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Comparison of different techniques to study the nanostructure and the microstructure of cementitious materials with and without superabsorbent polymers

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HIGHLIGHTS

- MIP, DVS, NMR and cryoporometry show the same trend in microstructure.
- The main nanometer pores have a size of 1.5–2 nm and 8–12 nm.
- There is a slight increase in the larger meso pore range when using SAPs.

GRAPHICAL ABSTRACT

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ABSTRACT

It is difficult to study the microstructural porosity in time without destroying the samples and stopping hydration. Current techniques mainly involve mercury intrusion porosimetry and microscopic analysis. These destructive techniques are able to give information on the microstructure, but the nanostructure is affected due to sample preparation. Dynamic vapour sorption is a technique which is not often used to study the nanostructure of cementitious materials and requires the application of different models. Furthermore, nuclear magnetic resonance can be applied to non-destructive study not only the total water content but also the pore size distribution by comparing the T_2 relaxation times, and can be combined with cryoporometry. In this paper, these different measuring techniques are compared and linked to each other. The obtained nano- and microstructures are compared to different models found in literature. Pore sizes in the range of 1.5–2 nm and of 8–12 nm are found, reflecting the gel pores. In addition, some bigger capillary pores are found. The measuring techniques are complementary to each other as they study different pore size ranges and are based on different phenomena.

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1. Introduction

Cement hydration causes the pore structure to evolve continuously over time. In time, the cementitious matrix is becoming

denser, affecting the nanostructure and microstructure of the material. It is interesting to study this change in porosity, but most techniques are destructive in nature and require sample handling [1]. In this paper, different techniques and their application on cementitious materials with and without superabsorbent polymers will be discussed. The techniques include Mercury Intrusion Porosimetry (MIP), Nuclear Magnetic Resonance (NMR) testing,

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complementary cryoporometry, microscopic analysis, and Dynamic Vapour Sorption (DVS).

SuperAbsorbent Polymers (SAPs) are interesting additives for the building industry [2–4]. Their application ranges from rheology modification [5] over internal curing of plastic shrinkage [6,7] and autogenous shrinkage [8–12] towards enhancement of hardened properties. They are able to increase the freeze-thaw resistance [13,14] and induce self-sealing [15,16] and self-healing [17,18] properties. As they are able to absorb a huge amount of liquid and to retain it, they will absorb part of the mixing water. To compensate for this absorption and the loss in workability, additional water is added to the mixture. By releasing their stored water for internal curing, they affect the microstructure of the material, mainly in the surroundings of a macro pore containing a SAP [19–21]. This effect is of interest and is the subject of this paper.

Due to the water release from the SAPs, there is further hydration and thus a decrease in micro-porosity at later ages [22] and in the amount of smaller capillary pores [23]. The existing pores are filled with hydration products and, as plastic and autogenous shrinkage are partially reduced, the micro-cracks in the interior of a cementitious matrix are reduced. Mercury Intrusion Porosimetry (MIP) and microscopic analysis [24,25] showed an increase in the total porosity due to macro-pore formation when SAPs and additional water are used. A lower total porosity was found for mixtures with SAPs without using additional water [22–24]. An important parameter for the mixtures with SAPs is the so-called effective water-to-cement ratio, comprising the water not stored in the SAP particles. The total water-to-cement ratio reflects the total amount of water, i.e., the sum of the effective water-to-cement ratio and the entrained water-to-cement ratio stored in the SAPs. Normally, when studying different mixtures with the same effective water-to-cement ratio, the capillary porosity should remain the same [26]. The amount of macro pores, however, will increase when using SAPs. All the above-mentioned studies conclude on capillary pores (10 nm–10 μ m). It would also be interesting to study the effects in the micro (<2 nm) and meso pore (2–50 nm) range. However, some authors believe that using MIP destroys the fragile microstructure, especially in the narrow range with the smallest pores, due to the high applied pressures [27–29]. The gel foils are displaced and the pores are widened and the neighboring pores are closed [30].

