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# Chemical aspects related to using recycled geopolymers as aggregates

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**Despite extensive research into sustainability of geopolymers, end-of-life aspects have been largely overlooked. A recycling scenario is examined in this study. This requires an investigation of alkali leaching potential from a geopolymeric matrix. To study the feasibility of geopolymer cement (GPC) recycling, the migration of alkalis was evaluated for the first time on a microstructural level through energy dispersive X-ray (EDX) scanning electron microscopy (SEM) elemental mapping and leaching tests. Macroscale impacts were assessed through an investigation of Portland cement (PC) mortar properties affected by alkali concentration. Leaching tests indicated that alkalis immediately become available in aqueous environments, but the majority remain chemically or physically bound in the matrix. This type of leaching accelerates the initial setting of PC paste. Elemental mapping and EDX/SEM analysis showed a complex paste–aggregate interfacial transition zone. Exchange of calcium and sodium, revealed by the maps, resulted in the migration of sodium into the PC paste and the formation of additional calcium–silicon-based phases in the geopolymeric matrix. Strength values of mortars with 25% and 50% recycled aggregates (RA) showed negligible differences compared with the reference sample. Screening tests indicated a low potential for GPC RA inducing alkali–silica reaction. Transport of GPC RA alkalis and the underlying mechanisms were observed. This transport phenomenon was found to have minor effects on the properties of the PC mortar, indicating that recycling of geopolymers is a viable reuse practice.**

**Introduction**

Increasing calls for sustainability in construction have led the cement industry to investigate low-carbon dioxide binders as replacements for Portland cement (PC). Geopolymers were popularised by Joseph Davidovits in the 1970s but have recently returned to the forefront of research due to their reported strong environmental credentials. Geopolymers are manufactured through mixing a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or alkali silicate solution (Duxson *et al.*, 2007). Among the various types of geopolymer cement (GPC), fly ash/ground granulated blast-furnace slag (FA/GGBS) mixes are deemed appropriate for high-volume applications such as construction due to their properties, as well as cost and availability of the raw materials (Gunasekara *et al.*, 2015; Heath *et al.*, 2013; Kumar *et al.*, 2010; Li *et al.*, 2013; McLellan *et al.*, 2011; Nath and Sarker, 2014; Shi and Day, 1999).

The environmental impact of GPC manufacture has been extensively investigated, but little attention has been given to reuse or disposal scenarios (Akbarnezhad *et al.*, 2015) and this information is crucial for accurate and complete life cycle assessment analyses. This paper presents part of a project examining the recyclability of FA/GGBS geopolymer paste concretes as aggregates in new concrete. The specific work presented in this paper was to determine an upper bound for pure

geopolymer paste processed to sand size and used as an aggregate in new PC-based mortars.

The experimental work focused on investigating the potential of alkali leaching from GPC recycled aggregates (RA) into PC mortars. Hypotheses on the alkali contribution from natural aggregates (NA) into cement paste have been investigated by a number of researchers (Bérubé *et al.*, 2002; Rajabipour *et al.*, 2015). It has been suggested that alkali release from non-reactive aggregates can be sufficient to influence concrete prism test results (Ideker *et al.*, 2010). In a particular study (Rajabipour *et al.*, 2015), alkalis in pore fluid were measured by means of hot water extraction and were found to exceed the calculated amount (assuming concrete with typical cement content) by 0.25–0.30% sodium oxide equivalent (Na<sub>2</sub>O<sub>eq</sub>) by mass of cement. The difference between the calculated and obtained value was attributed to the aggregates. However, the fundamental chemical and physical differences between an amorphous geopolymer matrix and crystalline NA mean that this previous work can only be used as a guide and not a comparison for the studies described in this paper. Geopolymeric matrices are highly alkaline, due to the activating solutions, and can have a higher porosity than NA. This makes it highly possible that the incorporation of recycled geopolymer as aggregate in a new mix will result in a significant increase in the overall alkalinity of the paste, which would affect a number of fresh and hardened properties.

Water-soluble alkalis from aggregates could diffuse almost immediately into the aqueous phase of the paste during mixing if they are available and there is sufficient mix water for dissolution. Some alkalis in the recycled paste are likely to be bound into solid phases and thus potentially unavailable to the mix water. Alkalis present in fresh paste can either be incorporated into calcium silicate hydrate (C–S–H) gel or become concentrated in the aqueous phase and remain present in the pore fluid (Hong and Glasser, 1999; Jawed and Skalny, 1978; Myers *et al.*, 2015). Findings regarding the capacity of alkali uptake by C–S–H are variable, but there is consensus regarding the factors affecting it. The underlying governing mechanisms are related to charge balancing processes and the overall incorporation depends on the initial concentration of alkalis in the aqueous solution, the calcium:silicon (Ca:Si) ratio of the paste and the presence of aluminium (Al) in the precursor (Hong and Glasser, 1999; Myers *et al.*, 2015). However, the high pH of the cement pore fluid, as reported by a number of researchers, provides strong evidence that a significant number of alkalis remain in the aqueous medium (Buckley *et al.*, 2007; Jawed and Skalny, 1978; Kim *et al.*, 2015; Rajabipour *et al.*, 2015; Taylor, 1987). This situation could increase the potential of alkali–silica reaction (ASR) occurrence in PC elements incorporating GPC RA because the pore fluid is the medium bringing alkalis into contact with the amorphous silica of the aggregates (Chatterji, 2005; Rajabipour *et al.*, 2015).

