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# Chemical aspects related to using recycled geopolymers as an aggregate

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## ABSTRACT

Geopolymer cements are alternative binders for concrete with low $CO_2$ footprint and distinct chemical composition. They consist of aluminosilicate macromolecules and have a highly alkaline matrix due to the activating solutions used for their production. This paper is based on a study examining the recyclability of fly ash-slag based geopolymer paste as fine recycled concrete aggregate (RCA) in Portland cement and geopolymer mortars. Given the intrinsic structure of geopolymers, leaching of chemical substances from the RCA into the new paste was considered possible. SEM images and elemental mapping of the hardened mortars were used to evaluate the effect of RA. The potential of alkali silica reaction occurrence and the effect of RA extract on the initial setting time of cement were examined.

## 1. Introduction

The call for sustainability in construction has lead cement industry to the investigation of low carbon binders as replacements for Portland cement (PC). Geopolymers were popularized by Joseph Davidovits in the 1970's but have been brought to the center of attention during the past years due to their low embodied carbon. They are manufactured by the interaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or alkali silicate solution (Duxson, Fernández-Jiménez et al. 2007). Amongst the various geopolymer types, fly ash and slag based geopolymer cement (GPC) is deemed appropriate for high volume applications such as construction, due to its' properties and availability of raw materials (Davidovits, J., 2015). Although the environmental impact of GPCs manufacturing is being investigated intensively, little attention has been given to reuse or disposal scenarios which are crucial for accurate Life Cycle Assessment (LCA) analyses.

The alkali limit of cement is suggested to be lower than 0.60 % by mass, expressed as the sodium oxide equivalent according to *BS EN 197-1:2000.* This is due to the potential of alkali silica reaction (ASR) occurring with the use of particular aggregates. Given that GPCs production involves the use of highly alkaline solutions, there is a concern that their incorporation in new concrete and mortar mixes might lead to an increase of the overall alkalinity of the paste. Additionally, considering their intrinsic chemical structure it is possible that other issues relating with their chemical composition might arise. This paper is presenting testing conducted as part of a study examining the recyclability of fly ash-slag geopolymer as fine aggregate in Portland cement mortars. The testing was focused on identifying leaching of chemical substances from the recycled aggregates into the paste of the new mixes. The effect of RA extract on the initial setting time of cement and its pH were recorded. SEM imaging and EDX element mapping was used in order to identify differences in the composition or morphology of the recycled aggregate mortars. The specimens were also subjected to a test for investigating the potential of alkali silica reaction. All the test results were compared with control mixes incorporating PC recycled aggregates and natural sand.

## 2. Materials

The Ground granulated blast furnace slag (GGBS) used for the GPC precursor was provided by the Hanson Heidelberg cement group from the Port Talbot works and the fly ash (FA) was CEMEX 450-S (BS EN 450 - 1 Fineness Category S; LOI Category B). The activating solution was produced by mixing sodium hydroxide pellets (NaOH, 98-100.5%) and sodium silicate solution $Na_2O\sim10.6\%$, $SiO_2\sim26.5\%$) with distilled water. The chemicals were both supplied by Sigma-Aldrich and the mixing of the solution took place 24 hours prior to casting. For the PC elements, General Purpose Portland fly ash cement/ Sulfacrete EN 197-1 – CEMII/BV 32,5R supplied by Tarmac Cement & Lime Ltd was used. The natural aggregate was standard sand complying with BS EN 196-1.

## 3. Experimental methodology

In order to limit chemical influences from the original aggregates, paste was used as the parent material for the recycled aggregates (RA). Cubes of 100mm were casted at the laboratory and after 28 days of curing, they were crushed. The pieces were put through a rock crusher with the jaws' opening set at 1mm in order to GPC-RA with

grading similar to that of standard sand. The proportion of FA to GGBS in the paste was 50/50, the $Na_2O/SiO_2$ ratio was 1 and the percentage of $Na_2O$ in the activating solution was 5% of the precursor mass. Portland cement RA, from paste with 0.5 water to cement ratio, (PC-RA) were produced with the same process. Then PC mortars with 0%, 25% and 50% replacement (by mass) of natural aggregates (NA) by RA were casted. The materials used for the production of the recycled aggregate mortars are presented in Table 1.

