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D12.1 Pre-test and post-test numerical analysis of coolant chemistry behaviour in the non-isothermal LBE loop MEXICO

Authors: Alessandro Marino, SCK CEN, Giacomo Gregori, SCK CEN, Jun Lim, SCK CEN



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DOCUMENT SUMMARY

At SCK CEN, a multi-physics thermal hydraulic-chemistry code has been developed based on the online coupling of commercial software Ansys Fluent and HSC-Chemistry. The coupling methods implemented were described and verified with respect to numerical accuracy as described in the *technical note MS28*. Relevant chemical species for coolant chemistry analysis of MYRRHA have been added to an initial version of the code. Furthermore, the thermodynamic database has been completed and improved based on new measurements of critical thermodynamic data such as iron solubility in LBE.

The code was preliminary validated against experiments in stagnant LBE pots. Oxygen concentration changes upon thermal cycling of the LBE were well reproduced. Additional validation has been carried out in the MEXICO loop. With respect to chemistry, the oxygen concentration drop expected from equilibrium simulations due to hematite formation upon cooling, were not observed experimentally. Because the thermodynamic conditions were similar to those tested in stagnant pots, this discrepancy may indicate that kinetic limitations occur due to the fast residence times upon cooling in MEXICO, or the absence of sufficient magnetite oxide suspended in the LBE, which is necessary to initiate the solid to solid reaction for hematite formation.

The findings in MEXICO loop are however very relevant, because the absence of significant oxygen gradients upon thermal cycling within the tested conditions means that efficient oxygen control in the actual reactor is possible. This will be further studied until completion of the project.

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Table of contents

1	Introduction to Task 12.1	7
2	Coupled thermal hydraulic and chemistry code development (MS28)	8
2.1	Theoretical framework.....	9
2.2	Transport operator and Fluent module	9
2.3	Chemical reaction operator and HSC-Chemistry module	10
2.4	Coupling methods	12
2.5	Coupling architecture	14
2.6	Implementation of relevant chemical elements and thermochemical database	15
3	Verification and preliminary validation of the code in stagnant pots and MEXICO loop (MS32). ..	18
3.1	Numerical verification	18
3.2	Preliminary validation in stagnant pots.....	20
3.3	Iron solubility measurement as input for GEM module.....	21
3.4	Preliminary validation in MEXICO loop	24
3.4.1	MEXICO loop installation.....	24
3.4.2	Thermal hydraulic validation.....	25
3.4.3	Chemistry validation.....	27
4	Summary and conclusions.....	29
5	References.....	30

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1 Introduction to Task 12.1

Chemistry control of the coolant is crucial for the safe operation of Gen. IV reactors cooled by LBE, such as MYRRHA [1]. The development of the optimal chemistry control strategy requires fundamental understanding of the main chemical processes in the coolant, including the physicochemical interactions of corrosion products with dissolved oxygen in the liquid LBE and the reaction mechanisms that govern solids formation and deposition onto reactor surfaces. Computational models have been used to complement limited experimental capabilities to predict chemical interactions within the coolant, and their potential impact on reactor safety.

The typical chemical system in an LBE coolant is a multi-phase and multi-component mixture, with elements that may exhibit highly non-ideal behaviour [2]. Furthermore, corrosion products and oxygen mass transport occurs in the presence of complex turbulent flow fields, which have an impact on local concentrations, driving forces for corrosion and ultimately effective reaction rates. An accurate modeling of such a system requires an interdisciplinary approach involving elaborate numerical codes for both turbulent transport phenomena and coolant chemistry. Hence, the goal of this task is to develop multi-physics numerical codes for the coupled simulation of reactor thermal hydraulics and LBE coolant chemistry.

Thermo-chemical equilibrium models that include many species that can occur in MYRRHA have been developed at SCK CEN in the past years [3]. These models are based on the Gibbs free energy minimizing method (GEM) [4]; this method provides an accurate resolution of heterogeneous chemical systems with multiple non-ideal multicomponent solution phases. Despite its advantages in term of modeling capability, the minimization process is a difficult task numerically: the problem is highly non-linear and non-convex while one is interested in the global minimum and not one of the many local minima. An efficient and stable GEM algorithm is essential, but its development is challenging and time-consuming [5]. For this reason, SCK CEN has chosen to use the commercial HSC-Chemistry code from Outotec to benefit from its proven solver accuracy (even at very low concentrations) and speed [6].

Concerning turbulent flows and species mass transport, the computational fluid dynamics (CFD) method offers the resolution required for both detailed design of components and overall plant behavior. The CFD method has been used for the study of nuclear reactor thermal hydraulics widely [7], and several tools have been proposed, including the open source library OpenFoam, and the commercial codes StarCCM+ and Ansys Fluent. For multi-physics chemistry and thermal hydraulics coupling, Fluent has been chosen at SCK CEN as the best compromise between the advantage of using a commercial code and its well-validated physical modeling capabilities, and also the flexibility of solver customization and multi-physics coupling, which can effectively be performed within UDF [8].

In summary, the idea of code development proposed in this project is to retain the advantages of well-documented and validated codes for the solution of each set of equations (hydraulics and chemistry, respectively) and to integrate them in a multi-physics environment using the well-known operator splitting (OS) approach [9]. An initial development of such code was available at SCK CEN and it is described in ref. [10]. Further improvements and additional numerical assessment, specifically required for this task, have been performed as part of MS28 and are summarized hereafter (see Table 1).

The high-resolution tool based on CFD and GEM is computationally expensive when envisaged to perform a long-term transient analysis of the full reactor system, mainly due to the computational cost of the CFD module [10]. It is consequently considered to study MYRRHA chemical behavior mainly in steady state normal operation. The second objective of Task 12.1 was to develop a lower resolution approach for transient analysis, encompassing the main chemical processes occurring in LBE systems at minimum computational cost. This objective was assigned to IPPE, Russia, with the MASKA code [11]. Prior to the final application of the codes to MYRRHA chemistry studies in normal operation (SCK CEN) and transients (IPPE), the work anticipated three preliminary milestones in Table 1, which aimed at acquiring the necessary modeling capabilities (MS28), comparing the two codes predictions (MS29) and validate them against experiments in MEXICO loop (MS32).

Milestone number	Milestone title	Lead beneficiary	Due Date (in months)	Means of verification
MS28	Coupled thermal hydraulic-chemistry codes developed	SCK CEN	12	Technical note
MS29	Blind benchmark on the MEXICO loop simulations performed	SCK CEN	24	Technical note
MS32	Model validated against experiments		30	

Table 1. Milestones foreseen prior to the final application of the codes to MYRRHA chemistry studies.

However, since 2022 the IPPE contribution was removed from the Project, and milestone MS29 was cancelled. MS32 included the simulation and validation of both tools in the MEXICO loop. Preliminary validation experiments in the MEXICO loop have been carried out at SCK CEN, mainly concerning the general GEM prediction of concentration profiles in equilibrium, and thermal hydraulics of the fuel assembly for the transport module. In order to provide additional means for validation of the tool and to compensate the reliability gain that should have been achieved by the blind-benchmarked exercise in MEXICO, SCK CEN have provided also experimental determination and validation of key modeling parameters such as iron solubility in LBE.

The structure of this deliverable is the following. First, the CFD-GEM code developed at SCK CEN is described with the coupling methods in Chapter 2, as a summary of the technical note already provided for MS28. Then, in Chapter 3, the code is verified numerically and part of the models such as hematite reaction are preliminary validated against experiments in stagnant pots. Further validation, as part of MS32, is performed in MEXICO loop in terms of thermal hydraulics and chemistry, with data from a long term blockage experiment performed for MYRRHA relevant normal operating conditions (see WP7.). MS32 is finally completed by adding experimental determination of key modeling parameters such as iron solubility.

2 Coupled thermal hydraulic and chemistry code development (MS28)

A starting point for the multi-physics coupling of CFD and GEM methods exists [10]. The preliminary implementation proved the feasibility of the coupling method, the accessible

computation cost required for a coupled simulation, the numerical accuracy for benchmark test cases, and the flexibility to implement more features, where more knowledge on the main physio-chemical processes governing LBE chemistry is available.

In order to achieve the aim of this task previously described, the following improvements have been considered from the current available version of the coupled tool:

- Continue evaluating systematically the numerical error induced by the coupling method (OS error).
- Based on the new insights of the CCP team on coolant chemistry behavior, implement additional species into the tool such as Ni, Cr, Fe₂O₃ (hematite), Ni oxides, mixed Fe-Ni oxides, intermetallic compounds, solid metallic impurities. The list definition shall be supported also by stand-alone chemical equilibrium calculations leading to thermodynamic stability diagrams.
- Definition/implementation of source and sink terms. This shall continue throughout the entire duration of the project, with updates and improvements based on experiments in MEXICO/others. In a first instance, steel oxidation is neglected because of the low temperatures (to be validated with experiments in MEXICO).

2.1 Theoretical framework

Species (turbulent) transport with the flow in the presence of chemical reactions is termed hereafter as '*reactive transport problem*'. For a multi-component system of n species, the problem can be described with the following general form:

$$\frac{dC_i}{dt} = L_i(C_i) + F_i(C_1, \dots, C_n) + S_i \quad i = 1, 2, \dots, n. \quad (1)$$

where C_i is the concentration of the species i , $L_i(C_i)$ is the transport operator related to the species i , $F_i(C_1, C_2, \dots, C_n)$ is the reaction operator which represents the chemistry influence over the i^{th} species and depends on the local concentration of the other species, and S_i a volumetric source or sink term different from a chemical reaction. Eq. 1 is solved for $n-1$ species where n is the total number of fluid phase chemical species present in the system. The n^{th} species mass amount is then computed from the total mass conservation equation. Eq. 1 is complemented with energy and momentum balance equations providing temperature and flow fields.

2.2 Transport operator and Fluent module

CFD is the method chosen here for solving thermalhydraulic fields and transport operator of the coupled problem. The theoretical basis for industrial CFD are the Reynolds Averaged Navier-Stokes equations (RANS), which consist in a time-averaged derivation of classic Navier-Stokes equations when the instantaneous velocity is decomposed into its time-averaged and fluctuating quantities. RANS equations and numerical aspects of the CFD method including turbulence modeling are well documented topics addressed in several textbooks, also specific for nuclear reactor simulations [7], [12]. In this technical note, only the transport operator is then described, in the framework of a RANS formulation.

The transport operator is composed by an advection term, a molecular diffusion term, and a turbulent diffusion term; assuming a single-phase flow:

$$L_i(C_i) = \vec{\nabla} \cdot (\rho U C_i) - \vec{\nabla} \cdot (D_i \nabla C_i + \rho \overline{u' C_i}) \quad (2)$$

where the velocity U is derived from RANS momentum equation, ρ is the fluid density, D_i is the species i diffusion coefficient, $\rho \overline{u' C_i}$ is the Reynolds flux. This term is usually assumed to be proportional to the concentration gradient, with a proportionality constant termed as Eddy diffusivity. The Reynolds flux reflects the enhanced mixing due to turbulent fluctuations [12].

