Estimation of Porosity and Pore Distribution in Hydrated Portland Cement at Elevated Temperatures using Synchrotron Micro Tomography

Harsha Praneeth Pavani¹, Tezeswi Tadepalli² and Ashish Kumar Agrawal³

Abstract

The porosity of concrete affects the mechanical properties and durability, during its exposure to extreme temperatures where the chemical and physical changes in PC affect the integrity of concrete as a whole because of its binding properties. An attempt is made to analyze the porosity in hydrated PC using synchrotron micro-tomography at temperatures of 27°C, 100°C, 400°C, 500°C, and 800°C. These temperatures are significant in the context of the mass loss and phase changes taking place during the thermal analysis. Image analysis is carried out to estimate porosity, radius, and circularity of pores for all the individual 2D slices. 3D analysis is carried out to estimate the diameter, area, and volume of pores present in the sample. The number of pores in the 2D slices has increased from 5974 to 11564 at 27°C and 800°C; while the total number of pores present in the sample at 27°C is 317 and at 800°C it is 3361. With the increase in temperatures, the area of pores 947 µm² contributed to 44.16 volume percent at 27°C, whereas at the temperatures of 800°C the area of 136 µm² pores volume percent is 41.

1. Introduction

Reduction in the mechanical properties, durability, physical changes, cracking, and spalling are often the outcomes when concrete is exposed to thermal loads, and the temperature to which the structure is exposed governs the damage behavior (Kim et al. 2013). Even though concrete is resistant to fire and also has relatively less thermal conductivity, its durability is often compromised when it comes in contact with heat, because the increase in porosity with temperature during fire deteriorates the concrete member. The effects of porosity need to be understood, as mechanical properties, transport properties, and durability are influenced by the porosity of the material (Wan and Xu 2014), and therefore the entire concrete structure (Kucharczyková et al. 2010). The individual pores contribute to the porosity, so there is a need to understand the type of pores present in concrete. The pores are classified into two categories (a) gel pore, capillary pores, entrapped and entrained pores are characteristics of pores, while (b) macro pores, micro pores, meso pores, and larger pores are categorized according to the sizes of pores (Vodák et al. 2004; Rivera et al. 2016). Many techniques are available to determine the porosity in concrete such as pressure method, air-void analyzer, stereoscopic and microscopic methods (Moravcová et al. 2016), torrent permeability tester (Kucharczyková et al. 2010), mercury intrusion porosimetry (MIP) method widely used by researchers (Piasta et al. 1984; Abell et al. 1999; Chan et al. 1999; Diamond 2000; Lee et al. 2017), ultrasound method (Benouis and Grini 2011), water vapor adsorption, nitrogen adsorption (Moravcová et al. 2016); but the limitation of these tests is that they assume that the pore geometry is regular and all the pores are interconnected. MIP measures capillary pores of size 0.005 µm to 10 µm while the adsorption techniques can predict the CSH gel pores of diameter less than 0.003 µm (Abell et al. 1999). Diamond et al. state that MIP is an inappropriate method to estimate the porosity in cementitious material (Diamond 2000). Scanning electronic microscopy (SEM) (Stutzman 2004; Durduziński et al. 2015), Transmission electronic microscopy (TEM) (Scrivener 2004) tests are confined to 2D analysis.

Many research articles have been published regarding application of computer tomography techniques to cementitious materials and a non-exhaustive list of literature is presented. Changes in porosity and unreacted clinker is quantified for PC binders (Wang and Dai 2017), while microstructure evolution and Pore network generation of alkali activated binders (Provis et al. 2012), porosity in leached cement paste at multi scales (Bossa et al. 2015), tortuosity and pore connectivity of cement specimen at different stages of hydration (Promentilla et al. 2008), reaction of anhydrous cement grains and porosity for hardened cement paste (Gallucci et al. 2007). Quantification and distribution of various phases, mass diffusivity of hardened cement (Valentini et al. 2011; Zhang et al. 2012). Ettringite-XRD-based image reconstruction linked with micro tomography for different period of hydration (Artioli et al. 2010). Dam-
age evolution in PC to estimate volume fraction and size distribution of anhydrous cement grains (Zhang and Jivkov 2014). Micro structure of cement paste at different curing ages to estimate moisture distribution and critical moisture content (Zhang et al. 2014). Air pore content in cement mixtures is estimated using pressure method, Air void analyzer, and CT (Moravcová et al. 2016). Cylindrical specimens are drilled from the cement mortar which are prepared by mixing polycrystalline (PAN) fibers, to monitor bonding and fiber orientation (Mishurova et al. 2017). Cement mortar morphology of pores such as appearance, size, volume, shape, porosity, tortuosity, permeability, and molecular diffusivity (Wang and Dai 2017). Size of the pore and connectivity for four different types of concretes cubes prepared with different mineral admixtures and at different spatial resolutions are investigated by (Lu et al. 2006). The Sealing effects on cracks formed in high strength and ultra-low permeable concrete is analyzed by (Fukuda et al. 2012). The effects of different scan rates and scan duration on quantifying the porosity of concrete are explored by (du Plessis et al. 2016). Void distribution in insulating concrete are monitored by (Chung et al. 2015), and entrained air-voids effects in concrete by (Lu et al. 2018). All these techniques are spread across various length scales of concrete. Limited literature is available to understand the thermal effects at different length scales in concrete: heating and curing effects on microstructure of high strength concrete and hydrated cement are investigated by (Henry et al. 2013, 2014); concrete prepared by different binding and aggregates exposed to 600°C and 900°C is the subject of study by (Sitek et al. 2015); Alkali activated geo binder and PC based binders from ambient temperature up 650°C are studied by (Rivera et al. 2016); mortar microstructure at room temperatures to 1000°C (Kim et al. 2012); concrete prepared with mineral admixture 400°C and 600°C is studied by (Su et al. 2016).