Another implication of potentially water-soluble alkalis is that their presence in the aqueous phase affects the hydration processes of cement. The solubility of calcium or calcium hydroxide (Ca(OH)<sub>2</sub>) suppresses the presence of alkalis (Hong and Glasser, 1999; Jawed and Skalny, 1978). On the contrary, silicon solubility increases with increasing alkali concentration. This, along with other interactions, results in alteration of the hydration kinetics and the growth, microstructure and morphology of the hydration products. The distinct effects of alkalis in cement are crystallisation of the C–S–H, acceleration of setting, an increase of early strength and a reduction in final strength (Jawed and Skalny, 1978; Mota Gassó, 2015).

## Materials

In this work, a geopolymer paste was used as the parent material for the RA. This was done to investigate an upper bound for the geopolymer paste and provide a simplified matrix system without the influence of other parameters such as aggregates or impurities. PC mortars with 0%, 25% and 50% replacement (by mass) of NA by GPC RA were cast (Table 1). The test results for GPC RA were evaluated against PC RA and natural sand.

For the geopolymer precursor, GGBS (procured by Hanson Heidelberg cement group from the Port Talbot works) and FA (Cemex 450-S, BS EN 450-1 (BSI, 2012) fineness category S; loss on ignition (LOI) category B) were used. The chemical composition of the precursors as obtained by X-ray fluorescence (XRF) is presented in Table 2. For the activating solution,

Table 1. Mix design for mortars with RA

Sample	PC: kg/m <sup>3</sup>	NA: kg/m <sup>3</sup>	PC RA: kg/m <sup>3</sup>	GPC RA: kg/m <sup>3</sup>	Water: kg/m <sup>3</sup>
PC_100%NA	960	2160	—	—	451
PC_25%PC	960	1620	540	—	451
PC_50%PC	960	1080	1080	—	451
PC_25%GPC	960	1620	—	540	451
PC_50%GPC	960	1080	—	1080	451

Table 2. Chemical analysis of precursors by XRF

	GGBS	FA
Silicon dioxide (SiO <sub>2</sub> ): wt%	35.15	49
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> ): wt%	13.07	23.5
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ): wt%	0.28	8.7
Calcium oxide (CaO): wt%	39.6	2.4
Magnesium oxide (MgO): wt%	8.47	1.4
Sulfur trioxide (SO <sub>3</sub> ): wt%	0.17	0.8
Sodium oxide (Na <sub>2</sub> O): wt%	0.14	3.06
Potassium oxide (K <sub>2</sub> O): wt%	0.51	0.87
Titanium dioxide (TiO <sub>2</sub> ): wt%	0.66	—
Manganese oxide (MnO): wt%	0.44	—
Phosphorus pentoxide (P <sub>2</sub> O <sub>5</sub> ): wt%	—	1.1
LOI: wt%	0.97	4.4

sodium hydroxide (NaOH) pellets (>98% purity) were mixed with distilled water and sodium silicate powder with a sodium oxide content of ~27.0% and silicon dioxide (SiO<sub>2</sub>) content of ~53.5%. The chemicals were supplied by Sigma-Aldrich.

For each batch of geopolymer paste, 10 kg of precursor with a FA to GGBS ratio of 1:1 were used. The corresponding activator was 906 g of sodium silicate solution mixed with 330 g sodium hydroxide and 2.375 l of distilled water. The total sodium (Na), calculated as sodium oxide equivalent per mass of precursor, was 5%, which is a level that was expected to result in some excess (unbound) alkalis. The activator solution was left to cool for 24 h prior to mixing as exothermic dissolution increased the temperature of the solution. For the PC RA, paste with a water to cement ratio of 0.5 was cast. For all PC elements, a low-alkalinity PC–FA cement was used (Sulfacrete BS EN 197-1 (BSI, 2011) CEM II/BV 32.5R, supplied by Tarmac Cement & Lime Ltd; LOI of FA <7%, minimum FA ~25%). Standard sand complying with BS EN 196-1 (BSI, 2016a) was used as NA.

The pastes for the RA were cast in cubes of 100 mm in the laboratory. They were cured for 28 d in sealed plastic bags at ambient temperature and then crushed according to BS EN 12390-3 (BSI, 2009) to determine compressive strength. The mean strength values were 45.5 MPa and 47.8 MPa for the PC and GPC pastes, respectively. The recycled pastes were designed to have equivalent strength in order to provide comparable results. The specimens were then put through a rock crusher with the jaw opening set at 1 mm. The material was then sieved and re-blended to a similar particle size

distribution as standard sand complying with BS EN 196-1 (BSI, 2016a). The final RA product was thus a sand with equal percentages of particle sizes of 2–1 mm, 0.5–1 mm and 0.5–0 mm.

## Methods

An extraction test to determine the water-solubility of the alkalis and other compounds of the geopolymer aggregates was conducted. The procedure was based on that described in BS EN 1744-6 (BSI, 2006a) for the duration and method of extraction. For the liquid to solids ratio, the recommendations of BS EN 1744-1 (BSI, 2006b) were followed. Aggregate test portions were mixed with demineralised water at a 1:1 water to solids ratio. Two extractions were carried out in parallel, for a total of 3 h with agitation by turning every 30 min. The pH of the extracts was measured just before the agitation took place at 30 min intervals. At the end of the immersion period, the extract was filtered and used as per the procedures of BS EN 1744-6 (BSI, 2006a) and described later.