In the multi-physics tool proposed, RANS equations (mass, momentum and energy equations), including the transport operator $L_i(C_i)$ and a source term S_i , are solved with the commercial CFD software Fluent [8]. As previously mentioned, this code has been chosen because of its well-validated physical modeling capabilities for turbulent flows and also its flexibility with respect to solver customization and multi-physics coupling.

Fluent solves the RANS set of equations using a finite-volume method: the domain is divided into control volumes where RANS equations are integrated to construct algebraic equations for the independent variables. A pressure-based segregated approach (SIMPLE, SIMPEC, PISO) is used for the pressure-velocity coupling, although a density-based solver is also available. The velocity is obtained from the momentum equation, and the pressure field is solved through a pressure correction equation obtained by manipulating the mass continuity and momentum equation. Different spatial discretization methods are available for each term of the equations, ranging from first and second order upwind methods to more complex methods such as MUSCL [8], which is a third-order accurate method. The choice of a specific discretization method for the transport operator in a multi-physics framework will also depend on the accuracy of the chemistry module and on the coupling method, as further discussed in Chapter 2.4. More information on the FLUENT code structure and solution methods are available in the extensive user manual documentation [8].

2.3 Chemical reaction operator and HSC-Chemistry module

The chemical reaction operator $F_i(C_1, C_2 \dots C_n)$ takes into account the contribution to the mass balance of a species i of all reactions. If the characteristic time of a chemical reaction is slower than the time scale of turbulent transport, the reaction is kinetic-controlled. Otherwise, the reaction is assumed to be at local chemical equilibrium.

The reaction operator can hence be divided for simplicity into the respective contribution of a combination of the N_e equilibrium reactions and/or N_k kinetic-controlled chemical reactions:

$$F_i^e(C_1 \dots C_n) = 0; \quad F_i^k(C_1 \dots C_n) = r_k; \quad (3)$$

where r_k is the rate of the specific reaction k .

The overall reactive transport system is composed of $n-1$ transport equations, a mass balance equation for the most abundant component, and $N_e + N_k$ equilibrium and kinetic reactions (in addition to RANS equations for the solution of thermalhydraulic fields).

Presently, a detailed kinetic mechanism for oxide formation in LBE is only available for PbO, which could form in the presence of undesirable oxygen in leaks and upon cooling; PbO

nucleation and growth has been characterized experimentally in ref. [13] and numerically [14] for analysis of abnormal conditions.

On the other hand, kinetic models for corrosion product oxide formation (normal operation), are not yet available. For this reason, the reaction operator for corrosion product impurity chemistry is initially assumed to involve reactions taking place under local chemical equilibrium. Chemical equilibrium is usually a conservative hypothesis in term of the amount of solid phases potentially formed during operation. It also enables the splitting of transport and chemical operators (no tight coupling between operators under equilibrium) and hence the possibility to choose an optimal, dedicated, solution algorithm for the chemistry operator.

An attractive method to model reactions under chemical equilibrium is the Gibbs free Energy Minimization method [4]. The GEM problem consists in the computation of a global equilibrium speciation and phase composition in a chemical system for a given temperature, pressure, bulk composition, standard state thermodynamic data for the dependent components, and all parameters used to describe non-ideal solutions in multi-component phases, such as activity coefficients. The mathematical formulation of the GEM method is described as follows. The chemical state is defined by the total Gibbs free energy G , and its differential changes with the progress variable, which is the number of moles of a reactant, normalized to the stoichiometric coefficient. The total Gibbs energy of a chemical system is the sum of the partial molar Gibbs energies of its components

$$G = \sum_{\alpha} \sum_k n_k^{\alpha} \mu_k^{\alpha} \quad (4)$$

where μ_k^{α} is the chemical potential of species k in phase α (or partial molar Gibbs energy) and n_k^{α} is the number of moles of species k in phase α .

Chemical potentials of pure condensed, (ideal) gas and dissolved species are expressed as follows:

$$\mu_k = \mu_k^{\circ}(T) \quad \text{where } \circ \text{ denotes the standard phase (pure stable phase at 1 bar)} \quad (5)$$

$$\mu_k(T, P) = \mu_k^{\circ}(T, P) + RT \ln P_k \quad \text{where } P_k \text{ is the partial pressure.} \quad (6)$$

$$\mu_k(T, P) = \mu_k^{\circ}(T, P) + RT \ln \gamma_k x_k \quad (7)$$

where γ_k is the activity coefficient of the species k and x_k the molar fraction.

The GEM method computes n_k^{α} such that $G = \min[G(n_k^{\alpha})]$ with elemental mass balance constraints.

The minimization process is a challenging task numerically. The HSC-Chemistry code from Outotec [6] has been selected to solve the reaction operator. This code utilizes its own proprietary algorithm for GEM, characterized by a combination of method of feasible directions with linear programming (LP) problem. The solution of the LP problem is integrated into the search for the new feasible direction, which improves the overall calculation speed [15]. HSC-Chemistry contains an extensive thermodynamic database that can be customized.

2.4 Coupling methods

Given the opportunity to decouple transport and chemistry under chemical equilibrium, and the advantage of using separate commercial solvers for CFD and GEM methods, the proposed multi-physics approach is based on the so-called OS method. The aim is to couple the component solution of each mathematical operator as previously defined, and retain the accuracy of the individual solver within the communication process.

The simplest OS formulation is the sequential non-iterative (SNI) method [16]. After one time step (transients) or iteration (steady state analysis) of a sub-problem, the partial solution is used as a new estimate or boundary condition for the next sub-problem. Studies have shown that species transport and chemical reactions taking place under equilibrium conditions can effectively be de-coupled and solved separately in a sequential mode [17], without the need to iterate between transport and chemical equations. This was also demonstrated in the early stage of development of the current multi-physics code [10] and it is further investigated here.

For the reasons above, an ordinary SNI method is implemented in the coupled code for steady state equilibrium calculations, where the computational procedure for the resolution of one iteration of the global problem is a sequence of one transport (including flow) intermediate iteration in Fluent (Step 1) followed by one chemical intermediate iteration in HSC-Chemistry (Step 2), as summarized in Table 2:

Algorithm 1: SNI method	
$L_i(C_i) + F_i^e(C_1 \dots C_n) + S_i = 0$	Iteration n (global initial problem)
$L_i(C_i) + S_i = 0 \Rightarrow \tilde{C}_i(\vec{x}, n)$	Step 1 $\rightarrow$ Fluent
$F_i^e(\tilde{C}_1 \dots \tilde{C}_n) = 0 \Rightarrow C_i(\vec{x}, n+1)$	Step 2 $\rightarrow$ HSC
$\Rightarrow$	next iteration

Table 2. Algorithm implemented for the SNI method with steady state solver and chemical reactions assumed at equilibrium.

where $\tilde{C}_i$ is the partial solution after the intermediate transport iteration performed in Fluent, $\vec{x}$ is the coordinates vector and C_i is the solution of the global problem after step in HSC.

In practice, Fluent performs a flow and species transport iteration with steady-state solver without bulk chemical reaction and based on the current boundary conditions (e.g. species fluxes at the walls). At the end of a Fluent iteration, arrays of species concentrations and temperatures are the required information passed to HSC to equilibrate the compositions and return local equilibrium concentrations to Fluent. Fluent updates concentrations at each cell as well as boundary conditions that depends on local concentrations, before moving to the next iteration. The iterative process ends when a certain convergence criterion is reached in Fluent for the hydraulic/transport equations and also species composition is at equilibrium.

Even when chemistry is treated under the assumption of local chemical equilibrium, the flow and transport solutions might depend on time, for example during reactor transients or when time dependent boundary conditions are used (e.g. surface steel corrosion/oxidation). The time evolution of the global problem will then consist in a series of steps where local chemistry is always equilibrated within a time step, while flow is evolving.

For such cases, a transient solver is used in Fluent and a number of internal iterations within each time step could be necessary, where the coupling variables are updated until a specified

convergence criterion is reached. In the literature, such a variant of SNI is termed sequential iterative method (SI) [18].

A SI method has been implemented in the code for transient analysis (Table 3), where an adaptive amount of internal iterations are defined between transport and chemistry until local equilibrium is reached within each time step. This strategy is useful to ensure convergence of the operator splitting procedure also using relatively large time steps. The time step size would then be limited by the internal convergence criteria of the flow and transport solver in Fluent. This gives a sort of implicit consistency to the method.

Algorithm 2: SI method

$$\frac{dC_i}{dt} = L_i(C_i) + F_i^e(C_1 \dots C_n) + S_i \quad \text{Time step } n \text{ (global initial problem)}$$

$$\frac{dC_i}{dt} + L_i(C_i) + S_i = 0 \Rightarrow \widetilde{C}_i^1(\vec{x}, t^n) \quad \text{Iteration 1} \rightarrow \text{FLUENT}$$

$$F_i^e(\widetilde{C}_1 \dots \widetilde{C}_n) = 0 \Rightarrow \widetilde{C}_i^2(\vec{x}, t^n) \quad \text{Iteration 2} \rightarrow \text{HSC}$$

$$\text{If Converged: } \widetilde{C}_i^2(\vec{x}, t^n) = C_i(\vec{x}, t^{n+1}) \Rightarrow \text{next time step}$$

$$\text{Else: } \Rightarrow \text{Iteration 3} \rightarrow \text{Fluent}$$

Table 3. Algorithm implemented for the SI method with transient solver and chemical reactions assumed at equilibrium.

where $\widetilde{C}_i^1$ is the partial solution of the problem after the first internal iteration (Fluent), and $\widetilde{C}_i^2$ is the partial solution of the problem after the second internal iteration (HSC).

The number of internal iterations within a time step can vary considerably between applications, and depends mainly on the time step size, spatial discretization, boundary conditions/ source-terms and flow conditions, among others.

A general disadvantage of both SNI and SI methods is the occurrence of numerical errors resulting from both the operator-splitting approach itself and from the time and spatial discretization [19]. Mesh refinement and time stepping are important aspects of a numerical simulation based on OS-method. Sensitivity studies are performed to address the impact of these factors on the numerical error induced by the coupling method.

Furthermore, the overall accuracy of the solution also depends on the discretization schemes of each stand-alone module. Assuming exact integration of the operators and homogeneous boundary conditions, SNI and SI are generally first-order accurate [20].

Additional coupling methods may be considered throughout the entire project if necessary for a specific application, for example when considering a number of kinetic limited reactions where the GEM module is used to calculate thermodynamic quantities required as input in the kinetic model, such as solubility products. The implementation of alternative and higher order coupling schemes is easily reachable in this coupled tool thanks to the flexible coupling architecture, described hereafter.

2.5 Coupling architecture

A specific software integration architecture may directly impact the flexibility of implementing features in a coupled tool, as well as the computational cost of a coupled simulation. Several coupled simulations based on the OS method are designed to perform data exchange between solvers via input/output files, which significantly slows down the overall computational speed.

