Pore-network distribution laws of cementitious materials detected by high-energy X-ray computed tomography imaging system

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Abstract. Pore networks of cementitious materials determine the materials’ properties and engineering safety. In this work, four kinds of cementitious materials which are geopolymer cement, foamed cement, ordinary concrete and pervious concrete were prepared, and a high-energy X-ray computed tomography imaging system was used to detect the samples’ inner structures. It was found that the pore network of such materials show similarity to social networks. However, the traditional mathematical degree which is the coordination number of a network is insufficient to characterize the pore networks, because such networks have volume limitations. Thus a new parameter, physical degree, was proposed in this work. By analyses of the pore networks of the samples, it was found the mathematical degrees follow Poisson distribution law whereas the physical degree can be fitted by power law. This indicates the pore networks are random and scale free. These findings may provide insight for future intelligent design of digital cementitious materials.

1. Introduction

Pore networks of cementitious materials determine the materials' strength[1], durability[2], permeability[3], and thermal resistivity[4] etc. Thus understanding the governing laws of pore-network distribution is crucial[5], especially from macroscopic perspective. On the other hand, with the rise of additive manufacturing, the 3D printing of cementitious materials [6] can also benefit from the thorough understanding of pore-network distributions.

The traditional methods to detect the pore network of cementitious materials are mainly indirect methods such as mercury intrusion porosimetry (MIP) [7] which is a destructive method that can give information about the connected porosity, pores volume and size distribution. Besides this method, the nuclear magnetic resonance (NMR) method [8] can also get the information of inner pore networks of cementitious materials by detecting hydrogen nuclear magnetization relaxation. This method is nondestructive and allows 3D image reconstructions. But it also needs the pores are permeable with detectable quantities of hydrogen nuclear, though the majority pores in cement are impermeable. Nevertheless, the X-ray computed tomography (CT) method has no such limitation, and thus it is widely used [9]. This method detects the X-rays attenuation when they pass through the materials and thus can provide detailed inner structure of the materials [10].

Usually, the CT image data are extremely huge whereas the sample size is very small. To correlate the sample's micro parameters with its macro properties, we may draw support from the network theories which are highly developed but lack enough application in the analysis of pore networks of
cementitious materials. Indeed, pore networks are quite similar to social networks, cf. Figure 1 where two pore networks of cementitious materials and two social networks [11] are compared. Their degree distributions show similarity to each other. Here the degree is also named as coordination number in literatures of porous media. From the similarity, it can be inferred that pore networks may follow similar laws of social networks. This paper was planned to check this point. Here, four kinds of samples of cementitious materials were prepared, and an industrial X-ray computed tomography imaging system was used to detect the samples’ inner structures. By data analysis, the pore-network distribution laws of such materials were concluded in this paper.

Figure 1. Degree distributions of four networks: (a) Pore network of foamed cement; (b) Pore network of pervious concrete; (c) Papers citation network of American Physical Society journals until 2005; (d) Twitter mention network during January 23rd and February 8th, 2011.

2. Materials and Methods

2.1. Samples
Four kinds of cementitious materials which are geopolymer cement, foamed cement, pervious concrete, and ordinary concrete were used in the experiment, cf. Figure 2. Specifically, Figure 2a is 3 pieces of geopolymer cement with the same dimensions of 50 mm × 50 mm × 50 mm. Figure 2b shows a piece of foamed cement with the dimensions of 78 mm × 86 mm × 200 mm. Figure 2c is a piece of ordinary concrete with the dimensions of 50 mm × 110 mm × 200 mm, which was made of ordinary Portland cement, water and aggregates. Figure 2d shows a piece of pervious concrete with the dimensions of 53 mm × 115 mm × 240 mm, which is made of Portland cement, water, slag and coarse recycled aggregates.

2.2. X-ray CT imaging system
All the samples were detected by a high-energy X-ray CT imaging system. The CT facilities mainly consist of three parts which are X-ray source, sample table and X-ray detector as shown in Figure 3. The maximum voltage of the X-ray source in this CT system can reach up to 450kV which can generate high-energy X rays that can penetrate large or dense samples.
Figure 2. Samples: (a) geopolymer cement, (b) foamed cement, (c) ordinary concrete and (d) pervious concrete.

In detection, the X-ray source of the CT facilities generate X-rays with an incident intensity $I_0$ to penetrate the samples on the sample table, and then the X-ray detector receives attenuated X-ray intensity $I$ which follows the Beer-Lambert law. Indeed, the intensity reflects material densities varying in space. Through the histogram of intensities, air (pore) can be differentiated from solid (structure) by the Otsu method. All the CT images were processed in VG Studio and Avizo. Then the PNext extract was used to extract the conventional pore networks from the processed image data. After that, the pore networks can be analyzed by OpenPNM and NetworkX which are specific Python packages for network analysis.

Figure 3. X-ray CT facilities.

