

# Synthesis of Fukushima Daiichi Cs-bearing microparticles through molten core-concrete interaction in nitrogen atmosphere

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## ABSTRACT

Cs-bearing microparticles, released during the accident of Fukushima Daiichi, are a significant concern for health and environment due to their abundance over wide areas, associated with a low solubility. Since their discovery, efforts have been made to characterise these particles and use them as direct witnesses of the various events inside the reactors. This study reports the experimental synthesis of micrometric particles through molten core-concrete interaction. Primary chemical analyses on Al/Si, K/Si and Na/Si atomic ratios seem to confirm concrete as source of Si. Cs has also been identified in low concentrations.

**Keywords :** CsMP, Fukushima Daiichi, experimental synthesis, molten core-concrete interaction

## MAIN BODY

In 2011, three reactors of the Fukushima Daiichi Nuclear Power Station (FDNPS) experienced core meltdown due to a loss of coolant in the primary loop. The total source term (excluding noble gases) is estimated to be of 520 PBq [1]. Radionuclides were released into the Pacific Ocean and on Japanese lands, depending on the wind direction [2].

On March 14<sup>th</sup> and 15<sup>th</sup>, radioactive Cs-bearing Microparticles (CsMP) were discovered on air monitoring filters at Tsukuba, Japan (170 km southwest of the FDNPS) [3] (Figure 1). CsMP are micrometric particles mainly made of amorphous silica, containing a diversity of other major elements (depending on the particle analysed) such as iron (Fe), zinc (Zn), tin (Sn), potassium (K), rubidium (Rb), chlorine (Cl), carbon (C), sodium (Na) and caesium (Cs) [4, 5]. Cs is the principal source of radioactivity of CsMP due to its radioisotopes <sup>134</sup>Cs and <sup>137</sup>Cs (half-lives of 2.2 and 30 years respectively [6]). Other elements such as actinides or fission products (FP) can also be found as traces or inclusions [7, 8]. It must be noted that this type of Cs-bearing particles had not been anticipated and is not currently taken into account in severe accident modelling. This paper reports the first achievement in the attempt of synthesising CsMP through molten core concrete interaction (MCCI), to provide key information about the FDNPS accident and improve the understanding of radioactive aerosol release after lower head failure and core relocation.

Experimental synthesis of type-A (*i.e.*  $\approx 1 \mu\text{m}$  diameter and high specific radioactivity) CsMP has been set up on the VITI facility of PLINIUS platform to investigate the generation process and the physicochemical conditions of the source reactor [9]. Among the few hypotheses justifying a sufficient source of Si, molten core-concrete interaction (MCCI) after molten fuel relocation on the concrete pedestal is supported by several researchers and investigated in this study [10, 11]. Structural stainless steel, silicate insulation materials or high-efficiency particulate air filters are also considered as possible source of Si in the literature [12, 13, 14]. The basaltic concrete used for FDNPS construction contains around 60% wt. of SiO<sub>2</sub> [15]. When the molten fuel, containing a significant fraction of sub-oxidised Zircaloy cladding, hits the pedestal, highly exothermic reactions take place, producing atomic Si or gaseous SiO, as the temperature increases [16]. Then, silicon-containing vapours spread in the Primary Containment Vessel (PCV) and may condense as SiO<sub>2</sub> in colder locations.

The experimental test section is composed of a zirconia crucible, containing a corium simulant and concrete in a closed zirconia chamber (Figure 2). The heating process is achieved by electromagnetic induction from a 4-turn cooled inductor, on a tungsten hollow cylinder, radiating on the chamber. The test section lies inside a 70L water-cooled stainless steel vessel filled with nitrogen at atmospheric pressure. The experimental set-up is also composed of a heated sample line (150°C) to carry (and

dilute) the aerosols from the vessel to a High-Efficiency Particulate Air (HEPA) filter and a particle counter (Pegasor®PPS-M).

