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Investigation of Microstructure of Cementitious Materials Exposed to High Temperature by Non-destructive Integrated CT-XRD Method

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ABSTRACT

Severe accident occurred in 2011 at the Fukushima Daiichi nuclear power plant and it can be assumed that the concrete building was exposed to high temperatures environment for a long time due to loss of the cooling function of the nuclear reactor. In order to prepare for the best scenario in the decommission plan, it should be first needed to clarify and evaluate the level of damage and deterioration of the contaminated concrete. To solve this problem, experiments were conducted for cementitious materials with the maximum temperature of 400 or 1000 degrees Celsius with durations of up to 2 hours. Subsequent results were evaluated microscopically. In this research, authors have employed a Non-Destructive Integrated CT-XRD Method using synchrotron white X-ray. The unique feature of this method is that both CT for measuring internal structure and XRD for identifying crystal structure can be performed on the same specimen at the same time. Therefore, in addition to other measurements such as the Thin film X-ray diffraction technique, the application of this method is expected to bring an interesting exploration with regard to the physical and chemical alteration of the concrete that was endured by high temperatures.

Keywords: Non-destructed integrated CT-XRD method, Thin film X-ray diffraction technique, High temperatures, Cement hydration system, Crack

1.0 INTRODUCTION

The concrete building damaged by the accident at the Fukushima nuclear power plant in 2011 was assumed to have been exposed to high temperatures environment for a long time due to loss of the cooling function of the nuclear reactor. Also, seawater was injected in to the reactor to cool it. Therefore, it is considered that the alteration mechanism of the concrete is complicated. In the event of final disposal in future, it is necessary to grasp the leaching of radioactive contamination from the altered concrete. To do so, the damage and deterioration of microstructure of the concrete that received the high temperature must be properly evaluated. However, in past studies of concrete exposed to high temperature, available data on normal strength fly ash concrete is seldom seen while concrete building of nuclear power plants is generally normal strength concrete. Therefore, it is difficult to evaluate the damage of nuclear accidents such as the case of the Fukushima. Therefore, this study aimed to evaluate the alteration of cementitious material with relatively high water to binder ratio and fly ash as the binder, which endured high temperatures using Non-destructive integrated CT-XRD method and Thin film X-ray diffraction measurement.

2.0 EXPERIMENT

2.1 Non-destructive Integrated CT-XRD Method

This method is carried out at the white X-ray diffraction beam line 28B2 of the large synchrotron radiation facility SPring-8. As a procedure of this method, cross-sectional images after reconstructing transmission image of specimen are first obtained using X-ray CT. Secondly, the X-ray diffraction measurement position is determined referred to the obtained cross-sectional image, and Energy-Dispersive XRD profiles of the determined position can be obtained. The feature of this method is that white X-ray with wide wavelength band is used. Hence angle scanning is unnecessary during XRD measurement. In addition, it enables us to measure the same sample over times because it is non-destructive. The experimental setup is shown in Fig.1. Compared with past experiments using this method (Sugiyama *et al*, 2014, Takahashi and Sugiyama, 2016), the position of silicon mono-crystal is moved from the downstream to upstream position of the specimen. In this way the distance between the specimen and the X-ray camera became shorter.

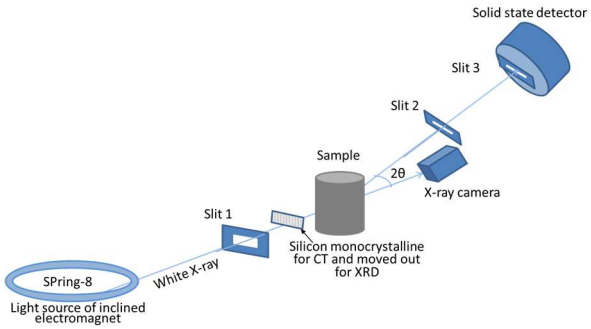


Fig.1. Schematic of the system for Non-destructive integrated CT-XRD method

Therefore this modification is expected to improve the quality of the image.

