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RESEARCH ARTICLE

Effect of exposure of metakaolin-based geopolymer cements to gamma radiation

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Abstract

The stability of cementitious materials under the harsh environment they will experience when used for radioactive waste disposal is incredibly important. Therefore, understanding the irradiation resistance of geopolymer cement, a potential alternative binder for the treatment of nuclear waste, is of the utmost importance when trying to develop a safety case for these materials. The study presented here addresses the structural and chemical changes of metakaolin-based geopolymers, designed with different water contents, and exposed to a total cumulative dose of 1 MGy of gamma radiation. The range of formulations that were tested showed a significant loss of free water related to the irradiation process, which has led to an increase in the porosity. Analysis of the chemical structure has shown minimal changes in the main binding type-gel phase, demonstrating high microstructural stability. Results showed that in samples cured for longer than 20 h, the bound/gel structure water remained in the sample when the water content was kept low enough. As the porosity and water content increase, more gel water is removed due to radiation exposure. However, the degree to which the water is removed from the gel structure is very small, and minimal changes can be seen across the geopolymers tested. Overall, metakaolin-based geopolymers appear resistant to irradiation up to 1 MGy, which offers a potentially viable alternative for the immobilization of problematic intermediate-level waste.

KEYWORDS
alkali activation, durability, geopolymers, nuclear waste

1 | INTRODUCTION

The UK expects to produce more than 4.5 million tonnes of nuclear waste by 2150, which is the current anticipated lifetime of the Sellafield site, where most of the waste is currently stored.[1] Intermediate-level waste (ILW), which is largely intended to be conditioned by cementation, comprises about 10% of this inventory; ILW is defined as waste that exceeds the radiation dose rate limits set for low-level wastes (4 GBq per tonne alpha and/or

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12 GBq per tonne beta/gamma) but is not significantly heat-generating, therefore heating is not considered in the design of storage or disposal facilities.[2] Cementation is an important environmental remediation technique for radioactive waste, as it offers a low-cost, high-throughput technique that can be used for a wide variety of wastes.[3] ILW is a diverse stockpile of wastes that contains many different types of waste with large compositional differences. These wastes can take many physical forms, including sludges, slurries, organic wastes, ion exchange resins, and reactive metals (principally Magnox, aluminum, and uranium). The organic wastes and the diverse chemical and physical nature of the other waste stream types mean that for some types of ILW, conventional cementation techniques may be a suboptimal treatment methodology.

Cementation using blends of Portland cement with blast furnace slag or fly ash is currently the UK baseline method for the conditioning of most ILW to produce a passively safe waste package. However, significant issues can arise when using blended Portland cement as the treatment method for so-called "problematic wastes". This includes restrictions on waste loadings as a result of chemical compatibility issues between waste and encapsulant or can relate to physical processes (rheology) of the system, such as the ability to satisfactorily mix viscous wastes with the cementitious matrix.[3,4] Therefore, alternative cementitious matrices are being considered. Geopolymers are an attractive potential alternative cementation method that could be used by the nuclear industry.[5,6] These materials have shown significant promise in the potential to treat and dispose of wastes with varying water contents.[7]

Geopolymers are most commonly produced from the reaction between an aluminosilicate precursor (typically a calcined clay such as metakaolin) and an alkali silicate activating solution. This results in the formation of an alkali aluminosilicate hydrate-type gel, which has a three-dimensional, highly polymerized, pseudo-zeolitic framework structure.[8] Potassium silicate-activated metakaolin-based geopolymers have been shown to produce a stable geopolymer product with desirable rheological properties without the need for high water content in the fresh cement paste.[9] Due to the nature of the ILW that they are intended to encapsulate, these cementitious materials are likely to experience high doses of gamma radiation when they are produced and placed in long term storage. Therefore, the gamma irradiation of cementitious systems has been studied in detail in the literature, with a specific focus on radiolysis of any free water present, as well as any carbonation of the cement that might be induced.[10,11] Radiolysis of the free water leads to the production of hydrogen gas[12] and causes cracks to appear within Portland cement systems.[11] As potassium silicate-activated metakaolin-based geopolymer formulations have significantly more free water than Portland cement, it could be expected that the cracking will be significantly greater within these cementitious systems.

