A new research program on accidents in spent fuel pools: the DENOPI project

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A new research program on accidents in spent fuel pools: the DENOPI project

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ABSTRACT: In the framework of the post-Fukushima actions, an experimental project named DENOPI has been launched by Institut de Radioprotection et de Sûreté Nucléaire in collaboration with research laboratories with the aim to study the behavior of spent fuel pools under loss of cooling and loss of coolant conditions. This paper describes the objectives and the strategy of this program which includes experiments at different scales and simulations based on CFD and system codes. Some results obtained on fuel cladding degradation due to oxidation under air/steam mixtures are also reported in the last section.

KEYWORDS: *Spent Fuel Pool, Loss-of-cooling/coolant accident, Clad oxidation, DENOPI*

I. INTRODUCTION

Since the Fukushima accident, increased attention has been paid to the vulnerability of the Spent Fuel Pools (SFPs). This vulnerability is of major concern for nuclear safety because SFPs which are large water-filled structures are generally placed outside the reactor containment building so that the fuel clad is the only one barrier against fission product release in case of dewatering. Furthermore, SFPs contain a number of Fuel Assemblies (FAs) that could be several times the one present in the reactor core (e.g. 2.5 times for French 900 MWe reactor). Accidental situation can be the result of a loss of cooling due to a prolonged breakdown of the pool cooling system or a loss of coolant due to a breach in the pool structure or in a connected fluid circuit. The latter type of accidents may lead to a rapid dewatering of the pool whereas for the former type the dewatering process is more progressive.

The phenomenology of SFPs accidents can be described according to the water level in the pool[a]. As long as fuel assemblies are completely covered with water, fuel damage is very unlikely due to heat exchanges by natural convection between fuel rods and pool water. If the spent fuel pool cooling system is not recovered and in absence of a sufficient water supply, 3 to 5 days are needed for the pool water level to reach the top of the fuel assemblies for a total residual power of 10 MW (maximum power authorized for a 900 MWe)[b]. During the decrease of the water level, boiling inside the FAs can occur according to the saturation temperature which is decreasing with the hydrostatic pressure. A local increase of the void fraction inside the FAs could then produce an excess of reactivity and thus a criticality accident. Once the water level drops below the top of the FAs, the cooling of the fuel is no longer ensured and the temperature of the uncovered part rises. The cladding temperature in the uncovered part increases with the reduction of the water level because less steam is generated below the water surface and because more length is available to overheat the steam flow. The temperature rise promotes the oxidation of zirconium by steam and potentially by air present in the fuel building hall. These reactions are highly exothermic and can result in large production of hydrogen and in a zirconium fire with severe degradation of the fuel.

The behavior of fuel assemblies fully uncovered was studied at Sandia National Laboratories in the framework of the OECD-NEA SFP project. Experiments included separate and integral effect tests and investigated zirconium burn propagation between adjacent assemblies. On the other hand, the behavior of spent fuel pools with FAs fully or partly covered by water is relatively unknown despite the challenges associated. Questions are still pending regarding the issues of convective flow under natural circulation, air ingress inside the FAs, spray efficiency but also zirconium oxidation under air/steam mixture. To gain knowledge in the above mentioned areas and in order to better evaluate the safety margins, the French Institut de Radioprotection et de Sûreté Nucléaire (IRSN) in collaboration with partners from French universities has launched in 2013 the experimental DENOPI project for a 6 year period. This program is composed of experiments, modeling works and validation of computer codes. It is based on an approach encompassing three different scales: the spent fuel pool scale, the assembly scale and finally the clad scale.

This paper gives an overall picture of the DENOPI

[a] The height of FAs is approximately 4 m. They are covered by 5 to 9 meters of water depending of the pool design. For a French 900 MWe reactor, the volume of the associated spent fuel pool is ~ 1300 m^3 and the depth is about 12 m.

[b] This maximum heat load is obtained just after full core off-load.

project. Section 2 describes the thermal-hydraulic part of the project with a brief review of the phenomena where a lack of knowledge has been identified. Section 3 is devoted to the experiments on Zr-oxidation under air+steam atmosphere planned in the DENOPI program.

