Alkali-activated cements for ground improvement

M. Mavroulidou^{1*}, C. Gray¹, M.J. Gunn¹

¹London South Bank University, 103 Borough Road, SE1 0AA, London, UK

*Corresponding author: E-mail: mavroum@lsbu.ac.uk

Abstract

The paper studies alkali-activated (AA) slag cements for soil stabilisation, as alternatives to traditional binders such as Portland cement or lime. A number of alkali activators were considered, containing also a range of salts and a material retrieved from waste (Paper Sludge Ash, PSA). The results are discussed in terms of unconfined compressive strength (UCS) at two different curing times. In general alkali-activated cements based on the use of alkali salts only had a modest performance in terms of strength improvement; a material that showed promise however as slag activator was the PSA. Further analysis is recommended in order to gain a better understanding of the complex mechanisms involved towards engineering uses for soil stabilisation.

Keywords: alkali-activated cements; soil stabilisation; paper sludge ash; ground granulated blast furnace slag

1. INTRODUCTION

Inferior geomaterials (soils and rocks, natural or man-made, e.g. concrete or soil-like waste such as mine tailings, sludges, dredged sediments) have always been a major problem for professionals who develop or maintain civil infrastructure. Geomaterials can be problematic due to inadequate engineering properties (strength or stiffness) causing hazards (e.g. erosion, landslides/slope failures, Engineering failures may lead not only to loss of life, property and soil liquefaction, etc.). infrastructure and environmental disasters, see e.g. Ajka Kolontár tailings dam failure, 2010). Current policies require infrastructure to be provided in an economical and environmentally responsible manner (reducing material use, embedded carbon and other impacts on the natural environment and ecosystems). Improving rather than replacing and landfilling inferior ground or geomaterials (including wastes) for civil infrastructure uses, will thus become critically important in future engineering practice towards low-carbon, sustainable solutions. However common soils stabilisers such as cement and lime are not impact free as they are energy-intensive and contribute to ca. 8% anthropogenic CO_2 emissions during their production. There is therefore intensive effort in finding alternative cements of lower carbon footprint and could also incorporate waste materials in their production. In this context, alkali-activated (AA) cements show potential in becoming more sustainable alternatives to Portland cement.

According to the definition of RILEM (Provis, 2014), AA cements are binder systems produced by the reaction of an alkali metal source (solid or dissolved) with a solid (alumino-)silicate powder, e.g. metallurgical slags, fly or bottom ash or natural pozzolans, whereas alkali sources can be various soluble substances that can supply alkali metal ions (hydroxides, carbonates, sulphates, aluminates or oxides) and raise the pH of the mixture thereby accelerating the dissolution of the solid precursor. This type of cements has a an established use in concrete but it is less widely researched in the context of soil cementation (e.g. Cristelo et al., 2013; Sargent et al., 2013; Du et al, 2016; Mavroulidou et al, 2019).

The aim of this paper is thus to assess the performance of a number of alkali-activated (AA) based on different activators of the slag in improving the strength of a silt soil. In some of the AA cement systems waste paper sludge ash (PSA) has been used in the alkaline activator system, towards a potential solid waste management route for this material.

2. MATERIALS AND METHODS

2.1 Materials

The soil used in this study was an industrially supplied silt soil. For the AA mixes the following analytical grade alkali activators were used supplied by Fisher Scientific: sodium silicate Na₂SiO₃ (waterglass-WG) solution of a modulus $M=SiO_2/NaO_2=2$; potassium hydroxide KOH pellets; anhydrous potassium carbonate pellets and sodium carbonate pellets. (Note than in a parallel study whose results are not shown here we also used low grade K₂CO₃ from the incineration of vegetable waste). In addition, a waste material Paper Sludge Ash (PSA) was provided by a newspaper recycling company in the South-East of England. It is the ash produced from the incineration of non-hazardous paper sludge (a semi-solid slurry collected in the effluent treatment units), which is the main waste stream of the paper recycling industry. The sludge is incinerated primarily to reduce the volume of sludge waste for landfilling (80-90% reduction) and partly to recover energy through co-combustion with biomass (although mechanically dewatered paper sludge has a low calorific value of 2.5-6.0 MJ/kg, Spathi, 2015). PSA is subsequently landfilled in large part. The precursor was GGBS from Hanson Regen which was found to be suitable for alkali activation (pH-basic, of high vitreous content of 98%, large specific surface of 450-550m²/kg and of adequate modulus of activity, Mavroulidou and Martynkovà, 2018).