To optimize communication, a compiled-linked-in code integration method is implemented, where data exchange occurs directly in the main memory and communication stages are handled by a custom-designed coupler class (also compiled and linked to the main software). Such procedure can be achieved thanks to the particular software customization features of HSC-Chemistry and Fluent.

In particular, the HSC installation package includes an application programming interface (API) which provides a flexible way to use HSC methods such as the equilibrium function *StreamEQA* [6], from other programs and libraries. The API uses Component Object Model (COM) approach [21], where objects can be used in environments different from the one in which they were created without knowledge of their internal implementation; thus, COM is an optimal format for the integration of existing codes. The interface is available as a Dynamic Link Library (DLL), which contains the actual program code for the interface and should be included in the codes that aims at accessing HSC methods.

Fluent solver can be accessed and customized with a C-programming interface named UDF. In UDF, a new C-routine or function can be defined and dynamically loaded with the Fluent executable to enhance its standard features [8]. In principle, a COM-interface could be called directly from a C-programming environment such as UDF. However, the HSC COM-interface is designed to deal with reasonably complicated data structures, such as SAFEARRAY, BSTR and VARIANT. Using these structures is more complex than the simple C-style arrays typical of UDF.

To overcome this limitation, the API DLL is firstly included into a custom-designed C++ coupler class, which contains a separate wrapper interface to provide a more reliable way to access COM interface from UDF, without memory leaks. This wrapper is also described in ref. [10]. A second piece of code takes care of interface “open/close” and memory management. Finally, the coupler class is used to define the chemical system, including list of species, chemical state and activity coefficients, as required from Eq. 7 in the GEM method.

To complete the codes integration process, the coupler class is included into a UDF code as a *header* file, so that its functions, including HSC methods, are accessible in Fluent. The OS coupling schemes (Section 2.2) are finally implemented directly in the UDF code to perform a coupled simulation.

In order to integrate the coupler class into UDF, a linking stage is also required. The coupler class, API and UDF code should be linked in the Fluent *user_nt* file [8] and compiled together with the appropriate flags, which have to be specified in the Fluent *makefile* [8]. After the compilation process, the resulting shared libraries (*libudf*) are dynamically linked with the Fluent executable at each run time. Such integration method also enables efficient parallel computing [5]. A schematic representation of the software coupling architecture is shown in Fig. 1.

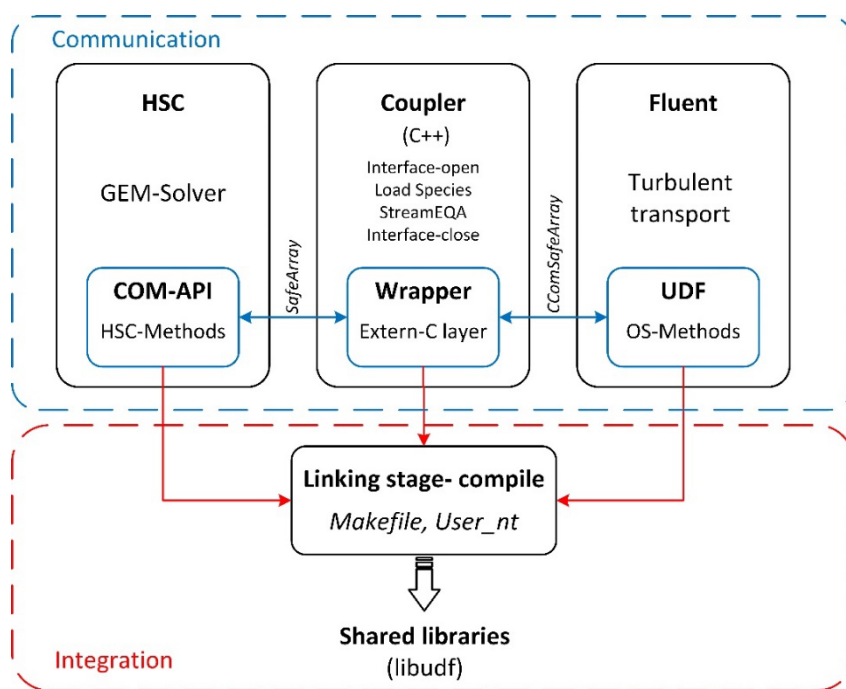


Fig. 1 Scheme of Fluent and HSC-Chemistry coupling architecture as reported in ref. [10].

2.6 Implementation of relevant chemical elements and thermochemical database

The initial development of the coupled code [10] included the implementation of the chemical systems O-PbO-LBE and Fe-O-Fe₃O₄-LBE. These systems define the upper and lower limit, respectively, of the desired dissolved oxygen concentration for MYRRHA temperature range. The oxygen control strategy for MYRRHA aims at keeping a sufficient amount of dissolved oxygen in LBE to promote the formation of protective oxide layers (at least a magnetite oxide) onto steel surfaces, while minimizing the risk of coolant oxidation (PbO is the most stable Pb or Bi oxide) and consequent transport of particles in the primary system. PbO and Fe₃O₄ formation are also well understood experimentally [3], [13].

However, these systems are not sufficient for a comprehensive assessment of all relevant chemical reactions in LBE, their impact on oxygen distributions and additional oxide formation and transport. The first step toward a more complete implementation of relevant chemical elements that could realistically simulate LBE chemistry in MYRRHA, involves the calculation of thermodynamic oxide stability diagrams (Ellingham diagrams).

Such a diagram as shown in Fig. 2 is built using the HSC-Chemistry thermodynamic database and considering the most abundant corrosion products (Fe, Ni, Cr), and other impurities initially present in the LBE. The diagram is only used as a preliminary screening method as oxides are considered to form from pure elements; the real behavior of species interactions in LBE is consequently not accounted. Also, potential non-stoichiometric compositions are initially not considered.

In the graph, one can see that Cr and Al containing oxides are more stable than magnetite. Excess Cr released from corrosion is expected to be fully oxidized in the LBE. During a thermal cycle from the hot region to the cold region of the reactor, Cr-oxides are mostly expected to remain stable, with minimal contribution to the oxygen concentration distribution inside the reactor.

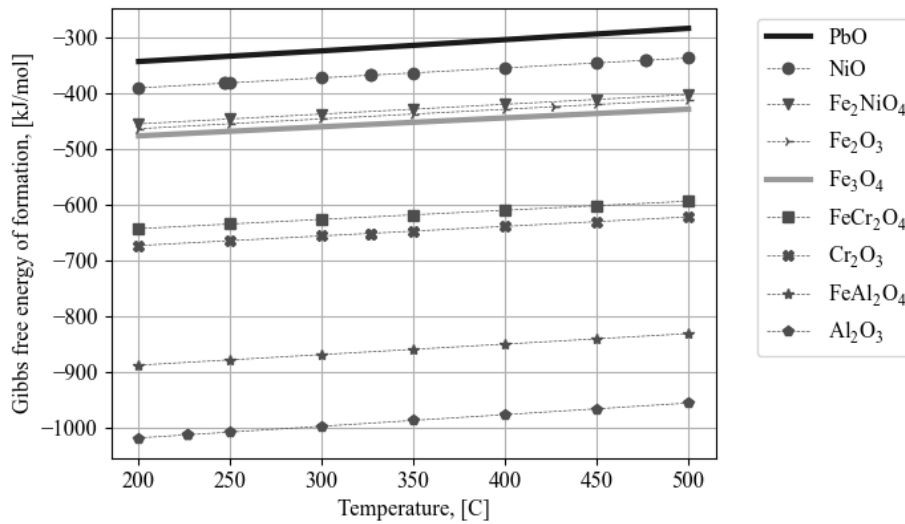


Fig. 2. Ellingham diagram for the oxides produced from the major LBE impurities. The Gibbs free energy of formation was calculated for one mole of oxygen. The data were extracted from the HSC-Chemistry database v.9.9.0.1, see website www.outotec.com/HSC.

On the other hand, three oxides are formed in the range between Fe_3O_4 and PbO : nickel oxide (NiO), mixed iron-nickel oxide (Fe_2NiO_4) and hematite (Fe_2O_3). The formation of Fe_3O_4 in equilibrium conditions is expected to consume almost all dissolved iron before the formation of these other oxides becomes thermodynamically favorable. Consequently, in an LBE system with magnetite present, it is reasonable to consider the formation of Fe_2NiO_4 and Fe_2O_3 from magnetite [22]. The respective reactions are the following:



The aforementioned new oxides are implemented in the coupled code. Their transport should be accurately tracked in the CFD module, as their formation/re-dissolution may impact the oxygen distribution inside the reactor primary system.

In summary, based on preliminary thermochemical calculations combined with experimental observations (see next section) the initial chemical system based on PbO and Fe_3O_4 has been extended with the implementation of dissolved Ni, Cr and relevant oxides. The transport of NiO , Fe_2NiO_4 and Fe_2O_3 should be accounted in the transport module, whereas oxides that are always stable in MYRRHA temperature and oxygen concentration ranges should be accounted for the total Gibbs energy calculation, but their transport in Fluent could be initially neglected as they are not expected to significantly contribute to oxygen concentration distribution in the primary system.

After the chemical system definition, the chemical behavior of the system is modeled based on the Gibbs free energy minimization method described above, which takes into account the real behavior of oxide formation from the elements present in the LBE. This is done by introducing in the formula of chemical potentials of each component, the definition of activity coefficient as in Eq. 6 and 7.

The thermodynamic database of HSC-Chemistry has been customized to implement the real behavior of dissolved Fe, Ni, Cr and O in LBE as well as Pb and Bi in the mixture LBE via their activity coefficients. The derivation of activity coefficients is done with theoretical methods and available experimental data. Specific experiments have been also performed at SCK CEN when the required data were missing, e.g. oxygen Sievert's constant in MYRRHA temperature range [23]. The calculation method and final derivation for the activity coefficients of Pb, Bi and O in LBE are reported in Ref. [24].

The activity coefficient for Fe in LBE is obtained, with a theoretical derivation similar to that reported in [24] using solid iron as a reference and initially solubility data from Gosse' [25]:

$$\ln(\gamma_{Fe(LBE)}) = \frac{10128}{T} - 1.33890 \quad (11)$$

This thermodynamic data is very important for LBE chemistry, as iron is the key element for oxide formation in the temperature range of MYRRHA. Therefore, the direct and accurate measurement of iron solubility has been performed within the task, which gives more reliability to the entire modelling package. This also compensates the missing contribution/benchmark from IPPE, as mentioned in the task introduction. The measurement of iron solubility, and the resulting new activity coefficient is presented briefly in Chapter 3.

Concerning the activity coefficient for Ni in LBE, it is derived with a model proposed by Gosse' [25], which analyses solubility data measured by Martinelli [26]. Gosse' model has also been updated to include the recent work on binary liquids Bi-Ni and Bi-Pb from Liu et al. and Gokcen et al., respectively [27]:

$$\ln(\gamma_{Ni(LBE)}) = 20.9479 - \frac{934.6764}{T} - 2.901 \cdot \ln(T) \quad (12)$$

The activity coefficient for Cr in LBE is derived from an assessment of the Bi-Cr system made recently by Gossé [25]:

$$\ln(\gamma_{Cr(LBE)}) = \frac{7036.93}{T} + 0.6348 \quad (13)$$

A detailed description of the thermodynamic calculations goes beyond the scope of this Deliverable and is therefore omitted. This description will be made available as part of reports on previous activities performed at SCK CEN.