An in-vessel corium composition has been defined to interact with concrete and simulate MCCI. For this set of trials, the corium composition is based on results of the OECD/NEA Benchmark Study of the Accident at the Fukushima Daiichi nuclear power plant (BSAF) project (Phase I, Unit 2) [17]. The corium is composed of depleted uranium oxide, Zircaloy-2, zirconia, stainless steel, stainless steel oxides, boron carbide and some fission products of interest available as stable isotopes (Table S1). The concrete used for the trials is basaltic concrete based on the real composition of FDNPS concrete.

Aerosols are not collected all along the heating process but only at a defined target temperature. This experimental procedure has been designed to keep the most volatile species inside VITI vessel until the end of the trial. The target temperature is defined as the temperature providing a vapour composition that best satisfies the desired aerosol composition (*i.e.* CsMP composition). This temperature has been estimated by thermodynamics calculations using the Thermodynamics of Advanced Fuels – International Database (TAF-ID) and ThermoCalc software, considering that the gaseous phase may be an indicator of the final composition of particles [18]. The collecting process starts as the crucible reaches 2200°C (corium temperature between 2100 and 2200°C) and lasts 10 to 30 seconds depending on the particle counting. Vessel pressure is slightly above the atmospheric pressure, ensuring the path of aerosols from the vessel to the sampling line. A moderate gas flow (5 L/min) blowing under the crucible (from the bottom to top direction) carries aerosols and prevents the pressure from dropping under 1 atm. A volumetric pump downstream ensures also that the gas flows through the HEPA filter.

The preparation process for Scanning Electron Microscopy (SEM) observations and Energy-Dispersive X-ray spectroscopy (EDX) analyses consists of taking a small HEPA filter portion ( $< 1 \text{ cm}^2$ ) with aerosols and transfer it into a test tube filled with a few millilitres of demineralised water. An energetic shaking of the tube (1 to 2 min) is performed to take off the aerosol from the filter, disperse them and dissolve soluble aerosols. The suspension is finally passed through a filter syringe (0.22  $\mu\text{m}$  pores) to keep the insoluble aerosols. The filter is then dried at room temperature and fixed with carbon tape onto a sample holder. Samples are coated with carbon through vapour deposition for electric conduction.

Macroscopic SEM observations show a large diversity of aerosols with irregular shapes and sizes on the filter. Close observations led to the identification of numerous spherical particles with a diameter varying between 250 nm and 6.4  $\mu\text{m}$  (Figure 3). The median diameter is around 2  $\mu\text{m}$ , which is consistent with most of identified CsMP from the FDNPS [19]. In total, 21 spherical particles have been studied, all having a spherical shape and some small background aerosols sometimes stuck on the surface. In comparison, a particle has been identified on a non-dispersed sample (directly transferred onto the carbon tape) and seems to have more aerosol stuck on its surface, implying that the water dispersion mostly removed or dissolved the background aerosols on other particles. A study suggests that particles greater than 1  $\mu\text{m}$  were mostly found because their radioactivity *i.e.* their radiocaesium content was higher, but even more minute particles exist. In this study, particles are only sought visually, with the microscope, implying that this bias is less likely to occur, although larger particles are easier to find [20]. Moreover, if some synthesised particles have a diameter below 200 nm, they may have passed through the filter during the preparation process. These particles would require ultrafiltration to be isolated, after a segregation from background aerosols.

EDX chemical composition has for now been conducted on a few particles. This experimental method provides qualitative or semi-quantitative results on major elements. Light elements such as boron (B) cannot be accurately identified. Carbon contents cannot be assessed as the sample is coated with carbon. Chemical analyses have been made on specific particles, chosen for their size or background, as larger particles will provide spectra with less background noise. Particle 59 (diameter of 1.5  $\mu\text{m}$ , very low background noise) is mainly made of Si and O, the other main elements are alkali elements (Na, K and Cs), Fe and magnesium (Mg) (Figure 4a). This EDX analysis suggest that the particle is mainly made of  $\text{SiO}_2$  like CsMP. Na and K are reliable elements for further comparisons with CsMP since they are inherent concrete components, but Cs has been artificially added to the concrete composition and the Cs content of the particles may directly be influenced by the initial corium content in Cs. The Fe content of the particles is mainly due to the presence of stainless steel, even if concrete aggregates are a minor source of Fe. The largest particle collected (Figure 3, bottom right, diameter of 6.4  $\mu\text{m}$ ) has the same spectrum with slightly different intensities.

