Investigation of fuel crud by means of ICP-MS and TEM

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Abstract

Dissolved and suspended solid corrosion products (crud) from structural elements in LWRs are of concern since the incorporation of short-lived nuclides like $^{60}$Co in such oxide layers is a dominant source of the radiation exposure. To determine the mechanisms of the nuclide incorporation, detailed information on the formation and nature of crud is required, especially regarding the chemical composition, molecular coordination and crystal structure. The paper describes the methodology for the characterization of the chemical composition of crud and of the Pt distribution in crud (relevant if Online NobleChem™ is applied) by means of ICP-MS and TEM as well as the sample preparation techniques.

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1. Introduction

Dissolved and suspended solid corrosion products from structural elements in light-water reactors (LWRs) - so called crud (Chalk River Unidentified Deposits) - are of concern to the nuclear power operators: a) large fraction of these corrosion products deposit on the outer surface of fuel rods, where they can compromise the thermal efficiency of the rods and lead to increased cladding corrosion and potential fuel failure; b) crud particles can migrate away from the cladding surface and can cause radioactive contamination in cooling-water systems.

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and spent-fuel storage areas [1, 2]. While the conditions leading to rod failure are not always fully understood, the failures are generally attributed to a combination of water chemistry, fuel duty, and cladding materials. The deposition and dissolution behavior of crud depends on its solubility in the coolant water mostly influenced by pH and temperature.

Fuel crud mainly consists of iron, nickel, manganese, and chromium oxides, most often, zinc is also observed on the fuel cladding. Investigations of the structure revealed that the main phases for boiling water reactor (BWR) crud are normally hematite and non-stoichiometric nickel ferrite spinels, whereas for pressurized water reactor (PWR) crud the main phases are shown to be non-stoichiometric nickel ferrite and nickel metal or oxide. The fuel rod crud deposits in the PWRs are normally consisting of a single, more adherent layer, whereas BWR fuel crud has a duplex layer structure with a relatively porous outer layer and a dense and more adherent inner layer [3, 4]. The exact composition of the oxide layer not only depends on the thermodynamics of the system, but also on the kinetics of the process. Therefore, many different types of microscopic oxide grains can be present. Zn is added to PWRs and BWRs to decrease the dose rates in the primary circuit by fixing the crud on the fuel rods and to reduce stress corrosion cracking. So far, no direct effects of Zn on cladding corrosion have been reported. However, a possible negative effect of Zn addition could appear through changes in the crud chemistry and morphology like the production of harder crud layers [5] and can not be totally excluded.

The structural characterization of dispersed crud has in recent years been expanded towards the characterization of Pt nanosize particles. Pt is added to BWR feed water in a method developed by GE Hitachi, called “Online NobleChem™” (OLNC). It is intended to prevent or minimize irradiation assisted stress corrosion cracking of structural components in the pressure vessel of BWR [6, 7] by enhancing the efficiency of Hydrogen Water Chemistry (HWC). Whenever high hydrogen injection rates are needed to attain low electrochemical potentials, high radiation fields may result. OLNC allows attaining low electrochemical potentials since Pt acts as a catalyst in order to achieve reducing conditions on the surface of the reactor internals while adding low amounts of hydrogen during normal operation. However, concerns have been raised about whether or not fuel cladding corrosion and hydrogen uptake could be accelerated by OLNC. Therefore, knowledge about the Pt distribution on reactor internals [8] and in crud is essential for proving the efficiency of the protection method.

So far, crud was comprehensively investigated in Swiss nuclear power plants mostly for BWRs. In the Hot Laboratory of PSI very detailed investigations have been performed during the last decade especially on crud samples from the nuclear power plant Leibstadt (KKL) also covering first studies about the implementation of Pt during OLNC in crud layers. The elemental composition of the crud deposits as well as the crud structure and the axial variations of the magnetic properties were studied in frame of periodic crud sampling and investigation programs at PSI [9, 10] and recently also in frame of a PhD thesis [11, 12] using advanced microscopic X-ray techniques at the Swiss Light Source (SLS). The results of such detailed structural investigations help to better understand crud formation and deposition and possible correlations with the applied water chemistry. Therefore, an improvement of the fuel reliability by minimizing corrosion product formation on fuel rods is expected on a long-term perspective.

