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UNGG Waste Retrieval – Comparison of general and galvanic corrosion of Magnesium alloy coupled to graphite in ordinary Portland cement and alkali-activated slag binders

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Introduction

Graphite and magnesium alloys wastes were generated during the reprocessing phase of spent fuel assemblies of the former nuclear reactors in France. Conditioning of these low to intermediate level wastes in cementitious materials is being addressed here. Magnesium is one of the most reactive metals with a standard potential of -2.37V/SHE [1]. Once embedded in a hydraulic binder with alkaline pH and high internal humidity, oxidation reactions occur. The subsequent formation of corrosion products around the alloy may result in tensile stresses development in the surrounding binder that could lead to cracking risks. Thus, general and galvanic corrosion (when coupled with graphite) of the metal in the packages should be properly addressed.

Materials and methods

The tested hydraulic binders are mortars with water to binder (w/b) and sand to binder (s/b) ratios of 0.5 and 2 respectively. Three different formulations are studied: a ground granulated blast furnace slag (GGBFS) – LA – activated with NaOH solution (2.5 M) and two different Ordinary Portland Cement (OPC). The first one – CB – has low amount of iron (CEM I 52.5 N CE CP2 NF « SB ») in its compositions while the second – SR0 – is free of sulfates (CEM I 52.5 N-SR0 CE PM-CP2 NF).

The studied magnesium alloy is Mg-1.2%Mn. Extruded graphite is used with high purity degree and a total porosity of 15%.

Mass loss experiments are conducted according to the NF ISO 8407 protocol. An average corrosion rate is determined in the three binder, up to 24 months, for the general corrosion (Mg pellets) and the galvanic corrosion (Mg/graphite assemblies, surface ratio 1/10)

The general corrosion is characterized with electrochemical impedance spectroscopy (EIS). A tow electrode system is used: Mg-1.2%Mn (2x2x1 cm) as working electrode, graphite (2x2x1.5 cm) as counter and reference electrode. Electrodes are embedded in 4x4x16 cm mortar samples covered with double layer of aluminum to ensure autogenous conditions.

Galvanic Corrosion measurements were performed in the three binders through the electrical coupling between Mg alloy and graphite (surface ratios 1:10 respectively), achieved with the zero-resistance ammeter (ZRA) technique.

SEM observations and EDS mapping were performed on the interfaces between Mg-1.2%Mn alloys and the different binders.

Results and discussion

Mass loss results: general and galvanic average corrosion rate

The experimental results indicate similar general corrosion behavior in all binders. The average corrosion rate is lower than 2 µm.year^{-1} for all studied ages.

However, the metal’s galvanic corrosion is lower in AAS mortar compared to the OPC ones. The damage seems to stabilize at a value of 10 µm within 6 to 12 month of embedment in LA mortar while the stabilization value in OPC mortars is close to 100 µm reached only after 1 month of encapsulation.

ZRA results: galvanic corrosion rate

Galvanic currents evolutions shows a fast decrease in the first days and a stabilization after 30 days for LA and CB. Stabilization is not achieved for SR0 after 90days and still decrease slowly. Once stabilized, LA shows a 0.25 µA current while CB is closed to 1 µA and SR0 remains over 2 µA after 90 days.

Comparing to mass loss measurements, gravimetric tests tends to overestimate the corrosion rate especially for CB and LA. A high variability is encountered in the case of corrosion in SR0 due to its highly aggressive nature. Comparison between both techniques for galvanic corrosion rate estimation is difficult but general trends seems to be respected.

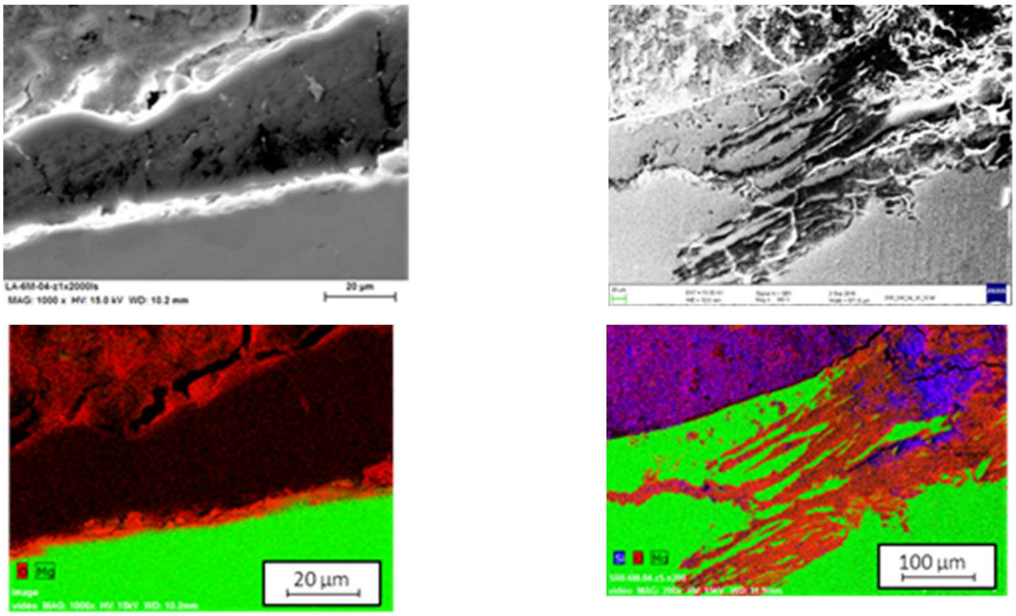
EIS results: general corrosion rate and electrolyte resistance

The results confirms once again the similarity of general corrosion behavior in the studied mortars. A maximum metal loss of 0.02 µm is calculated after 100 days of embedment for every mortar. An exception is observed for one of the SR0 specimens. These results cannot be faced up to gravimetric calculated damage because of the limitation and precision of the technique.

The computed electrolyte resistance determined from EIS measurements is a very important parameter to explain the galvanic corrosion behavior in the different binders. In fact, the galvanic corrosion depends strongly on the electrical conductivity of the electrolyte [10] and in our case the cementitious matrix. Results seems to be in accordance with the galvanic corrosion rate determined previously. The high resistivity of LA may explain the lower corrosion of the embedded metal.

Surface analysis (SEM/EDS)

The morphology of corrosion in AAS mortar is compared to that in OPC ones. SEM images and corresponding EDS mappings (Figures 1). The analyzed area corresponds to galvanic corrosion assemblies embedded for 6 months in the LA mortar (Figure 1a) and the SR0 one (Figure 1b).



(a)

(b)

Figure 1: SEM images coupled to EDS for Mg-1.2%Mn alloy in galvanic corrosion assembly embedded for 6 month in (a) the AAS mortar and (b) the SR0 OPC mortar (Green for Mg element – Red for O element – Blue for Si)

On one hand, the images show a general (homogenous) corrosion in the LA mortar. On the other hand, the aggressive nature of galvanic corrosion in SR0 OPC mortar is confirmed.

Conclusions

Mass loss results in accordance with ZRA measurements confirmed the advantage of alkali-activated slag mortar for the encapsulation of these wastes. In fact, the galvanic corrosion behavior of the metal in this particular hydraulic binder show lower corrosion rate than in the case of ordinary Portland cement binders.

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