One way of studying the nanostructure without using high pressures is using water vapour sorption, the relation between the moisture content and the relative humidity, also called Dynamic Vapour Sorption (DVS) [31]. Upon increasing relative humidity, water molecules are adsorbed on a substrate – in this case a cementitious material – mainly on the oxygen containing groups [32]. When water molecules are adsorbed, they will act as secondary sites for further adsorption. This process continues until the water vapour clusters form layers and fill a micro pore. Next, the bigger meso pores will be filled. The relationship between the increase in mass of the sample and the relative humidity, the moisture sorption isotherm, provides information on the porosity after applying different models (see *infra*). The method needs a limited amount of small samples and can still be considered a destructive technique.

Nuclear Magnetic Resonance (NMR) is a powerful non-destructive technique to study the porosity and the water amounts in a material. Hydrogen atoms will interact with the pore wall and will cause the NMR signal to decay. The signal's relaxation rate is indicative to the microstructure and may be quantified and visualized [33] and can be applied to study the cement hydration [10,34]. The technique can be combined with cryoporometry as a complementary technique on the formed porosity [35]. Only a limited amount of studies has investigated the use of NMR to study SAPs and internal curing [7,10,36,37]. The results on microstructural

properties still need to be linked to other quantitative measuring techniques.

In this paper, different techniques are used to study the formed nano- and microstructure of cementitious materials. The obtained results are compared and the appropriate models to be used with DVS are discussed.

2. Materials and methods

In this section, the used materials and mixtures are discussed first (2.1), followed by the used measuring techniques: MIP (2.2), NMR (2.3), NMR combined with cryoporometry (2.4), microscopic analysis (2.5) and DVS (2.6). In this paper, the pore structure is classified as gel pores (<10 nm), capillary pores (10 nm–10 μ m) and voids (>10 μ m) [38–40]. A second way of classifying pores is according to micro pores (<2 nm), meso pores (2–50 nm) and macro (>50 nm) pores [41,42].

2.1. Materials

Two different types of SAP were investigated, being SAP A and SAP B, both from BASF. SAP A is a cross-linked copolymer of acrylamide and sodium acrylate with a size of $100 \pm 21 \mu$ m. SAP B is a cross-linked potassium salt polyacrylate and has a size of $477 \pm 53 \mu$ m. Both SAPs are bulk-polymerized and showed similar absorption capacities of 305 ± 4 and 283 ± 2 g demineralized water per g SAP, as determined using the filtration method [43], respectively for SAP A and SAP B. To determine the absorption of mixing water, the flow values of different mixtures with and without a predetermined amount of SAP were investigated. The influence on the flow values reflects the absorption in a cementitious material. These amounts were 23 g/g SAP A and 11 g/g SAP B in cement pastes with an effective water-to-cement ratio of 0.30.

Different cement pastes were studied, having an effective water-to-cement ratio of 0.30. The total water-to-cement ratio is the ratio of the total amount of water added over the total amount of cement. It comprises the entrained water content. The difference between total and entrained water is the effective water-to-cement ratio. This means that a system with an initial water-to-cement ratio of 0.30 and an imposed entrained water-to-cement ratio in the SAPs of 0.054 has a total water-to-cement ratio of 0.354, an entrained water-to-cement ratio of 0.054 and an effective water-to-cement ratio of 0.30. The amount of additional water needed to counteract autogenous shrinkage can be calculated using the Powers' model [44], leading to the entrained water amount of 0.054. Two reference mixtures were studied with an effective water-to-cement ratio of 0.30 (R0.30) and 0.354 (R0.354). A polycarboxylate type superplasticizer (Glenium 51, conc. 35%, BASF) was added in amounts of 0.5 (R0.30) and 0.3 m% (mass percentage) (R0.354) of cement weight (CEM I 52.5N, Holcim). Two different mixtures with SAPs were studied, having an effective water-to-cement ratio of 0.30 and a total water-to-cement ratio of 0.354. These were mixtures A_e and B_e with 0.22 m% (of cement weight) of SAP A and 0.45 m% of SAP B, respectively, based on the absorption of mixing water. The amount of superplasticizer was 0.5 m% of cement weight. All samples showed the same workability and were stored in sealed conditions at a temperature of 20 ± 2 °C until the age of the respective testing.

2.2. Mercury intrusion Porosimetry (MIP)

To study the capillary porosity in the range of 7 nm–100 μ m, Mercury Intrusion Porosimetry (MIP) was used on hardened samples with an age of 3 months. The equipment was a Pascal 140

and 440 series of Thermo Fisher Scientific Inc. As a specific pressure corresponds to an aperture of a pore, and the amount of mercury intrusion approximates to the pores' volume, the amount and size of the pores could be determined. MIP does not directly measure the amount of macro pores, but the macro pores of the SAP do show up in the total porosity. With this test, the total pore volume and the critical diameter, i.e., most frequent diameter in the sample, could be determined.