CT measurement

Incident white X-ray irradiated to silicon mono-crystal to get itself monochromatic. Then, monochromatic X-ray goes through specimen and is captured by X-ray camera. At the time of measurement, the specimen is placed on the rotating stage, and radiated by monochromatic X-rays while rotating the specimen. Therefore, it is possible to obtain X-ray transmission images from all directions. From these obtained transmission images, cross-sectional images of specimens are reconstructed.

X-ray diffraction measurement

The region of interest is determined from the cross-sectional image obtained by CT measurement and X-ray diffraction measurement performed. Slits are used to obtain X-ray diffraction signals only from the region of interest. An X-ray diffraction signal can be obtained only from the area that is focused by the slit 1 installed in the upstream of the specimen and the slit 2 and slit 3 located in the downstream of it (See Fig.2). Here, the relationship of X-ray energy and the intensity of the diffracted X-ray on the region of interest can be obtained.

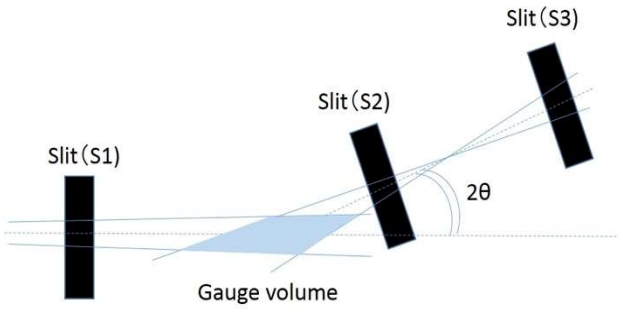


Fig.2. Concept of gauge volume

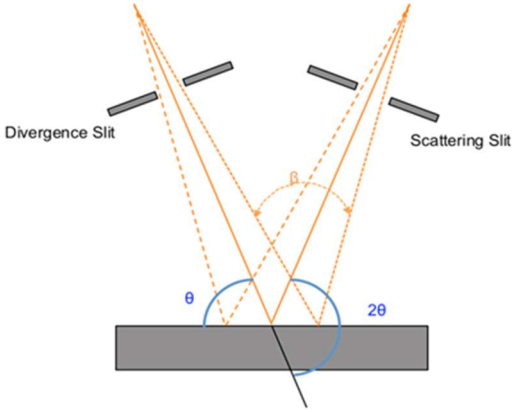
2.2 Thin Film X-ray Diffraction Technique

In order to investigate chemical alteration of cement hydrate subjected to high temperature compared with CT-XRD, a thin film X-ray diffraction method was carried out. Since this method can be performed nondestructively without special material preparation, there is an advantage that the same surface of the sample can be measured over time. The measurement conditions were as follows: tube voltage:45kV, tube voltage;200mA, step width; 0.01°, scan speed; 20°/min. The diffraction profile was analyzed using integrated powder X-ray analysis software PDXL (Rigaku Corporation). Fig.3 shows outline of the system. If irradiation width and height are determined as A and B shown in Fig. 3(b), the irradiation area can be expressed as following:

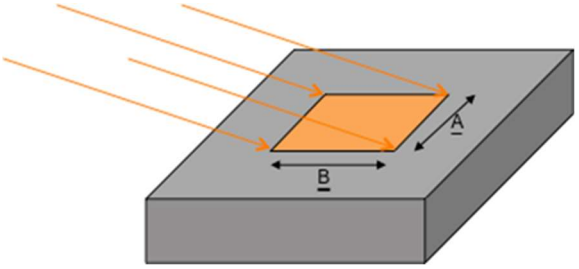
$$A = \left[\frac{1}{\sin(\theta + \beta/2)} + \frac{1}{\sin(\theta - \beta/2)}\right] \cdot R \cdot \sin\frac{\beta}{2}$$

$$B = a + 2r \cdot \tan\frac{\delta}{2}$$

where θ is the angle between incident X-ray and sample surface, β is the diverging angle of Divergence Slit, R is the radius of Goniometer, a is the width of longer arm slit, r is the distance between longer arm slit, and δ is the diverging angle of soller slit. All parameters except θ are fixed. Hence irradiation area is dependent on only θ.



