Inner changes of Portland cement and metakaolin-based geopolymer in the high-temperature environment

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Abstract. The inner structure of cementitious materials is crucial for the intelligent design and construction in civil engineering. In this work, two kinds of samples made from Portland cement and metakaolin-based geopolymer respectively were prepared to be exposed in high-temperature environment. In the experiments, the samples were placed on a heater with a 400°C surface for 40 minutes. A high-energy X-ray computed tomography (CT) facility was used to detect the macroscopic inner structure of the samples. In addition, the infrared-ray morphology of samples was also tested and compared. Results show that metakaolin-based geopolymer was relatively more resistant to heat compared with Portland cement. However, the cracks development of metakaolin-based geopolymer was severer due to the shrinkage in the high-temperature environment. In addition, based on the X-ray CT images, a method to show the distribution of pores’ sizes was proposed. It was found the distribution of pores’ volumes and area surfaces can be fitted by power laws which are straight lines in the logarithmic coordinates, and the geopolymer samples have relatively higher goodness of fit. Moreover, a lower intercept of the fitting line indicates the frequency of larger pores in the sample is lower, and a lower slope indicates a tighter distribution range of the pores’ sizes. These findings may provide insight for future intelligent design of digital cementitious materials used in harsh environment.

1. Introduction
Cementitious materials are important construction materials and also suitable for 3D printing. With the rise of intelligent design and construction in civil engineering, the inner structures of cementitious materials and their changes in different circumstances would been considered more and more seriously in relevant engineering. In addition, the Portland cement which is the traditional cementitious material consumes lots of energy in its production [1]. And the emission of waste gases such as carbon dioxide during the production is remarkably great. Thus, developing other environment-friendly cementitious materials such as geopolymer is of great importance. Indeed, the geopolymer (alkali-activated material) is often used as additive in cooperation with Portland cement in producing concrete, which show better performance in acid corrosion as well as heat resistance [2]. However, shrinkage cracks may be generated when the materials dehydrate. Thus, understanding the mechanism of cracks development in the materials is crucial.

Indeed, the pores in the materials play important roles in their resistance of heat as well as the crack developing process [3]. Thus, pore test is crucial to evaluate the performance of materials in harsh environment. Generally, the popular test methods are for microscopic samples, whose results would focus on the micro pores. For instance, the mercury intrusion porosimetry (MIP) usually require the
typical length of the sample around 1cm. Moreover, the test results of MIP are for connected pores in the sample whereas the isolated pores are undetectable [4]. Thus, it was found the porosity of cement was higher than that of geopolymer, though the geopolymer is more porous [5]. To directly describe the morphology of pores, the scanning electron microscopy (SEM) was usually employed [6], though it is also limited in microscopic and 2 dimensional scope. Indeed, the X-ray computed tomography (CT) can provide 3 dimensional morphology of the pores [7]. However the penetration power of traditional laboratory X-ray CT is also usually limited to a scope which is merely suitable for micro-samples [8]. Thus a macroscopic porosity detection would be valuable.

In this work, a high energy X-ray CT facility was used to detect the macroscopic degradations of Portland cement and metakaolin-based geopolymer in the high-temperature environment. On the base of the X-ray CT images, a method to show the distribution of pores' sizes was also proposed. The results may provide insights for the intelligent design of digital cement and geopolymer used in harsh environment.

2. Materials and Methods

2.1. Samples
The samples were made from Portland cement and metakaolin-based geopolymer, respectively, which have a cubic shape with 5 cm on each side, cf. Figure 1(a). The mineral compositions of Portland cement are mainly 3CaO·SiO$_2$ (C3S), 2CaO·SiO$_2$ (C2S), 3CaO·Al$_2$O$_3$·Fe$_2$O$_3$ (C4AF), whereas the main mineral of metakaolin is Al$_2$O$_3$·2SiO$_2$ (AS2) which is dehydrated from kaolin clay (Al$_2$O$_3$·2SiO$_2$·2H$_2$O) at a temperature of 600-900℃. For the cement samples, the ratio of water to cement is 0.35. The geopolymer samples were made from metakaolin and alkaline activators. Here the alkaline activators were NaOH and Na$_2$SiO$_3$ solutions. And the concentration of NaOH solution is 12 mol/L whereas the compositions of Na$_2$SiO$_3$ solution are 12.97% Na$_2$O, 29.03% SiO$_2$ and 58% H$_2$O by mass. The mass ratio of metakaolin, Na$_2$SiO$_3$ and NaOH solutions is 3.55:2:1. All samples had been cured in a chamber with a constant temperature of 20℃ and humidity of 95% for 28 days.