For solid oxides, the required data are only the standard state chemical potentials as in Eq. 5. Initially, standard state chemical potentials provided by HSC-Chemistry default database have been considered. Experiments should verify the reliability of those data. On this regard, an experimental work recently performed at SCK CEN in the framework of this project aimed at characterizing Fe₂O₃ equilibrium behaviour in LBE [22].

Based on this experiment, the default thermodynamic data of Fe₂O₃ from HSC-Chemistry database proved to be not sufficiently accurate in describing Fe₂O₃ equilibrium, at least in the extrapolation range of MYRRHA temperatures. On the other hand, standard state chemical potential data of Fe₂O₃ from Barin database [28] well reproduced experimental observations and for this reason it has been implemented in HSC-chemistry for this oxide.

3 Verification and preliminary validation of the code in stagnant pots and MEXICO loop (MS32)

This chapter presents the results obtained so far, which were focused on gaining the required confidence in the numerical tool, prior to the simulation to the MYRRHA system. This includes the numerical verification of the coupling methods firstly (Chapter 3.1), an initial validation of hematite formation against stagnant pots experiments (Chapter 3.2), the experimental determination of iron solubility in LBE, which is a separate section but it's also performed in the framework of improving database reliability (Chapter 3.3), and finally the comparison with experimental data from the non-isothermal operation of MEXICO loop (Chapter 3.4)

3.1 Numerical verification

The solution of a coupled simulation based on Fluent and HSC-Chemistry is verified hereafter against stand-alone HSC simulations, which is a clear way to verify how the coupling method retains the accuracy of the solution of the stand-alone modules.

The first example aims at verifying the newly implemented hematite formation reaction (Eq. 10). The computational domain consists of a pipe-flow uniformly cooled down from an inlet temperature of 500°C to an outlet temperature of 200°C. The boundary conditions are summarized in Fig. 3. Fe_3O_4 is expected to be converted into Fe_2O_3 according to Eq. 10, during cooling of the LBE, at sufficiently high inlet oxygen concentration.

Species fluxes and/or sources/sinks are neglected and the flow is highly convective. Excluded any transport limitations, a coupled transport-chemistry simulation should hence provide identical results of a stand-alone HSC- simulation. The goal of the example is therefore limited to verifying the numerical errors induced only by the coupling method.

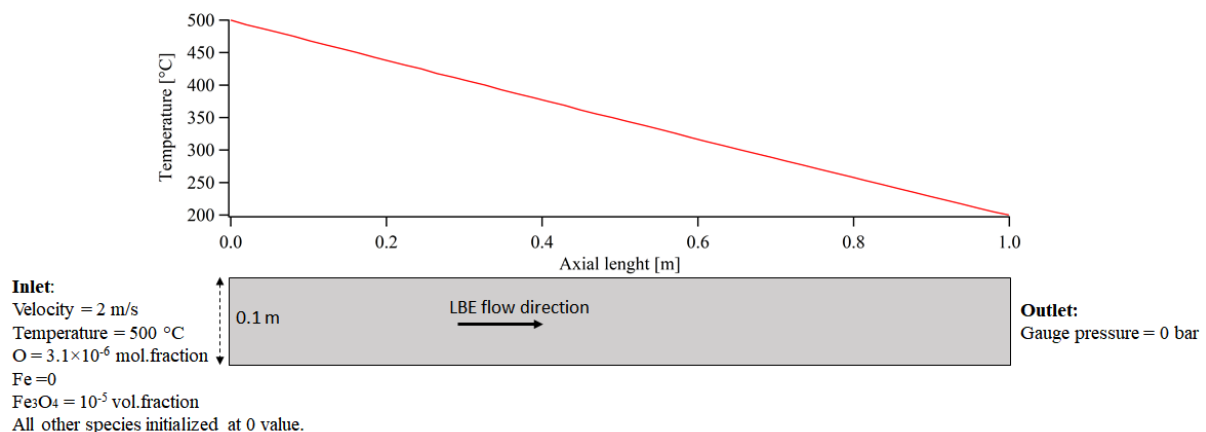


Fig. 3. Computational domain and boundary conditions for hematite formation example.

Concerning the numerical settings of the transport module (Fluent), sensitivity studies on the spatial discretization schemes and mesh refinement are performed to address their impact on the OS-error. In particular, a first order upwind, second order upwind, and third order MUSCL discretization scheme are tested. Two different mesh refinements are also considered (mainly relevant in the axial direction). The results are summarized in Fig. 4 and Fig. 5.

The results show the equilibrium oxygen concentration during cooling with the flow direction. With the defined inlet conditions, hematite formation starts at about 340 °C. The reaction

consumes dissolved oxygen upon further cooling. In Fig. 4, one can see a very good agreement between a coupled simulation and a stand-alone HSC simulation across the entire domain, even with a coarse axial grid resolution. The onset of hematite formation is magnified in the figure to show the (limited) effect of spatial discretization schemes. In a first-order upwind method, the face-value of a quantity is set equal to the cell-center value of the quantity in the upstream cell. With a low mesh refinement, this node lies upstream the onset of hematite formation, causing a slightly deviating prediction also in the cell downstream. A third order MUSCL scheme shows slightly better match with the expected trend in the reaction zone, for the given grid refinement. This method uses a central-differencing discretization scheme (three cells involved) which is also prone to ‘checker-board errors’ close to large discontinuities, causing the minor miss prediction to propagate one cell further downstream with respect to upwind. The difference between coupling schemes and with respect to stand-alone HSC becomes even less noticeable when mesh is refined in the axial direction, as shown in Fig. 5. In practice, minor differences in the predicted oxygen trends from a coupled simulation compared to stand-alone HSC may only be expected at onset temperature, where the onset of steep gradients occurs.

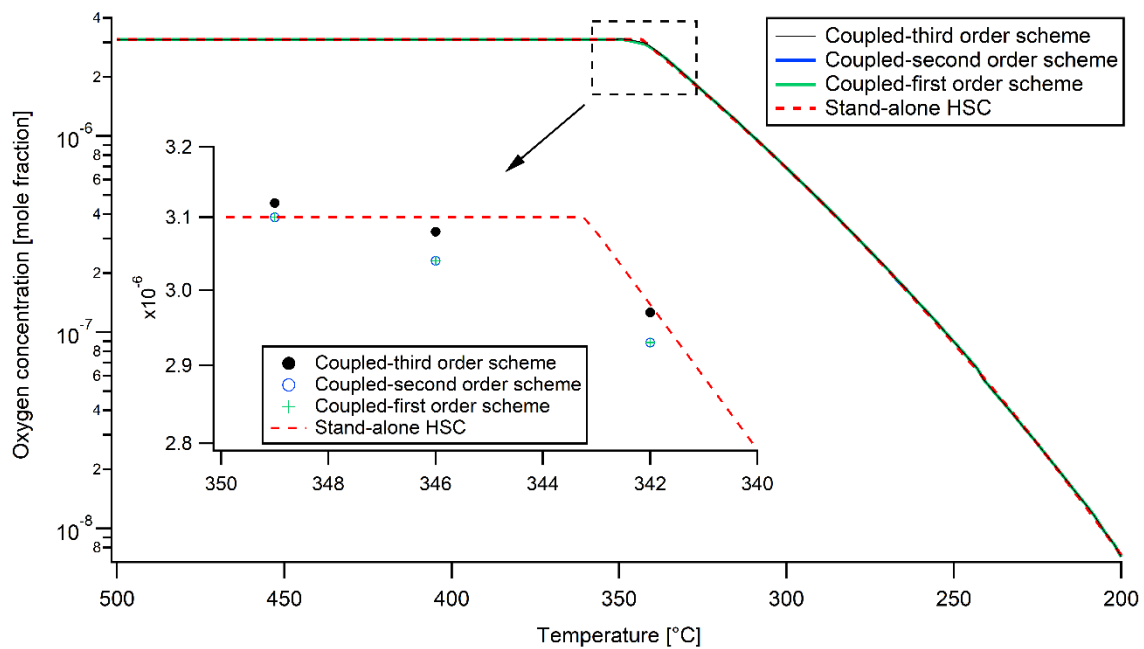


Fig. 4. Comparison between coupled simulation and stand-alone HSC calculation of Fe_2O_3 precipitation/dissolution equilibria. Sensitivity study on the spatial discretization methods of the transport module, for a coarse mesh of 6 x 60 cells.

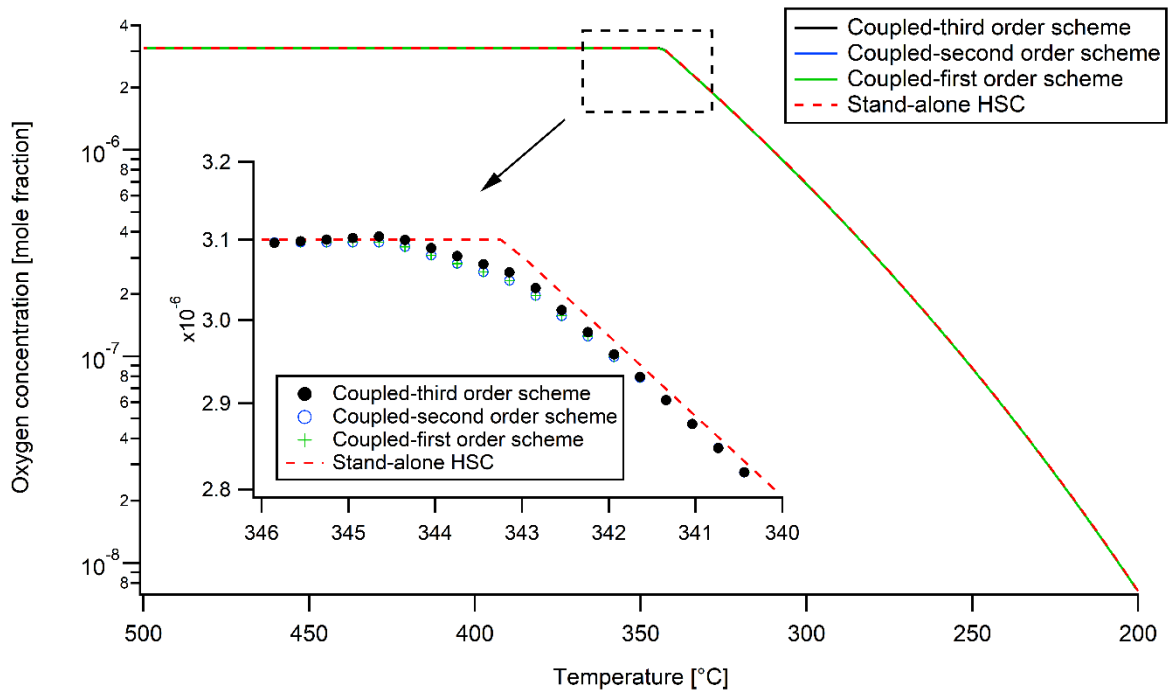


Fig. 5. Comparison between coupled simulation and stand-alone HSC calculation of Fe_2O_3 precipitation/dissolution equilibria. Sensitivity study on the spatial discretization methods of the transport module, for a fine mesh of 20 x 400 cells.

