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Thermochemical effect of fission products on sodium – MOX fuel reaction : the case of niobium.

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Abstract:

The influence of Niobium on sodium MOX fuel was studied by different heat treatments of airtight capsules containing fresh MOX, sodium and a niobium strip. The characterisation results evidenced a fast oxidation of the MOX followed by its reduction at a slower rate. This result was interpreted by considering the formation of sodium niobiate that captures oxygen from the MOX pellet but at a lower rate than the sodium MOX reaction. This interpretation is used to discuss the influence of niobium as fission product on the sodium –irradiated MOX fuel reaction.

1. Introduction

Worldwide Sodium Fast Reactors (SFR) have risen the most interest as Generation IV reactors, with over 400 reactor years of global experience in operating them^[1]. In France the research in this field was only recently renewed after the 1990 decision to decommission the SUPER PHENIX Reactor, with the design studies for the new ASTRID SFR^[2]. Among the design improvements considered for the ASTRID reactor relative to other CEA SFRs is the fuel pin failure management strategy. This reopens the scientific interest in the sodium – MOX ((U,Pu)O₂ mixed oxide) fuel interactions and requires a better, more detailed understanding of the reactions and mechanisms controlling the fuel pin failure evolution.

A fuel pin failure represents a breach in the first confinement barrier of the nuclear fuel inside the reactor core – the fuel pin cladding. This can lead to the contact between the coolant and the compounds inside the fuel pin including the nuclear fuel.

In the context of the ASTRID reactor the fuel used will be MOX, which can react with the primary sodium in the case of a fuel pin failure, to form the trisodium uranoplutonate (Na₃(U,PuO)₄) according to :



The physico-chemical properties of the uranoplutonate differ significantly from those of the initial MOX and if left unchecked the reaction could lead to the further degradation of the cladding with

possible dissemination of fissile matter in the primary sodium^[4]. Past experimental programs together with the direct observations from the reactor operation have provided significant experience concerning the fuel pin failure evolution and have set the safety limits governing the fuel pin failure management. These programs described the thermodynamic properties of the U-Pu-Na-O system and also provided hints to the sodium–fuel reaction rate and its variation with the main parameters of the system (oxygen potential, temperature, and MOX fuel composition)^[5-10]. There have also been studies showing that the fuel burnup as well as the presence of fission products like zirconium and some lanthanides favours the sodium – MOX reaction ^[11, 12]. Here we will focus on the influence of such metals as Nb on the fuel-sodium interactions. In previous papers the incorporation of some dopants miming the fission products resulted in changes of sodium reaction kinetics and increased swelling even at temperatures as low as 300° C. Two possible mechanisms have been proposed to interpret these changes. The first one considers fission products as substitution elements within the MOX crystalline lattice that would modify its overall behaviour. The second one considers the fission products as separated chemical phases that modify the chemical equilibria in the sodium-fuel system. Modelling the one or the other mechanism requires different approaches and modelling techniques, at the atomic scale in the first case, at a thermochemical macroscopic scale in the latter.

In this paper we focus on the thermochemical effects of the Nb metal on the sodium–fuel interactions. Incorporating such fission products in the MOX fuel however is known to lead to the fragmentation of the fuel pellet when in contact with sodium at high temperatures ^[7], rendering impossible observations on the MOX pellet evolution, such as the pellet swelling or the change in the MOX composition on the surface of the pellet relative to its bulk. For that purpose we developed a dedicated experiment in which niobium was added as a metal strip to the Na-MOX system. Niobium is indeed a fission product with a high production yield, and it can buffer the oxygen potential of the system as proposed in the thermochemical mechanism. The goal of the experiment is to check how effective is this buffering and consequently how to take it into account for the interpretation of the reaction between sodium and actual irradiated MOX fuel.

2. Experimental

Four MOX pellets with $\text{Pu}/(\text{U}+\text{Pu}) = 0.2$ were prepared and then heated at 800° C in sodium in contact with a strip of niobium (Nb) metal for different durations, using a modified Swagelok[®] connector closed at both ends as a reaction capsule.

