Influence of Drying on the Microstructure of Hardened Cement Paste: A Mercury Intrusion Porosimetry, Nitrogen Sorption and SAXS Study

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Abstract
Since the durability of concrete depends on the paste matrix, a sound knowledge of its pore structure is required. The most common methods to investigate the microstructure like mercury intrusion porosimetry (MIP) and gas sorption require the removal of free water in the pore space. However, the different drying methods used for this task either do not remove all free water or remove also chemically bound water and thus alter the microstructure. Small-angle X-ray scattering (SAXS) is one of the rare methods which allows to investigate the microstructure without complete water removal. Therefore, in order to compare the effect of different drying methods on the pore structure, hardened OPC paste samples (w/c = 0.5) were investigated with MIP, nitrogen sorption and for the first time with SAXS, after different drying was carried out. Since specific surfaces obtained for SAXS showed a similar trend as for MIP and nitrogen sorption, it can be concluded that SAXS can be utilized to predict the influence of drying on these methods as well. Solvent exchange appears to be a drying method that preserves the microstructure well, since for this the largest specific surface was obtained.

1. Introduction
The durability of concrete structures depends on the pore structure of the paste matrix, whose permeability is a measure of the ingress of gases, water and dissolved substances, which can potentially cause damage. Therefore, a sound knowledge of the pore structure enables the assessment of the susceptibility of concrete to chemical and physical damage mechanisms and is the key to the development of more durable concretes. Due to the wide pore size distribution and the hydraulic properties of cement paste, the investigation of its pore structure poses a major challenge.

The most common method to investigate the pore structure is mercury intrusion porosimetry (MIP), as it covers a wide range of pore sizes present in hardened cement paste and is a relatively fast measurement technique. The principle of measurement is based on applying an increasing pressure to force the intrusion of the non-wetting fluid mercury into pores while measuring the intruded volume for each pressure. In addition to the pore distribution, also a specific surface area can be calculated (Rootare et al. 1967). In some rare cases, mercury is replaced by molten Wood’s metal, which is similar to mercury but solidifies when it is cooled after the measurement has been stopped, allowing to investigate the locations where it has been intruded at the last pressure step of the measurement (Willis et al. 1998).

Gas sorption is another method often applied to determine the pore structure of cement-based materials with nitrogen being the most common gas while water vapor and argon are only occasionally used. With this method only small pores are detectable, the actual size depending on the utilized gas. In addition to determining the pore distribution, by applying the Langmuir theory (Langmuir 1969) or more common the extended BET theory (Brunauer et al. 1938), a specific surface area can be calculated which is often used as a measure to characterize the porous structure.

Since all methods described above are based on filling the pore space with a substance, all water contained in the pores of the cement paste must first be removed by drying prior to measurement. The difficulty is to remove as much free water from the pore space as possible and at the same time as little chemically bound water as possible. In addition, the water should be removed without damaging the pore structure by capillary hydrostatic stresses due to receding water menisci. Various methods are used for this purpose, which alter the microstructure of the samples in different ways during the drying process and which are evaluated differently in literature, sometimes even contradictorily.
Oven drying is the most widely used drying technique for cement-containing materials (Korpa and Trettin 2006). The sample is usually either dried for 24 hours at 105°C under atmospheric pressure or the mass of the sample is periodically checked to monitor the drying process, as it is necessary for more gentle drying temperatures below 105°C, where the process takes longer. Once a constant weight has been reached, drying is considered to be complete. Typically, temperatures between 40°C and 105°C are used for oven drying of cement paste (Aligizaki 2006). Oven drying at 105°C makes it possible to remove the largest amount of water in a short time (Moukwa and Aitcin 1988). It is assumed that the pore water has fully evaporated after 24 hours (Aligizaki 2006). However, although this drying method is considered to be the most effective method for water removal, it is also the method that most strongly alters the microstructure of the hardened cement paste (Gallé et al. 2001). Konecny and Naqvi (1993) assume that the pore structure is destroyed during oven drying and Moukwa and Aitcin (1988) assume that oven drying at 105°C partially dehydrates the calcium silicate hydrate (C-S-H) phases. Young et al. (1998) suspect that hydration products of the cement paste dehydrate far below 105°C. According to Snoeck et al. (2014), the destruction of the fine pores and the decomposition of hydrate phases during oven drying lead to an increase in the surface area of the cement paste compared to more gentle drying methods.

For oven drying with low pressure, the sample is connected to a desiccator with a vacuum pump. The vacuum causes the water to evaporate at lower temperatures. Zhang and Glaser (2000) found that drying with low pressure even without heating causes an enlargement of the surface with simultaneous degradation of ettringite and monosulfates. Investigations by Gallé et al. (2001) show that the samples dried by vacuum have similar micro-cracks to those subjected to oven drying.

Another drying option represents a solvent exchange based on the exchange of the pore water by a non-polar or low-polar solvent with a lower surface tension than water. Following the substitution of the pore water, one of the other drying methods can be used to remove the solvent from the pores. It is assumed that this technique preserves the microstructure of the cement paste very well (Konecny and Naqvi 1993; Collier et al. 2008). In the case of isopropanol as a solvent, it is assumed in literature that there is no reaction with the hardened cement paste surface (Feldmann et al. 1991; Snoeck et al. 2014). However, for the comparison within a sample series, the rate of solvent exchange is an additional variable. This can lead to fluctuations in the test results if the pore water is not exchanged sufficiently (Taylor and Turner 1987).

