

CORROSION BEHAVIOUR OF MG ALLOYS IN VARIOUS BASIC MEDIA: APPLICATION OF WASTE ENCAPSULATION OF FUEL DECANNING FROM UNGG NUCLEAR REACTOR

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Keywords: Magnesium-zirconium alloy, encapsulation, electrochemistry

Abstract

The dismantling of UNGG nuclear reactor generates a large volume of fuel decanning. These materials are based on Mg-Zr alloy. The dismantling strategy could be to encapsulate these wastes into an ordinary Portland cement (OPC) or geopolymer (aluminosilicate material) in a form suitable for storage. Studies have been performed on Mg or Mg-Al alloy in basic media but no data are available on Mg-Zr behaviour. The influence of representative pore solution of both OPC and geopolymer with Mg-Zr alloy has been studied on corrosion behaviour. Electrochemical methods have been used to determine the corrosion densities at room temperature. Results show that the corrosion densities of Mg-Zr alloy in OPC solution is one order of magnitude more important than in a geopolymer solution environment and the effect of an inhibiting agent has been undertaken with Mg-Zr alloy. Evaluation of corrosion hydrogen production during the encapsulation of Mg-Zr alloy in both OPC and geopolymer has also been done.

Introduction

The dismantling of UNGG nuclear reactor generates a large volume of fuel decanning. These materials are based on Mg-Zr alloy. The dismantling strategy could be to encapsulate these wastes into a mineral binder, namely an ordinary Portland cement (OPC) or geopolymer (aluminosilicate material) in a form suitable for storage.

Since 1990, scrap metal from the MAGNOX reactor in Great Britain based on Mg-Al alloy were packed with a mixture of Portland cement and blast furnace ash or fly ash [1, 2, 3]. The strategy of this formulation is to use a minimum of water for hydration of cement and a high pH (around 12.5) [2]. Hydrogen gas generation has been observed with the formation of magnesium hydroxide on the surface of magnesium metal, causing damage to the package [4]. An alternative to the use of Portland cement has been proposed with the use of mineral geopolymer [1, 5]. Encapsulations of Magnox waste containing

magnesium metal were made with organic polymers [6] to limit the amount of water to avoid a hydrogen gas.

In this work, we have studied the influence of representative solution of OPC and geopolymer with Mg-Zr alloy on corrosion behaviour. Electrochemical methods have been used to determine the corrosion densities at room temperature. Evaluation of encapsulation of Mg-Zr alloy in OPC and geopolymer has been done in term of corrosion hydrogen production.

Experimental procedure

The material used in the Mg-Zr corrosion tests was inactive fuel decanning plates from UNGG reactor whose composition was 0.49 % Zr and Mg balance. The samples were cut in order to obtain a rectangular shape, before being pickled in 1 M H₂SO₄ solution for 20 seconds and rinsed with distilled water.

For electrochemical measurements, the composition of representative solution of ordinary Portland cement (OPC) was NaOH 10g/L, KOH 3 g/L, Ca(OH)₂ 1 g/L, and the composition of geopolymer was NaOH 370 g/L, SiO₂ 333 g/L.

A classical three electrodes cell was used for the electrochemical investigations. A platinum counter electrode and a saturated calomel reference electrode (SCE) were used. The working electrode is made of Mg-Zr pieces partially recovered of epoxy resin for a well defined surface. The experiments were performed with a Princeton Applied Research Potentiostat VersaSTAT model. For potentiodynamic polarization, the scan rate was equal to 1 mV/mn.

The encapsulation of Mg-Zr alloy in OPC and geopolymer was completed and the hydrogen evolution has been measured in order to obtain the corrosion rates. The composition of the OPC and geopolymer used for corrosion rate measurements is reported in Table 1. Two binders were used:

- Geopolymer (Metakaolin of Pieri Premix MK, SiO₂ Tixosil of Degussa)
- Ordinary Portland Cement (CEM I 52.5 Lafarge Le Teil)

Table 1. Composition of the various mineral binders for the encapsulation of Mg-Zr alloy

Matrix composition	
Geopolymer	Metakaolin: 87.8 g SiO ₂ : 20 g NaOH: 22 g H ₂ O: 60 g
Ordinary Portland Cement	CEM I: 80 g H ₂ O: 32g

Measurements of hydrogen evolution are initiated by placing Mg-Zr samples encapsulated in binders in a fixed volume container.

The hydrogen analysis is undertaken by gas chromatography and the time dependant results are used to determine corrosion rates.