2.1. MOX pellet preparation

The MOX pellets (20%Pu) used in this study were prepared at the Nuclear Chemistry Department of Chalmers University. The pellets were prepared by mixing together stoichiometric amounts of UO₂ and PuO₂ powders using an agate mortar in an active glove box under Ar atmosphere with an oxygen content varying between 10 ppm and 100 ppm. The pellets were pressed for 1 minute at 600 MPa \pm 100 MPa using a Speac® manual press with a 4.5 diameter matrix. The pellets were then sintered for 4 hours at 1700°C with a heating ramp of 2° C/minute and a cooling ramp of 5° C/minute in a reducing atmosphere (Ar + 5% H₂). The pellets were afterwards polished on both faces using a 1µm diamond suspension and then reheated to 1400 °C for 4 hours with a heating ramp of 5° C/min and a cooling ramp of 5° C/min. The properties of the pellets obtained as well as the subsequent reaction time with the sodium are listed in Table 1.

Table 1. Prepared MOX pellets and the subsequent heating time at 800°C in sodium

pellet label	mass (g)	diameter (mm)	high (mm)	relative density (% TD)	reaction time (hours)
C	0.2848	3.79	2.47	90	4
D	0.2842	3.75	2.37	95	16
F	0.2874	3.83	2.47	90	48
G	0.2863	3.76	2.47	93	2

2.2. Reaction capsule and experimental setup

The capsule used was a Swagelok® connector modified and closed at both ends, with an internal volume of proximately 3 mL. The modification consisted in adding a stainless steel separator in the middle of the connector as to separate the capsule into 2 compartments (Figure 1)



Figure 1. Open Swagelok connector (a), closed experimental capsule (b), stainless steel separator (c).

In one compartment was placed the fuel pellet together with a rolled-up strip of Nb metal of ≈ 600 mg. In the other compartment was placed ≈ 1000 mg of sodium. The connector was close at both ends and places in an oven in a vertical position with the MOX pellet at the bottom. This ensures the contact between Na and the MOX pellet since at high temperature the Na melts and fills the bottom compartment. The pellet can be recovered from the sodium by turning the capsule upside down and reheating to 300°C . The melted sodium will thus leak into the bottom compartment while the MOX pellet remains in the top compartment, retained by the separator. In order to recover the pellet, the capsule had to be cut open, and a new similar capsule was used for each run.

2.3. Control of the oxygen potential

Analytical grade sodium was used for the reaction, provided by Sigma Aldrich[®] as ≈ 1.5 g metal cubes kept in a glass container in mineral oil. The sodium was kept and manipulated in the same glove box as the MOX fuel with an Ar atmosphere and an oxygen content varying between 10 ppm and 100 ppm.

For each experiment a sodium metal cube was taken from the glass container and cleaned by cleaving the oxidised surface layer on each side as to expose the pure sodium metal. It was however unavoidable that the sodium absorbs some traces of oxygen during handling in the glove-box. A Nb metal strip was added in the sodium in order to observe the effect of fission products on thermochemistry without having to incorporate them in the MOX crystalline structure.

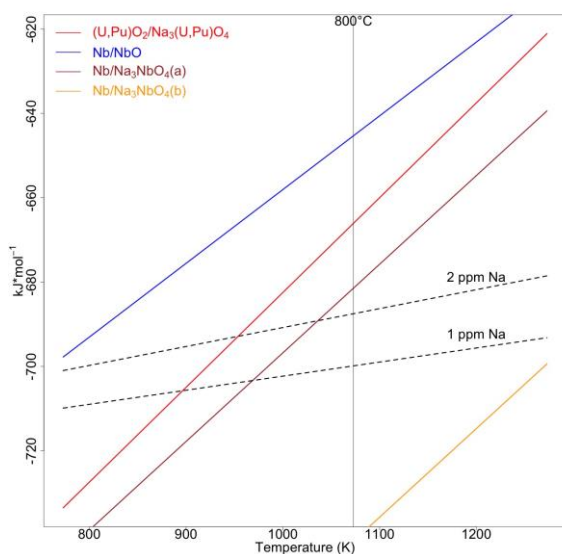


Figure 2. Equilibrium oxygen potential variation with temperature for the systems considered, relative to the oxygen potential in the primary sodium of the reactor expected to contain 1 to 2 ppm oxygen (dashed line). The data for the Nb/NbO equilibriums comes from the FactPS database of the FactSage[®]7.0 software, while the data for the $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_2/\text{Na}_3\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_4$ equilibrium comes from [2]

Niobium metal was introduced into the reaction capsule as a ≈ 600 mg rolled-up metal strip with a thickness 0.2 mm. Analytical grade niobium was provided by Sigma Aldrich[®].