The influence of the RA extract on the initial setting time of cement was evaluated according to BS EN 1744-6 (BSI, 2006a). For this test, the initial setting of a standard-consistency CEM I paste made with demineralised water was measured using the Vicat apparatus. Then, following the same method, the initial setting time of the paste made with the RA extract was determined. The influence on setting time due to the aggregate extract was then calculated.

The GPC aggregate was subjected to energy dispersive X-ray (EDX) scanning electron microscopy (SEM) analysis before and after the extraction and the obtained spectra were compared to identify the leaching of elements. A crushed uncoated sample was placed on carbon tape. The aggregate samples were examined at low, medium and high magnifications. The element used for optimisation of the spectra was copper. A threshold of  $1\sigma$  was set and all qualitative results below that were set to zero. The data were recorded as atomic percentages (atomic %) of elements in the examined area.

Backscattered electron (BSE) imaging and EDX/SEM elemental mapping was also conducted on 6 month old mortars. The purpose of this was to investigate whether alkalis are transferred to the PC matrix and to attempt to determine the mechanism through which the transfer took place. It was considered possible that if alkalis are easily soluble in water, transfer would take place during mixing. If any transfer occurred at a later age it would most probably be through the interfacial transition zone (ITZ). This hypothesis could easily be tested by elemental mapping as any patterns of sodium leaching from the GPC aggregate into the paste would be apparent.

Cubic specimens of 20 mm edge and 10 mm depth were cut from mortar prisms, cast into low-viscosity epoxy resin and then polished to reveal the top surface of the specimens. EDX

was conducted in low vacuum mode, at a pressure of 30 Pa. The time for the element mapping varied from 35 to 45 min. Results below  $2\sigma$  were set to zero.

For all EDX/SEM analyses, a Jeol JSM-6480LV SEM with Oxford Instruments X-Act EDX detector was used with an accelerating voltage of 20 kV and a process time of 5 s.

The potential for ASR was investigated according to the accelerated mortar bar method as described in ASTM C 1260-14 (ASTM, 2014) (this procedure is identical to that described in the withdrawn British DD 249:1999) and was the appropriate test for the fine aggregates used in this study. The test was conducted on four mortar bars of dimensions 25 mm  $\times$  25 mm  $\times$  250 mm with studs in the longitudinal direction. The bars were kept at 80°C for the whole duration of the test; in water for 1 d after demoulding, then in 1 M sodium hydroxide solution for 14 d. The total length change after the 14 d immersion period is the criterion to identify ASR occurrence: for a mean expansion greater than 0.10%, the formation of alkali-silica gel is considered possible and further investigation is required.

Additionally, the 28 d compressive strength of the mortars incorporating RA was tested according to the procedure described in BS EN 1015-11 (BSI, 1999).

## Results and discussion

### GPC RA extraction

The alkalinity of the water increased immediately after the GPC RA immersion, rising from a pH of approximately 7 to higher than 12. This is approximately a 39% increase in pH value, which corresponds to a rise in  $\text{OH}^-$  concentration from  $6.3 \times 10^{-7}$  to  $3.1 \times 10^{-2}$  mol/l. A slight and steady increase took place for the first 2 h and then the values appeared to stabilise, as shown in Figure 1. The duration of the test was short compared with standard leaching tests in order to better

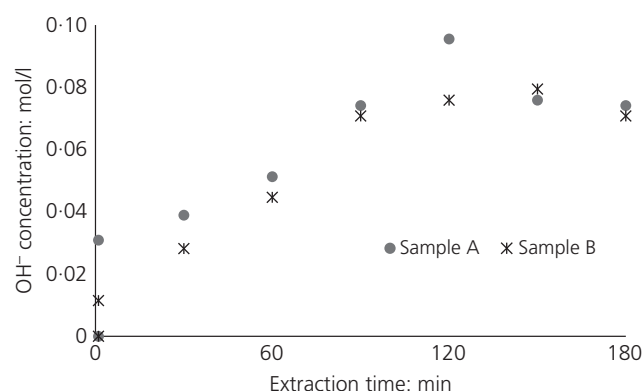


Figure 1.  $\text{OH}^-$  concentration of water GPC RA extract as calculated from pH measurements

replicate the situation where RA are combined with mix water. Therefore, the observations were more likely to relate to short-term processes such as dissolution or washout, rather than provide information for the diffusion mechanism of sodium through the geopolymeric paste. However, the sharp pH increase was indicative of alkalis that are soluble in water and therefore could immediately become available during mixing of mortar or concrete. The total amount of sodium oxide from the precursors and activators in 1 kg of the RA was approximately 66 g. If all of this leached in 1 l of water during the extraction process, the concentration of sodium oxide in the water would be just over 1 mol/l. Although sodium will not be in the form of sodium oxide in the aqueous solution, it does indicate that this level of soluble sodium will not result in an OH<sup>-</sup> concentration of only  $3.1 \times 10^{-2}$  mol/l, as indicated by the pH. Therefore, it can be concluded that the majority of sodium oxide is not available for dissolution during the time period of the leaching test. This is most likely because of a combination of chemical and physical bonding.

