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RE: Measuring Transport Properties for Concrete Containing CNC:
Porosity, Resistivity, and Chloride Ingress

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Background:

This work evaluated the transport properties of concrete containing cellulose nanocrystals (CNCs). Mortar samples were prepared without CNC for reference and with CNC (0.2% by mass). Samples were tested for (1) a conventional mixture using ordinary portland cement (OPC), (2) a mixture with an OPC+ limestone blend (OPC+20LS or OPC+30LS), (3) OPC+slag+limestone blend (OPC+50Slag+20LS). Seven mixtures were prepared consisting of three mixtures without CNCs (OPC, OPC+20LS, OPC+50Slag+20LS) and three mixtures with 0.2% CNC dosages by volume of binder (OPC+20LS, OPC+30LS, OPC+50Slag+20LS) were cast. For all mixtures, a water-to-cementitious material ratio (w/cm) of 0.40 was kept constant and mortar samples with standard sand (sand content 35% of total mass) were cast to reduce the influence of large aggregate. Table 1 provides a summary of the mixtures used in this study.

Table 1. The mixture details of the mixtures proposed in this study

	OPC	Limestone (LS)	Slag (SL)	Cellulose nanocrystals (CNCs)
OPC_0CNC	100 %	0 %	0 %	0.0 %
20LS_0CNC	80 %	20 %	0 %	0.0 %
20LS_0.2CNC	80 %	20 %	0 %	0.2 %
30LS_0.2CNC	70 %	30 %	0 %	0.2 %
20LS_50SL_0CNC	30 %	20 %	50 %	0.0 %
20LS_50SL_0.2CNC	30 %	20 %	50 %	0.2 %

The samples were tested at 91-days for compressive strength (AASHTO T22 [1]), 91-days for porosity (AASHTO TP-135 [2]), 91-days for resistivity (AASHTO TP-402 [3]), chloride binding isotherms ([4]), and the apparent chloride diffusion coefficients (ASTM C1556 [5]).

Task 1-Determination of 91-day compressive strength (AASHTO T22):

For compressive strength, 3 50 mm (diameter)×100 mm (length) cylinder samples were tested following AASHTO T22 at 91 equivalent days. The samples were cured under sealed conditions for 3 days at 23±1 °C and 25 days at 50±1 °C to accelerate curing so that a 91-day equivalent age was achieved. **Figure 1** shows the average compressive strength of 3 repeats of each mixture (MPa) vs the SCM replacement (%). The compressive strength decreases as the OPC is replaced. The strength of the systems containing CNC is similar to that of systems without CNC for similar mixtures.

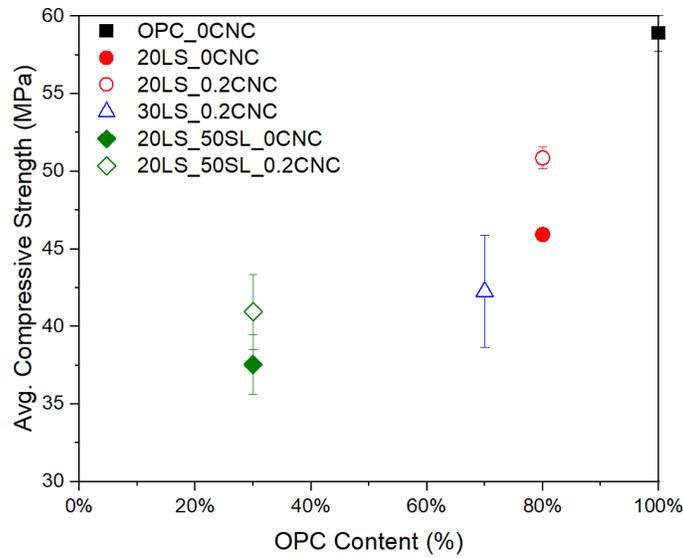


Figure 1. The average compressive strength (MPa) of the mixtures at 91 days

Task 2-Determination of electrical resistivity (AASHTO TP-119):