2.4. *Sample characterisation*

Since the formation of the uranoplutonate typically results in significant swelling of the MOX fuel^[5,7,8,10], SEM images of the pellets before and after the reaction were taken using a HITACHI TM300[®] table top scanning electronic microscope in order to quantify the pellet swelling and to observe the morphology of the phases in the sample.

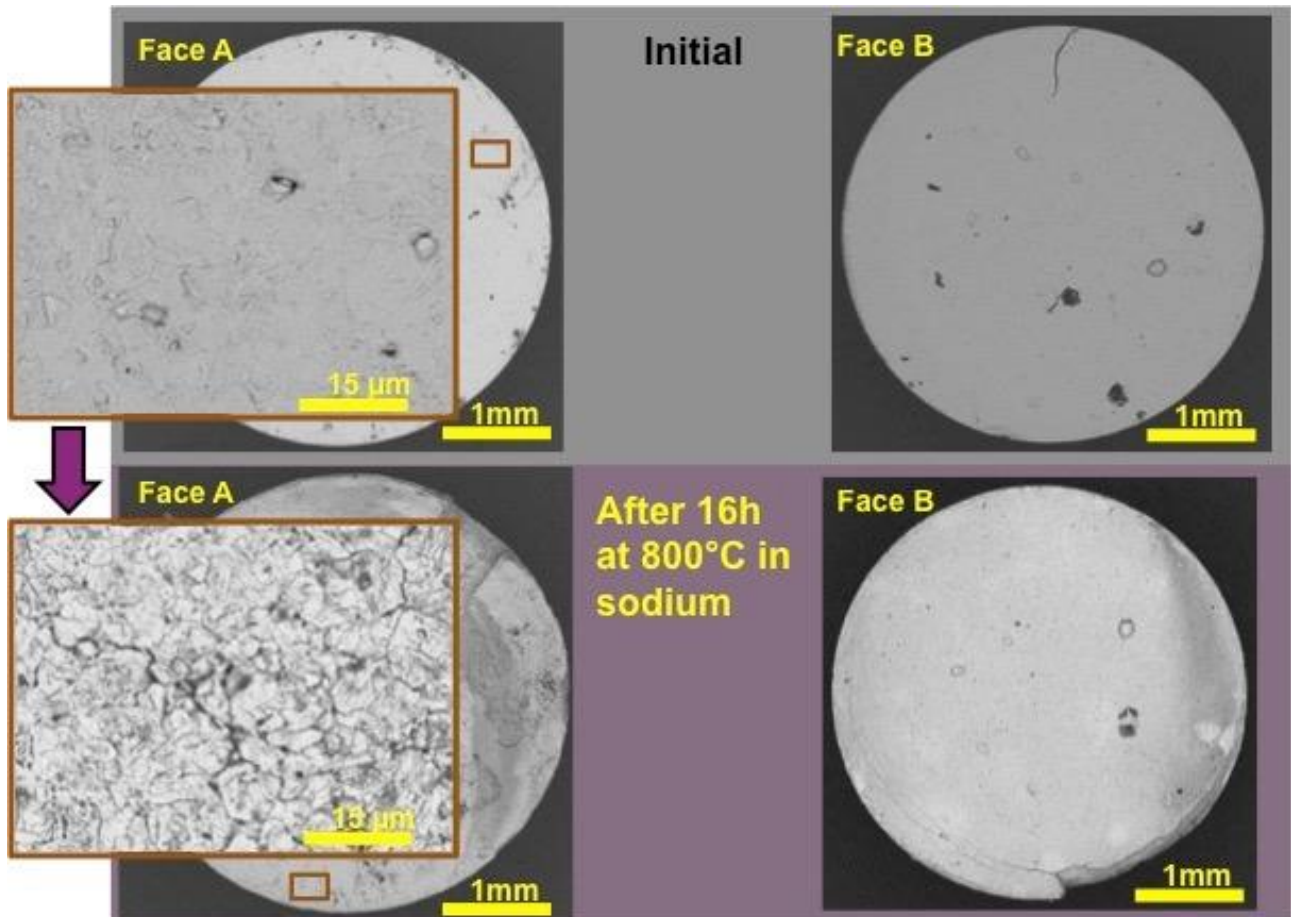
XRD analyses were performed using a Brüker D2 Phaser[®] diffractometer equipped with a Lynxeye[®] detector. Two types of XRD analysis were made. First an analysis was carried out on the surface of the pellet by placing the entire pellet on a plastic sample holder with adjustable depth, making sure that the surface of the pellet is in a horizontal plane. This analysis was only focused on identifying the phases on the surface of the pellet and it is not available for the 4 hours sample because the pellet was fragmented during removal from the capsule.

