PROPERTIES OF ALKALI-ACTIVATED CONCRETE BASED ON INDUSTRIAL WASTES OR BY-PRODUCTS

MARTYNKOVÁ R. and MAVROULIDOU M.*

London South Bank University, School of the Built Environment and Architecture, 103 Borough Road, London SE1 0AA, UK
E-mail: mavroum@lsbu.ac.uk

ABSTRACT

The presented research performed a laboratory study of alkali-activated concrete based on industrial wastes. This type of concrete has potentially twofold environmental advantages as its production would involve lower carbon dioxide emissions while at the same time it would provide an outlet route for the waste materials used for its production. The research focused on the workability and strength development of different mixes, in which the main source material activated by alkalis was ground granulated blast furnace slag (GGBS), a by-product formed during the production of iron. A particularly novel aspect of the research was the investigation of the use of paper sludge ash (PSA), a waste material produced by the incineration of paper mill sludge in Combined Heat and Power (CHP) plants. It is a consistent material due to high controls in the CHP plants, containing reactive silica and alumina (in the form of metakaolin) as well as lime (CaO); it is therefore thought to be a potentially a suitable pozzolanic material for cement production or alternatively, a source of alkali for the alkali activation of a different pozzolan in the making of alkali-activated concrete. Both these potential uses were investigated in this study.

The study assessed the effect of parameters such as (a) the alkali activator type namely NaOH, KOH or Ca(OH)$_2$ (due to the CaO contained in the PSA) with or without sodium silicate, Na$_2$SiO$_3$; (b) the alkaline activator concentration; (c) four different curing conditions and (d) curing time. Overall higher strengths and workability were obtained for KOH containing mixes which achieved higher strengths with lower activator concentrations (hence they would potentially be less costly). Curing at constant moisture and ambient temperature, which is probably a most practical curing condition for industrial production was very successful for most alkaline activators and mixes giving good concrete strengths at all curing times. It was soon established that the PSA could not act as a pozzolanic material to be activated by alkalis. However under the right curing conditions, the PSA was found to be one of the most effective alkaline activators of GGBS giving some of the highest observed compressive strengths. Whereas this shows promise for the successful use of this waste material in the production of concrete (which would not contain any Ordinary Portland Cement), the workability of the resulting concrete remained low; in addition accelerated mortar bar testing for alkali silica reaction (ASR) using waste cullet glass aggregate (a reactive silica aggregate) showed some expansion which could imply that there could be potential durability issues of the resulting concrete. The latter two aspects require further investigation before the use of this material in the making of alkali-activated concrete can be suggested with confidence.

Keywords: sustainable construction materials, alkali activated concrete, ground granulated blast furnace slag, waste paper sludge ash, solid waste management

1. Introduction
Alkali activated cements in the production of concrete containing no Portland cement could be a very effective way of reducing carbon dioxide emissions by up to five to six times (Davidovits, 2013). An additional advantage is that waste materials or by-products from industrial processes, which otherwise would be discarded /landfilled, can be used in the manufacture of
this type of concrete. Namely, the main components needed for the preparation of alkali activated binders are materials containing aluminosilicates and an alkali solution. An aluminosilicate material must be rich in silicon dioxide ($\text{SiO}_2$) and aluminium oxide ($\text{Al}_2\text{O}_3$), and must be present in an amorphous (glassy) phase in order to be capable of activation (Davidovits, 2013). Such characteristics are present in materials such as ground granulated blast furnace slag (GGBS), fly ash (FA) and metakaolin (MK) (the latter material usually comes from the calcination of clay however it can also be produced by waste materials such as paper sludge ash). These materials cannot set when mixed with water therefore they need to be activated using alkalis such as sodium hydroxide, potassium hydroxide or calcium hydroxide usually mixed with sodium or potassium water glass. The mixture then becomes hydraulic and is able to set and harden (Gluchovsky, 1959). The aim of this research was to assess the strength of different alkali-activated concrete mixes containing waste or by-product aluminosilicate materials and variety of alkali activators. Initially ground granulated blast furnace slag, a material previously investigated for its potential use in alkali-activated concrete, was used. The ultimate goal however was to assess the potential of using paper sludge ash (PSA), a waste material, whose use in in alkali activated concrete has not yet been established. PSA is produced by the incineration of paper mill sludge, a by-product of the deinking and re-pulping of paper, in controlled heat and power (CHP) plants. Both materials (waste paper sludge and paper sludge ash) are presently predominantly mostly discarded in landfill although some potential alternatives to paper sludge landfiling such as land-spreading of sludge as agricultural fertiliser and use as an alternative fuel (Class 2 - liquid alternative fuel) are also possible. Paper sludge and the resulting ash from its incineration are becoming abundant in the UK, as paper recycling rates are increasing; recent statistics report an annual production of approximately 1 million tonnes (Dunster, 2007).There is therefore a lot of interest in finding outlets for these waste materials as alternatives to landfilling.

