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Microstructural characterisation of alkali-activated PFA matrices for waste immobilisation

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Abstract

A variety of natural and industrial waste product materials rich in SiO_2 and Al_2O_3 may be activated with alkalis to produce cementitious systems which when cured under mild temperature conditions, set and harden to give a very compact paste. When fly ash is the activated material, fast setting and rapid strength development have been reported. In addition to their application in construction, they may have a role in the immobilisation of toxic waste.

Alkali-activated fly ash matrices containing arsenic were studied by a combination of scanning and transmission electron microscopy along with energy-dispersive X-ray analysis of argon-milled sections. Little arsenic was incorporated in the matrix of hydration product but it was apparently associated with iron derived from the hydration of the fly ash. There was no association of As with added Fe_2O_3.

Keywords: Geopolymer; Alkali-activated fly ash; Arsenic immobilisation

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1. Introduction

Geopolymers are representative of a class of cementitious materials derived from the alkaline activation of readily available natural or industrial by-product aluminosilicate materials. These alkali-activated cements are very attractive environmentally for a number of reasons. Their performance as construction materials is in many ways comparable with Portland cement but they differ from Portland cements because they do not require the thermal decomposition of limestone in their manufacture. This alone represents a considerable benefit in terms of reducing global CO_2 emissions. Further, the use of industrial by-products is consistent with the growing trend towards waste re-utilisation.

This paper is concerned with geopolymers [1] derived from the coal combustion by-product, fly ash. The solidification of alkali-activated fly ashes is thought to arise from a series of solution and polycondensation processes in which a randomly arranged, three dimensional network of corner-linked silicate and aluminate tetrahedra is established [2]. These systems, in which the framework alumino-silicate is negatively charged due to the incorporation of the AlO_4 tetrahedral units, require corresponding numbers of positive charges, these normally provided by cations held tightly within the geoplymer matrix. It is such properties which make geopolymers attractive matrices for the binding of metal wastes.

1.1. Microstructures

The present paper is concerned with the microstructures of geopolymers derived from the activation of fly ash by concentrated sodium hydroxide solutions. The work described here is part of a larger project aimed at assessing the suitability of these materials as immobilisation matrices for arsenic wastes and follows from an earlier investigation [3] which suggested that the degree of arsenic binding was correlated with the iron content of the fly ash. A more detailed analysis of leaching characteristics of fly ash- and metakaolin-based geopolymers incorporating iron oxide (and manganese oxide) additions is reported elsewhere [4]. We concentrate here on morphologies, surface textures and

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constitution of microstructural constituents of the leached matrices and attempt to identify specific associations between arsenic and the geopolymer system.

2. Experimental

2.1. Synthesis of geopolymers

The composition of the matrix studied is presented in Table 1. The arsenic content was constant (1 wt% added as $NaAsO_2$) and Fe_2O_3 (5 wt%) and MnO_2 (1 wt%) were included in the system studied. The chemical composition of fly ash used is presented in Table 2.

Fly ashes were activated using a NaOH (8M) solution (containing the appropriate amount of arsenate solution) using a liquid/solid ratio of 0:35. Pastes were mixed to give complete homogenisation, then poured and compacted into metallic moulds. Samples were then cured in an oven at 85 °C (20 h). After curing, the samples were removed from the oven and de-moulded.

2.2. Electron microscopy

Fresh fractures were coated with gold and examined in a JEOL 2000 EX Temscan operating at 20 kV in the SEM mode. Thin sections for TEM examination were prepared from petrographic thin sections by argon milling with an Atom Tech mill operating at 5–6 kV. The sections were coated with carbon and observed with a JEOL 2000 EX Temscan operating at 200 kV. EDX analysis was done with a Link AN10/85S EDX analyser. Quantification was done by the Cliff–Lorimer method [5], which gives results in terms of the ratios of the constituents.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The geopolymer microstructures (Figs. 1–4) are characterised by a dispersion of distinctive morphologies in a mass of predominantly featureless hydration product (aluminosilicate gel). Occasionally, cracking in the product is observed. This may be due to the thermal treatment carried out as part of the activation process, mechanical damage during sample preparation or to drying shrinkage in the vacuum of the electron microscope. The relatively low magnification images (Figs. 1 and 2) provide an overview of the distribution of various constituent phases with more local detail being provided in Figs. 3 and 4.