To the author’s knowledge there is lack of sufficient literature regarding the quantification of porosity parameters in hydrated PC subjected to different temperatures. The current research article focuses on characterizing the micro structure changes taking place in hydrated PPC specimen. The samples are obtained from the cores of the specimens exposed to temperatures of 100°C, 400°C, 500°C, and 800°C. These temperatures are selected based on thermal analysis (TG/DTA) of the hydrated PPC samples after 28 days of hydration. CHNS-O elemental analysis is conducted to estimate the elemental changes in the concentration of hydrogen, oxygen, carbon, and sulphur after the samples are exposed to 100°C and 800°C respectively. The samples collected from specimen cores are scanned using micro tomography, at the above specified temperatures to investigate the changes taking place in the micro level porosity of the specimen. The 2D images obtained from the scans are analyzed to estimate the radius, circularity, NND using 2D image analysis, while 3D analysis (integration of 3D analysis) study is carried out on the specimen to evaluate the diameter, area, volume, and sphericity of the pores.

2. Experimental investigation

Thermal analysis study is carried on the sample after 28 days of hydration to determining the critical temperatures at which micro tomography studies are to be conducted. For thermal analysis, the dried sample is collected after 28 days of hydration; as powder sample is needed for thermal analysis, the hard samples pieces obtained after testing the sample under compressive testing are ground using a planetary ball mill. For dispersing the solid sample in the whiles, acetone is used for milling; after 15 minutes of milling the wet sample are left to dry at air, and the obtained powder sample is used for thermal analysis. TGA and DTA thermal analysis, are carried on NETZSCH STA 2500 at a heating rate of 10°C/min in an argon atmosphere, for temperatures ranging from 27°C to 800°C. Elemental composition of C, H, N, S, and O elemental composition is determined using CHNS-O elemental analysis on a Thermo Finnigan, Model: FLASH EA 1112. The percentage of these elements present in hydrated PPC at temperatures of 100°C and 800°C is estimated; for the sample preparation we followed the same procedure adopted for thermal analysis; only exception is that the hydrated sample is collected after heating the sample at 100°C and 800°C respectively.

The sample for micro tomography is prepared using PPC cement manufactured in the industry which is commonly available at any cement supplier is used; the chemical oxide composition is estimated using XRF analysis and test are carried out on Bruker S4 Pioneer equipment. A total of 15 cubes are cast, i.e., three cubes are tested at each temperature, i.e., 100°C, 400°C, 500°C, and 800°C, and also at room temperature (27°C). PPC is mixed with a water-cement ratio of 0.33 and after mixing the sample is placed in a mold of 50 x 50 x 50 mm and compacted on a pan vibrator. The mold is air dried for 24 hours, and the specimen is taken out of the mold and placed in the curing tank for 28 days. At the time of testing the sample is taken out of the curing tank and air dried. The cubes are placed in a muffle furnace at a temperature loading of 5°C/min; once the desired temperature is reached, the temperatures are sustained in the furnace for a duration of 2 hours for 100°C, 4 hours for 400°C and 500°C; and 6 hours at 800°C. With an increase in temperature, the hold time is also increased so that higher temperatures can have their effects on the internal structure of the specimen. After the hold time, samples are brought to room temperature inside the furnace and tested under a compressive strength of the sample. After testing has been done the sample is collected from the sample of size ± 3 mm x 3 mm x 10 mm using a diamond precision cutter so that the sample is not disturbed. Then the sample is placed under Synchro-
2.1 Micro tomography measurements

The experimentation facility consists of storage ring energy of 2.5 GeV, and its maximum current is 135 mA. Unfocused monochromatic x-ray beam with an energy of 20 Kev, and a cross-sectional area of 100 x 5.25 mm² is used for irradiation. The voxel size for the current scan is 4.5 x 4.5 x 4.5 micrometer which is the input parameter, and the sample is mounted on a stage that allows the rotation and translation movement, and the data sets are obtained from the Micro-Tomography scans. The cross-sectional images obtained from the micro tomography are reconstructed using Octopus 3D reconstruction software which uses the filtered back projection algorithm (Kak and Slaney 1988). Data sets obtained from the micro tomography scans are processed to remove noise and due to beam temporal fluctuations which are a function of time, and the normalized obtained images are cropped to the ROI. After the normalization, the sinogram is built; then parallel beam reconstruction module is chosen, and the sinogram images are processed to remove any smears that are present in the image using the rotation axis option. After removing the smears, the volume reconstruction process is initiated and once the reconstruction is completed a histogram is generated. The upper and lower limit for the histogram is applied to the image and it is converted into an 8-bit image; this process is repeated for all the samples at the respective temperatures.