Similar results were obtained for verification examples of PbO equilibrium reaction presented in ref. [10], also characterized by sharp changes of the gradients at the onset of precipitation, whereas magnetite equilibrium proved to be less sensitive to grid refinement as this oxide is always present (stable in the domain) and partial formation/re-dissolution involve smoother reaction fronts.

From a numerical point of view, the coupled tool based on CFD and HSC-Chemistry proved to be accurate with respect to the coupling methods, and can be considered verified.

3.2 Preliminary validation in stagnant pots

An experimental campaign with thermal cycling in a small-scale LBE autoclave [22] has been performed, which aimed at confirming hematite formation reaction from magnetite, and its effect on dissolved oxygen.

Fig. 6 shows a very good agreement between oxygen trends predicted by a coupled simulation based on chemical equilibrium and the experimental results; even though the simulated autoclave does not include any relevant mass transfer limitation to require a coupled simulation, the comparison is useful to confirm that hematite formation is probably a key reaction for MYRRHA operating conditions; also the set of thermodynamic data chosen in Chapter 2.6 and implemented in the numerical tool proved reliable as a first approximation.

The few degree higher onset temperature measured by experiments, may be due to slight kinetic limitation or some minor error/uncertainty in the thermodynamic data-set for this reaction. This also justifies, direct iron solubility measurement in Chapter 3.3. However, most

recent analysis (to be confirmed) show an even better agreement by using JANAF database for magnetite and hematite thermodynamic properties.

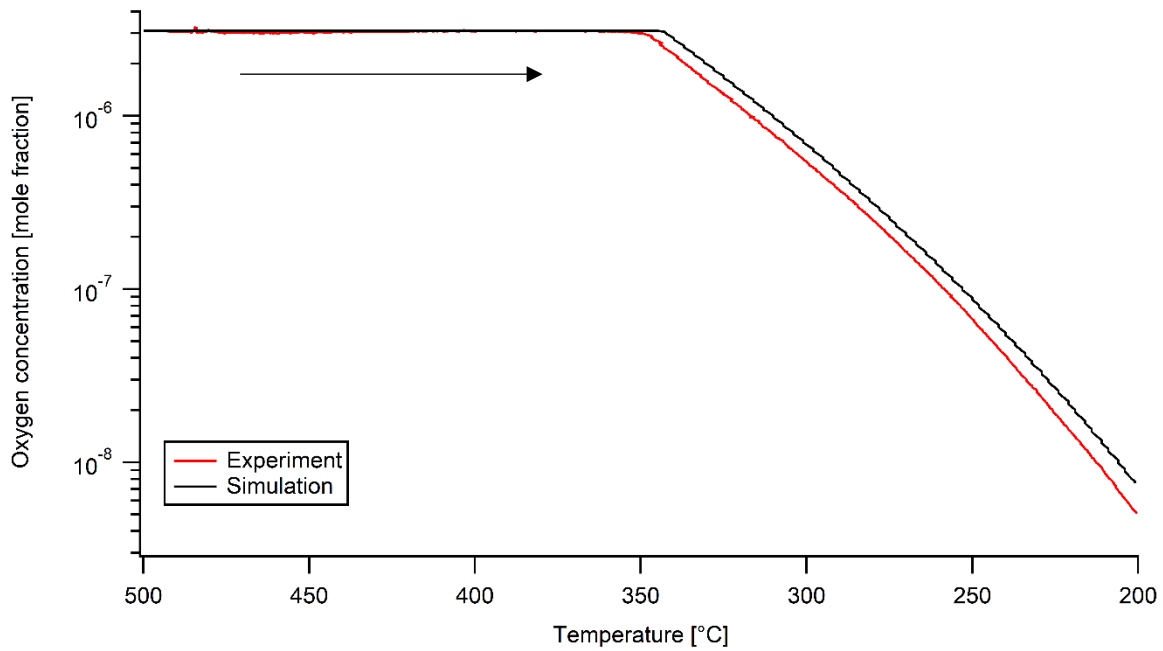
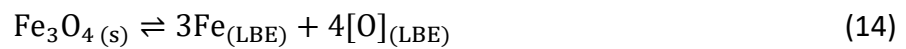


Fig. 6. Comparison between oxygen concentration trends during LBE cooling predicted by coupled simulation and experiments performed in small scale autoclaves LBE [22].

It should be noted that in the previous test-case simulation, the solid phase is assumed to be mixed at the molecular level with the LBE. In practical applications however, flotation and accumulation of particles is relevant; solid particles will hence be treated as an Eulerian phase in the transport module, when required.

3.3 Iron solubility measurement as input for GEM module

The characterization of Fe-O-Pb-Bi system is considered fundamental for a LBE-cooled ADS because Fe is the main component of steel, and because the $\text{Fe}_{(\text{LBE})}/\text{Fe}_3\text{O}_{4(s)}$ equilibrium can influence the local oxygen content of the coolant according to the following chemical process:



In a recent publication from Gregori et al. [23] an advanced electrochemical method was presented to measure the magnetite (Fe_3O_4) solubility product and the iron solubility limit in LBE by oxygen solid-state ionic devices: iron is dissolved in LBE closely to the solubility limit by dissolution of solid metal. Subsequently, a controlled amount of oxygen is added to LBE with an electrochemical oxygen pump (EOP) by a coulometric titration. This causes the oxidation of dissolved iron and the change of oxygen concentration in LBE, according to the following differential equation:

$$\left(\frac{dC_{O,\text{LBE}}}{dt} \right) = \frac{r_{O(t)}}{1 + \frac{16 M_O}{9 M_{Fe}} K_{sp}^{1/3} C_{O,\text{LBE}}^{-7/3}} \quad (15)$$

where K_{sp} is the magnetite solubility product, M_O and M_{Fe} are the molar mass of oxygen and iron respectively, and $r_{O(t)}$ is the time-dependent oxygen addition rate derived from the EOP.

The actual evolution of oxygen concentration can be measured by an electrochemical oxygen sensor (EOS). By fitting Eq. (15) to the measured oxygen trend and the oxygen addition rate with K_{sp} as the unique fitting parameter, an accurate measurement of the magnetite solubility product is achieved. Subsequently, the solubility product can be converted into iron solubility as follows:

$$S_{Fe} = \left(\frac{K_{sp}}{C_{O, Fe(LBE) \leftrightarrow Fe(s)}^4} \right)^{1/3} \quad (16)$$

where $C_{O, Fe(LBE) \leftrightarrow Fe(s)}^4$ is the oxygen concentration for the $Fe_{(LBE)}/Fe_3O_{4(s)}$ in Fe saturated-LBE, which can be easily derived from thermodynamic data in literature.

The experimental measurements were carried out in a small-scale facility (Fig. 7), by melting LBE in a alumina crucible, with one EOS and two EOPs connected in parallel to a constant potential generator.

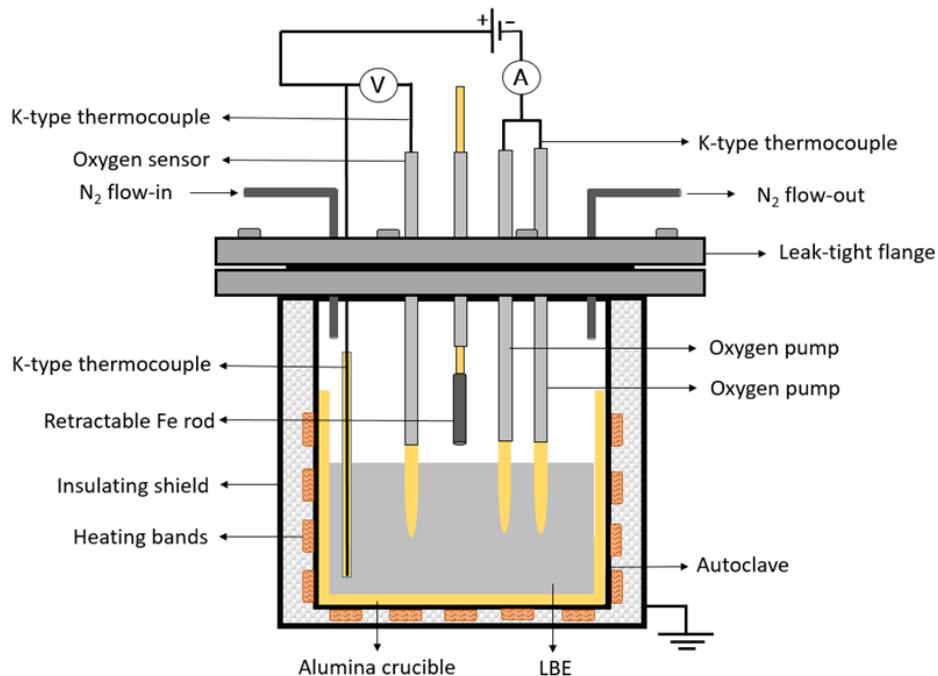


Fig. 7. Experimental facility used in this study [29].

Fig. 8-a shows an example of the typical exponential increase recorded in oxygen concentration during titration. Eq. (15) was fitted to this oxygen evolution to determine the solubility product. Subsequently, the value of K_{sp} was used to plot the fitted trend of oxygen along with the experimental value. As shown in Fig. 8-b, a good matching was obtained indicating the reliability of the experimental and numerical methods. Finally, the values of solubility product of magnetite were converted into the solubility. Fig. 9 depicts how the measured solubility follows the expected trend Hoff-like linear trend and matches perfectly with the values predicted by Martynov's law. In addition, this method allowed for the first time the measurement of iron solubility below 823 K.

