Proceedings of the 9th International Conference on Fluid Flow, Heat and Mass Transfer (FFHMT'22)
Niagara Falls, Canada – June 08-10, 2022
Paper No. 148
DOI: 10.11159/ffhmt22.148

Mass Transfer Induced Rayleigh-Taylor Instabilities between Two Immiscible Liquids: The Unique Case of Corium

Romain Le Tellier[1]
[1]CEA, DES, IRESNE, DTN, Cadarache
F-13108 Saint Paul-lez-Durance, France
romain.le-tellier@cea.fr

Abstract **-** Liquid pools composed of molten multicomponent materials are often multiphase systems and their behaviour is complex because the associated non-miscible phases can be chemically reactive. At the interfaces between phases, mass transfer occurs and can have a significant impact on the overall pool thermalhydraulics. The case of interest in this paper pertains to the behaviour of molten core materials – so-called corium – in a nuclear reactor during a severe accident like at the Fukushima Daiichi plant. These materials form a liquid pool in which inter-phase mass transfer occurs between an oxygen-rich phase (mainly composed suboxidized U and Zr elements from the fuel and cladding materials of the core) and an oxygen-poor phase (initially made of molten steel elements) that tend to segregate under the force of gravity.

The specificity of the underlying (O, U, Zr, steel) thermodynamic system is that the density difference between both phases under equilibrium can change of sign depending on the tie line under consideration. Accordingly, interface mass transfer can induce local density changes in such a way that, under certain conditions, Rayleigh-Taylor instabilities (RT) can occur, grow and lead to modification of the phase topology that are referred to as "stratification transients".

The coupling between mass transfer and hydrodynamics in the corium system composed of two immiscible liquid phases presents peculiarities that this paper aims at exposing to a broad fluid dynamics researchers' audience. In order to do so, a critical review of the coupled phenomena and the associated stratification flow regimes is proposed based on both state-of-the-art experimental data and recent simulation results.

Keywords**:** Miscibility gap, reactive interface, Rayleigh-Taylor instability, corium, nuclear reactor severe accident analysis

1. Introduction

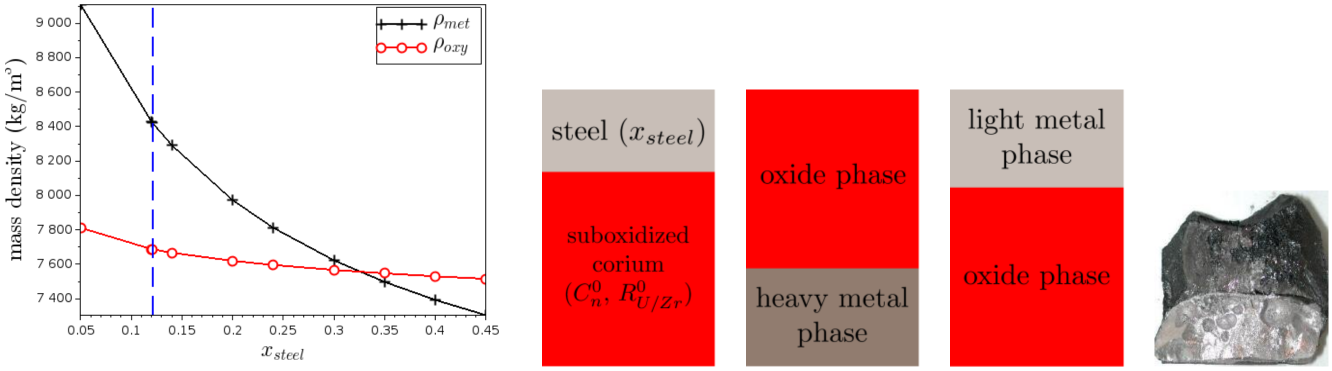
The study of liquids stratification is of interest in many industrial fields, and, in many cases, including carbon dioxide sequestration and oil recovery, chemo-hydrodynamics instabilities play a significant role in the behaviour of such multiphase systems [1]. Such instabilities can be related to viscosity or density profiles across the interface between the two phases that are affected by chemical reactions and mass transfers. In particular, in the literature, the case where the two phases are miscible and the interface reaction under consideration is of the type A + B → C has been the subject of many experimental [2] and analytical [3] studies covering both viscous fingering and buoyancy-driven instabilities. When considering immiscible phases, main body of work is associated with Hele-Shaw cells where an organic solution containing an acid (reactant A) is put in contact with an aqueous solution in which a base (reactant B) is dissolved. In such configuration, buoyancy effects take the form of plumes rising and fingers falling below the interface [4] that can be complicated by the presence of Marangoni effects due to surface tension gradients.