Other drying methods are desiccant drying over silica gel or calcium chloride, D-drying and freeze-drying [see Aligizaki (2006) for further information]. Despite different opinions in literature, it seems that isopropanol exchange and freeze-drying are the best options. According to Konecny and Naqvi (1993), both methods have different advantages: while isopropanol replacement preserves the pore structure of the majority of pores better, freeze-drying preserves only very small pores with radii smaller than 5 nm better.

Even by means of some image analysis techniques like the one based on scanning electron microscopy (SEM) it is not possible to investigate the pore structure of an unaltered sample since low pressure has to be applied during the measurement. Thus, only a few methods like environmental scanning electron microscopy (ESEM) (Diamond et al. 1994), 1H nuclear magnetic resonance (NMR) relaxometry (Muller et al. 2012), X-ray computed tomography (CT) (Benz et al. 2000) as well as small-angle scattering (SAS) offer the possibility to probe unaltered samples.

The microstructure of hardened cement paste can be investigated by means of SAS – either small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS). Applying these methods, information about the inner surface area, the roughness of the inner surface and – depending on the measuring range – about different structures defining this surface can be obtained. The signal is caused by the formed contrast of structural objects like hydration products to their surrounding medium (i.e., pore space). Since this contrast is sufficiently good not only in the absence of free water, but also if the pore space is partially or even completely filled with water, even undried or only partially dried samples can be measured with this method. In fact, there are some studies investigating the influence of water saturation on the information obtained with SAS on the inner surface of hardened cement paste (Völkl et al. 1987; Beddoe et al. 1994; Thomas et al. 2008; Maruyama et al. 2017). However, so far the drying which is necessary for these studies was only carried out in one way in each study (usually with low pressure) since only the effect of various relative humidity (RH) levels was studied and not the effect of various ways to reach such a specific RH level.

In the present study the effect of different drying procedures on hardened cement paste samples of an ordinary Portland cement (OPC) is investigated. The samples are investigated with the two most common characterization methods: MIP and nitrogen sorption. In order to be able to perform a comparison with an undried reference sample, SANS measurements are also performed. With all three characterization methods the inner surface area can be investigated. This first comparative SAXS study of different drying methods, combined with MIP and nitrogen sorption, enables new insights into advantages and disadvantages of different drying methods and thus allows a better assessment of the information obtained on the microstructure of hardened cement paste.
Table 1 Physical properties and mineralogical composition of the employed cement.

| Physical Properties / Cement Composition | Specification / Method | Dimension | Value |
|-----------------------------------------|------------------------|-----------|-------|
| Specific weight                         | ISO 1183-3 (DIN EN ISO 1183-3:1999 2000) | [g/cm³]   | 3.136 |
| Blaine value                            | EN 196-6 (DIN EN 196-6:2018 2019)       | [cm²/g]   | 3 100 |
| Water demand                            | EN 196-3 (DIN EN 196-3:2016 2017)       | [mass %]  | 27.0  |
| Tricalcium silicate                     |                         | [mass %]  | 64.4  |
| Dicalcium silicate                      |                         | [mass %]  | 14.1  |
| Tricalcium aluminate                    |                         | [mass %]  | 5.3   |
| Tetraalcium aluminate fritre            |                         | [mass %]  | 2.2   |
| Free lime                               |                         | [mass %]  | 0.4   |
| Periclase                               |                         | [mass %]  | 0.7   |
| Quartz                                  |                         | [mass %]  | 1.4   |
| Arcanite                                |                         | [mass %]  | 1.0   |
| Apaththlitic                            |                         | [mass %]  | 0.1   |
| Gypsum                                  |                         | [mass %]  | 0.2   |
| Bassanite                               |                         | [mass %]  | 2.1   |
| Anhydrite                               |                         | [mass %]  | 2.8   |
| Calcite                                 |                         | [mass %]  | 2.8   |
| Syngenite                               |                         | [mass %]  | 0.3   |
| Srebrodolskite                          |                         | [mass %]  | 0.7   |
| Silcocarnottite                         |                         | [mass %]  | 1.5   |

2. Experimental

2.1 Raw materials and sample preparation

All investigations were carried out with an ordinary Portland cement CEM I 42.5 R according to EN 197-1 (DIN EN 197-1:2011 2011) obtained by Wittekind Hugo Miesbach Söhne KG. The cement composition and physical properties as well as the methods by which they were obtained are given in Table 1. Water to cement ratio w/c of the investigated hardened pastes was adjusted to 0.5, guaranteeing a high porosity. All pastes were prepared using tap water. Depending on the investigation method, three different sample geometries were used. Drilling cores (height 20 mm, diameter 15 mm) were measured with MIP and 1.5 g to 2.0 g granules [diameter 0.5 mm to 1.0 mm, as typically used, for example, by Belie et al. (2010) and Snoeck et al. (2014)] prepared therefrom were investigated by nitrogen sorption. For SAXS measurements thin plates (10 × 10 × 1 mm²) were cast in a small formwork and then the upper face was sanded by hand to obtain a thickness of approx. 0.7 mm suitable for SAXS measurements. All samples were stored under water at room temperature until the investigations were carried out after approx. 112 days.

2.2 Experimental drying procedures

In order to study the influence of drying procedures on the investigation of microstructure, hardened cement paste samples were prepared using different drying methods. The degree of drying was evaluated by determining the loss of mass of the samples during these procedures. After drying, samples were stored in sealed containers under nitrogen atmosphere to prevent hydration and carbonation.