Stored samples were first crushed into samples of approximately 1 cm^3 in volume. These samples were subjected to liquid nitrogen and a subsequent lyophilisation period of 7 days, prior to testing. Freeze-drying was used as this is the main drying technique when performing MIP [45], even though the fragile microstructure may be affected [46].

2.3. Nuclear magnetic resonance (NMR) testing

Sealed sample containers with a diameter of 27 mm and a height of 100 mm filled with cement paste were put in the NMR setup. An external field of 0.8 T was applied corresponding to a proton frequency of 34 MHz. A coil was placed around the sample to create and receive radiofrequency fields during the NMR measurements. A magnetic field gradient of 0.3 T/m was used to offer a one-dimensional resolution of 1.0 mm. For a detailed description of the setup, we refer to [10]. The resulting measured relaxation was a complex summation of decaying signals. By means of Fast Laplace Inversion (FLI), the distribution of the relaxation times was found as a spectrum and could be analysed.

The peaks of the obtained signals were used to calculate the pore sizes using following relation [33]:

$$T_2 = \frac{V}{S \cdot \rho_2} \quad (1)$$

where V is the volume of the pore, S is the surface of the pore and ρ_2 is the surface relaxivity. When starting from planar pores with a diameter d , the planar volume-to-surface ratio is $d/2$ [34]. The surface relaxivity was assumed to be $3.73 \cdot 10^{-3} \text{ nm} \cdot \mu\text{s}^{-1}$ [34].

2.4. Complementary cryoporometry to NMR

Cryoporometry uses the melting point depression of a confined liquid in a pore. Whilst simultaneously performing NMR relaxometry measurements, the pore sizes can be estimated. The method can be used in the pore size range of 1 to 100 nm [35].

At 28 days and after being submerged for one day, specimens with a diameter of 20 mm and a height of 30 mm were vacuum saturated at 75 cm Hg. Subsequently, the specimens were super-cooled in liquid nitrogen for two hours. The samples were then quickly placed in a sample container with insulation at the top and bottom of the sample. A thermocouple was simultaneously inserted in the middle of the specimen through a pre-drilled hole and another thermocouple was placed at the exterior of the sample to investigate the thermal gradient in the sample. The sample container was placed in the NMR setup and the NMR signals were recorded in the middle of the specimen, as shown in Fig. 1. The first NMR signal was recorded at a temperature of -100°C . The total time to record all temperatures up to 20°C was approximately 2 h per sample. Afterwards, the specimens were stored in sealed conditions to perform the microscopic analysis.

2.5. Microscopic analysis

To study the amount of air voids and macro pores after conducting a cryoporometry test, thin sections ($20 \text{ mm} \times 30 \text{ mm} \times 25 \mu\text{m}$) were prepared from the cylindrical specimens at an age of 3 months, along the cylindrical axis. The sections were analysed with a microscope (Leica DMLP) mounted with a camera (DFC 295) under normal and fluorescent light. Normal light was used to characterize the formed SAP macro pores and to study their shape and size. Fluorescent light was used to quantify the amount of voids ($40 \mu\text{m} < \text{diameter } d$; macro pores and air voids), as the voids filled with fluorescent resin appeared as bright spots on a micrograph. Quantification of these bright spots gave the amount of macro pores. The cracking pattern due to performing cryoporometry was also studied and linked to the observed improvement in freeze–thaw resistance when using SAPs as an additive. Furthermore, a specimen with an air-entraining agent (AEA) was

Fig. 1. The NMR setup used to perform cryoporometry. A frozen sample of $\varnothing 20 \text{ mm}$ and 30 mm height was put in a sample container and insulation was put on the bottom and top to ensure a proper and steady temperature decrease.

made simultaneously to study the behaviour compared to a practically applied mixture with an AEA dosage of 0.025% by weight of cement to receive an air content of approximately 7% (not verified due to a small amount of cement paste) [13].