II. THERMAL-HYDRAULIC STUDIES IN THE DENOPI PROJECT

As indicated in the introduction of this paper, flows and heat exchanges are different during the uncovering process of the spent fuel and during the first phase of the accident when the fuel is fully covered by water. The two phases are studied in the DENOPI program with the objective to have a better understanding of natural convection and boiling phenomena in the pool and on thermal-hydraulic mechanisms in the fuel assembly.

1. Natural convection and boiling phenomena in the pool

In case of loss-of-cooling, the pool water is gradually heated up and natural convection is developing between the FAs (heat source) placed at bottom of the pool and the free surface. Through the FAs which are inserted side-by-side in rack blocks the vertical flow [c] is generated by the temperature-difference driven buoyancy. Despite its relative apparent simplicity, natural convection in the pool is complex. First, the overall flow structure is a function of the distribution of decay power in the pool [d]. The flow is rising more vigorously above the hot fuel assemblies than over the colder ones (see figure 1). CFD simulations indicate that in addition to the large convective loop rising above the assemblies and coming down between the racks and the pool walls, secondary convective loops are also expected above the FAs[1-2]. These convective loops could mix efficiently the flows and thus reduce the vertical thermal gradient in the pool. Boiling can occur in the pool in a region close to the free surface as soon as the water temperature reaches 100°C and also, when the water level decreases, in the upper part of the hot FAs. Preliminary CFD calculations [e] performed at IRSN clearly show that boiling occurs first in these two regions (see figure 2).

Natural convection in a spent fuel pool is poorly known and is mainly evaluated on the so-called expert judgment. Simulations currently used industrially for this type of problem - especially with single phase CFD codes - are likely far from representing the physics of the phenomena which is multiphasic. In addition, models for natural convection suffer from a lack of validation in spent fuel pool conditions. This is also the case for the safety system codes that have been mainly developed and validated for reactor accidents.

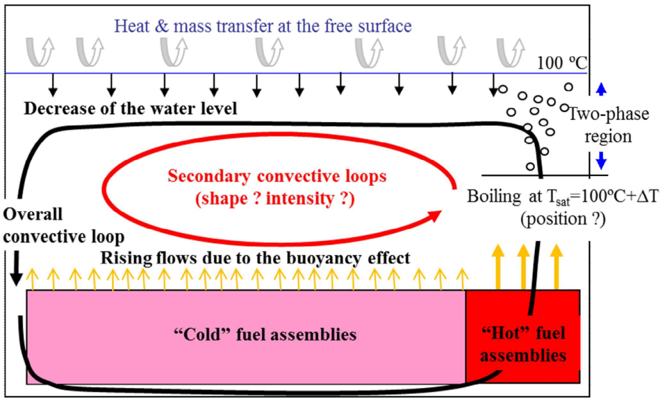

Figure 1 : Natural convection in the spent fuel pool

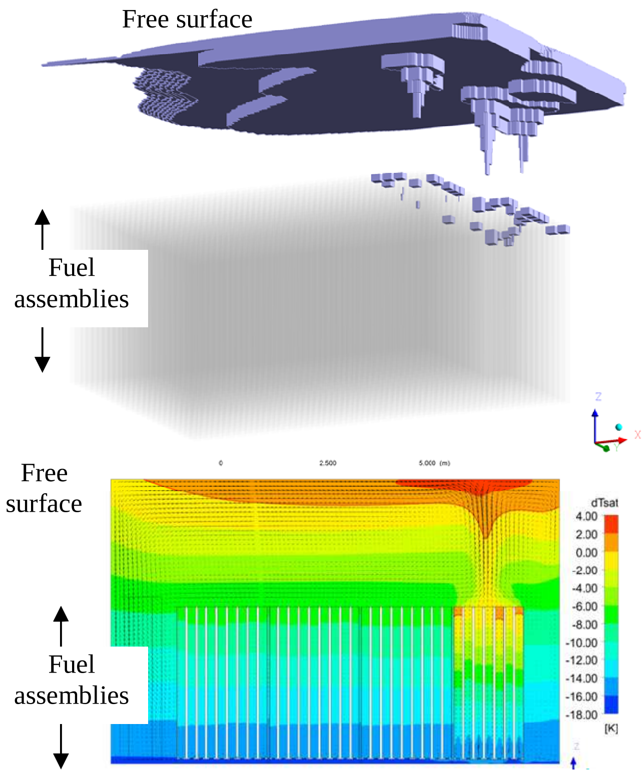

Figure 2 : Fluid saturation in the pool (dTsat > 0 indicates oversaturation of water). The upper part of the figure is 3-D visualization of the calculation cells where dTsat is > 0. Simulation was performed for a water level 4 m above the top of the fuel rods.