In this paper, we focus on another case of buoyancy-driven instabilities in a two-phase liquid system where the specificity of the underlying multicomponent thermodynamic system is that the density difference between both phases at equilibrium can change of sign depending on the tie line of the miscibility gap under consideration. This case of interest pertains to the behaviour of molten core materials – so-called corium – in a nuclear reactor during a severe accident [5] like at the Fukushima Daiichi plant. These materials form a liquid pool in which inter-phase mass transfer occurs between an oxygen-rich phase (mainly composed suboxidized U and Zr elements form the fuel and cladding materials of the core) and an oxygen-poor phase (initially made of molten steel elements) that tend to segregate under the force of gravity at the bottom of the reactor pressure vessel. Because interface mass transfer can induce local density changes, under certain conditions, Rayleigh-Taylor instabilities (RT) can occur, grow and lead to modification of the phase topology that are referred to as "stratification transients" and have a significant impact on the overall pool thermalhydraulics.

To the author's best knowledge, the coupling between mass transfer and hydrodynamics in the corium system presents peculiarities that make this two immiscible liquid-system rather unique. This paper aims at exposing it to a broad fluid dynamics researchers' audience by a critical review of the coupled phenomena and the associated stratification flow regimes. In order to do so, section 2 starts with an overview of the corium stratification phenomenology through its limited experimental characterization. Then, numerical simulation results are reported in section 3 in order to further discuss the possible coupled mass transfer/flow regimes and illustrate their main characteristics. Finally, short conclusions are given in section 4.

2. Overview of stratification phenomenology and associated experimental characterization

Considering the U-O-Zr-Fe(-Ni-Cr) system to be representative of in-vessel corium composition and thermodynamics, past experimental programs on suboxidized corium-steel interactions, in particular, OECD MASCA 1 and 2 [6], have shown that the miscibility gap exhibited at liquid state leads, at steady-state, to melt component partitioning into an oxygen-rich ("oxide") phase and an oxygen-poor ("metal") phase. When their density difference is large enough, these two phases tends to stratify into a two-layer pool. For a low Zr molar oxidation degree C_{Zr} or steel mass fraction x_{steel}, the "metal" phase density is higher than the oxide one (because of a relatively large mass fraction of uranium and zirconium) and tends to decrease when C_{Zr}or x_{steel} increases. Such a trend w.r.t. x_{steel} is illustrated in Figure 1 (a) by thermodynamic equilibrium calculation results where it can be seen that an "inversion threshold" value can be defined around 0.325 for x_{steel} in this case. Note that this threshold is also dependent on the U over Zr molar ratio ($R_{U/Zr}$) in the corium that is reactor design dependent. Accordingly, considering a two-phase stratified system initially composed of a steel upper layer on top of a suboxidized corium layer (see Figure 1 (b)) representative of the reactor situation, two possible steady-states are expected with either an "heavy" metal layer below an oxide pool (see Figure 1 (c)) or a "light" metal layer on top (see Figure 1 (c)). The example of such a stratified configuration characterized in the frame of the MASCA-MA experiment series is depicted in Figure 1 (d) where the post-mortem cut of a solidified system is shown with a metal layer below an oxide phase.



(a) mass densities of the phases at equilibrium as a function of x_{steel} – temperature is 2840K, C_{Zr}=0.365, $R_{U/Zr} = 1.14$ *i.e.* conditions close to the one of the MA-3 test [6] where x_{steel} =0.121 (blue dashed line)

(b) initial state

(c) equilibrium state with $\rho_{met} > \rho_{oxy}$

(d) equilibrium state with $\rho_{met} < \rho_{oxy}$

(e) cut of the post-mortem ingot of MA-3 test [6] – diameter is about 7cm

Figure 1: Illustrations of the two-phase equilibrium and possible stratification states associated with the U-O-Zr-steel system

