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Corrosion behavior of Mg-Zr alloy in alkaline solutions and in Na-geopolymer

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Introduction

The reprocessing of spent fuels from UNGG (Uranium Natural Graphite Gas) nuclear reactors in France generated cladding wastes mainly composed of Mg alloys. The management of these wastes involves their immobilization in a hydraulic binder with high pH interstitial solution (pH =12.5). As a result, the use of geopolymers as binders is being studied at the CEA for conditioning this metallic waste [1].

The choice of the immobilization matrix is not straightforward due to the characteristic reactivity of these alloys, which is caused by several aspects [2]. First, magnesium corrosion is strongly influenced by the pH, and thermodynamics predicts a passivation of Mg alloys with pH higher than 10.50 due to the formation of a superficial protective film of Mg(OH)₂ [8]. However, understanding the kinetics of formation for this passivating layer is important to the comprehension of the corrosion mechanisms of Mg in alkaline media. In addition, the electrochemical potential of Mg places this metal as an anode with respect to several materials [3] (e.g. residual graphite materials initially present in the fuel assemblies or steel from the container), which can create galvanic couplings and accelerate corrosion. Furthermore, magnesium corrosion results in hydrogen production [4], which must be understood to better manage the immobilization of the magnesium waste in a geopolymer matrix. The geopolymer used in this study was obtained by activation of an alumino-silicate source by sodium hydroxide solution in the presence of sodium fluoride (NaGeo/NaF). Fluoride is used here as a corrosion inhibitor for the Mg-Zr alloy [1] [6].

The aim of this work is to provide, through electrochemistry and gravimetric measurements, information about the corrosion processes that will occur once the alloy is in contact with its immobilization matrix, either in the case of general corrosion or in a galvanic coupling situation.

Experimental approach

This work is divided in two main axes. The first one focuses on the study of the general and galvanic corrosions of Mg in alkaline solutions by electrochemical methods (OCP, ZRA and polarization curves), covering the study of the effect of the pH, ions and conductivity. The second axis studies the corrosion of Mg in the geopolymer by gravimetric measurements.

Corrosion of Mg-Zr in alkaline solutions

The reference electrolyte chosen for this study is an interstitial solution of the geopolymer used for the immobilization of Mg waste. The pH, conductivity and the ions present in this solution will interfere in different ways during the corrosion process and, in order to understand the impact of these factors on the corrosion mechanisms, an individual study of each one of them was carried out.

The effect of the pH and the conductivity was studied directly in the case of galvanic coupling with graphite during 90 days by ZRA (Zero Resistance Ammeter). This technique allowed us to measure the current between Mg-0.5%Zr and graphite, where Mg becomes the anode and graphite the cathode, with a surface ratio Mg-Zr/Graphite of 1/1. Our pH range is between 10.45 (close to the equilibrium pH of Mg(OH)₂) and 13.70 (close to the pH of the pore solution of activated slag, which is

also used for storing Mg nuclear wastes). The corrosion rates and hydrogen evolution were subsequently calculated from the coupling current measured by ZRA.

Corrosion of Mg-Zr in the geopolymer

This test allowed us to access the average corrosion rates over hydration time for a maximum period of 373 days. Three cases were evaluated: general corrosion of Mg-0.5%Zr and galvanic corrosion of Mg-0.5%Zr/Steel S235JR and Mg-0.5%Zr/Graphite.

For the execution of this test the samples were weighed before and after the exposure to a corrosive environment for a certain time. For Mg alloys, the NF ISO 8407 (2014-05-02) standard specifies the solution used for removing the formed corrosion products.

Results

Galvanic corrosion of Mg in alkaline solutions

The conductivity increases with pH (values ranging from 0.072 to 242.7 mS.cm⁻¹). However, this parameter does not have the same major impact on the corrosion rate as the pH. An optimum pH value was observed for values higher than 12 (Figure 1.a), where the corrosion rate was kept under 15 $\mu\text{m}\cdot\text{year}^{-1}$, so binders with a pH above this value are relevant for embedding Mg-Zr alloys. The highest corrosion rate was observed for pH between 10.45 and 11.44. In this case, Mg(OH)₂ precipitates in a heterogeneous manner. For the pH with a lower corrosion rate (above 11.90) Mg(OH)₂ precipitates homogeneously in a thin layer on the surface of Mg (Figure 1.b). This difference in the homogeneity of the Mg(OH)₂ layer is related to the concentration of ions OH⁻ present in the solution : lower concentrations favor the growth of preexisting Mg(OH)₂ crystals, causing heterogeneous precipitations on the surface; higher concentrations favor the nucleation of new growth sites, generating a thinner and homogeneous layer on the surface which is apparently more protective than the Mg(OH)₂ layer formed at lower pH.

