CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS IMMOBILIZED IN MKPC MORTAR

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Abstract

Radioactive waste from nuclear activities must be managed responsibly to ensure their safe disposal, which is in fact the essential part of the radioactive waste management strategy. The commonly used conditioning matrix for low- and intermediate-level radioactive waste is based on Portland cement. In the case of waste containing metallic aluminium, the high alkalinity of the Portland cement matrix is a serious obstacle in obtaining an adequate waste form, as the Al reacts with the hyper-alkaline pore water leading to solid corrosion products and a significant amount of hydrogen. The release of significant volumes of hydrogen as a result of chemical reactions is a major drawback for embedding reactive metals in Portland cement matrix and represents the starting point in finding new conditioning matrices for reactive metals such as aluminium and its alloys. Magnesium and potassium phosphate cement (MKPC) is one of the alternative binders under investigation. This type of matrix has a pore fluid with a pH nearly neutral, which is a major advantage and a promising alternative in solving the management of reactive metals. This study compares the results obtained in the tests carried out on $AlMg_3$ alloy embedded in Portland and MKPC matrices, in the framework of the European project PREDIS (*Predisposal management of radioactive waste*) in which RATEN ICN is a partner. To measure the corrosion rates and the volumes of hydrogen released in the reactions between $AlMg_3$ and the two tested matrices, chemical tests and electrochemical tests were carried out.

Keywords: *$AlMg_3$ alloy, Portland matrix, MKPC matrix, Corrosion*

Introduction

Following the nuclear facilities decommissioning, all alloys (carbon steels, stainless steel and aluminium) present in these structures become low or medium level radioactive waste due to the activation of inpurities contained in these materials and/or their contamination by contact with the cooling fluids. Therefore these metals must be managed responsibly to ensure an acceptable level of environmental protection and a safety storage as an essential part of the radioactive waste management strategy.

TRIGA research reactor operated by RATEN ICN Pitesti is a dual core reactor, with ACPR (Annular Core Pulsed Reactor) and SSR (Steady State Reactor) located in a pool with walls from $AlMg_3$ alloy, with magnesium as the main alloying element for corrosion resistance and better weldability. After decommissioning of the TRIGA reactor, $AlMg_3$ liner will be considered a radioactive waste. For radioactive waste immobilization, Portland cement (PC) - a binder with many advantages - is used, but for Al alloys this is not an optimal solution. PC-type matrix is strongly alkaline and has a pH up to 12.6 at 20 °C, this high alkalinity being a serious obstacle in the immobilization due to the high reactivity of Al. It is well known that Al passivity is ensured by the protective layer of alumina present on its surface, but only for pH values in the range of 3-9. The alkaline solution destroys the protective oxide layer on Al surface, triggering the reaction between Al and water followed by production of hydrogen and solid corrosion products. Consequently, it is necessary to find new matrixes that present a better compatibility with this metal, therefore a neutral binder suitable for conditioning Al and its alloys [1, 2].

In recent years promising results were obtained using matrices based on magnesium and potassium phosphate (MKPC) with a nearly neutral pH. The advantages of using MKPC matrices are as follows: almost neutral pH, low water demand, low drying shrinkage, fast setting and high compressive strength. They are prepared by mixing basic magnesium oxide with acidic potassium dihydrogen phosphate (KH_2PO_4) in the presence of water, which explains their classification as acid-base binders.

In this paper, a comparative study was initiated, regarding evaluation of the corrosion rates of $AlMg_3$ alloy embedded in two conditioning matrices: one based on Portland cement, and the other one based on Mg and K phosphate cement [3, 4]. The matrix based on Portland cement generates a strongly alkaline pH in the porewater, reaching the value of 12.6 units, while the matrix based on Mg and K phosphate cement (MKPC) develops in the pores a solution with pH values in the range 7.25 - 8.5.

The tests carried out were long-term chemical and electrochemical tests, which helped to evaluate the corrosion rates and the release rate of hydrogen resulting from chemical reactions [3, 4].