Corrosion rates measurement

The simplest and most fundamental measurement of the corrosion rate is the metal weight loss rate, ΔW (mg/cm²/d). This can be converted to an average corrosion rate (mm/y) using [7]:

$$P_w = 3.65\Delta W/\rho \quad \text{Eq.1}$$

where ρ is the metal density (g/cm³).

For Mg alloys, ρ is 1.74 g/cm³, and Eq. (1) becomes:

$$P_w = 2.10\Delta W \quad \text{Eq.2}$$

In the overall corrosion reaction of pure Mg, one molecule of hydrogen is evolved for each atom of corroded Mg. One mole (*i.e.* 24.31 g) of Mg metal corrodes for each mole of hydrogen gas produced. Therefore, the hydrogen evolution rate, V_H (ml/cm²/d), is related to the metallic weight loss rate, ΔW_m (mg/cm²/d), using [8]:

$$\Delta W = 1.085V_H \quad \text{Eq.3}$$

So the corresponding corrosion rate, P_H , is equal to:

$$P_H = 2.279V_H \quad \text{Eq.4}$$

For Mg corrosion, there is excellent agreement [8] between the corrosion rate measured by the weight loss rate and that evaluated from the hydrogen evolution rate. In the Tafel extrapolation method for measuring the Mg corrosion rate, the corrosion current density, I_{corr} (mA/cm²) is estimated by Tafel extrapolation of the cathodic branch of the polarisation curve, and I_{corr} is related to the average corrosion rate using [9]:

$$P_i = 22.85 I_{corr} \quad \text{Eq.5}$$

Results and discussion

Electrochemical measurements

The corrosion properties of Mg-Zr alloy in representative solution of OPC (with sodium fluoride addition) and geopolymer have been evaluated by open circuit and potentiodynamic polarization. Figure 1 shows the open circuit potential measurements (E_{corr}) for Mg-Zr alloy in representative solution of OPC with addition of sodium fluoride ($[NaF] = 1.25$ M and $[NaF] = 2.5$ M). A previous study [10] has pointed out the effect of fluoride on corrosion rate decreasing in alkaline solutions with pure Mg. Consequently, the addition of sodium fluoride in representative solution of OPC has been performed to evaluate the performance of sodium fluoride inhibiting effect on Mg-Zr alloy. We can see in Figure 1 that the open circuit potential (E_{corr}) trends to a more anodic value with greater fluoride concentrations. Gulbrandsen et al. [10] have pointed out that the open circuit values give trend to corrosion current density I_{corr} ; the corrosion current density decreases when the open circuit potential is more anodic. So we can notice that in our basic media at a high fluoride concentration (2.5 M), the corrosion current density will be less important than at a medium fluoride concentration (1.25 M). In order to determine the corrosion current density, potentiodynamic polarization measurements have been carried out in OPC solution with fluoride addition and in activated geopolymer solution for 24 hours (Figure 2). Corrosion current densities have been evaluated with the cathodic branch provided a linear Tafel region [11]. The evaluated I_{corr} value is included in Table 2. We can see that the corrosion current density of Mg-Zr alloy decreases in OPC solution with fluoride addition. In activated geopolymer solution, the corrosion current density of Mg-Zr is one order of magnitude less important than in OPC solution, and addition of fluoride in OPC is necessary to obtain equivalent performance to an activated geopolymer solution. By using Eq.5, corrosion rates at 24 hours have been calculated and reported in Table 2. Ratios P_{OPC-i} / P_{sol-i} show that corrosion rates obtained with Tafel extrapolation of Mg-Zr alloy in OPC solution with fluoride at 1.25 M and in activated geopolymer solution are in the same order of magnitude. Corrosion rate value of Mg-Zr alloy in OPC solution with fluoride at 2.5 M evidenced high fluoride concentration for inhibiting efficiency.