A second XRD analysis was then carried out on pellet fragments that have been ground into a fine powder. The powder was then paced on a silica wafer single crystal low-background sample holder using alcohol to favour a homogeneous distribution of the powder and avoid preferential orientation of the particles.

3. Results

SEM analysis of the samples showed no change in the pellet's diameters regardless of the heating time in sodium. All samples presented a similar aspect after the thermal treatment as the example shown in Figure 3

Figure 3. SEM images of a MOX pellet before and after 16h at 800°C in sodium.



The conservation of the pellet diameter points to the absence of a significant amount of uranoplutonate and thus a very limited reaction between the MOX and the sodium in the conditions of the experiment. Detailed images however show a change in the morphology of the grains on the surface. Indeed the surface grains after the reaction appear to have developed multiple parallel fractures consistent with the lamellar morphology of the uranoplutonate phase. This seems to indicate that the MOX to uranoplutonate transition was initiated on the surface grains of the pellet but did not fully develop.

These observations are in agreement with the data from the XRD analysis Figure 4

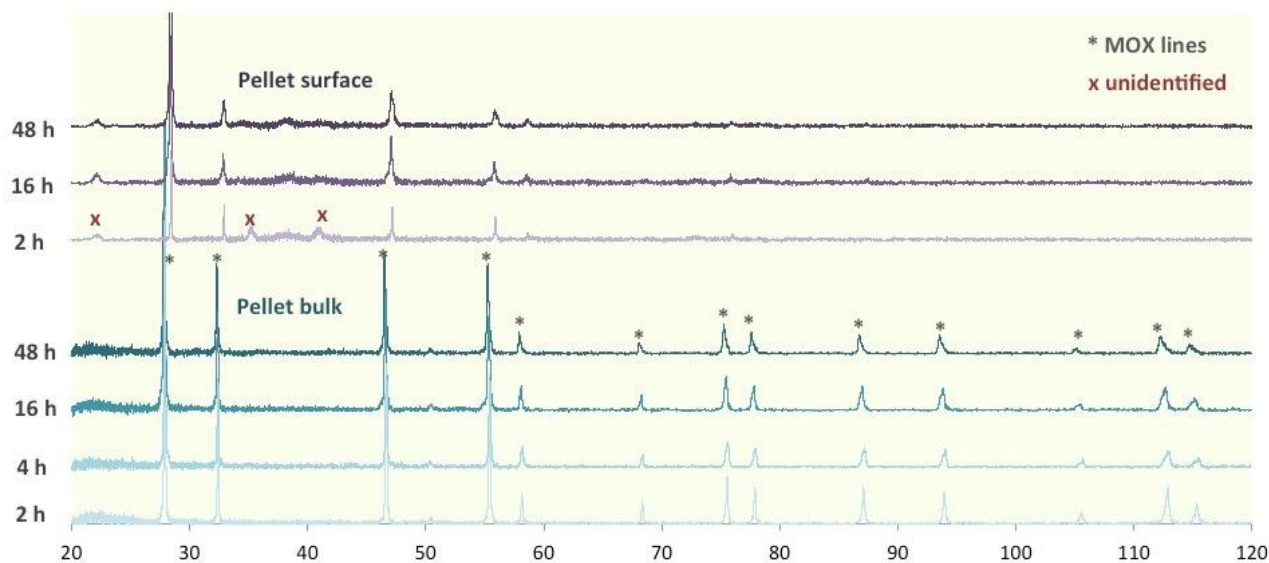


Figure 4. XRD lines of the four MOX samples after the reaction with sodium: pellet surface diffraction lines (purple shade lines) and pellet bulk powder diffraction lines (blue shade lines). The background due to epoxy used to fix the sample has been removed.

The XRD data shows the presence of a poorly crystallised secondary phase on the surface of the pellet that was not detected in the bulk powder XRD analysis. This phase could not be identified most likely due to its small quantity and poor crystallinity. It could correspond to Na_4UO_5 formed on MOX crystalline structure because 2 out of the three diffraction lines observed on Figure 4 could be assigned to Na_4UO_5 . Although not all Na_4UO_5 diffraction lines are observed this poorly crystallised phase seems to disappear with heating time.