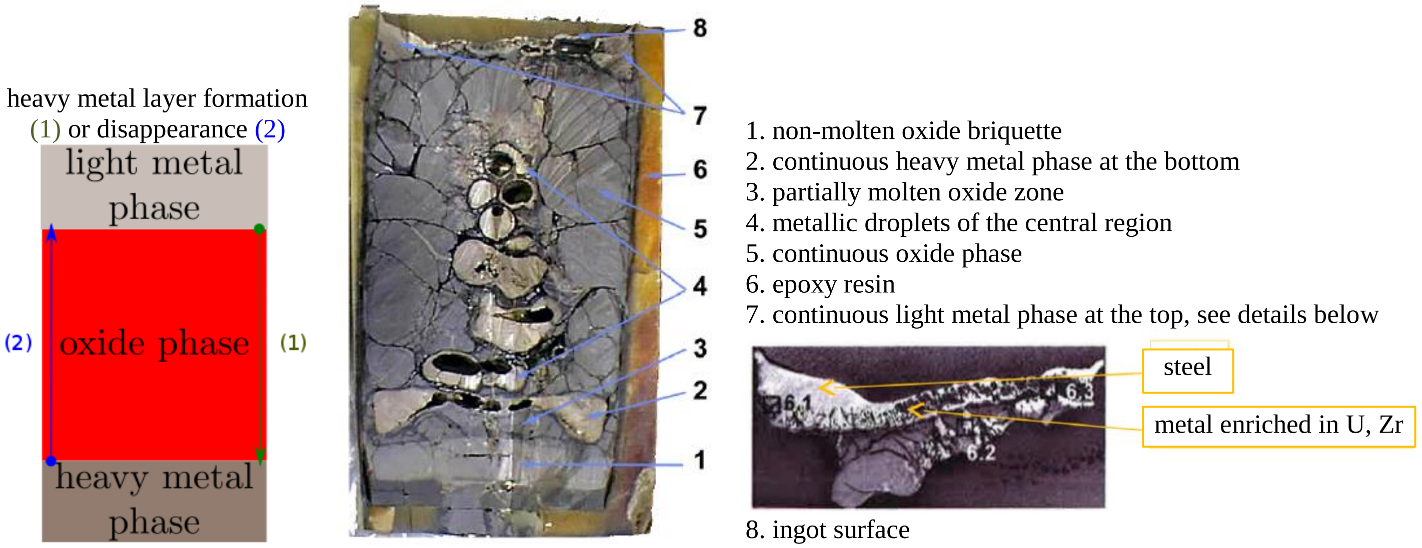
During a severe accident transient where C_{Zr} and x_{steel} are both likely to increase (because of the pool oxidation by steam and the melting of steel internal vessel structures), the stratification can be modified according to two possible transients illustrated schematically in Figure 2 (a) where a transient 3-layer configuration is depicted. Because of the materials at play, so-called prototypical experiments (where depleted uranium is used instead of enriched uranium) to characterize the corium pool behaviour are scarce. In any case, they are carried out at a spatial scale that is at least one order of magnitude (in length) smaller than the reactor one. Accordingly, because of the very small scale (≤ 2kg of corium) of all-but-one MASCA experiments, the transient kinetics is not well characterized. Only the RCW test where 5kg of molten steel were poured on top of about 45kg of suboxidized corium for a 22-min exposure time can be related to the heavy metal layer formation transient by the analysis of the solidified ingot (see Figure 2 (b)). The interpretation made of this experiment leads to consider this ingot as the solidified state of the system during the transient of relocation of the steel under the oxide and the metallic phases are distributed as follows:

- a continuous light metallic phase (7, in in Figure 2 (b)), above the oxide pool (5);
- metallic inclusions enriched in U and Zr interpreted as droplets (4) falling through the oxide (5);
- a continuous heavy metallic phase (2) under the oxide layer (5).

Qualitatively, the phenomenology associated with this experiment can be described by the following steps:

- the transfer of metallic U and Zr to the steel at its interface with the oxide (associated with the shift of the reaction $UO_2 + Zr \leftrightarrow ZrO_2 + U$ in the right direction in the oxide phase, at the interface);
- the formation and detachment by Rayleigh-Taylor instabilities (associated with this local enrichment of the metallic phase above the oxide) of metallic droplets heavier than the oxide phase that sink into the oxide;
- the droplets coalescence that leads to a continuous heavy metal phase at the bottom of the pool.

A more in-depth analysis of such an experiment shows that interfacial mass transfer with a characteristic time of 1000s appears as the limiting kinetic factor (in comparison with droplets hydrodynamics) and the overall metal relocation process is likely to be intermittent [7]. Accordingly, in the detail view of the upper metal phase (7 in Figure 2 (b)), it can be seen that U,Zr-enrichment of the upper metal layer is limited to a boundary region near the interface with the oxide phase.



