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Geopolymers from fly ash and their gamma irradiation

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Highlights

- The radiolytic H₂ generation from fly ash based geopolymers is presented
- A dose rate effect is observed
- Minimal change in pore structure is seen
- The effect of surface area and energy transfer from the geopolymer to the pore water is discussed

Declaration of interest: none

Abstract

In order to assess the suitability of geopolymers produced from fly ash for use in nuclear waste encapsulation, their behaviour when exposed to gamma radiation has been examined. Irradiation (400 KGy at 4 kGy/hr) was found to have had minimal effect on the

porosity of bulk samples. Radiolytic hydrogen production from the pore water exhibited a dose rate effect (9 kGy/hr up to 280 kGy and 24 kGy/hr up to 700 kGy). An effect of surface area was observed with a decrease in hydrogen production corresponding to a decrease in surface area; the effect of pore chemistry was not ruled out.

Keywords

Geopolymer; Alkali-activated material; Gamma radiation; Nuclear waste encapsulation; Radiolytic hydrogen

1 Introduction

Geopolymers are a porous material formed by reacting a concentrated alkali solution with a powdered aluminosilicate [1, 2, 3]. Common aluminosilicate sources include fly ash and metakaolin. Geopolymers share many properties with cement including compressive strength [4] and fire resistance [5]. They can also cure at room temperature [2] and have an environmental advantage over cement as the amount of CO₂ generated during their production is much smaller [6]. Cement is traditionally used in the nuclear industry to encapsulate nuclear waste [7]. Geopolymers could be used as an alternative [8, 9], however, the performance under irradiation must be understood. Irradiation can lead to the generation of hydrogen gas from water contained within the pores [10], and can also cause a change in the microstructure of a material [11] [12] [13]. Work on metakaolin-based geopolymers found that hydrogen production increased with water content [14,15], the pore structure changed after irradiation [14] and structural parameters such as pore size and surface area affect hydrogen generation [15]. Such studies have not been performed on fly ash geopolymers. We

examine the effect of γ -radiation on gas generation and on the microstructure of fly ash geopolymers.

2 Experimental

2.1 Sample production

Sodium hydroxide was first dissolved in water then added to sodium silicate (both VWR International) to produce a required Na content of 13.4 wt%. Cat N fly ash (Powerminerals Ltd) was then added and an overhead mixer used. The composition of the fly ash by wt% was: CaO 2.0 %; MgO 1.5 %; SiO₂ 49.8 %; Fe₂O₃ 10.7 %; Al₂O₃ 23.2 %; Na₂O 1.1 %; K₂O 2.7 %; SO₃ 1.0 %; <1 % Cl and P₂O₅. The amount of fly ash was varied (Table 1) as the type and concentration of the waste to be encapsulated will result in differing solid/liquid ratios. The resultant water wt% was calculated using the total amounts of water in the sodium hydroxide and sodium silicate solutions. Samples were cast into cylindrical silicon moulds 45 mm in diameter and 15 mm in height. They were covered and allowed to cure at room temperature for at least 24 hours, then heated in an oven for 42 hours at 60°C before irradiation and analysis.

Table 1: Details of the geopolymer samples, including amounts of pre-cursors used

Sample Name	Fly Ash (g)	Sodium Silicate (g)	Sodium Hydroxide (g)	Water (g)	Water wt%	Si/Al ratio
FA-0.4	317.01	66.67	16.67	43.37	24.51	2.03
FA-0.5	253.31	66.68	16.68	43.35	27.44	2.08
FA-0.6	211.14	66.69	16.68	43.37	30.00	2.13

2.2 Irradiation

A ⁶⁰Co source at the Dalton Cumbrian Facility [16] was used and the full experimental regime is described schematically in Fig. 1. For structural analysis using gas adsorption,

irradiation of monoliths was preferred in order to be representative of industrial applications to waste encapsulation. For gas analysis, two dose rates were applied to powdered samples; irradiation of monoliths was not possible. Dose was determined using Radcal® which has an error of $\pm 4\%$.