**Table 1.** Amount of materials for recycled aggregate mortar mixes in kg/m$^3$

The alkali silica reaction was investigated using an accelerated screening test as described in DD 249:1999. The particular method is under development in UK and proposes a procedure similar to that described in ASTM C1260-14.  It was

| Materials in kg/m$^3$ | | | | |
|---|---|---|---|---|
| Mix | PC | NA | RA | Water |
| PC_100%NA | 960 | 2160 | - | 451 |
| PC_25%PC | 960 | 1620 | 1080 | 451 |
| PC_50%PC | 960 | 1080 | 540 | 451 |
| PC_25%GPC | 960 | 1620 | 1080 | 451 |
| PC_50%GPC | 960 | 1080 | 540 | 451 |

considered advantageous due to the short duration of the test.  The test involved fabrication of mortar bars (25mm x 25mm x 250mm) with studs at the longitudinal direction. The bars were cured at 80$^O$C in water for 1 day and then in 1M NaOH solution for 14 days. The total length change after the 14 day immersion period is the criterion for identifying alkali silica reaction occurrence. For mean expansion higher than 0.10%, formation of alkali-silica gel is considered possible and further investigation is required.

The SEM imaging and element mapping was conducted using used is Jeol JSM-6480LV SEM with Oxford Instruments X-Act EDX detector on 6month old recycled aggregate mortars.
Cubic pieces with 20mm edge and 10mm depth were cut from mortar prisms, cast into low viscosity epoxy resin and then polished. Polishing revealed the top surface of the specimens, so that the elemental readings would not be affected by the presence of the resin.  The EDX was conducted at low vacuum mode, at pressure of 30 Pa, accelerating voltage of 20 Kvolts, 100 microns aperture and 350 magnification. The time for the element mapping varied from 35 to 45 minutes.
The effect of RA on the initial setting time of cement was investigated in accordance with *BS EN 1744-6:2006*. Additionally, the pH change caused by the immersion of RA in deionised water was recorded.

## 4. Results and discussion

The results of the ASR test indicated a trend relating to the aggregate type of the mortar mix.
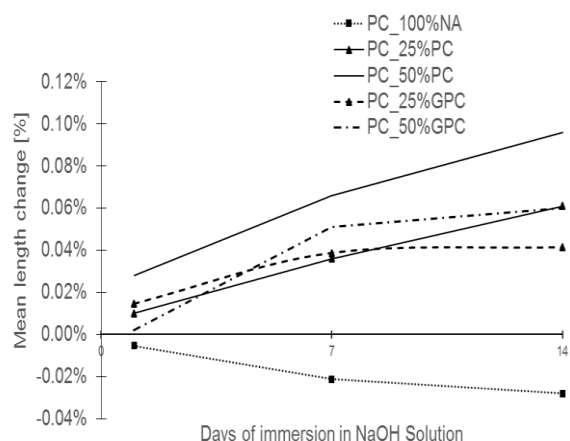


**Figure 1.** Mean % length expansion of all mixes after 14 days of NaOH immersion for identifying ASR

The reference mix with NA solely presented a distinct behaviour by being the only one exhibiting shrinkage. The mixes incorporating PC RA present a trend of gradual length increase.  Given the slope of the line 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 presents a total length increase close to the limit of 0.10%. For mixes with GPC RA a trend of sharper length increase during the first week of immersion is observed. Both mixes exhibited a total length change significantly lower than that of the criterion, with PC_25%GPC and PC_50%GPC presenting values of 0.04% and 0.06% correspondingly.