The data were fitted with a linear regression to the following thermal law for iron solubility in LBE:

$$\log_{10}(S_{Fe [wt.\%]}) = 1.961 - \frac{4335}{T_{[K]}} \quad (723-826 \text{ K}) \quad (17)$$

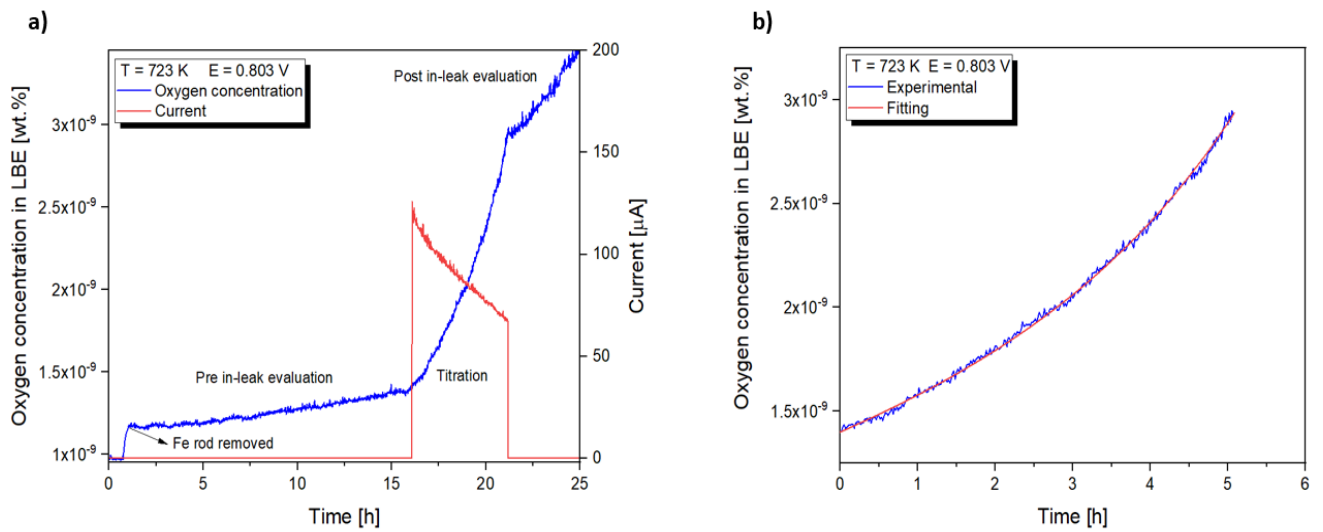


Fig. 8. a) whole experimental session of coulometric titration. b) comparison between experimental and fitted oxygen trends [29].

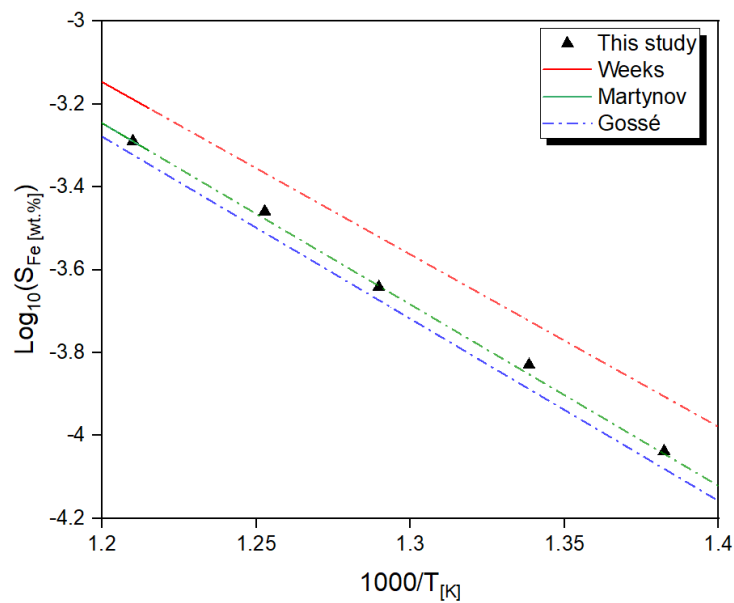


Fig. 9. Thermal trend of iron solubility compared to literature data [29].

Equation (17) is used as boundary condition for dissolution-corrosion modelling in a CFD simulation, and as an input for the activity coefficient for the GEM module.

3.4 Preliminary validation in MEXICO loop

3.4.1 MEXICO loop installation

The MEXICO loop is a forced convection, non-isothermal LBE loop designed for coolant chemistry measurements for the MYRRHA research program. The loop is also equipped with the necessary instrumentation for thermal hydraulic measurements, at specific locations. MEXICO was recently refurbished to host experiments with a heated fuel assembly for WP7.1.

A new test section has been installed with the 7 heated pins, which replaces the old one used to study oxygen control by a PbO mass exchanger. A newly installed, larger, air cooler removes 84 kW of power from the pins and has now differential pressure measurement and oxygen sensors installed at its inlet and outlet to monitor the chemical behaviour upon cooling. A new electromagnetic pump with permanent magnets has been installed in the cold-section of the loop, which now enhances reliability for long-term operation. A Coriolis flow meter is installed after the pump to measure the mass flow rate. The expansion tank of ca 100 liter located after the test section, in the hot region, enables regulation of the dissolved oxygen activity by an electrochemical oxygen pumping system. Filters are placed in the cold section of the loop, allowing purification of the coolant by cold trapping and or mechanical filtration. The filters mesh size is now 10 micron. In this test, a cold trap was used to purify the LBE.

Pressure drops can be measured over the whole loop, across the filters, air cooler and across the test section by differential pressure transducers from EMERSON. Thermocouples are located along the entire loop, including the test section. In order to monitor the dissolved oxygen concentration in the LBE during operation, there are several sensing ports including one before and one after the test section and the air cooler. Chemistry validation is in fact relevant upon heating up or cooling down the LBE streams. Fig. 10 shows a schematic of the refurbished MEXICO loop.

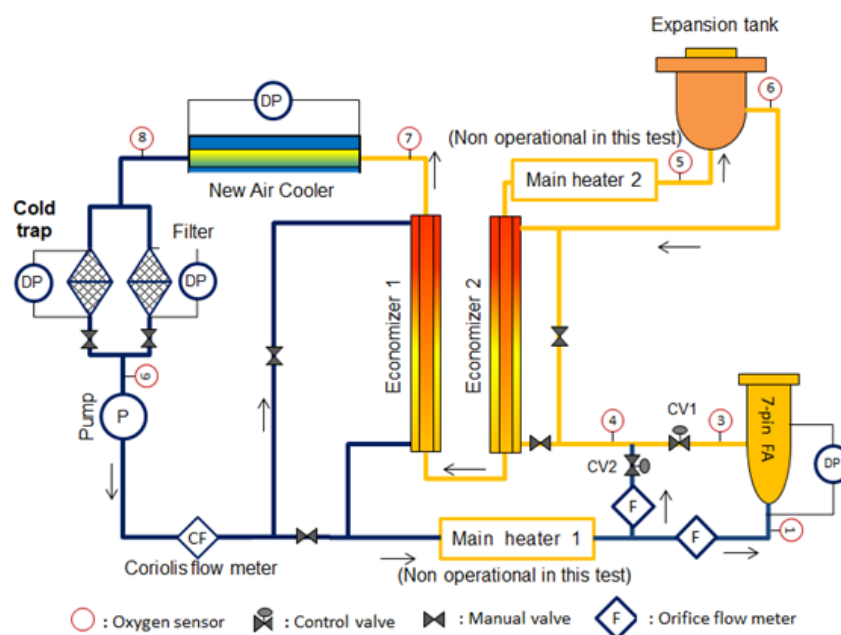


Fig. 10. Schematic drawing of MEXICO loop.

3.4.2 Thermal hydraulic validation

Although thermal hydraulic validation is not the main objective of this task, it is clear that the reliability of a coupled simulation depends also on the CFD module prediction. Within Task 7.1, a 7-pin heated fuel assembly experiment has been running in MEXICO, which provides a validation platform for the wire pitch pressure drop simulation of a scaled wire-wrapped MYRRHA fuel assembly, and also for temperature profiles prediction. To this aim, the bundle was equipped with three different differential pressure transducers along the axial direction and the so-called pressure station, which minimizes the experimental error due to setup, by flushing and venting the sensors from air pockets as well as keeping uniform temperature in the measurement region. The bundle is also equipped with thermocouple of only 0.25 mm sensing tip, placed at the outlet cross section. Wire functionality is replaced by multi-point thermocouples, as described more in detailed in *Deliverable7.1* of this project [30]. More details on the experimental set up, and experimental results (also in relation to chemistry) will be detailed in a separate Deliverable within Task 7.1. Hereafter, only a summary is given, with the simulations results shown in Fig. 11 and the comparison with the experiments in Fig. 12.

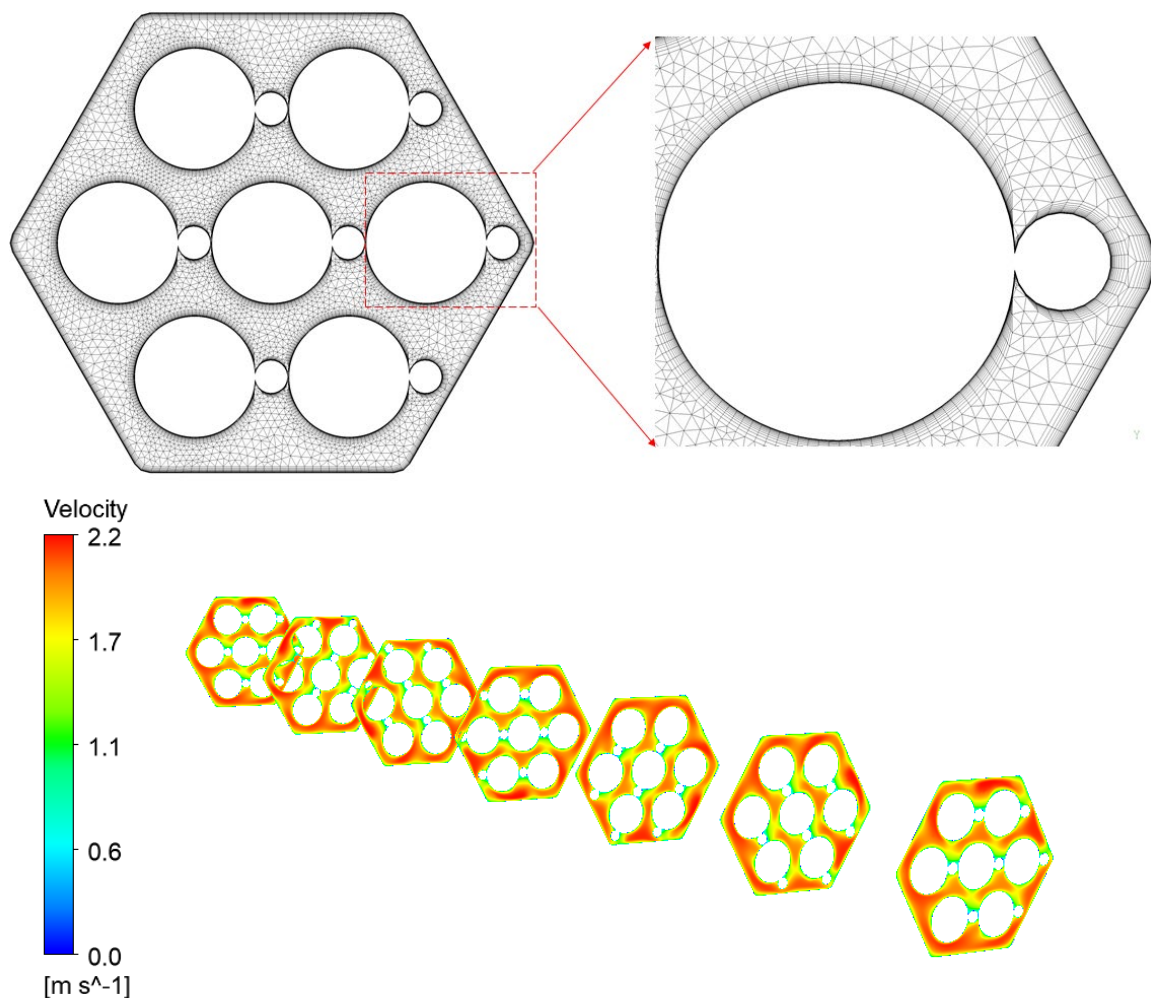


Fig. 11. Highest resolution mesh used for the simulations (top) and velocity contour at different cross sections of the 7-pin computational domain (bottom).