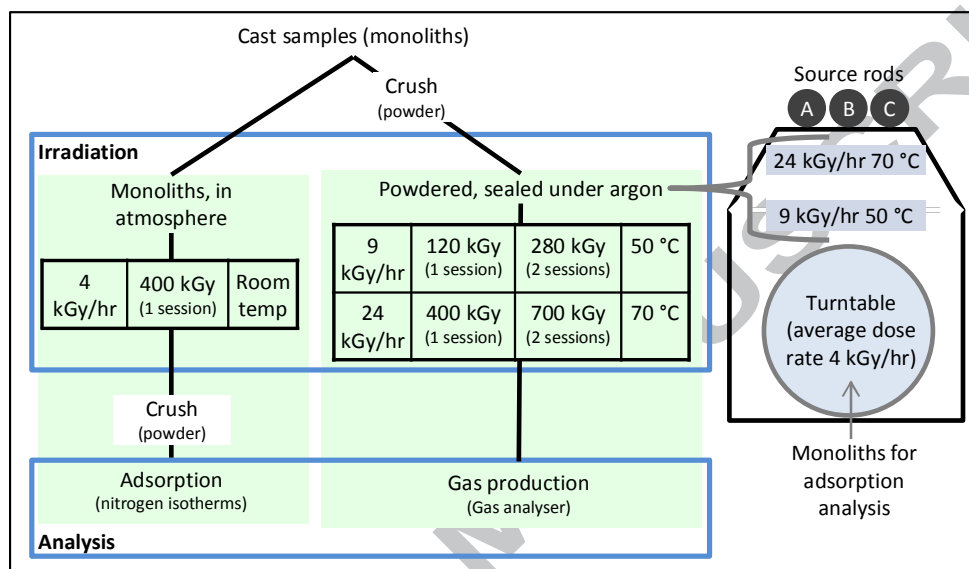


Fig. 1: Summary of the irradiation and analysis regime. A turntable was used to ensure an even dose to the monoliths. Powdered samples for gas analysis were placed in a rack and irradiated over multiple sessions.

2.3 Analysis

Powdered samples of 0.75 g were flame-sealed in 4.8 mL glass vials that were purged with argon for 20 minutes. The tube crush method described by Schofield *et al* was used to determine the presence of H₂ [17]. A gas analyser (SRI Instruments) was used with a molecular sieve 13X column (Alfa Aesar product no. 33550) at 40 °C and detected via thermal conductivity (TCD) at 120 °C. The carrier gas was argon; flow rate of 31.5 mL/min. A good seal between the tubing and the instrument was assured by observing the chromatogram. The headspace in the vial was sufficiently large that any gas generated was expected to have a negligible effect on pressure; the purging technique employed ensured atmospheric pressure. Radiolytic yield was calculated using the dose to the whole sample.

Nitrogen adsorption isotherms were collected using a Micromeritics TriStar II 3020. Approximately 2.3 g of powder was heated at 105 °C overnight in a vacuum oven at 1000 mbar then degassed at 105 °C overnight at 100 mTorr. All samples were analysed within days of each other to minimise the evolution of porosity over time [18]. Surface areas were determined using the BET method.

3 Results and Discussion

Adsorption isotherms for all samples (Fig. 2 provides an example) were type IV(a) with a hysteresis loop (type H3), indicative of a mesoporous material [19]. Comparison of the isotherms to those from metakaolin-based geopolymers [14] (γ -irradiated at 0.6 kGy/hr to 750 kGy) demonstrates a key difference: irradiation caused isotherms from the metakaolin-based geopolymers to change shape, indicating a change in the pore size distribution from monomodal to bimodal. This behaviour was not observed for the fly ash geopolymers suggesting that the structure of fly ash geopolymers is less susceptible to irradiation than metakaolin-based geopolymers.

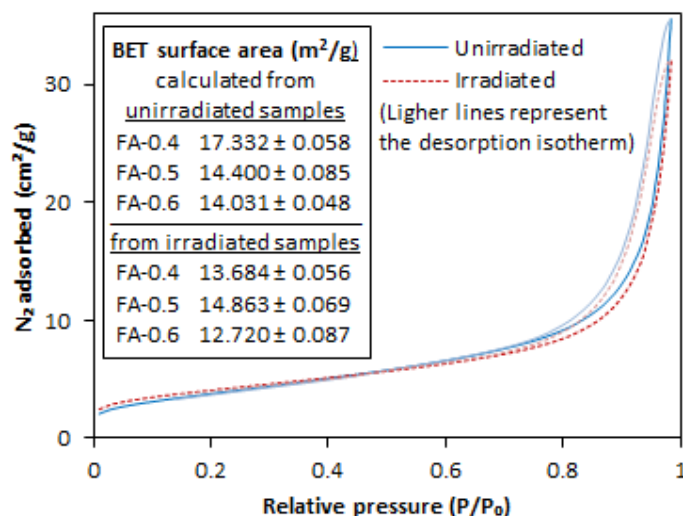


Fig. 2: Example isotherms (from FA-0.5) and surface areas for all formulations. Irradiation was to 400 kGy at 68 Gy/min.

