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ANALYSIS OF ACCIDENTAL SEQUENCE TESTS AND INTERPRETATION OF FISSION PRODUCT RELEASE: INTERDEPENDENCE OF Cs, Mo, AND Ba RELEASE.

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ABSTRACT

The behaviour of fission products (F.P.) during fuel life in a nuclear reactor is of particular importance as it plays a significant role in the release kinetics during hypothetical reactor severe accident transients.

A description of (¹³⁷Cs, ⁹⁹Mo, ¹⁴⁰Ba) chemical states after some UO₂ fuel irradiation stages is drawn. Molybdenum is supposed to be localised in a MoO₂ precipitate (volatile over 1273K) and chemical reactions with condensed Cs oxides and/or uranates are possible.

According to this description, a coherent interpretation is presented for some accidental sequence tests providing new ideas for release mechanisms of (Cs, Mo, Ba).

Keywords: Cs, Mo, Ba, fission product release, Vercors tests, release mechanisms.

1. INTRODUCTION AND EXPERIMENTAL DETAILS

This paper is dedicated to the analysis and interpretation of some analytical experiments called Vercors tests, performed at Commissariat à l'Énergie Atomique (CEA), France. These tests are performed on a fuel pin element consisted by three pellets of irradiated UO₂ and re-irradiated just before the test [1]. A temperature transient¹, without any irradiation, is applied to these specimens under various atmospheres (pure steam, pure hydrogen, or steam/hydrogen mixture). For all the tests, a temperature step is done (at around 1573K), under an oxidising gas flow, in order to get a full oxidation of the clad (Zr). The release kinetics are measured using online γ -spectrometry, which provides very accurate curves and high quality results. Therefore, Vercors test are very interesting in order to understand the release mechanism of fission products and for a further interpretation of integral tests (Phebus tests [2] for instance) as well as for simulations of a reactor accident scenario (with the ASTEC code [3] for example). The attention is focused here on (Cs, Mo, Ba) whose behaviour is not well known during temperature transients.

An interpretation of (Cs, Mo, Ba) release, during Vercors 4, 5 tests, is proposed here. It is based on the concept that F.P. release is ruled by the evolution of their chemical forms and localisations inside a fuel under a temperature transient and defined gas conditions.

This interpretation lays on observations of F.P. during the fuel life in reactor and a modelling (linked with an analysis of experimental results) of F.P. evolution during the test sequence.

In this sense, the scope of the present work differs from classical approaches concerning Cs for instance with the classical models of "Booth" [4] where intragranular diffusion is the only limiting phenomena for release and where no chemical reaction is taken into account.

¹ generally from 293K to the fuel degradation and relocation which most of the time occurs over 2573K.

2. INTERPRETATION PROPOSAL FOR VERCORS 4 AND 5 TESTS

Vercors 4 and 5 (see table 1 for experimental conditions and total amounts released) were deeply investigated on the basis of experimental release kinetics (figure 1), with a focus on Cs, Mo, and Ba.

If many thermodynamical studies have been performed on the systems (Cs, Ba)-(Mo, U)-O, only few are devoted to describe the real localisation of (Cs, Mo, Ba) inside an irradiated UO₂ fuel. Kleykamp [5, 6] indicates that Cs, Mo, Ba, and their respective oxides have a very low solubility. Moreover, due to oxygen liberation during fission, these three fission products are oxidised. Cs is supposed to precipitate under uranates forms of type Cs_xUO_y, [5, 7-11] the simplest one being Cs₂UO₄. Ba has been observed under BaO form [5, 6, 12, 13], and Mo under MoO₂ precipitate [5, 6, 12-16] coming from the oxidation of Mo directly from the solid solution or from Mo existing inside a metallic precipitate which contains also Pd, Rh, Ru, and Tc [5, 6, 12-16]. Moreover, in VERCORS tests, what is measured as Mo release is the release of ⁹⁹Mo which has just been recreated by re-irradiation. It is therefore supposed that this isotope does not have a sufficient time to form the usually observed 5-metals particles.

It is therefore possible to submit the following interpretation (figure 2): at the initial time (t₀) of the test, (Cs, Mo, Ba) are over their solubility limit (reasonable regarding the fuel specimen burnups) and Cs is supposed to be localised into Cs₂UO₄ precipitate, Mo into MoO₂ precipitate and Ba into BaO (or Ba_xO_y).

During Vercors 4 and 5 tests, all the MoO₂ is supposed to vaporise over 1273K [13]. A part of MoO₂ can react with some precipitates located at the grain boundaries. A similar mechanism of vaporization/reaction was observed in Phénix reactor bundle pins [16], where no Mo was found in the centre of the pellet whereas molybdates Cs were found at the periphery. In this case MoO₂ is supposed to vaporize from hot parts of the fuel then condense and react in colder parts.

