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Evaluation of the Cs–Mo–I–O and Cs–U–I–O diagrams and determination of iodine and oxygen partial pressure in spent nuclear fuel rods

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Abstract

This work provides three dimensions potential diagrams calculated in view of the evaluation of the iodine partial pressure in spent PWR fuel pellets intended to be stored for 100 years. These diagrams can be interpreted, on the basis of spent fuel examinations. It is shown that the iodine partial pressure could be controlled by the formation of cesium uranate Cs_2UO_4 from cesium iodide CsI in the fuel. If the formation of cesium molybdate Cs_2MoO_4 would take place during the storage, the iodine partial pressure is expected to increase. Such an evolution can't be excluded because of the temperature that could reach the spent fuel assemblies during the transport step up to the place of the storage.
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1. Introduction

Dry long term storage of Pressurised Water Reactor (PWR) spent nuclear fuel assemblies is currently under consideration in many countries. All causes of fuel rod failures have to be evaluated. In this context, the evolution of the chemical constitution of fuel pellets during this 100 years interim storage is of great interest.

Nuclear Fuel rods are composed of a Zircaloy cladding that contains fuel pellets made of uranium dioxide. The nuclear fission of uranium creates fission products liberated in the pellet. All these elements together with uranium dioxide and the cladding material form a very complex system.

Stress Corrosion Cracking of the cladding material induced by iodine fission product has been identified as a possible cause of failure, so that the iodine partial pressure in the fuel rod must be evaluated.

Both the production yield and the life time of each isotope are well known, so that calculations of the chemical constitution of the ceramic have been realised [1]. Thermochemical data have been determined, and calculations of the chemical state of the fuel have been performed [2–4].

These literature results underlines the role that could play cesium and molybdenum fission products on the chemical form of iodine in the fuel. In particular, chemical equilibria involved in the system may strongly depend on the oxygen potential of the fuel pellet. Irradiation effects on the chemical stability of iodine compounds have also been considered [5].

In this work, thermodynamic evaluations of the Cs–I–O, Cs–U–I–O and Cs–Mo–I–O systems are realized, using the BANK 97 thermochemical database provided by THERMODATA. Results are presented on the basis of three dimensional potential diagrams, calculated at the estimated temperature at the beginning of the storage, i.e. 623 K. Advantages of such a representation has been described elsewhere [6]. The stability domains of the compounds formed are shown versus oxygen, cesium and iodine partial pressures. Results are discussed on the basis of spent nuclear fuel pellets examinations. Finally, relationships between cesium, iodine and oxygen partial pressures are given and

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compared with similar equations derived from literature results.

2. Evaluation method of potential diagrams

2.1. Construction process of the diagram

Each of the three dimensions diagrams is constructed as follow:

1. for each system, compounds that could be formed are identified, using previous literature data and the compounds listed in the thermochemical database used for calculations, i.e. BANK 97 provided by THERMODATA
2. two dimensions diagrams of the cesium–iodine, cesium–oxygen and iodine–oxygen systems are constructed, by writing the constant of equilibria between compounds identified in step 1, as described in the following Section 2.2,
3. three dimensions diagram is constructed, by extruding the two dimension diagrams of step 2. Such a process provides a check-up, because it imposes each of the three coordinates of all the particular points of the diagram to be calculated twice. As far as the two dimensional diagram of the I–O system is concerned, the cesium partial pressure is taken as the saturated vapor pressure of this element, i.e. $P_{Cs}=10^{-2.013}$ bar at 623 K.

Gaseous iodine can exist either as atomic I or molecular I_2. The relationship between P_I and P_{I_2} can be calculated, using the BANK 97 database. At 623 K, one can obtain: $\log_{10}P_I = 0.5\log_{10}P_{I_2} - 3.681$. Atomic iodine I was used in calculations, because it is the preponderant form of gaseous iodine at partial pressures encountered in the nuclear fuel rods.

Iodine partial pressure is limited to $P_I=10^{-3.094}$ bar, which is the saturated vapor pressure of gaseous iodine I at 623 K, according to the BANK 97 database. In the same manner, cesium partial pressure is limited to $P_{Cs}=10^{-2.013}$ bar.

2.2. Calculation of the two dimensional diagrams

Two dimensional diagrams are calculated by writing the equilibrium constants of the chemical reactions involved in the system. As an example, for the following reaction, one can obtain:

$$2<CsI> + <UO_2> + O_2 \rightarrow <Cs_2UO_4> + 2I$$

$$\log_{10}P_I = 0.5\log_{10}P_{O_2} + 0.5\log_{10}K \quad (1)$$

The compound A is written $<A>$ when solid, (A) when liquid and A when gaseous. K is the equilibrium constant of the chemical reaction, calculated using the standard Gibbs energy, $\Delta_r G^o$. For all calculations, the chemical activity of the condensed state compounds are supposed to be equal to unity and the reference pressure is taken as 1 bar.

In the example presented above, (Eq. (1)) gives a linear relationship between $\log_{10} P_I$ and $\log_{10}$ k in the two dimensional iodine–oxygen diagram of the Cs–U–I–O system. The whole diagram is evaluated by taking into account all the chemical reactions involved.

3. The cesium–iodine–oxygen system

The Cs–I–O system is composed of cesium oxides as well as cesium iodides. No cesium oxi-iodide have been reported [4]. Three cesium oxides have been considered: $<Cs_2O>$, $<Cs_2O_2>$ and $<CsO_2>$. Oxidation potentials of these oxides are respectively −566, −102 and −75 kJ mol^{-1} at 623 K for the (Cs)/$<Cs_2O>$, $<Cs_2O>$/$<Cs_2O_2>$ and $<Cs_2O_2>$/$<CsO_2>$ equilibria.

The only cesium iodide is $<CsI>$ which is a very stable compound even if iodine and cesium partial pressures are very low.

All equations taken into account when constructing the diagram are given in Appendix A, where the Gibbs energy changes are given versus temperature. Appendix B gives all the relationships used in calculations. The whole diagram is presented in Fig. 1. An atmosphere of iodine and cesium cannot be stable if the product $P_I \times P_{Cs}$ is higher than the equilibrium constant of the reaction $<CsI> \rightarrow Cs + I$: a condensation of solid CsI is then observed. The three dimensional diagram shows four volumes labeled $<CsI>$, $<Cs_2O>$, $<Cs_2O_2>$ and $<CsO_2>$. Inside these volumes, the gaseous atmosphere is unstable and a condensation of the corresponding solids is observed.

Both iodine and cesium partial pressures can be decreased down to very low values by the formation of cesium iodide. When increasing the oxygen potential of the system, the formation of cesium oxides from cesium iodide takes place. Such reactions allow iodine partial pressure to increase.

4. The cesium–uranium–iodine–oxygen system

The oxidation of uranium must also be considered. The oxidation potentials of these compounds are respectively equal to −975, −253, −209 and −71 kJ mol^{-1} at 623 K for the $<U>$/$<UO_2>$, $<UO_2>$/$<U_4O_9>$, $<U_4O_9>$/$<U_3O_8>$ and $<U_3O_8>$/$<UO_3>$ equilibria [7,8]. These results are in agreement with the most recent assessments of the U–O binary system [9–11].

When adding uranium in the system presented above, the formation of cesium uranates takes place. Cs_2UO_{4-x}, $Cs_2U_2O_7$, $Cs_2U_4O_{13}$, $Cs_2U_4O_{12}$, and $Cs_4U_5O_{17}$ have been reported [12,13], but only two of them are encountered in the fuel pellets, namely Cs_2UO_4 and $Cs_2U_4O_{12}$. This observation

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