

Selection of Binders for a Reactive Metal (Tungsten) Encapsulation – 17211

David Lambertin^{*}, Charly Lemoine^{*}, Céline Cau-dit-Coumes^{*}, Fabien Frizon^{*},
Christelle Decanis^{**}

^{*}CEA, DEN, DTCD, SPDE, LP2C F-30207 Bagnols Sur Ceze, France

^{**}CEA, DEN, DSN, SGTD, LMDE F-13115 Saint-Paul lez Durance, France

ABSTRACT

Waste containing reactive metals is produced by nuclear activities, and the usual strategy is to encapsulate this waste in ordinary Portland cement (OPC) or alternative binders in a state suitable for storage. However, in the case of tungsten metal, corrosion by the pore solution of the binders could occur with hydrogen release. Based on Potential-pH diagram, tungsten metal corrosion depends on pH conditions. Consequently, studies have been performed with tungsten in a large pH scale relevant for various binders such as ordinary Portland cement (OPC), sodium geopolymer (Na-Geo), magnesium-phosphate cement (MKP) and wollastonite-based cement (Wo). The influence of representative pore solutions of OPC, Na-Geo, MKP and Wo on tungsten corrosion has been studied by electrochemical methods (Open Circuit Potential and impedance spectroscopy). The corrosion of tungsten encapsulated in OPC, Na-Geo, MKP and Wo has been investigated by measuring the production of hydrogen over time. It is shown that ordinary Portland cement is not a suitable binder for tungsten metal encapsulation while a binder producing a pore solution with a neutral pH such as MKP presents the lowest interaction with tungsten.

INTRODUCTION

The dismantling of legacy nuclear facilities produces radioactive waste materials, some of which contain tungsten metal. Prior to disposal, the waste must be conditioned in a stable, monolithic and confined form. Calcium silicate cements are widely used for conditioning low- or intermediate-level waste. Compared with other solidification techniques, the cementation process is relatively simple and inexpensive. Moreover, these binders can be easily supplied, are compatible with aqueous waste, and, after hydration, generally exhibit good mechanical strength, stability over time, and high alkalinity which allows precipitating, and thus confining, many radionuclides [1]. At the same time, however, this basicity could be an obstacle for conditioning tungsten metal. The potential-pH diagram of tungsten (Fig. 1) shows that this metal is not thermodynamically stable in an aqueous environment. The behavior of tungsten in aqueous solutions is governed by the high affinity of tungsten to oxygen and its complex speciation. No oxygen-free tungsten cation exists but only monomeric or dimeric species like WO_2^{2+} or monomeric tungstate ion like WO_4^{2-} . Water reacts with tungsten at room temperature. As a reaction product, the presence of hydrogen always has to be considered [2] and the resulting hydrogen release

would be detrimental to the safe storage of the conditioned waste packages. In acidic medium, formation of a tungsten oxide layer on surface is evidenced and, in basic solution, tungsten oxide is soluble as monomeric tungstate ion and metal corrosion continues until all the reactants have been depleted.

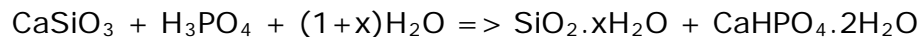
This paper presents studies on tungsten metal over a large pH range covering the pore solution pH values of various binders such as ordinary Portland cement (OPC), sodium geopolymer (Na-Geo), magnesium-phosphate cement (MKP) and wollastonite cement (Wo).

Portland cement (CEM I according to EN 197-1 standard) is widely used in France for waste conditioning and presents a pore solution pH close to 13. Alkali-activated binders are made by mixing solid aluminosilicates, such as fly ash, metakaolin, various clays usually activated by heat or blastfurnace slag, with an activating solution comprising high concentrations of alkali hydroxide and/or polysilicate. The reaction product, formed according to a polycondensation process, exhibits a network. Thus, the binders are sometimes called inorganic polymers or geopolymers. In our laboratory, we developed various sodium geopolymer formulations [3] with alkaline silicate solution exhibiting a high pH at early age and reaching an equilibrium pH close to 12.5 after setting. A magnesium phosphate cement known as Ceramicrete has been developed in the United States at the Argonne National Laboratory to stabilize hazardous waste [4]. It is prepared by reacting magnesium oxide with potassium dihydrogen phosphate (KH_2PO_4) to form a hydrated phase, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite).