Experimental set-up and methods

$AlMg_3$ coupons embedded in both matrices (PC and MKPC) were subjected to a continuous process of hydration on entire surface. During the chemical tests, the volume of hydrogen released as a result of the corrosion process was collected and measured. In the electrochemical tests (linear polarization resistance method) the relevant parameters were recorded: corrosion current (I_{cor}), polarization resistance, corrosion speed (v_{cor}), corrosion potential (E_{cor}), based on which volume of hydrogen was calculated. The experiments were carried out on $AlMg_3$ alloy samples in sheet form, classified as type 5754. The chemical composition from the technical specification is presented in Table 1.

Before the corrosion tests, $AlMg_3$ alloy samples were grinded and polished using SiC abrasive papers progressing up to P#4000 grain size. The finishing of the surfaces was done with diamond paste moistened with ethyl alcohol.

The samples were analysed through optical microscopy before their embedding into the two conditioning matrices and presence of some inclusions in the material were observed, both in the longitudinal and transverse sections (Fig. 1), [5].

The recipe formulations for the two conditioning matrices are presented in Table 2 (PC) and Table 3 (MKPC), [4].

The samples for chemical tests were prepared in specific moulds with or without $AlMg_3$ coupons embedded in the two selected matrices respectively and undergone a curing period of 28 days. Samples with $AlMg_3$ coupons embedded have been weighted before and after the curing period. After that, all the samples were removed from moulds, visually inspected for defects (cracks, voids), weighed and measured before the testing stage. The appearance of the samples for the chemical tests, after their curing, is presented in Fig. 2.

Table 1. Chemical composition of the 5754 Al-Mg alloy [%]

Chemical composition	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Min	0.07	0.13	0.01	0.05	2.65	0.16	0.02	97
Max	0.08	0.24	0.01	0.09	2.8	0.19	0.02	96

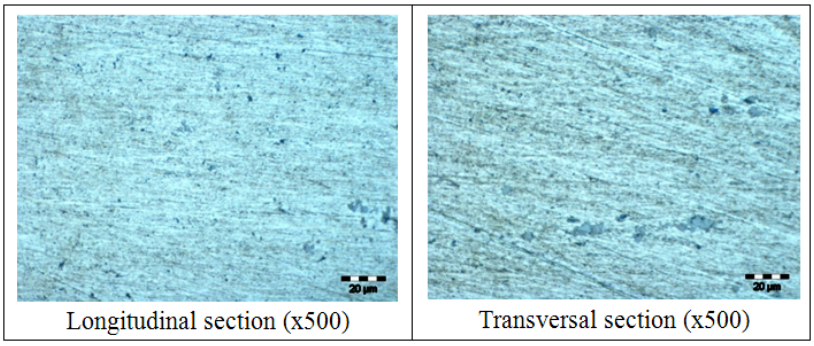


Fig. 1. Optical micrograph of AlMg3 coupons (as delivered, polished)

Table 2. Portland cement-based mortar recipe

Matrix	Water/Solid	Cement	H_2O [g]	Total [g]
PC1	0.4	125	50	175

Table 3. MKPC-based mortar recipe

Matrix	Water/Solid	MgO [g]	KH_2PO_4 [g]	H_2O [g]	Ash/Slag [g]	H_2BO_3 [g]	Total [g]
MKPC1	0.5556	30	110	100	40	6	286

