



Effects of magnesium content and carbonation on the multiscale pore structure of alkali-activated slags

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ABSTRACT

While CO₂-resistant cement materials are crucial in oil and gas industries, the CO₂ emissions associated with manufacturing oil-well cements have necessitated the development of lower-CO₂ alternatives with enhanced carbonation resistance. A higher magnesium content blast furnace slag precursor for alkali-activated slag (AAS) has been shown to increase resistance to accelerated carbonation-induced degradation. This investigation assesses the effects of sample age, AAS magnesium content, and carbonation (exposure to 100% CO₂) on the multiscale pore structure of AASs (nanometers to microns). The pore size distributions and diffusion tortuosities of ordinary Portland cement (OPC) and silicate-activated slag pastes are obtained through the techniques of nitrogen sorption, mercury intrusion porosimetry, and X-ray microtomography. These pore morphology properties show AAS to be more resistant to pore structural degradation following accelerated carbonation than OPC, and increased magnesium content in AAS is shown to improve its resistance to gel decalcification and capillary pore formation during carbonation.

1. Introduction

Concrete is an indispensable material for construction and infrastructure, and is the highest-volume product consumed by humans after water [1]. However, concrete production comes with a significant environmental cost due to its extensive utilization around the world: a large carbon footprint. Production of ordinary Portland cement (OPC), the most commonly used concrete binder material, accounts for 5–8% of all anthropogenic CO₂ emissions [2]. Recently, alkali-activated materials (AAMs) that use recycled industrial waste products or calcined clays as precursors have been investigated as sustainable alternatives to OPC. Alkali-activated slags (AASs) are a promising class of AAMs that are manufactured by mixing an alkali activator (such as sodium silicate) with ground granulated blast furnace slag (denoted as slag from hereon), a steel-making byproduct. Due to the recycling of slag, an industrial waste product, the production process of AAS releases 80–90% less CO₂ than that of OPC on a binder basis [3]. Although AASs have been gaining popularity in construction projects, a lack of knowledge on their long-term durability and resistance to degradation prevents more widespread usage. Furthermore, due to the limited availability of slag around the world together with its existing usage in OPC-based concrete, diversion of this resource to an alternative cement must be accompanied by extensive proof of the overall benefit to

society (e.g., mitigation of rogue emissions by capping abandoned oil-wells with carbonation-resistant AAS may offset the increased CO₂ emissions from OPC concrete as a result of the slag diversion) [3].

Carbonation is a common degradation process for both OPC- and AAS-based concretes. Carbonation occurs when CO₂ diffuses into, and lowers the pH of, the pore solution of a cementitious material [4]. In OPC, the pH is initially maintained at ~12.5 by the buffering effects of portlandite, while in AAS it has been shown that a hydrotalcite-like phase mitigates carbonation by acting as a sorbent for CO₂ [5]. However, once these phases are exhausted (loss of portlandite in OPC and CO₂ saturation of the hydrotalcite-like phase in AAS), this acidification causes decalcification of the strength-giving calcium-silicate-hydrate (C-S-H) gel in OPC, or sodium-based calcium-alumino-silicate-hydrate (C-(N)-A-S-H) gel in AAS [4,6,7]. The acidification also leads to the precipitation of crystalline calcium carbonate (CaCO₃) in both AAS and OPC [4,7]. Carbonation proceeds with simple exposure to air, but is accelerated in high CO₂ environments such as in the petroleum industry and in CO₂ geological storage applications [8]. This form of degradation is particularly dangerous for oil-well cements that are directly exposed to supercritical CO₂ and whose failure would lead to costly and environmentally harmful oil and gas leaks [9,10].

Traditional OPC is highly susceptible to accelerated carbonation damage due to the rapid dissolution of portlandite and subsequent

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decalcification of C-S-H gel [11,12]. For C-S-H and C(N)-A-S-H gels, both natural and accelerated carbonation have been seen to cause degradation of the binder resulting in an amorphous silica or aluminosilica gel while leached calcium arranges into an amorphous calcium carbonate (ACC) phase [13,14] before rapidly transforming into a more stable crystalline phase such as calcite or vaterite [15]. More recently, we have shown that an increased magnesium content improves the resistance of AAS to carbonation by decreasing the extent of C(N)-A-S-H gel decalcification [7]. This mitigation is likely made possible by the formation of a Mg-stabilized ACC phase. ACC possesses a higher solubility product ($K_{sp} = 10^{-6.39}$) than either calcite ($K_{sp} = 10^{-8.48}$) or vaterite ($K_{sp} = 10^{-7.91}$) and thus causes more Ca^{2+} ions to be present in the pore solution [16,17]. A higher Ca^{2+} concentration in turn prevents further leaching and decalcification of the C(N)-A-S-H gel as the system equilibrates with carbonates in the pore solution.

While Mg-stabilized ACC may offer resistance to carbonation, the AAS paste may have a higher susceptibility to subsequent chemical damage caused by sulfate attack or chlorides if the pore structure of AAS paste were to change [18]. Many studies have investigated the influence of precursor composition, chemistry of the activating solutions, and curing conditions on the strength and performance of AAMs [1,19–22]. However, few studies have offered a comprehensive picture on the permeability and pore structure of AAMs across length scales and how these attributes are affected by degradation. It has been shown for OPC that the pore size distribution, particularly in the mesopore region (2–50 nm), dictates the intrinsic permeability of cement [23,24]. However, such conclusions have yet to be drawn for AAMs, as pore size distributions are usually only investigated with one technique at a time. Each technique has access to a limited range of length scales (e.g., nitrogen sorption for micro- to mesopores and mercury intrusion porosimetry (MIP) for meso- to macropores, see Table 1 for pore size classification). It is crucial to understand the pore behavior from gel pores to large, interconnected capillary pores to determine how material characteristics are affected, such as transport properties, compressive strength, and susceptibility to harmful ions.

Previously, Shi et al. showed, using MIP analysis, that silicate-activated AAS paste possesses a lower overall porosity than that of OPC paste [26]. Furthermore, a majority of AAS porosity is accounted for by micro- to meso-pores with a smaller fraction being attributed to capillary pores. The opposite is true for OPC paste where macropores account for more than half of the paste porosity [27]. However, AAS experiences much more drying shrinkage than OPC which can result in significant cracking unaccounted for in nitrogen sorption and MIP powder experiments [27]. Nitrogen sorption and beam bending experiments have shown that for AAS, the percolated pore network is controlled by pores around 3 nm in size when activated with a silicate solution and by pores 50 nm in size when activated by a hydroxide solution [28]. In addition, extensive research based on OPC systems has shown that drying methods greatly influence the PSD obtained through

MIP and nitrogen sorption [29]. Oven-drying has been shown to significantly increase the sample porosity by evaporating structural water from the C-S-H gel and other hydrates, while solvent exchange and vacuum drying have been shown to alter the pore size distribution to a smaller degree [30]. Hence, care must be taken when comparing pore size distributions from the literature, since different drying methods may have been utilized, leading to non-material-based differences arising in the data.

In recent years, noninvasive techniques such as X-ray microtomography (μCT) and small angle scattering (SAS) have been explored as alternative pore structure characterization methods for cementitious materials [31–34]. In these techniques, a paste sample does not need to undergo any further drying treatment before analysis, thus preserving its morphology. However, both methods have historically required access to a neutron or synchrotron source for analysis. While both methods have been used extensively to study the pore structures of OPC and C-S-H gels, few studies have been performed on the AAS system. In addition, no studies of μCT analysis have been performed on carbonated AAS pastes.

This study examines the pore size distribution and diffusion tortuosity of low- and high-Mg AAS and OPC paste using nitrogen sorption, MIP, and X-ray μCT . Nitrogen sorption and MIP can elucidate the pore size distribution from micro- to mesopores and meso- to macropores, respectively, however both methods require extensive drying and crushing of the sample that may cause potential damage to the pore structure. Alternatively, μCT can produce a 3D reconstruction of a cured, intact sample with no additional preparation, with the voxel size obtained during the reconstruction process dictating the smallest pore feature that can be resolved ($\sim 0.7 \times 0.7 \times 0.7 \mu\text{m}^3$ on a laboratory-based μCT instrument). As is the case with MIP data, μCT can be utilized to calculate the total porosity of macropores, however, porosity attributed to pores smaller than the resolution of the instrument cannot be detected using μCT unless assumptions are made regarding the level of porosity associated with different solid phases identified from the grey scale values (e.g., gel porosity associated with C(N)-A-S-H gel). Additionally, a random walker method can be implemented in the reconstructed pore-space to calculate the tortuosity of the larger capillary pores [31].

Here, low- and high-Mg AASs (synthesized using ~ 7 and 13 wt% MgO slags) together with OPC paste are investigated using nitrogen sorption, MIP, and X-ray μCT , with the aim to discover how the magnesium content of the slag, and the associated formation of a Mg-stabilized ACC during accelerated carbonation, affect the resulting pore structure of the carbonated AAS. Firstly, the evolution of the multiscale pore structure during curing (1 to 180 days for AAS, 1 to 7 days for OPC) is elucidated using nitrogen sorption and MIP. These data are then used as references for quantification of the impact of accelerated carbonation on the pore structure, where exposure to CO_2 has been carried out at 1, 3, 7 and 180 days for the AAS pastes and at 1, 3 and 7 days for the OPC paste. In addition to nitrogen sorption and MIP analysis of the uncarbonated and carbonated pastes, the pastes at 7 days before and after carbonation are analyzed using μCT . The measured pore size distributions (from nitrogen sorption, MIP and μCT) and porosities and tortuosities (from μCT) reveal the impact of magnesium content of the slag on the susceptibility of AAS to chemical attack after exposure to accelerated carbonation conditions, together with the performance of AAS in comparison with OPC paste.