As SAXS provides the ability to investigate samples without removing porous water, the sample called RT in the following was not subjected to a rigorous drying process. It was instead only mildly dried overnight at room temperature to obtain an approx. stable moisture content during the measurement process, similar as it would be with an actual concrete at room temperature. X-ray diffraction was used to ensure that no significant carbonation had occurred.

Pure oven drying was performed at three different temperatures in ventilated ovens regulated at: 40±2°C, 60±2°C and 105±2°C. Drying was performed at 105°C for 24 h (sample 105°C), which is the most common drying method and considered to be the most efficient method for complete removal of pore water and also as the most damaging to the porous structure (Gallé et al. 2001, Beaudoin et al. 2002). A presumably more microstructure preserving oven drying was carried out at 60°C and 40°C. These samples were weighed each day until the mass loss was less than 0.001 g per gram hardened cement paste and day. This criterion for mass constancy (Copeland and Hayes 1953) was reached after 11 days at 60°C (sample 60°C) and after 21 days at 40°C (sample 40°C).

Attempting to prevent possible carbonation during long oven drying, in addition, oven drying at 60°C with silica gel and applied vacuum (less than 1 mbar) was also carried out. In order not to interrupt the evacuation for weighing, the samples were dried for 11 days, just as for the previous described drying procedure without vacuum applied.

Finally, solvent exchange was also performed. Samples were stored for seven days in approx. twenty times their volume of isopropanol. For the first two days, isopropanol was replaced two times a day and from then on once a day. After that, isopropanol was removed either by oven drying at 105°C for one day (iso+105°C) or just at room temperature (iso+RT) for SAXS investigations.

2.3 Characterization methods

Mercury intrusion porosimetry (MIP) was used to compare porosities and pore distributions dependent of the drying procedure. The non-wetting fluid mercury is pressed into the pores of the dried sample under high pressure. For each pressure step, the corresponding pore access diameter d can be calculated from the respective injection pressure P assuming cylindrical pores according to the Washburn equation (Washburn et al., 1921):

$$ P = \frac{4 \gamma \cos \theta}{d} \quad (1) $$

MIP measurements were performed with a Micromeritics Autopore III 9420 mercury porosimeter with a maximum injection pressure of 400 MPa. Assuming a surface tension of mercury γ = 480 mN/m and upon
recommendation of Ma et al. (2014) $\theta = 130^\circ$ as the contact angle between solid and mercury, a minimum pore access radius of about 1.5 nm is reached. For each sample two measurements were performed and therefore for the calculated measures the average is given. The mercury porosity $\Phi$ is calculated as the ratio between the total injected mercury volume and the total sample volume. In addition, the bulk density $\delta$ can be determined as the ratio of sample weight and its bulk volume. In addition, an estimation of the specific surface of a sample can be made by calculating the volume work performed by the system to intrude the mercury in the pores with the Rootare-Prenzlow equation (Rootare et al. 1967):

$$S_{\text{MIP}} = \frac{1}{\gamma \cos \theta} \int_0^\infty P \, dV$$  \hspace{1cm} (2)

However, pore distributions and specific surfaces obtained by MIP measurements should not be considered as an actual representation of the pore structure since the whole volume of a pore is assigned to its diameter on the surface of the sample. This only gives a correct tally of volume vs. pore diameter using the Washburn equation if the biggest diameter of a pore is on the surface of a specimen and not if a large pore is just connected to the outside through a small cylindrical pore. Due to this effect, the volume of pores is attributed to smaller radii than the actual ones (Diamond 2000). The volume of small pores is thus overestimated at the expense of larger pores. Also, the assumption that all pores are cylindrical is an unrealistic simplification resulting in errors. However, a recent study by Muller et al. (2017) reported an ‘excellent agreement’ between capillary porosity determined by MIP and NMR and thus that the ‘ink-bottle effect’ does not pose a problem for MIP. Nevertheless, in the present study only pore distributions performed with the same method – showing the same systematic errors – are compared with each other.

Nitrogen gas sorption experiments were carried out at 77.3K (-195.7°C) using a Micromeritics ASAP 2000. Different drying procedures of the samples (see Section 2.2) were followed by a degassing step using the vacuum pump of the ASAP 2000 combined with five hours of heating to the temperature used for prior drying, which resulted in a final pressure of approximately 0.03 mbar, depending on the temperature. The area occupied by one molecule of nitrogen was assumed to be 0.162 nm². Specific surface $S_{\text{BET}}$ was calculated using the Brunauer-Emmett-Teller (BET) theory according to ISO 9277 (ISO 9277 2010). With the multipoint method (linear fit of 13 points) good linearity (correlation coefficient > 0.999) was obtained.

SAXS measurements were performed using a Bruker AXS Nanostar instrument with a Cu-KαS microfocus X-ray source operating at a current of 6 mA and a potential difference of 50 kV. The X-ray beam was focused and monochromated using a MONTEL optic. Parasitic scattering was removed by two 550 µm pinholes placed prior to the sample chamber. In order to minimize further drying and possible alteration of the samples, only the beam path before and after the sample chamber was evacuated and not the sample chamber itself. Scattered X-rays were detected on a two-dimensional VANTEC-2000 detector (Bruker AXS) build on MIKROGAP technology. A $q$-range of 0.10 nm⁻¹ to 2.27 nm⁻¹ was covered at a wavelength of $\lambda = 0.154$ nm, with the length of the scattering vector $q = 4\pi\sin(\theta)/\lambda$ and $\theta$ being half of the scattering angle 2$\theta$. Calibration of the $q$-scale, i.e., of the detector pixels to the respective scattering angle, was done using silver(I) behenate (obtained by Alfa Aesar). The 2D data were azimuthally averaged to obtain intensity profiles and the background scattering of the air was subtracted from the raw intensity profiles. For each drying condition measurements at three different positions of a sample were performed. In the following always the average of such three measurements is given.

