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Influence of gamma ray irradiation on metakaolin based sodium geopolymer

D. Lambertin [a,*], C. Boher [a], A. Dannoux-Papin [b], K. Galliez [a], A. Rooses [a], F. Frizon [a]

[a] CEA, DEN, DTCD/SPDE/LP2C, F-30207 Bagnols-sur-Cèze, France
[b] CEA, DEN, DTCD/SPDE/LCFI, F-30207 Bagnols-sur-Cèze, France

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ABSTRACT

Effects of gamma irradiation on metakaolin based Na-geopolymer have been investigated by external irradiation. The experiments were carried out in a gamma irradiator with ^{60}Co sources up to 1000 kGy. Various Na-geopolymer with three H_2O/Na_2O ratios have been studied in terms of hydrogen radiolytic yield. The results show that hydrogen production increases linearly with water content. Gamma irradiation effects on Na-geopolymer microstructure have been investigated with porosity measurements and X-ray pair distribution function analysis. A change of pore size distribution and a structural relaxation have been found after gamma ray irradiation.

1. Introduction

Geopolymers are a class of inorganic binders which are solid, aluminosilicate, charge-balanced by alkali cations such as Na^+, K^+ or Cs^+ [1]. They are generally formed by reacting aluminosilicate powder (metakaolin, fly-ash) with highly caustic, aqueous alkali silicate solution. Geopolymers have been studied for immobilization of low and intermediate level nuclear waste [2] especially for Cs and Sr encapsulation [3–5] or Mg–Zr alloy fuel cladding immobilization [6]. Moreover, geopolymer is already used in nuclear industry to encapsulate sludges and organic ion exchange resins in Slovakia [7].

As cement matrices, geopolymers contain water in their pores [8] that could release hydrogen, the main product gas of water radiolysis. Previous experiments demonstrate that the radiolytic yield of hydrogen production $G_0(H_2)$ determined at 50 kGy on a Na-geopolymer dried under ambient atmosphere during one month after synthesis is 0.061×10^{-7} mol/J [9]. This result indicates a lower H_2 production by water radiolysis than that obtained in cement matrices [10,11]. In the present work, the effects of gamma irradiation on air-tightly stored sodium geopolymer material have been studied in terms of radiolytic hydrogen yields, mechanical properties, porosity measurements and structural characteristics with X-ray pair distribution function.

2. Experimental

The sodium geopolymer samples $Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}xH_2O$ ($x = 11$–13) thereafter called Na-Geo – have been prepared by mixing metakaolin powder with sodium silicate solutions. Silicate solutions $1.2SiO_2{\cdot}Na_2O{\cdot}xH_2O$ were prepared by dissolving amorphous silica (TIXOSIL 38, Rhodia factory) in sodium hydroxide solutions (NaOH pellets, Prolabo, 98%). The composition of metakaolin ($2.4SiO_2{\cdot}Al_2O_3$), Pieri PREMIX MK from Grace Constructions, is given in Table 1. After demoulding, the samples have been stored in sealed bags in order to prevent water evaporation. The water content of Na-Geo $Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}xH_2O$ with different water composition has been determined by water resaturation method (EN 1936) and is reported in Table 2.

To quantify the hydrogen gas produced by gamma irradiation, about 20 g of geopolymer samples were irradiated in 200 cm^3 sealed glass containers in an industrial irradiator using ^{60}Co γ-source (IONISOS – Dagneux, France) at a dose rate of 600 Gy/h until 750 kGy under argon atmosphere at room temperature. Dosimetry was realised with Perspex devices. After irradiation, the atmosphere of the glass container is analysed with a gas chromatography equipped with a TCD detector (Varian, CP3800). The standard error on the calculated radiolytic yield is about 10%.

Compressive strength measurements were performed on 4 × 4 × 16 cm prismatic samples (EN196-1). The samples were obtained by pouring fresh Na-geopolymer paste into 4 × 4 × 16 cm PTFE moulds, vibrated for a few seconds, and sealed from the atmosphere. Samples were cured for 4 days at 20 °C and at atmospheric pressure before removal from the mould and stored in sealed bags.

The pore microstructure was studied with isothermal nitrogen adsorption–desorption measurement performed with a Micromeritics ASAP 2020 device and with Mercury Intrusion Porosimeter (MIP) from Micromeritics Autopore IV 9500 with a maximum injection pressure of 420 MPa. Before the porosity measurements,

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* Corresponding author. Tel.: +33 466791480; fax: +33 466397871.
E-mail address: david.lambertin@cea.fr (D. Lambertin).

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Table 1
Chemical composition of metakaolin.

	Oxide weight composition (%)					
	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2
Metakaolin	0.1	54.4	38.4	1.3	0.6	1.6

Table 2
Hydrogen production radiolytic yields of Na-Geo samples with different water contents obtained at 750 kGy.

Sample	Storage	Water content (wt%)	$G(H_2)$ (10^{-7} mol/J)	Reference
$Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}11H_2O$	Sealed	32.5	0.090	This work
$Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}12H_2O$	Sealed	34.1	0.102	This work
$Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}13H_2O$	Sealed	35.9	0.113	This work
$Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}11H_2O$	Air	18.1	0.061	[9]
Portland cement (water/cement = 0.4)	Sealed	28.6	0.80	[22]
Water in free volume	–	100	0.45	[11]

freeze-drying technique was used as a low alteration technique of the pore structure [12].