Other spectra with possible background influence show also contents of Ca, Zn, Al, S, and W, the latter due to pollution from the susceptor (Figure 4b). Ca, Al and S are major or minor elements of concrete and have been found in several CsMP. The source (thus initial quantity) of Zn is uncertain but supposed to be from paint. It was added in the experimental composition as ZnO (Table S1).

Semi-quantitative chemical analyses have been carried out and are compared with CsMP from other studies [21, 7]. Note the impossibility to determine carbon concentration even though carbon has been measured, sometimes more than Si in some particles of the literature [7]. Hence, the present semi-quantitative ratios on Si may be significantly underestimated. Al, Na and K are elements that are only provided by concrete in the experiments. Al is not found in every CsMP and often as a minor element ( $< 1\% \text{ wt.}$ ), which is consistent with the three experimental particles considered here, as Al/Si ratios are in the same order of magnitude. K is found in every CsMP but seems to be in lower concentration compared to the synthesised particles with the same order of magnitude. In FDNPS, concrete is also the main source of K. On the other hand, Na is not measured

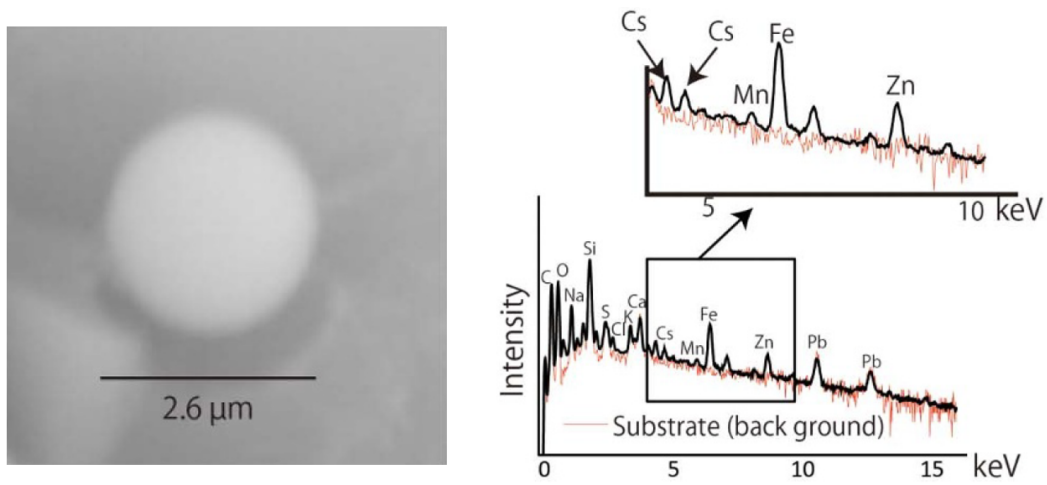
in every CsMP. In the first published papers, Na was not identified in EDX analysis as Zn and Na peaks overlap [21]. The synthesised particles have a similar Na/Si ratio with CsMP, but it may also be possible for Na to be brought by other source such as sea water, if CsMP were generated after sea water injection. Thus, results on Al/Si, K/Si and Na/Si tend to confirm MCCI as generation process compared to other sources of Si. Fe concentration of synthesised particles is at least one order of magnitude below CsMP. According to thermodynamics calculations, the Fe fraction in the gas phase is directly influenced by the stainless steel fraction in the corium. This result suggests that the corium responsible for CsMP generation may have been richer in stainless steel, or that CsMP were generated at interfaces rich in stainless steel, if the melt contained heterogeneities. Finally, Cs concentration seems lower in synthesised particles than CsMP (one order of magnitude) but this may be due to different effects. Cs is a volatile FP and there are different hypotheses on its behaviour before the core may have hit the concrete pedestal. Cs was probably mostly released from degraded fuel rods and may have condensed on colder walls and on the concrete pedestal. As for Fe, Cs concentration may have varied in the PCV. Plus, observed CsMP are isolated with Imaging Plates (IP), based on their radioactivity that is brought (mainly) by radiocaesium. Thus, studied CsMP are certainly not representative of all silicate aerosol particles in terms of size and Cs activity.