Porod formalism was applied to a high $q$-range (1.27 nm⁻¹ to 1.86 nm⁻¹) of the intensity plots (Porod 1951). Therefore, a linear fit in the Porod plot $[I(q)q^4$ vs. $q^2]$ was performed for each measurement resulting in the Porod constant $C_p$ as the intersection with the ordinate and a fluctuation background $K$ as the slope according to the following equation with the Porod exponent $p = 4$:

$$I(q)q^4 = C_p + Kq^p$$  \hspace{1cm} (3)

Since an absolute calibration of the scattering intensity was not possible, the Porod invariant $Q$ was used to calculate the specific surface area $S_{\text{SAXS}}$. For this purpose, the porosity $\Phi$ and bulk density $\rho$ determined by MIP were also required:

$$S_{\text{SAXS}} = \frac{4\Phi(1-\Phi)C_p}{\rho}$$  \hspace{1cm} (4)

As the Guinier region could not be measured, the Porod invariant could not be determined exactly. Instead, a lower estimate of the value was carried out. The scattered intensity blocked by the beam stop was approximated by a constant intensity equal to the one of the lowest $q$-value accessible. Then the Porod background $K$ was subtracted and $Q$ was determined by integration of the resulting $I^*q^4$ vs. $q^2$ plot. The slope of the linear region in the double logarithmic scale of the $I(q)/I(q=0.1 \text{ nm}^-1)$ vs. $q$ plot equals the negative value of the Porod exponent $p$. Consequently, $p$ was obtained by linear fitting of this region. This exponent provides information about the fractal character of the interface between hardened cement paste matrix and pores probed with SAXS as reported, for example, by Schmidt (1991).

The concept of fractal geometry (Mandelbrot 1983) is used to describe irregular forms that are self-similar. This means, that if one magnifies a region of a fractal
object, the structure of the magnified region should be either exactly or approx. similar to the original region viewed at a lesser magnification (Winslow 1985). Thereby, the term ‘fractal’ stands for the fractional number of dimensions (Winslow 1985). The region (here q-range) where this fractal dimensions can be observed determines the ranges of magnification of this self-similarity (Winslow 1985). For the point collimation used in this experiment, values of \( p = 4 \) are related to smooth Euclidean surfaces while values \( 3 < p < 4 \) are related to surface fractals and values \( 2 < p < 3 \) indicate mass or volume fractals as shown by Allen and Thomas (2007), for example. The concept of fractal geometry allows to quantify the irregularity of a structure. Using \( p \), the dimension of surface fractals \( d_s = 6 - p \) and of mass fractals \( d_m = p \) can be determined. For example, \( d_s = 2 \) represents a smooth Euclidean surface with the surface dimension 2 (e.g., \( \text{cm}^2 \)) while \( d_s = 2.3 \) stands for a fractal surface whose surface dimension is a fractional number (e.g., \( \text{cm}^{2.3} \)) (Häußler et al. 2009) and \( d_s = 2.4 \) would mean an even more irregular structure. A higher surface fractal dimension is attributed to an increased roughness of the surface while a higher mass fractal dimension stands for a more open, porous structure (Winslow 1985, Beddoe et al. 1994).

It should be noted that the values of \( S_{\text{SAXS}} \) determined like this correspond strictly speaking only for fully dried and fully water saturated samples to the specific surface area. The specific surface area of samples only partially saturated with water could be obtained by the following equations taking into account the interfaces between the hardened cement paste matrix and the empty pores (wall – air) as well as between the matrix and the water-filled pores (wall – water):

\[
I(q)q^4 = 2\pi[(\rho_{\text{wall}} - \rho_{\text{air}})^2S_{\text{wall-air}} + (\rho_{\text{wall}} - \rho_{\text{water}})^2S_{\text{wall-water}} + Kq^4] 
\]

where

- \( S_{\text{wall-air}} \): specific surface area between wall and air
- \( S_{\text{wall-water}} \): specific surface area between wall and water
- \( \rho_{\text{wall}} \): electron density of wall
- \( \rho_{\text{air}} \): electron density of air
- \( \rho_{\text{water}} \): electron density of water

Since using these equations the specific surface cannot be obtained solely from SAXS and since the electron density of water and air are rather similar compared to \( \rho_{\text{wall}} \) (which is mainly determined by the electron density of calcium silicate hydrates (Aligizaki 2006)), sometimes the simplified equations 3 and 4 are used to obtain information about the inner surface of partially saturated samples, for example, as in the work of Völkl et al. (1987). However strictly speaking, these values are only apparent inner surfaces and the restrictions should be kept in mind when interpreting these values.