As discussed in Mavroulidou (2018) and Mavroulidou et al., (2019a) PSA is mainly a calcium aluminosilicate, as the principal compounds are lime (CaO) (ca 60%), silica (SiO₂) and alumina (Al₂O₃); the total combined content of SiO₂ and Al₂O₃ and Fe₂O₃ is typically less than 50% hence it is not a pozzolan. The PSA used in this study is richer in CaO and SiO₂ compared to other PSA used elsewhere (e.g. Gluth et al. 2014 or Frías et al. 2008). It is cementitious and due to its high free CaO content it has a pH=12.3-12.4 (Mavroulidou, 2018). Although the chemical compositions of GGBS and PSA have some similarities, attempts to activate PSA itself in the context of structural concrete did not show evidence of such activation (Martynková and Mavroulidou, 2015). Therefore the PSA was now considered mostly as an alkaline activator of the GGBS in the system, with the free CaO hydrating to Ca(OH)₂ in the presence of water.

2.2 Sample preparation and testing

For AA systems, different mixes were prepared, in which activators in solution or powder form were thoroughly mixed with the dry soil and the GGBS powder. Compacted cylindrical specimens at a fixed target dry density $\rho_d = 1.56 \text{ g/cm}^3$ and water contents w=25% (adjusted for solution water) were used for all mixes. Cylindrical specimens of 100mm height and 50 mm diameter were then made by compaction in layers of 10mm. As a minimum, duplicate to triplicate specimens were prepared. The specimens were then left to cure at ambient temperature at constant moisture curing (i.e. wrapped in cling film and stored in a temperature and humidity controlled cabinet for the specified curing period of 7 and 28 days respectively). At the end of the required curing periods (7 and 28 days respectively), the dimensions and the mass of the specimens after curing were measured; Unconfined Compressive Strength (UCS) testing was then performed at a constant rate of strain of 1mm/min.

3. RESULTS AND DISCUSSION

Indicative results of our work presented in Figure 1 show that all alkaline activators increased the strength of the silt although the carbonates and silicate used on their own only led to modest strength increases (for soil stabilisation at least doubling of the strength is considered as having an effect of the soil but strength requirement may be much higher depending on application). GGBS used as a control mix (before alkali stabilisation) was found to have a minor effect on the strength after 7 days; 28 days later however, the strength had approximately doubled compared to the untreated silt (Fig. 1(a)). However, compared to the strength of the alkali-activated mixes with Ca(OH)₂ (from PSA) and KOH acting as the base activators, the strength increase with GGBS only, was very small (compare Fig 1(a) with Fig 1(b) and 1(c)). The carbonates are relatively weak activators compared to hydroxides so this was not a surprise but it was interesting that although the sodium silicate used in the same amount as the carbonates led to higher strengths, it did not have a very pronounced effect on the strength of the soil compared to the carbonates. This was not expected as silicate activators are commonly used in alkali activation to lead to higher strengths and the explanation offered in the literature is that as a consequence of the interaction of the carbonate ions $(CO_3^{2^-})$ from the carbonate activator with the calcium ions (Ca^{2^+}) from the dissolved slag, the development of calcium and mixed carbonates (e.g. sodium-calcium) is favoured instead of the formation of calcium silicate hydrate gels which are stronger cementing agents (Bernal et al., 2015).

Comparing Figures 1(a) and 1(b) KOH used on its own at the same percentage as PSA used on its own led to higher earlier strengths than PSA but at 28-day of curing the strengths developed by the PSA activator mix are practically the same as those of the respective KOH activator mix (note that the authors' experience of using PSA as an alkali activator of GGBS in concrete cement showed instead high early strength gain, so this was not expected).

The effect of increasing the amount of precursor without increasing the activator can be seen in Fig 1(b) comparing the strengths of mixes with 6% KOH activating 10% GGBS vs 6% KOH activating 15% GGBS in the latter case it can be seen that strengths are lower and in fact there is an apparent strength reversal so that the strength of the soil mix after 28 days of curing is lower than that after 7 days of curing. This is difficult to explain but it has been noted in a number of other occasions another example of which is the last mix at the right-hand side in figure 1(b) (we noticed this in several other occasions not shown here for brevity). Thus, although the UCS test is a crude quick test with little control of the testing conditions, this potential reversing of the effects on the strengths appears to be a trend unrelated to the experimental error; it could possibly be due to the reminiscence of material that was not used in reactions and which is of low strength compared to the cementing agent. On the other hand increasing the KOH content at the same time as increasing the GGBS content (keeping the same ratio of activator/precursor=0.6) increased in particular the 28-day strength by ca. 1000 kPa. Similarly, in Fig 1(c) one can see that increasing the GGBS amount to 15% while keeping the PSA content at 6% gave lower strengths at both curing ages compared to the mix with 6% PSA and 10% GGBS although the effect was less pronounced than in the case of KOH mixes.