2.2 2D Image Analysis

The 2D images obtained from the Synchrotron micro tomography after scanning are analyzed using ImageJ software. A total of 900 to 1100 images are produced from the scan of depending on the sample size, and the scanned images are analyzed using image processing technique to estimate the porosity, pore distribution, circularity, and NND. The threshold of the images and beam hardening effects play a significant role in quantifying the parameters mentioned above for which Otsu’s method (Smith et al. 1979) is adopted. Otsu’s method defines a threshold ‘t’ value for converting grayscale images to a binary image. This method is dependent on determining an ideal ‘t’ value that is achieved by minimizing the variance of the two-pixel group. Once the threshold value is determined, the value lower than ‘t’ are selected as pores and the rest as solids. The threshold images are imported into ImageJ using the import image sequence option; for the current analysis 500 images are considered by neglecting the image layers at the top and bottom. This method is followed so that the internal structure of the sample can be determined, for these imported images ROI is selected by omitting the external area of the sample, i.e., for all the samples dimensions of ±1.1 mm x 1.1 mm x 2.2 mm is selected. After the ROI is selected the voxel parameters of 4.5 x 4.5 x 4.5 micrometer are given as the image properties, and the threshold is set to default for separating the pores and the matrix of the sample for estimating the quantity of porosity. Analyze particles option is selected to obtain the values of the area of pores, and circularity. After the area of pores is calculated, the NND plugin is used to estimate the pore network. The radius of the pore is determined assuming that the area of the pores obtained from image analysis are in circular shape. The 3D view is obtained by stacking 2D slices in the z-direction using volume viewer plugin.

2.3 3D Image Analysis

2D analysis is useful in determining the pores present in the sample per slice as the analysis does not give the number of pores in the sample which is 3D quantity. Avizo software is used as this software treats the pores present in the immediate slice at the same coordinates as a single pore. Hence to estimate the pore parameters such as diameter, area, volume, and sphericity in the sample. For the 3D analysis, the threshold images that are analyzed in ImageJ software, are imported into Avizo software, and the voxel parameters of 4.5 x 4.5 x 4.5 micrometer are given as the image properties for the image sequence. Interactive threshold module is selected for separating the pores and matrix; the ortho slice option enables observation of the pores being threshold across the x-y-z-axis. To quantify pores in the cube, label analysis module is selected to calculate the diameter, area, volume, sphericity, and porosity of the sample and this procedure is repeated for all the samples at the respective temperatures.

3. Results and discussions

Micro tomography tests are conducted on hydrated PPC samples that are collected from the core of those samples exposed to different temperatures, and 2D data sets are obtained from the scans. These 2D images acquired are quantified using image processing; from the image analysis the porosity of the sample, radius, circularity, and NND of pores are calculated. The number of individual pores, diameter, area, volume, and the sphericity of the pores is quantified for the sample by 3D analysis and the following observations emerged:

3.1 CHNS-O elemental analysis

As water is added to PPC, hydration takes place, which means that elements such as hydrogen and oxygen play a crucial role in producing the bond between the Calcium, Silica, Alumina, Magnesia, etc. However, when PPC is exposed to elevated temperatures the elements present in PC are affected; as the boiling point of water is low, there is a reduction of the concentrations of hydrogen, Oxygen, and carbon. The elemental percentages of C, H, S, and O of PPC sample exposed to 100°C, are 2.12, 1.74, 0.25, and 8.23 respectively; among these elemental percentages oxygen has the highest percent,
the elemental concentrations of H and O are crucial for concrete to show a better behavior under fire. The C, H, S, and O elemental percentages at 800°C are 0.97, 0.27, 0.48, and 3.71 respectively. Elemental percentages of N are not observed in the sample at both temperatures. The O content present in PPC at 100°C is very high compared to other elements, while the oxygen content at 800°C is reduced by 55% when compared to PPC at 100°C. The H element is highly affected when compared to other elements in the CHNS-O elemental analysis, as it is reduced by 85% at 800°C, in comparison to PPC at 100°C. The C content reduced by 55.25% at 800°C. The inclusion of water (which composes of H and O elements), into Portland initiates the hydration process, while the major phases in unhydrated PC forms a hydrated gel of Calcium Silicate Hydrate ((CaO)1.7(SiO2)(H2O)1.8 : CSH) and Portlandite (Ca(OH)2) which constitutes to 60 - 70% and 20 - 30% of the hydrated cements (Taylor 1997). A reduction in the elemental concentration of H and O affects the bonds between the CSH gel and Portlandite, thereby weakening the microstructure, and reducing the mechanical properties. From the elemental analysis, one can conclude that the reduction in H and O elements from PPC is one of the crucial factors governing the reduction in mechanical properties at elevated temperatures. To the author’s knowledge CHNS-O elemental analysis has not been conducted previously for PC subjected to various temperatures.

3.2 XRF Analysis
The chemical oxides present in dry powder of PPC sample are estimated using the XRF analysis; the quantities of major oxides are as follows: PPC is replaced with 15 - 35% of fly ash (IS 1489-1) hence there is variation in the volume percent of silicon dioxide, the calcium oxide content is 37.65% in comparison, while in OPC the quantity of CaO is higher. While the silicon dioxide is 34.67% which is usually found in lower quantities in OPC, Al2O3 is 11.8% which is higher than the recommended values of 3 - 8%, and Fe2O3 content is 6.99% (see Table 1).