The most distinctive morphology in all images is that of the fly ash particles. The variation in fly ash reactivity ranges from no appreciable reaction (e.g. top right of Fig. 1), through surface dimpling (Fig. 1; middle left) to partial or complete reaction, and in some cases the

Table 1
Matrix studied

Fly ash (%)	Fe_2O_3 (%)	As (%)	MnO_2 (%)
93	5%	1%	1%

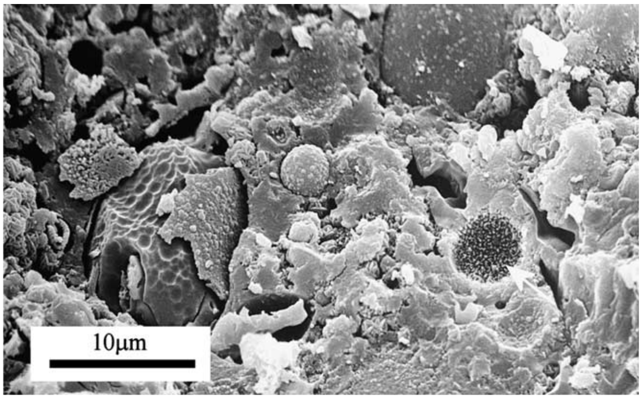

Fig. 1. SEM micrograph of fracture surface of alkali-activated PFA geopolymer. Fe_2O_3 is arrowed.

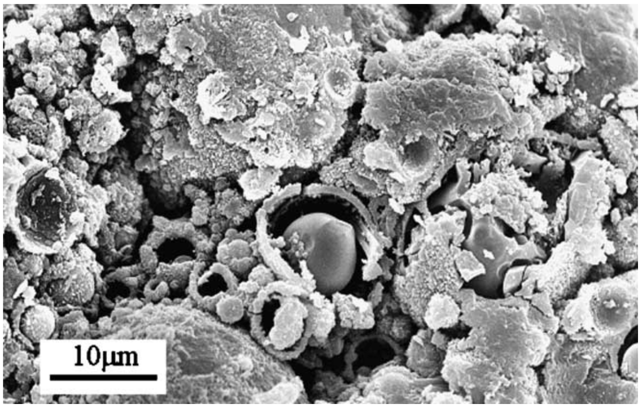

Fig. 2. SEM micrograph of fracture surface of alkali-activated PFA geopolymer.

Table 2
Chemical composition of fly ash

	LoI	IR	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Fly ash	1.80	0.40	51.51	27.47	7.23	4.39	1.86	0.15	3.46	0.70

LoI = Loss on ignition; IR = Insoluble residue.

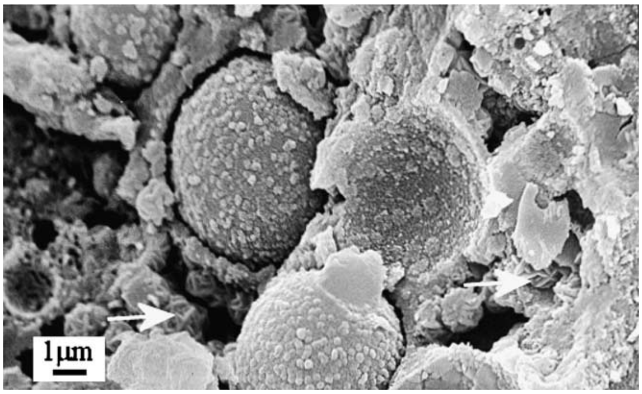

Fig. 3. SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing PFA particle with reaction shells and also unidentified spherical assemblages (arrowed).

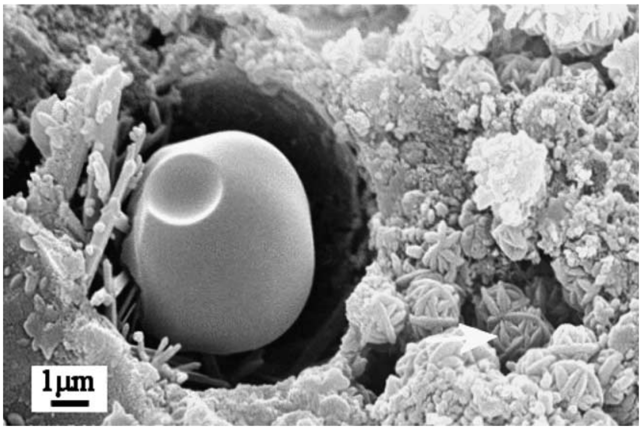

Fig. 4. SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing considerably eroded PFA particle and also unidentified spherical assemblages (arrowed).