Similarities can be drawn between aluminosilicate glasses and the gel structure of the geopolymer systems as both are comprised of silica and alumina tetrahedra with no long-range periodicity. The amorphous structure has led to geopolymers being referred to as "low-temperature glasses".[13,14] However the structure of glasses tends to be significantly more disordered when compared with geopolymer cements.[14] It has been shown that potassium-based activators do tend to yield geopolymers that resist any potential phase evolution or crystallization processes to a greater degree than those which are activated using sodium-containing activators.[15] Further to the structural changes, it is believed that metakaolin-based geopolymers show order on the nanoscale, and produce nanocrystalline products similar to that of zeolites when activated with sodium-based solutions.[16] For these systems to be accepted as a nuclear waste grout alternative, the cements need to be stable under irradiation and to not undergo significant changes in the main binding gel structure. To pass the stringent safety requirements of the UK nuclear industry, long-term stability to irradiation is required. Geopolymer cements have been identified[17–19] as a viable alternative to Portland cement-based wasteforms for the disposal of several problematic nuclear wastes. This is primarily due to them not following a hydration mechanism as does Portland cement, which may make them more compatible with some problematic wastes that can interfere with this hydration mechanism.

Gamma irradiation has been shown to remove additional water from geopolymer[20–22] or Portland cement[10,11,23] wasteforms when compared with specimens subjected to heating to the same temperature reached upon radiation exposure. The liberation of water is seen between 50°C and 150°C.[20] Gamma irradiation also induces carbonation within certain cement samples, which can be analyzed using thermogravimetric analysis coupled with mass spectroscopy (TG–MS).[11] This is believed to be due to the dehydration of the sample through radiolysis, removing the mobility of the free water, and increasing the effect of atmospheric carbonation on the sample with an increase in cracking.[24] However, the effects of sample preparation, exposure conditions, and the rate at which the radiation dose is applied to metakaolin-based geopolymers, have not yet been considered in detail.

This paper presents for the first time a clear and concise understanding of the changes to the chemical and physical structure of metakaolin-based geopolymers when exposed to different curing conditions prior to irradiation. The outcomes of this study provide important insight into the irradiation stability of geopolymer cements; information that is crucial for the development

TABLE 1 X-ray fluorescence data for the FC MK powder.

Product	Abbreviation	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	K_2O	Na_2O	LOI[a]	Other
Argicem	FC MK	70.4	23.4	1.1	2.9	0.7	0.3	0.1	0.4	0.8

Note: Results reported in wt.%.

[a] Loss on ignition (LOI).

of novel cement wasteforms that are stable under gamma irradiation.

2 | EXPERIMENTAL PROCEDURE

2.1 | Materials

The metakaolin powders used to produce the geopolymers in this investigation were supplied under the trade name Argicem (Argeco Developpement, France—flash calcined) and are denoted FC MK. The oxide composition of the FC MK is shown in Table 1. The alkali activating solution was prepared by blending K120 potassium silicate (30.2 wt.% SiO2, 21.4 wt.% K2O, 48.4 wt.% H2O, PQ Silicates) with reagent grade potassium hydroxide (pellets, >95%, Fisher Scientific) to produce an activating solution with a SiO2/K2O molar ratio = 1.0. The formulations were designed to have a water content such that the molar ratio H2O/K2O was equal to 11 or 13 as specified. Geopolymers were prepared by mixing the metakaolin powder with the activating solution, to give a molar ratio of Al2O3/K2O = 1.0. The samples were produced by high shear mixing for 10 min, and monoliths were produced by casting the paste in appropriately sized polymeric molds, which were sealed for procuring at 20°C until testing.

2.2 | Gamma irradiation

Gamma irradiation was performed at the Dalton Cumbrian Facility, University of Manchester, UK, using a 60Co gamma irradiator. The samples were exposed at a dose rate of approximately 12 $kGy{\cdot}hr^1$ to produce a total dose of 1.0 MGy. The dose rate that is experienced by these samples is much higher than the dose rate that an ILW wasteform will experience in its lifetime, prior to backfilling in a Geological Disposal Facility, with an approximate total dose of 10 MGy at a dose rate of 24 $Gy{\cdot}hr^1$.[25] The total dose that has been presented in this study equates to 1 MGy, experienced at 12 $kGy{\cdot}hr^{-1}$. Although the dose rate is significantly higher and the total dose is only 10% of the possible lifetime dose, the intention of this study is to present some preliminary stabilization data and also to provide a methodology for the analysis of these samples upon irradiation.

Control samples were heated to 50°C for the same duration as the irradiated samples to represent the conditions within the irradiator, and to de-couple the effects of heating and irradiation. Comparisons were also drawn to further control samples that were cured at room temperature (20°C).

2.3 | Chemical analysis techniques

TG–MS was performed using a Perkin Elmer TGA4000 connected to a Hiden mass spectrometer; 40 ± 2 mg of sample was analyzed at a heating rate of $10°C{\cdot}min^{-1}$, between 30°C and 950°C.[8]

The phase assemblage of the geopolymers was analyzed using a Panalytical X'pert3 Powder X-ray diffractometer, with a 2θ range of 5°–70°, a step size of 0.02°, and a time per step of 2.2 s.

