

SOME COOLANT CHEMISTRY ISSUES FOR CORROSION MITIGATION STRATEGY IN ADVANCED FISSION REACTORS

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1. GENERAL APPROACH

Increasing the advanced fission reactors safety is largely determined by the level of improvement of physical and chemical processes in the system coolant – structural materials – impurities present in this coolant. The objectives of this paper are to try to describe the key chemistry control issues expected in an advanced fission reactors, and to propose possible monitoring and control strategies to address these.

The chemical regime of advanced fission reactors should be developed and maintained in such a way as to ensure [1, 2]:

- Integrity of physical barriers (fuel elements and the boundaries of the coolant circuit of the reactor);
- Corrosion resistance of construction materials of equipment and pipelines of systems important for safety was ensured throughout the lifetime of the reactor unit by minimizing corrosion and corrosion erosion processes under all operating conditions;
- Minimum amount of deposits on the surfaces of fuel elements, equipment and pipelines in contact with coolant.

In order to ensure the radiation safety, the chemical regime of advanced fission reactors should help to reduce to a reasonably achievable level of radiation exposure to personnel caused by activated corrosion products forming deposits on the surfaces of equipment and pipelines and reagents to maintain the chemical regime.

The coolant of advanced fission reactors is never absolutely pure liquid, but always contained chemical additives or contaminated by corrosion products, gases, salts etc. (this is true for a variety of types of coolant, both for supercritical water (SCW) and for heavy liquid metal coolants (HLMC)). The basic condition for ensuring the safe use of the coolant, both for a supercritical water-cooled reactor and for liquid metal cooled reactor, is a high degree of purity and the ability to control this purity [3–5].

Chemistry requirements are set by the desires to minimize corrosion (general and localized), fouling and activity transport, optimize thermal performance and maximize component lifetime. Normally, chemistry regime is achieved by system design, the use of chemical additives, and operational methods (e.g., purification). A key requirement of any chemistry regime is that chemistry “control parameters” must be monitored and adjusted within a specified timeframe. To control the allowable – from the safety point of view – chemical additives or contamination level chemistry specifications have to be set up, as well as the means to maintain these specifications. To provide all above requirements is to have the instrumentation devices to control the process correctness, physical barriers, equipment and pipelines integrity [4, 5].

2. PROTECTIVE OXIDE FILMS

The compatibility of structural materials with various coolants is a rather complicated issue. At high temperatures and irradiation most structural materials, including iron-based ferritic-martensitic and austenitic steels, are unstable in coolant of advanced fission reactors without special measures (e.g. supercritical high purity water and HLWC) [2 – 8]. In this regard, the formation of thermodynamically stable films on the surface of metals is of great importance, and the properties of these films under various conditions, especially at high temperatures and irradiation, often determine the possibility of using certain metals as structural materials for innovative advanced fission reactors. The composition, physical and chemical stability of oxide films under various coolant conditions also determine an equally important process – contamination of the coolant with corrosion products, which are partly the same metal compounds that are part of the oxide films. The condition for the protective action of the oxide film is primarily its high density and good adhesion. The film must not be porous and must be free of stresses and cracks. The temperature along with redox conditions (e.g. oxygen and/or hydrogen content) in coolant are of key importance for creating the thermodynamic conditions required for the formation of a protective oxide layer on the structural steel surface [3, 4, 5].

As shown in Fig. 1(a) the structure of the oxide layer on the surface of conventional austenitic and ferritic/martensitic steels exposed to coolant (both supercritical water and lead) has a two-layer structure. Magnetite Fe_3O_4 is formed as an outer oxide layer on conventional austenitic stainless steels which is in contact with the coolant. The inner (adjacent to the metal) layer is a mixed spinel of the type $[\text{Fe}, \text{Ni}, \text{Cr}]_3\text{O}_4$ (depending on steel content) [5 – 7].

