The LBE Coolant Chemistry R&D Programme for the MYRRHA ADS: Chemistry and Control of Oxygen, Corrosion and Spallation products

Alexander AERTS\textsuperscript{1*}, Kristof GLADINEZ\textsuperscript{1}, Borja GONZALEZ PRIETO\textsuperscript{1}, Jun LIM\textsuperscript{1}, Alessandro MARINO\textsuperscript{1} and Kris ROSSEEL\textsuperscript{1}

\textsuperscript{1}Chemistry and Conditioning Programme, Belgian Nuclear Research Centre (SCK\textperiodcentered CEN), 2400 Mol, Belgium

\*E-mail: alexander.aerts@sckcen.be

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Compatibility with structural materials and activation are major challenges of the use of heavy liquid metal (HLM) spallation targets and coolants such as lead-bismuth eutectic (LBE). Steel exposed to HLM is prone to corrosion which results in the release of steel elements in the HLM coolant. A commonly accepted strategy to reduce corrosion rates is to maintain a sufficiently elevated dissolved oxygen concentration in order to stabilize a protective oxide layer on the steel surface in contact with HLM. We present a brief overview of the oxygen sensing and control technology for LBE, developed in the frame of the MYRRHA accelerator driven system (ADS) demonstrate its performance on a large scale in the MEXICO chemistry loop (Mass Exchanger In Continuous Operation). MYRRHA stands for Multi-purpose hYbrid Research Reactor for High-tech Applications accelerator driven system and is currently under development at the Belgian Nuclear Research Centre, and will operate between 200 °C and 400 °C with a target oxygen concentration level of $10^{-7}$ wt.-%. Numerical simulations allowed mapping of the local oxygen concentration in MYRRHA, enabling identification of the regions in the core which could be prone to corrosion.

On the other hand, oxygen concentrations must be sufficiently low to avoid formation of solid lead oxide (PbO) in the primary circuit. When designing a nuclear system such as an ADS, one must take into account accidents that may lead to increase of the oxygen concentration in the LBE and assess the probability for PbO formation and its consequences. In this context, we have studied the formation of lead oxide from oxygen-oversaturated LBE and determined the metastable limit for PbO nucleation.

Corrosion products that are released in the LBE will interact with dissolved oxygen in LBE to form corrosion product oxides. These interactions influence the concentration of both dissolved oxygen and dissolved corrosion products. This in turn can cause changes in the corrosion process itself by altering the driving force for steel element dissolution or protective oxide layer decomposition. Experimental results will be presented which provide evidence for the precipitation and dissolution of oxides of iron impurities in LBE. Numerical simulations based on computational fluid dynamics (CFD) and chemical equilibrium complement experiments in understanding the interactions between coolant chemistry and reactor thermal-hydraulics.

A similar approach was adopted for simulating the chemistry of spallation and other radioactive impurities in the primary LBE of MYRRHA. Simulations allow the prediction of released fraction, vapor composition and precipitation/dissolution phenomena in the LBE, as function of the oxygen concentration in the LBE and of the oxygen and humidity content of the cover gas in contact with the LBE. Simulations of the chemical behavior of several critical
radioactive impurities in the coolant such as iodine and polonium are discussed and compared with experimental results.

**KEYWORDS:** LBE, ADS, MYRRHA, polonium, oxygen control

1. Introduction

MYRRHA, a flexible fast spectrum research reactor (50-100 MWth) under design at the Belgian Nuclear Research Centre, is conceived as an accelerator driven system (ADS), able to operate in sub-critical and critical modes. It contains a proton accelerator of 600 MeV, a spallation target and a multiplying core with MOX fuel, cooled by liquid lead-bismuth eutectic (LBE).

The application portfolio of MYRRHA includes demonstration of the physics and technology of an ADS for transmuting long-lived radioactive waste [1], the testing of materials and fuels for fast spectrum reactor and fusion technology development, the production of radioisotopes for nuclear medicine and fundamental research. As an LBE cooled nuclear system, MYRRHA is also listed as the pilot plant for lead cooled fast reactor technology in the European demonstration programme for fast neutron reactors, ESNII [2].

In MYRRHA, LBE is besides the primary coolant also the spallation target. The use of LBE and the choice to implement several advanced safety features in the MYRRHA design presents several safety and technological challenges, which have been under investigation at SCK•CEN during the past years.