2. Materials and methods

2.1. Materials

Two types of slag were used as the AAS precursor with the main difference being their MgO contents (low- and high-Mg slag), as determined in a previous study using X-ray fluorescence (XRF, Table 2) [7], together with Type I OPC powder.

Table 1

Pore size classification by IUPAC and by Mendiss [25] for cement pastes. The cutoff between large gel pores and medium capillary pores is somewhat arbitrary.

Type of pore	Description	Size (diameter)	IUPAC pore classification (diameter)
Other features	Microcracks	50–200 μm	–
	Interfacial transition zone ^a	20–50 μm	
Capillary pores	Large	10 μm –50 nm	Macropores (> 50 nm)
	Medium	50–10 nm	Mesopores (2–50 nm)
Gel pores	Small	10–2.5 nm	Micropores (< 2 nm)
	Micropores	2.5–0.5 nm	
Interlayer spaces	Structural	< 0.5 nm	

^a Only applies when aggregates are present.

Table 2

Oxide composition (wt%) of two sources of slag, as determined using XRF [7].

Slag source	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	(Ca + Mg)/Si molar ratio	Mg/Ca molar ratio
13% MgO	26.1	34.5	10.5	12.7	2.7	1.67	0.49
7% MgO	42.5	34.5	11.5	7.3	1.7	1.64	0.24

Table 3

Sample naming convention for AAS and OPC pastes (sample type, age, and carbonation status).

Sample type	LMg	AAS synthesized using low-Mg slag (7 wt% MgO)
	HMg	AAS synthesized using high-Mg slag (13 wt% MgO)
	OPC	Ordinary Portland cement paste
Sample age	1	1 day old
	3	3 days old
	7	7 days old
	180	180 days old (mature sample)
Carbonation status	–	Uncarbonated
	carb	Carbonated

Example sample name: LMg1 carb – Low-Mg AAS carbonated after 1 day of curing.

AAS pastes were prepared by mixing slag with a sodium silicate alkali activating solution to obtain a Na₂O-to-slag weight ratio of 0.07 and a water-to-slag weight ratio of 0.50. The activating solution was prepared by mixing PQ Corporation Type D sodium silicate solution with the appropriate amount of deionized water and sodium hydroxide (reagent grade, Sigma-Aldrich) to achieve a SiO₂/Na₂O molar ratio of 1. The silicate solution was stirred for 24 h using a magnetic stirrer bar to reach equilibrium. OPC paste was prepared with a water/cement weight ratio of 0.50. Precursor powders and activating solutions were mixed at 1200 rpm for 90 s using a vortex mixer. Pastes were then poured in plastic cuvettes, sealed, and placed on the vortex mixer for an additional 30 s to remove air bubbles. The pastes were allowed to cure for 1, 3, or 7 days at room temperature to determine the dependence of pore structure on sample age. 180 day (6-month-old) mature samples were also prepared for both types of AAS. The naming convention used for the samples is described in Table 3.

For accelerated carbonation, samples were placed in a plastic tube and exposed to a 13 mL/s flow of 100% CO₂ from an industrial grade CO₂ gas cylinder for 24 h. A mineral oil bubbler was placed on the exhaust end of the plastic tube to prevent air from entering the carbonation chamber. Samples to be used for nitrogen sorption and mercury intrusion porosimetry experiments were ground and sieved to include only grains with diameters between 0.5 and 1.0 mm prior to carbonation. Samples to be used for μ CT were cured in a 0.5 mm inner diameter polyamide capillary tube and placed into the carbonation setup following curing. Carbonation of the samples was performed in a fume hood at ambient temperature and pressure.

2.2. Sample preparation for nitrogen sorption and mercury intrusion porosimetry

The dried and hardened pastes were removed from the plastic cuvettes and ground by hand using a mortar and pestle into coarse grains. The grains were sieved to include only the 0.5 to 1.0 mm diameter fraction. The grains were then submerged in isopropanol (IPA) for 48 h to halt the curing reaction and allow for solvent exchange before being dried under vacuum for a minimum of 48 h at ambient temperature. For carbonated samples, the grains were placed in the carbonation setup for 24 h before IPA exchange.

2.3. Nitrogen sorption

Samples were first degassed at 60 °C to 5.0 μ m Hg on a Micromeritics Smart VacPrep 067 before analysis. Nitrogen adsorption and desorption analyses were performed on a Micromeritics 3Flex instrument. Isotherms were analyzed using the BJH (Barrett-Joyner-Halenda) method [35] through the Micromeritics 3Flex software. Pore size distribution information was collected for pore diameters from 0.8–150 nm. Only pore size distribution data for pore diameters from 1 to 100 nm were used due to high intrinsic uncertainty at high relative pressures for nitrogen sorption. Nitrogen sorption results are presented in mL/g.

2.4. Mercury intrusion porosimetry

Samples were degassed to 200 μ m Hg and analyzed in a Micromeritics AutoPore V instrument. A model 10 5 cc powder penetrometer was used for all samples. Low pressure analysis was performed for pressures up to 30 psia and high pressure analysis was performed from 40 to 60,000 psia (0.28–413 MPa). Pore size distributions were collected for pore diameters 3–350,000 nm in size. Only pore size distribution data for pore diameters from 3 to 10,000 nm were used, since at larger diameters it is impossible to differentiate macropores from interparticle space filling. Mercury intrusion results are presented in mL/g. Bulk density values obtained from MIP are available in the Supplementary material.

2.5. X-ray microtomography sample preparation and data collection

AAS and OPC pastes were cured for 7 days in polyimide capillary tubes with a 0.50 mm inner diameter. Only 7-day old samples (rather than 1-, 3- and 7-day old samples) were imaged to prevent significant curing or morphology changes during the scan-time. For carbonated samples, the capillary tubes containing the pastes were placed in the carbonation setup for 24 h prior to imaging. A 24 hour exposure time to CO₂ was deemed sufficient for full sample carbonation, as powder AAS samples have been shown to reach equilibrium in a 100% CO₂ gas environment in ~40 min [7]. In addition, drying stresses create cracks that run down the length of the capillary tube and into the dried paste, thus increasing the exposure of the sample interior to CO₂.

X-ray μ CT was performed on a ZEISS Xradia 510 Versa, using a voltage of 40 kV, an exposure time of 75 s for each scan, a 20 $\times$ objective lens, and a binning of 2. In addition, a low energy filter was used. A long exposure time was necessary for sufficient image contrast at a recommended 5000 counts/voxel. 2001 projections were taken at a constant step angle size resulting in a measurement time of 41 h per sample, and a resolution of 1.02–1.17 μ m. Scan reconstruction and conversion to 2D image slices was performed on the Xradia Versa 520 Reconstructor Scout-and-Scan software.

The μ CT data were exported as 8-bit TIFF images of slices in the XY plane (perpendicular to the length of the capillary tube). Photoshop PS5 was used to crop out a volume-of-interest and segment the voxels into either solid- or pore-space. Solid voxels were colored completely white (grayscale value of 255) while pore-space voxels were colored black (grayscale value of 0). Two segmentation methods were explored. The first method, to be referred to as the capillary method, involved using the lowest threshold grayscale brightness value so that a large air bubble or crack within the sample became entirely black. The second method, to be referred to as the porosity method, involved selecting a threshold value that produced a bulk porosity value that matched the MIP-derived value. The segmented, black-and-white images from both methods were then input into Mathematica scripts to perform random walker simulations using the code written by Nakashima and Kamiya and modified by Provis et al. [31,36]. Every sample was analyzed with 6000 random walkers that performed walks of 200,000 steps each. This number of random walkers and steps was determined by Provis et al. to