2.6. Dynamic vapour sorption (DVS) testing

DVS is technique, which is not often used to study cementitious materials. Using this technique, the equilibrium is measured of water vapour and the vapour adsorption of the sample. An important influence for the interpretation is the pre-conditioning of the sample. Some techniques require drying of the sample which will influence the microstructure, e.g. by introducing drying cracks and the collapse of C—S—H [45,47]. The best drying technique to preserve the fragile microstructure for DVS measurements is the solvent exchange with isopropanol followed by vacuum-drying [46].

At three months of age, the samples were crushed to particles of a size of about 500 μm to 1000 μm and put in isopropanol with a concentration of 100 (isopropanol): 1 (sample) for one week. Subsequently, the crushed part was wet-sieved between 500 μm and 1000 μm . Circular movement during sieving separated the lighter small SAP polymer particles from the cement paste particles (resemblance with gold panning) [20]. The paste particles were collected, rinsed with isopropanol and vacuum dried for 14 days in the presence of soda lime to exclude the effect of carbonation. The temperature was always at $20 \pm 2^\circ\text{C}$.

The specimens (5–10 mg cement paste particles) were put in the DVS equipment (Surface Measurement Systems, London, UK) and the RH was set by means of mixing dry and humid nitrogen gas, carried out at 20°C . The samples were first conditioned at 0% RH followed by a cycle of adsorption and desorption. The RH was increased once the mass criterion ($\text{dm}/\text{dt} < 0.002 \text{ wt\%/min}$) was reached [46] and were subsequently equilibrated at 0–1–2–5–10–20–30–40–50–60–70–80–90–95–98% RH for the adsorption branch. Rinsing of the sample with a phenolphthalein indicator after performing the DVS test proved that the samples did not show carbonation when being tested.

Different models can be applied on the obtained sorption curves and in this paper the model of Brunauer-Emmett-Teller for the specific surface area accessible to gas molecules (S_{BET}) determined on 10, 20 and 30% RH [48], the model of Dubinin-Radushkevich for the micro pore volumes ($< 2 \text{ nm}$) determined on 1, 2, 5 and 10% RH [41,49], and the model of Barrett-Joyner-Halenda in the meso pore range (2–50 nm) [50] were applied to study pores in the micro- and meso pore range. These models need to be further investigated for their applicability to obtain quantitative conclusions. In this way, solid conclusions may be drawn on the effects of SAPs on the nanostructure of concrete. There are still a lot of questions regarding the best quantitative description of capillary porosity [51]. More detailed and comprehensive data thus must be provided to establish improved correlations between different measuring techniques and the porosity.

The ratio of the water amount adsorbed by the cementitious particles to the water amount adsorbed by the C—S—H served as basis to determine the C—S—H gel amount [31]. Multilayer adsorption was determined to occur at a value of 20% RH. Two values were used as the boundary condition for the C—S—H content. These were 0.219 g per cm^3 of C—S—H at 22.8% RH [31] and 0.26 g per cm^3 of C—S—H at 20% RH [52]

3. Results and discussion

In this part, the different proposed methods are applied on the same mixtures and compared. First, NMR and MIP are compared

(3.1), followed by cryoporometry and microscopic analysis (3.2), and DVS (3.3).

3.1. Comparison of MIP and NMR results

As cement is hydrating in time, the water will be consumed and the hydration products will be formed. As a result, the material becomes denser. This can be studied by means of NMR. The obtained NMR water signal is formed from different signals with respective relaxation times. These T_2 relaxation values are investigated in this paper and served as a basis for the microstructural characterization. Preliminary research showed distinct peaks in reference systems [10]. In SAP systems, additional peaks in T_2 relaxation times are found and allocated to the SAP-entrained water, as these signals are not found in the reference systems. As the T_2 relaxation times are proportional to the pore size distribution following Eq. (1) [33], the pore sizes could be investigated starting from the T_2 values. The indexes of the peaks in the T_2 spectra, as found in [10] were multiplied with the surface relaxivity while assuming planar pores.

The pore-size results are shown in Fig. 2. In this figure, the x-axis shows the pore size in nanometres and the y-axis the time, starting from top to bottom, for all studied mixtures when hydrating. In time, a decrease in pore sizes is found, reflecting the densification of the cement paste due to hydration. The main pore sizes in reference systems are 1.5 nm to 2 nm and 8 nm to 12 nm. Some bigger capillary pores of 10 nm–1000 nm are found additionally.