These experiments are a first milestone towards the synthesis of representative artificial CsMP and will be followed by other sets of trials to evaluate the influence of corium and atmosphere composition. Further analysis will also be carried out to study more precisely the concentration of key elements, to confirm if the matrix is amorphous SiO<sub>2</sub> and to study if the particle contains concentration gradients. Synthesis is accompanied by thermodynamic calculations. The comparison of CsMP observed in Japan with both modelling and particle synthesis under well-controlled conditions will provide a powerful help of using CsMP to assess accident evolution in Fukushima.

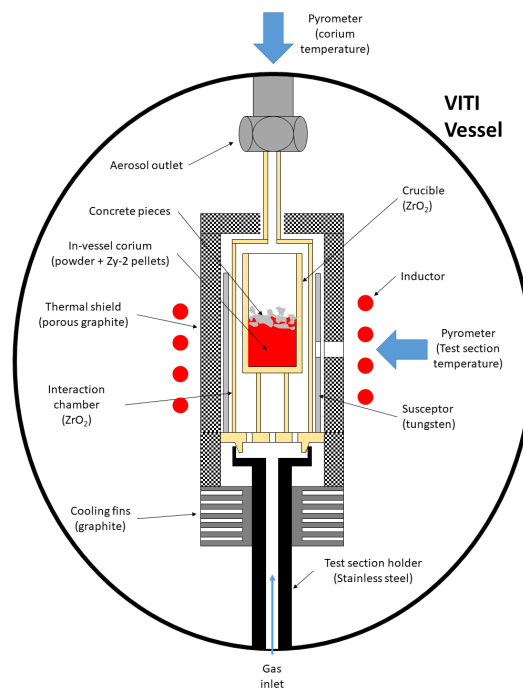
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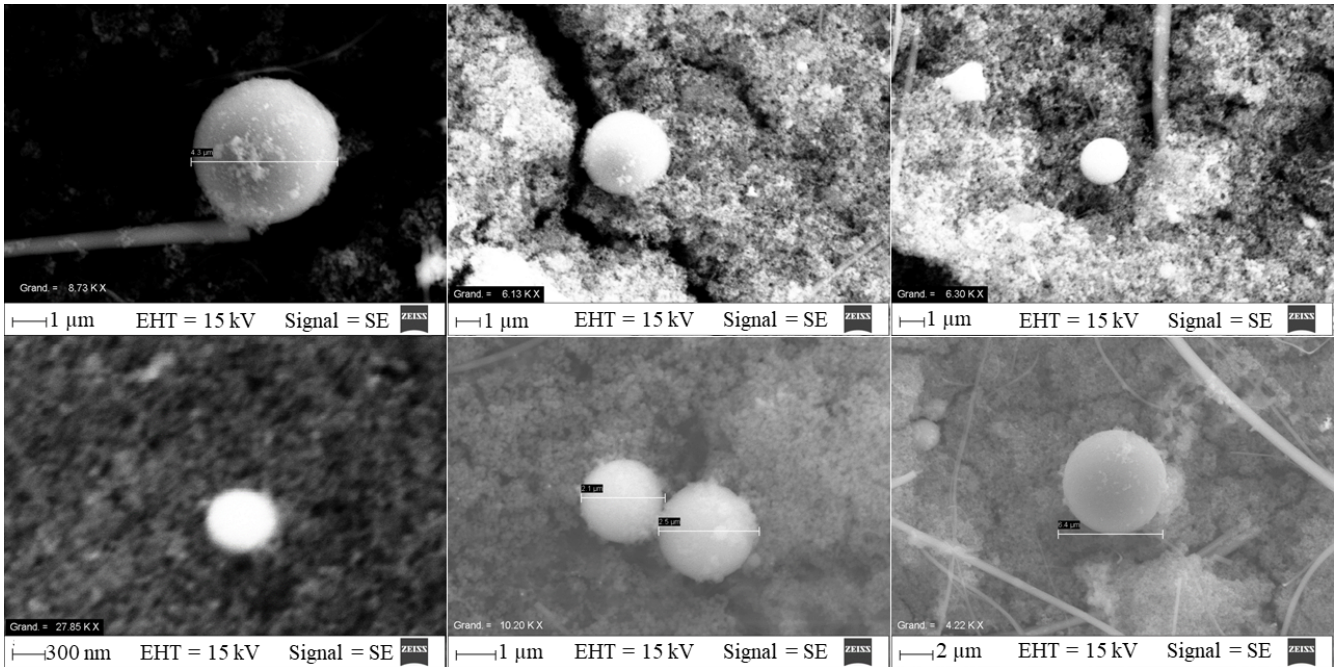