(a) schematics of possible stratification transients

(b) cut of the solidified ingot of the RCW experiment (adapted from [6]) – the diameter is about 18cm

Figure 2: Illustrations of in-vessel corium stratification transients

It should be noted that, in the reactor situation, a refractory solid phase is likely to be formed at the interface between the oxide pool and the top metal layer. The influence of this additional (mechanically unstable) phase on the overall stratification process is out of the scope of this paper and the reader is referred to [8] for an experimental characterization of this effect considering a stable crust.

In any case, even without considering this additional effect, the experimental characterization is very limited and, in particular, no experiment is available regarding the transient that is associated with heavy metal layer formation disappearance (transient (2) in Figure 2 (a)) when, in particular, x_{steel} is increased. Accordingly, the experimental data about coupling between mass transfer and hydrodynamics are very limited and the analysis of the corium pool highly relies on modelling and numerical simulations illustrated in the next section.

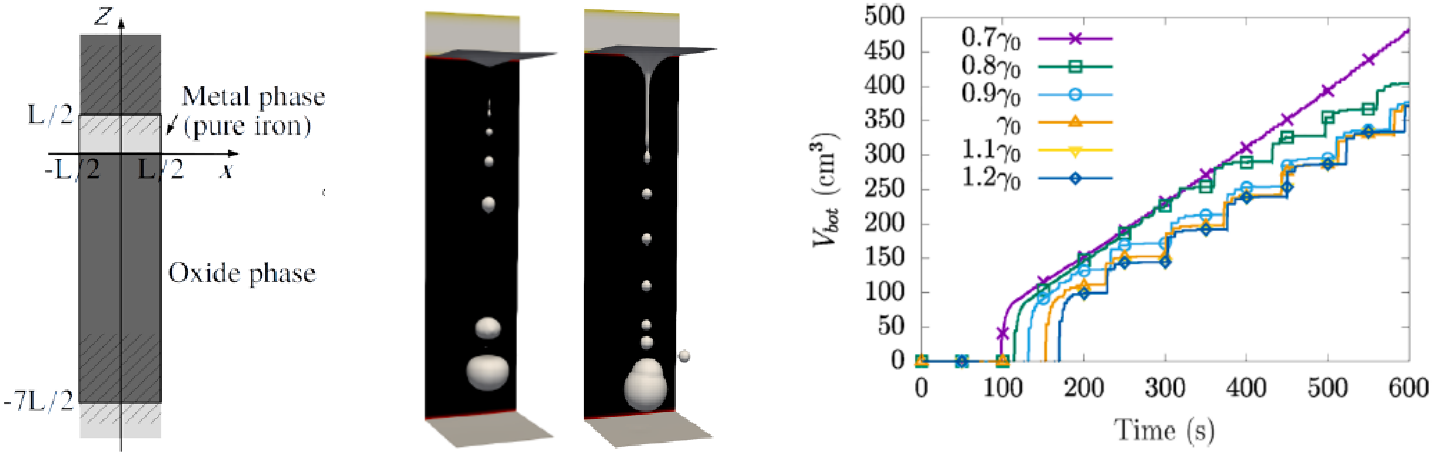
3. Modelling and Numerical Simulation

Two different types of models can be distinguished. Integral models are used in lumped parameter codes that simulate the overall pool behaviour during the in-vessel phase of the severe accident while distributed parameter models are to be coupled with Computational Fluid Dynamics (CFD) for finer analysis of stratification transients in order to calibrate or validate integral models.