interiors of ceno-and plero-spheres are revealed (Fig. 2). This variation, which has been reported before [6], suggests either: (i) differences in the properties of the fly ash on a granular level or (ii) that the availability of the hydrating medium to some fly ash grains is limited. Although it can be noted that the variability in bulk fly ash composition, even within the same batch from a single source, is well known, the permeability of the hydration product layer (or hydration barrier) may also contribute to the variability in reaction rate. The deposition characteristics of hydration product on fly ash surfaces is likely to depend on local chemistry (e.g. pH). On-going hydration will consolidate hydration product layers, thus influencing the pH gradient across the fly ash-hydration product interfacial zone. As hydration continues, the very high pH activator solution may not actually penetrate to the unreacted fly ash within the core of hydration product, reducing reaction rate. The variation in degree of reaction evident from the microstructures may suggest variability in the permeability of hydration product layers.

The existence of empty hydration 'shells' indicates that hydration of the underlying fly ash particle has arisen in cases where ionic diffusion through the hydration product shells has been relatively easy. These empty shells are not unique to geopolymers (nor indeed to fly ash systems) but are more likely in these alkali-activated matrices due to the more extreme alkaline conditions for hydrolysis of the fly ash (aluminosilicate) glass. The spaces in the partially reacted fly ash shells are empty in these images and support the idea that the optimum chemistry for product deposition is not necessarily on the reacting fly ash surface. During hydration, these spaces would be fluid-filled.

The Fe_2O_3 additions to the matrix are readily observed by SEM (Fig. 1) and appear not to have dispersed. Although EDX (see later) confirms the presence of iron in hydration product throughout the specimen, it is most likely that this more dispersed iron has originated from the hydration of fly ash particles.

At higher magnification, further interesting morphologies are clearer (Figs. 3 and 4). Small, apparently well-crystallised, rounded features containing what appear to be interlocking circular platelets are evident in the hydration mass. These may be zeolites of the hydroxy-sodalite and herschelite type as detected by XRD (see Fig. 5). Their existence in Figs. 3 and 4 is most pronounced in the vicinity of the fly ash particles. They are too small to resolve compositionally with confidence by EDX. Fig. 4 also shows apparently well-crystallised needles (probably mullite) within the reaction rim of the central fly ash particle. In contrast to the smooth texture of this particle, Fig. 3 shows fly ash with variable surface

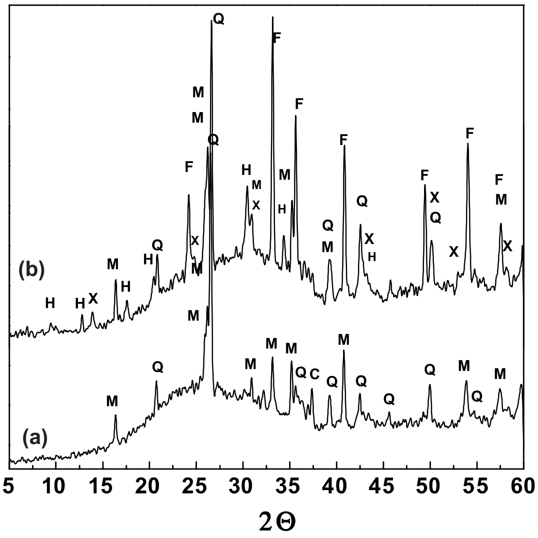

Fig. 5. XRD spectra (a) un-reacted fly ash; (b) alkali-activated fly ash 20 h at 85 °C. Q = Quartz; M = Mullite; F = Hematite; C = CaO; H = Herschelite; X = Hydroxysodalite.

textures, due principally to the nature of deposited hydration products. The morphologies range from granular (Fig. 4; centre) to thin layer type products (Fig. 4; lower right).