The moderate acidity of the KH_2PO_4 solution, near pH 4, makes it easy to use. After the reaction, the magnesium phosphate cement paste presents an equilibrium pH between 6 and 8.

Calcium phosphate cements are usually composed of one or several calcium phosphates, to which other calcic compounds can possibly be added, such as calcium hydroxide or calcium carbonate, as well as additives to control the setting rate and the properties of the hardened matrix [5]. Mixed with water, they can yield different end-products, such as stoichiometric or calcium-deficient hydroxyapatite, calcium octaphosphate or calcium phosphate, by an acid-base or hydrolysis reaction [6]. A calcium phosphate binder can be prepared from wollastonite (CaSiO_3), a natural calcium meta-silicate, and phosphoric acid (H_3PO_4), as firstly described by Semler [7]. The reaction starts in very acidic medium (pH ~ 1), but the pH increases rapidly to reach equilibrium at a value close to 6 [8]. For P/Ca molar ratios between 0.39 and 1, the sole precipitated calcium phosphate is brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Amorphous silica is also formed according following balance reaction



The influence on tungsten corrosion of solutions which mimic the pore solution of OPC, Na-Geo, MKP and Wo has been studied by electrochemical methods (Open Circuit Potential and impedance spectroscopy). The corrosion of tungsten encapsulated in OPC, Na-Geo, MKP and Wo has been investigated by measuring the

hydrogen production over time.

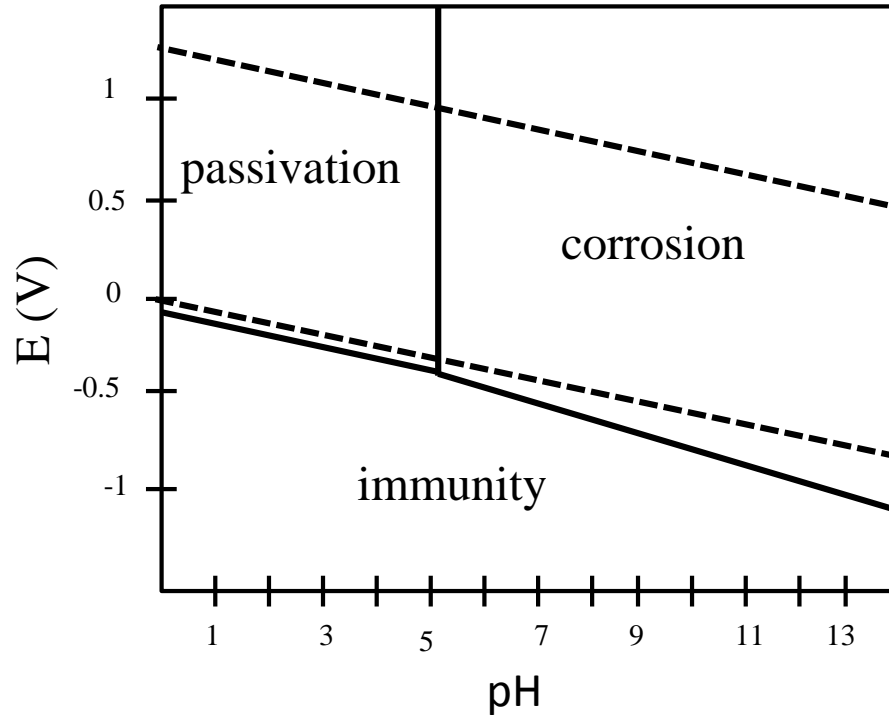


Fig. 1 : Pourbaix Potential-pH diagram for tungsten, from [2]

MATERIALS AND METHODS

Samples, solutions and binders

The material used in the tests was tungsten wire or plate (Goodfellow purity 99%). The samples were previously abraded and treated with ethanol under ultrasounds during 5 minutes and dried at 60°C during 5 minutes.