Several open issues have been identified that should need further analysis and experimental support. First, boiling at the free surface can lead to steam suction by the cooling system if the cooling is recovered before dewatering of the strainers [f] and restarted in a boiling pool situation. As a consequence, there is a risk of irreversible loss of cooling by pump cavitation. It is also essential to check that no boiling occurs in

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[c] In the storage racks, each fuel assembly is inserted in its own closed cell opened at the bottom inlet and the top outlet. With this design, no cross-flow is allowed between the FAs excepted when the walls of the cell are damaged.

[d] Various patterns are possible for fuel arrangement in the storage racks. Furthermore, the decay heat distribution in the pool is changing periodically due to the successive outages.

[e] These simulations were carried out with a modelling approach similar to the industrial simulations described further in this paper.

[f] Strainers are generally placed at the top of the pool. For a French 900 MWe reactor, the strainer of the spent fuel pool is located 4 m below the nominal level of the pool.

the FAs that could create a criticality issue. The configuration of the FAs in the pool can be seen as parallel and independent heated channels connected to a large upper volume. This configuration could induce unstable circulation and flow reversal inside low-power FAs leading to nucleate boiling at the wall rods[3)]. It is also suspected that the recovery of the cooling system could increase locally the flow rate below some racks and hence reduce temporarily the natural convection flow rate in the corresponding assemblies. This mechanism could produce transient boiling at the top of the assemblies.

In order to study boiling and natural convection flows in pool conditions, a three-step approach is proposed in the DENOPI project:

- Use of scale analysis to determine the dominant terms of the dimensionless equations that describe the whole physical system,
- Use of multiphasic CFD modelling to have a better understanding of the different convection loops and boiling conditions and to help in specifying the experimental devices,
- Perform experiments under conditions representative of normal operation, in a situation of loss-of-cooling and in case of recovery of the cooling system. These experiments will be conducted on analytical mock-ups and/or in a prototypical model of a spent fuel pool at reduced scale. To evaluate also properly the risk of steam aspiration by the cooling circuit, the void distribution at the exit of the FA and the dynamics of steam in the water column will be investigated on a full-scale assembly (see next section). All the results provided by these experiments will be used to develop and/or validate CFD models. The tests carried out on the mock-ups will be designed to assess the impact of different parameters such as water level, pressure losses, etc. The distribution of the heat decay in the storage rack is expected to have a noticeable effect and hence will be also studied. One challenge of this study is to reproduce with confidence the flow in the region area above the racks and to measure precisely fluid temperature and velocity. PIV measurements and Lagrangian sensors are currently investigated to get these parameters.

2. Thermal-hydraulics at the scale of the fuel assembly

The DENOPI project also addresses the issue of heat exchanges and two-phase flow patterns in a fuel assembly under loss of cooling and loss of coolant conditions. Experiments will provide better understanding of :

- Void distribution inside and above a 17x17 rod bundle. Void distribution at the outlet of the bundle is a boundary condition which is necessary to calculate properly the dynamics of steam bubbles and its transport in the water column up to the strainers of the cooling system. Void fraction inside the bundle is required to identify a possible return to criticality;
- Cladding peak temperatures of uncovered fuel assembly as a function of the decay heat load. Tests will be done for dewatering transients but also for steady-state conditions with different water levels in the assembly;
- Conditions for air penetration in the assemblies. Air flow inside the uncovered part of the bundle could change the chemical environment and hence impact significantly Zr-oxidation process (see next section). Several mechanisms that could lead to air ingress from the top of the assembly have been identified such as the effect of steam rising plume generated by a hot assembly on a next cold one, Rayleigh-Taylor instabilities producing local descend of air-rich gas from the pool building or flow reversal due to buoyancy forces in a vertical channel (see [4)] for this last mechanism). It should be mentioned that all these mechanisms are highly dependent of the thermal boundary conditions in the fuel assembly and in the pool building atmosphere;
- Coolability of dewatered assemblies by water spray. After a total pool dewatering, spraying could be a better solution than bottom reflooding. Indeed, it could avoid complete blockage of air circulation inside the FAs and thus a transient increase of the fuel temperature which is suspected for bottom-up refilling. Even if top-down reflooding has been extensively studied in the past for reactor loss-of-coolant accidents, models developed and implemented in the safety codes were not generally developed and validated for spent fuel pool conditions and rack geometries.