The XRD patterns were analysed using Fullprof and Topaze softwares for the bulk samples. For the surface samples the existence of the poorly crystalline phase disturbed the refinement of the MOX lines and no accurate conclusion could be drawn. It appeared that for pristine MOX and MOX that has reacted more than 4 hours with sodium, MOX peaks were better described using two diffraction lines. This experimental result was interpreted considering that the MOX composition of these samples lies within the miscibility gap of the (U-Pu-O) phase diagram. In this miscibility gap, two different crystalline phases having the same fluorite structure but different cell parameters coexist. The Rietvelt refinement of the XRD patterns led to the determination of the cell parameter and the relative intensity of each phase. Using this information the average O/M ratio of MOX was determined as follows:

- The value of cell parameter can be correlated to the pellet stoichiometry, considering that the unit cell, a , of $(\text{U}_{1-y}, \text{Pu}_y)\text{O}_{2-x}$ is given by $a = 547 - 7.4y + 32x$ pm (where $\text{O/M} = 2 - x$). For MOX having a 20% content in Pu ($y=0.2$), a cell parameter of 5.452\AA corresponds to stoichiometric MOX.

- The average O/M was determined using x value when the MOX peaks were refined with a single phase. When the MOX peaks were refined using two phases, it was taken as the averaged O/M of each phases weighted their relative intensities.

The cell parameter of the MOX phase was determined for each XRD pattern as listed in Table 2, together with the corresponding stoichiometry. The accuracy of the Rietveld refinements was estimated by comparing the results given by both software programs Fullprof and Topaze. This comparison not only accounts for statistical errors, but also for biases that can exist in numerical data processing. So the accuracy on average O/M is evaluated around 0.01-0.02. This value of accuracy allows us to conclude that the changes in O/M seen in Figure 5 are physically sounded.

Heating time	Phase 1			Phase 2			Average O/M
	a(Å)	O/M	Phase ratio (%)	a(Å)	O/M	Phase ration (%)	
pristine	5,453	2,007	26,4	5,468	1,961	73,6	1,97
2h	5,459	1,989	100,0	-	-	-	1,99
4h	5,454	2,003	61,2	5,464	1,973	38,8	1,99
16h	5,464	1,972	61,1	5,474	1,940	38,9	1,96
48h	5,464	1,973	34,2	5,477	1,932	65,8	1,94

Table 2 : results of XRD pattern refinement for different heating time

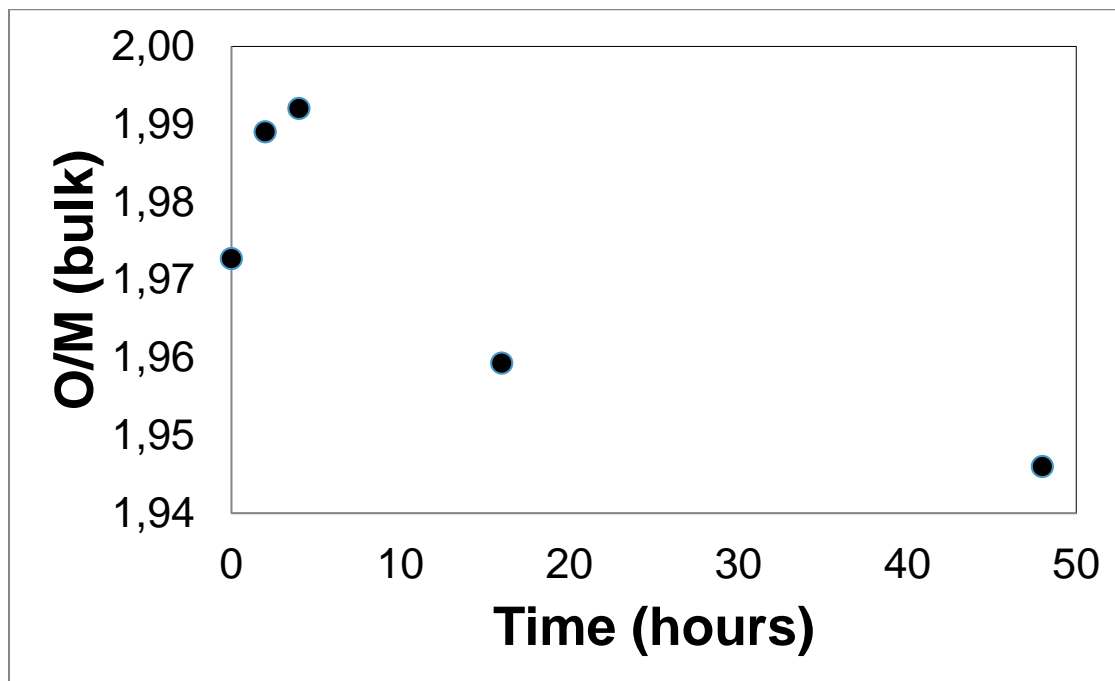


Figure 5. MOX O/M evolution with the heating time

The pristine bulk O/M = 1.97 is consistent with sintering conditions that are expected to lead to hypo-stoichiometric MOX^[13]. It first increased to 1.99 after 2 hours of heat treatment and then decreased again up to 1.945, a lower value than the pristine pellet. (Figure 5)