For electrochemical tests, various representative solutions were used (alkaline solution for geopolymer, Portland pore solution, initial potassium dihydrogen phosphate and interstitial pore solution for MKP and mixing of phosphoric acid and boric acid for calcium phosphate cement).

Portland cement grade CEM I 52.5 PM-ES was selected to prepare Portland paste with a water/cement equal to 0.4. The surrogate of the Portland pore solution comprised of NaOH (4 g.L⁻¹), KOH (28 g.L⁻¹) and Ca(OH)₂ (4 g.L⁻¹).

Magnesium phosphate cement was prepared by mixing "hard-burnt" magnesium oxide, potassium dihydrogen phosphate, fly ash, and boric acid in the following proportions (wt%): MgO: 11.31%; KH₂PO₄: 38.19%; fly ash: 49.51%; H₃BO₃ = 0.99%.

The calcium phosphate cement cement was a commercial binder (FOTIMINE, from Sulitec) comprising a powder (wollastonite – $d_{10} = 2.4 \mu\text{m}$, $d_{50} = 15.6 \mu\text{m}$, $d_{90} = 57.2 \mu\text{m}$) and a mixing solution (phosphoric acid + boric acid, $\text{pH} = 0.5$) to be mixed in the 125/100 mass ratio.

The sodium geopolymer samples $\text{Al}_2\text{O}_3\text{-xSiO}_2\text{-Na}_2\text{O-12H}_2\text{O}$ with $x=3.6, 3.8, 4$ (called Na-Geo) were prepared by mixing metakaolin powder with sodium silicate solutions. Silicate solutions $(x-2.4)\text{SiO}_2\text{-Na}_2\text{O-12H}_2\text{O}$ were prepared from commercial silicate solutions (BETOL 39T, Wollner). The composition of metakaolin Pieri PREMIX MK from Grace Constructions has been previously described [3].

Electrochemical measurements

A three-electrode cell was used for the electrochemical measurement: a working electrode (tungsten wire, Goodfellow purity 99%), a counter electrode (platinum wire, goodfellow purity 99.95%) and a calomel saturated reference electrode or a quasi-reference electrode (platinum wire). Figure 2 shows the experimental cell. The measurement setup consisted of a potentiostat (Princeton Applied Research model 263A) connected to a frequency response analyzer (Solartron model SI 1255) and driven with Solartron ZPLOT software. The analysis of the diagrams was performed using ZVIEW Software. EIS spectra were recorded at the open circuit potential with a 10 mV amplitude. Frequency ranged between 10^5 Hz to 0.01 Hz , with 10 frequency values per logarithmic decade.

Measurement of hydrogen production

Each tungsten test piece was plunged into 50 mL of fresh material poured into a polyethylene cell, then placed in a metal reactor with a cover tap that could be connected to a vacuum pump, to a nitrogen supply, or to a gas chromatograph (Figure 2). The reactor was hermetically sealed. It was placed under vacuum at a pressure of 150 mbar. Nitrogen was then introduced and pressurized to 750 mbar. The reactor was stored at room temperature ($22 \pm 2^\circ\text{C}$) and gas samples were taken at regular intervals for hydrogen analysis by gas chromatography (Varian CP 3800, argon carrier gas, capillary column, thermal conductivity detector, detection limit corresponding to 0.01% hydrogen in the reactor headspace). For safety reasons, each test was stopped when the hydrogen concentration reached 4% in the reactor headspace.