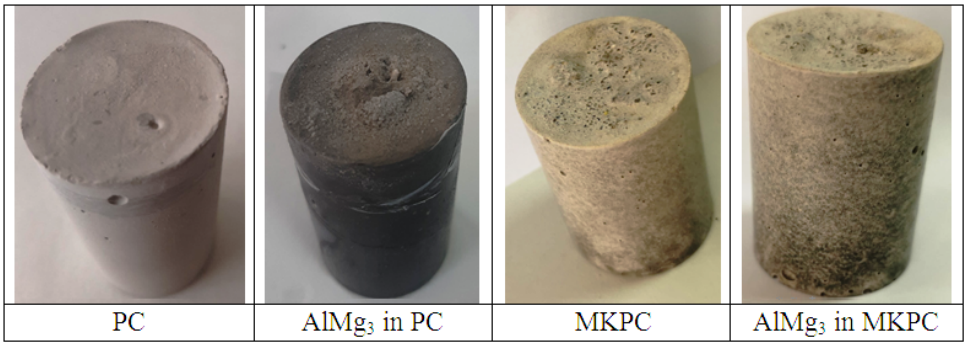


Fig. 2. Visual aspect of the samples prepared for the chemical test

Experimental setup for chemical test

Starting from the idea of collecting and measuring the volume of hydrogen released in chemical reactions, an experimental installation was designed and realized (see Fig. 3). The material is in direct and continuous contact with the chemical environment generated in the pores of the conditioning matrices, subject to the hydration process.

Linear polarization resistance method

For electrochemical tests, $AlMg_3$ coupons were embedded in both matrices together with two platinum counter electrodes. To perform the linear polarization resistance tests, an AUTOLAB 302N system (a potentiostat/ galvanostat interfaced with a Windows XP computer) was used (Fig.4 a).

A polyethylene recipient (Fig.4 b) was adapted to be used as electrochemical cell. The conditioning matrix (Fig.4 c), including three electrodes ($AlMg_3$ coupon and two counter platinum electrodes) together with an external reference electrode (Ag/AgCl electrode), were introduced inside of this cell. The electrolyte consisted of the solution generated and maintained by the cement matrix through continuous hydration during the test.

To draw the polarization curves, the potential was varied from -100 mV vs OCP (open circuit potential) up to + 100 mV vs SCE (saturated calomel electrode), with an increasing speed of 5 mV/s [6, 7].

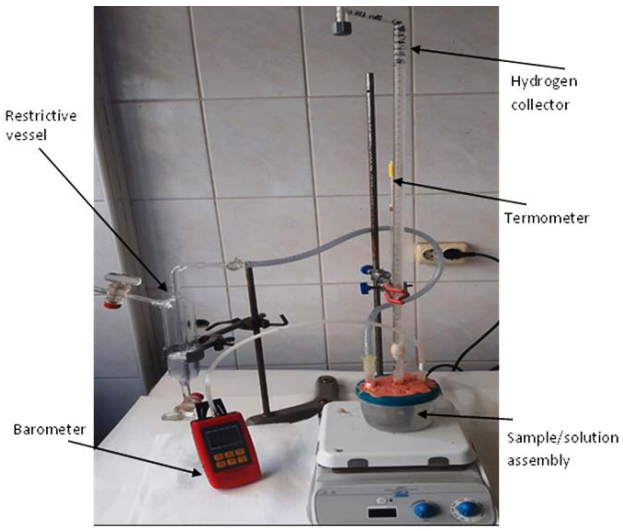


Fig.3. Chemical test experimental setup

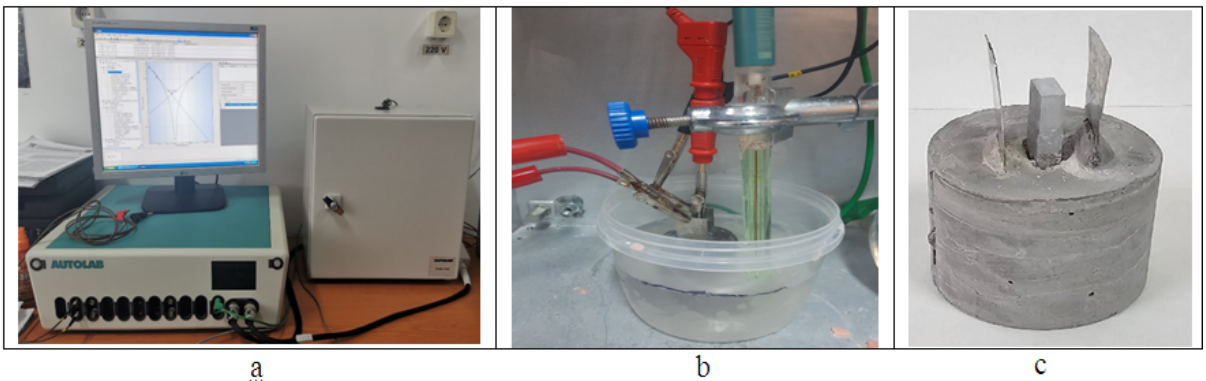


Fig. 4. a) AUTOLAB 302N electrochemical potentiostat/galvanostat assembly, b) adapted electrochemical cell, c) cement matrix with electrodes embedded