This was confirmed by EDX/SEM measurements, which were taken to determine the atomic concentration of sodium in the aggregates before and after 3 h of leaching. EDX/SEM measurements were also taken from an additional sample that was subjected to extended leaching (5 d). Fourteen different sites were used before leaching and seven were used after leaching. The EDX spectra indicated a broad range in sodium concentrations, which makes it difficult to conclusively determine how much the sodium oxide concentration had reduced. Analysis of variance of the data indicated that at the 95% confidence level it was not possible to determine if there was a significant difference in the overall sodium concentration in the RA before or after leaching. This demonstrates that the increase in pH of the leachate water is probably a better indicator of available alkalis than the decrease in concentration in the RA. The leaching test is, however, not the true representation of the mix process that the elemental maps represent as an actual mix situation, where the water available for leaching alkalis is influenced by hydration reactions and vice versa. It should be noted that as the quantity of sodium far exceeded the quantity of potassium (K) in the geopolymer mix, the movement of sodium was the focus of this investigation.

In addition to sodium, other elements may have leached from the RA and influenced the hydration products, but these were also not clearly discernible from the EDX spectra. This effect of leached elements on the hydration products was not directly examined in the work reported in this paper, but indirect effects were examined through measurements of setting time and compressive strength and BSE/SEM images.

#### Elemental maps of mortars

After the solubility of sodium from GPC RA was confirmed, elemental mapping was performed on the final mortars. The

mapping had two purposes. The first was to visually examine the distribution of sodium in the PC mortar paste to determine whether this was uniform or concentrated at the interface between the PC paste and the GPC RA. The second was a semi-quantitative analysis to estimate how the GPC RA affected the overall sodium concentration in the paste, compared to samples with PC RA and NA.

Each pixel of an elemental map is defined by a spectrum with known coordinates. The spectrum provides information about the detected elements in terms of atomic percentages. The values for a single spectrum are normalised to 100% by the analysis software INCA. Using this information, INCA derives the highest and lowest percentage for every element detected on the mapped area. These values are presented using the terms ‘max percent’ and ‘min percent’. Additionally, INCA generates a ‘sum spectrum’, which is the average value of the atomic percentages for a single element (Figure 2).

The sum spectra for a single map are normalised to 100% and provide information about the average concentration of each element in the examined area. Due to the averaging and normalisation, the presence of areas with a high concentration of a specific element can result in high values that are not characteristic of the whole map. Although, the mapped areas were chosen to provide representative results, this effect is inevitable in locations of interest with GPC RA such as those presented in Figures 3–7. For example, in Figure 4 the presence of NA increased the sum spectrum of silicon in relation to values of other elements. To reinforce the results, individual spectra from the paste of the mapped areas were taken. The average of sodium percentages was calculated and this is presented as the ‘paste average’ in Figure 2. All the results were normalised to the sum spectrum of the reference mix (PC\_100%NA) and are presented graphically in Figure 2.

Although the data are quantitative, they should be considered in a qualitative manner as the sample size was small compared

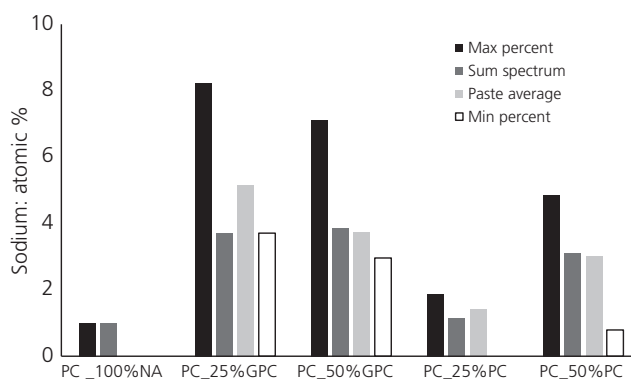


Figure 2. Measured atomic sodium of PC mortars according to EDX spectra from elemental mapping



with the aggregate dimensions; the trends are better illustrated in the BSE/SEM images (Figures 3–7). As expected, the sum spectra of the mortars with GPC RA showed higher sodium contents than all other mixes, but the variability between samples showed that a higher GPC replacement did not result in a proportionally overall higher sodium content. The samples with the PC RA also showed an increased sodium content in comparison with the NA sample. The PC RA had a higher sodium content than the standard sand used in the present study. When a proportion of sand was replaced by PC RA, the cumulative amount of sodium in the mortars was expected to be higher than that of the reference mix. However, the paste average data in Figure 2 do indicate that, as expected, the sodium concentration is likely to be more of a concern when using recycled geopolymer aggregate. Specifically, the paste averages for mortars with 50% and 25% GPC RA were 5% and 4% higher compared with the sum spectrum of the reference mix. In the case of mortars with PC RA, the corresponding values showed a relative increase of 1.4% and 3% for 25% and 50% PC RA, respectively. It should be noted that the absence of a column in Figure 2 indicates a recorded value below the threshold or zero. As mentioned earlier and better demonstrated in Figures 3–7, the values of max percent in samples with GPC aggregate and PC paste correspond to the GPC RA areas.

Elemental maps of the mortars incorporating GPC RA are presented in Figures 3–7. The images show the distribution of calcium and sodium along with SEM images of the examined areas. Calcium maps were used to distinguish the PC paste from the GPC RA and were also indicative of the ‘border’ between the two materials. The brightness of colour is proportional to the element concentration: white indicates a high concentration and grey corresponds to low or zero values.

