- Technical Paper -

STUDY ON FABRICATION OF ANISOTROPIC CEMENT-BASED MATERIALS WITH ALIGNED PORE STRUCTURES USING FREEZE CASTING METHOD

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ABSTRACT
This study fabricated cement-based materials with aligned pore structures via freeze casting. Temperature variations during the process were monitored, and the resulting pore structure, porosity, and mechanical properties were compared with those of conventionally prepared cement paste. The results showed that freezing speed strongly influences the freezing point, and significant anisotropy in porosity and mechanical properties was observed. Directional pore structures enhanced early-age mechanical performance along the lamellar alignment.
Keywords: materials circulation, freeze casting, mono materials, anisotropy, lamellar pores

1. INTRODUCTION

The excessive emission of carbon dioxide (CO_2) caused by human activities has led to a consistent rise in global temperatures over the past few decades [1]. In building materials, improving the material's recyclability is an effective way to reduce CO_2. In general, the construction projects often use composite materials to meet multifunctional demands, making it difficult to separate components after finishing their service life, leading to low recyclability. Moreover, building construction materials, like concrete, are composed of various components and exhibit low recyclability, due to the complex interfaces between different components [2]. These interfaces are often the weakest points, and their quantity increases with the number of cycles, leading to a rapid deterioration in performance [3].

Enhancing the recyclability of construction materials and developing multifunctional single-component materials are effective strategies to reduce carbon emissions during the construction, operation, and demolition phases of buildings. By simplifying the composition of construction materials to a single material, the variety and quantity of interfaces in the recycling process can be minimized, thereby improving recyclability [4]. Additionally, the primary functions of construction materials, such as mechanical strength and thermal insulation, can be achieved by creating anisotropic materials with tailored pore structures [5]. For example, in a building wall, the vertical direction requires high load-bearing capacity, while the horizontal direction focuses more on insulation and soundproofing. By precisely controlling the material's internal structure, we aim to achieve an optimized performance distribution while conserving materials. Therefore, low-carbon, highly recyclable construction materials should ideally be single-component and anisotropic.

In this study, freeze casting techniques were employed to fabricate anisotropic cement-based materials by directionally controlling the pore distribution within hardened cement paste. The core advantage of this method lies in its ability to generate an ordered pore structure through a controlled freezing process, endowing the material with superior mechanical and functional properties in specific directions while maintaining high recyclability. The freeze-casting method has demonstrated excellent anisotropic control in ceramics and polymer materials; however, its application in cement-based materials remains relatively unexplored. The freeze-casting technique relies on low-temperature directional freezing, and its energy consumption can be managed through process optimization or by implementing it in low-temperature environments or regions, making large-scale application feasible with further refinement.

Previous studies have explored the freeze-drying of cement paste and evaluated its multifunctionality [6-7], they have lacked temperature monitoring during the freezing process, as well as quantitative analysis and characterization of the pore structure. Furthermore, the anisotropic pore structures formed have not been correlated with the resulting anisotropic mechanical properties in three orthogonal directions. To address these gaps, this study investigated and evaluated the temperature variations, anisotropy of the pore structures, and mechanical properties of the samples. The findings of this research provide a valuable reference for the development of multifunctional and recyclable construction materials.

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2. TEST PROGRAMS

2.1 Materials

The cement used for the experiments comes from Taiheiyo Cement's high early strength (JIS R 5210) and Table 1 shows its chemical compositions. The viscosity powder F of KAO was applied to maintain the viscosity of the cement paste [8]. The mixed water is distilled water. The water to cement ratio (W/C) is 0.80, mixed with 3% viscosity powder, where no bleeding was observed based on rheological tests. The mixing device is ARE-500, Thinkymixer, with a centrifugal mixing speed of 1000 rpm and mixing time of 90 s.