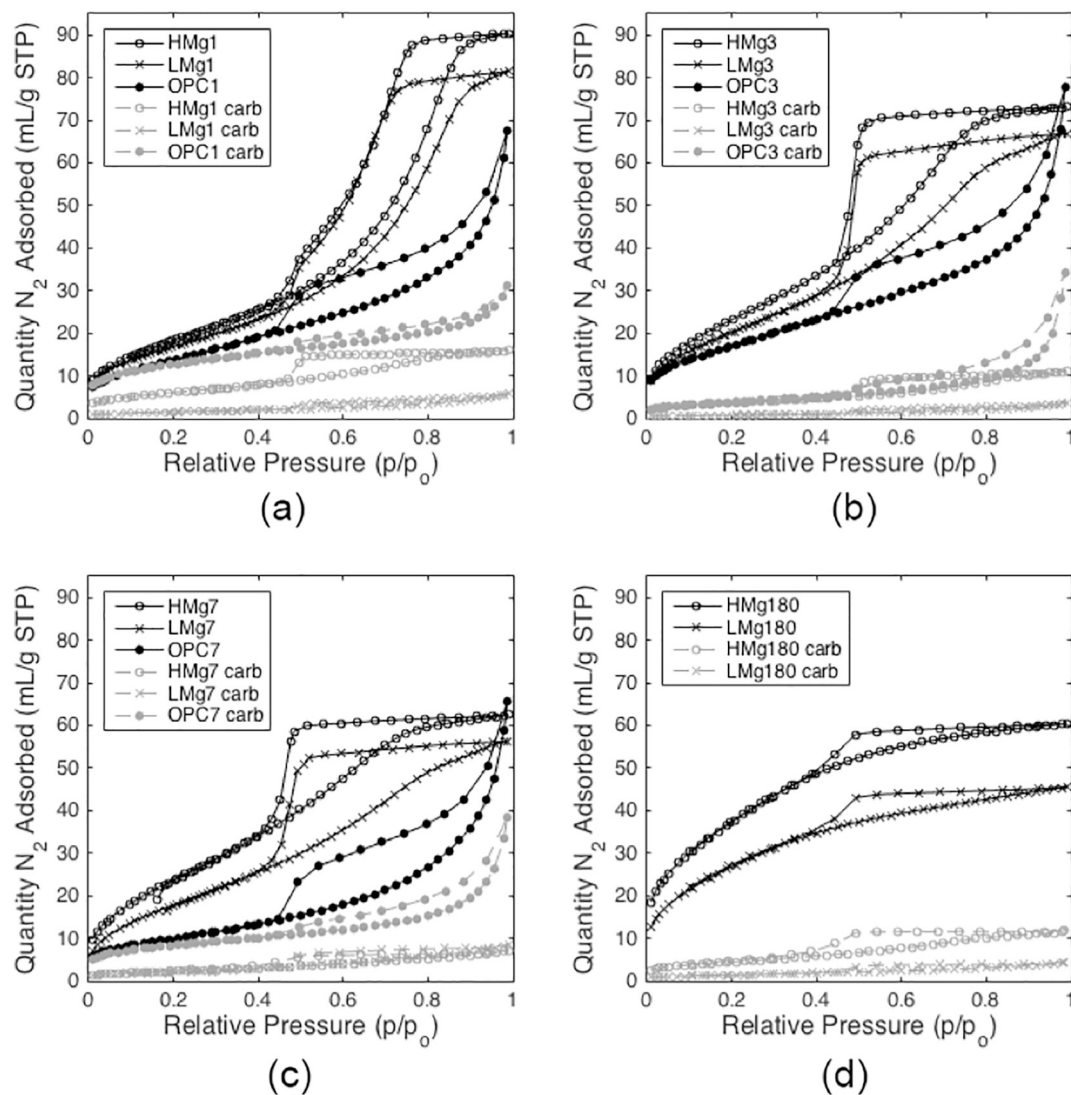


Fig. 1. Adsorption and desorption isotherms for high- and low-Mg AAS and OPC paste obtained using nitrogen sorption at (a) 1, (b) 3, (c) 7, and (d) 180 days of curing before and after carbonation. Note that OPC paste samples were measured up to 7 days.

be well above the limit of restricted diffusion specifically for AAS pore systems, and that increasing the number of walkers and steps above these values did not affect the calculated tortuosities [31]. Increasing the number of walkers and steps beyond these values likewise did not change the tortuosities reported in this study.

3. Results and discussion

3.1. Pore size distribution: pores smaller than 100 nm in diameter

The nitrogen adsorption and desorption isotherms for all samples are shown in Fig. 1. This figure shows that there are significant pore structure changes occurring in the samples as a function of curing age and CO₂ exposure. For instance, the value of the cumulative adsorption at a relative pressure of 1 is dependent on the sample type, sample age, and state of carbonation (uncarbonated versus carbonated), where a higher value indicates a higher the porosity in the pore region of 1–100 nm for the sample (adsorption curve is the lower curve of an adsorption-desorption isotherm). Fig. 1 shows that high-Mg AAS approaches a plateau at a higher quantity of adsorbed N₂ than low-Mg AAS for the same sample age regardless of the state of carbonation (uncarbonated and carbonated), thus showing that high-Mg AAS possess a higher porosity in the 1–100 nm pore diameter region (consisting

of gel pores and small capillary pores, see Table 1). Both types of AAS (low- and high-Mg) decrease in porosity as their sample age increases due to the ongoing alkali-activation reaction, where dissolution of slag and subsequent precipitation of C-(N)-A-S-H gel leads to a decrease in the size and/or quantity of capillary pores and an increase in the amount of gel pores. Both AAS and OPC samples show a decrease in porosity in the 1–100 nm pore diameter region after carbonation (Fig. 1).

A plateau of an isotherm near a relative pressure of 1 represents that there is little porosity at the higher bound of the pore sizes accessible with nitrogen sorption, and that most of the sample porosity can be captured with this technique. While both AAS isotherms near a plateau across all uncarbonated sample ages, the OPC isotherm continues to rise, showing that OPC has more porosity in the large capillary pore region (Fig. 1, i.e., porosity associated with pores larger than 100 nm). The porosities of OPC samples in the gel pore regime do not appear to change significantly with sample age (up to 7 days), since, as will be discussed later in this investigation, most of the porosity of early age OPC exists at larger pore diameters than what is accessible using nitrogen sorption.

BJH (Barrett-Joyner-Halenda) analysis was performed on the nitrogen adsorption curve, where the results are given in Fig. 2. While the desorption branch can reveal information about the percolation of the

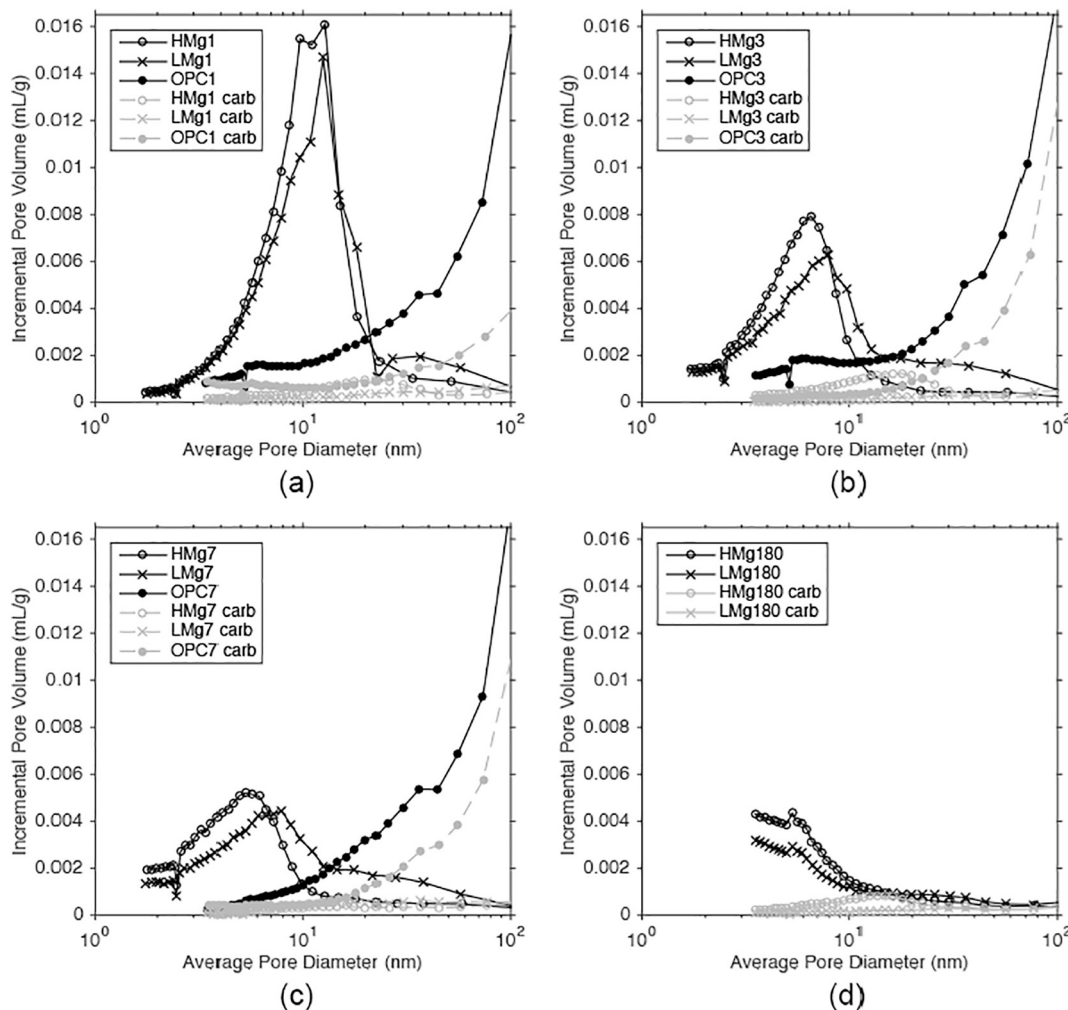


Fig. 2. Measured incremental pore volume versus average pore diameter obtained using the BJH method on nitrogen adsorption curves for (a) 1, (b) 3, (c) 7, and (d) 180 day old samples before and after carbonation. Note that the pore size is given on a logarithmic axis.

pore network, it was not selected due to the sharp drop in the curve near a relative pressure of 0.45 that corresponds to a pore diameter of 2.8 nm (Fig. 1). This drop is indicative of nitrogen cavitation that occurs in the ink-bottle shaped pores of cementitious materials [37,38]. Pore size cannot be extracted readily from the desorption branch below the cavitation pressure. Ink-bottle shaped pores also artificially shift the pore size distribution to left (i.e., represented by smaller pores than in reality) [37,39]. This is due to the fact that the smaller diameter bottleneck pores will fill first with adsorbed nitrogen and prevent the filling of a larger connected pore. Likewise, larger pores cannot empty during desorption even when thermodynamically favorable until the smaller pore necks empty at a lower pressure [37]. While this makes absolute, quantitative conclusions from nitrogen sorption pore size distributions prone to error for cementitious samples, nitrogen sorption is a technique well suited for the relative comparison of pore size distributions of similar sample types. As nitrogen sorption can access the entire range of pore sizes for uncarbonated silicate-activated slag, it is an excellent technique for comparing the pore size distribution of silicate-activated slag of different compositions and ages. However, it is important to note that other types of AAS (and AAMs) may consist of pores inaccessible via nitrogen sorption, such as hydroxide-activated slag, where the majority of pores are larger than what can be probed using nitrogen sorption [28].