Element mapping took place in order to investigate the distribution of sodium in the paste of the samples as cast. The element maps were examined together with the sum spectrum of the mapped area and the spectra of specifically chosen points. In Figure2  the SEM images of the examined areas are presented along with  the element maps that demonstrating the Na distribution and the quant maps presenting the Na distribution and concentration (as element %weight).
It is expected that the sum spectrum of the mixes incorporating GPC RA would present a higher sodium percentage as the accumulative result is affected by points with higher Na concentration such as the GPC RA. Therefore indicative spectrums of the PC paste were taken to complement the results and clarify whether the NA is affecting the alkalinity of the paste.  An interesting remark about the SEM images of mixes with GPC-RA is that the two different materials are quite distinct with a clear transition zone. On the other hand it is not possible to distinguish the OPC-RA in the corresponding mixes.
For the reference OPC_100% NA mix, very low percentages of sodium are identified in the maps

with the maximum value being 1%. Also the distribution in the elemental map seems quite scattered. This is in accordance with the spectra data, where the mean Na percentage of the examined area is reported to be 0.24%.

**Table 2.** Spectra data of main compositional elements as weight% for mix PC_100%NA

| Mix | | PC _ 100% NA | | | | |
|---|---|---|---|---|---|---|
| **Spectr** | **Spectrum location** | **Ca** | **Na** | **Al** | **Si** | **Fe** |
| **Sum** | Total Area | 12.17 | 0.24 | 2.91 | 18.87 | 1.08 |
| **2** | PC Paste | 30.49 | - | 6.89 | 8.53 | 4.99 |
| **3** | PC Paste | 22.27 | - | 4.64 | 10.44 | 1.93 |
| **4** | PC Paste | 30.2 | - | 3.22 | 8.37 | 2.01 |
| **5** | NA | 2.07 | - | - | 44.41 | - |
| **6** | PC Paste | 33.95 | - | 3.63 | 9.27 | 1.44 |
| **7** | PC Paste | 19.55 | - | 3.89 | 10.34 | 1.58 |

In the mixes with PC RA a similar scatter of sodium distribution in the paste is observed. It is remarkable though that OPC_25% OPC and OPC_50%OPC mixes present peak Na percentages of 5% and 4%; values higher than those of OPC_25%GPC. By close observation of the quant maps bright spots indicating concentration much higher than the rest of the map are identified. Therefore, the relatively high max percentages can be attributed to spots with concentrated sodium, while at the rest of the examined area the Na percentage appears relatively low. This is further confirmed by the spectra data. Specifically, for OPC_25%OPC the sum spectrum indicates 0.28% Na, while the percentages of the separate points range from 0.26% to 0.45%. For the mix with 50% OPC-RA, similar observations apply. The mean Na percentage is 0.75% while Na values from the paste vary between 0.54% and 0.95%.

In the case of OPC GPC-RA mixes the mapping results are much more distinct as the highest Na percentages are matching the RA outlines. A worth mentioning fact, which is seen more clearly in the OPC_25%GPC map, is the accumulation of Na in the transition zone. Also the Na distribution appears to be more homogenous.

As it would be expected, the maximum Na concentration of OPC_50%GPC is the highest amongst the mixes. But this number might not be absolutely representative as a high concentration point can be identified close to the transition zone. By observing the maps in correlation to the spectra data, is seems possible that Na leaching from the GPC-RA into the PC paste does take place. Specifically, the spectra values obtained from PC pastes incorporating GPC-RA range from 0.90% to 1.39% for 25% replacement and from 0.71% to 1.04% for 50%.