3. Results and discussion

3.1 Investigation with mercury intrusion porosimetry and nitrogen gas sorption

The microstructure of samples prepared with different drying procedures as described in Section 2.2 was investigated by means of MIP and nitrogen gas sorption. In Fig. 1 the most important range of the pore distribution measured by MIP (1 nm to 200 nm) is displayed as log differential pore volumes. In addition, the gravimetric determined mass loss by drying is given. All curves show a small dip at approx. radius \( r = 20 \text{ nm} \) which is an artifact produced by the MIP system. By comparing these measurements with a reference substance (Silica-Alumina, obtained by Micromeritics), it could be ensured that this artifact is identical for each measurement and has no effect on other measuring ranges. Since the main purpose here is to compare different samples that

\[
S_{\text{total}} = S_{\text{wall-air}} + S_{\text{wall-water}} 
\]

Fig. 1 Section of the pore distribution (log differential intrusion) for different drying conditions measured with mercury intrusion porosimetry, related to the mass loss by drying. Pore distribution changed dependent on the drying procedure. Note the small dip at approx. \( r = 20 \text{ nm} \) is due to an artifact of the MIP system. The following drying methods are compared: 40°C, 60°C, low pressure and subsequent heating to 60°C (lp_60°C), solvent exchange with isopropanol and subsequent heating to 105°C (iso+105°C), 105°C.
were measured identically, this artifact does not affect the interpretation.

As expected, mass loss increased with increasing drying temperature. Drying at 40°C resulted in the fewest mass loss of 15.1% and therefore the lowest removal of water. Increasing the temperature to 60°C increased the mass loss to 18.4%. Finally, most water removal was observed for 105°C, represented by a mass loss of 22.1%. Concerning the pore distribution determined by MIP, represented as log differential intrusion, increasing drying temperature is connected with a shift of the peak to larger pore radii from a maximum at approx. 35 nm at 40°C, over approx. $r = 50$ nm for 60°C and to approx. $r = 65$ nm observed at 105°C. In contrast, for pore radii smaller than 20 nm, there is practically no difference between these various drying temperatures.

Additional low pressure for drying at 60°C led to a mass loss of 20.6 %, an increase of 2.2 percentage points compared to drying at 60°C without vacuum. Also, the observed pore distribution changed. While the maximum pore radius is only approx. 5 nm smaller and the largest pore radius with significant intrusion also decreased about 20 nm, a substantial increase of pore volume between 15 nm and 2 nm was detected. Combination of solvent exchange with isopropanol and subsequent one-day heating to 105°C yielded with 21.6% a lower mass loss than without solvent exchange at 105°C. This is accompanied by a peak at a much smaller pore radius $r = 40$ nm. According to Konecny and Naqvi (1993) this implies that smaller pores are less damaged.

A frequently used parameter to characterize the pore structure is the specific surface area. While determining it from gas sorption measurements according to BET theory is a typical evaluation, calculating specific surface from MIP investigations is less common. Despite concerns about the resulting absolute values due to the overestimation of small pores and the assumption of cylindrical pores, this parameter can still be used to compare the results determined with the same method. For MIP measurements drilling cores have been probed instead of granules as for the gas sorption because using a single specimen avoids the intrusion of mercury between particles (in inter-particle voids) which could be confused with the porosity of the particles themselves (i.e., the intra-particle voids) (Aligizaki 2006; Hearn et al. 1992). In addition, crushing of samples in order to obtain granules may change the internal pore space, e.g., the volume of large pores will decrease when particles break along large pores (which would not affect nitrogen sorption) (Van Brakel et al. 1981). These reasons justify using different sample sizes for MIP and nitrogen sorption. Despite these systematic differences between the two characterization methods, comparing changes in a property like specific surface with varying sample pretreatment can provide valuable information about the effect of pretreatment and about the characterization method.

All drying procedures resulted in different values for the specific surface determined by MIP and gas sorption (Fig. 2). This is not surprising since different pore radii are accessible and different theoretical models are used. For both characterization methods the largest specific surface was determined for solvent replacement (iso+105°C), followed by low pressure combined with oven drying at 60°C and then the pure oven drying procedures. Assuming that the biggest difference between different drying methods is the preservation of small pores that mainly contribute to the inner surface, this implies that drying by solvent exchange is the gentlest drying method, followed by low pressure combined with heating to 60°C. This coincides with the conclusion drawn by Konecny and Naqvi (1993) as well as by Collier et al. (2008) who recommend solvent replacement with isopropanol as the drying method preserving the microstructure very well.

When comparing the two investigation methods, surface areas are often in good agreement. Deviation is usually reported for samples with large surface areas, whereby gas sorption provides the higher values (Aligizaki 2006). Winslow et al. (1974) attributed this to the fraction of the total pore space unintruded by mercury. Another explanation can be the role of the pore wall roughness (Aligizaki 2006). This roughness has less influence on the surface determined by MIP since this is calculated from the pore volume while in case of gas sorption more molecules are needed to cover the surface and therefore a larger surface is measured. In the present study, the samples with the largest surface areas (iso+105°C and lp_60°C) yielded much larger surface areas for nitrogen sorption than for MIP.

The influence of drying procedure on the specific sur-

![Fig. 2 Comparison of specific surface areas measured by MIP and gas sorption after different drying procedures. The influence of drying is more pronounced for gas sorption, although for both methods the same drying operations resulted in the largest $S_m$.](image-url)
face was much higher for gas sorption than for MIP. A possible explanation could be that with nitrogen sorption smaller pores are accessible and since they have a huge influence on the inner surface, the inner surface determined with gas sorption is more sensitive to changes of the pore structure caused by drying. However, Fig. 1 reveals clear differences in the pore distribution obtained by MIP as discussed before. These are not fully represented by $S_{\text{MIP}}$, which is a measure for the inner surface and not for the exact pore distribution.