It is noticeable that in all the electron images, the two materials presented quite distinct morphologies. In all cases, unreacted FA spheres were present in both the GPC RA and

the PC matrix, visible as circles in the images. Some unreacted GGBS is also visible in the GPC, indicated as a largely straight-sided form with high calcium concentration.

As far as sodium is concerned, a scattered distribution of the element in the paste is shown in Figure 3. A slightly higher concentration was observed at the area corresponding to the GPC RA but the results regarding the PC paste were variable. At the top/middle left-hand side, a continuous concentration beyond the ITZ is shown. On the contrary, in the middle right-hand area of the image, sodium seemed absent in areas of the PC paste. This continuous distribution was considered an indication of sodium transfer not only through water but also through the ITZ at later ages. In order to examine this observation further, samples were examined at higher magnifications.

By examining Figures 4 and 5 it became more obvious that sodium had been transferred in the PC paste not only through dissolution in water but also by leaching through the ITZ, as there was a gradual decrease in sodium concentration past the paste-aggregate boundary. A relatively highly scattered distribution in the paste was confirmed, while leaching through the ITZ is apparent in Figure 5. In these higher magnification images, the calcium outline appeared less sharp in comparison with Figure 3. A higher concentration of calcium close to the ITZ that cannot be related to GGBS particles was also revealed.

In Figures 6 and 7, the effect is more subtle and it appears there was a continuity in the sodium dispersion. This low contrast indicates that the sodium concentration in the two materials was similar and it appeared unaltered for at least 100  $\mu\text{m}$  beyond the paste–aggregate interface.

In addition, Figures 6 and 7 reveal the reverse phenomenon of calcium leaching from the PC paste into the geopolymeric matrix through the ITZ. The concentration of calcium at these

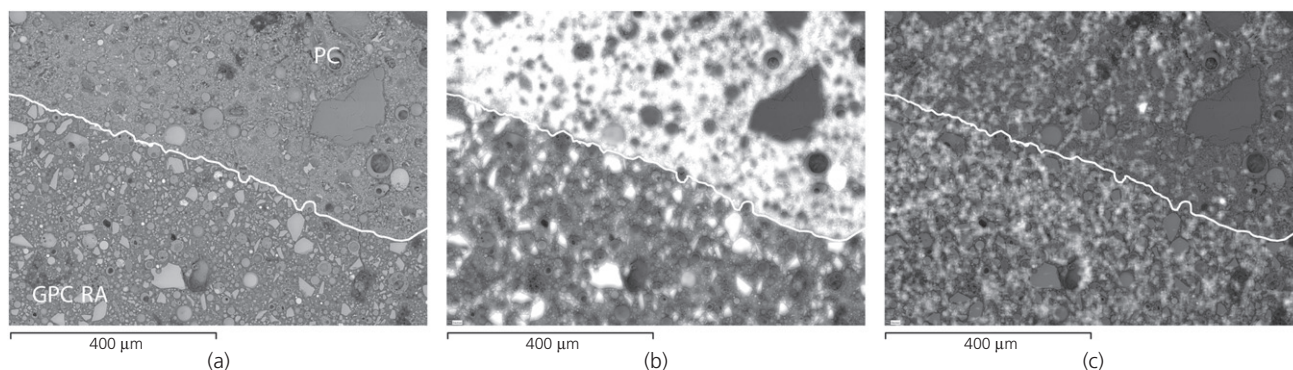


Figure 3. PC\_50%GPC site 1: (a) BSE SEM image of polished sample with the ITZ border drawn; (b) elemental map of calcium; (c) elemental map of sodium

points cannot definitely be related to GGBS particles, as indicated by the SEM images and the shape of the points. Instead, it appears that these points correspond to a geopolymeric phase with quite distinct morphology compared with the rest of the material. Additional spectra of those areas (not presented here)

showed high silicon and low aluminium concentrations, which concur with the high calcium concentration, and this may indicate the formation of a C-S-H type product. The physical appearance of that product seemed to be denser and more homogenous than the rest of the geopolymer material.

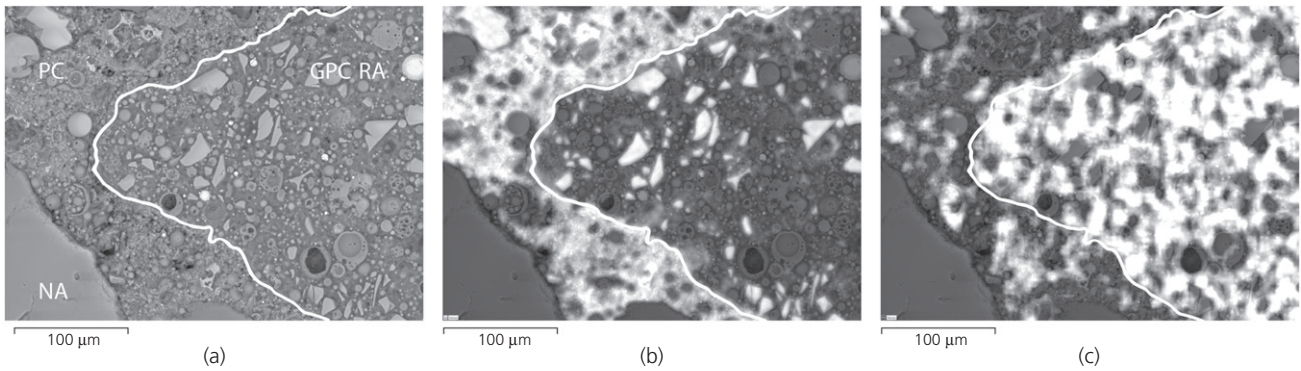


Figure 4. PC\_50%GPC site 2: (a) BSE SEM image of polished sample with the ITZ border drawn; (b) elemental map of calcium; (c) elemental map of sodium