Regarding the latter simulation approach, a recent attempt have been made to capture the coupled phenomena of such transients by more detailed simulations based on the coupled solution of the Cahn-Hilliard and Navier-Stokes equations [9]. This is part of a long-term collaborative work between the author and the PMC laboratory of Ecole Polytechnique with a special focus on a thermodynamically consistent modelling of the multicomponent mass transfer in a miscibility gap [10][11]. In this framework, simulations in [9] were a “proof of principle” considering a simplified pseudo-binary thermodynamics system constructed from equilibrium conditions representative of the RCW experiment. Based on a pseudo-spectral code, these simulations, illustrated in Figure 3, have shown a qualitative agreement with the experimental observations. The Rayleigh–Taylor instability at the interface between the iron and the suboxidized corium leads to the formation of a plume of heavy metal phase that breaks into droplets due to the Rayleigh-Plateau instability (see Figure 3 (b)-left). Moreover, a parametric study has shown that, beside the intermittent droplet detachment regime consistent with the RCW test, a quasi-continuous regime can be obtained depending, in particular, on the interfacial tension γ. Indeed, the plume of heavy metal phase is affected by the balance between inertial, viscous and capillary forces and when the latter decreases, the plume tends to be more stable so that a rather stable filament can exists between the top and bottom metal phases (see Figure 3 (b)-right). Interestingly, as shown in Figure 3 (c), the overall rate of transfer of metal from the top to the bottom is higher with a continuous regime. These results clearly showed that detailed simulations of such phenomena can be complementary to experiments and an effort is now pursued for the coupling of a quaternary Cahn-Hilliard model to Navier-Stokes in the frame of a CFD code.

Regarding integral models for reactor applications, they consist in a kinetic model of the inter-layer mass transfer at the interfaces where the droplets formation, relocation and coalescence is not described [12][13][14]. Accordingly, the inter-layer mass transfer drives the overall layer inversion process considering hydrodynamic metal droplets transport as fast in comparison. As a consequence, the intermittent process discussed in the previous section is modelled as an averaged continuous mass transfer between perfectly stratified layers. In a more recent analysis [15], it was shown that the mass transfer between the droplets and the oxide phase during their residence time in this continuous phase cannot always be neglected and can play a significant role in the overall stratification transient. Accordingly, in [16], an enhanced integral stratification model have been proposed where the dispersed metal phase is treated and the droplets dynamics is explicitly taken into account. It is constructed on “first-order” simplifying hypotheses (e.g. the quaternary thermodynamics system is treated a two pseudo-binary systems: (U,Zr)-O in the oxide and (U,Zr)-(Fe-Ni,Cr) in the metal) that were shown to retain the expected features of the phenomena at play.

Considering the RCW test conditions, preliminary simulation results associated with an ongoing validation exercise of this model are presented in Figure 4 for illustration purpose. It can be observed that the time evolution of the masses of the different metal phases (continuous – heavy and light – or dispersed) exhibits an expected intermittent relocation process during the formation of the heavy metal layer. Interestingly, the periodic nature of this process is shown to be highly dependent on the relative values of the mass transfer kinetic parameters properties between the oxide and metal phases. Indeed, the local chemical equilibrium conditions assumed at the oxide/metal interfaces directly depends on the diffusion coefficients in both phases. While such a model is parametric in nature, one should keep in mind that it has been proposed as a part of the overall ongoing research efforts to improve the level of knowledge associated with such stratification transients. Accordingly, it is expected that new planned experimental setups such as the STROMBOLI device with an enhanced instrumentation [17], or the multiphase CFD simulations previously reported will provide validated closure laws for such an integral model.



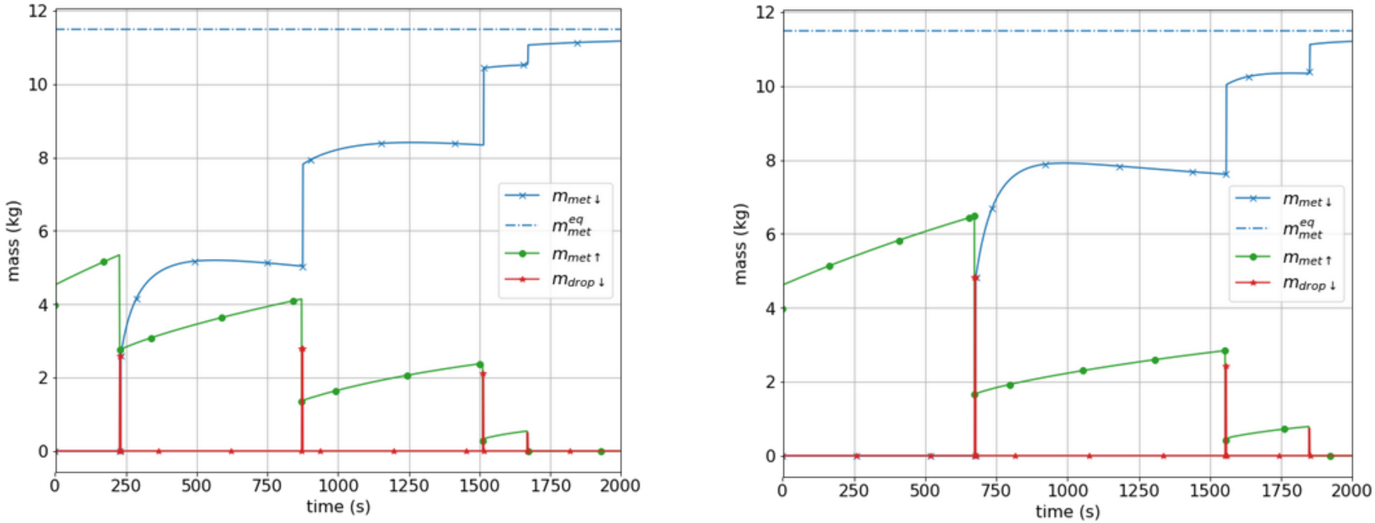
(a) simulation initial setup – periodic boundary conditions, hatched region correspond to zero-gravity