Results and discussions

Chemical tests performed on samples embedded in Portland cement-based matrix

One of the long-term chemical corrosion tests consisted of evaluating the corrosion behaviour of $AlMg_3$ coupon embedded in Portland cement-based matrices subjected to the continuous hydration process. The analysis was carried out taking into account the volume of hydrogen collected and measured, released from the chemical reactions between the environment generated by the matrix and the $AlMg_3$ sample during 153 days of testing.

In parallel with the matrix containing the Al alloy coupon, a control matrix of the same composition, cured under the same conditions, was tested. To avoid errors caused by the volume of gases released from the matrix volume, this experiment was conducted in parallel. Practically, the air volume from the matrix pores was measured and removed by replacing it with solution.

After fixing samples in the installation, 400 ml of drinking water with the initial pH of 7.233 and conductivity (c) of 453 µS/cm, were added into the installation's tank. Once this was accomplished, the solution was applied directly onto the matrix, covering it.

After each period of time between two measurements, the volumes of gases obtained were accounted for, the difference between the two measurements representing the volume of hydrogen generated by corrosion. The solution developed in the pores of the PC matrix is a saturated solution of calcium hydroxide, which, in contact with the $AlMg_3$ coupon, leads to a series of chemical reactions.

In the first stage, the aluminium oxide film is removed by the calcium hydroxide solution. Metallic aluminium, remaining without the protective oxide, reacts with water resulting in aluminium hydroxide and hydrogen according to the following chemical equation:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2 \quad (1)$$

The resulting volume of hydrogen was transformed into a volume of gas under normal conditions, using the formula:

$$pv/T = p_0v_0/T_0 \quad (2)$$

where: p = measured pressure [mmHg]; v = hydrogen developed volume [ml]; T = absolute temperature at the time of the measurement [K]; P_0 = 1atm. = 760 mmHg; T_0 = 273.15K = 0 °C; V_0 = normal volume of perfect gas.

The cumulative volume of hydrogen, transformed under normal conditions (normalized specific hydrogen volume), expressed in l/m^2, obtained after measurements at different time intervals is graphically represented in the Fig. 5.

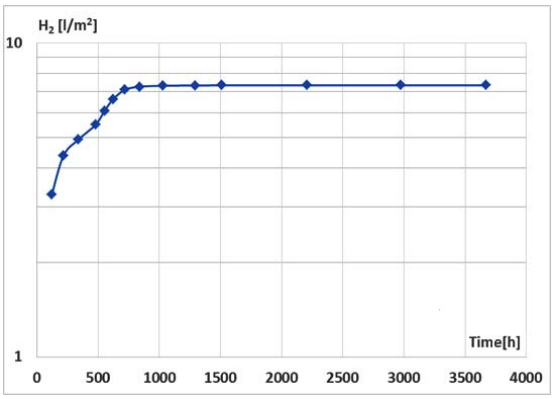


Fig. 5. Normalized specific hydrogen released in the chemical reaction

A total normalized specific hydrogen volume of 7.33 l/m^2 resulted at the end of testing period.

Knowing the volume of hydrogen released during the corrosion process, and the volume of hydrogen under normal conditions, the amount of alloy transformed into corrosion products have been calculated using the following formula:

$$m_{lost} = M_{Al} \times \frac{V_{measured}}{V_0 \times \frac{3}{2}} \quad (3)$$

Based on the mass loss, the corrosion rate was calculated using the formula given below:

$$V_{cor} = (K \times W)/(A \times T \times D)\ [mm/an] \quad (4)$$

with: $K = 8.76x10^4$, constant; T = exposure time [h]; A = sample area [cm^2]; W = mass loss [g]; D = alloy density [g/cm^3].