To study thermal-hydraulics at the scale of the assembly, three test devices are planned in the DENOPI project. The first set-up will be devoted to study counter-current air/water and steam/water flow limitations. Experiments will be performed within an unheated 17x17 rod bundle one meter long inserted in a representative cell rack (see figure 3).

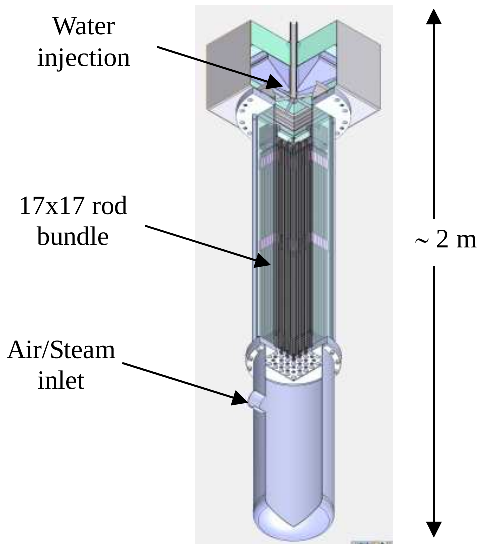

Figure 3 : Test device dedicated to reflooding studies

The bundle will be equipped with various prototypical upper tie-plates corresponding to the different types of fuel assembly inserted in the racks[g]. The second apparatus corresponds to a 7x7 bundle with electrically heated rods and spacer grids. It will be used to evaluate analytically air penetration inside a heated bundle for different thermal and flow boundary conditions. The air progression will be monitored with a gas

[g] The free flow area at the tie-plate is known to have a significant influence on the flooding curve[5)].

mass spectrometer at different level of the assembly by measuring oxygen and nitrogen concentrations. Experiments will be also conducted to measure quench front progression and rewetting of hot rods in pool conditions. These tests will allow checking the mechanical and thermal resistance of hot rods under spray flow. The last mock-up will be a full scale heated 17x17 rod[h] bundle with spacer/mixing grids and its cell rack. Dewatering tests will be carried out with this last set-up over a wide range of boundary conditions: decay heat load (from 2 kW to 80 kW), water level, thermal wall cell conditions, etc. Additional data on air ingress and spray cooling could be also collected with this full scale mock-up. The assembly could be covered by a water column of several meters long to explore the steam bubble flow in subcooled areas and under cross flows. Special attention will be paid on void monitoring in the assembly and in the water column. Void distribution will be measured using pressure transducers, optical probes and wire-mesh sensor (this last technique was already employed to characterize the transport and the condensation of bubbles inside large vertical channels[6)]).
Dewatering tests will be preceded by detailed analyses with the computer codes ASTEC[7)] and DRACCAR[8)] to provide trends and to precise boundary conditions. Figure 4 shows an example of ASTEC code results obtained for dewatering simulation of a fuel assembly.

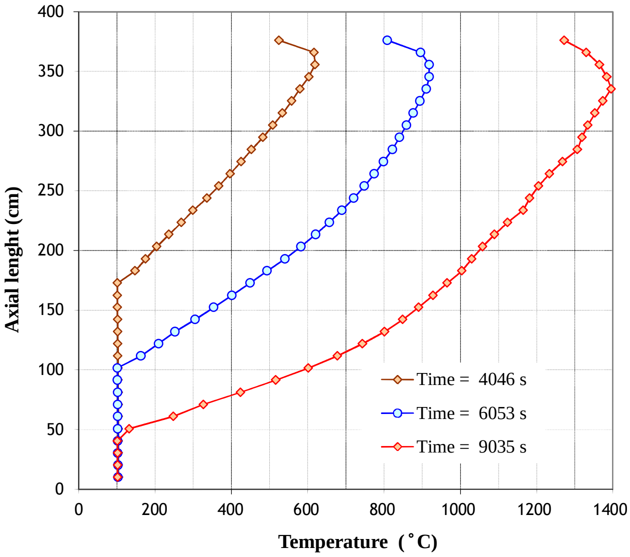

Figure 4: Axial temperatures of fuel rods in the central part of an isolated assembly (decay heat = 58kW) during dewatering