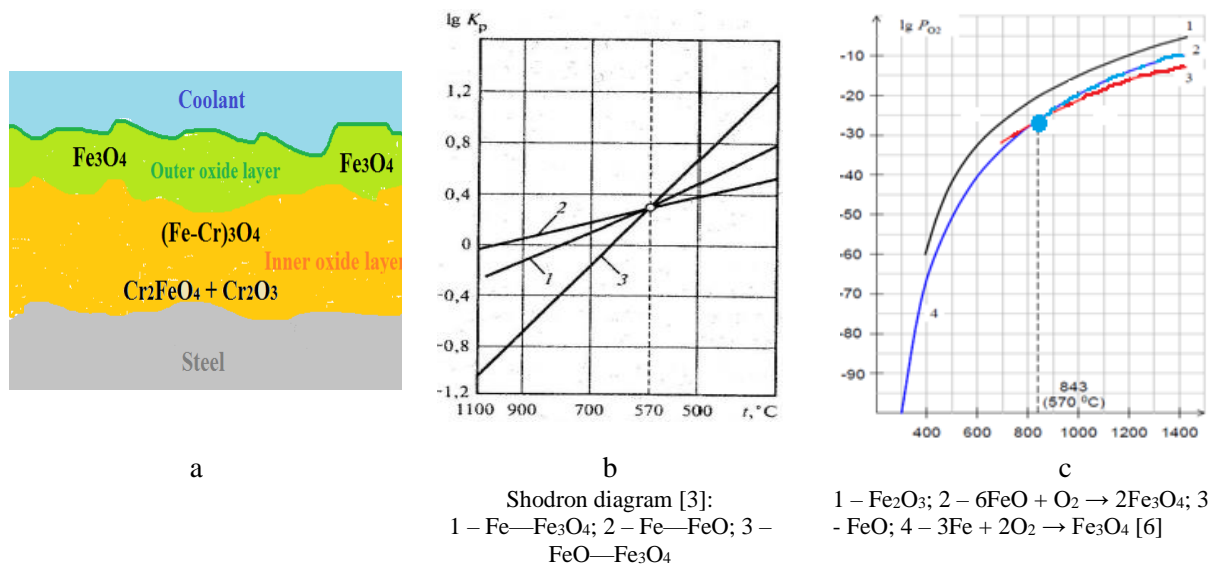


FIG. 1. Structure of the oxide layer and stable oxide phases of α -Fe depending on temperature and oxygen concentration [2–7]

The diagrams on Fig. 1 (b) and (c) shows that at the temperatures lower, than 570°C , magnetite – Fe_3O_4 is thermodynamically stable compound. At the temperatures above 570°C , ferrous oxide – $\text{Fe}_{0.947}\text{O}$ is more thermodynamically stable, but $\text{Fe}_{0.947}\text{O}$ does not exhibit protective properties [3]. An increase in the Cr content in the stainless steel leads to a significant decrease in the thickness of the oxide film and a change in the structure of the

oxide with the predominant formation of chromium oxide (Cr_2O_3), which has higher protective properties compared to mixed spinels [4–7].

Coolant temperatures of advanced fission reactors may be higher than 570 °C [9]. Consequently, in this temperature area, an outer protective film of magnetite may be unstable. However to select the optimum chemistry is necessary to have information on the conditions of formation the protective film on the construction materials surfaces.

2.1. CHEMISTRY CONTROL IN A HLHC

Heavy liquid metal coolants (HLHC) including lead-bismuth and lead make significant corrosion and erosion impact on construction steel elements. For example, liquid lead coolant used in the reactor contains suspended impurities, the content of which can vary due to corrosion of structural materials, erosion of oxide films, possible leaks in the steam generators, ingress of impurities into the primary circuit during repair work, etc. These impurities contained in the lead coolant may lead to the formation and accumulation of deposits on the surfaces of the heat exchange equipment, in the core and in the stagnant zones of the primary circuit. This may lead to a change in the thermal and hydrodynamic operating modes of the equipment [2, 3, 7-12].