Analysis of AAS using the BJH approach reveals that, while high-Mg AAS possesses a higher porosity in the gel pore region, it also possesses a smaller average pore diameter than that of low-Mg AAS at all ages

(Fig. 2). For the mature (180 days) uncarbonated AAS samples, the lower tail of the distribution is no longer visible, which implies that much of the gel pore diameters are smaller than those probed using nitrogen sorption mesopore analysis (Fig. 2). Following carbonation, the pore size distribution of low- and high-Mg AASs appear to flatten out drastically, representing reduced porosity in the 1–100 nm pore diameter range accessible by nitrogen sorption (Fig. 2). In addition, while carbonation significantly decreased the porosity in the gel pore region for all AAS samples, the high-Mg AAS appears to have been less affected than the low-Mg AAS, with its pore size distribution curve shifting less to the right and experiencing less broadening than that of low-Mg AAS (Fig. 2). OPC samples also displayed a decrease in overall porosity and a shift to larger average pore diameters following carbonation (Figs. 1 and 2).

3.2. Pore size distribution: pores between ~7 nm and 10 μ m in diameter

Figs. 3 and 4 show the incremental and cumulative pore size distributions, respectively, obtained using MIP for pores ranging from ~5 nm to 10 μ m in diameter in the low- and high-Mg AASs and OPC paste, before and after carbonation. Data above a pore diameter of 10 μ m are not considered in this investigation since this region cannot be solely attributed to macropore filling due to contributions from interparticle space filling between the sample grains that causes a sharp increase in measured intrusion volume at low pressures and large pore diameters. Furthermore, mercury intrusion below a size of ~7 nm may

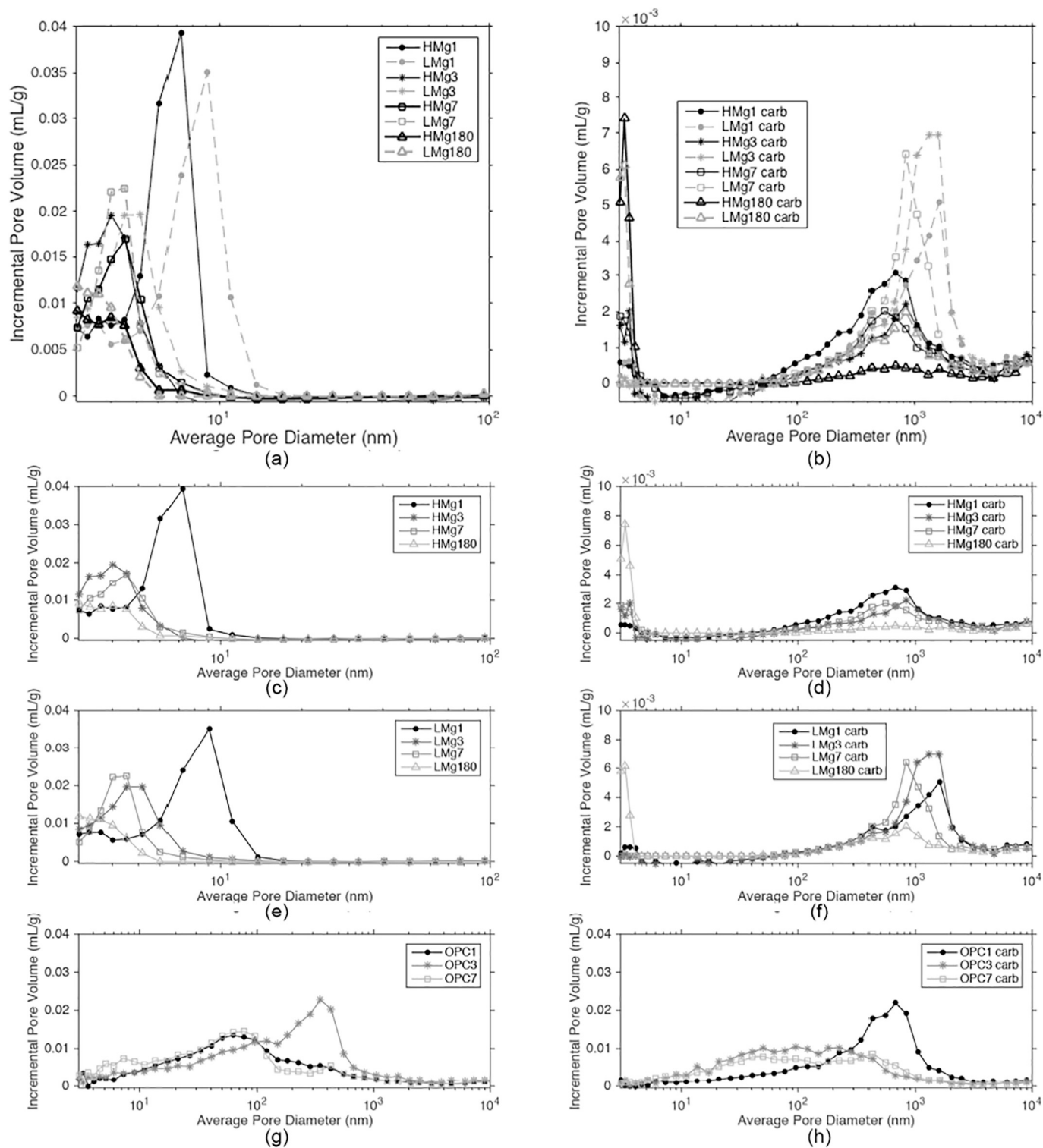


Fig. 3. Measured incremental pore volume versus average pore diameter obtained using MIP for (a) uncarbonated AAS samples and (b) carbonated AAS samples. Note that the y-axis scale for carbonated AAS samples is $4 \times$ smaller than that of uncarbonated AAS, and that the x-axis scale for carbonated AAS extends to 10^4 nm whereas the x-axis scale for uncarbonated AAS ends at 10^2 nm as there is no recorded porosity above this pore size. For clarity, (c) shows uncarbonated high-Mg AAS at every sample age, (d) shows carbonated high-Mg AAS at every sample age, (e) shows uncarbonated low-Mg AAS at every sample age, and (f) shows carbonated low-Mg AAS at every sample age. (g) Uncarbonated OPC samples and (h) carbonated OPC samples are shown with the same y-axis scale (different from the scale used for AAS samples). Note that the pore size is given on a logarithmic axis.

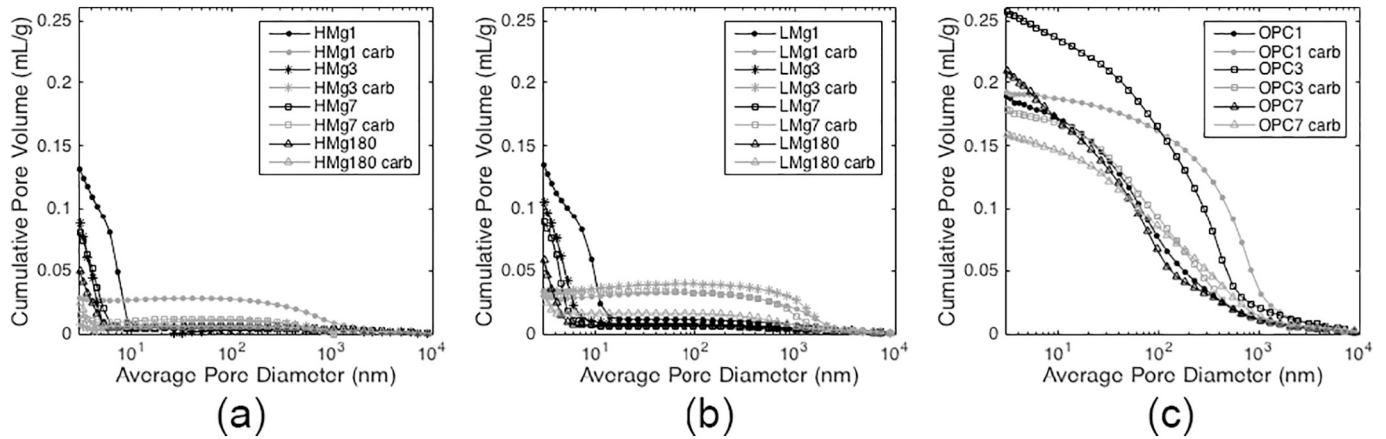


Fig. 4. Measured cumulative pore volume versus average pore diameter before and after carbonation obtained using MIP for (a) high-Mg AAS, (b) low-Mg AAS, and (c) OPC. The pore volume attributed to pores > 10,000 nm in diameter has been subtracted. Note that the pore size is given on a logarithmic axis.