(b) simulation snapshots at t=302s with nominal parameter values (left) and with $\gamma = 0.7\gamma_0$ (right)

(c) Time evolution of the volume of metal at the bottom for various values of γ

Figure 3: Illustrations of recent Cahn-Hilliard/Navier-Stokes simulations of the transient formation of the heavy metal phase in conditions representative of the RCW experiment (adapted from [11]) - γ is the interfacial tension with $\gamma_0 = 0.385$N.m^{-1}

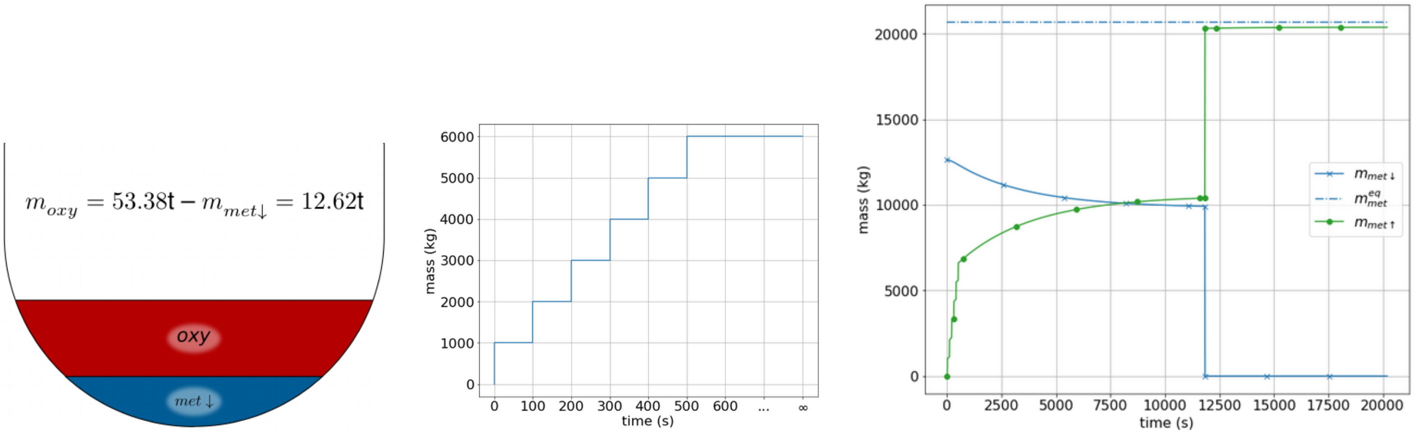
In the meanwhile, this enhanced integral model was found useful in [16] for performing a parametric study in order to "explore" stratification transients for which neither detailed simulations nor experimental data are available. In particular, as stated earlier, no experiment is available for the characterization of transient (2) in Figure 2 (a) *i.e.* the disappearance of the heavy metal phase when C_{Zr} or x_{steel} is increased. Such a transient was investigated with this model by considering the simulation setup illustrated in Figure 5 (a) and (b). Considering a two-layer corium pool at equilibrium with an heavy metal phase at the bottom, molten steel is added to the system during a limited time (600s) to form a continuous metal phase at the top. The amount of steel at the end is such that the associated x_{steel} is above the "inversion threshold". The results in terms of the time evolution of the metal phase masses is presented in Figure 5 (c). It is found that, contrarily to the heavy metal formation transient discussed so far (and illustrated with this model in Figure 4), this transient exhibits an "en bloc" inversion of the heavy metal phase position (around 11500s). This qualitative difference comes from the fact that, contrarily to the light metal layer, the heavy metal layer is formed from a metal under equilibrium conditions with the oxide phase. Then, heat and mass transfer at the bottom of the oxide layer is less effective than through its top surface in such a way that the interfacial mass transfer at its top surface is faster than at its lower boundary. As a consequence, with such a slower mass transfer, at any time, the heavy metal average composition follows very closely (in a quasi-static way) the interfacial composition (associated with the local equilibrium). Accordingly, contrarily to the upper metal phase depicted in Figure 2 (b) that exhibits a U,Zr-enriched boundary layer, the heavy metal layer is predicted to be rather homogeneous throughout the transient. Consequently, when its relocation to the top is triggered (*i.e.* when its mass density is sufficiently low so that Rayleigh-Taylor instabilities can grow), the inversion process is only limited by the plumes formation, pinch-off and the droplets dynamics that are very fast in comparison with the inter-layer mass transfer. This qualitative difference regarding these two transient types is an important finding that requires further confirmation. Nevertheless, it clearly illustrates the message of the present paper: the coupling between mass transfer and hydrodynamics in the corium system is complex and present peculiarities that can lead to the very different coupled mass transfer/flow regimes depending on the conditions. Because of the experimental difficulties to manipulate such materials, a strong modelling and simulation effort is required for a better characterization of these regimes.