AASHTO TP119-22 Option A was used to assess uniaxial resistivity measurements. Two specimens were selected with 50 mm (diameter) ×100 mm (length) cylinder dimensions and were cured in a sealed condition after casting until testing. After demolding, the specimens were placed under vacuum at 7 ± 2 Torr for 3 hours. The simulated pore solution consisting of 7.6g/L NaOH (0.19M); 10.64g/L KOH (0.19M); 2g/L Ca(OH)₂ (0.027M) was added and the specimens were allowed to saturate under a vacuum for 1 hour. The specimens were stored under simulated pore solution at 23°C+/-1.5°C for 24 ± 4 hours. The specimens were tested after the saturation at a single frequency of 10 kHz and the bulk resistivity was calculated according to equation 1:

$$\rho = R_{cylinder} \left(\frac{A}{L} \right) \tag{Equation 1}$$

where ρ is the saturated bulk resistivity ($\Omega \cdot m$); $R_{cylinder}$ is the vacuum-saturated resistance (ohm, Ω); A is the cross-sectional area of the sample (m^2); L is the length of the sample (m).

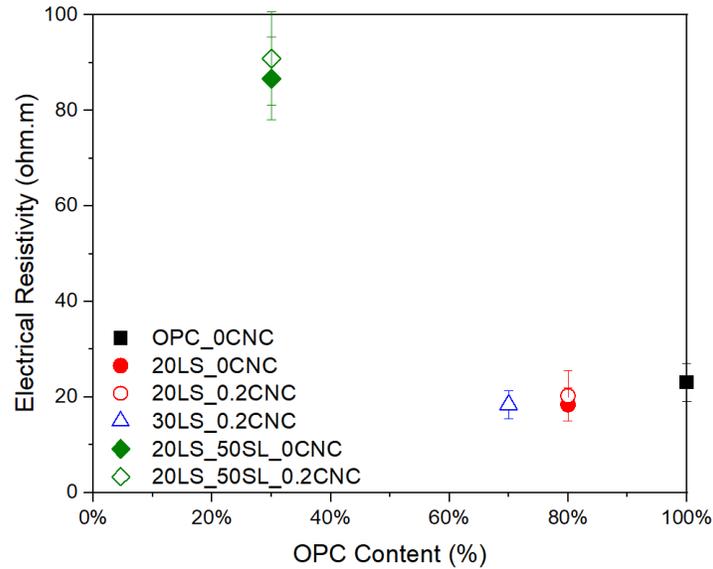


Figure 2. Electrical resistivity of the mixtures (ohm.m)

Task 3-Determination of porosity (AASHTO TP 135):

After bulk resistivity measurements, the saturated weight and the apparent weight were measured for two specimens from each mixture. Then, the specimens were then dried at 105°C to obtain dry weight until a constant mass was achieved. The porosity of the cylinders was computed using Equation 2:

$$\Phi = \frac{w_{sat} - w_{dry}}{w_{sat} - w_{app}} \quad (\text{Equation 2})$$

where Φ is the porosity of the mortar specimens; w_{sat} is the vacuum-saturated weight of the specimens; w_{dry} is the dry weight of the specimens; and w_{app} is the apparent weight of the specimens. For each mixture, two specimens were tested and the average of two specimens was reported in **Figure 3**.