III.OXIDATION EXPERIMENTS

From about 700-800°C, the oxidation kinetics of the cladding material become significant and heat released by the oxidation reactions contributes significantly to the heating power. Reaction runaway can occur if the heat released exceeds the heat exchange with the surrounding, which may result in degradation of the assembly.

1. Background

A specificity of the spent fuel pool accidents is the possible presence of air in the oxidant atmosphere around the rods when they are uncovered. Enthalpy of the Zr + O_2 reaction (-1100 kJ/mol of Zr at 298 K) is about 80% higher that of the Zr + H_2O reaction (-616 kJ/mol of Zr at 298 K). Furthermore, high temperature oxidation of Zr-based alloys is much faster in air compared to steam. On the one hand the breakaway transition occurs earlier and on the other hand the post-transition acceleration is stronger[9-12)]. A possible cause for the early breakaway is the incorporation of nitrogen in the first formed dense zirconia scale, recently evidenced by Raman spectroscopy[13)]. Regarding the post-transition regime, it has been early suggested that the marked acceleration in air was due to the combined action of oxygen and nitrogen[10)]. Based on metallographic observations, a detailed sequence, involving formation of zirconium nitride particles at the metal/oxide interface and their oxidation, was proposed to explain the fast progression of the oxidation front in the post-breakaway regime[14-15)]. The presence of the ZrN compound in the vicinity of the metal/oxide (M/O) interface has been confirmed by Raman spectroscopy[13)]. Recently, a detailed kinetic analysis has shown that the ZrN oxidation reaction contains the rate-limiting step in this post-breakaway regime[16)], thus confirming that, at least in the investigated conditions (initially bare Zircaloy-4, N_2+O_2 atmosphere without steam, T=850°C), the post-breakaway oxide is not protective (i.e. it does not limit the oxygen flux to the M/O interface).

2. Effect of steam on air oxidation

The effect on Zr alloy oxidation of adding steam in an air oxidant atmosphere has rarely been addressed. Tests performed at Karlsruhe Institute of Technology (KIT) with bare Zy-4 have shown that at 800 and 900°C, a rather low amount of steam inhibits the detrimental effect of nitrogen: at 800°C, weight gain after one hour oxidation is observed to be the same in a 90/10 vol. air/steam mixture than in pure steam. At 900°C, the same inhibiting effect is obtained with 30% vol. steam added[15)]. The effect of steam addition in air has also been investigated at IRSN by ThermoGravimetric Analysis (TGA). The corresponding tests were performed with bare Zy4 cladding samples, at 850 and 950°C, and with steam volume fraction ranging from 5 to 20%. During the first ~30 min, all weight gain curves merge (Figure 5), indicating that composition of the atmosphere does not strongly affect the diffusion limited regime. Results clearly confirm that steam slows down the oxidation process. However, the kinetic transition is only moderately delayed and occurs in air + steam mixtures much earlier than in pure oxygen or in pure steam[i]. The post-transition acceleration, even if significantly affected by adding steam in air, is still very pronounced compared to pure steam or pure O_2. Metallographic examinations confirm that nitriding, responsible for the fast acceleration in pure air, also occurs in air + steam mixtures, for the temperature and steam concentrations investigated.

[h] The cladding material will be chosen to avoid oxidation reactions.

[i] In pure steam, kinetics is close to the one in pure O_2.

