



## Oxygen diffusion in liquid (over)stoichiometric corium

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### ABSTRACT

Within the framework of pressurized water reactor severe accidents, the ICE research program is devoted to studies on a variety of fundamental mechanisms involved in Fuel-Coolant Interaction (FCI). Among them, the oxidation of liquid corium is expected to impact the premixing/fragmentation stage, thus possibly influencing the subsequent steam explosion. As a first step towards the exhaustive description of oxidation phenomena occurring in typical FCI layouts, the 1-D oxygen diffusion in liquid (over)stoichiometric spherical corium droplets is investigated in this article. A mesoscopic description is adopted, based on the evolution of oxygen concentration  $c_O$ , depending on space, time, corium composition and temperature. The underlying physical model is coupled with CALPHAD-based thermodynamic calculations. An asymptotic analytical solution is first determined, assuming that the apparent diffusion coefficient  $D_O$  does not depend on  $c_O$ . Then, the general variational form of governing equations is derived, leading to the implementation of a related numerical approach using the finite-element method, in COMSOL<sup>®</sup> software. This numerical approach is first benchmarked with the analytical calculation, and then extrapolated to the more general case where  $D_O$  varies with  $c_O$ . Finally, some case studies representative of FCI issues are selected, in order to determine typical oxygen diffusion transient times within a variety of liquid corium droplets.

## 1. Introduction

### 1.1. Outlines

Within the framework of pressurized water reactor severe accidents, the role of several fundamental mechanisms involved in Fuel-Coolant Interaction (FCI) must be clarified. In particular, the fundamental mechanisms linked to the oxidation of the corium melt have been pointed out as a major issue, one of the cornerstone of the ICE research program (Meignen, 2012). Especially, the influence of corium oxidation on the premixing/fragmentation stage is not yet fully understood, and requires a modeling effort, from analytical, numerical and experimental point of view.

Oxidation phenomena can have positive or negative impacts on FCI and steam explosion. During premixing/fragmentation phase of the corium, the generation of hydrogen in the gas film around droplets and around the jet directly impacts the distribution of the gas phase including hydrogen (light) gas. This mechanism, along with heat transfer of the gaseous phase (including hydrogen) can be a positive counter-effect, increasing void in the mixture. On the contrary, oxidation process with high exothermic energy release such as for pure zirconium will lead to a higher available liquid fraction with possible higher

energetics in steam explosion, the latter point directly depending of the ratio of zirconium present in the corium phase. Besides, the accumulation of hydrogen in containment might also be considered as negative for nuclear safety, considering the risk linked to hydrogen explosion.

The investigation of corium oxidation has been already undertaken in a collection of reference works. When scrutinizing the existing literature, two distinct approaches clearly stand out, beginning with the so-called “macro-scale” approach.

This “integral” approach can be first based on a phenomenological approach of oxidation, bearing on post-test analyses using for instance SEM (Scanning Electron Microscope) and EDS (Energy Dispersive Spectrometer) for the analysis of corium fragments, as emphasised by Sanchez-Brusset (2015) or Tyrpekl (2012). The morphology of corium debris, along with their crystallographic characterization and their chemical composition with respect to “integral” oxidation conditions are particularly investigated. Another experimental approach bears on the analysis of the effective flow rate of oxidant gases spent on the melt oxidation, as highlighted by Almyashev et al. (2016), by means of mass spectrometers. This on-line analysis of the difference between inlet and outlet oxidant gases is performed within the framework of in-vessel melt retention, the related series of corium oxidation tests being carried out on the RASPLAV test facility for liquid corium pools. The previous

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Nomenclature			
Symbol	Description (Unit)		
$c_i$ ( $C_i$ )	molar concentration of element (species) $i$ ( $\text{mol.m}^{-3}$ )	$T$	temperature (K)
$c_S$	surface molar concentration of oxygen ( $\text{mol.m}^{-3}$ )	$U$	typical velocity ( $\text{m.s}^{-1}$ )
$c_0$	initial molar concentration of oxygen ( $\text{mol.m}^{-3}$ )	$V$	volume ( $\text{m}^3$ )
$d$	droplet diameter (m)	$V_i$	partial molar volume of species $i$ ( $\text{m}^3.\text{mol}^{-1}$ )
$D_i$	diffusion coefficient of element or species $i$ ( $\text{m}^2.\text{s}^{-1}$ )	$w$	test function (–)
$\vec{J}_{\text{diff}} (\vec{J}_i)$	Flux of element O (of species $i$ ) ( $\text{mol.m}^{-2}.\text{s}^{-1}$ )	$x_i$ ( $X_i$ )	mole fraction of element $i$ (species $i$ ) (–)
$L$	Typical length (m)	<i>Greek letters and other notations</i>	
$n_i$	number of moles of element $i$ (mol)	$\alpha$	overstoichiometry (–)
Ox. rate	oxidation rate (%)	$\alpha_{\text{max}}$	maximum overstoichiometry (–)
Pe	Péclet number (–)	$\gamma_O^*$	relative oxygen concentration (–)
$r$	radial coordinate (m)	$\gamma_S^*$	surface relative oxygen concentration (–)
$R$	droplet radius (m)	$\gamma_0^*$	initial relative oxygen concentration (–)
Re	Reynolds number (–)	$\eta_a$	dynamic viscosity (ambient medium) ( $\text{Pa.s}^{-1}$ )
$R_{U/Zr}$	U/Zr molar ratio (–)	$\kappa$	dimensionless diffusion coefficient (–)
$t$	time (s)	$\mu_i$	chemical potential of species $i$ ( $\text{J.mol}^{-1}$ )
		$\rho_a$	density (ambient medium) ( $\text{kg.m}^{-3}$ )
		$\tau$	typical time scale (s)
		★	dimensionless notation (–)