2.2 Preparation procedure

Fig. 1 shows the developed preparation procedure of the freeze casting. The cement paste was first put into the mould, which was made of high heat insulation material, with a heat insulation factor of 0.034W/(m· K). The internal dimension of the mould is 2cm(x) × 12cm(y) × 18cm(z). The distance between the long sides in the mould along the freezing direction is 2 cm. After pouring the cement paste into the mould, the samples were put into a minus temperature environment, with three temperatures of -20°C, -60°C and -196°C. In the case of -20°C and -60°C, the sample was placed in a freezer at the designated temperature and cooled from the top of the sample, while in the case of -196°C, the liquid nitrogen was applied on the top of the sample for one-direction cooling (Fig. 2). The freezing of the sample was confirmed by embedded temperature sensors, where the entire sample's temperature dropped below 0°C. After freezing, the samples were demoulded and put into a low-temperature environment at 2°C for 48 h for primary curing, to stabilize the generated lamellar structures during the freezing process. Thereafter, the samples were placed in a curing chamber (20°C, 95%RH). After curing, the samples were cut and measured by various techniques for further investigation. The reference of curing time, such as 3d, are defined based on the duration after normal environmental curing. For comparison, normal cement pastes, with the same mix proportion and mixing procedure, were prepared. The normal cement pastes were cast in a 2-cm cube and demoulded after 1 day of casting, and then placed in a curing chamber (20°C, 95%RH).

Table 1 The chemical compositions of used cement

Composition	Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO
Mass ratio (%)	0.78	20.15	5.44	2.74	65.56
Composition	Na_2O	K_2O	SO_3	MgO	
Mass ratio (%)	0.34	0.28	0.47	0.89	

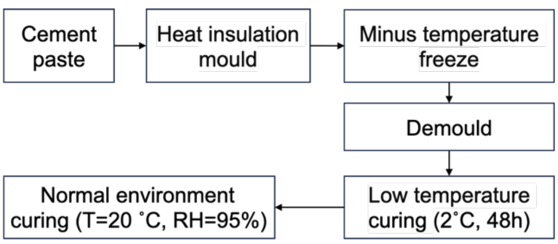


Fig. 1 The sample preparation process

2.3 Temperature monitoring design

In the preparation of cement-based materials via freeze casting, the formation of ice crystals relies primarily on directional control achieved through temperature gradient variations. Consequently, the temperature distribution within the sample plays a critical role. To monitor temperature changes at different locations within the sample during the freezing process, T-type thermocouples were embedded for real-time tracking. The experimental setup is illustrated in Fig. 2. Moreover, the global coordinate system is defined, the sample spans from 0 to 2 cm in the x-direction, from 5 to 7 cm in the y-direction, and from 2 to 4 cm in the z-direction, which is a cube with a length of 2 cm.

2.4 Evaluation method

(1) Mechanical performance test

Compressive strength was measured by a compressive machine. The samples were cut precisely with the diamond band saw EXAKT300, with the sample size of 2cm(x) × 2cm(y) × 2cm(z), since a smaller sample allows for better control of sample homogeneity. The compressive machine is the Shimadzu Autograph AG-250kN. The loading rate is controlled based on the JIS standard. Because of the anisotropy of the samples, the compressive strength of the three orthogonal directions was measured at least 3 samples for each.

(2) X-ray CT test

The X-ray CT device is Shimadzu Inspexio 100CT, the scanning sample size is 2cm × 2cm × 2cm. The scanning number of views is 1800, and the average count is 6×10 with high precision. After finishing the measurement, the image segmentation was performed using the classical Otsu's method [9], which defines the threshold value to convert gray-scale images to binary images.

(3) SEM test

Backscattered electron image (BSE) was adopted for microstructural analysis. The sample surface used for observation was embedded in epoxy resin. After resin hardening, the analytical surface was prepared by polishing the hardened resin. Carbon was deposited to impart conductivity to the analytical surface. The used device is SEM SU3900 (Hitachi High-Technologies Corporation), with an acceleration voltage of 15 kV.