3.3 Thermal Analysis
It is a preliminary analysis to determine the quantitative properties of the sample for understanding the thermal behavior of PC (Xu et al. 2005). In thermal analysis, TG/DTA analysis is carried out over PPC hydrated sample after 28 days of hydration. The TGA monitors the mass change against temperature over time, while DTA monitors over time, the temperature difference in the sample versus the reference. The TGA graph shown in Fig. 1 has three regions of interest i.e. a, b, and c; though there is a continuous mass change taking place in the sample, at regions ‘a’ and ‘b’, there is a sudden mass change. The mass loss in region ‘a’ which extends from the region of 90°C up to 200°C, is due to loss of water present in the Calcium Silicate Hydrate (CSH) gel layers. The mass loss happening in region ‘b’ at temperatures from 400°C to 500°C is due to the decomposition of Portlandite from the sample (Vedalakshmi et al. 2003; Gabrovšek et al. 2006). The DTA in Fig. 1 shows an exothermic reaction taking place at 80°C labeled region ‘a’ in Fig. 1, which is due to the evaporation of free and absorbed water (Masse et al. 2002). Endothermic peak is observed between 400°C and 430°C which is primarily due to the dehydration of calcium hydroxide and partially due to CSH. The peak after this drop shifts to exothermic peak as the temperature increases, because Portlandite (Ca(OH)2) is broken into CaO and H2O (Liu et al. 2017). Apart from the changes mentioned above, other chemical changes take place in hydrated PC at these temperatures by Collier (Collier 2016). Region ‘c’ is selected for the current analysis because of the minor changes in the physical structures of the hydrated PPC sample at temperatures of 800°C which is shown in Fig. 2(d). The temperatures corresponding to regions ‘a’, ‘b’ and ‘c’ are selected for further study.

3.4 Compressive strength
The compressive strength of the hydrated PPC sample is tested on 50 x 50 x 50 mm, after 28 days of hydration. The obtained compressive strength values are the aver-
The radius, circularity, and NND data are as follows: the internal pore structure samples obtained from the micro tomography scans at the specified temperatures of 100°C, 400°C, 500°C, and 800°C, along with 27°C are shown in Fig. 3. When the PPC samples are exposed to extreme temperatures there is an increase in the total number of pores for 500 slices as revealed by 2D analysis. At 27°C a total of 5974 pores of all sizes contributing to a porosity of 3.83%; at 400°C, the number of pores is 6589 with a porosity of 3.43%; and at 100°C the radii of the pores range from 2.54 µm to 235.14 µm corresponding to volume percentages of 83% and 0.22% respectively; at this temperature the pores tend to get finer, i.e. they attain values of 33.69 µm, 47.57 µm, 58.23 µm, and 67.23 µm and the relative volume percentages of these pores are 6.24%, 2.48%, 1.93%, and 1.43%. Below 400°C the dehydration of the Portland (Ca(OH)₂) takes place, as observed in Fig. 1 (Esteves 2011). The far end of the distribution of pore radii are centered on 218.8 µm (27°C), 235.14 µm (100°C), and 257.70 µm (400°C), which are larger than pore radii observed at 500°C and above, hence the corresponding porosity (up to 400°C) is higher. At 500°C the radii of pores range from 2.54 µm to 154.16 µm with relative volume percentages of 80.87 and 0.07 respectively; while the frequency bins (of radii distribution) which contribute to greater than 1% of total volume are centered on 18.22 µm, 25.64 µm, 31.35 µm, 36.17 µm and the volume percentages are 6.46%, 3.43%, 2.08% and 1.24% respectively. This dehydration process contributes to finer pores at macroscale in the temperatures ranges of 400°C to 500°C, as observed from the thermal analysis (Esteves 2011). At 800°C the radii of pores range from 2.54 µm to 134.18 µm with a volume percent of 55.81% to 0.02%, while the frequency bins (of radii distribution) which contribute to greater than 1% of total volume are centered on 14.77 µm, 20.73 µm, 25.33 µm, 29.22 µm,

(1) Radii of pores in 2D layer

The radii of pores by corresponding temperatures are plotted in Fig. 4(a); at 27°C the radii of pores range from 2.54 µm to 218.86 µm corresponding to volume percentages of 82.24 and 0.33 respectively. The radii of pores which contribute to greater than 1% of total volume are considered. At 27°C the frequency bins (of radii distribution) for these pores are centered on 36.05 µm, 50.92 µm, 62.34 µm, 71.98 µm and their corresponding volume percentages are 6.24%, 1.57%, 1.65%, and 1.40% respectively. At 100°C the radii of the pores range from 2.54 µm to 257.70 µm and the relative volume percentage is 79.13% and 0.25% respectively, while the frequency bins (of radii distribution) are centered on 38.46 µm, 54.33 µm, 66.51 µm and the relative volume percentages are 8.82%, 2.79%, and 1.72% respectively. At both these temperatures, the pores are spaced far apart. At temperatures of up to 150°C there is a mass loss which occurs due to the dehydroxylation of the CSH phase (Esteves 2011). At 400°C the radii of pores range from 2.54 µm to 235.14 µm corresponding to volume percentages of 83% and 0.22% respectively; at this temperature the pores tend to get finer, i.e. they attain values of 33.69 µm, 47.57 µm, 58.23 µm, and 67.23 µm and the relative volume percentages of these pores are 6.24%, 2.48%, 1.93%, and 1.43%. Below 400°C the dehydration of the Portland (Ca(OH)₂) takes place, as observed in Fig. 1 (Esteves 2011).
32.62 µm, 35.74 µm, 38.58 µm, 41.24 µm, and 43.73 µm; and the relative volume percentages are 11.44%, 7.19%, 5.64%, 3.95%, 3.15%, 2.01%, 1.73%, 1.46% and 1.08% respectively. A sudden drop in the frequency of pores of radii around 2.54 µm is observed at 800°C in Fig. 4(a) this is due to the pore expansion which increases the size of existing pores accompanied by an increase in the number of finer pores.