During the clad oxidation phase, as hydrogen is produced between the clad and the fuel, there is a lowering of the oxygen potential ($\Delta G_{O_2} = RT \ln(P_{O_2})$) leading to a decrease of the stability field of Cs₂UO₄ (a 2-d field where the first dimension is T and the other one is ΔG_{O_2}). This can provide some gaseous Cs release. Cs₂MoO₄ seems also to be affected as Mo release is observed at the end of oxidation temperature step. Some experimental evidences also show that Ba is released from the fuel during this phase, but trapped by the oxidised clad under the most probable form, which is BaZrO₃. Therefore, this Ba release is not visible on the release kinetics (figure 1).

This leads to a first step of Cs release at the end of the oxidation phase (~20%), all the non-released Cs is located into the Cs₂MoO₄ phase coming from the reaction of Cs₂UO₄ and gaseous MoO₂.

Then, when temperature is raised again to 2573K, the evolution changes from Vercors 5 to Vercors 4 because of a different injected atmosphere:

- for Vercors 5, under pure steam, Cs₂MoO₄ is vaporized (~2200K) leading to some Cs and Mo release, BaZrO₃ formed onto the clad is also vaporized (2500K) leading to Ba effective release,
- for Vercors 4, under pure H₂, Cs₂MoO₄ can be affected by the low oxygen potential coming from fuel reduction; this would lead to a decomposition of these two precipitates giving Cs release and a return of Mo into the metallic phase. Moreover it seems following experimental Mo release in Vercors 4 that a small part of Cs₂MoO₄ can be vaporized. There is a kind of a competition between the molybdates destruction and its vaporization. BaZrO₃ of the clad is also and in higher proportion than Vercors 5 due to the reducing atmosphere of this test.

3. CONCLUSIONS

The present interpretation concerning (Cs, Mo, Ba) release in Vercors 4 and 5 tests highlights that their behaviour is fully interdependent. Cs should not be considered as a “volatile” specie treated in the same way and with the same models as noble gases. Cs, Mo have interdependent chemistry in nuclear fuels.

Nevertheless, such an interpretation needs some microscopic experimental evidences. Scanning and Transmission Electron Microscopy should be useful to identify phase distribution before and after tests on irradiated UO₂. X-ray diffraction with an increasing temperature on irradiated pellet should be also a precious tool to follow the phase evolution.

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FIGURE CAPTION

Table 1: Vercors 4, 5 experimental conditions and corresponding Cs, Mo, and Ba released amounts

Figure 1: Vercors 4 and 5 release kinetics (% of the initial inventory after irradiation) for Cs, Mo, and Ba.

Figure 2: (Cs, Mo, Ba) release interpretation for Vercors 4 and 5 tests.

		Vercors 4		Vercors 5	
Fuel (Burnup)		UO ₂ (40 GWd/t _{UO2})		UO ₂ (40 GWd/t _{UO2})	
Clad oxidation temperature (K)		1523 (70 minutes)		1573 (80 minutes)	
Gas conditions					
Clad oxidation	After oxidation	H ₂ O/H ₂	H ₂	H ₂ O/H ₂	H ₂ O
Cs released fraction (%)		93		93	
Mo released fraction (%)		55		92	
Ba released fraction (%)		80		55	

Table 1: Vercors 4, 5 experimental conditions and corresponding Cs, Mo, and Ba released amounts