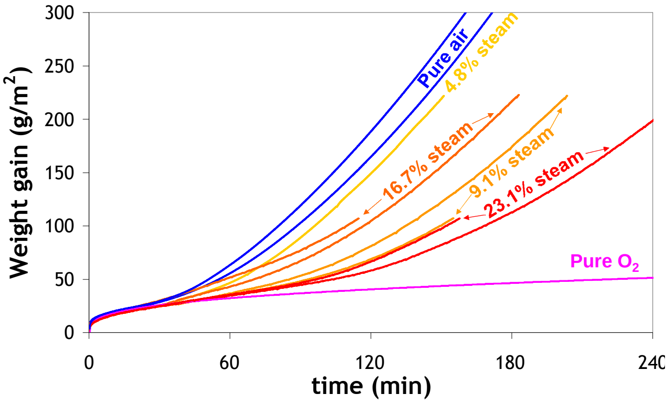

Figure 5: Bare Zy-4 oxidation at 850°C in air + steam mixtures. Two weight gain curves (except for the 4.8% steam atmosphere) are displayed for each air+steam composition. They correspond to repeatability tests.

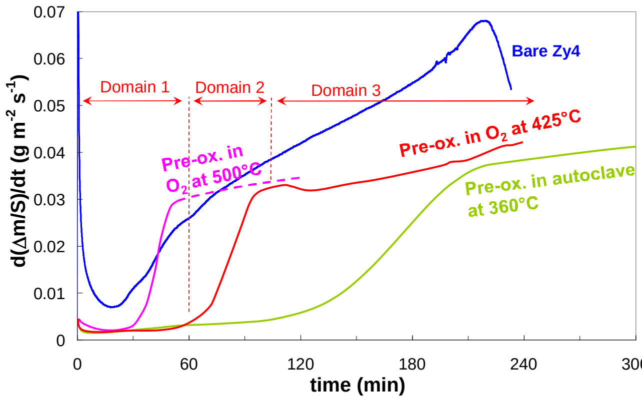

Figure 6: Bare and pre-oxidized (~30 µm pre-ox. thickness) Zy-4 oxidation in air at 850°C. Weight gain rate curves "cleaned" from spikes due to loss of oxide fragments during tests. Domains 1, 2 and 3 (see text) are delimited for the red curve.

3. Effect of pre-oxidation

Most of the kinetic investigations on the Zr-based cladding material oxidation in air at high temperature have used bare cladding samples. As far as spent fuels are concerned, the presence of corrosion oxide scale formed during normal operation in reactor has to be considered. In steam atmosphere and at temperature relevant to loss-of-coolant accident (LOCA) conditions (900-1200°C), a protective effect of the pre-oxide is generally observed[17-19]. Very limited work on the effect of a pre-transient oxide on the high temperature cladding behaviour in air has been performed so far. At Argone National Laboratory, small scale air oxidation tests were made in the 300-900°C temperature range with Zy-4, Zirlo and M5™ tubes, either bare or pre-oxidised in steam at 550°C up to 20-30 µm pre-oxide thickness[20]. It was observed for the pre-oxidized samples either no modification or even an increase of the oxidation kinetics compared to the bare ones. At IRSN, TGA was used to study in the 700-950°C temperature range the air oxidation kinetics of Zy-4 and M5 claddings pre-oxidised in different conditions: at 500°C in steam, at 500°C in oxygen, at 360°C in pressurized water (autoclave)[21] and recently at 425°C in oxygen. Results appear to significantly depend on the pre-oxidation conditions. For the same ~30 µm pre-oxide scale thickness, protectiveness is increasing in the following order: 500°C in O_2 < 425°C in O_2 < 360°C in autoclave.

Thanks to the on-line weight gain recording capability of the TGA technique, 3 different time domains can be identified on the weight gain rate curves obtained with pre-oxidized samples (Figure 6). During the first domain, the weight gain rate is low. Then, it increases progressively during domain 2, and finally stabilizes (linear regime, domain 3). The weight gain rate during domain 1 and 3 depends neither on the pre-oxide thickness nor on the pre-oxidation conditions. By contrast, significant differences are clearly observed regarding duration of domain 1 and domain 2, reflecting the protection efficiency differences from a pre-oxide to another.

4. Future experimental work

Objective is to have better understanding of the role of the various parameters above mentioned that can affect the degradation process, including the pre-oxide characteristics. Special attention will be paid to address conditions prototypic of spent fuel pool accidental transients, which means that the simultaneous presence of air and steam in the reactive atmosphere has to be considered.