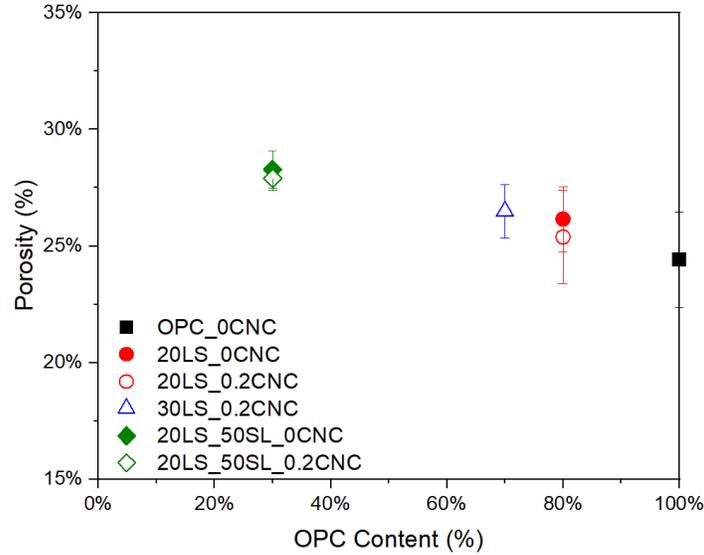


Figure 3. Porosity of the mixtures (%) vs SCM replacement

Task 4-Determination of apparent chloride diffusion (ASTM C1556):

ASTM C1556 test method was used to determine the apparent chloride diffusion coefficient. 100 mm (diameter)×200 mm (length) cylinder specimens, were cured for 91 days and then cut into samples with 75 mm test specimen heights. The specimens were vacuum-saturated with lime water and dried at 23±1 °C and 50±3 % RH for 24 hours. The samples were coated with a 2-part epoxy resin on all the surfaces except the surface that was exposed to chlorides to simulate one-dimensional ingress. The samples were then rewetted with lime water. The initial chloride content of the samples was measured at 0.0% by weight of the sample. The samples were exposed to 165 g/L NaCl solution according to ASTM C1556 for 56 days in sealed containers. After the chloride exposure, the samples were profile ground at 1 mm layer intervals to get samples at different depths by following the recommended depth in Table 1 (ASTM C1556). The powdered samples were used to determine acid-soluble chloride contents using ASTM C1152/1152M [6] by titration using a 0.05N silver nitrate solution. The surface chloride concentration and apparent chloride diffusion coefficient were computed by fitting the following equation to measured chloride-ion contents;

$$C(x, t) = C_s - (C_s - C_i) \operatorname{erf} \left(\frac{x}{\sqrt{4D_a t}} \right) \quad (\text{Equation 3})$$

where $C(x, t)$ is chloride concentration measured at depth x and exposure time t (mass %), C_s is the surface chloride concentration (mass %), C_i is the initial chloride concentration before exposure (mass %), x is the depth of exposure layer (m), D_a apparent chloride diffusion coefficient (m^2/s), t is the exposure time (s) and erf is the error function. The results for measured chloride contents versus depth below the surface and best-fit curve are presented in **Figure 4**. The estimated surface chloride concentrations and the diffusion coefficients obtained by chloride profile are given in **Table 2**.

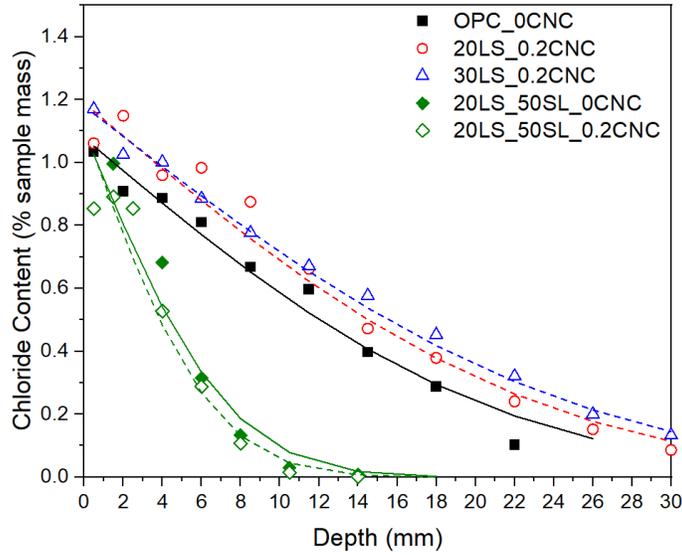


Figure 4. Chloride profile fit obtained from ASTM C1556

Table 2. The surface chloride concentrations and diffusion coefficients of the mixtures