Fig 3 3D reconstructed porosity in PPC samples at different temperatures.

Fig. 4 2D image analysis of PPC (a) radius of pores (b) NND of the pores.
(2) NND of pores in 2D layer

NND enables quantification of the pore network distribution across the sample. An NND value of ‘0’ indicates the pores are clustered, while values above ‘0’ indicate the pores are dispersed. The distribution of the NND values is shown in Fig. 4(b); at 27°C the NND value ranges from 0 µm to 56 µm and their corresponding volume percent is 34.71% and 0.01%; the frequency bins (of NND) contributing to volume percent greater than 2% of total volume are centered on 1.11 µm, 2.22 µm, 3.33 µm, 4.44 µm, 5.55 µm, 6.66 µm and their volume percent is 21.14%, 14.50%, 7.42%, 5.02%, 3.22%, and 2.31% respectively. At 100°C the NND range is 0 µm to 74 µm for corresponding volume percent of 53.70 and 0.02; while the distribution of radii contributing individually to more than 2% volume of porosity between these ranges is 1.19 µm, 2.39 µm, 3.59 µm, and 4.79 µm and the volume percentages are 22.97%, 8.78%, 5.61%, and 2.17%. But at 400°C the distribution has become finer i.e. the NND range is 0 µm to 51.04 µm for a volume percent of 21.71% to 0.012%; the frequency bins (of NND) which contribute to greater than 2% of total volume are centered on frequency bins 1.02 µm, 2.04 µm, 3.06 µm, 4.08 µm, 5.10 µm and the volume percentages are 17.41%, 13.19%, 10.05%, 7.69%, and 4.66% respectively (the values with volume percent greater than 4%). At 500°C and 800°C the volume percent of NND values closer to 0 µm decreased to 9.04% and 11.09%; at 500°C the NND values in the range of 0 µm to 4 µm are centered on frequency bins 0.56 µm, 1.13 µm, 1.70 µm, 2.27 µm, 2.83 µm, 3.40 µm, and 3.97 µm for volume percentages of 11.50%, 11.11%, 12.08%, 7.16%, 8.74%, 5.59%, and 6.44 respectively. One can observe from the frequency of NND ranges, that the distance between the pores reduce with an increase in temperature. At 800°C the NND values in the range of 0µm to 4µm are centered on frequency bins 0.50 µm, 1.00 µm, 1.5 µm, 2 µm, 2.5 µm, 3 µm, 3.5 µm, and 4 µm while the volume percentages are 15.06%, 13.68%, 10.54%, 10.82%, 6.18%, 6.18% 4.28% and 4.53% respectively. As the number and diameter of pores increase with the increase in temperature, this forms a dense pore network which enables the interconnection of pores due to external or internal stressed.

3.6 3D image analysis

The 2D analysis discussed above for data obtained from 500 2D slices characterizes the frequency distribution of NND, circularity and radii of pores within the plane of the 2D slice. Further, these 2D slices are integrated in the 3D analysis wherein the volume, area and sphericity of pores in the cube are estimated. The porosity estimated in 2D analysis remains the same in comparison with the more complex 3D analysis for the same image set. The 3D analysis treats the pores present in the next slice centered at the same coordinates as a single pore for estimating the total number of pores in the sample.

Figure 5 shows the 3D image with separate colors assigned to individual pores, across the sample. At the total number of pores in the sample corresponding to each temperature are: 27°C (317), 100°C (629), 400°C (2811), 500°C (4979) and 800°C (3361). There is a sudden increase in the total number of pores after 100°C, because of the increase in the smaller pores in the sample. However, there is a drop in the number of pores at 800°C which is due to the increase in the pore diameter caused due to the merging of the separate pores. To investigate the reasons for the sudden reduction in the pore numbers 3D analysis is carried and the pore diameter, area and volume of the pores are analyzed in the following sections.

(1) Diameter of pores

From the 3D analysis the diameter of pores ranges from 7.93 µm to 520 µm. For the estimation of the pore diameters the following equation (1) is used:

\[
\text{Equivalent diameter} = \sqrt{\frac{6 \times \text{Volume3D}}{\pi}} \tag{1}
\]