Phase analysis was made with a Siemens (Model D5005) X-ray powder diffractometer equipped with a Cu source ($\lambda_{K\alpha}$ = 1.5418 Å, 2θ range: 5–70°, steps of 0.02°, acquisition time of 1 h).

Structural characterisation of unheated geopolymers has been limited by their amorphous structure [2]. X-ray pair distribution function analysis (PDF) is appropriate for the study of materials with short coherence lengths including geopolymer materials [13–18]. PDF analysis, on the other hand, concerns the entire signal including Bragg peaks and diffuse scattering. The pair distribution function (PDF) represents the distribution of interatomic distances in a compound, regardless of its crystalline state, determined experimentally by a Fourier transform of the powder pattern. The experimental PDF is given by the following equation [19]:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1]\sin(Qr)dQ \qquad (1)$$

where $G(r)$ is the reduced PDF, $\rho(r)$ is the microscopic pair density, ρ_0 the numeric density of the compound (number of atoms per unit volume), and $S(Q)$ normalised scattering intensity, known as the total static scattering function.

It is important to obtain diffraction data with a high scattering vector ($Q = 4\pi\sin\theta/\lambda$) in order to maximise the resolution after the Fourier transform. We therefore used a PANalitycal (Model X'Pert Powder) X-ray powder diffractometer equipped with a Mo source ($\lambda_{K\alpha}$ = 0.70926 Å, 2θ range: 1.5–155.66°, steps of 0.017°, the total acquisition is the average of 4 runs recorded over 4 h) to attain Qmax = 17 $Å^{-1}$. The PDF and standard corrections were calculated with pdfgetX2 [20]. The calculated pair distribution function from structure was obtained with PDFGUI software [21]. Due to a limited Q resolution, a PDF Gaussian dampening (Q_{damp}) envelope has to be introduced in the refinement. The damping factor Q_{damp} was assigned to a value of 0.05.

Another parameter *s*-ratio is a reduction factor for PDF peak width accounting for correlated motion of bonded atoms.

3. Results and discussion

3.1. Hydrogen radiolytic yield $G(H_2)$

Geopolymers are porous materials. Like in cement matrices, water is contained in the pores of the material after setting. In literature, water radiolysis is well known to engage a series of reactions called Allen cycle with the formation of eight primary species (4 molecules: H_2, H_2O_2, OH^-, H_3O^+ and 4 radicals: e^-_{aq}, $H^\bullet$, $OH^\bullet$, $HO_2^\bullet$) [10]. One of the major stable products of water radiolysis is hydrogen gas. In free volume, the primary $G(H_2)$ issued from water radiolysis is 0.45×10^{-7} mol/J [11]. In a hydraulic binder, several parameters could interfere on the H_2 production such as the global water content, the pore size distribution or the interstitial water chemical composition. However, these effects have not been studied in geopolymers matrices to our knowledge. The results on Na-Geo samples $Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}xH_2O$ are shown in Table 2. From 32.5 to 35.9 wt% of water in the Na-Geo, the radiolytic yield $G(H_2)$ were between 0.090×10^{-7} and 0.113×10^{-7} mol/J. First, data indicate that the hydrogen production under gamma radiation increases with the water content in Na-Geo. The comparison of these results to the hydrogen radiolytic yield of 0.061×10^{-7} mol/J obtained in the previous study [9] indicate that in our case, hydrogen production was larger. Indeed, as the Na-Geo sample in the former study has been stored under air before irradiation, the water content was reduced to about 18% due to evaporation. As the water content also affects the pore size of the Na-Geo, an influence of the pore size on the hydrogen production might be expected but cannot be estimated through these few tests.

On the other hand, these radiolytic yield $G(H_2)$ are lower than the $G(H_2)$ of 0.8×10^{-7} mol/J obtained in Portland cement matrices with a water/cement ratio of 0.4 (water content = 28.6 wt%) [22]. Even though the water content in the Na-Geo is higher, $G(H_2)$ remain much lower than the cement reference value. This result can be explained not only by the difference in pore structure between cements and geopolymers but also by the disparity of pore solution [23,24] with regard to pH and chemical constitution. Indeed evolution of the primary yields of species depends on the alkaline medium, especially in the pH 12–14 range with cement and geopolymer pore solutions. The primary $G(H_2)$ can vary from 0.435×10^{-7} mol/J to 0.384×10^{-7} mol/J between pH 12.45 and 14 [10]. Besides, the ionic constitution (Ca, Na, Al, Si, K, etc.) of the pore solution are very different for cement and geopolymer [23,24]. These differences must significantly modify the stability of intermediates related to the radiolytic recombination of H_2 and therefore affect the production of hydrogen gas.

3.2. Microstructure

Radiations such as gamma ray could induce structural changes or even damages in solid materials. In order to reveal any structural modification on Na-Geo related to gamma radiation effect, compressive strength measurements have been done on non-irradiated and irradiated samples and for different doses at 50, 500 and 1000 kGy (Fig. 1). The results have shown an increase in compressive resistance by 10% after irradiation for the three absorbed doses. These observations assume a densification in the geopolymer network structure under gamma irradiation.

To provide explanations to this phenomenon, the porous network has been further characterised with nitrogen adsorption porosimetry measurements on $Al_2O_3{\cdot}3.6SiO_2{\cdot}Na_2O{\cdot}11H_2O$ in non-irradiated and irradiated conditions.

Fig. 2 presents the nitrogen sorption/desorption isotherms on non-irradiated and irradiated Na-Geo samples. The isotherms of non-irradiated Na-Geo present at first a pronounced stage of the