The evolution of corrosion rate is represented in Fig. 6. It is very clear that the corrosion rate has a downward evolution, in two steps. Practically, after 120 hours of testing, the corrosion rate starts at 379 µm /year and reaches 65 µm /year after 336 hours, after which there is a plateau period. Following the plateau period, the corrosion rate dropped and, after 2208 hours, it reached 0.25 µm/year.

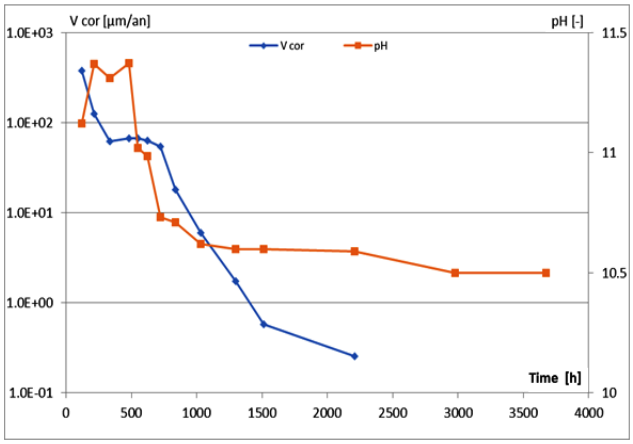


Fig. 6. Corrosion rate and pH vs time obtained in the chemical test (AlMg3 in Portland matrix)

It is important to note that the evolution of corrosion during the conditioned matrices curing process was not considered. The test was stopped after 153 days, a duration that was somewhat imposed by the test by recording two consecutive zero values at intervals of 30 days each.

Chemical tests performed on samples embedded in potassium and magnesium phosphate (MKPC) matrix

The MKPC matrix chemical tests were conducted using the same procedures and at the same time as the previous chemical test.

The tests included recording of the solution's pH evolution, the temperature for the environment and the solution, and the volume of hydrogen generated by the chemical reactions produced during the corrosion process. Based on the measured hydrogen volume, it was possible to evaluate the amount of material converted into various corrosion products. Fig. 7 displays a graphic representation of the cumulative hydrogen volume collected during this test i relation to the sample's surface.

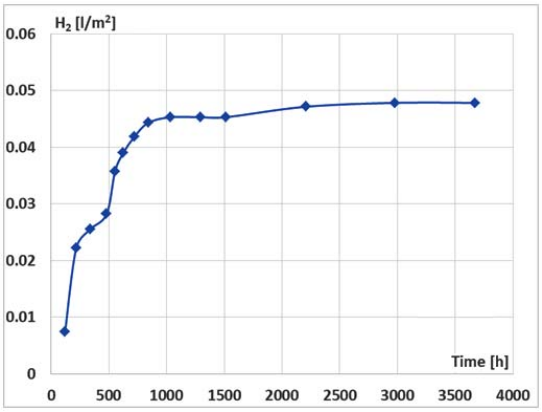


Fig. 7. Cumulative hydrogen volume in chemical test ($AlMg_3$ in MKPC matrix)

The hydrogen volume released in the corrosion process is much smaller compared with that measured in the PC matrix. Its measurement requires longer time intervals to avoid as much as possible reading errors in the correct assessment of the collected volume. The normalized specific volume of hydrogen was 0.047 L/m^2.

The corrosion rate was determined for each time interval between two successive measurements using Eq. (4), its graphic representation being displayed in Fig. 8.