The chemistry of LBE coolant involves the reactions of the main coolant constituents lead and bismuth, of dissolved oxygen and of a large variety of impurities, present either already in the non-irradiated LBE, released in the LBE by steel corrosion (Fe, Ni, Cr, Mn) or formed by nuclear reactions with the coolant. In an LBE-cooled ADS such as MYRRHA, critical nuclear reaction products are spallation products with masses close to that of the coolant atoms (such as mercury) and coolant activation products, most importantly polonium. Chemical reactions of LBE and its impurities have a strong influence on several safety related...
Dissolved oxygen has been shown to affect corrosion of steel used for fuel cladding in the core and structural components. Reactions of lead and corrosion products may cause the formation of solid particles and deposits in the narrow flow channels of the core and heat exchangers, frequently as oxides, and nuclear reaction products may evaporate from the LBE into the cover gas space.

Several chemical processes in the coolant are not well understood or lack sufficiently accurate data to allow predictive calculations and technology development [3]. With the conditioning and chemistry programme, SCK•CEN has addressed technological challenges and scientific gaps, in particular in the fields of oxygen control, impurity chemistry and release of safety-critical radionuclides from LBE. In the following sections we present an overview of the state-of-the-art of SCK•CEN's activities in these fields.

2. Oxygen measurement and control

Among possible chemical interactions in the coolant of MYRRHA, oxygen is a central element because of its high chemical affinity with most other elements. At SCK•CEN, the project on oxygen control is a continuous effort, with the aim to develop systems that are able to accurately measure and control the oxygen concentration in the LBE of MYRRHA to avoid coolant oxidation and reduce corrosion.

The range of allowed oxygen concentrations in the LBE depends on temperature and is bounded at high oxygen concentrations by the lead oxide (PbO) solubility line (top blue line in Fig. 2). On the low-oxygen concentration end, typically the lower magnetite stability line is taken to be the boundary (where magnetite is in equilibrium with solid iron). However, when considering a set of corrosion test results reported in the OECD handbook on heavy liquid metal technology (black markers in Figure 2) [3], it is clear that undesired dissolution corrosion may also occur above this magnetite stability line. On the other hand, dissolution corrosion does not seem to take place with high probability above the stoichiometric line for the magnetite solubility product (blue dash curve where the red lines in Figure 1 converge, see also Eq. 1).

In LBE cooled systems, it seems therefore desirable to target oxygen concentrations in the excess oxygen region. In MYRRHA, which will normally operate between ca. 200 °C and 400 °C, an oxygen concentration of about $10^{-7}$ wt-% is therefore envisaged.

![Fig. 2. Selection of the target oxygen concentration for the MYRRHA LBE cooled ADS. The data markers correspond to corrosion experiments at a given combination of temperature and oxygen concentration, for two types of stainless steel (316 and 1515Ti type fuel cladding steel) See text for further discussion.](image-url)
Oxygen sensors capable of measuring down to 200 °C have been developed to accurately measure the concentration of dissolved oxygen in the entire MYRRHA temperature range [4–6]. Ceramic solid electrolyte, reference electrode and sensor assembly methods have been optimized for application in loops, where the ceramic-to-metal joint is not exposed to LBE, as well as for application in deep LBE pools, where long sensors with submerged joint are required.

To allow for diversity, multiple approaches for oxygen control have been evaluated and developed. Oxygen control systems based on gas-LBE interaction, either via a cover gas or through bubbling have been studied [7]. Oxygen addition by controlled dissolution of lead oxide in a so-called PbO mass exchanger (PbO MX) has been evaluated experimentally and numerically [8,9]. A new approach toward oxygen control in LBE called electrochemical oxygen pumping (EOP) has been developed and tested in various experimental conditions [10]. Currently, oxygen reduction by means of cold trapping is also investigated.

LBE chemistry and oxygen control in large systems has been studied at SCK•CEN in the MEXICO, HELIOS 3 and CRAFT installations. MEXICO is a pilot-scale non-isothermal loop with an LBE inventory of 7 tons, where cold and hot leg temperatures are representative for MYRRHA, i.e. ~200 °C and ~400 °C, respectively (Figure 3). At present MEXICO accumulated more than 10000 h of operation, during which it has been used for oxygen control, lead oxide deposition, and impurity filtering experiments (Figure 4). Accurate oxygen control in MEXICO has been achieved using the PbO MX technology [11] (Figure 4, top) and electrochemical oxygen pumping
[12] (Figure 4, bottom). During the test with PbO MX, starting from ca. 1050 h, the oxygen concentration in the loop was increased stepwise with $1 \times 10^{-7}$ wt-% increments. In a subsequent test with the EOP system (PbO MX off), after reaching uniform concentration in the hot and cold parts of the loop, the oxygen concentration could be increased as well as decreased with a $1 \times 10^{-7}$ wt-% step.