2.4 | Microstructural analysis techniques

Geopolymer samples were placed in isopropanol to avoid any further supplementary reaction during the sample preparation.[26] The samples were then mounted into epoxy before being polished and carbon coated. Backscattered electron scanning electron microscopy was conducted using a low vacuum Hitachi TM3030 at a magnification of 1000× and an accelerating voltage of 15 kV. All images that were collected were then balanced considering a grey scale histogram to adjust the brightness and contrast.

3 | RESULTS AND DISCUSSION

3.1 | Structural integrity and bound water

The gamma irradiation of different cement types has been shown to affect the free water content, and this includes geopolymer cements.[22,27] Induced changes can also appear in the formation of carbonates and other chemical species.[11,22,28] Clear differences are seen in the changes in water content (Figure 1) and also in the degree of carbonation for all the geopolymer formulations tested here. The control sample results are important when discussing the effects of irradiation in geopolymer cements and this study

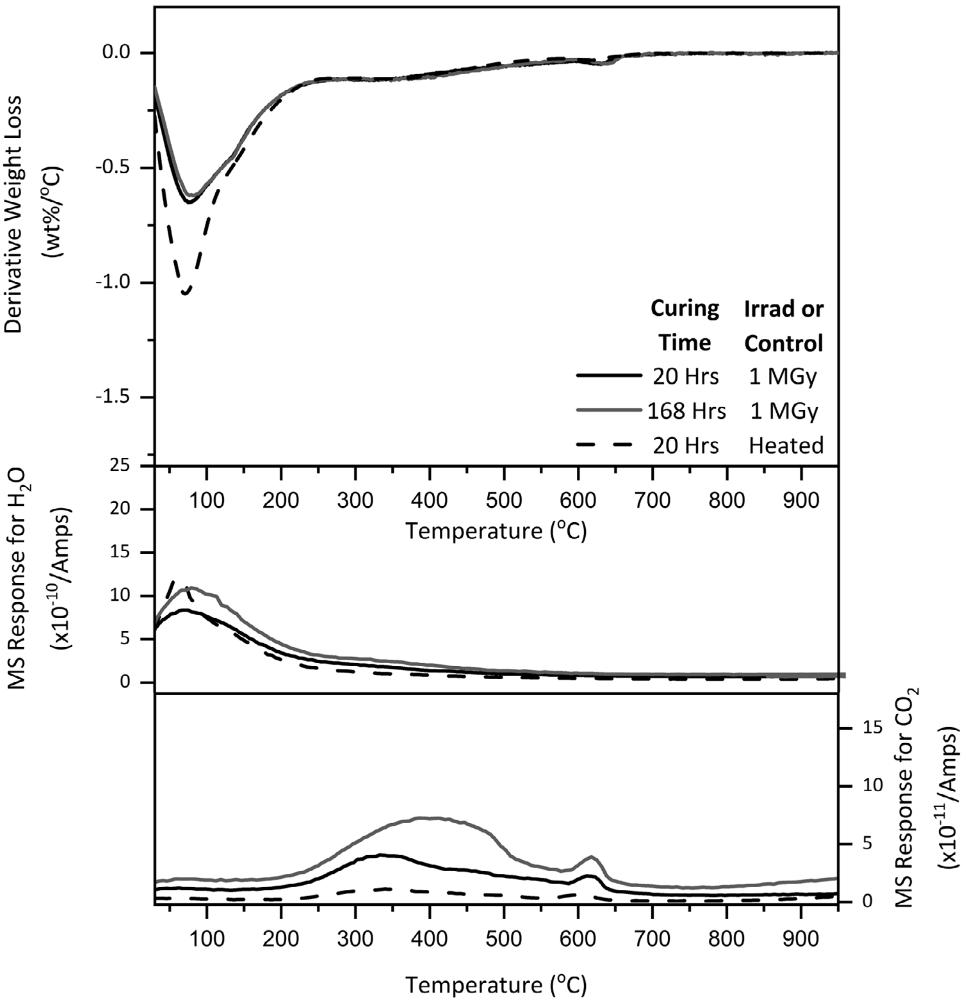

FIGURE 1 Derivative thermogravimetric analysis (dTG) for the H2O/K2O = 11 FC MK geopolymer samples (top), and MS data for H2O and CO2 (middle and bottom, respectively).

has used a sample heated to 50°C, denoted as the "heated control", to match the elevated temperature within the irradiation unit and thus aid in isolation of which effects are truly induced by the radiation exposure. The heated control (50°C) sample is selected to be based on the 20 h preirradiation-cured sample, to give a comparison to the worst-case scenario of water loss through heating. Heating a sample that has only been cured for a short period of time will be anticipated to release more free water due to the relatively immature microstructure.[29] The loosely bound water that can be easily removed upon heating or irradiation is therefore in the structure or gel phase of the geopolymer, a potassium aluminosilicate hydrate phase (sometimes referred to as K-A-S-H).

