GALVANIC CORROSION OF MG-ZR ALLOY AND STEEL OR GRAPHITE IN MINERAL BINDERS

David Lambertin, Adrien Rooses, Fabien Frizon

CEA, DEN, DTCD, SPDE, LP2C F-30207 Bagnols Sur Ceze, France

Abstract

The dismantling of UNGG nuclear reactor generates numerous nuclear wastes such as fuel decanning commonly composed of Mg-Zr alloy. A conditioning strategy consists in encapsulating these wastes into a hydraulic binder in a suitable state for storage. The eventual presence of steel and graphite accompanying the magnesium wastes could imply corrosion by galvanic coupling. This work is an experimental investigation of the galvanic coupling between Mg-Zr alloy and steel or graphite using ZRA electrochemical method in Portland cement or geopolymer pastes. The lowest corrosion activity of magnesium alloy while coupled to graphite or steel cathode has been observed in geopolymer pastes. Indeed, in this binder, an efficient corrosion protection of the magnesium alloy maintains the galvanic current very low during all the hardening process. In geopolymer paste, current densities of anodised Mg-Zr alloy is not dependent of the cathode/anode surface ratio in the range of 0.1 to 5 due to the dominance of the anode resistance.

Keywords: galvanic corrosion, Mg-Zr alloy, cement, geopolymer

Introduction

This study takes part of magnesium waste processing project of UP1 plant of Marcoule site in France. The dismantling of Uranium Natural Graphite Gas nuclear reactor generates a large volume of fuel cladding materials. Nuclear wastes such as Mg-Zr alloy fuel cladding, graphite and steel bars have been stored conjointly in tanks, and a solution for their processing is their immobilisation in a hydraulic binder [1]. Mg and its alloys act as anode in contact with other metals, and could suffer from a severe galvanic corrosion attack. Previous works [2] have evidenced the existence of intermediate Mg^+ which leads to the formation of Mg^{2+} and H_2. Therefore, in the case of magnesium alloy coupled to another metal such as steel, the hydrogen can be produced either by the water reduction or by AHE (Anodic Hydrogen Evolution) [3] on magnesium alloy (1).

$$Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + \frac{1}{2} H_2 \qquad (1)$$
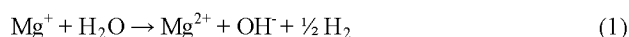
The knowledge of the corrosion activity while immobilizing the wastes is essential to avoid any damage of the storage container on the long run. If corrosion studies have been carried out on anodised magnesium in solutions [4-7], no data on the corrosion behaviour of anodised magnesium alloy in hydraulic binders such as Portland cement or geopolymer is available in the literature.
A theoretical and conceptual relation of the galvanic current i_{galv} between an anode and a cathode is proposed in the literature by:

$$i_{galv} = (E_c - E_a)/(R_c + R_a + R_s + R_m) \qquad (2)$$

where $E_c - E_a$ is the electrical potential difference of the cathode and anode, R_c and R_a their resistances, R_s the resistance of the solution between the electrodes and R_m the resistance of the metallic path between the cathode and the anode. R_m is normally considered negligible.

In the case of Graphite|Mg and Steel|Mg couples, the electrical potential difference is usually high, whatever the media. However, the binder paste media evolve chemically and physically, due to the dissolution of particles and to the curing processes respectively. The level of the solution resistance R_s could therefore change drastically. Furthermore, aggression or protection phenomenon on the surface of the magnesium anode may also modify the values of R_a during the immersion in the binder pastes.

The purpose of this study is to compare and understand the galvanic corrosion behaviour of Mg-Zr alloy coupled with graphite or steel in different Portland cement and geopolymer pastes to propose a suitable embedding binder for these wastes.

Experimental

The two selected Portland Cements are CEM I 52.5 N CE CP2 White from Calcia Cruas factory (WPC) and CEM I 52.5 PM ES CP2 from Lafarge Le Teil factory (OPC). Their compositions are reported in Table 1. The cement pastes were obtained by mixing the cement powder with water, with a water to cement mass ratio of 0.40.

Table 1 – Compositions of Portland cements WPC and OPC.

