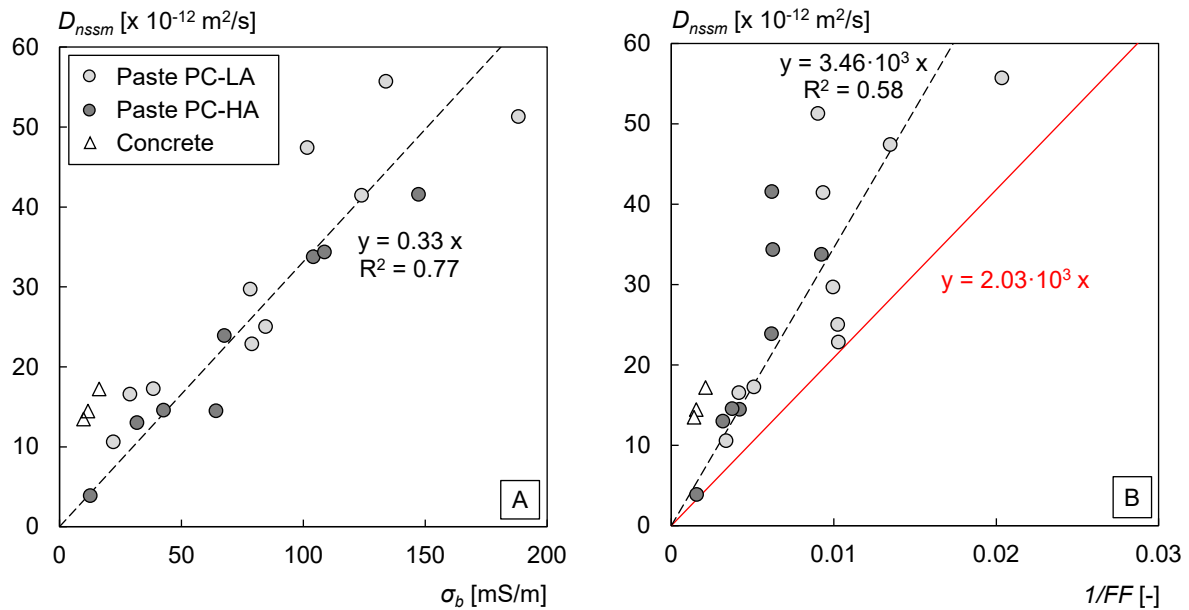


Figure 9 – Non-steady-state migration coefficient (in $10^{-12} \text{ m}^2/\text{s}$) at 28 days. A: as a function of the bulk conductivity. B: as a function of the reciprocal of the formation factor. Best linear fits are represented by dashed lines, and Equation (2) by a red solid line.

None of the studies mentioned in the introduction [4,9,10] concluded on a correlation between D_{nssm} and σ_b . Huang et al. [4] did see a correlation between D_{nssm} and $1/FF$, however the data in Figure 9B do not match the theoretical coefficient of proportionality. Given the large variations for conductivities and for $1/FF$ illustrated in Figure 7, it seems not so surprising to find different conclusions across the studies.

Assuming that the relationship found in Figure 5 holds true for all mixes, the correlation between D_{nssm} and σ_b exists whether the specimens are sealed cured or cured in their pore solution. Indeed, Figure 5 is a pure proportionality relationship, so using one value or the other in Figure 9A would only change the slope and not the R^2 value. By using the proportionality coefficient from Figure 5 (0.73), one can also “correct” $1/FF$ and estimate what the value would be for saturated and non-leached specimens. This is shown in Figure 10, and results in a significantly better fit with Equation (2), except for concrete specimens (triangles) and mixes containing BA1 and BA2 (circled in green).

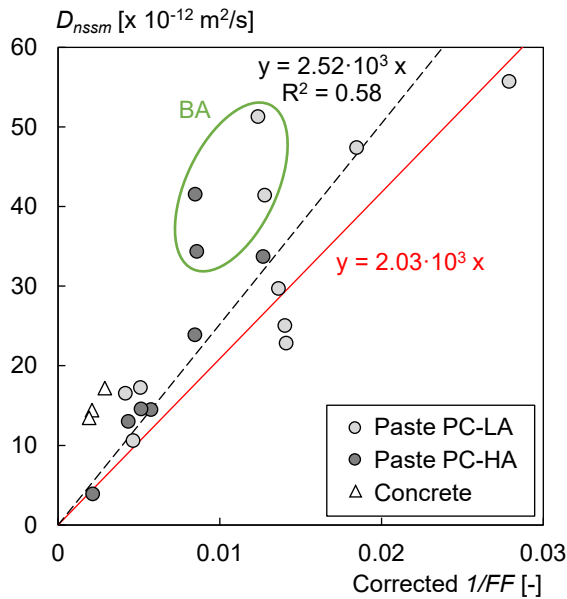


Figure 10 – Non-steady-state migration coefficient (in $10^{-12} \text{ m}^2/\text{s}$) at 28 days as a function of the reciprocal of the formation factor, corrected according to the relationship found in Figure 5 (division by 0.73 of the bulk conductivity measured on sealed cured specimens).