Drying at higher temperatures resulted in larger BET specific surface, more than doubling from 40°C to 105°C. This observation contradicts findings by Snoeck et al. (2014) who obtained for six months old samples with water vapor sorption a larger BET surface for 40°C than for 105°C, which they explained with an increasing cracking and microstructure alteration with increasing drying temperature. A possible explanation could be the difference in the accessible pore range due to the different diameter of water and nitrogen molecules. One nitrogen molecule covers approx. 50% more area than a water molecule and can therefore enter less pore sizes. Therefore a change in surface area of the small pores cannot be detected with nitrogen (Winslow 1985) while a change of the surface area caused by larger pores is therefore overproportionally weighted.

3.2 Investigation with SAXS

In order to investigate further the influence of the type of drying method on the microstructure of hardened cement paste, samples prepared using the drying procedures given in Section 2.2 were measured with SAXS. Since this method does not require complete drying of the samples, it was also possible to measure a sample that was only stored over night at room conditions to obtain an approximately stable water content. The resulting intensities were normalized to the intensity of the smallest $q$-value measured to enable an easy comparison despite slightly different sample thicknesses influencing the absolute intensities (see Fig. 3). The smallest $q$-value was selected for normalization since in this region the curvature of the different data sets was most similar.

There is clearly a big difference in the shape of the curves between the dried samples and the undried sample (note the logarithmic scale). The scattering intensity of the undried sample (RT) almost decreases linearly with the logarithm of the modulus of scattering vector over the whole measured $q$-range, except for large $q$-values. Linear fitting resulted in a slope of approx. $-3.2$, i.e., $p = 3.2$. Values of exponent $p$ between three and four can be interpreted as a surface fractal whose fractal dimension is defined by $d_f = 6 - p$ as has been reported by Allen and Thomas (2007) and others, instead of a smooth Euclidean one. Since the linear range covers almost the entire measured $q$-range, the range of self-similar structures extends over a broad size range. In contrast, the dried samples have a more curved shape overall with only short linear segments and thus only narrow size ranges with fractal character. Linear fitting in the range between $q = 0.24 \text{ nm}^{-1}$ and $q = 0.46 \text{ nm}^{-1}$ (meaning structure sizes of approx. 20 nm to 25 nm) resulted for the dried samples in absolute values of exponents between $p = 2.2$ and $p = 2.7$ (see Table 2). These are considered as mass fractals (sometimes called volume fractals) where $p$ corresponds to the fractal dimension ($d_f = p$). The further $p$ deviates from three (i.e., the higher $d_f$ and the lower $d_m$ are, whereas $p = 2$ would again imply no fractal character), the greater becomes the fractal character of the interface which is attributed to an increased roughness of the surface (for surface fractals) or a more open, porous structure (for mass fractals) (Winslow 1985, Beddoe et al. 1994). For the structure size covered with this evaluation, the following change with drying was observed. The sample only dried at room temperature showed a very rough surface while the other samples exhibited mass fractals. 105°C and iso+RT showed a rather closed structure which gets more open, porous for 60°C and even more for iso+105°C.

This could be interpreted as follows: Pure heating at 105°C leads to coarsening of structures (Korpa and Trettin 2006) and therefore results in a rather closed mass fractal. The structure for drying at 60°C is more open, since there is less coarsening of the structure. Finally, iso+105°C shows the most open structure because there is the least coarsening induced by the milder drying. A
Table 2 Overview on mass loss obtained by drying; porosity $\Phi$, bulk density $\delta$ and $S_{MIP}$ obtained with MIP; $S_{BET}$ obtained by gas sorption as well as $S_{SAXS}$, exponent $p$ and fractal dimensions $d_m$ and $d_s$ respectively evaluated from SAXS. The following drying methods are compared: room temperature (RT), 40°C, 60°C, 105°C, solvent exchange with isopropanol and subsequent heating to 105°C (iso+105°C), solvent exchange with isopropanol and subsequent drying at room temperature (iso+RT), low pressure and subsequent heating to 60°C (lp_60°C).

| Method          | Mass Loss [%] | $\Phi$ [g/cm³] | $\delta$ [g/cm³] | $S_{MIP}$ [m²/g] | $S_{BET}$ [m²/g] | $S_{SAXS}$ [m²/g] | $p$ [-] | $d_m$ (-) | $d_s$ (-) |
|-----------------|---------------|-----------------|------------------|------------------|------------------|------------------|--------|-----------|-----------|
| RT              | -             | -               | -                | -                | -                | -                | -      | -         | -         |
| 40°C            | 15.1          | 27.8            | 1.58             | 27               | 11               | 156              | 3.2    | 2.8       | -         |
| 60°C            | 18.4          | 28.5            | 1.53             | 25               | 16               | 183              | 2.5    | 2.5       | -         |
| 105°C           | 22.1          | 28.5            | 1.53             | 27               | 25               | 189              | 2.7    | 2.7       | -         |
| iso+105°C       | 21.6          | 28.8            | 1.53             | 34               | 91               | 225              | 2.2    | 2.2       | -         |
| iso+RT          | -             | -               | -                | -                | -                | 241              | 2.7    | 2.7       | -         |
| lp_60°C         | 20.6          | 28.1            | 1.53             | 31               | 51               | -                | -      | -         | -         |