Portland Cement type		WPC	OPC
Clinker mineral composition	C_3S	73.5 %	67.9 %
	C_2S	13.5 %	19.9 %
	C_3A	12.0 %	4.1 %
	C_4AF	1.0 %	7.9 %
Gypsum content %wt	$CaSO_4 \cdot H_2O$	5.5%	2.7%

The geopolymer binders (Na-GEO) were activated in waterglass alkali solutions and formulated with a $Al{:}Si{:}Na{:}H_2O$ molar ratio of $1{:}1.8{:}1{:}11.5$. Waterglass activating solutions were prepared by dissolving sodium hydroxide pellets (Prolabo, Rectapur, 98 %), and amorphous silica provided by Rhodia (Tixosil 38) in Milli-Q water. Solutions were then stirred for 24 h. Metakaolin was purchased under the brand name of Pieri Premix MK from Grace Construction Products. The oxide composition of metakaolin determined by X-ray Fluorescence (XRF) can be found in Table 2. Geopolymer pastes were then prepared by mixing metakaolin and waterglass solution with a standard laboratory mixer and then directly used for electrochemical measurements.
Small pieces of a few square centimetres of non-radioactive Mg-Zr alloy fuel decanning from UNGG reactors stored for long time under ambient atmosphere were used as electrodes. The weight composition of this alloy is Mg 99.48 %, Zr 0.49 % and Mn 0.016%.

Table 2 – Oxide composition of metakaolin.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2
% weight	54.4	38.4	1.3	0.6	1.6

Steel and graphite electrodes were respectively made of 2 mm wire of SAE 1020 steel and 6 mm pure graphite cylinder.
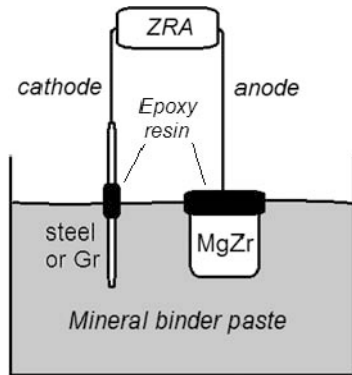

Fig. 1. Test arrangement diagram.

Zero-Resistance Ammeter test (ZRA) has been used to register the galvanic current density (J_{galv}) of coupled metals immersed in a mineral binder paste versus time. Galvanic current densities were calculated as a function of the magnesium surface. The experiments were performed with a Princeton Applied Research VersaSTAT 4 model. The electrodes distance has been kept equal to 2 cm as described in Fig 1. As binder pastes are changing media, the experiment duration has been fixed at 14 hours to cover the dissolution and curing steps.

Results and discussions

Galvanic corrosion of Mg-Zr alloy coupled to graphite and steel in Portland cement and geopolymer pastes.

Galvanic currents densities of Mg-Zr alloy coupled to graphite and steel immersed in WPC, OPC and Na-GEO are presented in Fig. 2. The surface ratio of graphite or steel to Mg-Zr (called S) has been kept equal to 0.1.
The current densities of magnesium alloy in the binder pastes present quite same evolutions either coupled to graphite or steel.
In OPC and WPC pastes, for both couples, anodised Mg-Zr alloy first displays an increase of current and then progressively decreases. Indeed, as anhydrous cement compounds are dissolving in the aqueous solution, the concentrations of aggressive soluble species increase and enhance metal corrosion. Theoretically, this can be explained by a decrease of both solution and anode resistances R_s and R_a while the electrical potential difference remains unchanged. When the point of saturation concentration of ionic constituents is reached, a maximum of magnesium current density is observed [8]. Then, the setting of the binder occurs and the consumptions of water and dissolved elements lead to a progressive decrease of the corrosion activity. Indeed, from then on, the solution resistance R_s is rising continuously. It has been noticed that the level of anodic current density is more important in OPC binder than in WPC binder. This difference can be explained by the effect on R_s and R_a of the cement constituents

