



Water content and porosity effect on hydrogen radiolytic yields of geopolymers



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HIGHLIGHTS

- Water radiolysis is mainly responsible of hydrogen production in geopolymers.
- Mechanisms explaining porosity effect on hydrogen released are proposed.
- A LET effect on hydrogen production is revealed.
- Porosity effect is not observed for ³⁶Ar irradiation (high LET).

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ABSTRACT

The behavior of geopolymers under irradiation is a topic that has not been thoroughly investigated so far. However, if geopolymers are considered to be used as radioactive waste embedding matrices, their chemical and mechanical stability under ionizing radiation as well as low hydrogen production must be demonstrated. For that purpose, a particular focus is put on water radiolysis. Various formulations of geopolymers have been irradiated either with γ -rays (⁶⁰Co source) or 95 MeV/amu ³⁶Ar¹⁸⁺ ions beams and the hydrogen production has been quantified. This paper presents the results of radiolytic gas analysis in order to identify important structural parameters that influence confined water radiolysis. A correlation between geopolymers nature, water content on the one side, and the hydrogen radiolytic yield ($G(H_2)$) on the other side, has been demonstrated. For both types of irradiations, a strong influence of the water content on the hydrogen radiolytic yield $G(H_2)$ is evidenced. The geopolymers porosity effect has been only highlighted under γ -rays irradiation.

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1. Introduction

Water radiolysis is of particular concern for the conditioning of radioactive waste. Indeed, one of its products is molecular hydrogen [1] which is potentially explosive. Its release must thus be accounted for and limited during disposal and nuclear waste storage. Consequently, the study of water radiolysis is important to understand the behavior of hydrated immobilization matrices under irradiation.

Usual solutions to condition low and intermediate level activity

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nuclear wastes rely on the use of calcium silicate cements thanks mainly to their low cost, low temperature process, good mechanical strength and chemical stability. Furthermore, the high pH of cement interstitial water insolubilizes many radioelements. Nevertheless, these matrices present an important limitation with regard to reactive metals such as aluminum [2] or magnesium. The corrosion of magnesium alloys from the fuel cladding materials in conventional Portland cement environment leads to a high hydrogen gas release [3]. In principle, the formation of a magnesium hydroxide layer on the alloy surface inhibits the magnesium corrosion by surface passivation. Consequently, the hydrogen release should be limited. However, in the case of calcium silicate cements, the presence of gypsum and other additives affects the protective layer efficiency and magnesium corrodes and

hydroxylates. Thus, H_2 is continuously released over time [4]. Fluorine can be added to the formulation to inhibit this corrosion by forming a fluorinated passivation layer [5,6]. It is well known that the addition of a low concentration of fluoride ($<10^{-1}$ mol/l) to the corroding solution strongly decreases the corrosion rate depending on the concentration, the pH and nature of the counter cations. However, the presence of calcium in cementitious matrices, which readily precipitates as calcium fluoride, prevents the fluorine ions from reaching the magnesium alloy surface. An alternative solution consists on finding a new material with properties similar to those of Portland cements but devoid of calcium in its formulation. Geopolymers synthesized with metakaolin as aluminosilicate source correspond to this description. Geopolymers are amorphous and mesoporous (2–50 nm pore sizes) [7] materials formed by alkaline activation of an aluminosilicate source. Their structure is composed of silicate (SiO_4) and aluminate (AlO_4) tetrahedrons where the negative charge on aluminum is balanced by extra-framework alkali cations. They have been studied for the immobilization of low and intermediate level nuclear waste [8–13] containing Mg-Zr alloys [14] prior to disposal. But very few publications deal with the geopolymer behavior under irradiation [15–17].

If the literature on radiolytic hydrogen production in geopolymers is scarce, the water radiolysis in porous structure has been already carefully studied in other systems using gamma-rays or electrons irradiations.

The H_2 production mechanism under irradiation has been studied in various materials: cement [18,19], zirconia [20], zeolite [21], clays [22] and Controlled-Pore Glasses (CPG) [23]. In CPG, the effect of pore size distribution on the radiolytic yield of hydrogen ($G(H_2)$) and of other molecular products has been demonstrated [23]. $G(H_2)$ values increase when specific surface area increases and pore size decreases. In confined media, energy transfers by way of excitons in interstitial water are responsible for a release of hydrogen gas under electron irradiation higher in CPG than in bulk water. The same type of phenomenon has also been observed in porous zirconia [20]. This is due to the fact that the Compton electrons diffusion at the solid/liquid interface induces a higher energy deposition in interstitial water due to the difference of electronic density between the solid and the liquid.