(a) $D_{met}^{steel} = 10^{-9}$m^2.s^{-1}, $D_{oxy}^{O} = 2 \times 10^{-9}$ m^2.s^{-1}

(b) $D_{met}^{steel} = D_{oxy}^{O} = 10^{-9}$m^2.s^{-1}

Figure 4: masses of the different metal phases as a function of time as calculated by a macroscopic model coupling inter-phase mass transfer and droplet dynamics in a simulation setup representative of the RCW experiment - $m_{met\downarrow}$: bottom metal layer mass, $m_{met\uparrow}$: top metal layer mass, $m_{drop\downarrow}$: mass of the falling metal droplets, m_{met}^{eq}: mass of the metal phase at thermodynamic equilibrium - D_{met}^{steel} (resp. D_{oxy}^{O}): effective diffusion coefficient of steel (resp. oxygen) in the metallic phases (resp. oxide phase).



(a) initial state

(b) accumulated mass of molten steel added to the pool as a function of time

(c) time evolution of the mass of the continuous metal phases

Figure 5: setup and illustrative results for an "inversion stratification" transient simulated by a macroscopic model coupling inter-phase mass transfer and droplet dynamics - $m_{met\downarrow}$: bottom metal layer mass, $m_{met\uparrow}$: top metal layer mass, m_{met}^{eq}: mass of the metal phase at thermodynamic equilibrium (adapted from [16])

4. Conclusion

This paper has given an overview of the stratification phenomenology associated with corium during the severe accident of a nuclear reactor in terms of the coupling between mass transfer and hydrodynamics. The limited but critical experimental characterization of the phenomena at play has been discussed and different numerical simulation results have been used to further illustrate the possible coupled mass transfer/flow regimes depending on both the material properties and the accidental scenario. It is the author's opinion that legacy modelling of such phenomena in severe accident dedicated codes are not sufficient to adequately capture the complexity of such transients. Accordingly, in order to reduce the uncertainty and conservatism associated with corium retention evaluations in reactor safety analysis, this paper advocates for a stronger research effort on the basic physical phenomena associated with corium pool stratification. Hopefully, bringing this interesting subject to the attention of a broader scientific research community will serve this purpose.

Acknowledgements

This work has mainly been carried out within the framework of the PROCOR software platform development funded by CEA, EDF and Framatome. The author would like to thank its collaborators from PMC laboratory at Ecole Polytechnique, namely Mathis Plapp and Hervé Henry along with the students involved in our ongoing collaboration on phase-field simulation of stratification (Clément Cardon, Raphaël Zanella and Mirantsoa-Aimé Rasolofomanana).

References

[1] A. De Wit, "Chemo-Hydrodynamic Patterns and Instabilities", *Annual Review of Fluid Mechanics*, vol. 52, no 1, p. 531-555, 2020.