In parallel, several small LBE setups are used to test new oxygen sensors. An autoclave equipped with a stirrer called CHECKMATE is used to investigate mass transfer effects on oxygen control by the electrochemical pumping method. Small autoclaves are also being used for the measurement of key chemical properties of dissolved oxygen in LBE, such as the Sieverts constant which describes the equilibrium between dissolved and gaseous oxygen [13].

Finally, a numerical model of oxygen mass transfer in a 19-pin scaled fuel assembly (FA) representative of the MYRRHA reactor core was developed. Oxidation of steels and oxygen transport from the bulk of the LBE to the surface of steels were simulated simultaneously. The simulations provide a local oxygen concentration mapping at steel/LBE interface enabling to identify the regions of the core which could be prone to corrosion due to oxygen depleted LBE. Operation recommendations for the MYRRHA reactor were given based on the simulation results [14].

3. Impurity chemistry and management

Impurity chemistry and management deals with dissolved and solid impurities in the coolant which are released to that extent that they may accumulate to macroscopic amounts during the lifetime of MYRRHA. Corrosion products are expected to be released continuously in the LBE of MYRRHA in amounts that can potentially cause blockages of narrow flow paths inside the primary system. Blockage formation may occur if dissolved corrosion-derived impurities deposit on surfaces, or first precipitate in the bulk of the LBE and then deposit. The driving forces for precipitation and deposition are governed by the thermodynamics of solids-forming reactions. In a first step toward predicting the location and amount of deposits in MYRRHA, it is therefore important to gain understanding in the precipitation-dissolution equilibria in LBE.

One of the abundant corrosion products expected to be released in the LBE of MYRRHA is iron. The reaction between dissolved iron, and

![Fig. 5. Oxygen concentration variation in the hot (red curves) and cold (blue) zones of the CRAFT LBE loop. The trend in the cold zone starts deviating from that in the hot zone after about 65 h due to magnetite precipitation, as indicated by the arrows. The inset shows the evolution of hot and cold zone oxygen concentrations in the magnetite solubility product diagram [15].](image-url)
dissolved oxygen in liquid LBE has been characterized [15]. It was found that many experimental observations, such as the change of dissolved oxygen concentration during temperature changes in a system with constant composition, can be described by the simple equilibrium:

\[ \text{Fe(lbe)} + \text{O(lbe)} = \text{Fe}_3\text{O}_4(s), \]  

where solids and dissolved species are indicated by (s) and (lbe), respectively.

This reaction was also found to have a strong impact on the local oxygen concentration and precipitate formation in larger LBE installations such as the CRAFT corrosion loop [15]. Large differences of the oxygen concentration between the hot leg, where the oxygen control point was located, and the cold leg were observed under certain conditions. To investigate these effects, a dedicated test was conducted (Figure 5) in which the oxygen concentration was gradually decreased. At a certain oxygen concentration in the hot leg, the oxygen concentration in the cold leg started to deviate strongly from that in the hot leg (Figure 5, blue curve). The concentration at which the deviation started was close to the stoichiometric point of the magnetite equilibrium, suggesting the involvement of the iron-oxygen-magnetite equilibrium and that the deviation occurred upon transition of the LBE from an excess oxygen to an excess iron regime.

Another important step toward prediction of impurity particle and deposit formation in a nuclear system such as MYRRHA is the characterization of the formation kinetics of solids in the LBE coolant. Figure 6 shows experimental results of the ratio of the measured dissolved oxygen in LBE to the concentration in equilibrium with lead oxide at each temperature, i.e. the degree of oversaturation. In an experiment in which the temperature of the LBE was cycled between 300 °C and 450 °C, the trend of the oversaturation can be attributed to nucleation and growth (upon temperature decrease).
and dissolution (upon temperature increase) of lead oxide particles in the LBE. The observed trends were well-described by a model based on classical nucleation and growth theory (Figure 6) [16].