on-line or post-test analyses are often coupled with the development of dedicated models, allowing to trace back to fundamental oxidation mechanisms by making use of inverse methods. They can consist of algebraic or 0-D models coupling e.g. oxidation and solidification for the binary system U-O, as described by Cardon and Nicaise (2014) or Manara et al. (2005), the latter focusing on solidus/liquidus transitions depending on the oxidation rate. These models may also investigate the oxidation kinetics of a corium pool by calculating oxygen molar fluxes to the melt surface, as presented by Sulatsky et al. (2013), whose results are further discussed in the next section. Finally, such models may consider the diffusion of oxygen across the gas film surrounding the liquid corium droplet, as emphasized by e.g. Loisel et al. (2017). In the latter, mass balances are completed by correlations based on dimensionless groups characterizing the mechanism of steam-gas film inter-diffusion. This “correlation-based” approach is also found in Veschnukov et al. (2005), which proposes an insightful molten corium oxidation-solidification model that could be qualified as pseudo 1-D. Indeed, in this model, three layers are distinguished between the (outer) oxide crust, a transition thickness and the (inner) liquid bulk. Their thickness vary with time, but for a given time, the concentrations and temperatures in the oxide crust and the liquid bulk are supposed to be homogeneous (hence the pseudo-1D denomination), the matching being performed within the transition thickness layer, thanks to appropriate mass transfer correlations.

On the other hand, the “lower-scale” approach adopts a more local description of oxidation phenomena. A collection of works is thus based on thermodynamic calculations in order to predict the 1-D multi-component diffusion in a variety of thermodynamic systems, e.g. binary U-O for *ab initio* calculations at micro-scale, as shown by Kupryazhkin et al. (2008), or binary Zr-O, as detailed by Mazeres (2013), at meso-scale. Some of these works adopt the strategy consisting in coupling thermodynamic equilibrium calculations, based on e.g. the CALPHAD method (to determine interface conditions within the assumption of instantaneous local equilibrium), with an additional model describing the oxidation kinetics in the adjacent phases (for instance: binary U-O systems (Cardon et al., 2016), with an upcoming extension to ternary U-Zr-O and then quaternary U-Zr-O-Fe (Cardon, 2016)).

In order to bridge the gap between both approaches, and as a first step towards the overall coupling between the physical phenomena involved in corium oxidation (e.g. those related to advection, heat transfer, phase change), the 1-D single-component diffusion of oxygen in liquid (over)stoichiometric U-Zr-O ternary systems is investigated in

the present article. These systems consist of spherical droplets of corium with various compositions, at a given homogeneous temperature. This choice allows us to assess our modeling strategy, partly based on the original reduction of the multi-component diffusion theory to the single-component diffusion of oxygen, in link with CALPHAD-based thermodynamic calculations. Moreover, in view of the dimensioning of an experimental test-bench dedicated to the study of corium oxidation mechanisms, the present work could be used to determine relevant experimental working conditions in order to magnify related phenomena.

For this purpose, after introducing the phenomenology of liquid corium oxidation in Section 1.2 and some fundamental notions of chemical transport in Section 2.1, the overall physical modeling is set up in Sections 2.2 and 2.3. The definition of governing equations, initial and boundary conditions brings some thermodynamic issues into play, requiring the aforementioned coupling with CALPHAD-based data, as highlighted in Section 3. A dimensionless analytical calculation is first performed, assuming that the diffusion coefficient  $D_O$  does not vary with  $c_0$ , as enhanced in Section 4. The general variational form of governing equations is then derived, leading to the implementation of a related numerical approach based on the discretization of diffusion equation using the finite-element method (FEM), as proposed in Section 5. This method is first benchmarked with the analytical calculation, as shown in Section 6.1. The latter results are then compared to the more general case where  $D_O$  varies with  $c_0$ , as highlighted in Section 6.2. Finally, some case studies representative of FCI issues are selected, in order to determine typical oxygen diffusion transient times within a variety of corium droplets, as explained in Section 6.3. For future prospects, some opening comments about internal mass transfer issues are given in Appendix A.3.

## 1.2. Phenomenology of liquid corium oxidation

Let us consider the fundamental case of a single corium droplet, suspended into liquid water, as shown in Fig. 1. The droplet is surrounded by a gaseous film, a mixture made of steam and other incondensable gases (e.g. hydrogen). Let us highlight the different mechanisms involved in liquid corium oxidation kinetics.

In the present analysis, the thermal dissociation of steam in the gas film is not taken into account: we shall indeed consider that the gas membrane at very high temperature is thin enough, so that water dissociation is only located in the first few molecular layers. Besides, as

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