[2] C. Wylock, A. Rednikov, B. Haut, and P. Colinet, "Nonmonotonic Rayleigh-Taylor Instabilities Driven by Gas−Liquid CO_2 Chemisorption," *J. Phys. Chem. B*, p. 7, 2014.

[3] V. Loodts, P. M. J. Trevelyan, L. Rongy, et A. De Wit, "Density profiles around $A + B \rightarrow C$ reaction-diffusion fronts in partially miscible systems: A general classification," *Phys. Rev. E*, vol. 94, no 4, p. 043115, 2016.

[4] D. A. Bratsun and A. De Wit, "Buoyancy-driven pattern formation in reactive immiscible two-layer systems," *Chemical Engineering Science*, vol. 66, no 22, p. 5723-5734, 2011.

[5] B. R. Sehgal and SARNET, Nuclear Safety in Light Water Reactors: Severe Accident Phenomenology. *Academic Press*, 2011.

[6] D. F. Tsurikov, V. F. Strizhov, S. V. Bechta, V. N. Zagriazkin, and N. P. Kiselev, "Main Results of MASCA1 and 2 Projects," RRC Kurchatov Institute, 2007.

[7] G. Ratel, F. Deffort, K. Froment, B. Tourniaire, and J. M. Seiler, "Considerations on mass transfer kinetics for layer inversion and layer oxidation: from MASCA program to the reactor situation," in *Proc. of MASCA-2 Seminar*, Cadarache, France, 2007.

[8] V. I. Almjashev, V. S Granovsky, V. B. Khabensky, S. Y. Kotova, E. V. Krushinov, A. A. Sulatsky, S. A. Vitol, V. V. Gusarov, F. Fichot, B. Michel, P. Piluso, R. Le Tellier, M. Fischer, C. Le Guennic, and N. Bakouta, "Experimental study of transient phenomena in the three-liquid oxidic-metallic corium pool," *Nuclear Engineering and Design*, vol. 332, pp. 31–37, 2018.

[9] R. Zanella, R. Le Tellier, M. Plapp, G. Tegze, and H. Henry, "Three-dimensional numerical simulation of droplet formation by Rayleigh–Taylor instability in multiphase corium," Nuclear Engineering and Design, vol. 379, p. 111177, 2021.

[10] C. Cardon, R. Le Tellier, and M. Plapp, "Modelling of Liquid Phase Segregation in the Uranium-Oxygen Binary System," *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry*, vol. 52, pp. 47–56, 2016.

[11] M.-A. Rasolofomanana, C. Cardon, , M. Plapp, T. Philippe, H. Henry and R. Le Tellier, "Diffuse-interface modelling of multicomponent diffusion and phase separation in the U-O-Zr ternary system," *Computational Materials Science* (submitted).

[12] F. Fichot and L. Carénini, "Some Consequences of Material Interactions for In-Vessel Melt Retention," in *Proc of International Congress on Advances in Nuclear Power Plants. ICAPP 2015*, Nice, France, 2015.

[13] R. Le Tellier, L. Saas, and S. Bajard, “Transient Stratification Modelling of a Corium Pool in a LWR Vessel Lower Head,” *Nuclear Engineering and Design*, vol. 287, pp. 68–77, 2015.

[14] R. Le Tellier, L. Viot, L. Carénini, F. Fichot, N. Bakouta, and A. Filippov, “Transient stratified corium pool modelling for In-Vessel Retention analysis,” in *Proc. of International Seminar “In-Vessel Retention: Outcomes of IVMR Project,*” Juan-les-Pins, France, Jan. 2020.

[15] R. Le Tellier, “Mass transfer between a continuous oxide phase (U-O-Zr) and a steel droplet at liquid state: Potential impact on corium pool behaviour during in-vessel melt retention,” *Nuclear Engineering and Design*, vol. 385, p. 111525, 2021.

[16] R. Le Tellier, “Integral modelling of continuous/dispersed phases mass transfer during in-vessel corium stratification transients,” in *Proc. Of The 10th European Review Meeting on Severe Accident Research (ERMSAR2022)*, Karlsruhe, Germany, 2022.

[17] M. Cavaro, K. Paumel, N. Chikhi, P. Fouquart, J. Delacroix, R. Le Tellier, and V. Bouyer, “Probing Corium in severe nuclear accident experiments: Development of acoustic techniques resisting very high temperatures,” in *Proc. of Meetings on Acoustics*, vol. 38, no. 1, p. 030006, 2019.