Phenomena related to lead oxide nucleation, growth and dissolution in LBE flowing in a non-isothermal system were clearly observed in the MEXICO chemistry loop (Figure 6, right) [17]. Using the PbO MX, the oxygen concentration in the hot leg (350 °C) was increased to 1.53 times the saturation concentration at the cold leg (210 °C). Subsequently, oxygen addition was stopped. When flowing from hot to cold leg, the oxygen oversaturation in the LBE dropped to 1.12, indicating PbO formation either as suspended particles or as deposits. Redissolution of PbO was observed by an increase of the oversaturation to 1.52 measured in the intermediate temperature region (280°C) which is located downstream of a filter section in the cold leg. This indicated that most of the PbO precipitated as small particles in the LBE bulk. These particles are transported to the intermediate temperature zone, rather than deposited on the walls of the cold leg or captured in the filter.

Coupled CFD simulations of LBE flow, heat transfer and oxygen and lead oxide mass transfer in the air cooler of the MEXICO LBE loop are able to explain the experimentally observed drop in oxygen concentration from hot to cold leg attributed to PbO nucleation and growth. Local cold spots in the installation’s air cooler are found to initiate PbO nucleation. The temperature field obtained in the CFD simulations is coupled directly with PbO formation kinetics in a two-phase Eulerian calculation. Experimental results indicate that also at high cooling rates, inside the MEXICO air cooler, the previously proposed model of PbO nucleation and growth is valid. It is found that PbO particles nucleate, grow and dissolve continuously in the MEXICO loop in the studied conditions.

Thermodynamic and kinetic models of solids forming reactions due to corrosion products impurities and PbO are being implemented in CFD models to predict solids formation, transport and deposition in the complex geometry, flow and temperature fields of the MYRRHA primary system. For example, a single-phase chemical equilibrium model was recently developed in order to identify the regions in the reactor with the highest probability for magnetite formation [18]. Figure 7 shows a quadrant of the MYRRHA core and upper plenum. The color scale indicates the concentration of dissolved iron (mass fraction) in equilibrium with magnetite at the local temperature and oxygen concentration in LBE in a quadrant of the MYRRHA core and upper plenum. The transport of already formed impurity particles in the primary system was studied with a multiphase particle tracking model [18]. This allows to investigate the behavior of

Fig. 7. Predicted concentration of dissolved iron (mass fraction) in equilibrium with magnetite at the local temperature and oxygen concentration in LBE in a quadrant of the MYRRHA core and upper plenum.
a dispersed phase having a drift velocity with the main flow due to buoyancy and the effect of particle size. This is of primary importance to identify whether the formed particles will accumulate and where accumulation might occur, for example at the cover gas – LBE interface, or whether the particles will remain suspended in the LBE and follow the flow. Such models are used for safety evaluations and to engineer LBE filter systems for MYRRHA.

Dedicated experiments which address deposition phenomena have been carried out in the MEXICO chemistry loop. In MEXICO, a test section is equipped with a scaled MYRRHA fuel bundle (Figure 8) to study lead oxide deposition and associated increase of the pressure drop under both normal operating and accidental conditions. Such experiments are only feasible because of the very accurate control and measurement of dissolved oxygen in both hot and cold legs of the MEXICO loop.

**Fig. 8.** (left) Pictures of the MYRRHA fuel assembly mock up used to study deposition phenomena in the MEXICO LBE chemistry loop and cross-sectional velocity field predicted by CFD. The Figure on the right depicts a simulation of impurity particle transport in the fuel assembly.

### 4. Fission and spallation product chemistry and evaporation

Volatile fission products (I, Cs, Te, …) may be released into the LBE coolant after a breach in the fuel cladding. As input for safety calculations, the release of fission products from LBE needs to be known quantitatively under various MYRRHA relevant conditions and scenarios. To a certain extent, the chemical properties of fission products are known or can be estimated from existing data. Therefore, we currently focus our experiments to cases where literature data are lacking.

Iodine is an example of a radiologically important element for which thermochemical data in literature were insufficient to evaluate its equilibrium evaporation from LBE. Iodine is commonly believed to be well retained in lead alloy coolants [3]. To verify this claim, we have characterized iodine evaporation from dilute solution in LBE by the so-called transpiration method and confirmed, consistent with experiments at much lower concentrations using a different source of iodine [19], that iodine evaporation from LBE is indeed strongly suppressed compared to evaporation of pure iodine.