2. Materials, mixes and specimen preparation
The materials used for the production of alkali activated concrete mixes were ground granulated blast furnace slag, paper sludge ash, aggregate (< 10mm in diameter), river sand, water and alkali activators. The two main waste materials/industrial by-products used were (a) GGBS (provided by Hanson Regen); (b) PSA from non-hazardous paper sludge, provided by Aylesford Newsprint Ltd. (Kent, UK). The chemical compositions of GGBS and PSA are fairly similar. However as the total content of the three major oxides in the PSA (namely silicon dioxide, aluminium oxide and ferric oxides) is approximately only 45%, the material is not strictly speaking a pozzolan. On the other hand, due to the high CaO content (almost double of that usually found in type C fly ash), the material is likely to have cementitious properties. The alkaline activators used in this study were: (a) Sodium hydroxide solution (NaOH) mixed with sodium silicate solution (Na$_2$SiO$_3$); (b) Potassium hydroxide solution (KOH) mixed with sodium silicate solution (sodium water glass, Na$_2$SiO$_3$); (c) Potassium hydroxide solution (KOH); (d) Sodium hydroxide solution (NaOH); (e) Ca(OH)$_2$ produced from the hydration of CaO contained in the PSA. All chemicals were supplied by Fisher Scientific; NaOH and KOH came in the form of pellets; therefore solutions in deionized water had to be prepared first. Alkaline activators were mixed at least one day before casting and left in plastic bottles closed securely. Details of the mix design are shown in Table 1. To investigate the effect of different curing regimes on the strength of the resulting alkali-activated concrete, specimens were then subjected to four different curing methods:

- Method 1 (after Adam, 2009) consisted in curing at room temperature for 24 hours. The samples were then demoulded, water cured for six days in a water tank at 20°C, wrapped in cling film and kept to cure at room temperature until required for testing
- Method 2 consisted in wrapping the samples immediately after casting in multiple layers of cling film for 24 hours; subsequently the samples were demoulded and wrapped again in multiple layers of cling film to cure until required for testing.
- Method 3 consisted in wrapping the samples immediately after casting in multiple layers of cling film; the samples were then put in the oven at 65°C for 5.5 hours; the selection of
this time period was based on Brough et al. (2002) and also on practical considerations given the working hours of the laboratory. Then the wrapped samples were left to cool down overnight; the following morning they were demoulded and left to cure in a water tank at 20°C until required for testing.

- Method 4 consisted in wrapping the samples (still in moulds) and placing these immediately after casting in an environmental (humidity and temperature controlled) cabinet at a temperature of 25°C and a relative humidity of 95%. After 24 hours, the samples were demoulded and put back into the humidity cabinet until required for testing.

Table 1. Details of alkali-activated concrete mix design

| Mix ID         | GGBS (g) | PSA (g) | River sand (g) | Coarse aggregate (< 10mm) (g) | Water glass Na$_2$SiO$_3$ (g) | Hydroxide NaOH (g) | KOH (g) | Added Water (g) |
|----------------|----------|---------|----------------|-------------------------------|-------------------------------|--------------------|---------|----------------|------------------|
| G_1.5WG_1N_10M| 415      | 0       | 784            | 1039                          | 71                            | 46                 | 0       | 136             |
| G_1.5WG_1N_6M | 415      | 0       | 784            | 1039                          | 59                            | 58                 | 0       | 136             |
| G_1WG_1N_10M  | 415      | 0       | 784            | 1039                          | 59                            | 58                 | 0       | 136             |
| G_N_10M       | 415      | 0       | 784            | 1039                          | 0                             | 117                | 0       | 136             |
| G_1.5WG_1K_4M | 415      | 0       | 784            | 1039                          | 71                            | 0                  | 46      | 136             |
| G_P_WG        | 407      | 8       | 784            | 1039                          | 117                           | 0                  | 0       | 136 (+50.4)    |