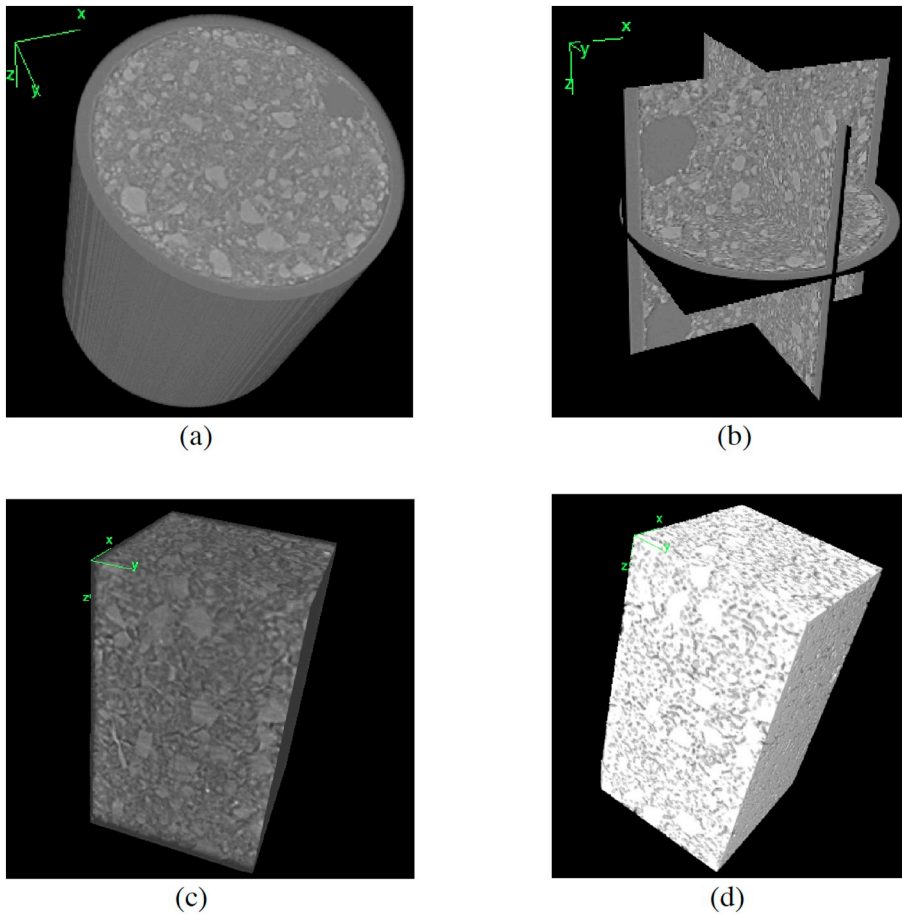


Fig. 5. (a) X-ray μ CT measurement of 7 day carbonated low-Mg AAS in a 0.50 mm diameter polyimide capillary tube and (b) a cross-sectional view showing the interior of the sample. (c) A $275 \times 260 \times 560 \mu\text{m}$ rectangular prism is cropped out and (d) segmented into black and white using the capillary thresholding method for analysis.

be associated with crushing of the sample at high pressures, as opposed to pore filling. Analysis of Fig. 3 reveals some general trends for the AAS samples. Specifically, minimal porosity is attributed to pores above 30 nm in diameter for the uncarbonated samples (in agreement with the nitrogen sorption data), while in carbonated samples pores with diameters around 1 μm are seen to emerge (Fig. 3a and b). Furthermore, across all sample ages a higher magnesium content of the initial slag is correlated with a lower extent of formation of coarse capillary pores (pores between 100 nm and 10 μm) resulting from carbonation, as seen in Fig. 3b and by comparing Fig. 3d and f (note that all carbonated MIP results for the AAS samples are plotted using the same scale for the incremental pore volume (mL/g)). The lower extent of coarse capillary

pore formation during carbonation in the high-Mg AAS compared with the low-Mg system is accompanied by the retention of more gel and small capillary pores (3–50 nm, see Fig. 3b, d and f). It is clear from Fig. 3 that the mature AAS samples (180 days) are significantly more resistant to pore structure changes as a result of exposure to CO_2 compared with the early age samples (up to 7 days).

The pore size distributions of both types of AAS are significantly different from that of OPC. Prior to carbonation AAS samples only display porosity in the micro- to mesopore region, below 20 nm in diameter (Fig. 3a), while OPC samples display a broad distribution of pore sizes with an average pore diameter near 100 nm (Fig. 3g, cumulative pore volume plot shown in Fig. 4c). These pore size

distributions obtained for uncarbonated AAS and OPC samples match those found in literature, with AAS having a higher fraction of micro- to mesopores and OPC having a wider distribution of macropores [27]. While previous studies have shown very mature OPC samples (1 year old) to have an average pore diameter closer to 3–5 nm, younger samples (1–7 days) have been shown to have average pore diameters of near 100 nm, similar to what has been found using MIP in this article (Fig. 3g) [27,40,41]. Note that the 1 day OPC sample has a much lower cumulative pore volume than at 3 days (1 day is similar to the 7 day sample), which may be attributed to subsequent hydration reactions occurring in the 1 day sample after solvent exchange and vacuum drying. As is evident in ref. [41] the 1 day OPC sample should have a higher cumulative pore volume than the 3 day sample.

Following carbonation, AAS samples show a decrease in gel and fine capillary porosity along with an increase in coarse capillary porosity at ~100–2000 nm in diameter (Fig. 3b). However, the carbonated AAS samples possess minimal porosity attributed to pores between ~10 and 100 nm (Figs. 3 and 4). On the other hand, the already broad pore size distribution of OPC (centered at ~70 nm at 7 days) shifts toward larger pores after exposure to CO₂ (centered at ~100 nm), but retains porosity across length scales (~5 nm–1 μ m). Although the average pore size for the carbonated OPC samples is smaller than that obtained for the carbonated AAS samples, analysis of the cumulative MIP results shown in Fig. 4, where all data are given on the same scale, shows that the total pore volume of the OPC samples after carbonation is significantly higher than the AAS samples (~0.15–0.20 mL/g compared with ~0.03 mL/g). Only the 1 day high-Mg AAS, and 1 and 3 day low-Mg AAS, carbonated samples have slightly higher intruded volumes for pores between ~500 and 1000 nm compared with the carbonated OPC samples. Hence, overall the carbonated AAS samples have significantly lower porosities after carbonated compared with the OPC samples.

3.3. Pore size distribution: micron-sized pores and voids

Analysis of the micron-sized pores and voids in the 7 day AAS and OPC samples before and after carbonation has been carried out using X-ray μ CT. Figs. 5 and 6 show images derived from the X-ray μ CT measurements for the 7 day carbonated low-Mg AAS sample, and the 7 day uncarbonated high-Mg AAS sample, respectively. Fig. 5 displays a rectangular prism volume-of-interest (VOI) selected from the cylindrical scan volume to avoid large cracks and air bubbles, and then the VOI after thresholding using the capillary method as described in Section 2.5. 2D slices of high-Mg AAS before and after thresholding using the (i) capillary and (ii) porosity methods are shown in Fig. 6. Porosity and diffusion tortuosity (τ) results are summarized in Table 4.

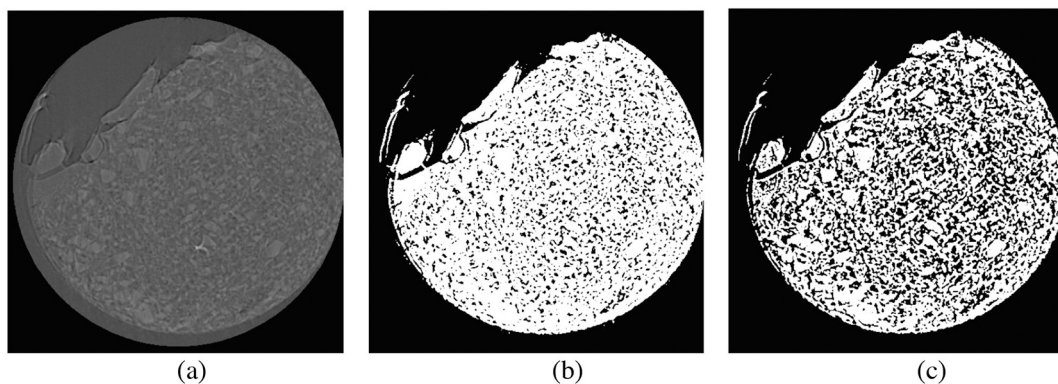


Fig. 6. Example of the two thresholding methods applied to the uncarbonated 7-day high-Mg AAS sample in a 0.50 mm diameter capillary tube, where (a) is an unedited image of a cross-section of the μ CT scan and (b) shows this scan after applying the capillary thresholding method that uses an air bubble to determine the thresholding brightness value. A threshold value of 70 (on the grayscale range from 0 to 255) was selected as the lower limit where the air bubble in the upper left corner appears black. (c) Shows the scan after applying the porosity thresholding method where a threshold value of 75 was selected to match the measured MIP porosity value for the uncarbonated 7-day high-Mg AAS sample.

Table 4

Diffusion tortuosity (τ) and porosity values determined using X-ray μ CT analysis and random walker simulations. The capillary method for thresholding is based the grayscale value of a large air bubble or crack located within the VOI. On the other hand, the porosity method utilizes the porosity value obtained from MIP to determine the grayscale value for thresholding, such that the resulting porosity from the X-ray μ CT analysis matches the value from MIP.

