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Selection of a mineral binder with potentialities for the stabilization/solidification of aluminum metal

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HIGHLIGHTS

- Binders capable of reducing the pore solution pH compared with Portland cements are reviewed.
- The binders are then tested against aluminum corrosion.
- Corrosion of aluminum metal is minimal with magnesium phosphate cement.
- The H_2 release can be reduced still further by adding $LiNO_3$ to the mixing solution.
- Electrochemical characterizations show that aluminum tends to a passive state.

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ABSTRACT

In a strongly alkaline medium, such as that encountered in conventional cementitious materials based on Portland cement, aluminum metal is corroded, with continued production of hydrogen. In order to develop a mineral matrix having enhanced compatibility with aluminum, a literature review was first undertaken to identify binders capable of reducing the pore solution pH compared with Portland cement. An experimental study was then carried out to measure the hydrogen production resulting from corrosion of aluminum metal rods encapsulated in the different selected cement pastes. The best results were achieved with magnesium phosphate cement, which released very little hydrogen over the duration of the study. This production could be reduced still further by adding a corrosion inhibitor (lithium nitrate) to the mixing solution. Open circuit potential measurement and Electrochemical Impedance Spectroscopy of aluminum electrode encapsulated in two pastes based on Portland cement and magnesium phosphate cement showed different redox behaviors. In the Portland cement paste, the electrochemical data confirmed the corrosion of aluminum whereas this latter tended to a passive state in the magnesium phosphate binder.

1. Introduction

The dismantling of legacy nuclear facilities produces radioactive waste materials, some of which contain aluminum 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 [1,2]. At the same time, however, this basicity is an obstacle for conditioning aluminum. The E-pH diagram of aluminum (Fig. 1) shows that this metal is not thermodynamically stable in an aqueous environment [3,4]: it is oxidized into Al^{3+} cations (acidic medium), alumina (near neutral solution) or aluminate ions (basic solution), while water is reduced with production of dihydrogen. Fig. 1 also illustrates the amphoteric behavior of aluminum. Passivation of the metal by a surface coating of poorly soluble alumina occurs between pH ~4 and 9, and the corrosion rate of aluminum is strongly reduced within this range of pH values [5] (Fig. 2). In more acidic media (Eq. (1)) or more basic media (Portland cement paste, Eq. (2)) [6], alumina is soluble and metal corrosion continues until all the reactants have been depleted. The resulting hydrogen release would be detrimental to the safe storage of the conditioned waste packages [7].

$$2Al + 6H_3O^+ \rightarrow 2Al^{3+} + 3H_2 + 6H_2O \quad (1)$$

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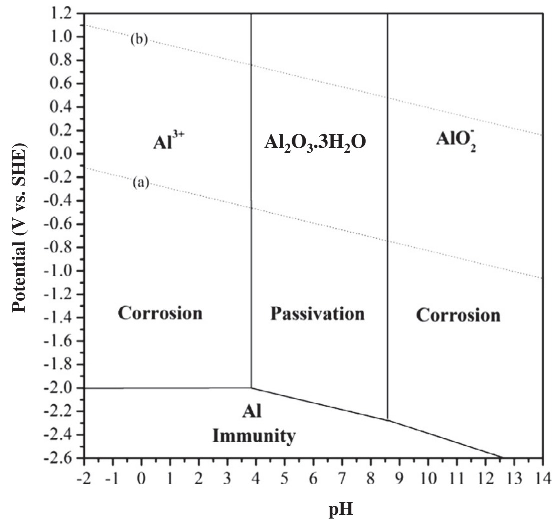

Fig. 1. E-pH diagram for pure Al at 25 °C in aqueous solution (adapted from Pourbaix [5]). The lines (a) and (b) define the water stability domain.

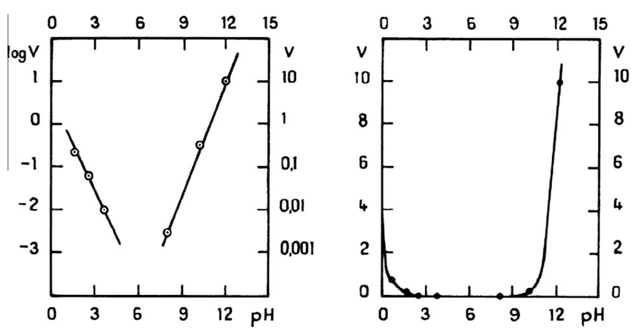

Fig. 2. Influence of pH on the corrosion rate of aluminum (*v*: corrosion rate in mg dm^{-2} h^{-1}) [5].