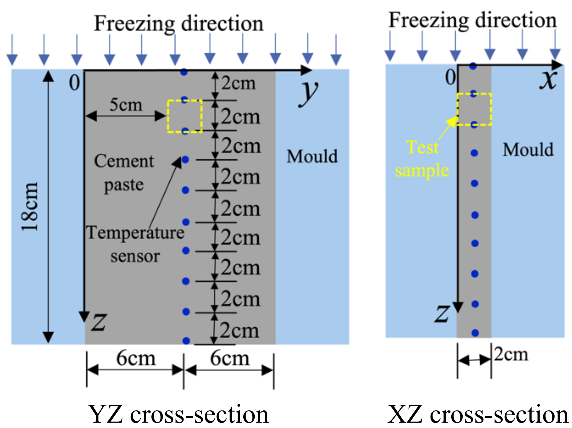


Fig. 2 Temperature monitoring setup

(4) Nanoindentation test

The test device is BRUKER Hysitron TS 77 Select. The nanoindentation test setup is shown in Fig. 3. The maximum load is 10,000 μN, the load and time relationship are shown in Fig. 3(a). The number of test points of one series in the *x*- and *y*-direction is 30 and 15, respectively, and the spacing between the tests are 5.19 μm, which is illustrated in Fig. 3(b).

3. RESULTS AND DISCUSSIONS

3.1. Freezing temperature

The temperature variations under different freezing temperatures along the freezing direction were monitored. Take the freezing temperature of -196°C, W/C of 0.80 as an example. The temperature monitoring results are shown in Fig. 4. The monitored positions ranged from *z* = 0 to -18 cm (define the freezing surface as *z* = 0 cm). It can be observed that as the freezing depth increases, the reduction rate of temperature tends to slow down and stabilize after reaching a certain temperature. Additionally, as the distance from the surface was larger, the stabilized final temperature gradually increased.

Fig. 5 gives an example of temperature variation in the position of *z* = -2.0cm. A distinct peak was observed in the freezing point, which is due to the heat absorption associated with the phase transition from liquid water to solid ice [10]. It can be observed that as the freezing speed decreased, the ice crystallization temperature also decreased. This phenomenon could be attributed to the rapid freezing process. Initially, the rapid thermal conduction in the cold zone caused the freezing temperature to be significantly lower than 0°C. As the conduction rate slowed with the increasing freezing distance, the freezing temperature graduallyapproached and stabilized at 0°C, as shown in Fig. 6.

The freezing temperatures significantly influenced the temperature variations in the sample as well. As the freezing temperature decreased, the temperature fluctuations at the same position became more pronounced. For instance, under a freezing temperature of -20°C, the sample at *z* = -2.0 cm required 6 hours and 5 minutes to reach 0°C. When the freezing temperature was reduced to -60°C, this time decreased to 2 hours and 40 minutes. At a freezing temperature of -196°C, the required freezing time at this position was further reduced to just 16 minutes.

3.2 Pore structures of freeze casting samples

X-ray CT was utilized to examine the 3D pore structure of the sample, and the reconstructed 3D image of the cement paste is shown in Fig. 7. From Fig. 7, distinct pore alignments can be observed, with lamellar structures primarily aligned parallel to the XZ plane. Using relevant calculations, the overall porosity of the sample, as well as the variation of porosity along the freezing direction, was determined. When the W/C ratio was 0.80, segmentation of the cement paste and pores based on grayscale thresholding using the Otsu method yielded a volumetric porosity of 54%.

The pore distribution curves along three orthogonal cutting planes were plotted, as shown in Fig. 8. Along the *z*-axis, the interlayer porosity in the XY plane exhibited a trend of initially decreasing (from *z* = 20 to 25 mm), then increasing (from *z* = 25 to 35 mm), and finally stabilized (from *z* = 35 to 40 mm). In both the

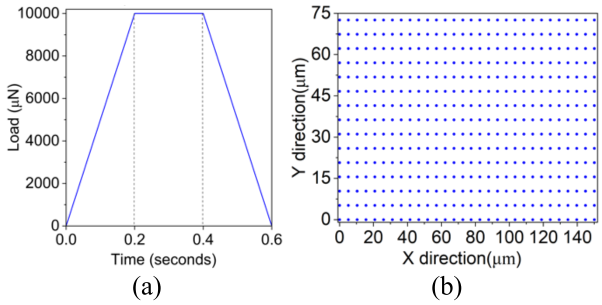


Fig. 3 The nanoindentation test setup: (a) loading regime, (b) test points distribution