where V and A are volume, and surface area of the pores respectively. The pores in the sample at 27°C range from 20.35 µm to 493 µm with corresponding volume percentages of 60.88% and 0.31%. The frequency bins (of diameter distribution) which contribute to greater than 1% of total volume are centered on 49.88 µm, 79.42 µm, and 108.98 µm and the volume percentages are 22.98%, 10.09%, and 1.92%. At 100°C the diameter of the pores are between 15.73 µm to 502.80 µm and the volume percentages are 65.65% to 0.15%. The frequency bins (of diameter distribution) which contribute to greater than 1% of total volume are centered on 36.02 µm, 56.32 µm, and 76.61 µm and the volume percentages are 14%, 7.95%, and 5.56% respectively. At 400°C there is reduction in the diameter ranges which is 10.48 µm and 520 µm respectively, and volume percentages are 84.24% and 0.03%. The distribution of diameter of pores has become finer with an increase in temperature, and the preceding values of higher percentages are for pores 20.28 and 30.07 µm, and the volume percentages are 8.44 and 2. After 50°C the minimum diameter of pore size reduces to 8.26 µm for 59.10% of pores and 77.76 µm for 0.02% of pores, the finer diameter of pores distribution in the sample is represented pictorially in Fig. 5, while the distribution of the pores diameters 13.61 µm, 18.97 µm, and 24.32 µm for a volume percentage of 20.57%, 9.87%, and 4.70% respectively are shown in Fig. 6(a). At 800°C the diameters distribution is 7.93 µm, 12.61 µm, 17.30 µm, and 21.97 µm for volume percentages of 50.67%, 16.22%, 8.13%, and 5.50%. The maximum diameter of pore is 270.17 µm which has a volume percent of 0.03. From Fig. 5(a) it is observed that the reduction in the distribution of the diameters of pores for the region 20.35 µm at 27°C volume has been reduced to 7.93 µm at 800°C. Overall it is observed that the pore diameter decreases with increase in temperature.
(2) Area of pores
The areas of pores range from 31.67 µm$^2$ to 1.07x10$^6$ µm$^2$, with 95% of the pores having areas less than 10500 µm$^2$ and these are plotted in Fig. 6(b). At 27°C the areas of pores range from 108.12 µm$^2$ to 9813 µm$^2$ and these contribute to 81.70% of total area of pores with the maximum area of pores being 998452 µm$^2$ with a volume percent of 0.31. At 100°C the area of pores range from 431.52 µm$^2$ to 848303 µm$^2$ for volume percentages of 45.62% and 0.16% respectively, while the area of pores with areas between 431.52 µm$^2$ to 9328 µm$^2$ constitutes to 82.36% of total area. With the increase in temperature the volume percentage of finer area of pores increases i.e., at 400°C, and the area of pores range from 159.13 µm$^2$ to 9989 µm$^2$ constitute 96.37% of volume. At 500°C with the changes taking place in Portlandite and CSH phases which have an effect on the microstructure, a temperature of 500°C the area of pores of range 99.15 to 5353 µm$^2$ contribute to 97.85% of total area volume. At 800°C the pores of areas 135.72 µm$^2$ to 8293 µm$^2$ contribute to 95.16% i.e. at 500°C the pores of area 99.16 µm$^2$, 175.80 µm$^2$, and 252.46 µm$^2$ contribute to volume percentages of 31.67%, 12.92%, and 7.03% while for 800°C the pores of area 135.72 µm$^2$ and 285.47 µm$^2$ contributed to 40.97% and 11.90% of volume. It is observed that there is a sudden increase in the areas of individual pores in the temperature range of 500°C to 800°C (Fig. 5), which occurs due to the interconnection of pores, and this causes a reduction in the total number of non-connected pores.

(3) Volume of pores
For the sample at 27°C the volume of pores 13213 µm$^3$ has a relative volume of 67.12%, while the relative volume of pores of 433107 µm$^3$ is 0.34%. At 100°C the volume of pores ranges from 4279 µm$^3$ to 188552 µm$^3$, and their volume percentages are 72.42% to 0.54%. The pores of volume 788.40 µm$^3$ have a volume percentage of 84.21% at 400°C. At 500°C the pores of volume 310.57 µm$^3$ and 750 µm$^3$ have a volume percentage of 53.48% and 15.28% respectively. At 800°C the volume of pores of 650 µm$^3$, 1766 µm$^3$, and 2882 µm$^3$...
while their volume percentages are 68.23%, 8.88%, and 4.30% respectively. Beyond temperatures of 500°C the pore volume increases and this same phenomenon is observed in the area of pores.

3.7 Circularity and sphericity
Circularity is a 2D quantity and for estimating these values, the pores in the 2D image layers are analyzed using ImageJ. The pores which are initially circular in shape tend to get interconnected with the neighboring pores due to which the pores become elongated in shape, as observed in the samples exposed to temperatures greater than 500°C. This phenomenon can be understood based on circularity of the pores. Circularity is plotted on a scale of ‘0’ to ‘1’ where ‘0’ indicates the pores are elongated polygons in shape while ‘1’ indicates the pores are perfectly circular in shape. As the temperature increases the mean sphericity of the pores has tendency to decrease. This is an artifact of the resolution limit of the micro-CT scan which causes pixilation and hence deviation from spherical shape of finer pores. Figure 7(a) displays the circularity of the pores using 2D analysis. At 27°C for a circularity value of 0.478 the volume percentage of pores are 0.30%. At temperatures of 100°C, 400°C, 500°C, and 800°C the circularity values are 0.469, 0.482, 0.339, and 0.332 for volume percentages of 0.25%, 0.48%, 0.391%, and 0.20% respectively. At 800°C, the distribution of elongated pores is spread between frequency bins of 0.356, 0.38, 0.40, 0.42, 0.45, and 0.475 respectively, and the total volume percentage of all corresponding elongated pores is 3.02%. Based on these values, one can conclude that the pores get interconnected with an increase in temperature. The percentage of elongated pores is very low initially, however, as the temperature increases there is a relative percentage increase in the elongated pores. This increase in the elongation helps in the interconnection of pores, thereby forming longer elongated pores which further coalesce into micro cracks and contribute to the failure of the material.

