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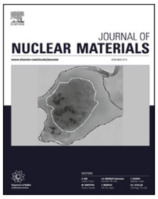

New sacrificial material for ex-vessel core catcher

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HIGHLIGHTS

- A sacrificial material (SM) was developed for ex-vessel core catcher.
- Suitable proportions in the $SrFe_{12}O_{19}$–$Al_2O_3 \cdot CaO$–Fe system were determined.
- Hydrogen release limitation was shown for ex-vessel corium retention with the SM.
- Calculated temperature of the active initiation of corium/SM interaction is 1716 °C.
- Functional properties of the SM were measured.

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ABSTRACT

A new functional (sacrificial) material has been developed in the Fe_2O_3–SrO–Al_2O_3–CaO system based on strontium hexaferrite ceramic in concrete matrix. The method of producing SM has been advanced technologically; this technological effectiveness allows the SM to be used in ex-vessel core catchers with corium spreading as well as in crucible-type core catchers. Critical properties regarding the efficiency of SM in ex-vessel core catchers, such as porosity, pycnometric density, apparent density, solidus and liquidus temperatures, and water content have been measured. Suitable fractions of $SrFe_{12}O_{19}$ and high alumina cement (HAC) were found in the SM based on thermodynamic analysis of the SM/corium interaction. The use of sacrificial steel as an additional heat adsorption component in the core catcher allowed us to increase the mass fraction range of $SrFe_{12}O_{19}$ in the SM from 0.3–0.5 to 0.3–0.85. The activation temperature of the SM/corium interaction has been shown to correspond to the liquidus temperature of the local composition at the SM/corium interface. The calculated value of this temperature was 1716 °C. Analysis of phase transformations in the SrO–Fe_2O_3 system revealed advantages of the $SrFe_{12}O_{19}$–based sacrificial material compared with the Fe_2O_3-contained material owing to the time proximity of $SrFe_{12}O_{19}$ decomposition and corium interaction activation.

1. Introduction

In general, the nuclear power industry has achieved a high level of safety for the nuclear power plants (NPPs) that are currently in operation [1]. However, the current level of efficiency and reliability of safety systems and integrated technical measures aimed at preventing severe accidents (SAs), which constitute the major risk to the public associated with potential radioactive releases from nuclear power plants, cannot completely eliminate SA scenarios involving substantial degradation and melting of the core [2–4].

After the recent accident at the Fukushima plant, the reactor safety community recognizes the need to improve the balance between accident prevention and consequence mitigation. The main thrust of the development strategy for NPP safety systems involves the implementation of severe accident management (SAM) guidelines. SAM should adequately protect the public with concise emergency planning requirements, primarily with respect

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to rapid evacuation of the surrounding population.

An effective SAM strategy for high power light water reactors (LWRs) [5–8] necessitates localization of the core melt within the ex-vessel core catcher (CC). This device can be considered a back-up system for reactor containment: in other words, it is the last protective barrier according to the currently used "defense-in-depth" philosophy. The primary functions of CCs are ensuring the retention, crystallization, and reliable long-term cooling of core melt and debris and minimizing the release of hydrogen, other non-condensable gases, and fission products into the containment atmosphere.

The concept of localizing the core melt for VVER-1000 and VVER-1200 NPPs was described in Ref. [9]. This concept envisages using a new class of functional materials [10], i.e., an oxide SM and a sacrificial steel (SS), located in crucible-type core catchers. These materials interact with metal and oxide core melt during the progression of an SA to modify the physicochemical properties of the melt in order to enable reliable operation of the core catcher. The use of SM and SS also decreases the temperature and volumetric power of the melt. Interactions between the SM and the core melt lead to reduction of the oxide melt density and to gravitational inversion of the oxide/metal molten layers. These changes naturally prevent heat focusing at the top of the metal melt and limit heat fluxes from the external surface of the core catcher vessel to the cooling water. This concept was validated [5,11,12] and was realized in the VVER-1000 NPP [13], resulting in the building of the first ex-vessel core catcher at the Tianwan (Lianyungang) VVER-NPP [14].

Interest in NPP passive safety systems for corium melt localization stimulated the development of new functional materials with improved properties [8] as well as studies of their interactions with corium [15,16]. The interaction mechanisms between SM and corium were determined, and models were developed on the basis of the experimental data that were obtained from these studies [11,12].

Several ceramic SMs in the Fe_2O_3–Al_2O_3 system with SrO, CeO_2, Gd_2O_3, Eu_2O_3 functional additives have been developed for crucible-type core catchers [5,6], and concrete SMs have been developed for EPR core catchers with melt spreading [17,18], as well as for some new projects [6,19].