The thermogravimetric curve for the FC-MK geopolymer with H2O/K2O = 11 (Figure 1), shows a clear mass loss between 50°C and 200°C, which is associated with the removal of both free and bound/structural water. Changing the preirradiation curing time between 20 and 168 h causes very minimal changes in the water content after irradiation to 1 MGy. When comparing this to the heated control, the water that has been removed during irradiation is not only the free water that is removed up to 100°C but also the bound water that is removed between 100°C and 250°C. Bound water, although present in quantities much lower than in Portland cements, has an important role in the structural development of geopolymer cements by mediating the reaction process,[30] and in this system has remained relatively unchanged.

The free water that resides within the open and accessible pore structure of the geopolymer cement originates from the excess water that is required to provide a fluid mix; some of this also results from water that had previously been bound as hydroxyl groups but is released during condensation reactions as the geopolymer binder forms. This release of free water is not expected to cause large changes in the chemical structure of the alkali aluminosilicate gel product, but it could cause significant changes in the porosity.[12] The mechanism for the radiation-induced removal of water from cements is understood to involve

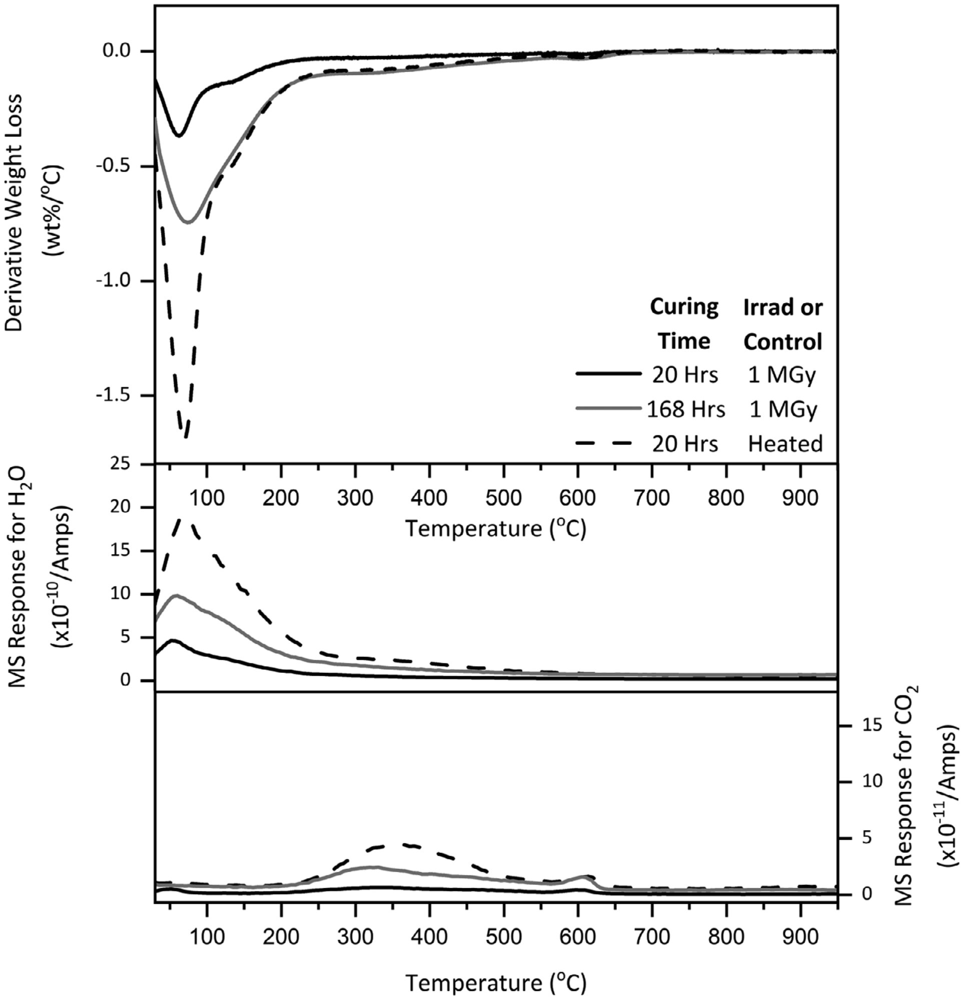

FIGURE 2 Derivative thermogravimetric analysis (dTG) for the H2O/K2O = 13 FC MK geopolymer samples (top), and MS data for H2O and CO2 (middle and bottom, respectively).