3.2. Transmission electron microscopy (TEM)

Figs. 6–9 are transmission electron micrographs of the geopolymer matrices featured in the scanning images (Figs. 1–4). The familiar spherical morphologies of the fly ash particles are again evident as discs amongst other features including hydration rims and the protuberances associated with them but, this time, more detail can be derived both from morphological and compositional information, the latter being available from energy dispersive X-ray analysis (EDX). Transmission microscopy is capable of providing the resolution necessary to focus on small microstructural features enabling microanalysis within hydration rims. Such information is useful in correlating compositions with specific morphologies. Fig. 10 summarises the raw analytical data obtained from EDX acquired from the points numbered 1 to 24 in Figs. 6–9. The values are expressed as atomic percentages normalised for all the elements analysed (Na, Mg, Al, Si, S, K, Ca, Ti, Fe and As) and take no account of the presence of oxygen or water. Although they are not absolute percentages they are, nevertheless, a useful indicator of relative amounts. Note that the penetration of beam electrons into the specimen at these points may lead to interaction of the electrons with underlying phases, although analytical

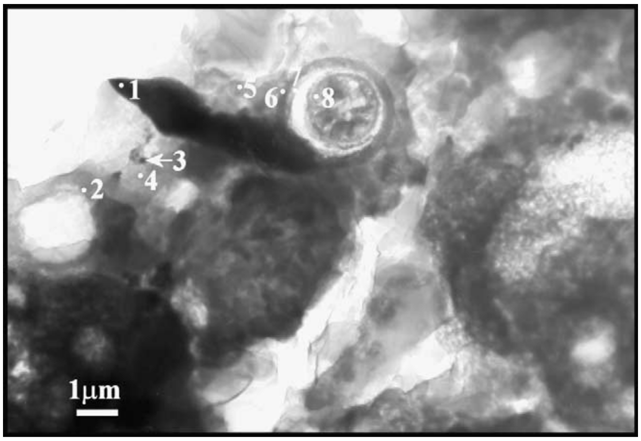

Fig. 6. TEM micrograph of argon-milled section. Numbers correspond to analytical points referred to in text.

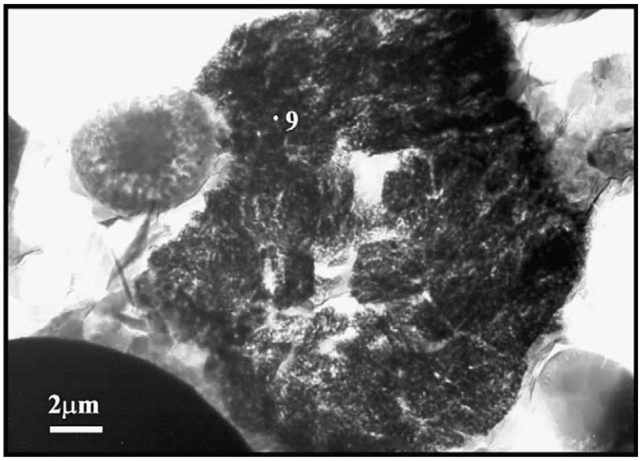

Fig. 7. TEM micrograph of argon-milled thin section showing large, unreacted cluster of Fe_2O_3 crystals. Number corresponds to analytical point referred to in text.

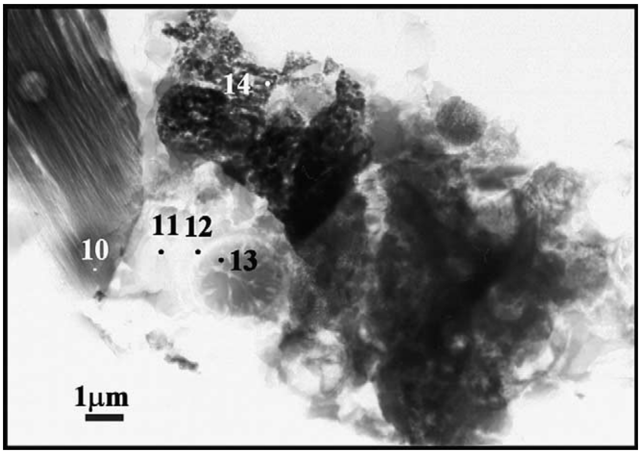

Fig. 8. TEM micrograph of argon-milled thin section showing quartz, PFA, Fe_2O_3 and hydration product. Numbers correspond to analytical points referred to in text.