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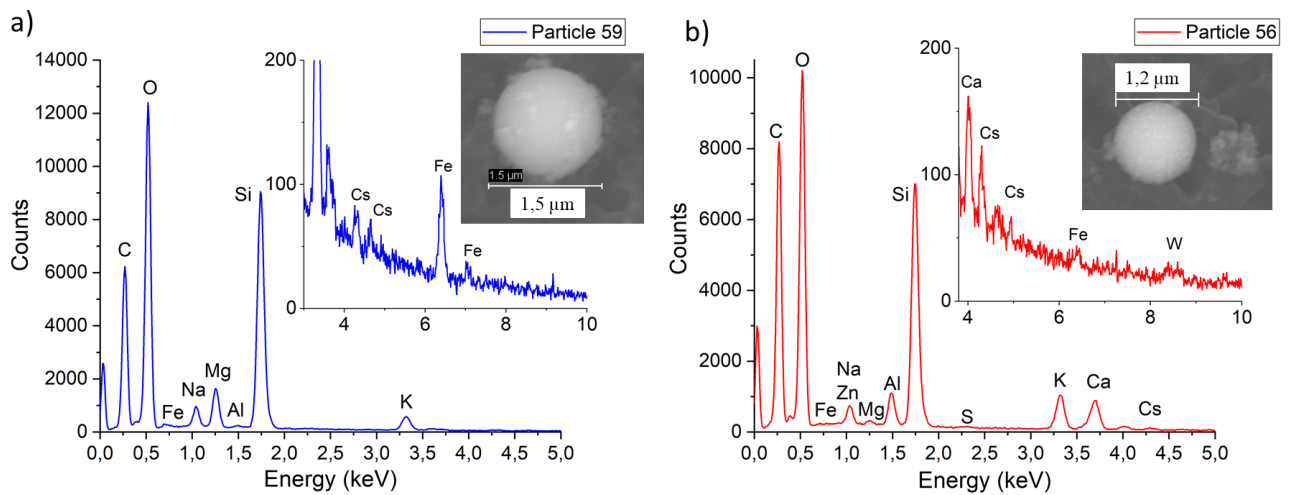
**Figure 1.** (left) SEM image of a spherical particle collected at Tsukuba (Japan) in the days following the accident and (right) its associated EDX spectrum (black line) [3].



**Figure 2.** Test section schematic view for aerosol generation inside the vessel.



**Figure 3.** Several synthesised particles identified after the preparation process. Fibres are borosilicate strands from HEPA filter deterioration.



**Figure 4.** EDX spectra of two synthesised particles with a low background noise. Carbon is due to the coating used for sample preparation even though particles may contain carbon. Tungsten (W) is a pollution from the susceptor for induction coupling.