a radiolysis process, that causes the water to be broken down with production of radiolytic hydrogen and oxygen species[23]; this has also been shown in geopolymers.[12] This liberation process has been shown in the literature to lead to a change in the surface porosity of MK-based geopolymers.[12]

When the water content is increased to H2O/K2O = 13, then significant differences are seen between the differential thermogravimetry results (Figure 2). The quantity of water present postirradiation is similar to that of the lower water content formulations when the sample is cured for 168 h. However, for the formulation that has only been cured for 20 h, a large reduction in the free water content and a large reduction in the bound water content postirradiation is observed. This suggests that chemical changes have occurred in the gel structure. Dehydration of cementitious gel structures can lead to a significant change in their stability, particularly in the case of Portland cement and other hydraulic cements where the bound water is an intrinsic and essential part of the binding phase. Geopolymers, which do not bind water to the same extent as hydraulic cements, may therefore be expected to be less prone to loss of structural integrity via such mechanisms, and this will be explored in more detail later in this paper. In the 20 h cured sample, insufficient structural development has occurred to enable the aluminosilicate geopolymer phases to resist the effect of irradiation on the free and bound water content. It is evident from this data that when the sample is cured for 168 h, minimal changes have occurred in the degree of bound water within the structure when compared with the heated control for both the H2O/K2O = 11 and 13 mix (Figure 1). Therefore, further studies on the effect of water content, both bound and free, and how the radiolysis of this water affects the structural formation needs to be examined in further detail. However, this study shows that the irradiation of a structure does not fundamentally affect the bound water in samples that are cured for times in excess of 20 h.

Carbonation within the geopolymer samples is clearly shown in the mass spectrometry data in Figures 1 and 2

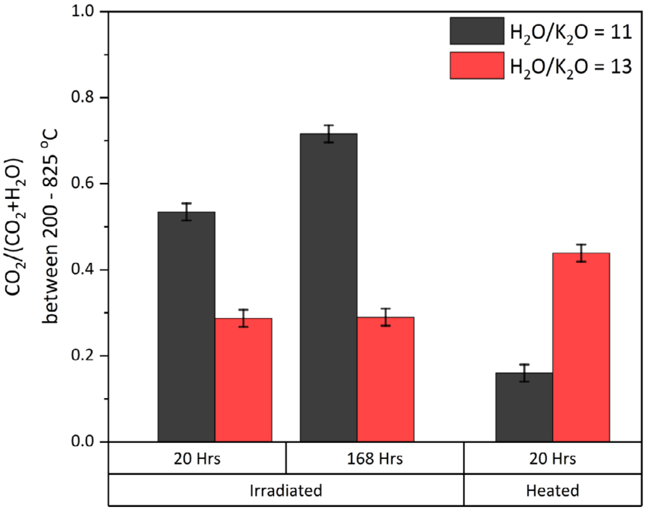

FIGURE 3 Integrated mass spectrometry data showing the fraction of the mass loss attributed to CO2 that is present in the heated controls and the irradiated samples.

(bottom segments). Using the difference in the mass spectrometry data in the H2O and CO2 MS response, the distribution in the wt.% loss given for both species was equated, and upon integration of the thermogravimetry data between 200°C and 825°C the results presented in Figure 3 can be used to show the degree of carbonation that has been induced as a result of the irradiation of the samples. The driving force for the carbonation of the geopolymer cements is the dissolution of atmospheric CO2 into the pore solution causing the production of alkali carbonate phases.[31]

The carbonation of the H2O/K2O = 11 samples is driven by the irradiation process, which causes the liberation of some of the pore water. By reducing the water content in the pore and consequently the degree of saturation, the irradiation allows the CO2 to diffuse through the sample using the free space and also by dissolving into the remaining pore solution. The lower water content sample therefore undergoes a greater degree of carbonation under irradiation than the higher water content system. Carbonation within the paste has occurred due to the formation of a potassium carbonate type species, to a very small degree which resulted in the lack of formation of surface efflorescence, below that visible in the X-ray diffraction (XRD).[32] As air has entered the sample, through incomplete sealing, N2 and CO2 have diffused into the remaining pore solution and reacted with the potassium species to drive the formation of potassium carbonate in a similar manner to that outlined by Anstice et al.[33] for sodium. Air entered the sample due to incomplete sealing, which occurred due to the irradiation of the polymer structure in the sealing film, which appeared tacky and porous postirradiation.[12,34,35] The presence of CO2 within the sample leads to the formation of a small quantity of carbonate (<1 wt.%).[31,34,36,37] Precuring of the H2O/K2O = 11 geopolymers has affected the carbonation level. A longer curing time will help to produce a higher compressive strength and consequently form a denser pore structure.[38]