The order of magnitude of the values correspond to those found by Müller et al. [34]. They addressed the found pores of 2.5 nm to gel pores and the 8 nm pores to interhydrate pores. Furthermore, there are different models describing the formed C—S—H within the cementitious matrix [51,53]. The Powers-Brunauer model focuses on colloidal particles, each containing a few closely-bonded structural layers, randomly arranged. The Feldman-Sereda model also considers the basic structural unit to be a layer but instead of forming particles, the layers are distributed randomly with nanometre-sized irregularities and interlayer spacings through the C—S—H. The Munich model is a physical model which considers discrete particles bonded together by van der Waals forces [51]. Another model describes C—S—H formed by spherical building blocks (2 nm) with a high specific surface area, which flocculate to form larger units [54]. It is believed that there are two types of C—S—H in the cement paste: a dense form near the clinker grains and a less-dense form which grows outwards into the pore structure [55]. Additionally, the Jennings Colloidal Model (CM-II) proposed three different pore size categories:

- Intraglobular pores ($< 1 \text{ nm}$);
- Small gel pores ($< 3 \text{ nm}$);
- Larger gel pores (3 nm–12 nm).

These categories are also found when studying the T_2 relaxation times.

In SAP systems, clear peaks in T_2 were assigned to the entrained water even though the sizes themselves do not correspond to the macro pore sizes of the swelling SAP particles. Smaller sizes are found with NMR. The respective macro pores found by means of image analysis on polished cross sections of hardened cement paste were $270 \pm 54 \mu\text{m}$ and for SAP A and $827 \pm 173 \mu\text{m}$ for SAP B [19,56]. The intrusion of solutes from the cement pore solution in the SAPs may lead to an increased relaxation due to paramagnetism. Secondly, the formation of precipitates in the SAPs may also cause the increase in relaxation [36]. Thirdly, the water molecules in SAPs may have a diffusive exchange with the water molecules at the interface of the cementitious matrix [37], especially

Fig. 2. Comparison of NMR and MIP results showing the pore size distribution [nm] as a function of the logarithm of time [days] for R0.30, R0.354, Ae and Be mixtures. The cumulative intrudable specific pore volume [mm^3/g] and the derivative $dV/d\log(D)$ [-] as a measure of the pore size distribution in the range of 7 nm–100 μm are shown as overlay graphs on the respective dot distributions.

Table 1

The accessible porosity [%], the total pore volume [mm^3/g], the average, the median and the first and the second modal pore size [nm] determined with MIP.

	Accessible porosity [%]	Total pore volume [mm^3/g]	Average pore size [nm]	Median pore size [nm]	First modal pore size [nm]	Second modal pore size [nm]
R0.30	3.01	13.73	30	38	13	44
R0.354	3.74	18.00	45	56	14	49
Ae	4.71	23.17	51	51	12	44
Be	4.74	23.31	34	45	12	39

when the particles themselves have an irregular size due to the production method, being bulk polymerization.

The NMR results were compared to the observed pore size distributions obtained with MIP. The results are shown in Fig. 2, together with the cumulative intrudable specific pore volume. The MIP mea-

surements cover pore ranges from 7 nm (due to the maximal possible applied pressure in the MIP setup) up to approximately 100 μm . The formed SAP macro pores are bigger than these sizes and only the smaller pores are found with MIP measurements. The macro pores, however, may occur in the total porosity (see infra).

The results show a good correlation with the observed 8 nm–12 nm peaks found with NMR. The smaller sizes found with NMR were not found with MIP but are likely to be observed if higher pressures are used when performing the MIP tests.

However, such high pressures may disturb the fragile microstructure [27]. Some larger pores are found in the SAP mixtures and may be the filling of some irregular parts of the macro pores or inkbottle effects.

Fig. 3. The obtained NMR signal intensity [a.u.] as a function of the increasing temperature and the relaxation times T_2 for R0.30, R0.354, A_e, B_e and AEA, respectively.

The accessible porosity, the total pore volume and the average, the median, the first and the second modal pore sizes for all mixtures as obtained by performing MIP measurements are shown in Table 1.