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2 \quad (2)$$

For this reason, the quantity of aluminum acceptable in a cement-based matrix is currently very low. For example, the maximum surface area acceptable in the 330-L cement-encapsulated waste packages disposed at the French Centre de Stockage de l'Aube disposal facility is 0.1 m^2 [8].

This article reports the first results of a project aiming at formulating a new inorganic matrix having significantly enhanced compatibility with aluminum metal compared with existing materials. In a first part, a literature review was performed to identify binders producing a lower pore solution pH than the one imposed by the conventional calcium silicate cements. In a second part, an experimental study was performed to test different cement pastes against aluminum corrosion. Two methods were selected to measure the corrosion reaction:

(i) Determination of the hydrogen released by gas chromatography. According to Eqs. (1) and (2), the amount of hydrogen produced is directly proportional to the quantity of aluminum corroded.
(ii) Electrochemical techniques by measuring the open circuit potential and by recording the electrochemical impedance spectrum. Indeed, it has already been shown that Electrochemical Impedance Spectroscopy (EIS) is a powerful technique to study the corrosion of metal or alloy embedded in a cement-based material [9–15]. This method offers the advantage to avoid any perturbation on the metal/paste interface if the measurement is carried out at the open circuit potential.

2. State of the art

According to the literature, five types of inorganic binders have been examined as replacements for conventional calcium silicate cements to stabilize waste containing aluminum metal: (i) ettringite cements, (ii) magnesium phosphate cements, (iii) magnesium silicate cements, (iv) phosphate-modified calcium aluminate cements, and (v) geopolymers. They are briefly described below. Other potential binders generating pore solutions with a pH in the aluminum passivation range are then evaluated.

2.1. Ettringite cements

The hydration of ettringite cements forms large amounts of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). They are obtained by mixing calcium aluminate cement with a source of calcium sulfate (gypsum, anhydrite, hemihydrate, etc.) or from a calcium sulfoaluminate cement rich in ye'elimite. It has been shown that the corrosion of aluminum bars [16] or twisted pieces of aluminum alloy 1050 [17] is significantly reduced in calcium sulfoaluminate cement paste compared with Portland cement. Two complementary explanations have been advanced.

– The pore solution pH of a calcium sulfoaluminate cement paste (between 10 and 11 as long as the mineral assemblage contains gypsum) is lower than for Portland cement paste (which exceeds 13) [18], and the aluminum corrosion rate is therefore lower.
– The chemical water demand (the amount of water necessary to fully hydrate the anhydrous phases of the cement) of a calcium sulfoaluminate binder, which increases with the initial gypsum content, exceeds that of Portland cement [19]. Consequently, the residual water content of a calcium sulfoaluminate cement paste having reached a high degree of hydration is low, thereby limiting the long-term corrosion of aluminum.

Recently, an ettringite binder prepared by mixing calcium aluminate cement (Fondu type) and plaster was used in a decommissioning project at the Savannah River site in the United States [20]. An injection grout was formulated to inert a reactor vessel containing aluminum internals. The authors reported an equilibrium pH of 9.5 for the hydrated material and very limited hydrogen release due to corrosion of aluminum. About 92 m^3 of material had been implemented at the end of 2010.

Several reservations must nevertheless be stated here.

- The hydrogen release resulting from corrosion of aluminum was measured over relatively short periods (up to 40 days) and the longer-term values must still be validated.
- Ettringite binders have a lower pore solution pH than Portland cement, but which still lies outside the aluminum passivation zone (pH 3–9). The pore solution pH of calcium sulfoaluminate cement – initially 10–11 – even increases by one unit after depletion of gypsum, further increasing the aluminum corrosion. Consequently, even though hydration results in self-desiccation of the material, renewed corrosion of aluminum cannot be excluded over the long term in the event of resaturation of the porosity by water.