However, this change is not consistent in the H2O/K2O = 13 formulations cured under the same conditions, which cannot be attributed directly to the curing regime. The carbonation of the H2O/K2O = 13 formulations is greater in the heated control than in the samples that have been irradiated. These samples contain a greater volume of water in the pores when compared with the H2O/K2O = 11 samples, although the irradiated H2O/K2O = 13 samples have notably less water remaining in their pores than do their heated counterparts. It is not immediately clear why this should have led to these higher water content samples showing more carbonation than any of the others depicted in Figure 3 upon heating; it is possible that different degrees of degradation of the polymeric films used to wrap the samples have led to discrepancies here, but it is not possible to provide a fully conclusive explanation for the observed behavior.

Most importantly, the level of carbonation within these samples is low (Figure 3). Higher degrees of carbonation (10–30 vol.%) have been shown to significantly affect the structural properties of geopolymer cements.[39] However, as these samples have a low proportion of carbonation (<1 wt.%) induced by gamma irradiation, the overall effect on the structural integrity of the samples through carbonation will be expected to be minimal. A study presented by Yeoh et al.[40] has shown that for a total dose of 1.5 MGy, the gamma irradiation experiment has produced a sample with greater compressive strength compared with that of an ambient cured sample. This is due to the increased curing temperature which will occur within the irradiator. Therefore, overall the structural integrity of these samples exposed to a high dose rate has shown minimal carbonation and cracking/structural deformity on the micrographs presented in Figure 5.

Irradiation is an aggressive process that can lead to structural changes, which are dependent on the dose rate and total dose and can lead to both positive and negative changes in the cross-linking and gel structure formation.[40] To identify any structural changes to the ordering of the gel structure of the geopolymers, XRD was used. Very small changes in the amorphous and crystalline gel network of the geopolymer that has been exposed to gamma radiation can be seen in the XRD data (Figure 4). These changes can be seen in the insets, where the amorphous region expands over a larger range upon irradiation showing a greater degree of disorder within the gel structure. Figure 4 shows a comparison of the X-ray diffractograms for the 20 and 168 h precured samples, and the 20 h cured heated control. The FC MK contains a significant content of quartz