The accessible porosity and the total pore volume increase with an increasing water-to-cement ratio. Upon adding SAPs, the amount is also higher, due to the formation of macro pores. The amount is irrespective of the type of SAP as the same amount of entrained water was used. This means that the entrained water was consumed for internal curing purposes, after the time of final setting, as was confirmed in previous research [10].

The same first (most dominant) and the same second modal pore sizes were found for all studied mixtures. In addition, when comparing with NMR results, there is no difference for the different mixtures in observed size of pores in the lower nanometre range. A slightly higher median and modal pore size was obtained for the R0.354 mixture. Mixtures with the same effective water-to-cement ratio show approximately the same pore sizes. The capillary porosity is thus approximately the same.

3.2. Use of cryoporometry as a qualitative complementary technique

The results for the cryoporometry are shown in Fig. 3. In this graph, the intensity of a signal with a certain relaxation time T_2 is shown as a function of the increasing temperature. The observed temperature in the middle of the specimen and at the exterior did not vary more than 2 °C, both before and after the completion of one single complete NMR scan. When performing an empty scan, no significant signals were found.

Almost no signal is found below −70 °C and starting from this temperature, a signal starts to emerge. This is attributed to a layer of water molecules at the surface of the pore walls with approximate sizes of 0.35 nm and a relaxation time of 1 μs–300 μs [35].

From −60 °C onwards, this is linked to the dense gel pores with a size of around 1 nm [35]. At −20 °C an additional signal intensity occurs, corresponding to the open gel pores with a size of 1 nm to 10 nm [35]. At −10 °C, this signal increases in intensity as ice in the capillary pores is melting. These pores correspond to more than 10 nm in size [35]. In the AEA mixture, no larger pores are noticed. However, due to paramagnetism (see supra), the SAP intensities are found, starting to show melting around −20 °C. The results confirm the obtained microstructural parameters with NMR relaxation and MIP.

The crack patterns in the samples after performing cryoporometry are shown in Fig. 4. Abundant crack formation is found in the reference samples. In the sample with an air-entraining agent (AEA), the cracks are narrower and tend to follow the air pores. When adding SAPs, the same tendency is noticed and the cracks tend to follow the formed macro pores. The macro pores act as a crack initiator [57] and are thus beneficial as the macro pores become accessible for the expansion due to freezing. This led to the observed increase in freeze-thaw resistance [13].

The SAP macro pores could also be measured in size. The SAP A macro pores have a size of $253 \pm 66 \mu\text{m}$ and SAP B shows $891 \pm 194 \mu\text{m}$ wide macro pores ($n=100$). This corresponds to the previously found macro pore sizes of $270 \pm 54 \mu\text{m}$ and $827 \pm 173 \mu\text{m}$ for SAP A and SAP B, respectively [19,56]. This confirms that the correct amount of additional water was used. This water is then used for internal curing purposes, supported by the above-mentioned findings with the other experimental techniques.

3.3. DVS to study the formed nanostructure

The results for the DVS measurements are shown in Fig. 5. In the top part of the figure, the sorption isotherms are visualized.

Fig. 4. Fluorescent microscopic analysis on thin sections of the samples after performing cryoporometry, showing the porosity and the observed crack pattern for R0.30/R0.354, AEA, Ae and Be, respectively. The scale bars amount to 1000 μm.

Fig. 5. The dynamic water vapour sorption results for R0.30, R0.354, Ae and Be showing the mass water content as a function of the relative humidity (top) and the calculated microstructure with the BJH method.

The curves clearly show hysteresis as is expected in cementitious materials. The steep rise from a relative humidity of 60% onwards indicates that all samples have mainly meso pores, also typical for cementitious materials. The adsorption branch and the desorption branch are depicted but only the adsorption branch is studied. In the bottom part of Fig. 5, the calculated pore size distribution in the meso pore range by means of the BJH method is shown for all studied mixtures.

A higher water-to-cement ratio results in a relatively higher observed sorption isotherm. This is due to the expected higher amount of capillary porosity and a less fine pore network compared to a system with a lower water-to-cement ratio. This is also reflected in the pore size distribution as obtained with the BJH method, as shown in the lower part of Fig. 5. A clear peak is observed in all mixtures around 6 nm to 8 nm. The results tend to confirm the Jennings Colloidal Model (CM-II). When comparing the graphs of systems with SAPs and additional water, they are shifted upwards from the reference with the same effective water-to-cement ratio, especially in the range of 10 nm–12 nm, the larger meso pore range.