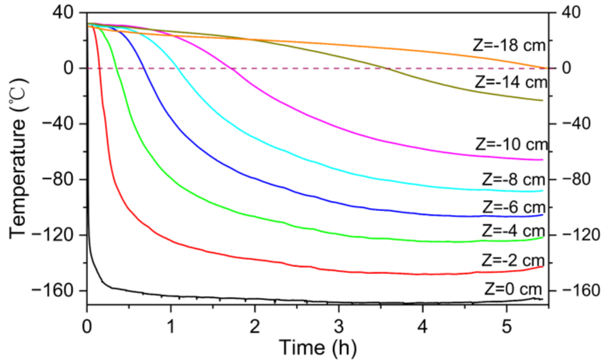


Fig. 4 Temperature variation in different freezing depths

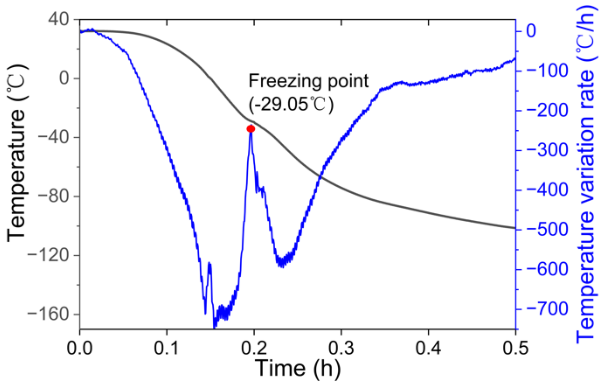


Fig. 5 The temperature variation rate and freezing temperature point illustration

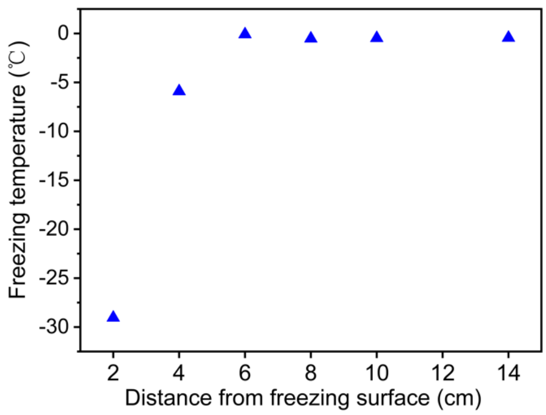


Fig. 6 The calculated freezing temperature at different freezing positions

YZ and XZ planes, a similar trend of decreasing followed by increasing porosity is observed. The observed trend of first increasing and then decreasing can be attributed to the temperature distribution. Near the edge of the mould, the difference in thermal conductivity between the mould and the cement paste results in a greater temperature gradient closer to the edge. Along the *z* direction, the cooling temperature shows a decreasing transfer speed, however, in the YZ and XZ planes, the temperature gradient is affected by temperature difference of mould and cement paste, which shows a certain symmetry around the center of the sample. This variation in the temperature gradient leads to differences in porosity [11].

Specifically, in the XZ plane, the porosity was larger at y = 50 and 70 mm than at y = 60 mm, with periodic fluctuations observed. These fluctuations are associated with the alignment of the lamellar structures. Since the lamellar planes are primarily parallel to the XZ plane, cutting along this plane results in a distinct and periodic porosity distribution influenced by the lamellar arrangement. In contrast, the pore distribution in the other two directions has different underlying causes. In the YZ plane, fluctuations in porosity are primarily attributed to temperature distribution.

3.3 Comparison with normal cement paste

The comparison between normal cement paste and lamellar structures prepared using the freeze casting method, under identical mix proportions, was conducted through SEM analysis (Fig.9). Based on the grayscale segmentation techniques of Otsu method [11], the porosity in two perpendicular directions (*x* and *y*) was extracted from the images. The variation of porosity with position is illustrated in Fig.10 and Fig. 11, the W/C ratio of both two samples is 0.80.