	Surface Concentration, C_s (% sample mass)	Diffusion Coefficient, D_a (m^2/s)
OPC_0CNC	1.08	2.79×10^{-11}
20LS_0.2CNC	1.19	3.35×10^{-11}
30LS_0.2CNC	1.18	3.90×10^{-11}
20LS_50SL_0CNC	1.10	3.50×10^{-12}
20LS_50SL_0.2CNC	1.11	2.70×10^{-12}

Task 5-Determination of chloride binding:

In order to determine bound chloride, the samples were crushed/powdered and exposed to simulated pore solutions containing different chloride concentrations of NaCl solutions. The powder-to-exposure solution ratio was kept as constant value of 2. The prepared chloride solutions had concentrations equal to 0.1 M, 0.5 M, 1.0 M, 2.0 M, and 3.0 M of chloride ions. The samples were equilibrated for 14 days and occasionally agitated to ensure uniform exposure to the chloride solutions. After this duration, 30-100 μ l of the equilibrated solution was used in potentiometric titration with 0.05 N silver nitrate to determine free chloride concentration. From the initial concentration (c_0) of the solution and the final concentration of the solution (c_1), the bound chloride concentrations (c_b) were determined by following equation;

$$c_b = \frac{(c_0 - c_1)V_{sol}M_{Cl}}{m_{paste}} \quad (\text{Equation 4})$$

where V_{sol} is the volume of solution (ml), M_{Cl} is the molar mass of chloride, and m_{sample} is the mass of the sample (g). Free chloride concentrations were plotted against the bound chloride concentrations and the data was fit with the Freundlich isotherm to determine the isotherm parameters: alpha and beta.

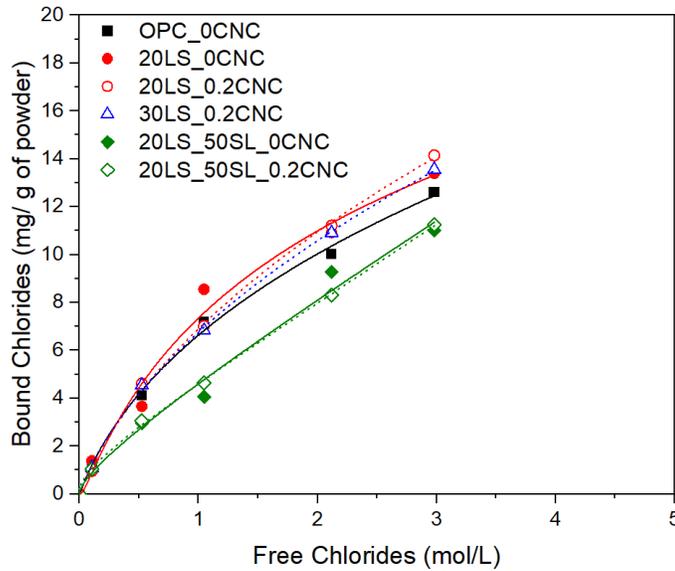


Figure 5. Chloride binding isotherms of the mixtures

Table 3. Fitted Freundlich parameters of the mixtures

	alpha	beta	R ²
OPC_0CNC	6.64	0.63	0.996
20LS_0CNC	7.35	0.65	0.974
20LS_0.2CNC	6.90	0.69	0.998
30LS_0.2CNC	6.75	0.67	0.999
20LS_50SL_0CNC	4.60	0.79	0.978
20LS_50SL_0.2CNC	4.60	0.76	0.999

Task 6-Simulated chloride profiles for concrete:

In this task chloride profiles are provided for hypothetical concrete samples produced with the six cementitious mixtures. The concrete is assumed to have a paste content of 26% (after the incorporation of coarse aggregate) giving the concrete a unit weight of 2310 kg/m³. Porosity and formation factor measurements have been used to calculate the diffusion coefficient of concrete without considering the aging effect. It is assumed that the concrete is 75% saturated and exposed to a marine environment. The information presented in Task 5 is used to model chloride binding. Figure 6 illustrates the free chloride profiles of these mixtures after exposure to a marine environment for 10 years. It can be noted that the CNC do not reduce the service life of the concrete. Rather the 20%LS sample with CNC provides similar performance to the OPC system.