Sphericity ($\Psi$) is a 3D quantity defined as the ratio of the surface area of a sphere to the particle surface area obtained from formula given below shown in equation (2):
Conclusions

(1) The CHNS-O elemental analysis has shown a reduction in the elemental percentages of hydrogen, oxygen, sulfur, and carbon, while there are no traces of nitrogen present in the PPC sample subjected to heat. XRF analysis indicates higher concentrations of SiO$_2$ and Fe$_2$O$_3$ in PPC at room temperature in comparison to OPC. Thermal analysis is conducted for obtaining the critical mass loss and heat flow changes taking place in the sample at temperatures of 100°C, 400°C and 500°C.

(2) Acquisition of 3D images to visualize the microstructure changes taking place with respect to temperature is enabled using Micro tomography analysis.

(3) The open source software such as ImageJ is found suitable to quantify the porosity parameters such as radius, area, circularity, NND of the pores present in individual 2D slices of the sample. However, while ImageJ allows 3D reconstruction from 2D slices, it does not enable 3D analysis of data. The commercial software Avizo® enables extraction of the 3D porosity statistics such as diameter, area, volume, and sphericity of the pores present in the sample. Both 2D and 3D analysis of the obtained Micro tomography images enables quantification of spatial distribution of the pore network at micro scale to similar accuracy.

(4) In random samples extracted from the hydrated cement, the frequency of pores of any given radius (especially smaller pore sizes), increases with temperature up to 500°C. This phenomenon may be due to the reduction in the concentration of elements such as hydrogen and oxygen, as indicated from CHNS-O elemental analysis, which have severe effects on the phases such as Portlandite, CSH etc.

(5) The NND analysis indicates an increase in spatial distribution of pore network with temperature expressed as an increase in the number of pores per 2D slice. The circularity of pores decreases with an increase in temperature, due to interconnection of the pores, which further causes an increase in the frequency of elongated pores. The mean pore diameter, mean area and mean volume reduces with the increase in temperature up to 500°C. However, at 800°C slight relative increase in mean pore parameters are indicated due to the interconnection of pores, which also causes a reduction in the mean sphericity of pores.

(6) Due to the increase in the frequency of smaller pores with temperature, the load carrying capacity of the hydrated cement sample is reduced, because the frequency of finer pores as well as their spatial distribution increases in the sample in relative to coarse pores. When a critical external load or internal stress due to increase in temperature is achieved, these pores get interconnected to form preferential failure planes along pore networks.

(7) At the micro scale the distribution of inaccessible pores is observed to increase with temperature in the sample. Hence, the mean porosity values observed in this study at microscale, are higher in comparison to the published data obtained from MIP conducted by other researchers. From this study one can conclude that micro tomography studies has various of advantages over the traditional methods such as MIP, nitrogen adsorption test etc. in quantifying the various porosity parameters.

Acknowledgment

The authors are thankful for the support extended by Dr. Amar Sinha (NXPD, BARC), Dr. Ravindra D Makde (RRCAT) and Mr. Balwant Singh (BL-04, RRCAT) along with Indus-II staff for helping us with Synchrotron Micro-Tomography study, also to Akhi mood from IIS’c, Banglore for his support and expertise on Avizo software, also we are thankful to CAM-NIT Warangal, SAIF-IIT Bombay, and Arbro pharmaceuticals Ltd-New Delhi for the facilities made available to carry out the experiments.

References

Abell, A. B., Willis, K. L. and Lange, D. A., (1999), “Mercury intrusion porosimetry and image analysis

\[ \psi = \frac{\pi^{1/3} \cdot 6V^{2/3}}{A} \]
of cement-based materials.” *Journal of Colloid and Interface Science*, 211(1), 39-44.

Artioli, G., Cerulli, T., Cruciani, G., Dalconi, M. C., Ferrari, G., Parisatto, M., Rack, A. and Tucoulou, R., (2010). “X-ray diffraction microtomography (XRD-CT), a novel tool for non-invasive mapping of phase development in cement materials.” *Analytical and Bioanalytical Chemistry*, 397(6), 2131-2136.

Benouis, A. and Grini, A., (2011). “Estimation of concrete’s porosity by ultrasounds.” *Physics Procedia*, 21, 53-58.

Bossa, N., Chaurand, P., Vicente, J., Borschneck, D., Levard, C., Aguerre-Chariol, O. and Rose, J., (2015). “Micro-and nano-X-ray computed-tomography: A step forward in the characterization of the pore network of a leached cement paste.” *Cement and Concrete Research*, 67, 138-147.

Chan, Y.-N., Peng, G.-F. and Anson, M., (1999). “Residual strength and pore structure of high-strength concrete and normal strength concrete after exposure to high temperatures.” *Cement and Concrete Composites*, 21(1), 23-27.

Chung, S.-Y., Han, T.-S. and Kim, Y.-W., (2015). “Evaluation of the hydration of Portland cement and Concrete Research.” *In: 3rd Int. Conf. on Sustainable construction materials and technologies, Tokyo, Japan*, 263-271.

Henry, M., Darma, I. S. and Sugiyama, T., (2013). “Analysis of cracking in high-strength cementitious materials under heating and re-curing using X-ray CT.” *Cement and Concrete Research*, 37(3), 360-368.

Kucharczyková, B., Misák, P. and Vymazal, T., (2010). “Determination and evaluation of the air permeability coefficient using Torrent Permeability Tester.” *Russian Journal of Nondestructive Testing*, 46(3), 226-233.

Lee, N. K., Koh, K. T., Park, S. H. and Ryu, G. S., (2017). “Microstructural investigation of calcium aluminate cement-based ultra-high performance concrete (UHPC) exposed to high temperatures.” *Cement and Concrete Research*, 102, 109-118.