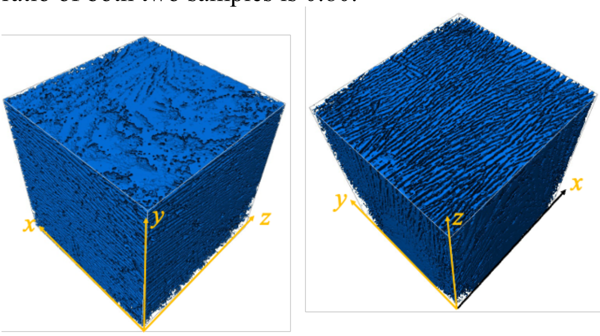


Fig. 7: The CT results of lamellar structures (2cm by 2cm by 2cm, black color represents pores)

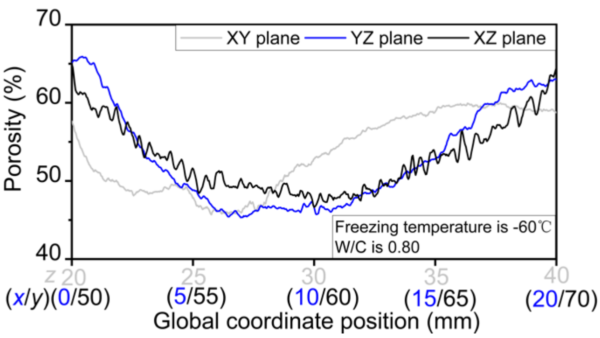
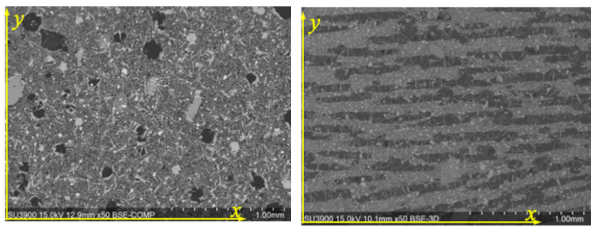


Fig. 8 The porosity in different plane

The overall porosity of samples prepared using the freeze casting method is higher than that of ordinary cement paste. Observing the porosity distribution in two directions, it was found that in the *y*-direction, the porosity of samples prepared by the freeze casting method fluctuates within a range of approximately 50%, whereas for ordinary cement paste, the porosity fluctuation is limited to around 15%. The higher porosity in the freeze casting samples is attributed to the consistent porosity distribution along the *y*-direction.

Along the *x*-direction, the porosity of ordinary cement paste exhibits a fluctuation pattern similar to that observed along the *y*-direction, with a range of approximately 15%. In contrast, the porosity of freeze casting samples along the *x*-direction shows larger and more periodic fluctuations, with a range varying from 20% to 70%. These greater fluctuations are caused by the lamellar structure's directional alignment.

Thus, the freeze casting method enables the fabrication of pore structures with directional distributions, resulting in anisotropic characteristics. The formation of directional pores introduces anisotropic properties in the material, which can be advantageous for applications requiring specific directional performance. For example, controlled anisotropy can enhance compressive strength in the load-bearing direction, reduce thermal conductivity in the desired orientation, or optimize fluid permeability. Therefore, this anisotropy can be utilized to achieve functional anisotropy, making it advantageous for applications requiring specific directional properties.



(a) (b)

Fig. 9 The BSE results of samples: (a) normal cement paste; (b) freeze casting cement paste