The present paper describes the analytical methodology for the characterization of the chemical composition and of the Pt distribution in crud collected on filter holders by means of inductively coupled plasma mass spectrometry (ICP-MS) and transmission electron microscopy (TEM) including the necessary sample preparation steps in detail. The objectives of the crud investigation programs are the understanding of the crud deposition as a function of the rod elevation and the observation of the depth of Pt penetration into the crud layer.

2. Experimental

2.1. Samples and sample preparation for ICP-MS

The crud sampling and analysis equipment (CRUDSAM, developed by Westinghouse) was installed in the KKL spent fuel pool. The device can be equipped with different work pieces to grind or to scrape off crud from the rod surface. This allows a differentiation in the sampling between the outer loose and the inner tenacious crud
components. The crud was collected on membrane filters in Millipore filter holders (type Swinnex™, 25 mm in diameter). The filter holders were placed in a filter cassette below the sampling equipment in the pool water. In addition to crud samples, water samples for background correction were taken. After sampling the filter holders were dried, covered with a Mylar foil and mounted in special sample holders for subsequent analysis. Few active filter samples were selected and transported to PSI for the analysis of the chemical composition and Pt particle distribution.

Primarily, all Millipore membrane filters including the Mylar foils had to be removed by cutting from the sample holder in a shielded fume hood. Afterwards the filters plus Mylar foils were transferred within plastic boxes into a shielded dissolution box in the Hot Laboratory. All Millipore filters plus Mylar foils were completely dissolved in a mixture of HNO₃ (69 %, VLSI, Fluka), HF (48 %, Ultrapur, Merck), H₂O₂ (30 %, Suprapur, Merck) or HCl (37%, VLSI, Fluka) in a microwave digestion system with Teflon containers (1200 MEGA, MLS, Leutkirch, Germany). In order to determine the efficiency of the dissolution procedure, the samples with the highest crud loading were filtered through 0.2 µm filter units after the microwave digestion procedure to retain possible non-dissolved residues. The filter samples as well as the crud solutions were analyzed by means of gamma spectrometry. For none of the nuclides more than 0.25% of the total activity of these nuclides was found on the filter proving the high efficiency of the chosen dissolution procedure. In order to determine the impurities in the acids used for filter digestion and possible memory effects between the different filters in the microwave digestion vessels an “acid blank” was mixed, treated in the same way in the microwave system before and after the active sample dissolution and analyzed by ICP-MS.

2.2. ICP-MS

The Hot Laboratory of the PSI is equipped with a sector field ICP-MS (Element 2) and a multi collector ICP-MS (Neptune, both from Thermo Fisher Scientific, Bremen, Germany) for elemental analysis. For handling and analyzing highly toxic radioactive samples the sample introduction part of the ICP mass spectrometers is encapsulated within glove-boxes (Fig. 1).

The measurements of crud solutions were performed with the Element 2 in low mass resolution mode for Zr, Sn (indicating the release of cladding material during the sampling process) and Pt (deposited due to the OLNC application), whereas the Cr, Fe, Mn, Co, Ni, Cu, and Zn isotopes (crud elements) have been measured in medium resolution mode in order to eliminate Ar based interferences in the mass range below 80 amu. The elements were quantified by an external calibration method using a mixture of TraceCert single element standards (Fluka Sigma Aldrich) with In (Spex) as internal standard.
In order to separate the analyte elements from the sample matrix or from interfering elements, the ICP-MS systems can be online connected to a chromatographic separation device. An online HPLC-MC-ICP-MS coupling [13] was performed in order to investigate the isotopic composition of Zn in the crud samples. Due to the injection of Zn depleted in the isotope $^{64}$Zn in KKL [9] a non-natural isotopic composition for Zn in crud was expected and could be proven. The total Zn concentrations in the crud samples were calculated based on the measured isotopic vectors.