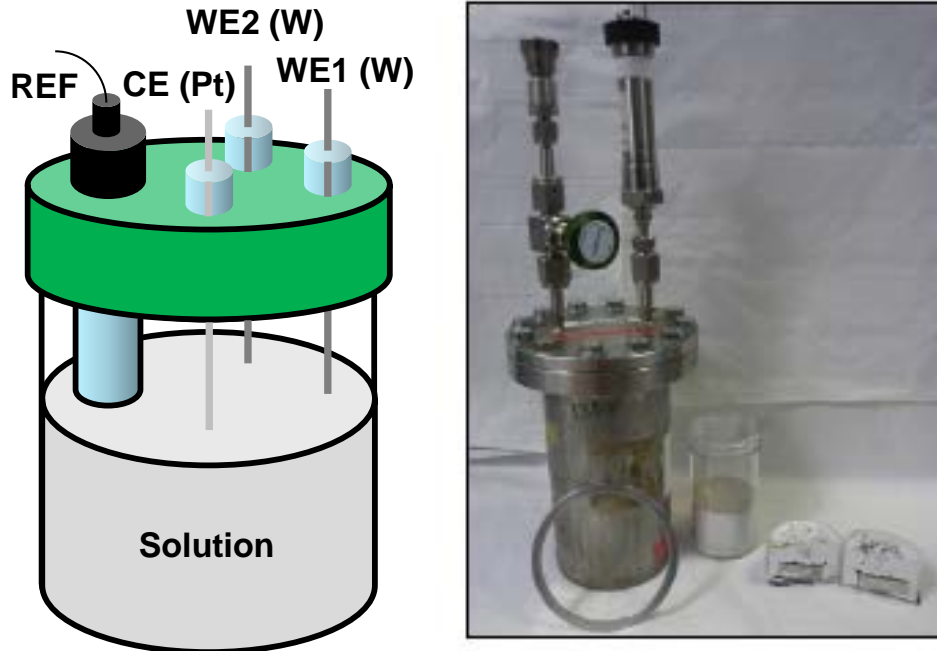


Fig. 2 : Electrochemical cell for OCP and impedance measurements (left) and container for hydrogen production measurements (right)

RESULTS AND DISCUSSIONS

Electrochemical measurements in synthetic pore solutions of the different binders

First, the open circuit potential (OCP) was measured with tungsten metal immersed in synthetic solutions representative of the pore solution of the different binders at early age (Figure 3). The OCP characterizes the reaction taking place at the electrode interface. When corrosion occurs, the chemical reaction potential is given by the two half-reactions corresponding to the two redox systems involved in the reaction. In the case of a chemical reaction between a metal and the solvent (the pore solution in this case), the potential is close to the cathodic limit of the solvent. The measurement of the OCP with time provides some data about the evolution of the corrosion process and the passivation of the interface against the solvent attack.

In the Fotimine initial solution, the tungsten electrode potential increases during 15 minutes and stabilizes at a high potential. For MKP pore solution and MKP initial solution, the tungsten electrode potentials are more anodic and stabilize between -0.3 and -0.2 V. These results suggest that in Fotimine and MKP solutions, tungsten metal is not strongly reactive and tends to a state of passivity.

In the case of alkaline solution corresponding to geopolymer and Portland cement binders, the tungsten electrode potentials are more cathodic which indicates a stronger corrosion reaction.