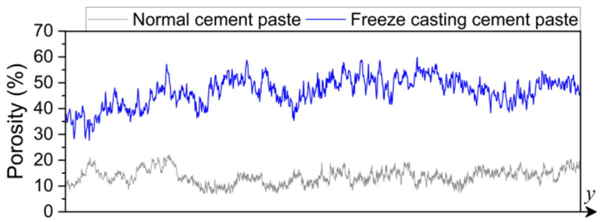


Fig. 10 The porosity distribution along *y*-direction

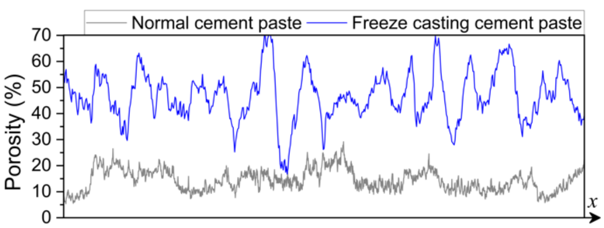


Fig. 11 The porosity distribution along *x*-direction

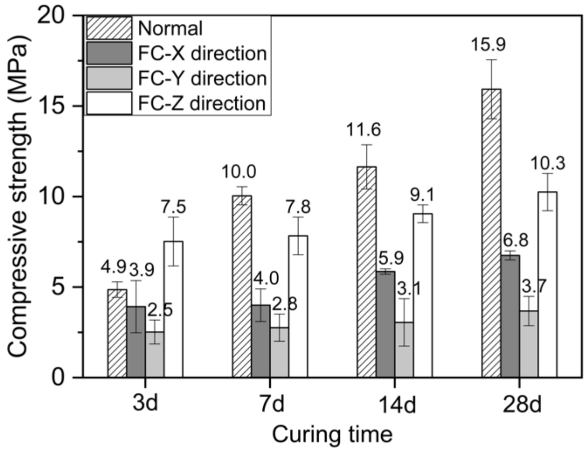


Fig. 12 The compressive performance of normal cement paste samples and freeze casting cement paste samples (W/C=0.80)

3.4 Mechanical performance

(1) Compressive strength

The compressive strength results are presented in Fig. 12, comparing the hardened cement paste prepared by the conventional method with that prepared using the freeze casting method under the same mix proportions. Based on the previous pore structure analysis, it was observed that samples prepared via freeze casting exhibit anisotropy, resulting in different strengths along the three principal directions. The strength data for each direction corresponds to the load applied parallel to that specific direction. First, comparing the compressive strengths of the freeze casting samples in the three principal directions, it was found that for all curing times, the *z*-direction exhibited the highest strength, followed by the *x*-direction, while the *y*-direction showed the lowest strength. With increased curing time, the strength in all three directions improved, with the *z*-direction consistently achieving the maximum strength. After 28 days of curing, the *z*-direction strength exceeded 10 MPa.

When comparing the compressive strengths of hardened cement paste prepared by the two methods, the *z*-direction strength of freeze casting samples at an early age (3 days) was 53.1% higher than that of conventionally prepared samples. However, as curing time increased, the strength of conventional samples surpassed that of the freeze casting samples by 7 days.

In conclusion, samples prepared by the freeze casting method exhibit anisotropic strength properties, with the highest strength observed parallel to the lamellar direction and the lowest strength perpendicular to it. At early stages, the maximum strength of freeze casting samples exceeds that of conventionally prepared cement paste, highlighting the potential benefits of this method for early-age applications. This is attributed to the lamellar structure formed during freeze casting in a specific direction, which enhances strength parallel to the layered structure.

(2) Indentation modulus results

The investigation of samples prepared using the freeze casting method revealed distinct anisotropic behavior, primarily attributed to the directional alignment of their internal pore structures. For cement paste cured for 3 days, the strength in one principal direction was higher than that of conventionally prepared cement paste under the same conditions. Further microscopic analysis of the elastic modulus was conducted. The color maps of the modulus results of the freeze casting cement paste samples and normal cement paste samples are shown in Fig. 13 and Fig. 15, respectively. Moreover, the average values of the two types of samples along the *y*-axis were calculated as well. The corresponding results are illustrated in Fig. 14 and Fig. 16, respectively.

The modulus color map results of freeze casting cement paste samples shown in Fig. 13 and Fig. 14 demonstrated that the modulus varied between the lamellar pore regions and the cement paste matrix. In the pore regions, the elastic modulus was uniform. The nonzero values in these regions were attributed to the hardened epoxy resin used to fix the samples during processing, with the modulus reflecting that of the resin. In the cement paste matrix, the elastic modulus increased with increasing distance from the pore boundaries.

Additionally, the elastic modulus color maps showed multiple prominent peaks concentrated within the lamellar structure, with a high density of these peaks. By contrast, the normal cement paste also exhibited peaks in its elastic modulus map, but these were less densely distributed, as shown in Fig. 15. These peaks corresponded to unhydrated cement particles. The results suggest that under the same W/C ratio, freeze casting led to the formation of lamellar structures due to water crystallization. This, in turn, caused a higher density of cement particles within the cement paste regions between lamellar structures compared to normal cement paste.