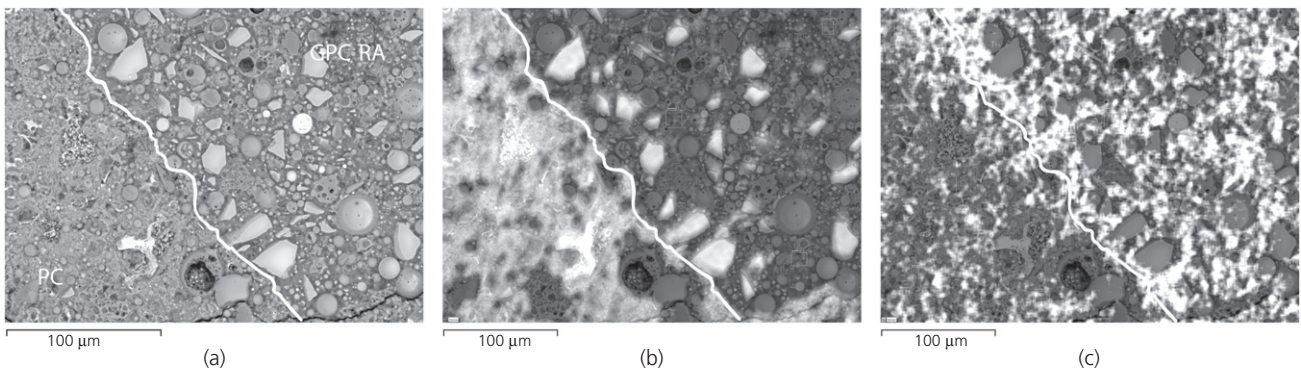


Figure 5. PC\_25%GPC site 1: (a) BSE SEM image of polished sample with the ITZ border drawn; (b) elemental map of calcium; (c) elemental map of sodium

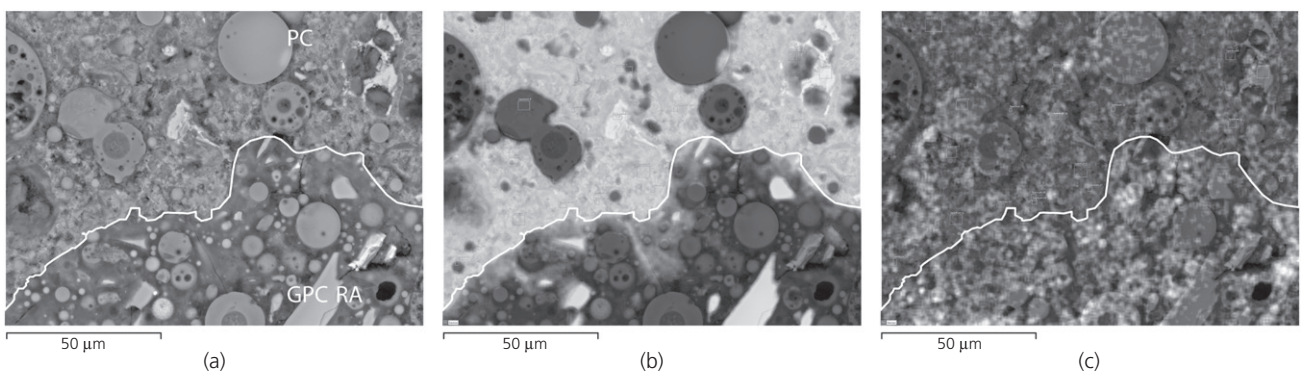
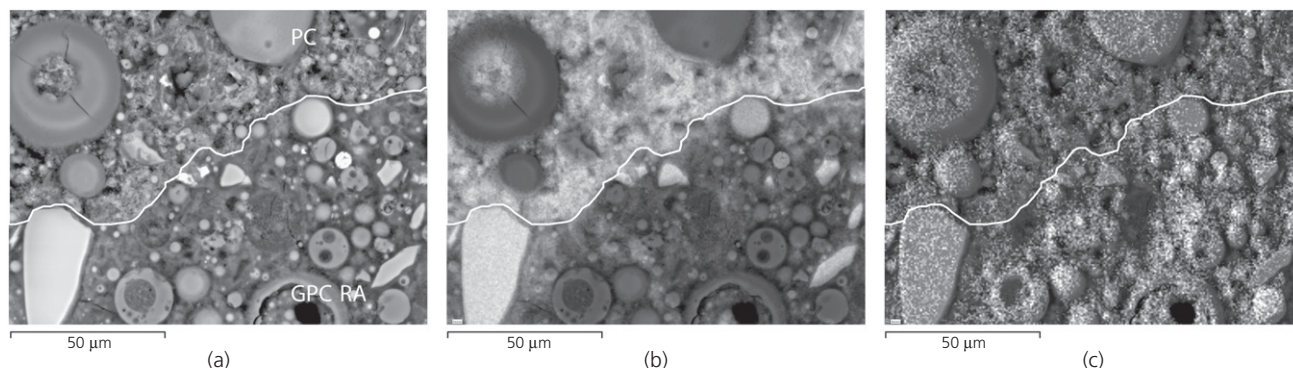
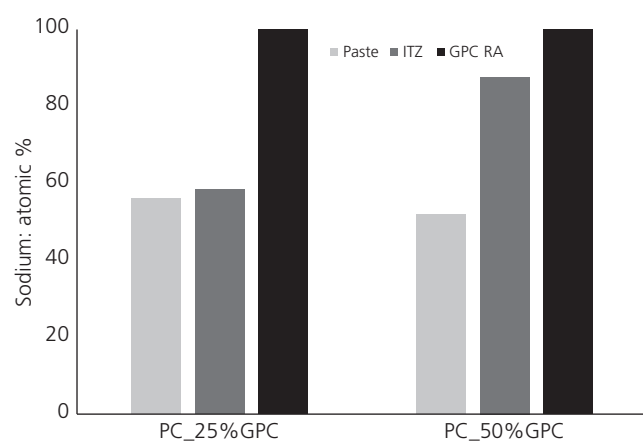