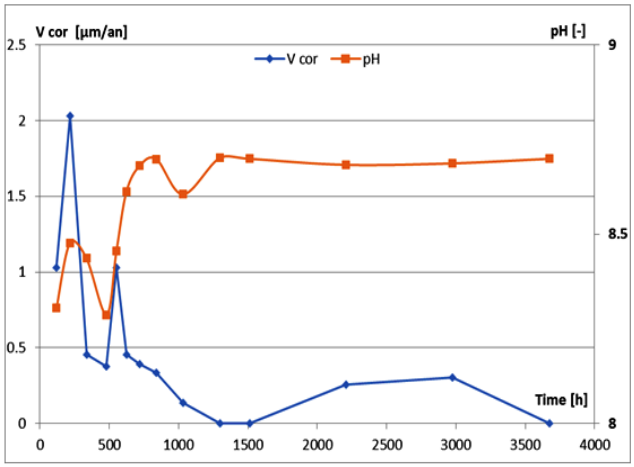


Fig. 8. Corrosion rate and pH vs time obtained in the chemical test ($AlMg_3$ embedded in MKPC matrix)

Fig. 8 illustrates how the corrosion rate changes within relatively narrow limits. It reaches the maximum after 216 test hours (2 µm/year), then it follows a downward trend over the two-time intervals before registering a new peak (after 555 hours) with a value of 1 µm/year. Following these two peaks, the corrosion rate gradually decreases until it reaches zero value after 1032 hours and remains there until 2208 hours, when it starts to slightly increase up to 0.306 µm/year. Analysing the corrosion rate over the entire time interval, alternative activation and passivation periods can be observed.

Another important aspect analyzed was the pH of the solution generated by the matrix, which seems to evolve in tandem with the corrosion rate, but only in first part of the test, during the matrix hydration period. This conclusion is based on the fact that the maximum value of pH=8.701 recorded after 1296 test hours overlaps the first zero recorded by the corrosion rate. However, the pH evolution during the test is rather insignificant (between 8.287 and 8.701) as can be seen in Fig.8.

Electrochemical corrosion tests

The electrochemical tests were conducted on $AlMg_3$ coupons embedded in Porland and MKPC conditioning matrices in order to determine the corrosion rates. The solution in equilibrium with each matrix was used as the test environment, and it had the same characteristics as in the previous performed tests.

The testing of the $AlMg_3$ coupon in a Portland-type matrix was performed for 84 days. The coupon's tested surface measured 8.69 cm^2, and its initial mass was 5.0099 g. The test involved the recording of the solution's pH evolution and, in addition, the electrochemical parameters (corrosion potential, corrosion current density, polarization resistance and corrosion rate).

Using the same algorithm based on the chemical reaction that occurred during the corrosion process, the hydrogen volume generated in the electrochemical tests was determined.

In the first stage, using the I_{cor} values recorded during the electrochemical test, the mass of Al transformed during the corrosion process is calculated using the formula:

$$M_{lost} = \frac{I_{cor} \times t \times M}{z \times F} \quad (4)$$

where: I_{cor} = corrosion curent, [A]; t = exposure time [h]; M = molar mass of the substance [g/mol]; Z = number of electrons participating in the reaction; F = Faraday constant = 96485.33 [C/mol].

Fig. 9 shows the evolution of hydrogen volume calculated as given below, after the converted Al mass was obtained:

$$V = \frac{3}{2} \times \left(\frac{M_{loss}}{M} \right) \times \frac{R \times T}{P} \quad (5)$$

where: M_{loss} = mass transformed into corrosion products [g], M = molar mass of the substance [g/mol]; R = 0.082, universal gas constant; T = absolute temperature [°C]; P = atmospheric pressure [mm Hg].

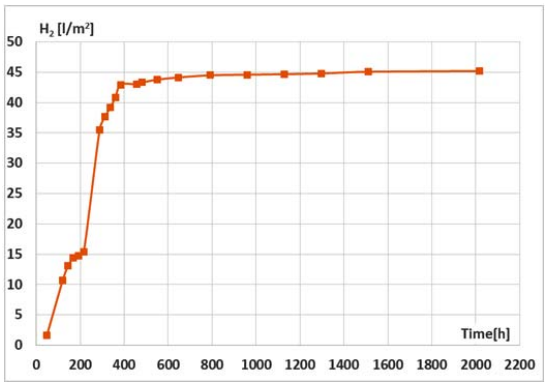


Fig. 9. Volume of hydrogen in electrochemical test on $AlMg_3$ embedded in PC matrix

In the electrochemical test, the normalized specific volume of hydrogen determined by calculation was 45.19 L/m^2. After 2016 hours of testing, the $AlMg_3$ coupon had a calculated cumulative mass loss of 0.0003679 g from the average initial mass.