(a) Outline of the Thin film X-ray diffraction



(b) Concept of irradiation area

Fig.3. System of thin film X-ray diffraction

2.3 Specimens Preparation

Cement paste and mortar with a water-to-binder ratio of 0.6 using Ordinary Portland Cement (OPC) mixed with fly ash were used. The fly ash was replaced by 15% for OPC for all specimens. For mortar the amount of fine aggregate was 20% of the total volume of the specimen. The specimen was formed into a

prism shape having a height of 5 mm and a square with one side being 2.5 mm.
The specimens were heated up to the maximum temperatures of 400 and 1000ºC at a temperature rise of 10ºC/min and continued heating at the maximum temperature for 2 hours (see Fig. 4). To denote the type of specimen, cement paste and mortar are defined as F6 and F6M2, respectively, and each setting maximum temperature (400 or 1000ºC) is defined as 4 and10, respectively. For example, cement paste heated at 1000ºC can be expressed as F6-10.

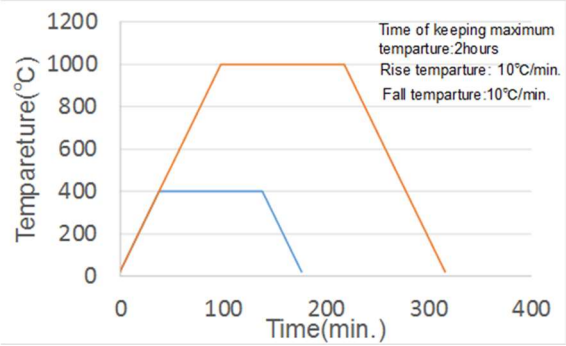
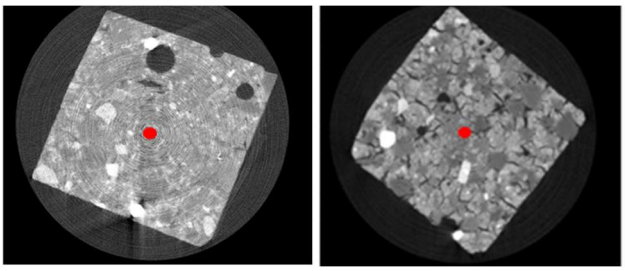


Fig. 4. Temperature program

3.0 RESULTS AND DISCUSSION

3.1 CT images

Figure 5 shows CT sectional views of each specimen heated at a given temperature (400 and 1000 ºC) with measured XRD point in this research (red circle point). The length of the view is 4.15 mm each of the square. The CT section shows white as the density becomes higher and black as the density lower.



(a) F6M2-4-2h (b) F6M2-10-2h

Fig.5. CT images with XRD points (Mortar)

From Fig. 5(a), little cracks are confirmed. It appears that the resolution of the CT image is limited so that microcracks are hardly observed. However, large cracks are confirmed from Fig. 5(b). It was considered that with this high temperature (1000 ºC) the volume change of the matrix and aggregates became an inequivalent so as to generate cracks at the interfaces and edges of the specimen.

3.2 XRD analysis

Figure 6 shows the diffraction profiles of hardened cement pastes with the same binder-water ratio as those of the mortar specimens using the Thin film X-ray diffraction technique. The XRD profiles were obtained after being heated at the temperatures of 400 and 1000°C for 2 hours (F6-4-2h and F6-10-2h). In addition, no heated sample was measured (F6-no heat). Ettringite and Monosulfate were detected in unheated specimens, but were not detected in specimen heated at 400°C for 2 hours. Portlandite was determined in the specimen without heating. Also, Portlandite was determined in the specimen heated at 400°C for 2 hours. However, it was not determined in the specimen heated at 1000°C for 2 hours.