Slump testing on fresh concrete mixes (BSI, 2009a) showed that most mixes with NaOH (with the exception of those with very high NaOH concentrations of 10M) had high slumps corresponding to pumpable concrete. The highest slumps were obtained by KOH containing mixes (some of these showed collapse). On the other hand mixes with PSA had zero slump.

3. Experimental results – concrete strength

Figure 1 represents 28-day curing cube compressive strengths (BSI, 2009b) of mixes whose 7 day curing strengths were found to be satisfactory. The results are arranged in descending order of strength magnitude. All mixes except those with PSA and waterglass plus NaOH (in an attempt to activate the PSA, which was not successful) showed good compressive strengths; they could all be adequate for concrete depending on the design specifications. Specimens with waterglass gave higher strengths than those containing only a base activator (NaOH or KOH); moreover the higher the waterglass content with the same base activator concentration the higher the strength (see e.g. the G_1.5WG_1N_10M vs the G_1WG_1N_10M mix); this is presumably due to the enhanced level of alkalinity when waterglass is used. Potassium base activator with the same content of waterglass gives higher strength than the respective mix with sodium base activator of a much higher molarity (see e.g. the G_1.5WG_1K_4M vs the G_1.5WG_1N_10M mix); this can be attributed to the fact that K+ is more basic providing a greater extent of dissolution and a higher reactivity of the prime pozzolan (GGBS); in addition the saturation point of mixes with KOH would be exceeded if concentrations above 10M were used, as opposed to solutions with NaOH; (Petermann et al, 2010); therefore comparatively lower KOH concentrations are sufficient.

Figure 2 shows the strength evolution with curing between 7 and 28 days for indicative mixes. It can be seen that there is little strength evolution in time when using curing method 3. On the other hand all curing methods showed good strength evolution of strengths during curing, with variable relative success from the point of view of progress of curing, depending on the alkaline activator; it is notable that the 7 day strengths obtained using curing method 1 were relatively
low for most mixes however the subsequent strength gain rate with curing was faster; thus the 28 day strengths of the respective mixes were close to those developed using methods 2 and 4 (which showed the highest early strengths already in day 7). Interestingly, mixes with a base activator only, also performed less well under temperature curing (method 3) compared to mixes with the same base activator plus waterglass (see mixes with KOH, i.e. G_1.5WG_1K_1M and G_1.5WG_1K_4M vs G_K_6M), unlike findings reported in Pettermann et al (2010).
of curing; therefore it was confirmed that the PSA did not act as a pozzolanic material which can be activated by alkalis. On the other hand under the right curing conditions, the PSA could be an effective alkaline activator of GGBS giving some of the highest compressive strengths observed. Some expansion of PSA-activated mixes was however noted during accelerated mortar bar testing for alkali-silica reaction (ASTM,2003) (to create worst-case conditions crushed waste glass cullet, a reactive aggregate, was used in the mortar instead of sand). This aspect requires further investigation, also for the rest of the studied alkali-activated mixes.

![Figure 3: Strength evolution with curing of selected mixes](image)

4. Conclusions
This study investigated suitable ways of producing alkali-activated concrete based on two waste materials (GGBS and PSA) using different alkaline activators and curing methodologies. Overall mixes containing KOH achieved higher strengths with lower activator concentrations (hence these would be less costly). Curing at constant moisture and ambient temperature, which is probably a most practical curing condition for industrial production, was successful for most alkaline activators and mixes giving good concrete strengths at all curing times. A novel aspect of the research was the investigation of whether PSA could be used in alkali-activated concrete. It was concluded that PSA did not act as a pozzolanic material to be activated by alkalis but that under the right curing conditions PSA was an effective alkaline activator of GGBS giving some of the highest compressive strengths observed. For the successful use of this waste material in alkali activated concrete, further research on workability and durability aspects is required.

REFERENCES