**Table 3.** Spectra data of main compositional elements as weight% for mixes PC_25%PC & PC_50%PC

| Mix | | PC_25%PC | | | | |
|---|---|---|---|---|---|---|
| **Spectr** | **Spectrum location** | **Ca** | **Na** | **Al** | **Si** | **Fe** |
| **Sum** | Total Area | 16.08 | 0.28 | 4.38 | 14.73 | 1.44 |
| **2** | PC Paste | 18.89 | 0.26 | 2.79 | 7.26 | 0.95 |
| **3** | PC Paste | 24.78 | 0.26 | 5.92 | 13.08 | 1.16 |
| **4** | PC Paste White formation | 24.04 | 0.42 | 6.02 | 13.09 | 2.54 |
| **5** | NA | 4.24 | 0.42 | 14 | 27.2 | 1.6 |
| **6** | NA | 2.7 | 0 | 0.79 | 44.26 | 0.2 |
| **7** | PC Paste | 23.34 | 0.45 | 5.26 | 13.63 | 2.18 |
| **8** | PC Paste | 24.35 | 0.34 | 5.62 | 12.55 | 1.95 |
| Mix | | PC_50%PC | | | | |
| **Sum** | Total Area | 18.26 | 0.75 | 4.71 | 13.11 | 1.52 |
| **2** | PC Paste | 23.87 | 0.95 | 3.1 | 10.36 | 1.19 |
| **3** | PC Paste | 29.07 | 0.54 | 4.78 | 13.15 | 3.05 |
| **4** | NA | 2.7 | 0.19 | 0.71 | 44.81 | 0.2 |
| **5** | PC Paste | 19.96 | 0.81 | 4.53 | 9.51 | 1.52 |
| **6** | PC Paste | 14.76 | 0.77 | 9.03 | 17.1 | 1.43 |
| **7** | PC Paste | 7.42 | 0.58 | 14.26 | 22.42 | 1.86 |
| **8** | PC Paste | 16.06 | 1.17 | 6.5 | 12.09 | 1.79 |

**Table 4.** Spectra data of main compositional elements as weight% for mixes PC_25%GPC & PC_50%GPC

| Mix | | PC_25%GPC | | | | |
|---|---|---|---|---|---|---|
| **Spectr** | **Spectrum location** | **Ca** | **Na** | **Al** | **Si** | **Fe** |
| **Sum** | Total Area | 11.45 | 0.89 | 5.8 | 12.68 | 1.58 |
| **2** | GPC-RA | 10.61 | 1.63 | 12.85 | 20.12 | 1.32 |
| **3** | PC Paste | 15.19 | 0.9 | 3.42 | 8.36 | 0.92 |
| **4** | GPC-RA | 11.22 | 1.98 | 10.44 | 21.61 | 4.53 |
| **5** | PC Paste | 22.95 | 1.39 | 3.69 | 10.11 | 1.22 |
| **6** | GPC-RA | 10.21 | 1.36 | 7.87 | 15.99 | 1.82 |
| **7** | PC Paste | 20.88 | 1.23 | 3.51 | 10.68 | 1.01 |
| **8** | PC Paste | 15.32 | 1.04 | 8.74 | 13.97 | 1.24 |
| Mix | | PC_50%GPC | | | | |
| **Sum** | Total Area | 9.91 | 0.93 | 5.21 | 11.61 | 1.31 |
| **2** | PC Paste | 14.07 | 1.04 | 4.32 | 9.99 | 1.14 |
| **3** | PC Paste | 4.58 | 0.71 | 5.1 | 18.71 | 1.09 |
| **4** | GPC-RA | 10.42 | 1.71 | 9.6 | 20.36 | 1.68 |
| **5** | GPC-RA | 10.33 | 1.28 | 11.06 | 21.08 | 1.79 |
| **6** | GPC-RA | 9.6 | 1.08 | 5.53 | 12.39 | 1.11 |
| **7** | PC Paste | 16.54 | 0.99 | 4.01 | 9.68 | 1.57 |
| **8** | Transition Zone | 14.51 | 0.82 | 2.93 | 7.12 | 0.7 |

These values are overall higher compared to those of the other mixes. Additionally to this observation though, there is also indication that Na leaching might not be proportional to GPC-RA percentage in the mortar. The Na percentages of the paste with