Fig. 10 displays the evolutions of the corrosion rate and the solution's pH during the electrochemical test.

The corrosion rate changes over several stages before showing a decreasing caused by the transition to a passive zone with higher chemical stability. Consequently, the corrosion rate doubles in the first stage, going from 150 µm/year to 290 µm/year, between two consecutive measurements taken a day apart. The maximum corrosion rate of 640 µm/year was recorded 216 hours after the test began. The test was continued until no significant jumps in the corrosion process were recorded, the corrosion rate reaching at the end of the test a value of 0.03 µm/year.

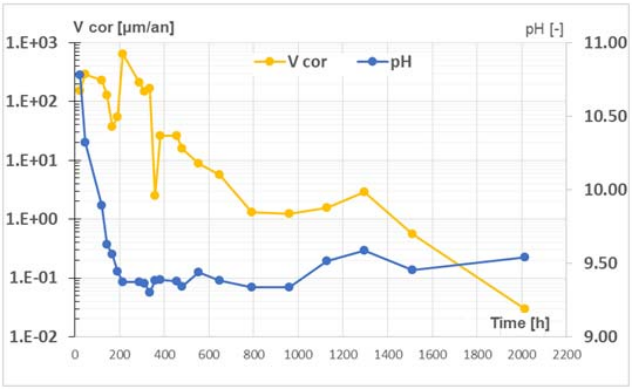


Fig. 10. Corrosion rate and pH vs. time in electrochemical test on $AlMg_3$ embedded in PC matrix

The electrochemical test on $AlMg_3$ coupon embedded in MKPC was similar, the differences consisting only in the sample's initial mass and surface (mass was 5.14904 g and surface was 10.22 cm^2). Data analysis revealed extremely low values for every parameter characterising the corrosion.

After 2016 hours of electrochemical testing, the $AlMg_3$ coupon showed a calculated cumulative mass loss of 0.000009774 g compared to the initial average mass at an exposed test surface of 10.78 cm^2.

As in the case of test on $AlMg_3$ coupon embedded in PC matrix, the formula used to calculate the hydrogen volume is based on the mass loss, determined from the corrosion rate calculated in electrochemical test. The corrosion rate has an exact and precise value, but only for the moment in which electrochemical parameters is recorded.

Since the corrosion rate is known to vary from one moment to another, the total hydrogen volume determined is based on the assumption that this rate remains constant over the time interval between two consecutive measurements. The normalized specific hydrogen volume calculated was 1.49 L/m^2.

For the time being, the hydrogen volume remains clear and accurate because the cumulative hydrogen volume may change only if the corrosion rate is extrapolated over the whole period of time between two successive measurements. The evolution of hydrogen volume, calculated from electrochemical parameters, is displayed in Fig. 11.

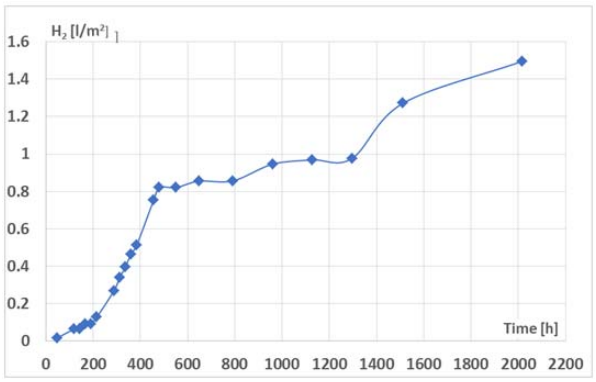


Fig. 11. Hydrogen volume calculated in electrochemical test on $AlMg_3$ embedded in MKPC matrix

The corrosion rate obtained using the Tafel slope method (see Fig. 12) exemplifies very well the behaviour of this type of material in MKPC matrix. The corrosion rate registers low values during the test, fluctuating repeatedly between measurements. It begins at 3.5 µm/year and reaches its maximum of 7.7 µm/year after 384 testing hours. After that, it trends downward to a minimum of 0.016 µm/year after 480 testing hours. The sample continues this trend of changing states until the end of the test; this trend is shown on the graph as saw teeth, reaching a small corrosion value (0.24 µm/year) at the end of the test.