The metakaolin-based geopolymers [14] had a water content of 32.5–35.9 %. Our fly ash geopolymers had a similar water content (24.5–30.0 %) but exhibited much lower H₂ yields: No more than 0.021x10⁻⁷ mol/J (Fig. 3) for the fly ash geopolymers compared to 0.090x10⁻⁷ – 0.113x10⁻⁷ mol/J for the metakaolin-based ones. Chupin *et al* [15] suggest that the geopolymer structure is linked to radiolytic H₂ production, specifically: the surface area influences a transfer of energy from the solid to the liquid phase and so correlates with H₂ production. The surface area of these fly ash geopolymers was much lower than the surface area found by Chupin *et al*: for metakaolin-based geopolymers synthesised with sodium hydroxide, the surface area was 66 m²/g and the H₂ yield was 0.13x10⁻⁷ mol/J (γ -irradiation at 0.5 kGy/hr up to 517 kGy). The surface area of these fly ash geopolymers was no more than 17.3±0.5 m²/g.

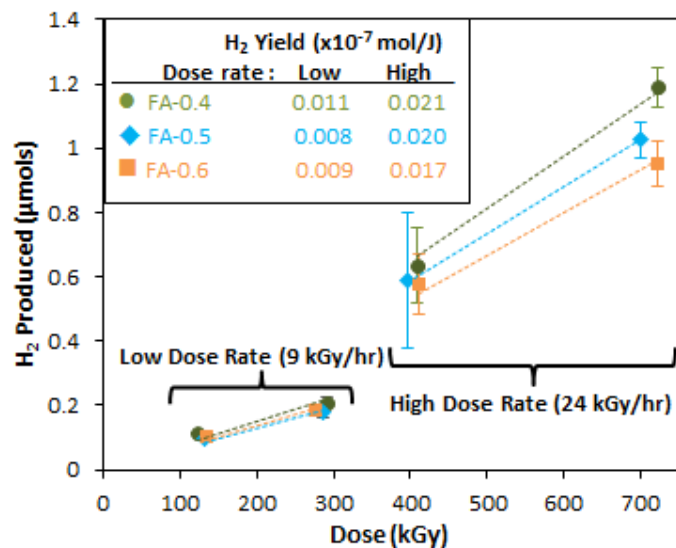


Fig. 3: Hydrogen production as a function of total dose. Error bars are calculated as the standard deviation from up to four samples. The gradient of the lines of best fit provides the H₂ yield.

Fig. 3 shows that less hydrogen was produced by samples that received a lower total dose at a lower dose rate when compared to those at a higher total dose and dose rate. The irradiation regime meant that the application of differing dose rates also led to a difference in temperature. To assess the effect of temperature on H₂ production in bulk water, FACSIMILE was used with a comprehensive set of chemical reactions relevant to the pH of this system [20]. The simulation was carried out at pH 11 with an initial dissolved oxygen concentration [21] of 2.4×10^{-4} mol/dm³. At 50 °C the computed steady-state concentration of H₂ was 3.2×10^{-4} mol/dm³ while at 70 °C this value was calculated to be 1.7×10^{-4} mol/dm³ indicating that H₂ generation should decrease at higher temperatures. This suggests that the elevated H₂ production at 400 and 720 kGy was caused by increased dose rate rather than the total dose or temperature.

Fig. 3 shows that the amount of H₂ produced at the higher dose rate reduced as the wt% of water increased. The data in Fig. 2 also show that the surface area decreased as the water wt% increased which may explain this phenomenon however, it is well known that

dissolved chemical species affect the radiolytic H₂ yield from water [21]. The decrease in water content while using a constant amount of fly ash may increase the concentration of various ionic species in the pore water. In similar systems, an increase in iron content coincides with increased radiolytic H₂ production [22]. Calcium has also been seen to have an effect [23]. Both of these species were present in the fly ash.

4 Conclusions

Under gamma irradiation, changes in pore structure of a fly ash geopolymer due to irradiation were found to be minimal suggesting that irradiation did not lead to structural changes. A dose rate effect was observed for H₂ generation which is in opposition to the associated temperature effect for a system of this pH. H₂ generation was also influenced by the transfer of absorbed energy from the solid geopolymer to the pore water. Further work is required to determine the influence of pore chemistry on H₂ production.

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