論文の内容の要旨

論文題目 **Interaction of cesium with calcium silicate insulator materials** (セシウムとカルシウムシリケート保温材との相互作用に関する研究)

氏 名 リザール ムハンマド

1. Introduction

In January-February 2017, series of internal investigation of primary containment vessel (PCV) of Fukushima Daiichi (1F) nuclear power station unit 2 were performed by Tokyo Electric Power Company Holdings, Inc. (TEPCO). The main task of the investigation was to inspect the condition of the platform inside PCV, fuel debris fallen to the control rod drive (CRD), and the pedestal internal structure. The recording device managed to record the information of temperature, dose rate, and conditions of various structures in pedestal vicinity. The recorded dose rate exhibited unexpected distribution. The pedestal area, in regard to the accident progression, should exhibit a higher dose rate than those of any other locations at its vicinity because pedestal area was the most affected area after the accident by molten fuel. In contrast, the dose rates were 10 Gy/h at the pedestal while 70-80 Gy/h at the pedestal vicinity. In addition, at this pedestal vicinity, deposits in the form of black pastes and thin pieces of gravel-sized materials were found, which might act as one of the causes for such a high dose rate condition. To the date of recent report [1], it remains unknown how these deposits were created. Nevertheless, using information about the condition and location where these deposits existed, suspected materials for the deposit can be narrowed to those used in a large quantity and most affected by high temperature steam blast in PCV, and one of such materials is calcium silicate insulation used for the primary piping systems.

The formation of these deposits is assumed to be originated by high temperature steam containing fission products such as cesium, leaking from safety relief valves (SRV) components which then directly hit the adjacent line of main steam piping thermal insulation. Then, the chemical adsorption of cesium on thermal insulation occurs subsequently which may lead to high dose rate of pedestal vicinity.

Calcium silicate insulation material is a common insulation material used in piping systems for high temperature purposes. In unit 2 of Fukushima Daiichi nuclear power plant primary piping systems, this calcium silicate type of insulation was utilized.

To authors' knowledge, there is no report of cesium interaction to calcium silicate insulation materials at severe accident because most researches were centered on cesium adsorption/interaction on structural material such as stainless steel. The present study is aimed to investigate chemical interaction between calcium silicate insulation and cesium. The study consists of batch solution adsorption, thermogravimetry and differential thermal analysis, and gas-phase interaction by means of electric furnace.

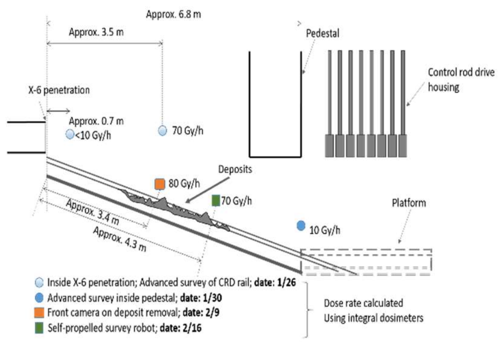

Fig. 1. Dose rate survey during investigation of platform inside pedestal Unit 2 of 1F

2. Room-temperature adsorption of cesium on calcium silicate

2.1 Adsorption study

The objective of this section is to obtain kinetics and concentration-dependency adsorption of cesium on calcium silicate at room temperature condition. For the experiments, Milli-Q grade pure water and analytical-grade chemicals from Wako Pure Chemical Industries were used, unless otherwise noted. Cesium chloride (CsCl) was used in this study. Calcium silicate insulation block, with specified insulation grade of nuclear primary coolant system was used as an adsorbent. The X-ray diffraction spectroscopy results (XRD, MiniFlex600SC, Rigaku Inc.) shows that the calcium silicate insulation was composed of xonotlite ($Ca_6Si_6O_{17}(OH)_2$) and some small amount of tobermorite ($Ca_5Si_6O_{12}(OH)_{10}$).

The results of adsorption kinetics showed that the adsorption process of cesium followed the pseudo-second order reaction model that highly indicated chemisorption of cesium.

3. Thermochemistry of calcium silicate-CsOH systems

The chemical reaction temperature between calcium silicate insulator material (calsil) and cesium hydroxide (CsOH) was experimentally investigated under Ar-5%H_2 and Ar-4%H_2-20%H_2O atmosphere with temperature up to 1100°C. Two type of pre-conditioned calcium silicate insulation materials led to distinct reaction temperature with CsOH: 575°C to 730°C for calsil while 700°C to 1100°C for PHT calsil. Despite of the reaction temperature and difference in initial chemical compounds (calsil: $Ca_6Si_6O_{17}(OH)_2$; PHT calsil: $CaSiO_3$), the end product of those calsils after subjected to reaction with CsOH in temperature up to 1100°C yielded similar XRD pattern regardless the atmosphere condition, which corresponded to the formation of cesium aluminum silicate: $CsAlSiO_4$. Elemental distribution analyses of Cs, Si, O, and Al have revealed the congruent distribution in samples after the experiment to signify the formation. The benchmark heating tests using high purity reagent grade $CaSiO_3$ were supplemented to the analyses for the purpose of proving the previous findings in calsil and PHT calsil that the formed cesium compound was cesium aluminum silicate. The results have proved that such a cesium aluminum silicate was not formed in all benchmark samples but in turn yielding the Cs water-soluble compound and Ca_2SiO_4.