While increasing the drying temperature and pressure, the water removal rate increased significantly. However, the influence of solvent exchange before heating on the water content was reduced and the mass loss was in the same order of magnitude of differences determined by MIP. The increase in $I(q)/I(q = 0.1 \text{ nm}^{-1}) \cdot q^4$ with increasing $q$ implies the greatest effect of solvent exchange for small pores, showing the highest values of all drying methods for approx. $q > 1.7 \text{ nm}^{-1}$. Probably small pores are preserved best with this drying method. Using the Porod theory, internal surfaces can also be derived from SAXS investigations. These are shown in Fig. 5 and discussed in Section 3.3. However, their absolute values are subject to uncertainties due to the restrictions described under Section 2.2. In addition, for the calculation of $S_{SAXS}$, the porosities and bulk densities determined by MIP are required [see Eq. (4)]. Since they could not be determined for the only partially dried samples, for sample RT and iso+RT the values obtained for 40°C (the sample with the least water removed) were used. To compare a characteristic value that is independent of another method, instead of the specific surface, the quotient $C_\text{SAXS}/Q$, which is proportional to $S_{SAXS}$ according to Eq. (4), is also shown in Fig. 5. The similar structure should be expected from iso+RT, but remaining fluid (water or isopropanol) could influence the scattering in a way (changing the electron contrast for small pores) resulting in a similar fractal dimension than observed for pure heating. RT being the only sample showing a surface fractal could either mean that any type of drying results in a transition from surface fractal to mass fractal.

The trend observed here that samples with higher water saturation (RT) show surface fractals while samples with lower water saturation (iso+RT, 60°C and 105°C) exhibit mass fractals contradicts the findings of Winslow et al. (1995). They obtained for a broader range of the same order of magnitude of $q$ with increasing relative humidity a change from rough surface fractals ($d_s = 2.0$) to a smoother surface and at about 50% RH a crossover to rather closed mass fractals which get more open, porous until $d_m = 2.5$ at 100% RH. However, they obtained a similar trend as in the present study for smaller $q$-values. This indicates, that the fractal character of the sample RT in the present study is determined by the water content.

Differences between related data sets are emphasized when multiplying the normalized intensities by $q^4$ like in Fig. 4 as typically used. For example, by Thomas and his co-workers (Thomas et al. 2008). For small $q$-values, the shape just reflects the different fractal dimensions. For large $q$-values interesting differences can be observed. Here it can be seen, that all three drying procedures with heating involved (60°C, 105°C, iso+105°C) show a similar curvature except for the very large $q$-values (approx. $q > 1.5 \text{ nm}^{-1}$). As expected, severe heating to 105°C and milder drying at 60°C resulted in a similar curve shape with a greater deviation from RT for smaller temperature. Surprisingly, combined solvent exchange and heating at 105°C resulted in the greatest deviation from the curve of RT. The strong influence of heating becomes clear when comparing iso+105°C with the samples dried only by heating. Despite exchanging the solvent before heating, the shape of the curve is fairly similar to drying by only heating, although more pronounced. Only drying by pure solvent exchange without heating (iso+RT) resulted in a different curvature.
values are normalized to that of the undried sample as a reference to allow for easy comparison. However, a comparison of the normalized quotient \( C_P/Q \) with \( S_{\text{SAXS}} \) shows that the influence of porosity and bulk density is relatively small since both plots exhibit a similar trend. Drying by solvent exchange with isopropanol (iso+RT and iso+105°C) resulted in the largest normalized \( C_P/Q \). Within the framework of the SAXS investigations, a distinction was also made as to whether the isopropanol was subsequently removed at 105°C or only at room temperature. The latter led to the highest value, 50% higher than RT. The samples prepared with oven drying showed lower normalized values than with solvent drying. While most publications usually argue that the drying method which yields the largest specific surface area changes the pore structure least, for example, in the works of Collier et al. (2008) and Snoeck et al. (2014), here it seems to be the other way round. Only the sample 60°C shows a similar value for \( C_P/Q \) as the undried sample. This can at least to some extent be explained by the only partial drying. It is well known that such a partial drying results in a smaller specific surface area measured with SAXS as has been demonstrated, for example, by Winslow et al. (1995), though both pores filled with water and air can be detected. This is attributed to shrinkage of the gel pores caused by a reduction in disjoining pressure (Völkl et al., 1987). Although, Völkl et al. obtained for 2.5 year old samples only a decrease in specific surface due to incomplete drying in adsorption of about 15%. In contrast, the difference between the largest value obtained and the one for the undried sample in the present study is approx. 50%. Although X-rays are both scattered at pores filled with water and with air, the electron contrast is different in both cases and so is the scattering. To prevent this, sometimes dried samples are re-saturated with water to ensure a constant electron contrast as reported by Thomas et al. (2008), for example. In this study, though, priority was given to examining the samples in the state in which they are analyzed by MIP and nitrogen sorption and thus were not re-saturated.

### 3.3 Comparison of all methods

Comparing the specific surfaces of samples after preparation with different drying methods, the same trend is observed for determination with MIP, nitrogen sorption and SAXS (see Table 2). Solvent replacement with isopropanol yielded the largest surface area followed by drying at 105°C and drying at 60°C gave the lowest specific surface. This is surprising, since it is believed that both at 105°C and at 60°C capillary hydrostatic stresses due to surface tension of the receding water menisci and removing of non-evaporable water due to dehydration of hydration products alters the microstructure (Snoeck et al. 2014). Since mass loss by drying at 40°C was less than by solvent replacement, this is maybe due to lack of water removal in small pores.