Figure 6. PC\_50%GPC site 3: (a) BSE SEM image of polished sample with the ITZ border drawn; (b) elemental map of calcium; (c) elemental map of sodium





**Figure 7.** PC\_25%GPC site 2: (a) BSE SEM image of polished sample with the ITZ border drawn; (b) elemental map of calcium; (c) elemental map of sodium



**Figure 8.** Average of atomic sodium from EDX spectra on points of interest in the paste, the ITZ and GPC RA for samples PC\_25% GPC (site 2) and PC\_50%GPC (site 3)

A number of researchers have reported distinct products from FA and GGBS alkali activation, with the latter resulting in the formation of a denser C–S–H type gel (Chi and Huang, 2013; Gunasekara *et al.*, 2015; Ismail *et al.*, 2014; Li *et al.*, 2013). The phase shown in Figures 6 and 7 has similar morphology to such gels. However, the absence of GGBS particles in the specific location allows consideration of the adjacent PC paste as a potential source of calcium.

Substitution of  $\text{Na}^+$  by  $\text{Ca}^{2+}$  in silica networks is considered a plausible mechanism for alkali exchange during ASR (Rajabipour *et al.*, 2015), while substitution of calcium oxide (CaO) by sodium oxide in aluminates and silicates is reported by Jawed and Skalny (1978). The latter attribute this phenomenon to the similar ionic radii of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , which allows substitution in the crystal matrices without significant alteration of the free energy of the system. Another identified phenomenon was the accumulation of sodium on partly or non-reacted FA particles. It is noticeable that calcium was largely absent from the FA particles, as shown in Figures 6 and 7.

Spectra from specific points were taken from PC\_25%GPC site 2 and PC\_50%GPC site 3. The points of interest were located in the paste, close to the ITZ (approximately up to 9  $\mu\text{m}$  from the interface) and in the GPC RA. The average of the sodium atomic percentages was calculated and normalised to the average sodium percentage of the corresponding GPC RA area of each site. The results, presented in Figure 8, indicate the relative sodium concentration of the mortar paste close to and further from the ITZ. The gradient in sodium concentration was more obvious in the case of PC\_50%GPC, with the relative percentage changing from approximately 85% close to the ITZ to less than 60% in the paste. This transition did not seem to take place in PC\_25% GPC, as the average sodium concentrations close to the ITZ and further away were almost equal (approximately 60% that of the GPC RA area).

### Mechanical and physical properties

#### Initial setting time

The influence of the aggregate extract in terms of differences in initial setting times was calculated using equation 1 of BS EN 1744-6 (BSI, 2006a).

Two pastes of standard consistency (according to BS EN 196-3 (BSI, 2016b)) were prepared using 500 g of CEM I and 175 g of demineralised water and extract. The initial setting times, determined using a manual Vicat apparatus, showed the aggregate extract to cause an acceleration of 13 min.

This accelerating effect is in accordance with most literature findings about the effect of alkalis on cement setting, and is considered an indication of the presence of alkalis in the extract. Most literature findings describe the acceleration of hydration as a distinct effect of alkalis in the aqueous solution (Jawed and Skalny, 1978; Salvador *et al.*, 2016). In this specific case though, no ‘flash setting’ took place but an acceleration of 6.4% of initial setting was observed. It is possible that other water-soluble elements were made available in the extract, but

this cannot be confirmed from the EDX spectra obtained in the present study.

### ASR test

The results of the ASR test indicated a trend relating to the aggregate type in the mortar mix (Figure 9).

The reference mix (with only NA) presented distinct behaviour, being the only one that exhibited shrinkage. The mixes incorporating PC RA presented a trend of gradual length increase. Given the slope of the lines, it appears that almost the same pace of length change was preserved during the test. Only the mix with 50% replacement of NA by PC RA presented a total length increase close to the limit in ASTM C1260-14 (ASTM, 2014) of 0.10%. For mixes with GPC RA, a trend of sharper length increase during the first week of immersion was observed. Both mixes exhibited a total length change significantly lower than that of the ASTM limit, with PC\_25%GPC and PC\_50% GPC presenting values of 0.04% and 0.06%, respectively.