	I_{corr} (mA/cm ²)	E_{corr} (V/SCE)	P_{i-24h} (mm/y)	P_{OPC-i} / P_{sol-i}
OPC solution	$5.5 \cdot 10^{-4}$	-1.51	$1.25 \cdot 10^{-2}$	1
OPC solution +[NaF]=1.25 M	$6.7 \cdot 10^{-5}$	-1.15	$1.53 \cdot 10^{-3}$	8.16
OPC solution +[NaF]=2.5 M	$3.1 \cdot 10^{-5}$	-0.71	$7.08 \cdot 10^{-4}$	17
Activated geopolymer solution	$5.9 \cdot 10^{-5}$	-1.28	$1.34 \cdot 10^{-3}$	9.3

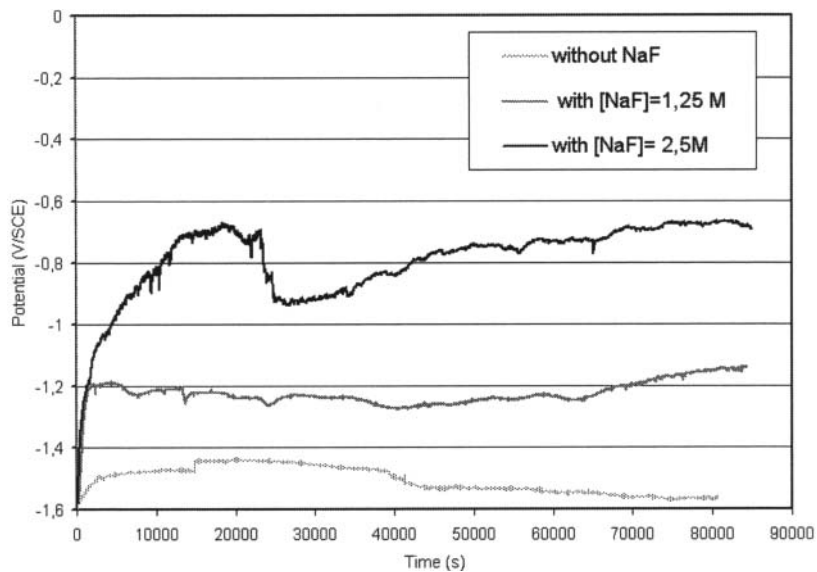


Figure 1. Open circuit evolution of Mg-Zr in OPC solution with addition of fluoride as a function of time

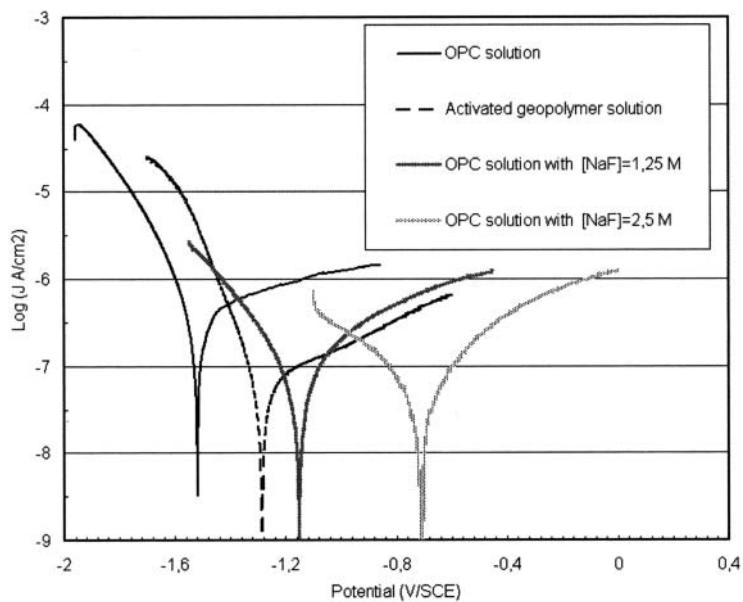


Figure 2. Potentiodynamic curves of Mg-Zr alloy in OPC solution with fluoride addition and in geopolymer solution at 24 hours

Encapsulation tests of Mg-Zr alloy in OPC and in geopolymer

In order to estimate corrosion rates P_H of Mg-Zr in OPC with addition of fluoride and in geopolymer, encapsulation of Mg-Zr pieces have been undertaken and analysis of hydrogen evolution have been performed as a function of time. Corrosion rates have been deduced by using Eq.4 and the hydrogen evolution rate V_H (ml/cm²/d). The results are reported in Table 3. In order to compare results obtained by Tafel extrapolation and hydrogen evolution at 1 day, P_{H-24h} / P_{i-24h} ratios have been calculated and reported in Table 4. Table 5 represents calculated $P_{OPC-H} / P_{binders-H}$ ratios from Table 3 results.