such as the clinker composition, the gypsum content and the use of different adjuvants part of cement making process.
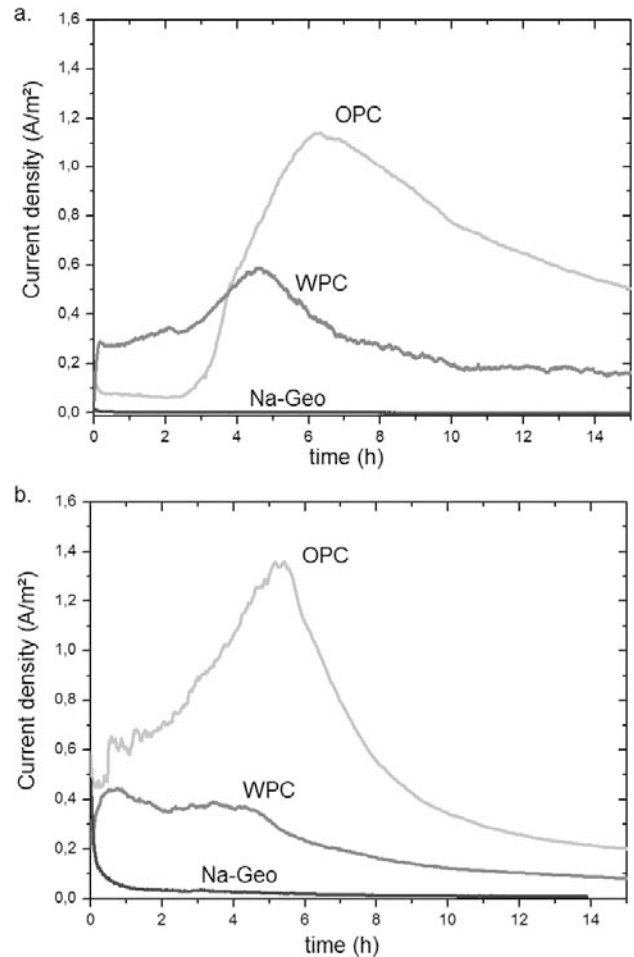

Fig. 2. Galvanic current densities of Mg-Zr alloy coupled to graphite (a) and steel (b) immersed in OPC, WPC and Na-Geo binder pastes for a $S_{cathode}/S_{Mg-Zr}$ ratio equal to 0.1.

In Na-geo paste, the magnesium current densities exhibit a totally different behaviour than in Portland cements. The anodic current evolution presents a sharp decrease as soon as the electrodes are immersed in the Na-geo paste. This important decrease of i_{galv} is a result of the formation of a efficient corrosion protection on the surface of the magnesium alloy which considerably amplifies R_a. The anodic protection could be a result of the formation of layers such as silicates [9], quickly after immersion in the geopolymer paste. For both cases, galvanic current densities remain very low over time and no not evolve during the material setting. This underlines that the R_s evolution is negligible towards the fast rise of R_a and that the latter leads by itself the electrochemical system. Nevertheless, the decrease seems to be faster with graphite than with steel cathode because of the difference of the cathode potentials E_c.
As a conclusion of the very low corrosion activity of anodised magnesium alloy in Na-Geo pastes, sodium geopolymer binders tend to be an appropriate matrix for the waste embedding in order to minimise the production of hydrogen gas related to corrosion.
Nevertheless, as the metal wastes could have been positioned randomly in the tanks, the contact surface ratio between

154

magnesium alloy and the other metals could change significantly. The next part of this study will assess the influence of the surface ratio on the corrosion activity of Mg-Zr alloy coupled to steel.

Influence of the metal surfaces ratio on the corrosion of Mg-Zr alloy coupled to steel in geopolymer paste.

In a medium, galvanic current densities depend on the nature of the connected metals but it is also related to the cathode/anode surface ratio. Indeed, an increase of the cathode/anode surface ratio lead to a decrease of the values of R_c and consequently to a rise of i_{galv}. It is well known that the worse combination is to have a high area ratio of cathode to anode. Indeed, G. Song et al. [10] have evidenced the linear increase of the anodic current density of Steel|Mg couple while increasing cathode/anode area ratio in 5% NaCl aqueous solutions.
The current densities of Mg-Zr alloy coupled to steel in Na-Geo paste with different Steel/Mg-Zr surface ratios (S) are presented in Fig. 3. On the one hand, the curves of anodic current density for the four surface ratios from 0.1 to 5 remain very close. This points out that the galvanic current density of Steel|Mg-Zr in geopolymer pastes is not dependent on the surface ratio of steel to magnesium. On the other hand, for all surface ratios, anodic current densities

are very low and unaffected by the material hardening as already seen in the previous part. This two observations illustrate not only the high values of the anode resistance R_a related to the magnesium surface protection, but also the negligibility of evolution of R_c whatever the cathode/anode surface ratio in the range of 0.1 to 5.