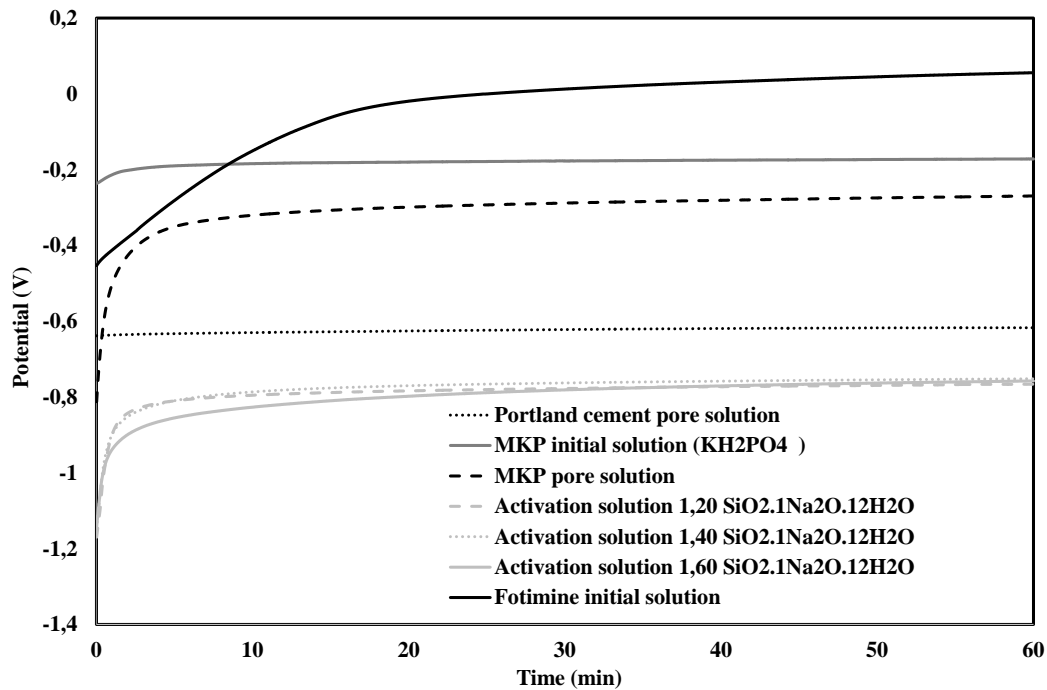


Fig. 3 : Open circuit evolution of tungsten immersed in various representative interstitial solutions.

Impedance spectroscopy provides information on the reaction mechanism and associated kinetics. Also, if the measurements are performed at Open Circuit Potential, the metal/mortar interface is not distorted. Therefore, this technique is well suited to study the corrosion. Impedance spectroscopy also can determine low corrosion rates that cannot be obtained by the usual methods, such as mass loss measurements or dihydrogen evolution by gas chromatography. This technique has already been used to study the corrosion of rebar steel in cementitious materials [9, 10]. Figure 4 presents the impedance spectra in Nyquist representation recorded on a tungsten electrode in various cement solutions. In Fotimine solution, the Nyquist plot tends to a linear vertical curve. This shape corresponds to a ideal capacitive behavior and a non-corroding sample [11]. The Nyquist curves differ in the initial mixing solution of the magnesium phosphate cement and in the solution simulating the pore solution after one day of hydration. This can be explained by the change in the composition of the pore solution with ongoing hydration. The corrosion is more important initially because of the lower pH of the solution. As wollastonite dissolves, the pH increases, which reduces the rate of corrosion of tungsten [2]. With the Portland cement pore solution, the Nyquist plot tends to a low impedance amplitude with loop, that characterizes a corrosion reaction [11]. With the high pH activation solution, the tungsten behavior is between that of MKP and Portland. This behavior

may result from the presence of silicate ionic in solution, which are known to induce a passivation layer [2].