Table 5 showed that at 1 day, corrosion rate P_H of Mg-Zr in OPC is higher than with fluoride at 1.25 M and in geopolymer. Ratios

$P_{OPC-H} / P_{binders-H}$ at 8 and 29 days pointed out that corrosion rates obtained with hydrogen evolution of Mg-Zr alloy in OPC with fluoride at 1.25 M and in geopolymer are in the same order of magnitude. The ratio P_{H-24h} / P_{i-24h} showed that determination of corrosion rates obtained by Tafel extrapolation and hydrogen evolution rate are in the same order in OPC, but with fluoride and in geopolymer a deviation is observed. We can see also that corrosion rates ratio obtained by Tafel extrapolation and with hydrogen evolution are what??

To compare various corrosion environments, corrosion rates determined by Tafel extrapolation (P_i) give a good evaluation of Mg-Zr behaviour, however corrosion rates P_H are always larger than P_i due to the NDE effect evidenced by Song *et al.* [9].

	1 day		8 days		29 days	
	V_H (ml/cm ² /d)	P_{H-1d} (mm/y)	V_H (ml/cm ² /d)	P_{H-8d} (mm/y)	V_H (ml/cm ² /d)	P_{H-29d} (mm/y)
OPC	$6,7010^{-3}$	0,015	$3,30 10^{-3}$	$7,52 10^{-3}$	$1,13 10^{-3}$	$2,99 10^{-3}$
OPC with [NaF]=1.25 M	$2,82 10^{-3}$	$6,42 10^{-3}$	$1,73 10^{-3}$	$3,95 10^{-3}$	$5,62 10^{-4}$	$1,28 10^{-3}$
OPC with [NaF]=2.5 M	ND	ND	$3,28 10^{-4}$	$7,46 10^{-4}$	$2,58 10^{-4}$	$5,90 10^{-4}$
geopolymer	$2,2 10^{-3}$	$5 10^{-3}$	$1,42 10^{-3}$	$3,25 10^{-3}$	$5,70 10^{-4}$	$1,29 10^{-3}$

	P_{H-24h} / P_{i-24h}
OPC	1.2
OPC with [NaF]=1.25 M	4.2
OPC with [NaF]=2.5 M	ND
geopolymer	3.73

	1 days	8 days	29 days
OPC	1	1	1
OPC with [NaF]=1.25 M	2.33	1.9	2.33
OPC with [NaF]=2.5 M	ND	10	5
geopolymer	3	2.3	2.3

Conclusions

The objectives of our study were to evaluate Mg-Zr alloy behaviour in OPC solution and activation geopolymer solution by electrochemical methods and to compare with hydrogen evolution of Mg-Zr in OPC and geopolymer binders. We have evidenced that the corrosion rate P_i of Mg-Zr alloy in OPC solution is one order of magnitude more important than in geopolymer solution environment. Evaluation of encapsulation of Mg-Zr alloy in OPC and geopolymer has been done by determination of corrosion

rates using hydrogen evolution, so we have evidenced that order of corrosion rates P_H can be summarized as follows:

$$P_{OPC-H} > P_{OPC+[NaF]=1.25M-H} \approx P_{GEO-H} > P_{OPC+[NaF]=2.5M-H}$$

To compare various corrosion environments, corrosion rate order determined by Tafel extrapolation (P_i) gives a good evaluation of Mg-Zr behaviour.

References

- [1] J. Morris, Proceedings of the 12th International Conference on Environmental Remediation and Radioactive Waste Management ICEM2009 October 11-15, (2009), Liverpool, UK.
- [2] G.A. Fairhall, J.D. Palmer, Cement and Concrete Research, Volume 22, Issues 2-3, Pages 201-514 (1992).
- [3] L.M. Spasova, M.I. Ojovan, Journal of Nuclear Materials 375 (2008) 347–358.
- [4] A. Setiadi, N.B. Milestone, J. Hill, M. Hayes, Adv. Appl. Ceram. 105 (4), (2006) 191-196.
- [5] A. Zosin, Atomic Energy, 85, 510-514, (1998).
- [6] G. Turner, Proceedings of the 15th International Symposium on the Packaging and Transportation of Radioactive Materials (PATRAM 2007), (2007), Miami, Florida.
- [7] D.A. Jones, Principles and Prevention of corrosion, Prentice-Hall, Englewood Cliffs, NJ, 1992.
- [8] G. Song, A. Atrens, Advanced Engineering Materials 5 (2003) 837-858.
- [9] G. Song, Advanced Engineering Materials 7 (2005) 563-586.
- [10] E. Gulbrandsen, J. Taftø, A. Olsen, Corrosion Science, Vol 34, N°9, (1993), 1423-1440.
- [11] X. Hallopeau, Ph D. University of Paris XII, 1996.