Conclusions

- Na-Geo paste is the binder that implies the lowest corrosion activity of magnesium alloy while coupled to graphite or steel cathode. The galvanic current remains very low during the hardening process thanks to the efficient corrosion protection once immersed in the geopolymer paste.
- In geopolymer paste, the current density of anodised Mg-Zr alloy is not dependent to the cathode/anode ratio in the range of 0.1 to 5 due to the dominance of the anode resistance R_a in the electrochemical system.
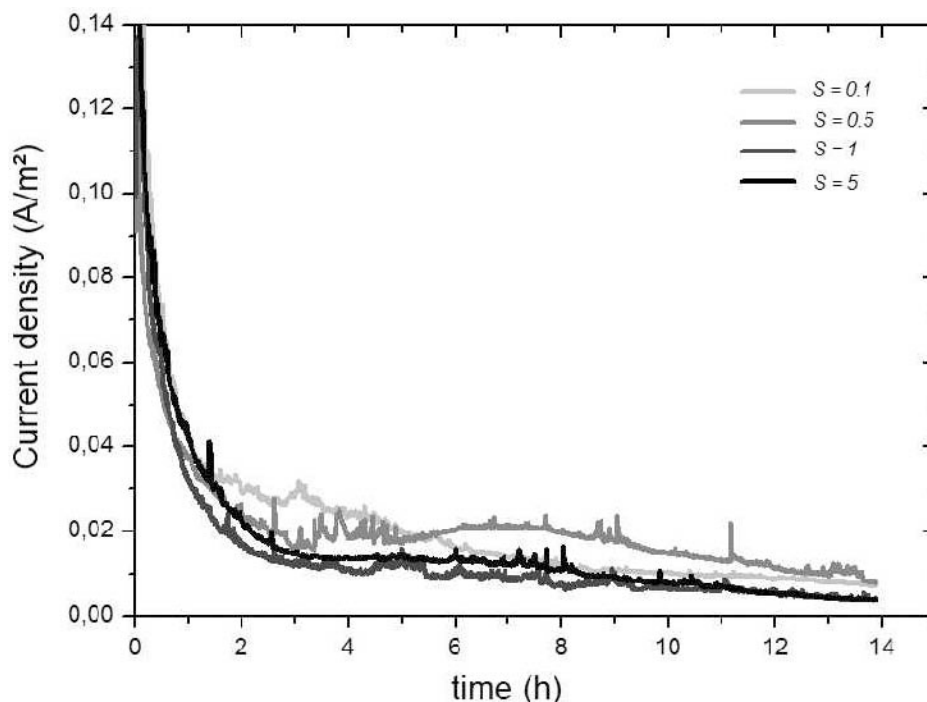- Na-Geo paste appears to be a suitable encapsulation matrix for magnesium wastes

Fig. 3. Galvanic current densities of Mg-Zr alloy coupled to steel with cathode/anode surface ratios of 0.1, 0.5, 1 and 5 in Na-Geo paste

References
[1] D. Lambertin, F. Frizon, F. Bart, Surface and Coatings Technology, 206 (2012) 4567-4573.
[2] G.L. Song, A. Atrens, Advanced Engineering Materials, 1 (1999) 11-33.
[3] G.L. Song, in, Woodhead Publishing in Materials, USA, 2011.
[4] S. Bender, J. Goellner, A. Heyn, E. Boese, Mater. Corros., 58 (2007) 977-982.
[5] J.X. Jia, G.L. Song, A. Atrens, Corrosion Sci., 48 (2006) 2133-2153.
[6] D. Lambertin, A. Blachère, F. Frizon, F. Bart. W.H. Sillekens, S.R. Agnew, M.R. Neelameggham, M.O. Pekguleryuz (Eds.) Magnesium Technology 2011.
[7] Z.M. Shi, J.X. Jia, A. Atrens, Corrosion Sci., 60 (2012) 296-308.
[8] J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, K.L. Scrivener, J.J. Thomas, Cement and Concrete Research, 41 (2011) 1208-1223.
[9] J.E. Gray, B. Luan, Journal of Alloys and Compounds, 336 (2002) 88-113.
[10] G. Song, B. Johannesson, S. Hapugoda, D. StJohn, Corrosion Sci., 46 (2004) 955-977.