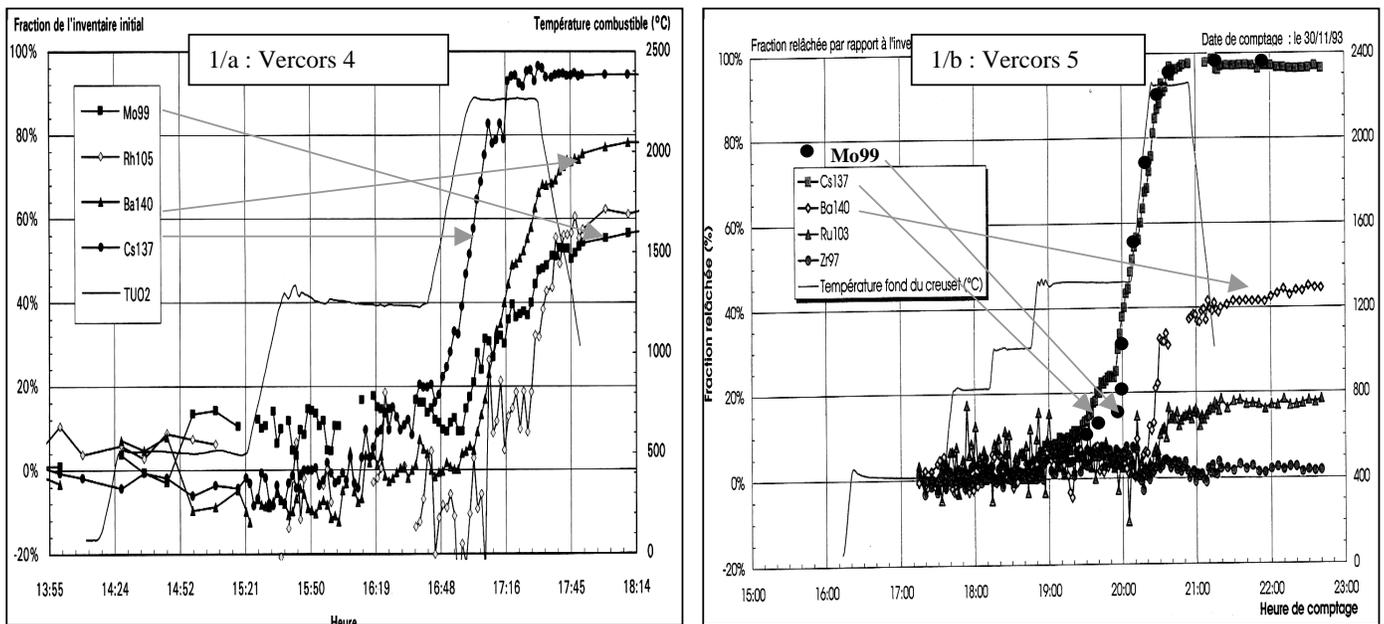


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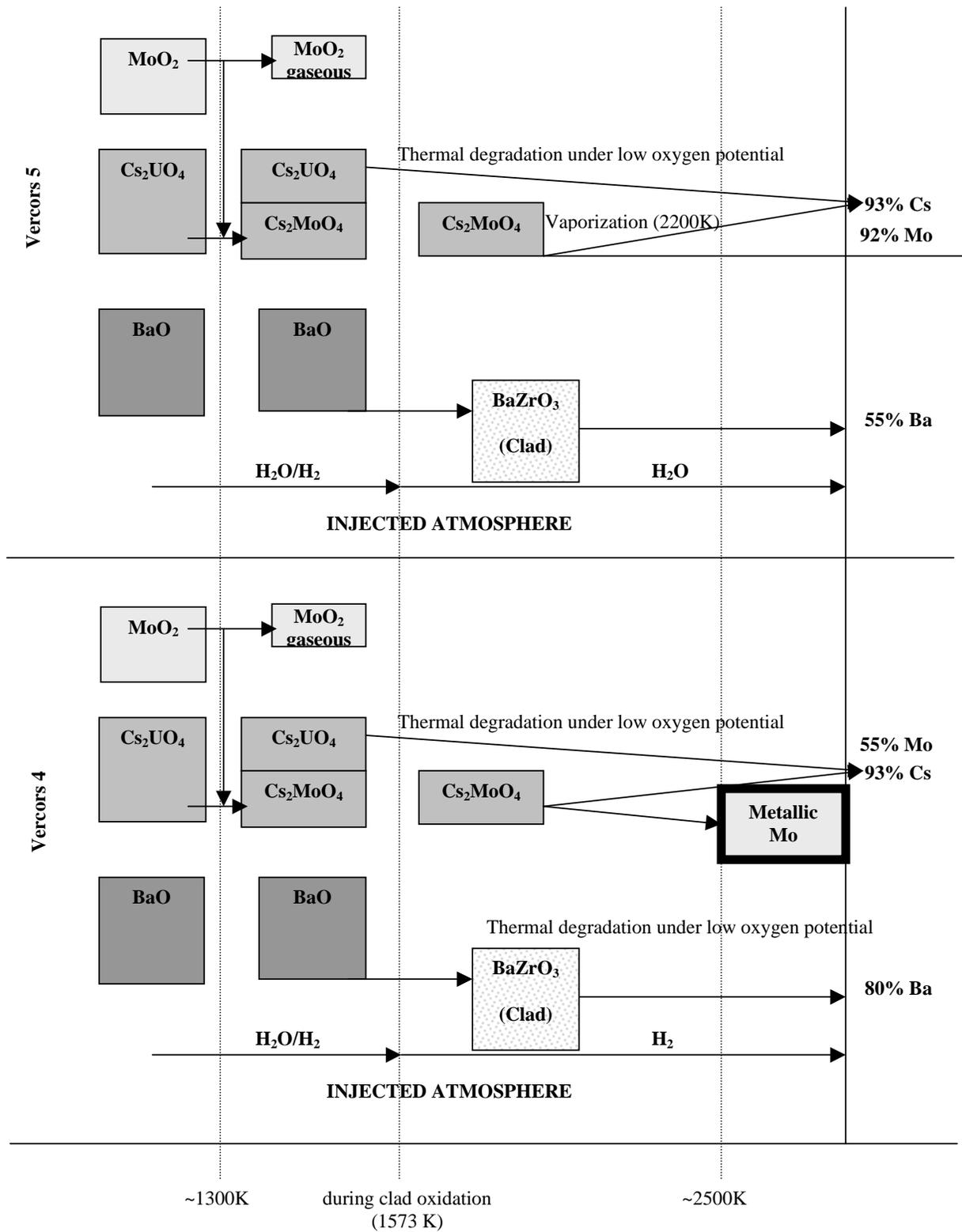


Figure 2: (Cs, Mo, Ba) release interpretation for Vercors 4 and 5 tests.