Introduction
When concrete structures in contact with water for a long time, there will be a chance of leaching which degrades the performance of structures. Leaching changes the pore structure which has significant effects on physical as well as chemical properties of concrete. There are many methodologies that have been applied to evaluate the pore structure of the leached cementitious materials. However, along with the advances in technology, X-ray CT can be used considering microstructural variations of cementitious materials. With the aid of Synchrotron-based microtomography, the detectable order of measurement could be 0.5 μm. But, differences in the X-ray absorption characteristic of minerals present in a hydrated cement system are small, resulting in lower contrast in a CT image. So the distribution of a mineral in three dimensions is difficult to evaluate for a hydrated cement system. On the other hand X-ray diffraction is a very useful technique to identify a crystalline mineral. X-ray diffraction is based on the scattering of x-rays. The diffraction pattern produced depends on the atoms present, their locations, and thermal motion. Every crystalline substance produces a unique diffraction pattern, which is a fingerprint of the material. In polycrystalline materials, each phase produces its pattern independent of the others. X-ray diffraction analysis is thus ideally suited for the characterization and identification of phases. So in this study, the leaching behavior of hardened cement paste has been studied by means of nondestructive integrated CT-XRD method. X-ray computed tomography (CT) images provide the physical information like the cracks geometry, air voids as well as high and low density substances present in the hydrated cement system. On the other hand XRD measurement gives mineral information.

RESEARCH OBJECTIVES
The prime objective of this study is to investigate the pore structure of leached cementitious materials using newly developed Non-destructive Integrated CT-XRD method. To achieve the main objectives following sub-objectives are discussed in this study:
1) To characterize the physical change in a deteriorated cementitious material due to leaching using synchrotron X-ray CT
2) To investigate the chemical change over time and space of the deteriorated cementitious material using X-ray diffraction
3) To determine the portlandite dissolution front in-situ condition

Materials and Methods

Non-Destructive Integrated CT-XRD Method
The Non-destructive Integrated CT-XRD Method was conducted at BL28B2, SPring-8, Japan. In this method white X-ray was used as the incident X-ray which covers a wide range of wave length. The energy of X-ray for CT measurement was 25 keV. The overall field of view was about 5 mm. The angle of diffraction (θ) was fixed at 10°. The preset time was 300 s. Solid-state detector was used to get the energy-intensity relationship. First CT measurement was carried out to get the reconstructed cross-sectional images. By observing the reconstructed image in three dimensions, the regions of interests (ROI) were determined for the XRD measurement. However, to extract the signal of the X-ray diffraction only in the ROI, various slits were used. The relationship between X-ray energy and the intensity of the diffracted X-ray was obtained from XRD detector. Then this energy-intensity relationship was converted to diffraction angle-intensity relationship where energy was converted to diffraction angle using Bragg equation and specific wavelength.

Specimen Preparation
There are two types of cement paste specimens used to evaluate the leaching effect in cementitious material. The two specimens were the ordinary Portland cement (OPC) paste with water to binder ratio of 0.3 and 0.5. First hardened OPC paste (40 mm x 40 mm x 160 mm) was made with water to cement ratio of 0.3 and 0.5. After curing in the water, it was cut to get the cylindrical specimen of about 5 mm diameter and 5 mm height. Then Crack was induced on that cylindrical specimen. Aluminum tape was used to cover the crack specimen and to connect plastic tubes of 2 mm inner diameter at both ends of that specimen.

Leaching Test
Tubing pump was used to circulate the water through the specimen. Demineralized water was kept at a tank from which water was circulated through the cracked specimen via the tube pump. Water flow rate was 50 cc/h and it was continued for a period of 9 months. After certain leaching period, the specimen was moved to SPring-8 for conducting nondestructive integrated CT-XRD measurement. In addition, the tank leaching test was used as a supplemental test of the water flowing test, where the specimen was submerged in water for 80 days.
RESULTS AND DISCUSSIONS

Figure 1 Cross Sectional CT images with XRD measurement result of OPC-30 specimen

Figure 1 shows the cross sectional image of the cracked specimen which are located at the central portion of the specimen (1.90 mm from the top surface of the specimen). Using gray scale value (GSV), CT image provides the physical information like location of crack, air voids, low or high density substances etc. But to know the chemical change XRD was conducted on some specific position.

Before leaching one region of interest (A) was selected for the XRD measurement (Figure 1a) of OPC-30 specimen. Diffraction spectrum of position A (before leaching) is shown in Figure 2. After getting the XRD spectrums from XRD measurement, the observed diffraction peak energy was compared with the calculated diffraction peak energy of different cement hydrates (portlandite, calcite). Calculated diffraction peak energy was obtained using the Bragg’s law, specific wavelength, different combination of possible miller indices \((hkl)\) and lattice parameters of specific cement hydrates. Besides the energy-intensity spectrum, observed diffracted energy was converted to diffraction angle to get the angle-intensity spectrum and compared with ICSD (Inorganic Crystal Structure Database) spectrum. From Figure 2 it is observed that before leaching most of the significant peak energy of positions A is matched with portlandite peak energy which represents the presence of portlandite at position A. As before leaching other positions were not affected, so it can be considered that before leaching other positions were similar to A (Figure 1a).

After six months leaching to know the proper distribution of chemical change, many regions of interest (1–66) were selected for XRD measurement. Some positions situated near crack region and some are far from the crack (Figure 1b). Figure 3 shows diffraction spectrum of position 6, 14 and 15 which are situated near crack region. From Figure 3 it is noticed that almost all peak angle are matched with calcite peak angle. Similar behavior that is calcite region was also observed for other measured positions (red marked position in Figure 1b). It was also observed that, after 6 months leaching portlandite present region was far (more than 0.54 mm) from the crack (green marked position in Figure 1b). From Figure 1b it is noticed that for 6 months leaching sample, the nearest portlandite present region is located at position 29, which is 0.54 mm perpendicular from the crack boundary. So it can be considered that for 6 months leaching sample, the portlandite dissolution front is more than 0.54 mm.

Similar measurement was conducted for other specimens of different leaching periods and following conclusion can be drawn from this research.

CONCLUSIONS

After one and two months leaching, near the crack region, where the water was passed portlandite was dissolved. As the leaching time increased portlandite dissolution front is increased. The dissolution zone became larger as the water to cement ratio was increased. In addition, during the leaching test it appeared that the cement paste at and near the crack boundary was carbonated. The formation of the calcite might reduce the rate of the portlandite dissolution front as well as porosity.