Also noticeable is the very big difference in the absolute values. The differences between MIP and nitrogen sorption have already been discussed in Section 3.2. As far as SAXS is concerned, it is known that this method provides very large surfaces, for example, in the work of Thomas et al. (1999). The main reason is the different fraction of pores that are detectable. While with MIP and gas sorption only pores are accessible which are interconnected to the surface by necks large enough to intrude for the mercury or gas, with SAXS also isolated pores are detectable (Aligizaki 2006). Due to the difference between open and closed porosity, the specific surfaces determined by these different characterization methods are a fundamental different physical measure. Depending on the current scientific/technical question, one or the other type of specific surface may be more helpful. Since the same pattern of specific surface values was found here for the three characterization methods, this demonstrates that SAXS is suitable for investigating the influence of different drying methods on the microstructure.

Comparing the methods applied in the present study with other typical methods like NMR, SANS and water vapor sorption results in a more complex picture. With NMR and SANS similar values of the specific surface area are obtained which are lower than the values determined with SAXS, although all three methods detect open and closed pores (Thomas et al. 1999). The difference between SAXS and SANS is attributed to the fact that the surface area is sensitive to the morphology of the C-S-H gel phase (Thomas et al. 1999). Water vapor sorption interestingly gives larger inner surfaces than sorption with any other liquid or gas (including mercury and nitrogen) and the differences are greater than ex-

![Fig. 5 Influence of different drying conditions on the quotient $C_P/Q$, which is related to surface area, normalized to the value obtained for room temperature (RT). Comparison with absolute values of $S_{\text{SAXS}}$ shows the influence of porosity and bulk density.](image-url)
pected when considering the different diameters of the molecules (Thomas et al. 1999). Surprisingly, specific surface areas determined with water vapor sorption of dried paste are in the order of magnitude of values obtained with SAS (Winslow et al. 1974), although closed pores should not be detectable. Since water vapor results are – against expectation – independent of w/c, Thomas et al. (1999) suggest to use other methods. In the light of the comparison of these different methods, it seems that it is not only important to distinguish whether a method can detect closed porosity in addition to open pores, but also how sensitive it is to changes in the morphology of the C-S-H gel phase.

In addition, the SAXS results offer a possible explanation for the large difference between surface areas found by MIP and nitrogen sorption for the sample dried with solvent replacement and subsequent heating to 105°C (iso+105°C). This sample showed by far the highest fractal character of the dried samples (\(d_{\text{fr}} = 2.2\), \(p\) deviates the furthest from three) and thus a rather open, porous structure. Hence this open structure, which has a much higher influence on gas sorption than on MIP, could actually be responsible for the larger BET surface.

4. Conclusions

The effect of different drying procedures on hardened cement paste samples of an OPC has been investigated by means of MIP, nitrogen sorption and for the first time with SAXS. Measurements with MIP revealed different pore distributions but only small differences in surface area for various drying procedures. In contrast to this, nitrogen sorption showed large differences in \(S_{\text{BET}}\).

Using SAXS, similar intensity distributions and thus similar pore structures for the measuring range were observed for all samples subject to a kind of oven drying, even after solvent replacement. Only solvent replacement without oven drying resulted in a different curvature. Although, the sample only air-dried overnight at room temperature exhibited a completely different intensity distribution, more or less linear without showing any features, except for higher \(q\)-values.

As expected, SAXS measurements yielded much larger surface areas than MIP and gas sorption. However, all three methods provided the same order of surface areas: solvent exchange and subsequent drying to 105°C lead to largest surface areas followed by drying at 105°C and finally drying at 60°C. This implies, that solvent exchange is the drying method which best preserves the microstructure.

This study shows that despite the fact that SAXS also measures closed pores, the influence of different drying methods on MIP and gas sorption can be investigated. This provides new insights into the alteration of hardened cement paste microstructure and therefore the reliability of data determined with MIP and gas sorption. In ongoing approaches, SAXS studies will be extended to more drying methods and the measured \(q\)-range will be broadened. Finally, samples will be re-saturated with water after drying to study whether this re-saturation has a different influence on samples prepared with different drying procedures.

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**List of notations**

- $C_P$: Porod constant
- $I$: scattering intensity
- $K$: fluctuation background
- $P$: injection pressure
- $Q$: Porod invariant
- $d$: pore diameter
- $d_m$: mass fractal dimension
- $d_s$: surface fractal dimension
- $p$: exponent of Porod Fit
- $q$: modulus of scattering vector
- $r$: pore radius
- $S_{BET}$: specific surface per mass determined with gas sorption using BET theory

- $S_{MIP}$: specific surface per mass determined with MIP
- $S_{SAXS}$: specific surface per mass determined with SAXS
- $S_{wall-air}$: specific surface area between wall and air
- $S_{wall-water}$: specific surface area between wall and water
- $\gamma$: surface tension
- $\Delta \rho$: scattering contrast
- $\theta$: scattering angle
- $\lambda$: wavelength
- $\delta$: bulk density
- $\Phi$: porosity
- $\rho_{air}$: electron density of air
- $\rho_{wall}$: electron density of wall
- $\rho_{water}$: electron density of water