The reason for the mixes containing biomass ashes to deviate from Equation (2) in Figure 10 may be due to the inaccuracy of the pore solution conductivity. As explained in Section 2.5.2, it was calculated by only considering $[\text{Na}^+]$ and $[\text{K}^+]$, and deducing $[\text{OH}^-]$ to maintain the charge balance. However, BA1 and BA2 contain some chloride [13], so a significant amount of Cl^- is probably present in the pore solution. Because the conductivity of Cl^- is about 2.6 times lower than that of OH^- [23], the actual conductivity of the pore solution is likely lower than the one calculated previously. As a result, the actual $1/FF$ may be larger than the one shown in Figure 10, which would bring the data points closer to the expected relationship. This could be verified by measuring the OH^- and Cl^- concentrations in the pore solution, but high-pressure extraction would be needed instead of Cold Water Extraction. Indeed, in the latter portlandite is dissolved during leaching, so the OH^- concentration is not representative of what it was in the initial pore solution [37].

Regarding concrete mixes, the deviation is probably due to the presence of aggregates that do not affect bulk conductivity and non-steady-state migration in the same way. Different conclusions may be drawn from steady-state experiments [9], where the presence of aggregates strongly affects the migration coefficient. In this case, the ratio between concrete and paste is expected to be significantly more related to the volume fraction of aggregates than in Figure 3.

3.5 Perspectives with respect to ASR testing

The beneficial effect of SCMs against ASR is generally associated with a reduction of the pore solution alkalinity [38]. However, the results presented in the previous sections combined with the conclusions of other studies [4,12] suggest that the influence of SCMs on transport properties can also greatly affect the kinetics of the ASR, particularly in accelerated tests. As an example, the permeability of blended mixes was listed as a key factor to consider when using ASTM C1567 [39] to test SCMs (immersion in 1 M NaOH at 80°C) [40]. In addition, there are indications that

soluble aluminium supplied by Al-rich SCMs slows down the dissolution of amorphous silica, which influences ASR kinetics [41].

The role of the alkali content on transport properties (Figure 8) is particularly relevant to consider. Even though high alkali contents are associated with a larger ASR risk, it was shown that they also contribute to lowering the permeability of the paste. Thus, there might be a sensitive area where both phenomena have a comparable influence but an opposite effect on the results, which should be factored in when interpreting the outcomes of the test. However, as mentioned in Section 3.3, a high alkali content may also favour the pozzolanic reaction. Thus, the difference in permeability between low- and high-alkali mixes may be largely due to different degrees of reactions of SCMs, and therefore possibly only visible in the short run.

4. CONCLUSIONS

The present study investigated the relationship between the non-steady-state migration coefficient (D_{nssm}), the bulk electrical conductivity (σ_b) and the formation factor (FF) for 18 different binders. Most of the experiments were carried out on paste specimens, however a comparison with concrete was made for a selected set of binders. The following conclusions can be drawn:

- For paste, a proportionality relationship was observed between D_{nssm} and σ_b measured on sealed cured specimens. A clear link was also observed with $1/FF$, even though the data were more scattered. From a practical perspective, measuring the bulk conductivity on sealed cured specimens has the advantage of being completely non-destructive, so that the same specimen can be measured over time or used for another test.
- Increasing the PC alkali content reduces D_{nssm} and σ_b , for both plain PC and blended mixes. Moreover, the effect of SCMs varies significantly from one type to another and is correlated with their reactivity. The simple R^3 bound water test seems able to predict the change in D_{nssm} compared to a reference PC sample.
- The methods used to determine electrical conductivities significantly influence the results, both for the bulk specimen and the pore solution. In particular, curing the samples in their own pore solution increased σ_b by nearly 40%. Using this value to calculate FF seems to better fit with the expected theoretical relationship between D_{nssm} and $1/FF$. This also calls for a more specific definition of the formation factor.
- There is a clear link between the properties measured on paste and concrete, which appeared to be independent of the binder type. However, D_{nssm} and σ_b seem to be affected in different ways by the presence of aggregates. As a result, the proportionality between D_{nssm} and σ_b seems to hold, but with a different coefficient.
- The points mentioned above suggest that comparing transport properties of concrete can be done on corresponding pastes, provided that the type, the volume fraction and the grading curve of aggregates are the same across all concrete mixes.

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