25% NA replacement are in their majority higher than those of the mix with 50% replacement. In addition, in the maps of the former mix, a more homogenous distribution of sodium throughout the whole investigated area is observed and the brighter outline indicating high percentage is potentially expanding beyond the transition zone.
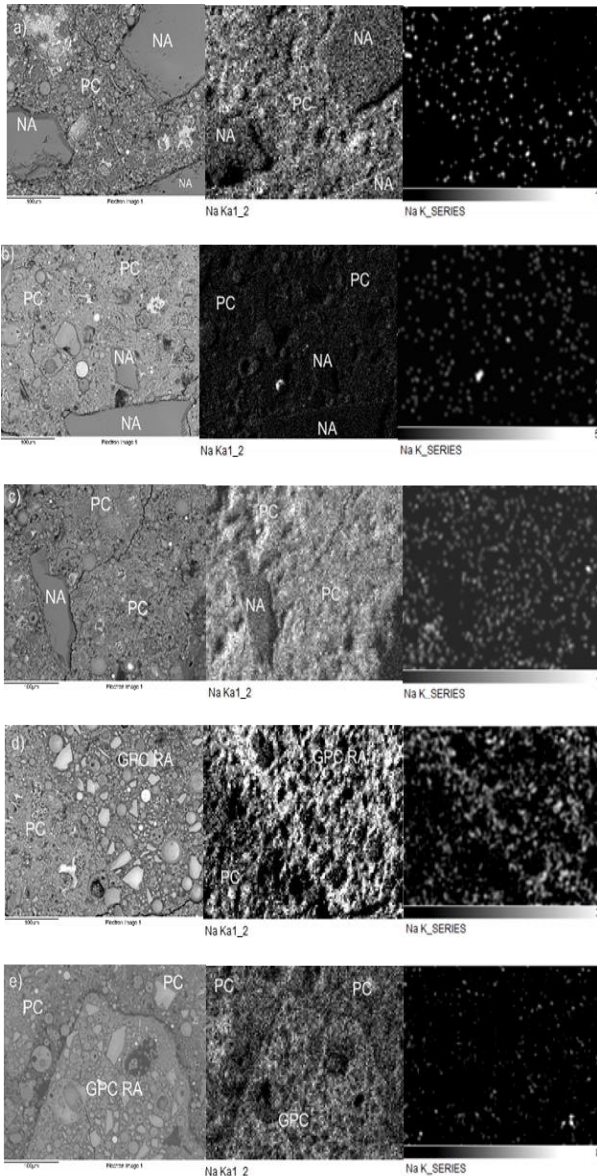


**Figure 2.** SEM image, elemental map & Quant map of a) PC_100%NA, b) PC_25%PC, c) PC_50%PC, d) PC_25%GPC, e) PC_50%GPC

Finally, the results of the effect of GPA –RA extract did not reveal any significant effect on the initial setting time of cement paste. Specifically, the control paste mixed with deionised water demonstrated initial setting 203 minutes after mixing, while the one mixed with GPC-RA extract after 190 minutes. It should be noted that the PH of the deionized water increased from 7.5 to 13.5 immediately after the RA immersion indicating that at least some Na in the RA is in a highly soluble form. This may be slower for larger recycled aggregates.

## Conclusions

The results mainly indicate that alkali leaching from GPC-RA to the mortar paste is happening. Both element distribution obtained through mapping of the specimens and spectra results strongly support this conclusion.

The main concern relating to highly alkaline pastes, alkali-silica reaction, was assessed through the accelerated test mentioned above. According to the corresponding standard the particular test should be used as a screening method and the results have to be corroborated by further examination of both the mortars and the aggregates. Despite that, the fact that no initial indication of ASR occurrence associated with the use of GPC RA appeared, is considered encouraging.

Also the setting time of cement did not appear to be affected by the alkaline solution leached form the RA. This test will be repeated with PC including fly ash addition since this type of cement is more widely used and the pozzolanic materials may be more affected by increases in alkalinity.

Despite these results showing no initial reason why geopolymer concretes should not be used as recycled aggregates, further investigation is clearly required. It is important to examine in what percentage this leaching takes place, which are the parameters affecting it and to what extend it does affect the other final mix properties, and in particular the durability of concretes.

## References

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