The velocity contours show typical profiles of wire-wrapped configuration, with local and global swirl motion due to the wire pitch. Sensitivity studies were performed on mesh and

discretization schemes. Parametric studies were also performed on different modelling approaches of the wire, more specifically the wire to surface contact region. In summary, the discretization order for turbulence turned to have an important effect on the results. y^+ has been extensively evaluated in literature, and also in this work it was confirmed that it should be kept below one and be aware of possible inconsistency when placing the first node in the viscous sublayer. The modelling of the wire can also account for a few percent of the pressure drop so the optimal geometrical model should be implemented for validation.

Based on the aforementioned, simulations have been compared with experimental wire pitch pressure drops. The agreement was always within 5%, for each model and/or setting. The best agreement was found for the high resolution schemes, the contact point between wire and surface, y^+ around one -as expected. This validation exercise increases the confidence on the use of CFD codes for design of fuel assemblies in flowing LBE.

Mass flow [kg/s]	Experiment [bar]	Model #1 $Y^+ = 1$ 2 rd order turbulence	Model #2 $Y^+ = 1$ 2 rd order turbulence	Model #3 $Y^+ = 1$ 2 rd order turbulence	Model #3 $Y^+ = 1$, 1 st order turbulence	Model #3 $Y^+ = 4$ 2 rd order turbulence
5.3	0.255±0.0004	0.2435	0.2466	0.247	0.243	0.254

Table 3. Summary of the sensitivity studies for the reference flow rate of the experiment (highest Reynolds number in Fig. 11).

In the figure, one can see an excellent agreement between simulations and experiments for different value of flow rate (Reynolds number) in the fully turbulent region. The validation of the heat transfer simulation is currently ongoing and it will be presented in the following reporting period.

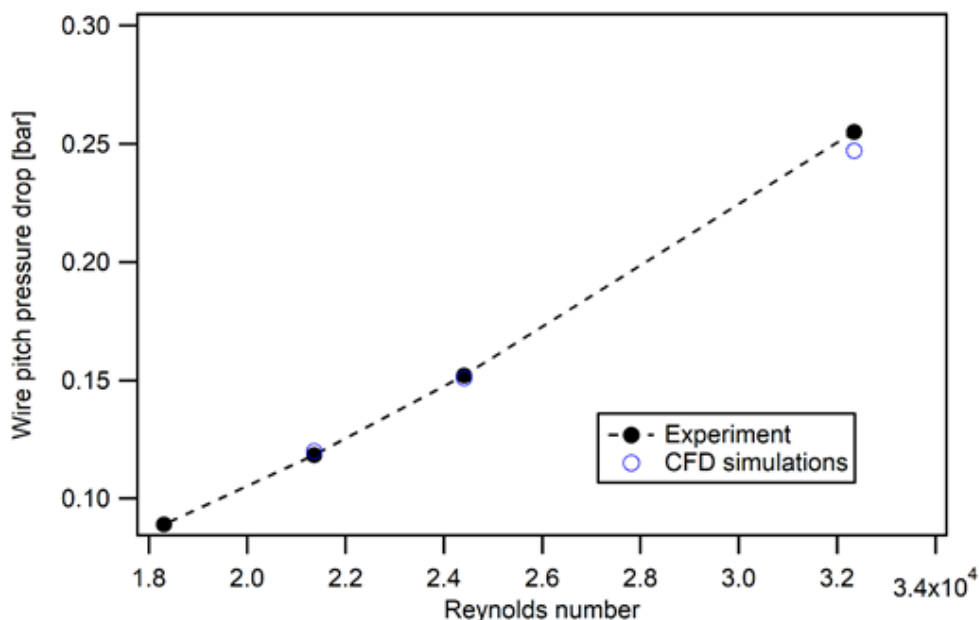


Fig. 11. Comparison between experimental and CFD prediction of wire-pitch pressure loss of the 7-pin isothermal bundle at 200°C as a function of the Reynolds number.

3.4.3 Chemistry validation

After verification of the coupling method, and the preliminary chemistry validation in LBE stagnant pots previously reported, the following milestone aimed at extending the prediction capabilities to large scale non-isothermal loops. An initial validation of this code was already performed on magnetite equilibrium reaction in the CRAFT loop at SCK CEN, as reported in ref. [10]. Within this task, the goal was the prediction of the main chemistry behaviour of MEXICO loop, and in particular the validation of the chemical behaviour due to the newly implemented elements and oxides, such as hematite.

MEXICO has been operating for a long term blockage and clad corrosion experiment, in the framework of Task 7.1. The operating conditions of the loop could not be parametrically changed, in order not to disturb the current test. However, the current operating conditions of MEXICO should be representative of MYRRHA reactor nominal operation, and therefore relevant to the final goal of the MYRRHA normal operation coolant chemistry simulation.

Fig. 12 shows the steady state oxygen concentration and temperature profiles over part of the long-term experiment, in the cold leg, FA inlet, and hot leg, respectively. In the figure, one can see that the oxygen trend is rather constant in time: since no active oxygen supply¹ is provided in this time interval, one can conclude that oxidation kinetics at the steel surfaces and across the FA are limited. This confirms the validity of the initial hypothesis of neglecting steel surface oxidation at these temperatures, and focusing on bulk chemistry mainly.

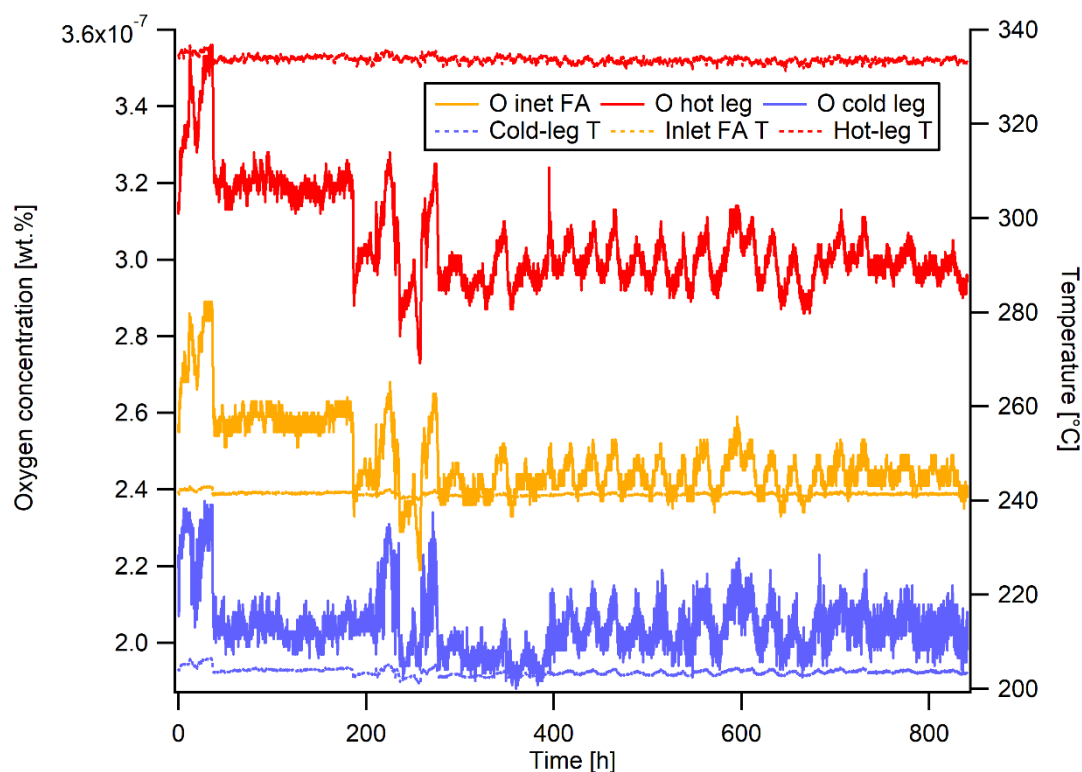


Fig. 12. Experiment performed in MEXICO loop: Oxygen concentration profiles in the different temperature regions of the loop.

¹ In practice it is possible that minor oxygen sources are present in the loop, such as PbO deposited in the pipelines after maintenance that re-dissolve. That is compensated by the cold trap, that in these conditions works in the so-called PbO grow region [13], and therefore with minor oxygen removal rate.

The most relevant outcome of the experiment is however the oxygen concentration trend upon the cooling and heating sections, where chemical reactions are expected to occur based on thermodynamic equilibrium calculations.

From the figure, one can see that there is a gradient between oxygen concentration moving from the hot leg at about 330 °C and 3×10^{-7} wt.% to the cold leg at 200 °C and 2×10^{-7} wt.%. Oxygen increased slightly again to 2.5×10^{-7} wt.% passing through the main heater 1 (inlet FA) at 240 °C. It is evident that these differences are small, and almost within uncertainty range of the oxygen sensor (including its correlation to convert voltage to partial pressure/concentration).

Simulations were then performed to mimic the MEXICO experiment, firstly considering only the HSC stand-alone module. This enables to identify eventual discrepancies with the experiment either in the hypothesis of chemical equilibrium, or in the hypothesis that mass transfer is not limiting reaction rates in a loop-type configuration. This approach is justified by the fact that numerical modelling of magnetite and hematite formation have been validated already in stagnant pots, under conditions close to chemical equilibrium.

The results (Fig. 13) show that the oxygen concentration upon cooling down to 200 °C should decrease to about 7×10^{-8} wt.% according to equilibrium reaction of hematite formation, whereas the equilibrium concentration after heating up to 240 °C should re-increase to about 3×10^{-7} wt.%, as the hot leg concentration. The predicted equilibrium oxygen concentration at 240 °C is closer to the experiments than that predicted in the cold trap outlet.