2.3. Degrees

The degree, also named coordination number, means the number of links attached to a pore in a network, which plays crucial roles in network theories. However, the traditional degree is insufficient to describe the pore networks, because these networks, unlike social networks, have space dimensions. That is to say they are affected by their volumes. Thus a new parameter, physical degree $d_p$, was defined in this work, and the traditional degree is renamed as mathematical degree $d_m$. The physical degree $d_{pi}$ for the $i$th pore in a pore network can be written as

$$d_{pi} = V_{pi} + \sum_{j=1}^{n} V_{tj},$$  \hspace{1cm} (1)

where $V_{pi}$ represents the volume of the $i$th pore which has $n$ throats attaching to it, and $V_{tj}$ represents the volume of the $j$th throat of the $i$th pore.
2.4. Distribution laws
Two kinds of distribution law were considered in this work, which are power law and Poisson law. The power law is the only scale-free distribution law and also the main concern of this work, which can be written as

\[ f = yd^{-\alpha}, \]  
\( (2) \)

where \( d \) represents the degree, \( f \) represents the frequency of degrees, \( y \) and \( \alpha \) are fitting coefficients. In logarithmic coordinates, the power law can be written in a form of linear function which is

\[ y = -\alpha x + \beta, \]  
\( (3) \)

where \( y = \log f, \beta = \log y, \) and \( x = \log d \). The Poisson law, which is also widely used to demonstrate the randomness of variables, can be written as

\[ f = \frac{e^{-\lambda \lambda^d}}{d!}, \]  
\( (4) \)

where \( e \) is the Euler’s number, \( \lambda \) is a fitting coefficient.

The Levenburg-Marquardt algorithm in SciPy, which is a Python package, was used to fit the data, and the coefficient of determination was used to show the goodness of fit, which is

\[ r^2 = 1 - \frac{\sum(y - \hat{y})^2}{\sum(y - \bar{y})^2}, \]  
\( (5) \)

where \( y \) represents the sample data, \( \hat{y} \) represents the fitted data, and \( \bar{y} \) represents the mean of sample data. When \( r^2 \) approaches 1, the fitting result is the best.

3. Results and discussion
The Poisson distribution law can demonstrate the randomness of variables, which was used to fit the mathematical degrees. Results are shown in Figure 4. Basically, the Poisson distribution law catches the trends of mathematical degrees. The fitting formula as well as its related goodness of fit \( r^2 \) are also shown in each sub-figure of Figure 4. The expectation (\( \lambda \)) of mathematical degrees of each sample can be found in each fitting formula. Specifically, the \( \lambda \) of foamed cement in Figure 4b is 3.998 which is the highest expectation among the four pore networks. This indicates the majority degree of foamed-cement pore network is around 3.998 (i.e. 4). Besides the foamed cement, the \( \lambda \) of pervious concrete (\( \lambda =1.373, \) cf. Figure 4d) is also beyond 1. These higher expectations (i.e., higher \( \lambda \)) indicates the pores in the networks are well connected. On the contrary, the \( \lambda \)s of geopolymer cement (\( \lambda = 0.036, \) cf. Figures 4a) and ordinary concrete (\( \lambda =0.274, \) cf. Figures 4c) are less than 1. That is to say the pores of such samples are mainly isolated, which indeed can be also conjectured from their CT images shown in each subfigures of Figure 4.

![Figure 4. Fitting results of Poisson distribution law for the mathematical degree of (a) geopolymer cement, (b) foamed cement, (c) ordinary concrete and (d) pervious concrete.](image-url)
It can be inferred from Figure 1 that mathematical degrees of cementitious materials do not perfectly follow the power law which should be a straight line in the logarithmic coordinates. From another point of view, the physical degree (Equation 1) proposed in this work was meant to demonstrate the preferential-attachment mechanism, and thus the physical degree may follow the power law. Indeed, the fitting results of physical degrees of each sample are shown in Figure 5, where it can be found the goodness of fit for each sample approaches 1. This indicates the fitting results are excellent and the physical degree follows the power law. Nevertheless, the data of foamed cement (Figure 5b) show slight deviation from the power law although the coefficient of determination $r^2$ is greater than 0.8 which is indeed a high value for fitting results. The reason for this deviation is due to the special pores of foamed cement, and these pores are not totally controlled by the preferential-attachment mechanism. Indeed, the pores in foamed cement are made by blowing agent and they are usually uniformed. This contributes to the slight deviation of the fitting result. For the parameters in the fitting formula, $\alpha$ is the slope of the fitting line, which satisfy $2 < \alpha < 3$. This is coincident with social networks [13]. $\beta$ represents the intercept of the fitting line. In Figure 5, it can be found the absolute value of $\beta$ for the geopolymer cement is the highest. This indicates the frequency of larger pores in geopolymer cement is the lowest. In other word, there are many more small pores in geopolymer cement whereas the pores in other samples are relatively larger.

4. Conclusions

To find the macroscopic pore-network distribution laws of cementitious materials, four kinds of cementitious samples were scanned by a high-energy X-ray CT imaging system. By analyzing the reconstructed CT pore structures of each sample, conclusions were drawn as below:

- The pore networks of cementitious materials show similarity to social networks. But the pore networks are limited by their volume space and the traditional degree distribution laws are insufficient to describe the particular properties of pore networks. Thus a new parameter, physical degree was proposed in cooperation with the traditional mathematical degree to characterize the pore network of cementitious materials.
- The Poisson distribution law is suitable to describe the mathematical degrees and showed excellent fitting agreement and reasonable parameters. For the physical degree, which was defined to represent the preferential-attachment mechanism that pervades a scale-free network,
the power law can describe the data trend, though the physical degrees of foamed cement deviate a little since their pore networks are also controlled by other mechanisms.

- the fitting parameters also show specific physical meanings. Larger $\lambda$ of the Poisson distribution law indicates the pores in the sample are mainly connected whereas smaller ones, especially when $\lambda < 1$, indicate the pores are isolated. The slopes of power law for the physical degrees show $2 < \alpha < 3$. And the lower intercepts of the fitting lines (power law) indicates the frequency of larger pores in the samples are lower.

These findings may provide insights for the design of cementitious materials. Especially, a model could be proposed based on the findings. And such model could be developed and used in optimizing both the permeability and strength of cementitious materials in future.

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