![Figure 1. (a) Samples of cement (left) and geopolymer (right); (b) Schematic heating process.](image)

2.2. Heating process
The heating process is schematically shown in Figure 1(b), where the samples were baked on a heater for 40 minutes during the experiments. The heater uses electricity to generate far infrared ray to heat the sample. And the temperature of the heater surface can reach to 400℃. During the baking process, an infrared thermal imager which can translate the thermal radiation into temperature was used to take the temperature-distribution images of the samples' surfaces with a resolution of 160×120.

2.3. X-ray computed tomography
The inner structures of all samples were detected by a high-energy X-ray CT (computed tomography) imaging facility which is shown in Figure 2. The CT facility consists of three parts which are X-ray source, sample table and X-ray detector. The X-ray source has a maximum voltage of 450kV which
can generate high energy X-rays to penetrate 5-cm steel plate, and thus the macroscopic inner structure of 5-cm cement and geopolymer samples whose density is around 1/3 of steel can be easily detected by such kind of X-rays.

In detection, the X-rays radiate from the source with an incident intensity $I_0$, then penetrate the sample, and last is received by the detector with an attenuated X-ray intensity $I$ which follows the Beer-Lambert law:

$$I = I_0 e^{-\mu x}, \quad (1)$$

where $\mu$ is an attenuation factor affected by material densities, and $x$ is the sample's thickness in the direction of X-ray transmission. Thus the intensity reflects material densities varying in space. From the intensity histogram of the samples, the pores and structure can be differentiated by the Otsu method. The CT reconstruction images have a resolution of $2048 \times 2048$ which would generate a pixel of 0.05mm for a scanning range of 10cm$\times$10cm. The images can be processed and analyzed by VG Studio and Avizo.

2.4. Curve fit

In this work, the pores of all samples were extracted from the CT images, and the pores' volumes and surface areas were also calculated and exported to Python to analyse the corresponding distributions. The main concerns are their frequencies which were fitted by the power law in this work. And the power law can be written as

$$f = \gamma v^{-\alpha}, \quad (2)$$

where $v$ represents the variables, i.e., volumes $V$ or areas $S$ in this work, $f$ represents the frequency of $v$, $\gamma$ and $\alpha$ are coefficients. In logarithmic coordinates, the power law can be written in a form of linear function like

$$y = -\alpha x + \beta, \quad (3)$$

where $y = \log f$, $\beta = \log \gamma$, and $x = \log v$.

The Levenburg-Marquardt algorithm in SciPy, which is a Python package, was used to fit the data, and for the goodness of fit, the coefficient of determination was used, which can be written as
\[ R^2 = 1 - \frac{\sum (y - \hat{y})^2}{\sum (y - \bar{y})^2}, \tag{4} \]

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

3. Results and discussion

During the heating process, the temperature distributions of the samples were taken by a thermal imager, and the results of 0 minute, 5 minutes, 15 minutes and 40 minutes later after the samples were placed on the heater were shown in Figure 3. Generally, the heat-transfer speed of cement samples is slightly faster than that of geopolymer samples. The reason for this is the lower thermal conductivity and higher porosity of geopolymer samples [9]. And indeed, the temperature-distribution curves of geopolymer samples were also more crooked, especially in the last images (i.e., images in column of 40 minutes). Thus, the heat-resistance capability of geopolymer samples is slightly higher than that of cement samples. This is consistent with previous researches [9].