This testing was carried out to determine whether the recycled geopolymer aggregate itself could react and lead to ASR. Accelerated mortar bar testing is recommended as a screening method, especially for concrete RA (Gress *et al.*, 2000), and therefore additional testing will be conducted to determine whether the additional alkalis introduced through the recycled geopolymers could result in ASR when combined with potentially reactive aggregates.

### Compressive strength testing

The compressive strength results indicated that the incorporation of GPC RA led to a reduction in strength (Figure 10). The mix with 25% PC RA had the highest strength of all the mixes, followed by the mix with 25% GPC RA. It is remarkable that all the mixes, with the exception of PC\_50%GPC, presented 28 d strength values higher than that of the reference mix.

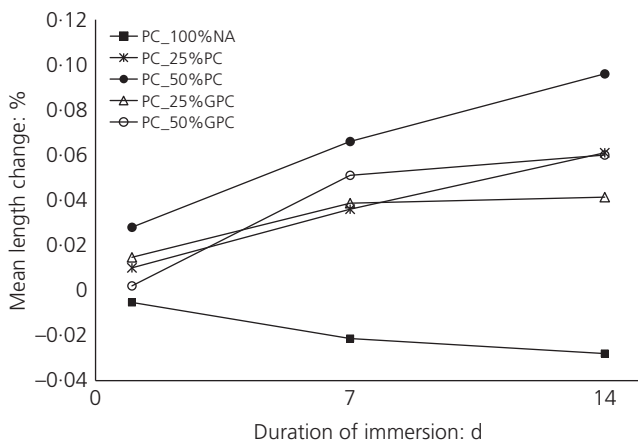


Figure 9. Mean length change for PC mortars after 14 d of immersion in 1 M sodium hydroxide solution as a means of identifying ASR

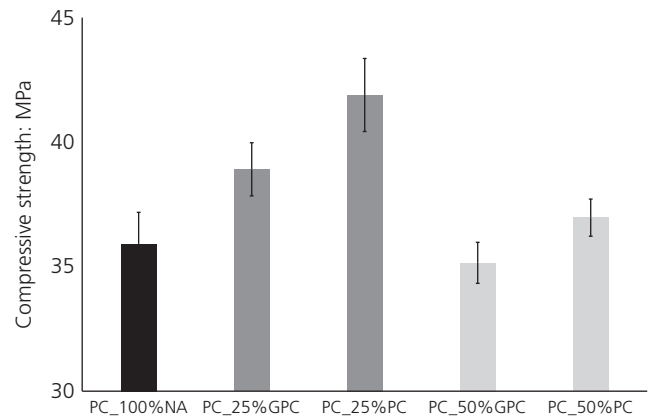


Figure 10. Compressive strength of mortars at 28 d

In the case of RA concrete or mortar, the final strength is dependent on numerous parameters, both physical and chemical (Pepe *et al.*, 2014; Tam *et al.*, 2009). One of the most distinct characteristics of RA – high water absorption – can affect the nominal water to cement ratio and therefore the final strength (De Pauw *et al.*, 1998; Kwan *et al.*, 2012; Malešev *et al.*, 2010). In this work, it appeared that, for mortars with the same replacement levels, the incorporation of GPC RA resulted in lower values compared with PC RA. This could be related not only to the chemical composition of the RA material but also the workability of the mix, as the mixes used in this study had a constant water content. As mentioned in the literature, the presence of alkalis in mortar leads to lower strength at later ages (Jawed and Skalny, 1978; Mota Gassó, 2015).

### Conclusions

EDX/SEM elemental mapping coupled with leaching tests proved to be a valid approach for investigating alkali migration from recycled geopolymers. The following results were obtained.

- The findings of this work showed that the incorporation of GPC RA in mortars could increase the alkalinity of the mix through two distinctive mechanisms.
- Alkali solubility in water: the sharp increase in leachate alkalinity demonstrated that there is a short window, during and after mixing, in which unbound alkalis become available in the aqueous phase. As a consequence, the chemistry of the mixing water and the paste is altered.
- Alkali migration through the paste–aggregate interface: the findings indicated that sodium migration can occur through the interface, by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  exchange between the two materials. Elemental mapping coupled with EDX spectra showed higher sodium concentrations close to the paste–aggregate interface than in the rest of the paste.



The corresponding calcium maps indicated transport from the PC paste into the GPC RA.

- BSE/SEM images revealed a complex paste–aggregate ITZ, while the formation of additional calcium–silicon-based phases in the geopolymeric matrix was identified by EDX spectra.
- GPC incorporation resulted in minor effects on PC mortar properties susceptible to presence of additional alkalis in the mix.
- GPC RA leachate accelerated the initial setting time of PC paste by 13 min. However, further investigation is required to determine its chemical composition.
- All mixes with the exception of PC\_50%GPC demonstrated higher compressive strength than the reference mix. The results did not show a distinct effect of GPC on strength, but strength is also dependent on mix design parameters and the age of testing. GPC RA demonstrated an effect comparable to that of PC RA.
- The screening test for ASR indicated that GPC RA did not show a tendency to expand or indicate ASR any more than recycled PC aggregates. More complex systems taking into account the action of potentially reactive aggregates are to be investigated.
- This research contributes to developing fundamental understanding of the mechanisms and effects of alkali transport on the behaviour of recycled geopolymer paste. No detrimental effects were observed on PC mortars due to the incorporation of GPC RA, implying that this recycling practice is feasible. However, further investigation of more complex systems is required.

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