This observation shows the effect of Nb metal on the MOX-Na system. In the first four hours of the reaction there seems to be significant oxygen diffusion from the sodium to the bulk of the MOX pellet with the increase of the O/M ratio close to stoichiometry. After this initial first step of approximately 4 hours the formation of the Na₃NbO₄ starts to compete for oxygen with the pellet oxidation and thus the MOX fuel starts to be reduced, at a slower rate than the initial oxidation, up to an O/M value of 1.94 after 48h.

The results from the SEM analysis together with the XRD analysis show that very little reaction occurred between the pellet and the sodium, with similar results regardless of the heating time in sodium of the pellets in the 2h to 48 hours interval. However the Nb metal strip used as oxygen buffer suffered a considerable change in its aspect and it seems to have played an important role to prevent the available oxygen in the sodium from fuelling the sodium-MOX reaction and it seems to have thus inhibited the formation of the uranoplutonate phase (Figure 7).



Figure 7. Niobium metal strip used as oxygen buffer before (a) and after the reaction (b)

The aspect of the metal strip changed from the initial shiny silver colour to a dull grey -yellow, indicating that it underwent visible oxidation although no significant change in the initial mass could be observed.

4. Discussion

The changes in oxygen potential observed during our experiment are consistent the data of Housseau *et al*^[10]. In their experiment of reaction between sodium and doped MOX, Mignanelli observed that

the oxygen potential became constant after a relatively short time (3 hours) but then drifted to a more negative value. This evolution can be interpreted as a two steps kinetics^[11, 12].

In the first step the sodium–MOX reaction is the faster, leading to the formation of sodium uranoplutonate. The oxygen potential of the system is then fixed by the MOX-sodium uranoplutonate redox couple. For 20% Pu MOX fuel in equilibrium with uranoplutonate and sodium at 800°C Lorenzelli^[9] proposed the oxygen potential value of -667 kJ/mol, while for the uraninite in equilibrium with sodium and sodium uranate Smith found an oxygen potential value of -670 kJ/mol^[8]. The authors did not mention the errors associated with these values but the two are close enough that they could be considered identical within experimental error. In our case the lower 20% Pu content of the MOX used in the present experiments is not enough to account for the lack of pellet swelling since the equilibrium oxygen potential between the MOX and the Uranoplutonate does not seem to vary significantly with the Pu content in the 0% Pu to 30% Pu interval^[5].

In the second step the system moves with a slower kinetics towards the most stable sodium niobate, which imposes an oxygen potential at -752 kJ/mol, by the Nb/Na₃NbO₄ equilibrium at 800°C.

These results confirm that the fission products can effectively modify the sodium-MOX reaction, but with a time scale that can be different from the time scale of sodium uranoplutonate formation. The characteristic time scale of the reaction is a very sensitive parameter with regard of the incidental scenario the MOX fuel is faced to. In a first case, we consider an accidental scenario of a breach in the cladding during in core operation. Then the MOX fuel temperature is high and the fuel-sodium reaction is fast (usually within the first 30 minutes of the breach detection), so the influence of the fission products having a low kinetic reaction with sodium can be neglected. In a second case, we consider an accidental scenario of a breach in the cladding during in internal storage in the core. The internal storage can last several months and fission products having a low kinetic reaction with sodium cannot be neglected anymore.

5. Conclusion

Our results evidenced that Fission Products can change the manner in which sodium interacts with the MOX fuel by controlling the oxygen potential of the system. In other words, fission products may be viewed as an oxygen sink that could immobilise a given amount of oxygen and sodium. This effect depends on the formation kinetic of the fission product made-of phases. It can be advantageous as long as these metals are not incorporates in the fuel pellet since it could slow down the formation of sodium urano-plutonate. But it could also be disadvantageous if the newly formed phases swell inside in the MOX ceramic, which could create some cracking and pellet fragmentation as observed in doped MOX interacting with sodium.

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