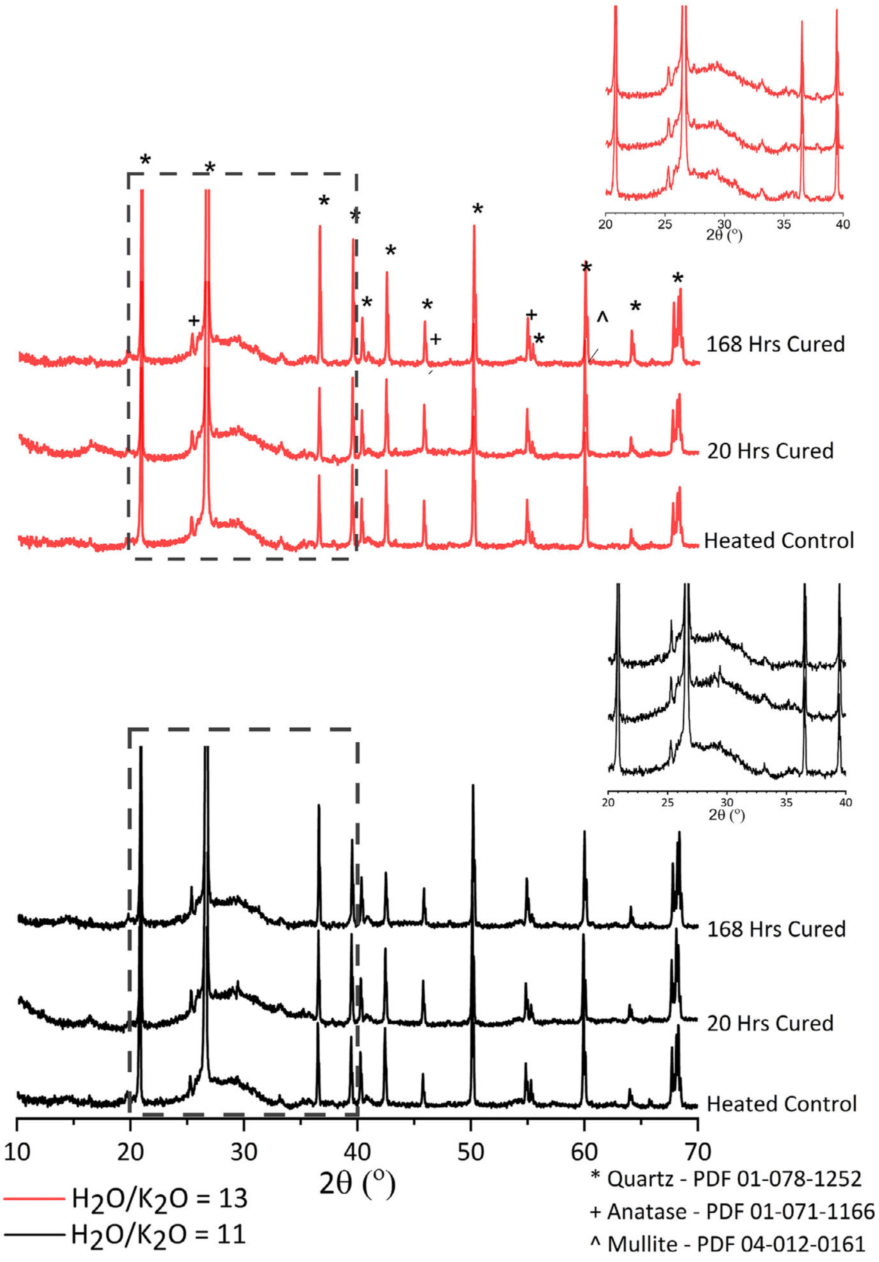

FIGURE 4 X-ray diffractograms of the 20 h cured heated control sample and the 20 and 168 h irradiated geopolymer samples, for H2O/K2O = 11 (bottom) and 13 (top). Insets show the region between 20 and 40° 2θ, with crystalline peaks cropped to highlight the changes in the underlying feature due to disordered materials.

and this leads to the highly crystalline features that dominate the XRD patterns. The slight carbonation seen in the TG–MS data (Figure 1) is not reflected by the formation of crystalline carbonation products; this may mean that the low level of carbonation does not yield observable peaks in comparison to the strong quartz peaks, and/or may be related to the formation of amorphous potassium carbonates. The lack of changes in the diffractogram does indicate that the FC MK geopolymer is resistant to irradiation doses of 1 MGy, independent of the preirradiation curing regime used in this study, in terms of any changes in crystalline ordering. This is a positive step when developing a safety case for these materials and also in understanding the effects of preirradiation curing on the chemical stability of these materials.

Scanning electron microscopy was also used to assess the microstructural changes in these potassium silicate-activated geopolymers exposed to 1 MGy of gamma radiation. The morphology of these samples shows a large proportion of voidage (Figure 5), produced from the removal of the large quartz content present in the FC MK (shown in Figure 4), via the polishing methodology used