The experimental iodine evaporation data from LBE were then analyzed by thermochemical modeling (Figure 9, left), which allowed estimating the distribution and chemical speciation of iodine among liquid, condensed and gas phases. Under the
conditions of the experiment (Figure 9, right), most of the iodine is dissolved in the LBE above 250 °C. Similar calculations were performed for the MYRRHA system. The partial pressure of all iodine species combined is then used to determine the contribution of iodine to the gaseous source term for the evaluation of the radiological consequences of accidents.

As opposed to fission products, spallation products are unique to ADS systems such as MYRRHA in which coolant and spallation target form a single entity. One important spallation product is mercury, which is both volatile and produced with high yield. In the frame of MYRRHA, mercury evaporation from LBE has been characterized using a dedicated setup [20].

Even when considering only the fission products, the number of possible interactions in the primary system is extremely large. It is therefore not feasible to perform experiments that fully cover the range of compositions and conditions to be expected in MYRRHA. For example, the currently performed iodine evaporation experiments do not take into account interactions with other fission products which may affect retention capacity of LBE for iodine, both positively and negatively. Thermochemical modeling is used to study such complex interactions and identify possible safety issues. Targeted experiments are then conducted to verify the model predictions. Results from the MEGAPIE experiment serve as cases to test model predictions against.

Besides the simple experimental setup for transpiration-type evaporation experiments, the thermochromatography technique is being used in the frame of MYRRHA, at the Swiss Paul Scherrer Institute (PSI), to characterize vapors of fission products that emanate from LBE [21].
5. Polonium chemistry in LBE

In addition to spallation and fission products, radionuclides will also be formed due to neutron activation of the coolant. The presence of 55% bismuth in the LBE leads to the production of relatively large quantities of polonium-210 during operation of MYRRHA. The chemistry of polonium and especially its release has been one of the focus points of the conditioning and chemistry programme at SCK•CEN. Using the transpiration method, the release of polonium from dilute solution in LBE has been quantified under various experimental conditions [22–26], importantly the composition of the gas atmosphere in which polonium evaporates (inert, reducing, oxidizing, humid). To enable constructing models which describe the observed evaporation behavior, the thermochemical properties of the relevant polonium gas molecules need to be known. These properties cannot be measured using traditional methods because of the low concentration of gaseous polonium molecules in experiments. We rely instead on thermochromatography experiments [27–30] which provide qualitative information on the nature of the gas species under various conditions, and on modeling. Two approaches towards modeling are adopted in parallel, viz. methods that rely on extrapolation of trends in the chalcogenide group and quantum chemical methods [31,32]. Since polonium gas molecules involve heavy atoms, these quantum chemical methods need to take into account relativistic effects in order to produce accurate results.

Besides providing insight into the nature of polonium gas molecules, thermochromatography experiments also allow the characterization of the interaction of polonium vapors with surfaces. Recent important results obtained in collaboration with PSI include the characterization of adsorption (sticking) of polonium-bearing vapor molecules on surfaces, and the derivation of the corresponding thermochemical interaction properties. Concurrently, ab initio studies of the interaction of polonium with LBE and metal surfaces have been performed [33,34]. The latter results are used in safety studies to assess transport of polonium vapors, after their release from LBE, in various components of MYRRHA such as the proton beam tube.

6. Conclusions

The main coolant chemistry issues encountered in LBE-cooled nuclear systems are addressed by the Chemistry and Conditioning programme at SCK•CEN in the frame of MYRRHA.

In the field of oxygen control and impurity chemistry and management, significant progress has been made. Oxygen sensors capable of measuring in the full MYRRHA temperature range (200 °C - 400 °C) have been developed and control methods to maintain the oxygen concentration at the target level of $10^{-7}$ wt-% have been designed and tested on pilot scale. The chemical behavior of impurities such as lead oxide from coolant oxidation and iron released by steel corrosion has been studied, allowing to make improved predictions of the effect these impurities on oxygen control as well as their precipitation and deposition behavior in the primary system. Future research will focus on the further improvement of predictions of impurity behavior, impurity management methods and on the chemistry of corrosion products such as nickel, which is known to have caused blockages in experimental loops.

Using a combination of experiment and modeling, the understanding of fission, spallation and activation product chemistry in LBE has been greatly improved. Complex interactions are also thought to be important and will be addressed in future studies. To
refine polonium release calculations from LBE, future research will include, among others, the determination of the thermochemical properties of polonium gas molecules with oxygen and hydrogen.

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