Because the atmosphere composition around the fuel rods can vary strongly depending on the accidental scenario, on the location in the pool and on axial and radial positions within a given assembly, influence of the partial pressure of the different gases on the reaction kinetics have to be addressed. The so called "partial-pressure jump" technique, developed at Ecole des Mines de Saint-Etienne (EMSE) for TGA measurements[22], is particularly well suited for that purpose, as it allows to determine, within a limited number of experiments, the dependence of the reaction kinetics with the partial pressure of the reactants. The kinetic regimes of the successive domains of the degradation process will be studied by this technique.

TGA experiments will be supported by in situ X-ray diffraction (XRD) investigations and post-test characterization by micro-Raman mapping of the oxide scales. In situ XRD experiments will be performed at the Laboratoire Vellave sur l'Elaboration et l'Etude des Matériaux (LVEEM), where a high temperature in situ XRD apparatus devoted to corrosion studies and having the capability to manage humid atmospheres has been developed[23]. Evolution of the pre-oxide and formation of the high temperature oxide in air+steam atmospheres will be investigated from a crystallographic point of view. Post-test analysis by micro-Raman spectroscopy will provide local information (resolution < 1µm) on phases, composition and stress state of the scales. The micro-Raman imaging technique, perfected at the Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI) for the study of oxide scales formed at high temperature in air on the Zy-4 and M5 alloys, has proved interesting mapping capabilities for Zr oxidation scales[13].

A set of ^{18}O tracer oxidation experiments will be performed to gain information on the oxygen transport through the pre-oxide and the high temperature oxide at various stages of the oxidation sequence.

A cross-analysis of the TGA, XRD, Raman and ^{18}O data will allow identification of the detailed reaction paths involved in the different steps of the cladding degradation process. A physically-based kinetic model taking into account the influence of temperature and atmosphere composition will be developed. Final goal is its integration in the severe accident code ASTEC.

IV. CONCLUSIONS

The DENOPI program is a challenging experimental program which addresses a large number of phenomena involved in spent fuel pools under loss of cooling and loss of coolant conditions: natural convective phenomena and boiling in the pool, thermal-hydraulic behavior before and during FAs uncovery as well as cladding degradation due to oxidation under air/steam atmosphere. It involves several experimental devices with the aim to assess efficiency of spray cooling mitigation, risk of steam aspiration by the cooling system or potential risk of return to criticality in the assembly. Launched in 2013 for 6 year period, this program federates Insitut de Radioprotection et de Sûreté Nucléaire and French research laboratories to take benefit of complementary equipments and skills.