4. High temperature interaction of cesium hydroxide with calcium silicate insulator materials

The purpose of this part of study is to investigate the interaction between cesium hydroxide with calcium silicate insulator materials at the reaction temperature obtained from thermochemical investigation in previous section. The gas-solid interaction test between calcium silicate insulator materials (calsil) and cesium hydroxide (CsOH) was experimentally investigated under Ar-4%H_2-20%H_2O atmosphere with temperature of 800°C. The temperature was chosen based on the suggested reaction temperature in thermochemical investigation. The interaction was realized by using horizontal electric furnace where cesium hydroxide was vaporized in the upstream of furnace and then transported by steam flow to the downstream where calcium silicates were located. After the gas-solid interaction test, series of characterizations were conducted including crystallography, elemental, morphological, and vibrational analyses. The XRD patterns of those calsils had been changed from their original crystal phase of xonotlite to $CsAlSiO_4$ and Ca_4SiO_4 meaning that the interaction with gaseous cesium hydroxide prevailed, Fig. 2.

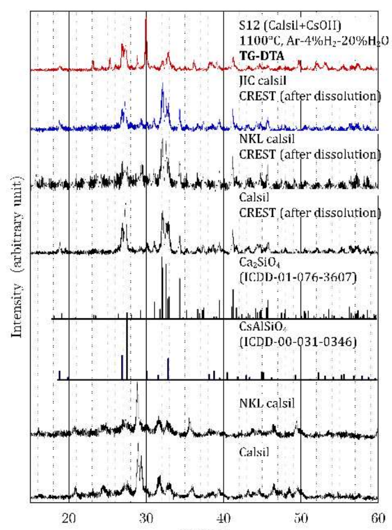

Fig. 2 Comparison of XRD patterns of calsil, NKL calsil, JIC calsil before and after the heating test as well as sample S12

Additionally, to support the result of cesium aluminum silicate formation, the elemental distribution analyses of Cs, Si, O, and Al was performed by EDS which showed the congruent distribution in the samples after this gas-solid interaction test. Infrared spectra of those samples also showed the similar stretching vibrational mode of Si-O-Si(Al) at 994 cm^{-1} band and bending vibration mode of (Al)Si-O at 449 cm^{-1} to that of $CsAlSiO_4$ reference.

5. Conclusions and future work

In the effort of emulating real interaction between calcium silicate insulator material and cesium hydroxide, the gas-solid interaction test was investigated under Ar-4%H_2-20%H_2O atmosphere with temperature of 800°C. The temperature was chosen based on the suggested reaction temperature in thermochemical investigation. The interaction was realized by using horizontal electric furnace where cesium hydroxide was vaporized in the upstream of furnace and then transported by steam flow to the downstream where calcium silicates were located. To elaborate the prevalence of interaction, two additional calcium silicates from different manufacturers were included in the test. After the gas-solid interaction test, series of characterizations were conducted including crystallography, elemental, morphological, and vibrational analyses. The XRD patterns of those calsils had been changed from their original crystal phase of xonotlite to $CsAlSiO_4$ and Ca_4SiO_4 meaning that the interaction with gaseous cesium hydroxide prevailed. Additionally, to support the result of cesium aluminum silicate formation, the elemental distribution analyses of Cs, Si, O, and Al was performed by EDS which showed the congruent distribution in the samples after this gas-solid interaction test. Infrared spectra of those samples also showed the similar stretching vibrational mode of Si-O-Si(Al) at 994 cm^{-1} band and bending vibration mode of (Al)Si-O at 449 cm^{-1} to that of $CsAlSiO_4$ reference. All the findings had proved that water-insoluble Cs compound, namely cesium aluminum silicate ($CsAlSiO_4$), formed on calcium silicate upon interaction with cesium hydroxide at high temperature.

It had been noticed in the main chapter that parametric study on threshold aluminum amount in calcium silicate would be an underlying case. However, considering the high cost for the purification technique of aluminum, it was not possible to be realized in the present study. This path will open new insight on calcium silicate manufacture process because most of the starting materials at certain limit contain alumina. Reduction of alumina would induce many consequences of finding the alternative starting materials that still could maintain the physical properties of the insulation and withstand harsh environment. The inclusion of other structural materials such as concrete and stainless steel during the gas-solid interaction test would be imperative in the next step. The transport itself will involve sequential process from reactor core where these structural materials are chosen as a representation of material at each stage when FPs transportation progress into lower temperature region. To which stainless steel represents internal structure of reactor and coolant system; piping insulation (i.e. calcium silicate) represents material existed just after coolant system; concrete represents the primary containment vessel and reactor building material. Therefore, the integrated test involving the materials would provide better understanding on the fission product interaction.

Bibliography

[1] Tokyo Electric Power Company. Evaluation of the situation of cores and containment vessels of Fukushima Daiichi nuclear power station units-1 to 3 and examination into unsolved issues in the accident progression. Japan: Tokyo Electric Power Company (TEPCO); 2017, Progress report no. 5.