The possible way to ensure the long-term reliable operation of steels of the primary system components operating in contact with HLHC is to provide protective layer on the structural steel surface [2, 3, 7, 8, 11]. For this purpose, it was developed oxygen-based technology of structural steel surface passivation [7, 8, 11, 12]. This technology implies formation of protective oxide films on the steel surface and assurance of their integrity during plant operation by maintaining specified oxygen potential of coolant (i.e. *providing the concentration of oxygen in the coolant in a given range*). In case of HLHC circuits operation without purposeful supply of dissolved oxygen to the coolant spontaneous deoxidization of coolant takes place down to the level, at which corrosion protection of structural steels cannot be provided. In lead (lead bismuth alloy), the formation of oxides may have protective properties and high chromium steels improve the corrosion resistance, but a strict range of oxygen concentrations needs to be followed in order to avoid dissolution of the oxides and precipitation of lead oxide.

This technology may be successful only through a strict control and accurate measurements of the oxygen and/ or hydrogen (at the stage of hydrogen treatment) content in the whole facility. Ensuring the good resistance of these oxide layers first requires understanding their formation mechanism, then modeling the oxidation kinetics in order to predict long term steel behavior under given conditions [11, 12].

Analysis of the current state of work on the technology HLHC shows the need to solve the following main tasks of heavy liquid-metal coolant technology (lead, lead-bismuth), fundamentally important for ensuring the safety of reactor plants [2, 7, 8, 11, 12]:

- ensuring the *required purity* of the coolant to maintain design limits and conditions specified in order to maintain the integrity of physical barriers in the path of ionizing radiation;
- *excluding the slagging* with lead oxides and corrosion products of structural materials of heat transfer surfaces of safety-important systems, as well as safety systems;

- providing the minimum corrosion of structural steels of equipment and pipelines in contact with lead coolant;
- providing the minimum deposits on the heat transfer surfaces of fuel rods, equipment and in pipelines of safety-important systems (including in gas systems);
- providing the *instrumentation devices to control* the process correctness, equipment and pipelines integrity;
- excluding the generation of *hydrogen explosive* concentrations in systems and equipment where the hydrogen accumulation is possible (at the stage of hydrogen dosing).

Protective oxide layer can be formed on the solid's surface by finely controlling the dissolved oxygen content and avoiding lead oxide precipitation. First of all it allows minimizing, general corrosion. Localized corrosion is not fully understood and is one key issue [8]. An analysis of the causes of the increased localized (pitting) corrosion, even providing the concentration of oxygen in the HLWC in a given range, and the identification of factors affecting them, seems to be a very urgent task.

2.2 CHEMISTRY CONTROL IN A SCWR

Also for supercritical water coolant it is necessary to control and maintain water chemistry conditions that will minimize corrosion and the transport of both corrosion products and radionuclides. Despite extensive experience in the use of water coolant of supercritical parameters in fossil power plants (FPPs), the concepts of maintaining chemical regimes, which have proven themselves well in FPPs units, may be limitedly suitable for advanced fission reactors. For supercritical water-cooled reactors major challenge will be [4, 5, 13, 14]:

- The development of cladding materials to withstand the high pressure and high temperature environment. The experimental data are very limited to estimate the construction materials behavior under the such conditions, to validate materials integrity and assess water radiolysis, and to validate computational codes;
- The establishment of a chemistry-control strategy to minimize water-radiolysis effect and activation-product transport. A major challenge will be to find an effective means of suppressing the net radiolytic production of oxidizing species in the reactor core. If a suitable means cannot be found, material degradation could be very high at the core outlet due to the combination of highly oxidizing conditions and high temperatures [13, 14].

3. CONCLUSIONS

The limitations of the current understanding of the physical-chemical processes in the coolant, along with the lack of data on the properties of candidate structural materials, are among the main problems that need to be solved to ensure the safety and reliability of advanced fission reactors.

In both cases (HLWC and SCW) interaction of coolant with oxide film is of key importance. Since direct measurement of chemical and physicochemical parameters under extreme conditions of temperature, pressure and radiation fields is difficult, the most promising approach seems to include a combination of theoretical calculations, chemical models and experimental work.

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