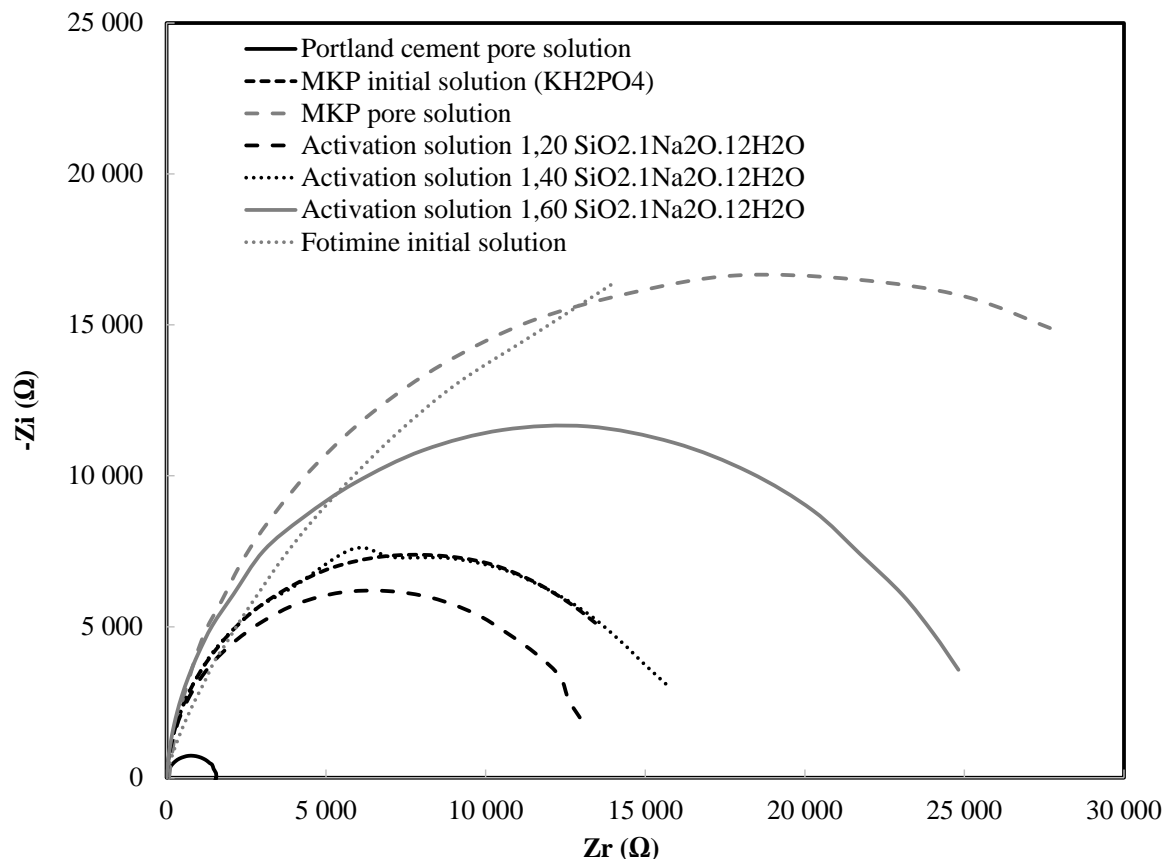


Fig. 4 : Impedance spectra in Nyquist representation recorded on tungsten electrode immersed in various representative cement solutions

Encapsulation of tungsten metal in various binders

Figure 5 compares the hydrogen production of tungsten metal immobilized in four binders (Portland cement, geopolymer, magnesium phosphate cement and calcium phosphate cement). As expected from the previous electrochemical measurements, the sample prepared with Portland cement releases massive amounts of hydrogen. This can be attributed to the alkaline pH of the pore solution and oxidation of tungsten into soluble species with no passivation.

With geopolymer, the hydrogen release is rapid during the first 10 days as observed with Portland cement, but then slows down until 55 days. Although the pore solution of the geopolymer exhibits a high pH, the reactivity with tungsten is low and this confirms the potential presence of a passivation layer on tungsten due to silicate ions in solution [2]. This still needs to be confirmed by metal/geopolymer interface analysis (MEB, XPS ..).

The calcium phosphate cement produces hydrogen only during the first days. Then, the hydrogen content increases very slowly and stabilizes after 15 days. This phenomenon is explained by the calcium phosphate cement hydration and the evolution of the pore solution pH with time. At the beginning, the pH of the mixing solution (phosphoric acid + boric acid) is very low, but as wollastonite starts to dissolve, it increases rapidly to reach equilibrium at a value close to 6. It is known that tungsten metal is dissolved in concentrated phosphoric acid and is resistant in diluted phosphoric acid [2].

In magnesium phosphate cement, the hydrogen production is very low (0.2 L/m²), which can be explained by the initial pH of potassium dihydrogen phosphate (pH ≈ 4) and the slight pH increasing during hydration until a pH equal to 7 falling within the passivation domain.

To summarize, over the duration of the study, the production of hydrogen is the most important with the Portland cement paste, and the least important with the magnesium phosphate binder.