Although there are few studies on geopolymers under gamma irradiation, no study on their behavior under alpha irradiation can be found. The energy deposition of alpha particles differs from that of gamma-rays in their energy deposition pattern. Alpha particles, as swift heavy ions, deposit their energy in a localized pattern, along the ion path, in a cylinder of a few nanometers, whereas gamma-rays deposit energy in a homogeneous manner. Besides, ion beams induce a high linear energy transfer (LET). This difference may influence radical mechanisms and so the radiolytic yields. In water radiolysis, the LET effect results in an increase of the primary yield of molecular products such as hydrogen and hydrogen peroxide [24,25]. With high LET, radiolytic precursors directly react in the track core where the ionization density is high. Thus, the high concentration of formed radicals promotes the formation of molecular products such as H_2 and H_2O_2 . Alpha particles (5 MeV) emitted by actinides can be simulated by swift heavy ions, provided the LET and the radial dose deposition induced by the two types of radiations are identical. Based on Monte Carlo calculations, actinides emitted alpha particles can be simulated by 95 MeV/A³⁶Ar beams or 13 MeV ¹³C or ¹⁶O beams.

The aim of this study is to highlight the importance of water radiolysis in geopolymers, to describe the influence of the porosity and to determine the impact of the type of irradiation (heavy ions, γ), i. e. the LET effect, on the hydrogen release.

2. Experimental

2.1. Materials

The aluminosilicate source chosen was a metakaolin (*Argical M1000, Imerys*) with a molar ratio of 2.4 SiO_2 for 1 Al_2O_3 . An aluminosilicate source devoid of calcium, namely metakaolin, was chosen instead of one leading to the precipitation of calcium hydrate phases mixed with geopolymeric materials [26]. The choice of metakaolin was also motivated to avoid the compositional variations resulting from the use of by-products such as fly ash or blast furnace slag.

The activating solutions were prepared by dissolving reagent grade NaOH, KOH (*Analar Normapur, Prolabo, VWR Chemicals*) and/or CsOH.H₂O (99.9%, *Alfa Aesar*) in Milli-Q water (18.2 M Ω /cm at room temperature). The silica used was the *Tixosil 38* provided by *Rhodia*. The molar reference composition of the activating solutions was 1.6 SiO_2 : 1 M_2O : 12 H_2O with “M” standing for Na, K or Cs. The formulation of these synthetic geopolymers is 1 Al_2O_3 : 4 SiO_2 : 1 M_2O : 12 H_2O . According to whether they are synthesized from sodium, potassium or cesium, this reference formulation will be referred to as Geo Na, Geo K and Geo Cs. Some geopolymers were also synthesized with an equimolar mix of cations. In this case, the activating solution was 1 Al_2O_3 : 1.2 SiO_2 : 1 M_2O : 12 H_2O with “M” standing for Na, K, Cs or a mix of Na-K, Na-Cs, K-Cs or Na-K-Cs and prepared with *Tixosil 331* silica (*Rhodia*).

2.2. Geopolymer synthesis and curing

The hydroxide solution was prepared from Milli-Q water and solid hydroxide. The activating solution was obtained by adding silica to the hydroxide solution under stirring at ambient temperature. After silica dissolution, the metakaolin was added and the mixing was performed with a standard laboratory mixer (*European Standard EN 196-1*). The fresh mixture was then transferred in 30 ml polypropylene tubes where the samples were cured for several days in atmospheric conditions after sealing. Finally, they were unmolded and stored at 100% RH (relative humidity) controlled by the presence of a distilled water tank in a controlled atmosphere enclosure placed at 20 °C. For experiments aiming to vary the water content, samples were stored at various RH at 20 °C using the saturated salts method: 75% with NaCl, 54% with $Mg(NO_3)_2$, 23% with $K_2C_2O_4$. Some samples were freeze-dried for complete removal of free water. Finally, in order to efficiently dry samples, further thermal treatments were used on freeze-dried samples: at 80 or at 150 °C during 24 h with an oven and 350 °C during 24 h with a furnace under atmospheric conditions. For heavy ions irradiations, geopolymer samples were cut with a circular saw into 10 mm height, 7 mm wide and about 1.3 mm thick wafers, except for Cs-geopolymer since this sample proved to be not mechanically stable under water.

2.3. Irradiations

For each type of irradiation and geopolymer, four geopolymers are synthesized and irradiated at two different doses (two geopolymers for each dose).

For γ -irradiation, samples were placed in 100 ml Pyrex glass ampoules sealed by fusion under argon at about 900 mbar and then sent to an industrial irradiator (*Ionisos, Dagneux, France*) equipped with a ⁶⁰Co source. Geopolymers were irradiated to a total absorbed dose between 114 and 517 kGy with an average dose rate of 500 Gy/h at room temperature. From an irradiation experiment to another, the dose rate could be different but in the range of 400–600 Gy/h. The introduced mass varied between 30 and 35 g. The glass

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