Sample	Capillary method		Porosity method	
	Diffusion τ	Porosity	Diffusion τ	Porosity
HMg7	80 $\pm$ 10	0.18 $\pm$ 0.05	11 $\pm$ 2	0.39 $\pm$ 0.05
LMg7	100 $\pm$ 10	0.16 $\pm$ 0.05	9 $\pm$ 2	0.40 $\pm$ 0.05
OPC7 ^a	7 $\pm$ 2	0.53 $\pm$ 0.05	7 $\pm$ 2	0.53 $\pm$ 0.05
HMg7 carb ^a	28 $\pm$ 2	0.32 $\pm$ 0.05	28 $\pm$ 2	0.32 $\pm$ 0.05
LMg7 carb ^a	24 $\pm$ 2	0.31 $\pm$ 0.05	24 $\pm$ 2	0.31 $\pm$ 0.05
OPC 7 carb ^a	8 $\pm$ 2	0.45 $\pm$ 0.05	8 $\pm$ 2	0.45 $\pm$ 0.05

^a Capillary and porosity methods yield the same results.

For uncarbonated AAS, thresholding using the capillary method (i.e., using a crack or air void to select the grayscale for pores) results in lower porosity values and higher tortuosity values than thresholding using the porosity method (Table 4). Since the capillary method thresholds to large voids such as cracks and air bubbles, it does not account for the presence of gel pores with diameters smaller than the μ CT scan resolution of 1 μ m. Therefore, the porosity and tortuosity values it produces are representative of only the larger, coarse capillary pores. As shown in Table 4, the capillary and porosity methods produced the same results for uncarbonated and carbonated OPC, and carbonated AAS samples. This convergence is due to the minimal amount of micro- and mesopores and presence of large macropores in both OPC and carbonated AAS that allows the capillary method to access a majority of the sample porosity. As such, the capillary method calculates a porosity value close to the overall sample porosity measured by MIP (MIP data taken for pores from 3 nm to 350 μ m) for these samples, and thus produces the same results as the porosity method. Overall, AAS porosity and tortuosity values are significantly lower and higher, respectively, than those of OPC both before and after carbonation.

The large differences between the tortuosity and porosity values obtained using the capillary and porosity thresholding methods for uncarbonated AAS are due to the fact that most of the porosity for these samples lies within the gel pore region (as determined above using nitrogen sorption and MIP). As the gel pore diameters are smaller than the resolution of the X-ray μ CT scans, the presence of gel pores results in a voxel brightness value that is in-between that of air or pure pore-space and a non-porous calcium aluminosilicate solid phase (e.g., unreacted slag). Thus, the capillary thresholding method offers insight into the

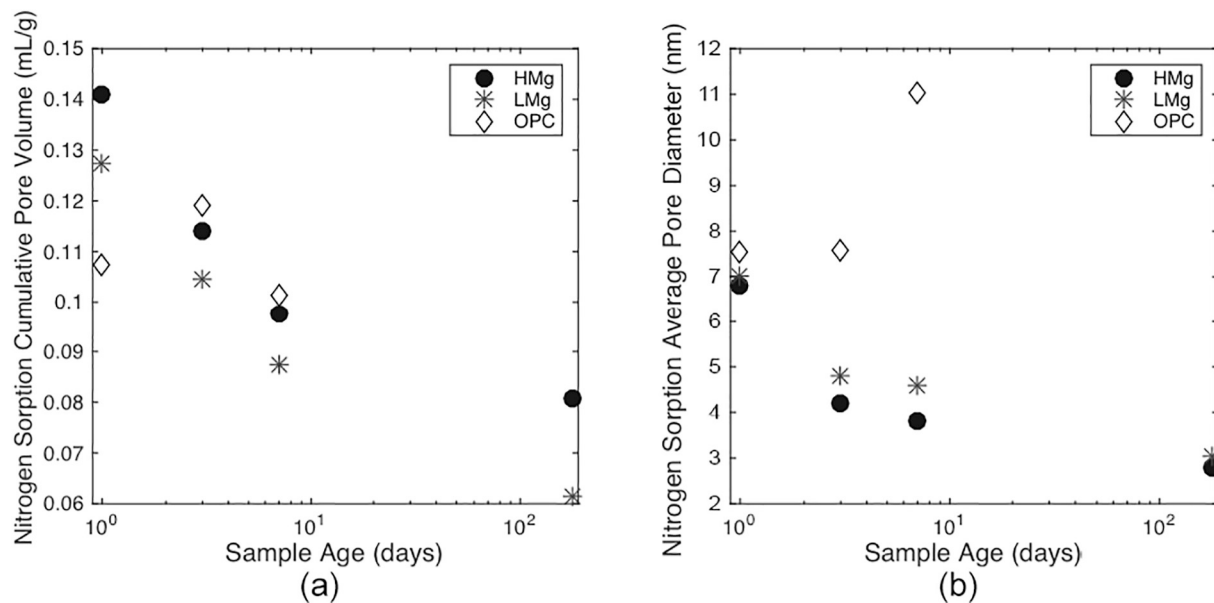


Fig. 7. (a) The total cumulative pore volume measured using nitrogen sorption for pore diameters between 0.14 and 150 nm and (b) the average sample pore diameter as calculated using BJH analysis versus sample age. Both AAS samples decrease in porosity and average pore diameter as sample age increases. Note that the sample age is given on a logarithmic axis.

connectedness of the coarse capillary pore region (i.e., consisting of pores $> 1 \mu\text{m}$). On the other hand, the porosity thresholding method locates an average brightness value so that voxels with a high density of gel pores that appear darker are counted as entirely pore-space, whereas brighter voxels with a low gel pore density are counted as entirely solid paste.

The uncarbonated AAS porosity values from the capillary method are lower than those measured from MIP (i.e., the values reported for the porosity method in Table 4), yet higher than the porosity that can be attributed to capillary pores between $1 \mu\text{m}$ (the scan resolution) and $10 \mu\text{m}$ (the limit for pores unaffected by interparticle space filling) in diameter for this region (12% for uncarbonated high-Mg AAS and 11% for uncarbonated low-Mg AAS, calculated from the MIP data for pores $< 10 \mu\text{m}$ in diameter). This is due to the presence of air bubbles and microcracks that cannot be accounted for through powder sample analysis using MIP. In particular, AAS is prone to drying shrinkage and therefore crack formation which will show up in the X-ray μCT data [40]. While cropping out a VOI can help avoid some of the larger bubbles and cracks, unavoidable smaller airspaces are still present within the sample. However, such information is important for a realistic tortuosity measurement in a bulk sample environment.

The tortuosity values for the uncarbonated AAS samples are roughly $10 \times$ higher when calculated using the capillary method compared with the porosity method (Table 4). This disparity shows that the capillary pore region itself is not well percolated, and that larger pores are connected by smaller, gel pores. However, applying the capillary method on carbonated AAS samples yields porosities similar to those measured by MIP and the porosity method (Table 4). This agreement between the capillary and porosity methods also occurs for both carbonated and uncarbonated OPC samples. For these samples, the bulk of the sample porosity exists in the coarse capillary pore region ($> 1 \mu\text{m}$) and thus can be more accurately captured by the X-ray μCT technique compared with samples containing a significant percentage of gel and fine capillary pores.

The X-ray μCT analyses reveal that the overall diffusion tortuosity calculated from the porosity method increases after carbonation for AAS, while the coarse capillary pore tortuosity ($> \sim 1 \mu\text{m}$ pore diameter) calculated from the capillary method decreases following carbonation. Previous measurements of tortuosity using a chloride diffusion cell test before and after carbonation (5% accelerated carbonation

for 42 days) of a 28-day OPC mortar have revealed that the tortuosity value increases as a result of carbonation (from ~ 2 to 10) [42]. However, for OPC mortars blended with slag or class F fly ash the tortuosity values were seen to decrease when exposed to the same carbonation conditions. Furthermore, research on AAS has shown that carbonation leads to an increase in permeability, which will be caused by, at least partially, a decrease in tortuosity [43]. Hence, the capillary method for analysis of the X-ray μCT data provides the most realistic results, where the tortuosity values of low- and high-Mg AAS decrease by 75 and 65%, respectively, after carbonation (Table 4). Furthermore, high-Mg AAS possesses a 17% higher diffusion tortuosity than low-Mg AAS following carbonation, as seen in both thresholding methods (Table 4). As shown through MIP analysis, high-Mg AAS has a lower amount of capillary pore development due to carbonation and a lower overall porosity than low-Mg slag (Figs. 3 and 4). These factors may explain its higher tortuosity, and also point to a higher resilience against other forms of chemical degradation.

There is too much uncertainty associated with the tortuosity values of the uncarbonated AAS samples to determine which of their pore structures is truly more tortuous (i.e., low- or high-Mg AAS), but results for the porosity analysis align closely with results from Provis et al. who first used X-ray μCT on AAS [31]. Much of the uncertainty is due to selecting a threshold value. For uncarbonated AAS samples, changing the selected grayscale value (0 to 255) by a value of 1 can alter porosity values by 5 vol% and tortuosity values by up to 10. Provis et al. found similar fluctuations when altering the grayscale threshold value [31]. Due to the fine pore size of uncarbonated AAS and the limited resolution of X-ray μCT , this technique appears more useful for obtaining the order-of-magnitude of tortuosity values attributed to the coarse capillary pore region ($> 1 \mu\text{m}$) rather than being able to accurately compare tortuosities between two similar samples. However, for experiments interested specifically in the coarse capillary pore region or for samples with larger pore sizes such as early age OPC, X-ray μCT analysis is an efficient way to nondestructively image and analyze the micron-scale pore structure without the need for extensive sample preparation.