2.3. TEM sample preparation and instrumentation

For TEM investigations the filters had less crud material on them due to the need of direct handling of the samples. The filter papers with the collected crud particles were transferred to small beakers for suspension in water. Small volumes of these suspensions were then further transferred to a different beaker. Particles suspended in the water were measured by gamma spectrometry and the activity of the suspension confirmed the presence of crud particles in the solution. A micropipette was used to disperse a drop of this suspension on a TEM copper grip coated with a thin carbon film. Several TEM samples were prepared for each crud filter.

A JEOL 2010 TEM equipped with LaB$_6$ filament and operating at 200 kV was used for the examination of the crud samples. An Oxford Instrument energy dispersive spectrometer (EDS) equipped with INCA software was used to perform the chemical analysis of the Pt and crud particles. The micrographs were acquired with a CCD camera with 4008 x 2672 pixel resolution (Orius, GATAN) providing a sub-nanometric resolution. The presence of Pt was confirmed with qualitative EDS measurements due to the fact that the particles deposited on the crud have different compositions.

3. Results

3.1. Chemical composition of crud

The typical composition of crud from the filter samples determined by ICP-MS is presented in Fig. 2. The quantification shows in this case a clear tendency of higher total crud concentrations in the upper part of the fuel rods (data not shown). This coincides with higher Pt concentrations in crud in the upper parts when OLNC is applied. In earlier examinations the opposite behavior concerning the amount of crud was also observed.

![Fig. 2. Relative composition of the crud forming elements sampled at different elevations of a fuel rod](image-url)
3.2. Pt detection and its particle size distribution, obtained by TEM

The prepared TEM samples normally showed in more than one region large signals from Pt particles. A micrograph representing typical Pt particles is shown in Fig. 3a.

![Fig. 3. (a) TEM bright field micrograph of a crud particle showing several Pt particles attached to it. The Pt particles show a size from 4 to 10 nm in diameter. (b) Particle size distribution of the Pt particles](image)

Since several different materials could give similar contrasts, it was possible to conclude for the presence of Pt particles only due to the EDS analysis. It is therefore necessary to perform a systematic analysis of the particles in order to evaluate the distribution of Pt in the crud. The EDS analysis of the largest particles indicates a very clear Pt signal (approx. 20 wt.% of Pt based on the semi-quantitative analysis of the spectrum, data not shown). The other particles also show Pt signals but with lower signal intensity. The presence of individual Pt particles on the carbon film was not very often observed, in most cases Pt particles were observed to be “linked” to iron oxide crystals. In some regions, agglomerations of spinel particles giving a large Pt signal were also observed.

The Pt particle size distribution (Fig. 3b) was determined by analyzing the TEM micrographs. The highest population of Pt particles was typically observed to be in the range of 5 to 11 nm. However, a number of larger Pt particles was also observed, these might be agglomerates of small particles or single large particles. From the crud samples investigated till present in frame of the KKL program the presence of Pt particles was only proven for the outer loose crud samples indicating that the Pt did not penetrate into the inner layers of crud on the fuel rods.

4. Discussion and Conclusions

In frame of periodic crud sampling and investigation programs in collaboration between KKL, WSE and PSI the methodology for crud sampling and analysis will be developed and continuously improved. The chosen concept of combining an analytical technique to determine the bulk chemical composition (ICP-MS) of the crud material collected on filter samples with an electron microscopic determination (TEM) of the Pt particle size distribution on crud was proven to be successful. The observation of crud particles by SEM (performed in parallel but not discussed in this paper) brings a large amount of information about the nature of crud and its local composition. Pt particles could occasionally be observed by SEM, however, since the Pt particles are often too small to be analyzed by SEM and EDS, the use of the more sophisticated TEM method is recommended and is now a standard method for crud characterization at PSI.
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