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Introduction

The reprocessing of spent fuels from UNGG (Uranium Natural Graphite Gas) nuclear reactors in France has generated cladding wastes mainly made of Mg alloys [1] (Figure 1). The waste will be conditioned in a waste-package, ensuring durability, handling capability, and confinement of the radionuclides during further storage period and final disposal [2]. The embedding and conditioning of magnesium waste are based on their immobilization in a hydraulic binder (Figure 2). Several binders were tested: OPC, cement with blast furnace slag, cement with fly ash, geopolymer, etc. In any case, they imply that the waste will be exposed to a very basic environment (pH> 12). Corrosion of magnesium could have consequences on the structural integrity of a cemented long-term package, due to the expansive corrosion products that form and cause stress within the coating matrix. In addition, corrosion leads to H_2 production, which has to be taken into account to ensure the safety of the storage of conditioned waste packages.

Figure 1: Pieces of Magnesium cladding stored in CEA Marcoule

Figure 2: Magnesium alloy cladding immobilized in a geopolymer matrix (200L drum cut in its height)

Nuclear wastes constituted by magnesium alloy fuel cladding used in the UNGG reactors represent a significant amount of waste and their conditioning is a challenge for many countries. In France, 1,119 tons of radioactive magnesium are thus stored at CEA Marcoule and 1,100 tons at Orano La Hague.

Several treatment/conditioning solutions of this waste are currently being studied in order to find a safe solution for their storage. The project will provide essential elements to decide for a possible implementation of the coating of magnesium waste with geopolymer, a solution envisaged by the CEA at present time.

DECIMAL program

The DECIMAL project (October 2017 – September 2021) focuses on the validation of a corrosion study methodology for a Mg/binder alloy pair. The approach is illustrated and tested via the concept envisaged by the CEA: MgZr/Geopolymer. An alloy and a reference binder will be used: MgZr and a geopolymeric cementitious matrix. To study parameters that may differ from one waste package producer to another, the effects of alloys will be studied with MgZr, MgMn and MgAl. The presence of passivating agent (NaF) in the cement matrix, ions contained in the pore solution, chlorides (water pollution of COx for example) as well as the pH of the solution will also be taken into account. The impact of irradiation will be evaluated on model and industrial materials. The intrinsic properties of the geopolymer will be characterized and the impact of Mg corrosion on its durability determined.

Objectives

DECIMAL is a basic research project whose objective is to better understand the geopolymer matrix behavior in storage conditions, in particular phenomena occurring at the magnesium/geopolymer interface and the consequences on the integrity/durability of the containers in which the waste will be conditioned. These data will be used to consider different magnesium alloys conditioning in cementitious matrixes.

Conduct

DECIMAL is a four-year project which involves six research groups. It is based on experimental parametric studies and a modeling of the integrity of the container. The effect of many parameters (environmental chemistry, nature of the alloy, irradiation) will be studied through the use of classical electrochemical techniques or specific ones, associated with gravimetric and physico-chemical characterizations and microstructures analyses at several scales. The study of sustainability, which is a complex approach, will integrate both the specificities of the geopolymer, the behavior of the waste and its evolution in interaction with the matrix. The study of several alloys (Mg-Zr, Mg-Mn) and industrial analogues (Mg-Al), pre-oxidized or not, will validate the approach.

Expected results

DECIMAL will allow the acquisition of new fundamental data currently unknown in the field of corrosion of magnesium alloys. Experimental protocols developed within the project will make it possible to carry out *in situ* analysis, to measure the amount of hydrogen produced by corrosion, and the amount of magnesium involved in chemical reactions (Figure 3). An innovative approach will also be implemented through the manufacture of thin layers geopolymer on Mg-Zr substrate so to have model materials, usable for the study of metal interfaces/binding under irradiation. An electrochemical-mechanical gantry previously developed [3] will allow the recording of the corrosion current of Mg electrodes embedded in a cement matrix, as well as induced deformations on the binder by the growth of a layer of corrosion products at the magnesium surface (Figure 4).

Figure 3: Electrochemical-gas measurement coupled reactor

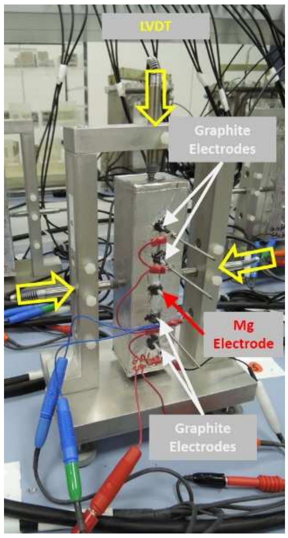

Figure 4: Measuring gantry coupling electrochemical-mechanical measurement

Conclusions

The novelty of this project is the originality of the partnership bringing a wealth of complementary skills to study in depth the mechanisms of corrosion at the interface metal/matrix and its impact on the mechanical behavior of the package. This will allow the acquisition of new fundamental data currently unknown in this field: electrochemistry of metal/matrix interfaces, composition, morphology, microstructure of a layer of corrosion products in the presence of a geopolymer; the stability of this layer out and under irradiation, the impact of this layer and the release of H_2 and on the mechanical behavior of the geopolymer.

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