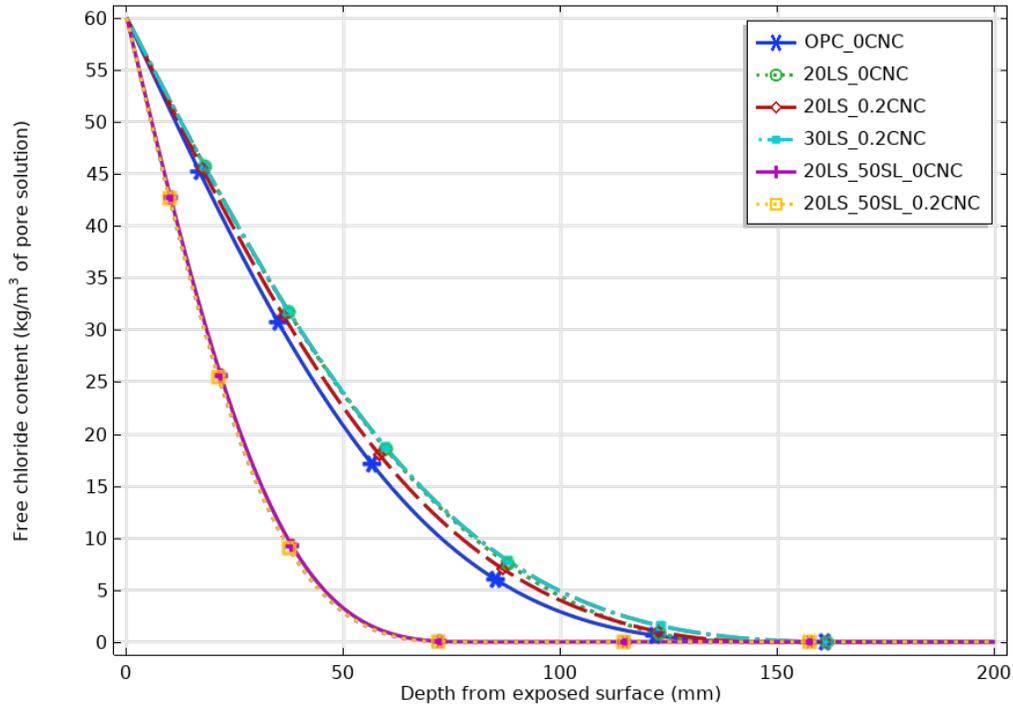


Figure 6. Chloride profiles of the hypothetical concrete samples produced with the six cementitious mixtures after exposure to a marine environment for 10 years. The effect of aging is not included in the simulations.

References

1. AASHTO. 2022. Standard Method of Test for Compressive Strength of Cylindrical Concrete Specimens. AASHTO T 22M/T 22-22. Washington, DC: American Association of State Highway and Transportation Officials.
2. AASHTO. 2022. Standard Method of Test for Determining the Total Pore Volume in Hardened Concrete Using Vacuum Saturation. AASHTO TP 135-22. Washington, DC: American Association of State Highway and Transportation Officials.
3. AASHTO. 2022. Standard Method of Test for Electrical Resistivity of a Concrete Cylinder Tested in a Uniaxial Resistance Test. AASHTO TP 119-22. Washington, DC: American Association of State Highway and Transportation Officials.
4. Then, N. W. (2021). Chloride Binding of Portland Limestone Cement containing Supplementary Cementitious Materials.
5. ASTM C1556-22: Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion. ASTM International, West Conshohocken, PA, 2022.
6. ASTM C1152/C1152M-20: Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete. ASTM International, West Conshohocken, PA, 2020.