![Figure 3](image-url)

**Figure 3.** Temperature distributions (infrared thermal images) of the (a) cement sample and (b) geopolymer sample during the heating process.

The inner pores, especially their distributions, affect the properties of cement and geopolymer samples [10]. In this work, a high-energy X-ray CT facility (cf. Figure 2) was used to detect the macroscopic inner structure of the samples, and the results before and after the heating are shown in Figures 4 and 5, respectively.
Figure 4. Distributions of pores’ volumes and surface areas before the heating: (a) structure, (b) pores, pores’ (c) volumes and (d) areas distributions of cement sample; (e) structure, (f) pores, pores’ (g) volumes and (h) areas distributions of geopolymer sample.

In Figure 4, excluding the data in the tail, the distributions of the remaining data are more likely to follow a straight line (power law). Thus, the whole data were split into two parts and fitted separately by the power law. Generally, by the goodness of fit $R^2$, the linear fits of areas are better than those of volumes, and the fits of geopolymer samples are better than those of cement samples. This is due to the heavier tail shown in cement samples, which indicates the sizes of a large part of pores in cement are distinctly larger whereas most pores in geopolymer are smaller [9]. Moreover, the absolute values of fitting parameters, i.e., $\alpha$ and $\beta$, of geopolymer samples are greater than those of cement samples. Here, $\alpha$ represents the slope of the fitting line, which distributes in the interval of (-2, -1). Indeed, the slopes of the oblique fitting lines affect the distribution range of the variables (i.e., $V$ and $S$). The higher absolute value of the slope indicates a tighter distribution range for the variable, $\beta$ is the intercept of the fitting line, which indicates the frequency of larger pores. From the results in Figure 4, the frequency of larger pores in geopolymer is lower than that of cement. For all samples, the data in the tail form a horizontal straight line with an intercept ($\beta$) around -3 whereas the remaining data form an oblique line whose intercepts distributes around -10. Moreover, for the tail data of the same sample, the intercepts ($\beta$) of fitting curves of volumes distribution and areas distribution are equal to each other.

After the heating, the samples were also scanned by the X-ray CT imaging facility, and results are shown in Figure 5, where it can be found distinct cracks appeared in the geopolymer sample whereas no more visible cracks appeared in the cement sample. The reason for the cracks is due to the shrinkage caused by dehydration. This is a distinct drawback of geopolymer samples. For the distributions of pores’ volumes and areas, as before, each dataset was fitted by two independent power laws. In comparison with the corresponding parameters ($\alpha$ and $\beta$) in Figure 4, the fitting parameters of cement sample change little whereas those of geopolymer sample change distinctly. This indicates the pores in geopolymer changed a lot and indeed is coincident with their morphology changes, cf. Figure 5(f) where a bunch of new cracks appeared at the bottom of the sample, and most of them were distributed in the inner central part of the sample. These cracks are usually difficult to be detected by other methods [4].
Figure 5. Distributions of pores' volumes and surface areas after the heating: (a) structure, (b) pores, pores' (c) volumes and (d) areas distributions of cement sample; (e) structure, (f) pores, pores' (g) volumes and (h) areas distributions of geopolymer sample.

4. Conclusions
Two kinds of samples made from Portland cement and metakaolin-based geopolymer respectively were compared for the inner structure changes in the high-temperature environment. Optical, infrared, and X-ray images of the samples were obtained and analyzed. The following conclusions were drawn:

- In high-temperature environment, the heat resistance of metakaolin-based geopolymer is higher than that of Portland cement due to its high porosity and newly generated cracks during the heating process.
- The distributions of pores' volumes and area surfaces of metakaolin-based geopolymer and Portland cement can be fitted by the power law, and those of geopolymer samples have relatively higher goodness of fit.
- The fitting parameters of the power law indicate the distribution law of pores' sizes. A lower intercept (higher absolute value) of the fitting line indicates the frequency of larger pores in the sample is lower, and a lower slope (higher absolute value) indicates a tighter distribution range of the pores' sizes.

These findings may provide insights for the future intelligent design of digital cementitious materials used in harsh environment.

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