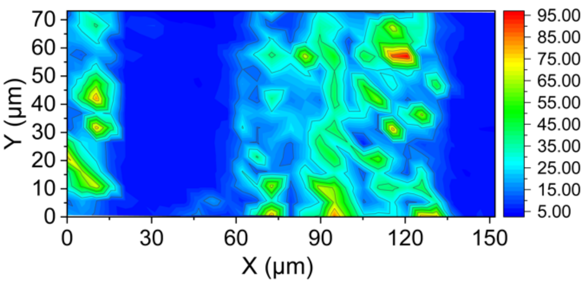


Fig. 13 The color map of nanoindentation test results with W/C of 0.80

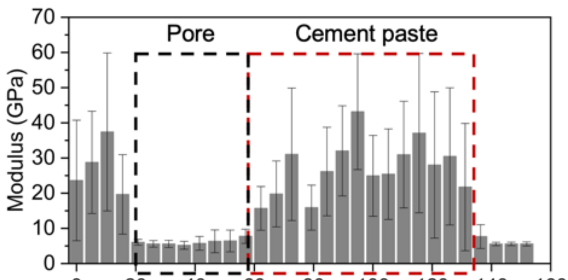


Fig. 14 The nanoindentation test results of freeze casting cement paste samples with W/C of 0.80

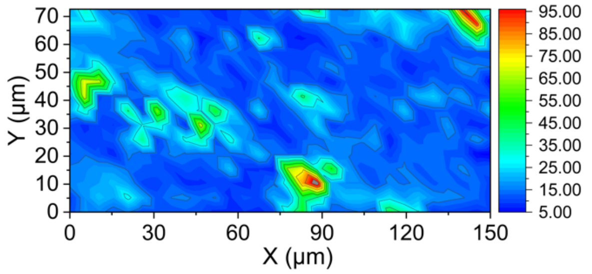


Fig. 15 The color map of nanoindentation test results with W/C of 0.80

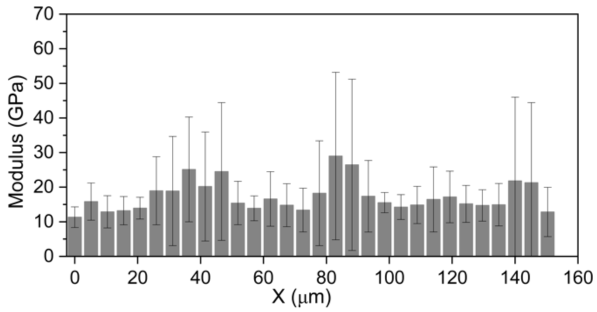


Fig. 16 The nanoindentation test results of normal cement paste samples with W/C of 0.80

Comparing the modulus results of normal cement paste, as shown in Fig. 16, the 3 days cured samples displayed uniform modulus values, mostly fluctuating within the 20 GPa range, with a lower mean value than the freeze casting cement paste samples, whose values range from 20 to 50 GPa (Fig. 14). During the freezing process, water in the cement paste migrates and forms a lamellar structure, and the cement particles tend to accumulate between these lamellae, resulting in a higher density compared to normal cement paste. During the subsequent hydration process, due to the increased density of cement particles in the accumulated regions, the elastic modulus of these regions becomes higher than that of normal cement paste. Therefore, despite the higher porosity of the freeze casting samples, their higher modulus of cement paste could explain their early-age (3 days) compressive strength compared to normal cement paste samples.

4. CONCLUSIONS

This study fabricated anisotropic cement paste using freeze casting, achieving directional pore alignment and confirming anisotropic mechanical properties through nanoindentation. Freezing temperature depended on heat transfer rate, with high rates causing subzero freezing. Freezing cast samples exhibited lamellar pores aligned with the temperature gradient, increasing in size as the gradient decreased. Overall porosity (~50%) was significantly higher than in conventional cement paste with the same W/C ratio.

The anisotropic pore structure led to directional variations in compressive strength, peaking along the maximum temperature gradient. Early-age strength exceeded that of conventional samples but gained strength more slowly over time. Nanoindentation revealed that despite high porosity, the cement matrix between pores was denser with a higher modulus, explaining the superior early-age strength in freezing cast samples.

ACKNOWLEDGEMENT

The authors would like to thank Prof. Takuzo AIDA (The University of Tokyo) and Prof. Ippei MARUYAMA (The University of Tokyo) for their valuable comments. They also extend their gratitude to Kodai NAKAGAWA (The University of Tokyo) and Heng LI (Shimizu Corporation) for their support in conducting the experiments involved in this study.

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