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REFERENCES

1. T.-C. Hung et al., "The development of a three-dimensional transient CFD model for predicting cooling ability of spent fuel pools", *Applied Thermal Engineering*., 50, 496-504 (2013).
2. P. Aude, M. Sakiz and I. Rupp, "Numerical simulation of the restart of the cooling system in a storage pool under boiling conditions", Proc. ICAPP-2007, May 13-18, 2007, Nice, France, (2007). [CD-ROM]
3. A. Bousbia Salah and J. Vlassenbroeck, "Survey of some safety issues related to some specific phenomena under natural circulation flow", Proc. EUROSAFE-2012, Nov. 5-6, 2012, Brussels, Belgium, (2012).
4. C.-H. Cheng et al., "Buoyancy-assisted flow reversal and convective heat transfer in entrance region of a vertical rectangular duct", *International Journal of Heat and Fluid Flow*, 21, 403-411 (2000).
5. R. Spatz and D. Mewes, "The influence of walls and upper tie plate slots on the flooding mechanism in fuel elements with and without heat transfer between steam and water", *Nuclear Eng. and Design*, 110, 413-422 (1989).
6. H.-M. Prasser et al., "Evolution of the structure of a gas-liquid two-phase flow in a large vertical pipe", *Nuclear Eng. and Design*, 237, 1848-1861 (2007).
7. P. Chatelard et al., "ASTEC V2 severe accident integral code – main features, current V2.0 modelling status and perspectives", *Nuclear Eng. and Design*, 272, 119-135 (2014).
8. G. Repetto et al., "DRACCAR : a 3D-thermal mechanical computer code to simulate LOCA transient - status of the development and the validation", Proc. ICAPP-09, May 14-19, 2009, Tokyo, Japan, (2009).
9. E.T. Hayes and A.H. Roberson, "Some effects of heating zirconium in air, oxygen and nitrogen", *J. Electro-chem. Soc.*, 96, 142-151 (1949).
10. E.B. Evans, N. Tsangarakis, H.B. Probst and N.J. Garibotti, "Critical role of nitrogen during high temperature scaling of zirconium", Proc. Conference on Metallurgical Society of AIME, Symposium on High Temperature Gas-Metal Reactions in Mixed Environments, May 9-10, 1972, Boston, USA, (1972).
11. C.J. Rosa, W.W. Smeltzer, "The oxidation of zirconium in oxygen-nitrogen atmospheres", *Zeitschrift Fur Metallkunde*, 71, 470-475 (1980).
12. S. Leistikow, H.V. Berg, "Investigation under nuclear safety aspects of Zircaloy-4 oxidation kinetics at high temperatures in air", Proc. of the 2nd Workshop of German and Polish Research on High Temperature Corrosion of Metals, Dec. 2-4, 1987, Jülich, Germany, (1987).
13. I. Idarraga et al., "Potentialities of Raman Imaging for the Analysis of Oxide Scales Formed on Zircaloy-4 and M5® in Air at High Temperature", *Oxid. Met.*, 79, 289-302 (2013).
14. C. Duriez, T. Dupont, B. Schmets and F. Enoch, "Zircaloy-4 and M5® high temperature oxidation and nitriding in air", *J. Nucl. Mat.*, 380 (1-3), 30-45 (2008).
15. M. Steinbrück, "Prototypical experiments relating to air oxidation of Zircaloy-4 at high temperatures", *J. Nucl. Mat.*, 392, 531-544 (2009).
16. M. Lasserre, O. Coindreau, M. Pijolat, V. Peres, M. Mermoux and J.P. Mardon, "Study of Zircaloy-4 Cladding Air Degradation at High Temperature", Proc. 21st International Conference on Nuclear Engineering (ICONE21), July 29 - August 2, 2013, Chengdu, China, (2013).
17. S. Guilbert, C. Duriez, C. Grandjean, "Influence of a pre-oxide layer on oxygen diffusion and on post-quench mechanical properties of Zircaloy-4 after steam oxidation at 900°C", Proc. WRFPM-2010, Sept. 26-29, 2010, Orlando, USA, (2010).
18. M. Le Saux, J.C. Brachet, V. Vandenberghe, D. Gilbon, J.P. Mardon, and B. Sebbari, "Influence of Pre-Transient Oxide on LOCA High Temperature Steam Oxidation and Post-Quench mechanical Properties of Zircaloy-4 and M5TM cladding", Proc. WRFPM-2011, Sept. 11-14, 2011, Chengdu, China, (2011).
19. S. Guilbert, P. Lacote, G. Montigny, C. Duriez , J. Desquines, C. Grandjean, "Effect of pre-oxide on Zircaloy-4 high temperature steam oxidation and post-quench mechanical properties", *J. ASTM Int.*, STP 1543 (2013).
20. K. Natesan and W. K. Soppet, *Air Oxidation Kinetics for Zr-based Alloys*, Argonne National Laboratory Report 03/32, NUREG/CR-6846, June 2004.

21. C. Duriez, D. Drouan, G. Pouzadoux, “Pre-oxidised Zircaloy-4 and M5® claddings reaction in air and in nitrogen”, *J. Nucl. Mat.*, 441, 84-95 (2013).
22. M. Pijolat, F. Valdivieso, M. Soustelle, “Experimental tests to validate the rate-limiting step assumption used in the kinetic analysis of solid-state reactions” *Thermochimica Acta*, 478, 34-40 (2008).
23. H. Buscail, R. Rolland, C. Issartel, F. Rabaste, F. Riffard, L. Aranda, M. Vilasi., “Effects of water vapour on the oxidation of a Nickel-Base alloy between 900-1100°C”, *Journal of Materials Science*, 46, 5903-5915 (2011).