It was attempted to determine the Portlandite using the Thin film X-ray diffraction technique in cement paste heated at 400°C for 12 hours (Oshiro, 2016). However with that accumulated temperature of 4800 (°C x hour) Portlandite wasn't determined. From this, it is considered that the accumulated temperature rather than the maximum temperature contributes greatly to the alteration of Portlandite. In addition, the Lime, Belite and Felite were determined in the specimens heated at 1000°C for 2 hours. It is known that the Ettringite is decomposed at a heat receiving temperature of 70 to 100°C. And the Monosulfate hydrate is decomposed at 100 to 200°C (JCI, 2017. In this measurement, the Ettringite and Monosulfate were determined in the unheated specimen, but these were not identified in the 400°C specimens. This is consistent with the past research results (JCI, 2017). Furthermore, it is known that when $CaCO_3$ is present when heated at 600°C to 800°C, decomposition takes place and CaO is formed. From Fig. 6, it is understood that CaO could be determined in the specimen heated at 1000°C for 2 hours. This suggests that $CaCO_3$ may have been present in the specimen. Table.1 shows referenced minerals in this research and the comparison of the results by the Non-destructive CT-XRD integrated method and Thin film X-ray diffraction technique. In non-destructive integrated CT-XRD method, it was considered that the X-ray energy (20 kev or less) in the low energy band was absorbed by the sample. Then it is difficult to determine Ettringite and Monosulfate.

3.3 Durability concern in heated concrete

This basic study clarified the formation of relatively larger cracks in mortar at 1000°C. These cracks can have negative effects on the durability by the increased transport properties such as permeability and diffusivity. However cracks could not be clearly found in the heated mortar at 400°C. It may be due to the inadequate resolution of the CT measurement to obtain the micro-cracks that may occur. If this is true then the transport properties would be increased as well although the widths of the cracks are fine.

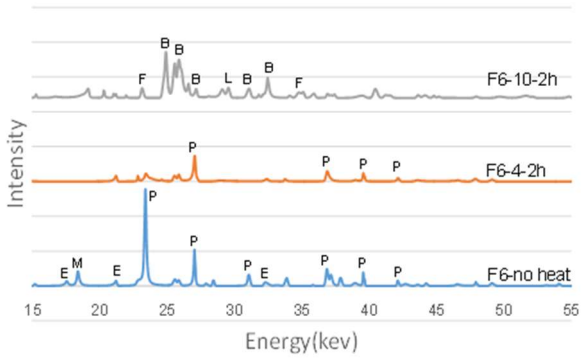


Fig. 6. The diffraction profile of F6 obtained by Thin film X-ray diffraction technique

4.0 CONCLUSIONS

CT image showed significant cracks in the mortar specimen heated at 1000°C while microcracks were hardly observed at 400°C. In this regard the permeability and diffusivity can be significantly changed. Ettringite and Monosulfate were detected using Thin film X-ray diffraction method in unheated specimens, but were not detected using Thin film X-ray diffraction method as well as Non-destructive CT-XRD Integrated method in specimen heated at 400°C for 2 hours. Portlandite was determined in the specimen heated at 400°C for 2 hours using both methods.

Acknowledgement

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The authors would like to thank Dr. Hitomi and Dr. Kajiwara for their assistance in the measurement.

Table 1. Referred minerals in this research and results of Non-destructive CT-XRD integrated method and Thin film X-ray diffraction technique

Mineral name (Notation)	Chemical Formula	Non-destructive CT-XRD integrated method		Thin film X-ray diffraction technique	
		400°C	1000°C	400°C	1000°C
Portlandite(P)	$Ca(OH)_2$	y	n	y	n
Belite(B)	$2CaO \cdot SiO_2$	n	y	n	y
Lime(L)	CaO	n	y	n	y
Felite(F)	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	n	y	n	y
Ettringite(E)	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	nd	nd	n	n
Monosulfate(M)	$C_3A \cdot CaSO_4 \cdot 12H_2O$	nd	nd	n	n

(y: could determine, n: couldn't be determined, nd: couldn't be detected)

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