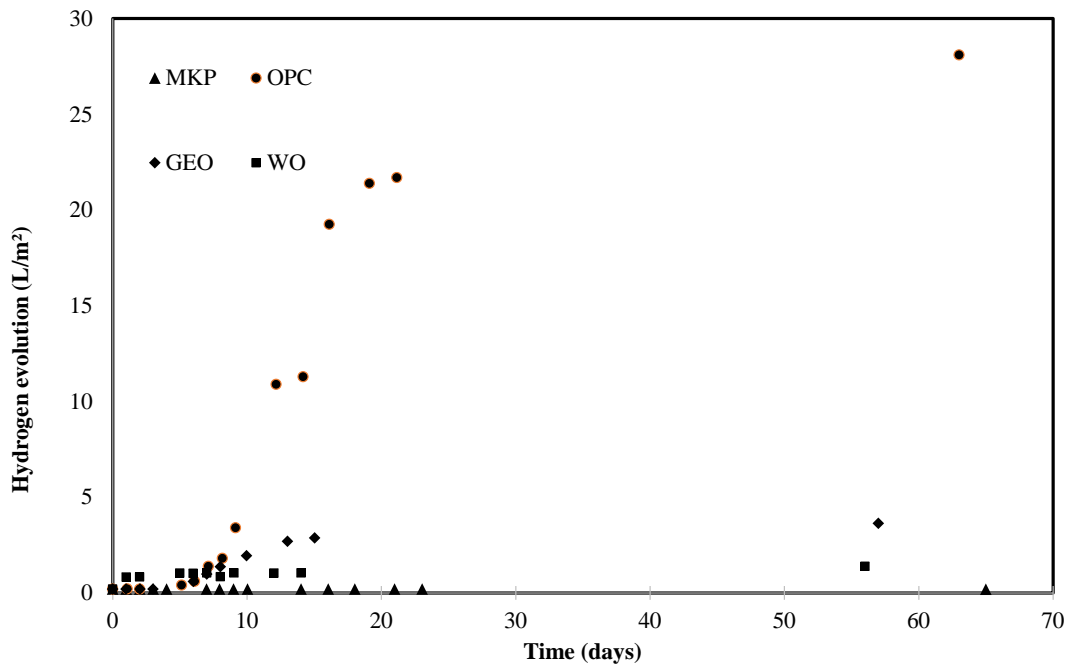


Fig. 5 : Hydrogen evolution of tungsten metal embedded in various binders (geopolymer, magnesium phosphate cement, Portland cement and calcium phosphate cement)

CONCLUSIONS

An experimental study was performed to measure by electrochemical techniques the behavior of tungsten metal in acidic and basic solutions representative of pore solutions of different cement pastes. In addition, the production of hydrogen by the corrosion of tungsten samples encapsulated in various cement pastes was measured over a period of 2 months. It confirmed that Portland cement is not an appropriate binder for tungsten metal encapsulation due to its high hydrogen production. On the contrary, this production can be strongly limited with alternative cements such as calcium phosphate and magnesium phosphate. The next step will be to get more information on the tungsten corrosion (mechanism, rate) in those alternative binders.

REFERENCES

1. Atkins, M. and F.P. Glasser, *Application of portland cement-based materials to radioactive waste immobilization*. Waste Management, 1992. **12**(2): p. 105-131.
2. Lassner, E. and W.D. Schubert, *Tungsten: Properties, Chemistry, Technology of the Elements, Alloys, and Chemical Compounds*. 1999: Springer US.
3. Rooses, A., et al., *Encapsulation of Mg-Zr alloy in metakaolin-based geopolymer*. Applied Clay Science, 2013. **73**: p. 86-92.
4. Wagh, A.S., *Chemically Bonded Phosphate Ceramics: Twenty-First Century Materials with Diverse Applications*. 2016: Elsevier Science.
5. Odler, I., *Special Inorganic Cements*. 2003: Taylor & Francis.
6. Lemaitre, J., *Biocéramiques et biociments résorbables pour le comblement osseux*, in *Presses Polytechniques et Universitaires Romandes*, C. Janot, Ilchner B., Eds, Editor. 2001: Lausanne. p. 289-314.
7. Semler, C., *Lime silico-phosphate cement*. 1974.
8. Mosselmans, G., et al., *Thermal hardening and structure of a phosphorus containing cementitious model material*. Journal of Thermal Analysis and Calorimetry, 2007. **88**(3): p. 723-729.
9. Nóvoa, X.R., *Electrochemical aspects of the steel-concrete system. A review*. Journal of Solid State Electrochemistry, 2016. **20**(8): p. 2113-2125.
10. Cau Dit Coumes, C., et al., *Selection of a mineral binder with potentialities for the stabilization/solidification of aluminum metal*. Journal of Nuclear Materials, 2014. **453**(1–3): p. 31-40.
11. Bard, A.J. and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*. 2000: Wiley.