Liu, S., Wang, H. and Wei, J., (2017). “The role of various powders during the hydration process of cement-based materials.” *Advances in Materials Science and Engineering*, 2017, 1-9.

Lu, H., Peterson, K. and Chernoloz, O., (2018). “Measurement of entrained air-void parameters in Portland cement concrete using micro X-ray computed tomography.” *International Journal of Pavement Engineering*, 19(2), 109-121.

Masse, S., Vetter, G., Boch, F. and Haehnel, C., (2002). “Elastic modulus changes in cementitious materials submitted to thermal treatments up to 1000°C.” *Advances in Cement Research*, 14(4), 169-177.

Mishurova, T., Léonard, F., Oesch, T., Meinel, D., and Margaritondo, G., (2007). “3D experimental investigation of the microstructure of cement pastes using synchrotron X-ray microtomography (μCT).” *Cement and Concrete Research*, 37(3), 360-368.
Bruno, G., Rachmatulin, N., Fontana, P. and Sevostianov, I., (2017). “Evaluation of fiber orientation in a composite and its effect on material behavior.” In: Proceeding of 7th Conference on Industrial Computed Tomography, Leuven, Belgium.

Moravcová, B., Possl, P., Misak, P. and Blazek, M., (2016). “Possibilities of determining the air-pore content in cement composites using computed tomography and other methods.” Materiali in tehnologije, 50(4), 491-498.

Piasta, J., Sawicz, Z. and Rudzinski, L., (1984). “Changes in the structure of hardened cement paste due to high temperature.” Materiaux et Constructions, 17(4), 291-296.

Promentilla, M. A. B., Sugiyama, T., Hitomi, T. and Takeda, N., (2008). “Characterizing the 3D pore structure of hardened cement paste with synchrotron microtomography.” Journal of Advanced Concrete Technology, 6(2), 273-286.

Provis, J. L., Myers, R. J., White, C. E., Rose, V. and van Deventer, J. S., (2012). “X-ray microtomography shows pore structure and tortuosity in alkali-activated binders.” Cement and Concrete Research, 42(6), 855-864.

Rivera, O. G., Long, W. R., Weiss Jr., C. A., Moser, R. D., Williams, B. A., Torres-Cancel, K., Gore, E. R. and Allison, P. G. (2016). “Effect of elevated temperature on alkali-activated geopolymeric binders compared to portland cement-based binders.” Cement and Concrete Research, 90, 43-51.

Scrivener, K. L., (2004). “Backscattered electron imaging of cementitious microstructures: Understanding and quantification.” Cement and Concrete Composites, 26(8), 935-945.

Sitek, L., Bodnarova, L., Souček, K., Staš, L. and Gurkova, L., (2015). “Analysis of inner structure changes of concretes exposed to high temperatures using micro X-ray computed tomography.” Acta Geodyn. Geomater, 12(1), 177.

Otsu, N., (1979). “A threshold selection method from gray-level histograms.” IEEE Transactions on Systems, Man, and Cybernetics, 9(1), 62-66.

Stutzman, P., (2004). “Scanning electron microscopy imaging of hydraulic cement microstructure.” Cement and Concrete Composites, 26(8), 957-966.

Su, Y. M., Hou, T. C., Lin, L. C., Chen, G. Y. and Pan, H. H., (2016). “The nondestructive evaluation of high temperature conditioned concrete in conjunction with acoustic emission and x-ray computed tomography.” Nondestructive Characterization and Monitoring of Advanced Materials, Aerospace, and Civil Infrastructure, 9804.

Taylor, H. F. W., (1997). “Cement chemistry.” Thomas Telford Publishing.

Valentini, L., Dalconi, M. C., Parisatto, M., Cruciani, G. and Artioli, G., (2011). “Towards three-dimensional quantitative reconstruction of cement microstructure by X-ray diffraction microtomography.” Journal of Applied Crystallography, 44(2), 272-280.

Wang, Y. S. and Dai, J. G. (2017). “X-ray computed tomography for pore-related characterization and simulation of cement mortar matrix.” NDT & E International. 86(3), 28-35.

Xu, W., Li, S., Whitely, N. and Pan, W. P., (2005). “Fundamentals of TGA and SDT.” In: Proceeding of International Seminar: “Thermal analysis and rheology.” (2003), 1-7.

Zhang, M., He, Y., Ye, G., Lange, D. A. and van Breugel, K., (2012). “Computational investigation on mass diffusivity in Portland cement paste based on X-ray computed microtomography (μCT) image.” Construction and Building Materials, 27(1), 472-481.

Zhang, M., Xu, K., He, Y. and Jivkov, A. P., (2014). “Pore-scale modelling of 3D moisture distribution and critical saturation in cementitious materials.” Construction and Building Materials, 64, 222-230.

Zhang, M. and Jivkov, A. P., (2014). “Microstructure-informed modelling of damage evolution in cement paste.” Construction and Building Materials. 66, 731-742.

**Notations**

- $\Psi$: Sphericity
- CHNS-O: Carbon hydrogen nitrogen sulphur and oxygen
- DTA: Differential thermal analysis
- NND: Nearing neighboring distance
- OPC: Ordinary Portland cement
- PPC: Portland pozzolona cement
- PC: Portland cement
- ROI: Region of interest
- TGA: Thermo gravimetric analysis
- XRF: X-ray fluorescence