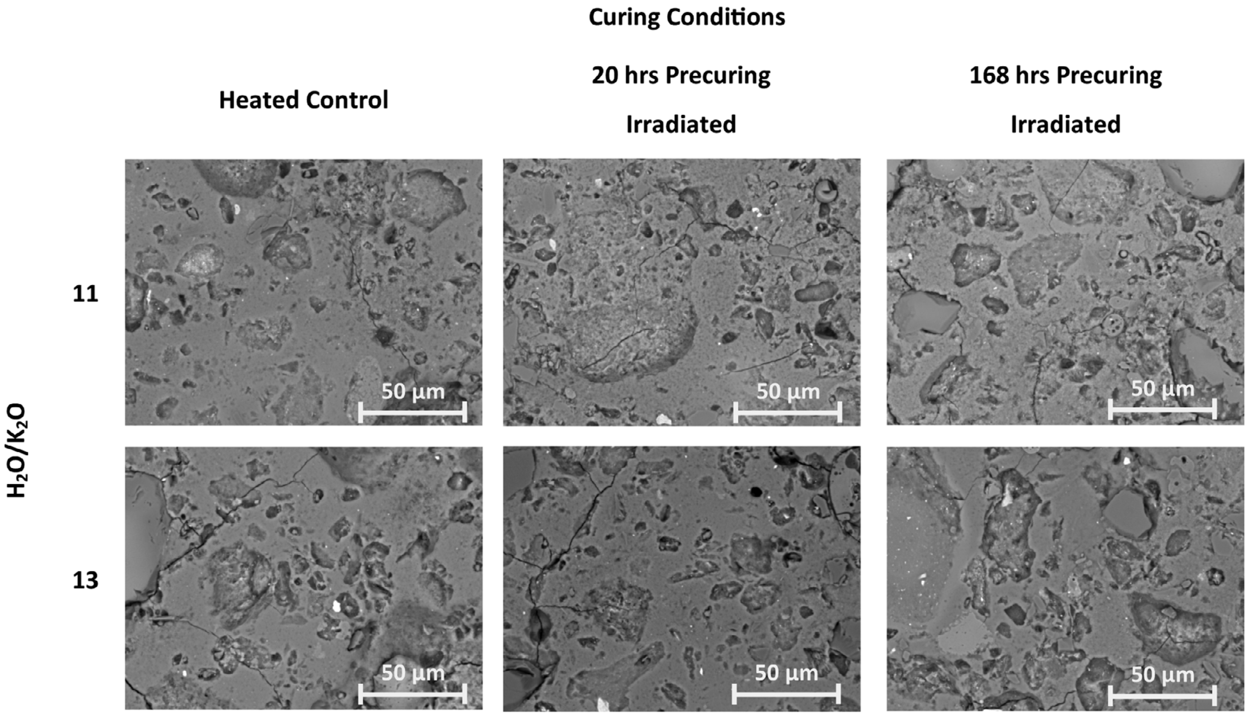

FIGURE 5 Backscatter scanning electron microscopy images demonstrating the morphology of the samples that have been heated to 50°C (heated control) and those irradiated to 1 MGy.

for the production of SEM samples. Quartz particles can be clearly seen as angular, large-diameter (≥20 μm) particles. The voidage can be observed; it does not appear to have dramatically increased in these samples with irradiation for both H2O/K2O ratios but may be more significant in the higher water content system. The 20 h precured sample does appear to contain a greater number of voids with larger volume than the 168 h precured sample, which can lead to a reduced strength within the samples. Increasing the precuring time produces a denser microstructure which helps the sample to withstand the harsh conditions within the irradiator.

In reality, it is noted that the geopolymer encapsulant will be subject to irradiation upon immediate mixing with nuclear waste. However, the exposure radiation doses used in this study are generally greatly increased compared with what can be experienced in a real-world scenario. The removal of the quartz particles (angular voids) appears to be more significant in the irradiated samples. This shows that the binding strength of the unreactive quartz to the geopolymer gel matrix has reduced and it can therefore be inferred that the strength of the paste as a whole has been reduced. Unfortunately, due to the sample size limitations, in the Foss 60Co irradiator,[41] for the dose rate required at this test a sample size of 35 × 35 × 8 mm ($w \times l \times d$) was required and this does not fit the sample size required for standard strength testing. Therefore, inference about the structural properties from standard physicochemical testing is required. Overall, the structure and morphology of these samples remain relatively unchanged, and the effect of precuring and also irradiation appears to have had a minimal effect on the porosity.

This set of results shows that geopolymer cements appear stable to changes induced by irradiation up to 1 MGy at a relatively high dose rate presenting minimal structural changes. However, this study is limited, and further studies at different dose rates, greater total dose, and simulant waste inclusion will be required to examine conditions closer to those experienced by ILW wasteforms. In addition, a direct assessment of the porosity could provide more information on the shape, size, and structure of the porosity within these formulations.

4 | CONCLUSION

Chemical and microstructural analysis has shown that gamma irradiation of potassium silicate-activated metakaolin-based geopolymer materials has a minimal effect on the structural stability of these cements. Thermogravimetric analysis coupled with mass spectrometry, and X-ray diffraction, were used to probe the chemical changes that occurred within these samples upon irradiation. For the first time, carbonation has been shown to occur in geopolymer cements under gamma irradiation (similar to Portland cement blends). However, the degree of carbonation is below 1.0 wt.% of the samples tested, and when compared with the heated control only a small increase is seen in most cases, with natural variation in CO2 levels being partly responsible for small variations. This shows that the carbonation has minimal effects on the microstructural stability of these materials. The reduction in free-water content is expected for cementitious materials and gel structures that have undergone irradiation, while bound water is retained to a greater degree.

Scanning electron microscopy showed that the microstructure of these materials is affected to a limited capacity by gamma radiation. Small changes indicative of cementitious strength properties have been shown, demonstrating minimal changes in structural properties. Changes in the porosity have not been determined, but small changes would empirically be consistent with the small degree of carbonation increase shown. However, SEM images appear to show an increase in voidage. Therefore, further studies of the porosity, including MIP measurements, are required in order to quantify the changes in porosity but overall, the samples appear to have resisted irradiation and not shown any structural changes.

The findings presented here have shown significant advancement in the understanding of not only the gamma irradiation stability of potassium silicate-activated geopolymer cements but also the conditions in which the samples are pretreated before irradiation. This understanding will inform experimental procedures and also develop the knowledge base surrounding the use of geopolymers for nuclear waste disposal.

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