Considering the various phenomena that occur during core melt localization, it is important to minimize the highly exothermic corium oxidation by water/air and to limit additional hydrogen production to ensure hydrogen safety in the containment vessel [20,21]. Additional loads on the containment vessel that may be critical to its integrity include significant heat release from hydrogen oxidation by oxygen and the possibility of explosion at certain temperatures and O_2 and H_2 partial pressures (see Reaction 1).

$$2H_2 + O_2 \rightarrow 2H_2O\ (+125.6\ \text{kJ}\cdot\text{g}(H_2)^{-1}) \quad (1)$$

If SM is absent from the core catcher, corium active reducers react with external cooling water flooded on the surface of non-fully oxidized corium (Reactions 2.1, 2.2), atmospheric oxygen (Reactions 3.1, 3.2), and water steam (Reactions 2.1, 2.2). Heat generation in Reactions 2.1, 2.2, 3.1, 3.2, 5.1, 5.2, 6.1, 6.2, 7.1, 7.2, 8.1, and 8.2 is calculated at 1716 °C [22].

$$Zr + 2H_2O\ (\text{atmospheric, cooling flow, steam}) \rightarrow ZrO_2 + \mathbf{2H_2}\ (+6332.7\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (2.1)$$

$$U + 2H_2O\ (\text{atmospheric, cooling flow, steam}) \rightarrow UO_2 + \mathbf{2H_2}\ (+2441.5\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (2.2)$$

$$Zr + O_2\ (\text{atmospheric}) \rightarrow ZrO_2\ (+11841.2\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (3.1)$$

$$U + O_2\ (\text{atmospheric}) \rightarrow UO_2\ (+4551.7\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (3.2)$$

Nearly every oxidation process is accompanied by a significant release of hydrogen: 43.85 $g(H_2)/kg(Zr)$ and 16.8 $g(H_2)/kg(U)$.

When SM is present in the core catcher, corium active reducers react with SM components, namely, Fe_2O_3, Fe_3O_4 and O_2. Magnetite (Fe_3O_4) and oxygen form owing to iron oxide (III) decomposition (at approximately 1380 °C), according to Reaction 4. When water is supplied, there are no active reducers present in corium, and Reactions 2.1, 2.2 do not occur. Interactions between SM oxidants and corium active reducers follow and form ZrO_2 and UO_2 without hydrogen release (Reactions 5–7). A small amount of hydrogen can form during the interaction of Zr(U) with water vapor released from the SM (Reaction 8). Water can be released from the SM surface (physically adsorbed water) and from the bulk SM during decomposition of water-containing SM components (chemically bonded water). In both cases, the water/steam flow rate depends on the composition, structure, and physicochemical properties of the SM (e.g., dispersion, porosity, adsorptive capacity).

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2\ (-500.9\ \text{kJ}\cdot\text{kg}(Fe_2O_3)^{-1}\ \text{at}\ 1380\ ^\circ\text{C}) \quad (4)$$

$$3Zr + 2Fe_2O_3 \rightarrow 3ZrO_2 + 4Fe\ (+6489.8\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (5.1)$$

$$3U + 2Fe_2O_3 \rightarrow 3UO_2 + 4Fe\ (+2501.4\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (5.2)$$

$$2Zr + Fe_3O_4 \rightarrow 2ZrO_2 + 3Fe\ (+6429.9\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (6.1)$$

$$2U + Fe_3O_4 \rightarrow 2UO_2 + 3Fe\ (+2478.4\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (6.2)$$

$$Zr + O_2 \rightarrow ZrO_2\ (+11841.2\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (7.1)$$

$$U + O_2 \rightarrow UO_2\ (+4551.7\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (7.2)$$

$$Zr + 2H_2O\ (\text{from SM}) \rightarrow ZrO_2 + \mathbf{2H_2}\ (+6332.7\ \text{kJ}\cdot\text{kg(Zr)}^{-1}) \quad (8.1)$$

$$U + 2H_2O\ (\text{from SM}) \rightarrow UO_2 + \mathbf{2H_2}\ (+2441.5\ \text{kJ}\cdot\text{kg(U)}^{-1}) \quad (8.2)$$

Using oxygen resources that have accumulated in the SM for corium melt oxidation without hydrogen formation, in addition to minimizing the water content in the SM, can significantly improve hydrogen safety during core catcher operation.

Two approaches can be used to produce SM for NPP passive safety systems: ceramic and concrete technologies. Concrete sacrificial materials have advantages owing to their simple construction technology and low manufacturing cost. However, the relatively high water content in concretes severely limits the use of concrete materials in localization devices [23].

Therefore, one of the main objectives of the present study was to develop concrete SM with a low water content.

2. Experimental setup

2.1. Specimen material production

SM samples were prepared using a two-stage technique. In the first stage, $SrFe_{12}O_{19}$ ceramic was synthesized using a solid-state method according to Reaction (9). In the second stage, $SrFe_{12}O_{19}$ ceramic and HAC were mixed to produce the SM specimens.

$$6Fe_2O_3 + SrCO_3 \rightarrow SrFe_{12}O_{19} + CO_2 \quad (9)$$

The initial charge was produced by dry-mixing a stoichiometric ratio of Fe_2O_3 and $SrCO_3$ powders in a mill. The weight ratio between the grinding bodies (steel balls) and the charge was 9:1. After