The results on the amount of micro pores as determined with the Dubinin-Radushkevich method, the amount of meso pores as determined with the Barrett-Joyner-Halenda model, the C–S–H

gel amount and the specific surface area are given in Table 2. The amount of micro pores is lower than the amount of meso pores, an intrinsic characteristic of a cementitious material.

Previous results show that cement pastes with SAPs and without additional water show a slight decrease in porosity in the micro- and meso pore range [20]. The cement pastes with SAPs and with additional water show no significant change of porosity in the micro pore range and a slight increase in the larger meso pore range. The micro pore amount of SAP samples tends to go towards the R0.354 system.

The amount of C–S–H gel, reflected by the gel pores, is higher with a higher water-to-cement ratio and also in mixtures with SAPs. This can be due to the further hydration by internal curing after the time of final setting. This causes a further densification of the C–S–H as stored mixing water is released by the SAPs towards the cementitious matrix during internal curing. The same trend is noticed when comparing the obtained specific surface areas and the values are typical values for cementitious materials reported in literature [31,44]. There are various types of water-filled spaces including nanometer-thick layers in between the C–S–H and the larger gel pores between the nanocrystalline regions, all in the nanoscale region. The C–S–H thus consists of a network of very fine gel pores giving it an extremely high specific surface area and making the total surface area determined by its C–S–H gel content.

4. Conclusions

Based on the obtained results in this paper, the following conclusions may be drawn:

- With NMR, most nanometer pores were found in the range of 1.5 nm–2 nm and with a size of 8 nm–12 nm. These can be attributed to the gel pores and the interhydrate pores, respectively. Some larger capillary pores are found in the range of 10 nm–1000 nm. The range in pore size of 8 nm–12 nm was also confirmed by MIP. Due to the limit of applied pressure, the smaller pores were not seen. DVS showed a clear peak in the pore size distribution around 6 nm–8 nm. The technique also showed an amount of micro pores.
- Cryoporometry is an interesting additional technique to state the range of pores in a cementitious material when heating a specimen after being supercooled. Qualitatively the method shows pores with a size of 1 nm, and 1 nm–10 nm. This is the expected range of pore sizes.
- The NMR and DVS results fit the Feldman and Sereda model and the Jennings Colloidal Model (CM-II) for C–S–H predicting intraglobular pores (<1 nm), small gel pores (<3 nm) and larger gel pores (3 nm–12 nm). They are both interesting methods to study the formation of the pores in a cementitious material over time.
- There is a slight increase in larger meso pore range noticed with DVS when using SAPs and additional water. There is no significant difference in the micro pore range but it is closer to the value of a reference with the same total water-to-cement ratio.

Table 2

The amount of micro pores [mm³/g], the amount of meso pores [mm³/g], the C–S–H gel amount [mm³/g] and the specific surface area (SBET) [m²/g] for all studied samples. The IUPAC pore classification is: micro pores (<2 nm), meso pores (2–50 nm) and macro pores (>50 nm).

	Amount of micro pores [mm ³ /g]	Amount of meso pores [mm ³ /g]	C-S-H gel amount [mm ³ /g]	Specific surface area (S _{BET}) [m ² /g]
R0.30	26.7 ± 2.4	87.5	127–182	109
R0.354	29.4 ± 2.6	95.4	141–201	128
Ae	28.1 ± 2.8	95.4	145–207	126
Be	29.0 ± 2.9	98.7	149–211	129

Fig. 6. The complementary techniques to study the porosity in cementitious materials.

- The SAP macro pores were seen in the accessible porosity and the total pore volume when using MIP. Microscopic analysis is also a good technique to study this pore range.
- The incorporation of SAPs leads to the formation of a system of macro pores, beneficial for the freeze-thaw resistance as is the case when using an air-entraining agent.
- DVS is able to provide information on the C–S–H gel amount and the specific surface area. Both are higher in mixtures with SAPs and additional water compared to the reference system with the same effective water-to-cement ratio and similar to a mixture with the same total water-to-cement ratio. This can be due to the further hydration caused by internal curing after the time of final setting leading to a denser C–S–H.
- The complementary techniques are able to provide information on the different classification of pores, as shown in Fig. 6.

Declaration of Competing Interest

None.

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Compliance with Ethical Standards

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