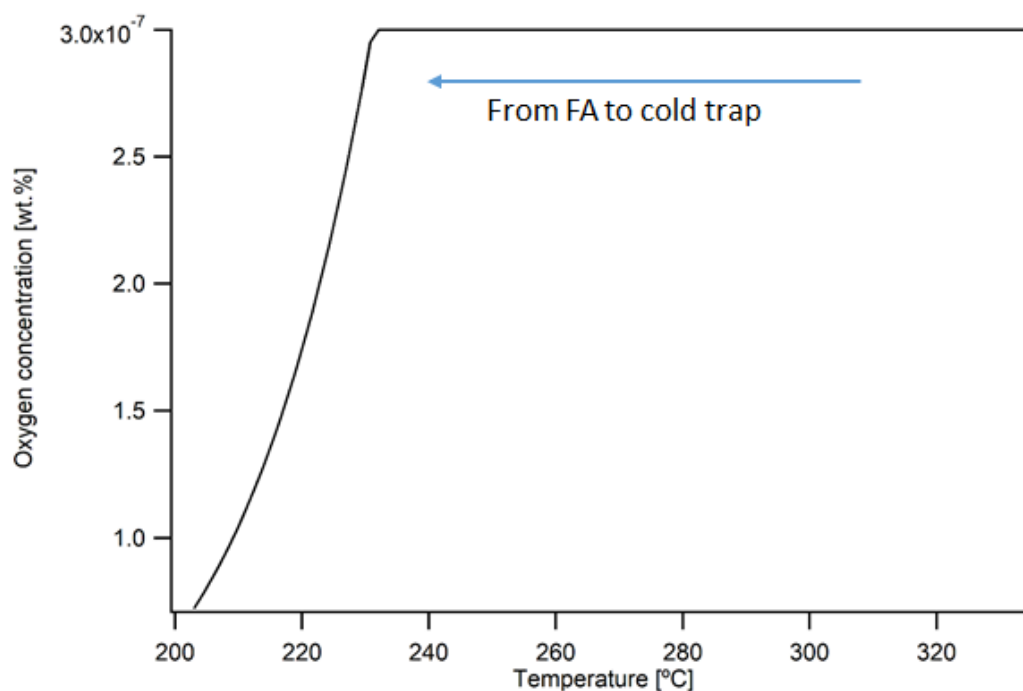


Fig. 13. Simulation of MEXICO loop experiment: oxygen concentration profiles along different temperature regions of the loop.

As anticipated, the reasons of this difference may be related to kinetics. It is possible that equilibrium is not reached because cooling/heating rates are much faster than the kinetics of oxide formation and dissolution. This was already previously observed in stagnant pots, where

the effect of cooling rates was addressed in ref. [22]. This hypothesis can be confirmed when the current long-term experiment in MEXICO will be completed, and the flow rate in the loop can be decreased parametrically.

The second possibility is that the reaction of conversion of magnetite into hematite is precluded by the absence of enough magnetite suspended particles in the LBE. This could be possible due to the relatively low operating temperatures of MEXICO and consequently low corrosion product release rate. The current corrosion experiment may release by the end of the test a sufficient amount of impurity to enable solid-to solid oxide reaction, although flotation of particle to the free surface of the MEXICO expansion tank cannot be excluded as well.

It is also not straightforward to verify the presence of suspended magnetite indirectly by trying studying magnetite solubility products in MEXICO, because in the current excess oxygen region, the oxygen concentration is expected to stay rather constant upon heating/cooling [3].

Kinetic studies of hematite formation are currently being performed at SCK CEN that could provide more insights in the future and extend the current chemical equilibrium model to take into account reaction kinetics. Although this initial validation test could not confirm the predicted hematite equilibrium behaviour fully, it suggests that oxygen drop upon cooling due to hematite formation in MYRRHA (with similar heating/cooling rates of the experiment) may be avoided based on the obtained results. This is a positive outcome of this work, because an oxygen drop in the cold plenum such as that predicted by chemical equilibrium, may create issues for the oxygen control system that should compensate for that “sink”, before the inlet of the FA. If this is confirmed at different cooling rates, it would imply that LBE coolant chemistry behaviour in MYRRHA is dominated mainly by magnetite equilibrium during normal operation, and PbO formation during accidents.

4 Summary and conclusions

A multi-physics computational tool based on the coupling of CFD and GEM methods has been developed at SCK CEN for the accurate simulation of coolant chemistry in the MYRRHA reactor. The coupling method is based on the operating splitting approach, with different coupling schemes implemented for communication and time stepping, including sequential iterative and non-iterative methods. Furthermore, a software integration technique based on *DLL* and *COM* enables fast data-transfer through the main memory, and efficient parallel computing.

The code includes now several species such as dissolved iron, nickel and chromium, oxygen, iron oxides such as hematite and others that have been implemented specifically for this task. The choice of the additional chemical species to be implemented was defined by preliminary GEM simulations with HSC-Chemistry for MYRRHA reactor relevant operating conditions. Key modelling parameters were also identified for further investigation, or direct measurement for the most critical, such as iron solubility.

The coupled code was verified against standalone HSC calculations for highly convective flows (where the same solution can be expected) and very good numerical accuracy was found, even for test cases dealing with stiff chemical reaction fronts, such as PbO formation. In general,

for those cases, mesh refinement and order of the discretization schemes should be verified case by case, for optimal accuracy.

Simulations were then compared with experiments, initially in stagnant pots. Oxygen profiles during thermal cycles were well reproduced, particularly for the thermodynamic condition where hematite is expected to be stable and an oxygen drop is expected at low temperatures. Further validation was attempted with the simulation of the non-isothermal loop MEXICO, in operating conditions typical of MYRRHA operation. In this case, simulations predicted a higher oxygen decrease across the cold leg than the actual experiment. Because the expected reactions are well reproduced in stagnant pots, this difference may be attributed mainly to two reasons: either the kinetics of hematite reaction are too slow with respect to LBE residence times upon cooling and heating in MEXICO (which are representative of MYRRHA), or there is not enough magnetite particles suspended in the LBE to enable the transition from solid magnetite to hematite. Further investigations will be performed, when additional impurities release during the corrosion experiment might generate a sufficient source term. At the end of the current FA long-term experimental run, also tests at different cooling/heating rate with fuel assembly operation can be performed to verify the effect of kinetics versus residence time.

To enhance the reliability of the multi-physics simulator, and compensate for the missing contribution initially expected from IPPE, the solubility of iron has been measured directly by electrochemical methods for temperature ranges representative of MYRRHA. Having reliable thermodynamic data of iron solubility in LBE gives also more confidence in the interpretation given of the validation exercise in the MEXICO loop.

5 References

- [1] J.-L. Courouau, J.-C. Robin "Chemistry control analysis of lead alloys systems to be used as nuclear coolant or spallation target", *Journal of Nuclear Materials*, 335 (2004), 264-269.
- [2] A. Aerts et al., "The Chemistry and Conditioning Programme for MYRRHA", *International Conference on Fast Reactors and Related Fuel Cycles: Next Generation Nuclear Systems for Sustainable Development (FR17)*, IAEA-CN245-211, 28 June 2017.
- [3] A. Aerts et al., "Oxygen-iron interaction in liquid lead-bismuth eutectic alloy", *Physical Chemistry Chemical Physics*, 18 (2016), 19526-19530.
- [4] S. Ebel Denton et al., "Gibbs energy minimization in gas + liquid + solid systems", *Journal of Computational Chemistry*, 21 (2000), 247-256.
- [5] D.A. Kulik et al., "GEM-Selektor geochemical modeling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes", *Computational Geosciences*, 17 (2013), 1-24.
- [6] A. Roine, HSC-Chemistry® [Software], Outotec, Pori 2019. Software available at www.outotec.com/HSC.
- [7] F. Roelofs, "Thermal Hydraulics Aspects of Liquid Metal cooled Nuclear Reactors", ISBN 978-0-08-101980-1. DOI <https://doi.org/10.1016/C2016-0-01216-0>.

- [8] ANSYS Inc, ANSYS Fluent Theory Guide, Release 15.0, November 2013.
- [9] J. Carrayrou et al., "Operator-splitting procedures for reactive transport and comparison of mass balance errors", *Journal of Contaminant Hydrology*, 68 (2004), 239-268.
- [10] A. Marino et al., "A multi-physics computational tool based on CFD and GEM chemical equilibrium solver for modeling coolant chemistry in nuclear reactors", *Progress in Nuclear Energy*, 120 (2020), 103190.
- [11] IPPE report N224/5.42.02-16/13231, Verification and MASKA-LM code revision, 2017.
- [12] K. Hanjalić and B. E Launder, "Modelling turbulence in engineering and the environment: second-moment routes to closure", Cambridge, UK: Cambridge University Press, 2011.
- [13] K. Gladinez et al., "Nucleation and growth of lead oxide particles in liquid lead-bismuth eutectic", *Physical Chemistry Chemical Physics*, a journal published by the Royal Society of Chemistry, DOI: 10.1039/c7cp05068b, 2017.
- [14] K. Gladinez et al., "Formation and transport of lead oxide in a non-isothermal lead-bismuth eutectic loop", *Nuclear Engineering and Design*. 349 (2019), 78-85.
- [15] M. Peltomäki, HSC-Chemistry Outotec private communications.
- [16] J. Carrayrou et al., "Operator-splitting procedures for reactive transport and comparison of mass balance errors", *Journal of Contaminant Hydrology*, 68 (2004), 239-268.
- [17] P. Engesgaard, and K. L. Kip, "A geochemical model for redox-controlled movement of mineral fronts in ground-water flow systems: A case of nitrate removal by oxidation of pyrite", *Water Resources. Research*, 28 (1992), 2829-2843.
- [18] W. Hundsdorfer and J.G. Verwer, "A note on splitting errors for advection-reaction equations", *Applied Numerical Mathematics*, 18 (1995), 191-199.
- [19] D. Jacques et al., "Operator-splitting errors in coupled reactive transport codes for transient variably saturated flow and contaminant transport in layered soil profiles", *Journal of Contaminant Hydrology*, 88 (2006), 197-218.
- [20] D. Jara et al., TReaLab: "An object-oriented implementation of non-intrusive splitting methods to couple independent transport and geochemical software", *Computers and Geosciences*, 109 (2017), 281-294.
- [21] Website: Component Object Model: <http://www.microsoft.com/com/>.
- [22] A. Tsybanev et al. "The New Insight on Iron-Based Oxide Formation in Lead-Bismuth Eutectic", NURETH-19, 2021.
- [23] J. Lim et al., "Electrochemical Measurement of Sieverts' Constant and Solubility of Oxygen in LBE at 598–748 K", *Journal of the Electrochemical Society*, 164 (2017), 743-747.
- [24] A. Aerts et al., "Behavior of Spallation, Activation and Fission Products in LBE", *Comprehensive Nuclear Materials* 2nd edition doi:10.1016/B978-0-12-803581-8.11612-1.

- [25] S. Gossé, "Thermodynamic assessment of solubility and activity of iron, chromium, and nickel in lead bismuth eutectic", *Journal of Nuclear Materials*, 449 (2014), 122-131.
- [26] L. Martinelli et al., "Nickel solubility limit in liquid lead–bismuth eutectic", *Journal of Nuclear Material*, 400 (2010), 232–239.
- [27] Liu, Y.; Liu, S.; Zhang, C.; Lu, X.; Chen, C.; Du, Y.; Živković, D. J. *Electron. Mater.* 2015, 45 (2), 1041–1056.
- [28] Barin, I. *Thermochemical Data of Pure Substances*; Wiley, 1995.
- [29] G. Gregori *et al.*, *Electrochimica Acta*, 432 (2022) 1412020.
- [30] A. Marino, D7.1 Design and fabrication of the 7-pin heated bundle and integration into 15-15Ti cladding tubes, PATRICIA H2020.