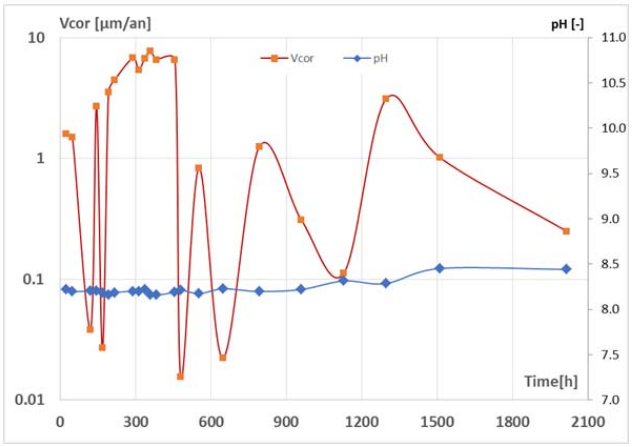


Fig. 12. Corrosion rate and pH vs. time recorded in electrochemical test on $AlMg_3$ embedded in MKPC matrix

Table 4 comparatively presents the initial and final values of corrosion rates and hydrogen volumes measured by the two considered methods, for $AlMg_3$ coupons embedded in PC and MKPC matrices.

Table 4. Corrosion rates and hydrogen volumes measured using LPR and chemical methods

Testing environment	Method	Initial time [h]	End of test time [h]	Corrosion rate initial [µm/y]	H_2 initial [L/m^2]	Corrosion rate end [µm/y]	Total H_2 [L/m^2]
PC	Chemical	120	3672	**379**	3.28	**0.25***	7.33
	LPR	24	2016	**150**	1.59	**0.03**	45.19
MKPC	Chemical	120	3672	**1.02**	0.007	**0.306***	0.047
	LPR	24	2016	**1.59**	0.015	**0.249**	1.495

Volume of hydrogen developed for electrochemical testing is estimated at 24h at the first measurement
* Final V_{cor} for chemical test in MKPC paste was reached at 2976h
* Final V_{cor} for chemical test in PC paste was reached at 2208h

Conclusions

Long-term chemical and electrochemical tests on $AlMg_3$ alloy embedded in PC and MKPC matrices were carried out. Based on their results it was possible to evaluate the corrosion rate and the volume of hydrogen resulting from the reactions occured during the corrosion process.

The two types of long-term tests revealed similar results indicating a corrosion rate lower by at least 2 orders of magnitude in the environment developed by MKPC matrix in comparison to that in the environment developed by PC matrix.

Consequently, the volume of hydrogen generated in the case of $AlMg_3$ coupons embedded in MKPC matrix is much smaller than the volume of hydrogen generated when embedding the $AlMg_3$ in PC matrix.

In conclusion, a MKPC matrix in comparison with a Portland Cement matrix represent a promising solution for the conditioning of reactive waste such as aluminium alloy Moreover, the aluminium alloy shows a low reactivity and a greater tendency to passivation the chemical activity throughout the tests being insignificant in the environment created by the MKPC matrix.

Comparing the hydrogen volumes values obtained by the two types of tests, a difference can be observed. This occurs after the extrapolation of the corrosion rate recorded in the electrochemical test (between two consecutive measurements) which is reflected in the cumulated hydrogen volume calculated at the end of the test.

Another aspect that should be mentioned is that the chemical tests allowed the evaluation of the air volume included in the matrix from the beginning of test (the volume of air collected being related to the effective volume of the matrix). Thus, it was observed that a 10 times more air volume was developed in Portland matrix comparatively to that developed in MKPC matrix.

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