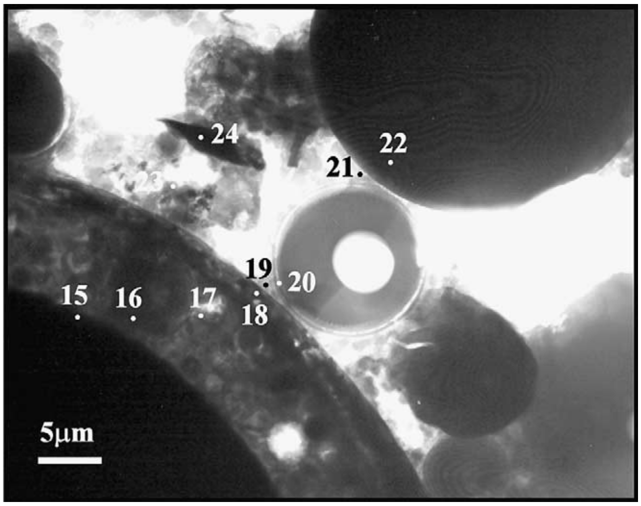

Fig. 9. TEM micrograph of argon-milled thin section showing PFA with hydration rims. The dark particle bottom left is an iron-rich PFA grain, readily distinguishable from the added Fe_2O_3. Numbers correspond to analytical points referred to in text. It is not entirely clear whether the circular features in the rim surrounding the large, Fe-rich particle on the bottom left are unreacted PFA particles or reaction products.

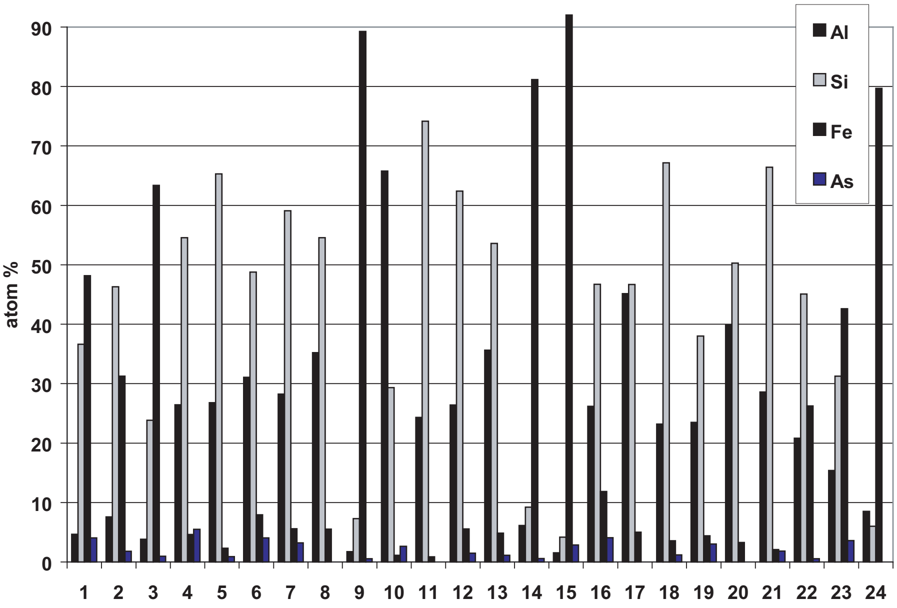

Fig. 10. EDX data on geopolymer paste. For clarity, only Al, Si, Fe and As data are shown.

points were chosen to minimise such interferences. Electron diffraction showed that the hydration products were amorphous.

For example, Fig. 10 suggests that the composition associated with the point 9 (position 9 on Fig. 7 is predominantly Fe (Fe_2O_3). This is consistent with the darker image and relative opacity expected of a Fe_2O_3-rich region of the sample but the analysis may be influenced by surrounding aluminosilicate hydration product which could be obscured by the very electron-dense Fe_2O_3 and which might also contribute Al, Si and As X-rays.

Although the fly ash is predominantly an amorphous aluminosilicate, it also contains other phases such as quartz, mullite and spinels. Indeed the glassy phase contains other chemical constituents, see Fig. 10 and points 8 (Fig. 6), 13 (Fig. 8) and 15 and 22 (Fig. 9). Fig. 6, point 1 indicates a crystalline (by electron diffraction) iron silicate and Fig. 8, point 10 is well-crystallised quartz (with underlying hydration product according to the analysis— Fig. 10). Those PFA grains which give featureless sections are probably wholly glassy, as in Fig. 9, while the textures seen in Figs. 6–8 suggest the presence of refractory crystals such as mullite which are eroded more slowly by the Ar beam than the glass. No features corresponding to the clusters of interlocking crystals observed by SEM were seen in the sections; this may be because they eroded rapidly, or it may be purely by chance.