3.4. Evolution of AAS pores during curing

As evident from Fig. 2 (nitrogen sorption) and Fig. 3. (MIP), the pore size distribution of the uncarbonated AAS samples can be fully

captured using nitrogen sorption since all pores have diameters below ~ 20 nm. Nitrogen sorption reveals that the AAS porosity and average pore diameter decrease as sample age increases, and that high-Mg AAS possesses a higher porosity at all ages but a lower average pore diameter (Fig. 7). As the alkali activation reaction proceeds, the slag particles continue to dissolve to form a mesoporous C-(N)-A-S-H gel phase [44]. The higher porosity yet smaller pores of high-Mg AAS in the mesopore region points to a higher volume of C-(N)-A-S-H gel (and associated gel pores) present in this sample compared with low-Mg AAS, especially at later ages. At 180 days, high-Mg AAS possesses 31% more pore volume in the gel/small-to-medium capillary pore region (calculated by including data from 0.14–150 nm (Fig. 2d)) than low-Mg AAS at roughly equal average pore sizes.

As the majority of OPC porosity is outside the range measurable by nitrogen sorption, it is difficult to draw conclusions from this technique alone. While the pore diameter appears to increase with curing age, this could simply be an effect of the OPC pore size distribution shifting to the left from the larger capillary pores to the small capillary pores and gel pores as the hydration reaction proceeds and additional C-S-H gel forms (Fig. 7).

3.5. Loss of gel and small capillary pores due to AAS carbonation

Following carbonation, the appearance of larger capillary pores ($> \sim 50$ nm) in the AAS samples prevents nitrogen sorption from providing a complete picture of the pore size distribution (see MIP results in Fig. 3b). However, nitrogen sorption can reveal with precision the changes that occur in the gel pore region after carbonation. As shown in the nitrogen isotherms (Fig. 2), mesoporosity significantly decreases following carbonation for all samples. This is primarily attributed to the decalcification of the C-(N)-A-S-H gel and associated loss of gel pores due to the lower pH conditions induced by CO_2 . The leaching of calcium near these sites thus increases the gel pore diameter as the C-(N)-A-S-H gel degrades, resulting in large capillary pores that cannot be measured using nitrogen sorption. However, formation of carbonation products such as CaCO_3 can also fill or plug mesopores, thus decreasing the measured porosity in this region (< 50 nm) [45]. Fig. 8 shows the volume fraction of gel pores lost after carbonation. This is calculated by dividing the difference in cumulative pore volume measured by nitrogen sorption between uncarbonated and carbonated samples by the cumulative pore volume for uncarbonated samples. In general, the high-Mg AAS samples retain more of their gel pores (and small capillary pores) after carbonation, as evidenced by the lower fraction of gel pore

volume reduction in Fig. 8, except for the 7 day sample. The retention of porosity in the mesopore region after exposure to CO_2 points to less calcium leaching or carbonation product formation. It is important to note that while the uncarbonated AAS samples consist solely of gel pores attributed to C-(N)-A-S-H ($< \sim 10$ nm in diameter, see Fig. 2), a limited amount of small capillary pores (between ~ 10 and 50 nm in diameter) emerge during carbonation (Fig. 2), which will contribute to the values calculated for the retained gel pores.

3.6. Effect of sample age and carbonation on macropores, porosity and tortuosity

Overall, the porosity is seen to decrease as a function of curing age for uncarbonated samples (Fig. 9a and b). This trend is particularly noticeable when considering the porosity attributed to pores with diameters below $10 \mu\text{m}$ as this region of the data does not contain interference from interparticle space filling (Fig. 9b). However, considering only the porosity due to pores smaller than $10 \mu\text{m}$ excludes contributions from larger voids such as microcracks and air bubbles. As such, the porosity in this region is roughly two times lower than bulk porosity measurements calculated from weight loss due to oven drying at 105°C (39% and 41% for 7-day low- and high-Mg AAS, respectively; similar values obtained by MIP when considering data for all pore sizes, see Fig. 9a). Despite the loss of information on the larger voids, the trends of gel and capillary pore structure development are much clearer when looking at pore sizes without interference from interparticle space filling (Fig. 9b and e). The correlation between pore diameter and sample age is difficult to observe for uncarbonated samples using MIP due to the poor resolution in the gel pore region (Fig. 9c). However, it is clear that the average pore diameter for OPC is up to $2\text{--}3\times$ greater than AAS samples.

It should be noted that the porosity of OPC measured using the capillary and porosity μCT methods and MIP (0.53) is higher than that of 0.5 water/cement ratio OPC pastes reported by Cook and Hover (0.36, 7-day-old sample) [41] and Gallé (0.38, 5-month-old sample) [46] measured using MIP. This discrepancy is likely due to the different drying conditions used by Cook and Hover [41] (D-drying in their study compared with alcohol exchange and mild vacuum drying here) and the age of the sample measured by Gallé (at 5 months). In a study by Vichit-Vadakan and Scherer [47], OPC with a w/c ratio of 0.5 had porosity values between ~ 0.54 (at early age, ~ 3 days) and ~ 0.45 (at later age, ~ 20 days), where porosity was measured using oven drying at 105°C . Nevertheless, irrespective of the total porosity values reported in the different studies, the pore size distributions from MIP in this study match those reported for OPC in the literature, with average pore diameters around 100 nm in diameter (Fig. 3g) [41,46]. This indicates that while the porosity may be different from curing conditions and/or sample pretreatment, AAS can still reliably be understood as having significantly finer pores and thus an overall smaller porosity than OPC.

There appears to be little correlation between sample age and porosity following carbonation for low-Mg AAS (Fig. 9e), while a decrease in porosity is seen for high-Mg AAS (Fig. 9e) and OPC (Fig. 9d) as sample age increases. On the other hand, consistent results are seen for the average pore diameters for all carbonated samples, where a decrease in average pore diameter occurs as sample age increases. Compared with the uncarbonated samples (Fig. 9c), the average pore diameters for carbonated low- and high-Mg AAS are approximately 1 to 2 orders of magnitude larger due to the development of macropores (pores $> 50 \text{ nm}$), while the average pore diameter of OPC increases by a factor of two (Fig. 9f). As mentioned earlier, carbonation products such as calcium carbonate can block gel pores that are originally open to the percolated pore network, which will prevent mercury intrusion and therefore alter the measured value of sample porosity. This phenomenon should not significantly alter the pore size distribution, as pores that are accessible by MIP after carbonation should still have a similar size distribution and therefore average pore diameter as the

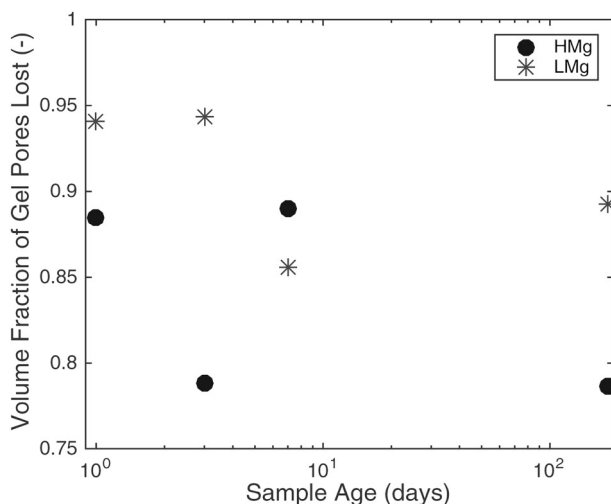


Fig. 8. Volume fraction of AAS gel and small capillary pores (< 50 nm in diameter) lost following carbonation as a function of sample age, measured using nitrogen sorption. Note that sample age is given on a logarithmic axis.