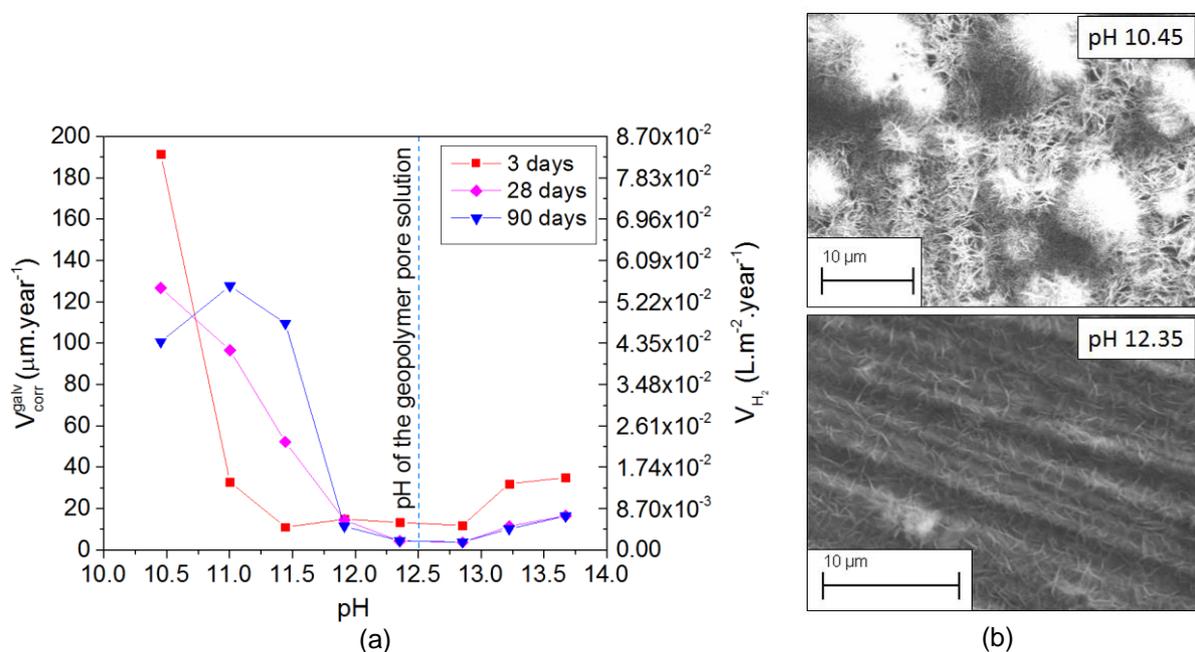


Figure 1: (a) Comparison of the galvanic corrosion rates between Mg-Zr/Graphite (ratio 1:1) at 3, 28 and 90 days in alkaline solutions at different pH. (b) SEM images of the Mg surface after 90 days at pH 10.45 and 12.35.

Mg corrosion in geopolymer mortar

The evolution of the average corrosion for the general corrosion of Mg-0.5%Zr and the galvanic corrosion of Mg-0.5%Zr/Steel S235JR and Mg-0.5%Zr/Graphite is shown in table 1. The samples

were embedded in a Na-Geo/NaF geopolymer up to 373 days. In all cases the average corrosion rate decreased with time, the coupling Mg-0.5%Zr/Graphite inducing the highest corrosion rate values. This difference is less evident when comparing these values to the ones obtained until 28 days – however, even if the coupling Mg-0.5%Zr/Graphite induces higher corrosion rates than the other cases, these values remain low ($2.3 \mu\text{.year}^{-1}$).

	Average corrosion rate ($\mu\text{.year}^{-1}$)			
	3 days	28 days	90 days	373 days
General Corrosion	29.4 ± 5.7	6.7 ± 1.1	2.4 ± 0.3	1.0 ± 0.4
Mg-0.5%Zr / Graphite	37.8 ± 8.3	8.2 ± 1.6	5.9 ± 0.7	2.3 ± 0.1
Mg-0.5%Zr/Steel S235JR	27.9 ± 9.4	5.8 ± 0.2	2.2 ± 0.5	0.6 ± 0.1

Table 1: Average corrosion rates for the general corrosion of Mg-Zr and the galvanic corrosion of Mg-Zr/Steel S235JR and Mg-Zr/Graphite obtained by gravimetric methods.

Conclusions

Based on our results for the pH effect, the optimal pH for reducing Mg-Zr corrosion and hydrogen evolution is around 12.50. This confirms the results obtained previously in the coating matrix and shows the good choice of this material for immobilizing this type of waste even in a situation of a galvanic coupling with graphite, which induces the highest corrosion rates. The pH is a major parameter to understand the corrosion of magnesium, because small variations strongly affect the kinetics of corrosion and the formation of a passive layer on the surface of the metal. It was also found that graphite is the most penalizing coupling for Mg-Zr, presenting nonetheless a small corrosion rate.

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