It is evident when considering the immobilisation potential of this geopolymer matrix that arsenic is not associated in high levels with hydration product. This is consistent with the high leach rates reported elsewhere [4] for arsenic from these matrices. The highest relative As concentration in any of the analyses (Fig. 10) is associated with points 1, 4, 6, 7, 10, 15, 16, 19 and 23. With the exception of point 1 (the crystalline iron silicate), the others are in (or close to) the hydration rims of fly ash particles. It is clear from the analysis at point 9 that the arsenic is *not* concentrated in the iron oxide cluster. Nonetheless, the association of arsenic with iron originating from the fly ash (which contains 7.23% iron expressed as Fe_2O_3) cannot be ruled out based on the proximity of arsenic accumulation in and around fly ash particles. If one analyses the As:Fe (As/Si:Fe/Si) ratios at the points associated with hydration products only, i.e. points 4, 6, 7, 10, 15, 16, 19 and 23, a reasonable correlation is observed (see Fig. 11). The implication of this observation is that it is the speciation of iron which

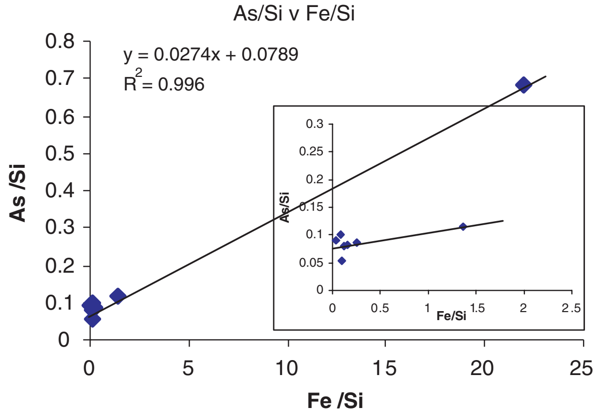

Fig. 11. Effective As/Fe ratio derived from EDX of 'iron-rich' hydration product.

is important in binding arsenic. The localised alkaline conditions in which the fly ash reacts is quite likely to provide an environment in which *aqueous* iron would exist as a hydroxy complex or precipitate as an oxyhydroxide (goethite). The As is associated with amorphous Fe-rich regions, arising from a through solution mechanism and the original state of the Fe in the fly ash is unlikely to affect this association. The persistence of iron added as Fe_2O_3 suggests that in these regions of the microstructure, the chemical environment is quite different. The lower reactivity of Fe_2O_3 (active in the protection of steel in concrete) would limit the conversion of this iron source to iron compounds with adsorption characteristics for As. Consequently, the Fe_2O_3 additions have not clarified the position regarding the role of Fe in As immobilisation within fly ash-derived geopolymers.

3.3. Comparison with OPC–PFA paste

The gel hydration product differs markedly from that obtained in PFA/OPC blends, the main difference being the very low Ca content, although the morphology revealed by TEM is similar [7]. In PFA/OPC pastes, even at long ages (6 yr), unreacted mullitic PFA grains were observed, whereas in the present study, Figs. 6–9 show mullitic grains (Fig. 6; point 8) with clear zones of hydration. This is probably a consequence of the higher alkalinity used here.

4. Conclusions

The morphological and compositional development of alkali-activated PFA geopolymers containing As has been studied by SEM and TEM. Only small amounts of As are incorporated in the hydration product. There is an apparent association of As with Fe arising from the hydration of the PFA, but iron added to the paste as Fe_2O_3 does not react with the As. We conclude therefore that it is the chemical form of Fe available to the aqueous phase that defines the immobilisation performance of fly ash geopolymer matrices and that the hydration conditions at the reacting fly ash surface provides the necessary chemistry for arsenic uptake by iron-containing hydration products. Due to the absence of distinct arsenic compounds within the hydration products, we believe that the small amount of As that is held within the matrix is therefore chemically bound, rather than physically encapsulated.

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