

Atmospheric effects on the formation of cesium-bearing deposits on concrete and aggregate at 200 °C

*Vu-Nhut Luu¹ and Kuniyasa Nakajima¹

¹ Japan Atomic Energy Agency

Chemisorption tests of CsOH onto concrete and aggregate were carried out at 200 °C in both dry and humid conditions to investigate the source of high dose rates at the concrete shield plugs of Units 2 and 3 at 1F. Post-test analyses using XRD, Raman, and SEM revealed that water-insoluble Cs-bearing deposits formed different morphologies under dry and humid conditions. Namely, uniform and large Cs deposits were formed under humid conditions, while heterogenous growth and smaller size Cs deposits were observed under dry conditions.

Keywords: Cesium-bearing materials, cesium aluminum silicate, concrete shield plug, Fukushima

1. Introduction

High radioactivity (>20PBq) was recently found in the concrete shield plugs of units 2 and 3 of 1F [1]. This indicates that released radioactive materials, such as CsOH and CsI, may have been trapped on the concrete surface at high temperatures during the severe accident. Although the interaction of CsOH with stainless steels at high temperatures (> 800 °C) has been intensively studied [2], the interaction of CsOH in the gaseous phase with the concrete at elevated temperatures was not fully understood. Our recent preliminary study using thermal analysis and the X-ray diffraction (XRD) method has confirmed the formation of Cs compounds by the interaction of CsOH·H₂O with pulverized concrete/aggregate below 300 °C, but the reacted products were difficult to observe due to the convolution of phases in pulverized samples [3]. This study aims to identify the chemistry and morphology of formed products in the gas-solid reaction (i.e., the interaction between concrete and CsOH present in the gas phase) that may occur in severe accidents.

2. Experimental method

Because the interaction behavior of CsOH with different concrete phases may differ, two types of samples were prepared: surface concrete and siliceous aggregate, both of which were cut/extracted from a cylindrical concrete (φ100 x 200 mm). By XRD and SEM analysis, SiO₂, NaAlSi₃O₈, KAlSi₃O₈ (minor), and Mg-Fe chlorite ((Fe, Mg, Al)₆(Si, Al)₄O₁₀(OH)₈) (minor) were detected in aggregate, while the predominant crystalline phases on surface concrete are CaCO₃ and SiO₂ (minor) though fine aluminosilicate aggregates were also observed by SEM. For chemisorption tests, CsOH·H₂O (4 - 5 g)-containing crucible was heated at 650 °C for 3 hours under a constant flow (100 ml/min at 0.1MPa) of dry gas (Ar + 5% H₂) and humid gas (Ar + 5% H₂ + 20% H₂O) from the top to the bottom. The sample temperature was kept at around 200 °C. The chemisorbed samples were soaked in water for 1 hour to remove water-soluble Cs before XRD, Raman, and SEM/EDS analyses.

3. Results and Discussion

Fig.1 shows the XRD analysis and the distribution of insoluble Cs-bearing deposits in both conditions. Under humid conditions, a large Cs-Al-Si-O deposit was observed on aggregate, while micro-size Cs-Al-Si-O deposits were found on surface concrete. The XRD and SEM/EDS analyses detected the formation of CsAlSiO₄ on both samples, which was thought to be due to the CsOH – aluminosilicate interaction [3]. Under dry conditions, Cs-Al-Fe-Mg-Si-O deposits and small size Cs-Al-Si-O deposits similar to those found under humid conditions were observed by SEM on aggregate. The elemental mapping on aggregate suggested that Cs-deposits could be trapped at Mg-Fe chlorite sites (i.e., a clay mineral). The elemental mapping also showed the congruency of Cs, Al, Fe, Mg, Si, and O elements on surface concrete. However, XRD did not detect any crystalline Cs phase on either the surface concrete or the aggregate. There was little reaction in the case of dry conditions, even though it is thermodynamically possible for CsOH – aluminosilicate reaction to occur [3]. This could be due to the less contact between CsOH and feldspar in solid-solid reactions. However, in humid conditions, CsOH aerosols absorbing water can lead to the generation of liquid CsOH [4], which makes it easier for the liquid-solid reaction to occur.

References

- [1] N. Kuwabara, 2020. <http://www.asahi.com/ajw/articles/14071742>; [2] S. Nishioka et al., J. Nucl. Sci. Technol., vol. 56, no. 11, pp. 988–995, 2019; [3] V. N. Luu and K. Nakajima, J. Nucl. Sci. Technol., in press, 2022; [4] Krischer W, Rubinstein MC. Elsevier Applied Science: London (UK). 1992. p. 340.

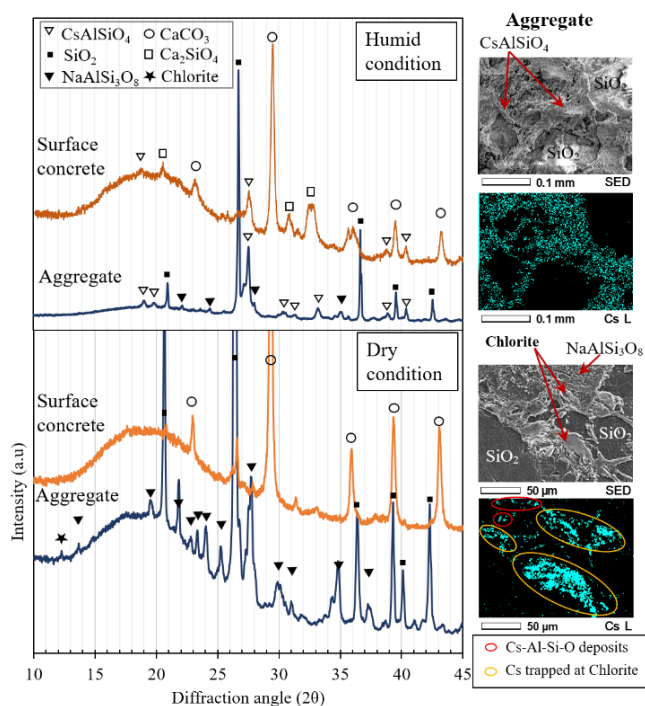


Figure 1: XRD analysis and distribution of Cs on water-washed samples in humid and dry conditions