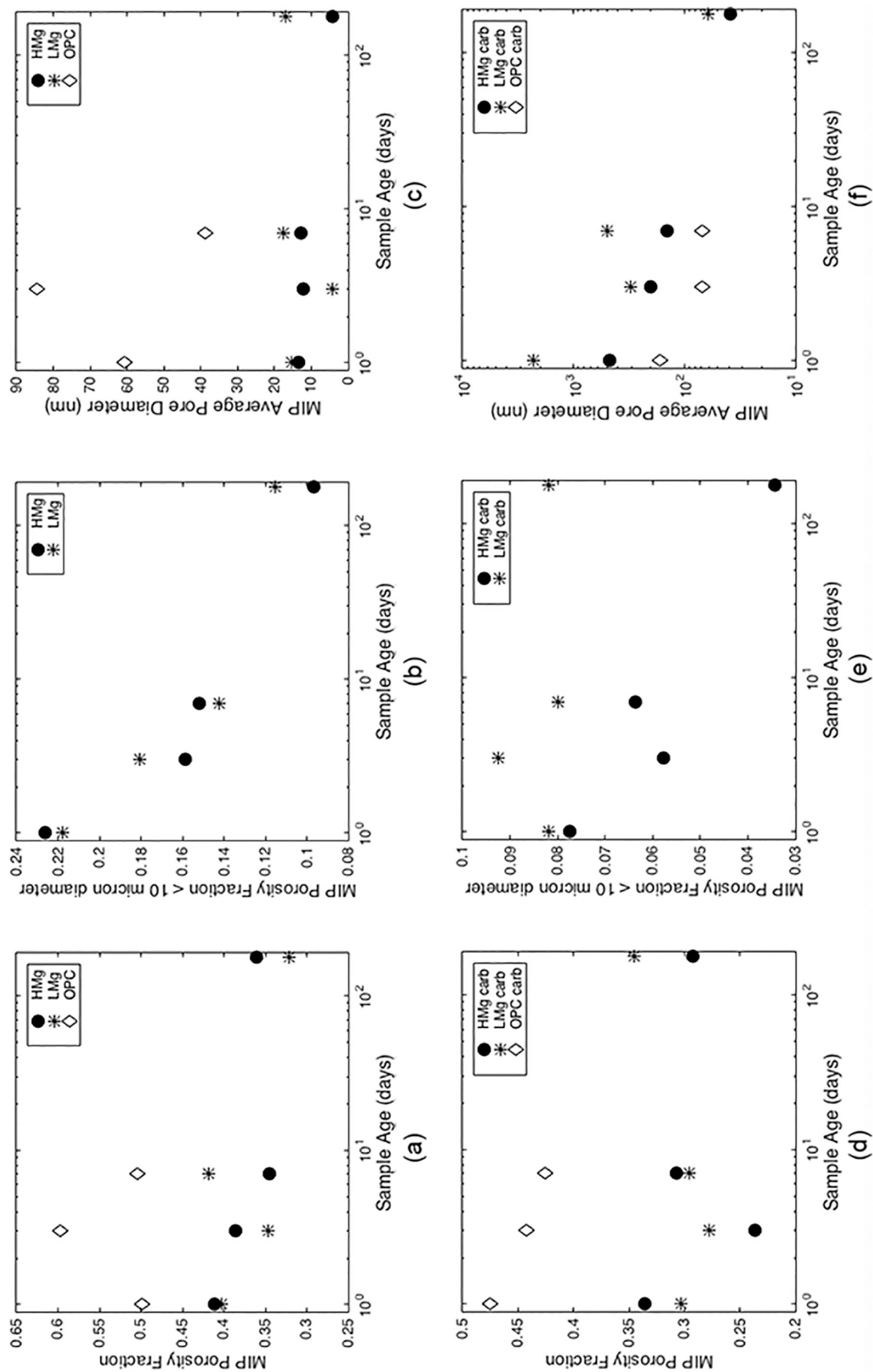


Fig. 9. (a) Porosity (volume fraction) of uncarbonated samples measured by MIP and (b) porosity of uncarbonated AAS samples when only considering pore sizes below 10 μm in diameter to avoid contributions from interparticle space filling. OPC data were not included to preserve the axis scale, and to focus on differences between high- and low-Mg AAS. (c) The average pore diameters measured by MIP for uncarbonated samples excluding contributions from voids that are $> 10 \mu\text{m}$ in size. (d) Porosity of carbonated samples measured by MIP, (e) porosity when only considering pore sizes below 10 μm . (f) The average pore diameters measured by MIP for carbonated samples excluding contributions from voids that are $> 10 \mu\text{m}$ in size. Note that the sample age is given on a logarithmic axis.

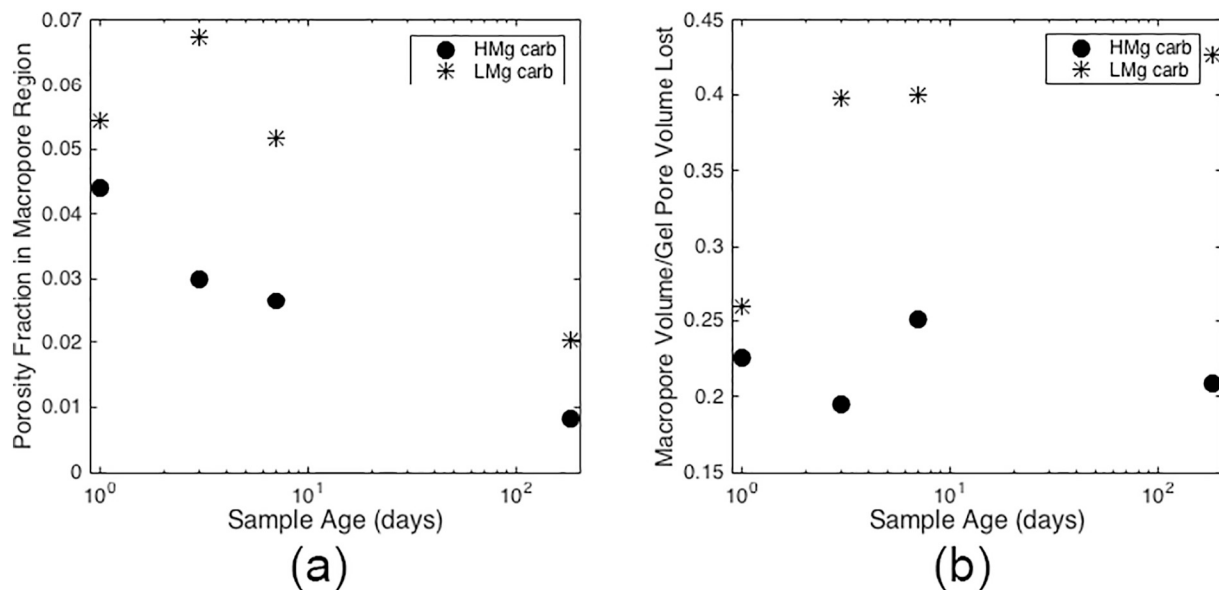


Fig. 10. (a) Porosity attributed to macropores (50–100,000 nm pore diameter) that form following carbonation and (b) the volume of macropores that form over the volume of gel pores lost to carbonation. Note that the sample age is given on a logarithmic axis.

entire pore-space (both accessible and blocked off pores). Furthermore, the ink-bottle nature of AAS and OPC pores also affects MIP measurements by shifting the pore size distribution to the left and over-representing the presence of smaller pores [39]. As such, the volume associated with larger diameter pores may be incorrectly attributed to smaller diameters due to the higher mercury pressure necessary to intrude the bottlenecks.

As mentioned previously in Section 3.2, carbonated high-Mg AAS possesses both a lower porosity (Fig. 9e) and a smaller volume of macropores (pores > 50 nm, see Fig. 10a) compared with carbonated low-Mg AAS, despite having a higher initial porosity prior to carbonation (Fig. 9b). The lower amount of macropores in carbonated high-Mg AAS is indicative of less C-(N)-A-S-H gel decalcification occurring near the acidified pore solution and hence less degradation. This can be directly seen in Fig. 10b, where the ratio between the volume of macropores created as a result of carbonation to the volume of gel pores lost (approximated as pores < 50 nm) is provided. Thus, the proposed formation of the Mg-stabilized ACC phase appears to also prevent damage to the pore structure by reducing the extent of decalcification of the mesoporous C-(N)-A-S-H gel (Fig. 8) and therefore lowering the extent of macropore formation. This observation is consistent with results from Morandeau and White, where pair distribution function (PDF) analyses of low- and high-Mg carbonated AAS pastes show that the paste synthesized using high Mg content slag experiences less decalcification of C-(N)-A-S-H gel (and thus less pore augmentation) compared with paste made using low Mg content slag, attributed to the formation and long-term existence of an amorphous Mg-stabilized ACC phase in the high-Mg AAS paste during exposure to CO_2 [7]. Furthermore, the lower porosity of high-Mg AAS compared with low-Mg AAS following CO_2 exposure indicates that the Mg-stabilized ACC does not introduce significant porosity to the AAS paste. However, more studies must be performed to determine the exact nature of the pore structure of this ACC phase and any changes that occur due to its formation. Lastly, the volume of capillary pores gained by the carbonated AAS samples is only ~25% and ~40% of the gel pore volume lost after carbonation for high- and low-Mg AAS pastes respectively (Fig. 10). Thus, the remaining gel porosity has either been lost to pore-filling with carbonation products or blocked off from analysis due to pore plugging truncating the percolated pore network.

4. Conclusions

In this investigation the influence of (i) magnesium, (ii) sample age and (iii) exposure to 100% CO_2 (accelerated carbonation conditions) on the multiscale pore structure of sodium silicate-activated blast furnace slag have been elucidated and compared with OPC paste using nitrogen sorption, MIP and X-ray μCT . Nitrogen sorption and MIP analysis reveal that the pore structures of these uncarbonated AAS samples are largely composed of gel pores, and that the porosity and average pore diameter decrease as sample age increases. This is in contrast to the larger capillary pores (average size of ~100 nm) found in OPC paste. Furthermore, low-Mg AAS consistently possesses a lower porosity in the 1–50 nm pore diameter region than high-Mg AAS, but is seen to have a higher average pore diameter. The lower porosity in the gel pore region of low-Mg AAS compared with high-Mg AAS points toward lower quantities of C-(N)-A-S-H gel present in the low-Mg AAS.

High-Mg AAS displayed less pore structural changes than low-Mg AAS and OPC paste after carbonation. An increased magnesium content results in less volume of gel pores lost and less volume of macropores developed. Both of these findings point toward lower levels of gel decalcification for high-Mg slag. While it remains inconclusive whether the Mg content affects tortuosity prior to carbonation due to the inability of X-ray μCT to resolve gel pores, high-Mg AAS possesses a higher tortuosity than low-Mg AAS (and OPC paste) for carbonated samples at 7 days, attributed to the fact that high-Mg AAS develops less capillary porosity during carbonation than low-Mg AAS. Despite initially having a slightly higher porosity than low-Mg AAS as measured by nitrogen sorption, high-Mg AAS experiences less pore structural degradation from carbonation, thought to be due to its ability to form an Mg-stabilized ACC phase. The decreased capillary pore formation, reduced extent of gel pore loss, and increased tortuosity following carbonation associated with high-Mg AAS indicates that this cement-based material may have enhanced resistance to subsequent types of chemical degradation (e.g., sulfate or chloride ingress following carbonation) compared with low-Mg AAS and OPC.

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CRediT authorship contribution statement

Sarah Y. Wang: Investigation, Validation, Data curation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Eric McCaslin:** Methodology, Supervision, Writing - review & editing. **Claire E. White:** Conceptualization, Methodology, Supervision, Writing - original draft, Writing - review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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