Still in Fig 1(b) one can notice that replacing partially the KOH by K_2CO_3 or otherwise keeping the same amount of KOH and adding carbonate led to lower strengths which is difficult to explain without further material analysis but it could be due to the excess amount of activator. Conversely adding carbonates or silicate in the PSA mix led to clearly improved strengths in particular at early curing times; it is also interesting that carbonates perform quite well with the PSA and that strength differences compared to the combination of PSA with sodium silicate were very small. On the other hand, replacing partially the PSA by a carbonate led to lower strengths as in the case of KOH replacement.

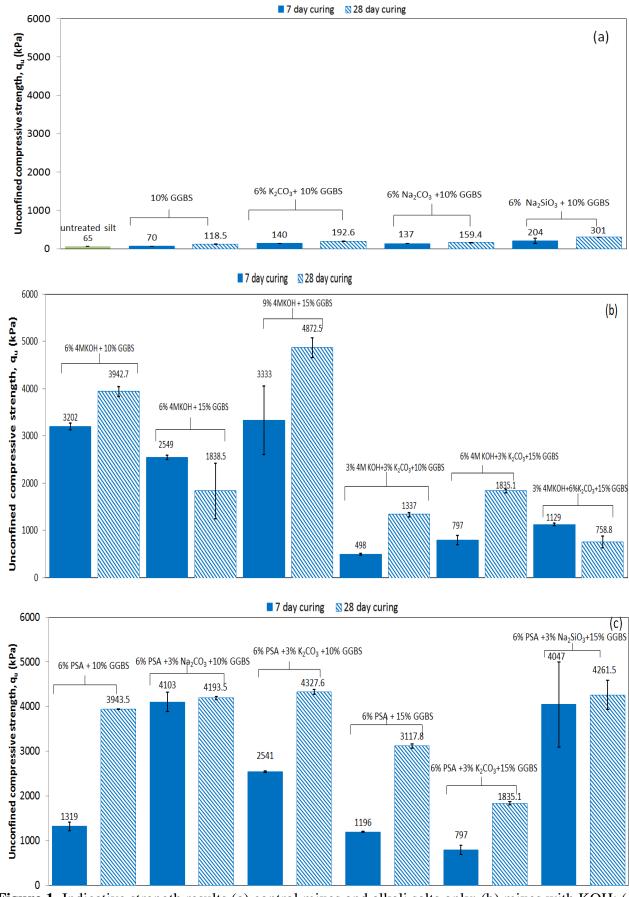


Figure 1. Indicative strength results (a) control mixes and alkali salts only; (b) mixes with KOH; (c) Mixes with PSA.

The very good performance of the PSA is consistent with a number of previous studies by the authors where the material used either as an activator of GGBS or used directly on the soil (fully or partially replacing cement or lime) is found to give similar or better strengths than traditional stabilisers (cement or lime) for a number of soils in particular different clays, silt and the paper sludge itself which could then be used as a fill material instead of soil (Mavroulidou et al, 2017; Mavroulidou, 2018; Mavroulidou et al, 2019a and Mavroulidou et al, 2019b). This is very interesting for finding an outlet for this material as a soil stabiliser. Other that the fact that it is caustic due to its high pH (12.3-12.4) –but so are cement and lime-, the two traditional stabilisers- it is non-hazardous and as opposed to other industrial process ashes could be used in the soil with less concern for potential long term environmental impacts.

4. CONCLUSIONS

The study considered treatment of a fine grained soil treated by mixing with different alkaline activators including waste materials. The unconfined compression strength was found to be very sensitive to the composition of the activator mix. All AA mixes showed improvements in the strength great however to establish the beneficial effect of using carbonates on their own or as partial replacements of the other activators needs to be further researched as at the moment these mixes gave lower strengths compared to others. However it must be noted that depending on the application the strengths developed may be sufficient. A material that has shown consistently a lot of promise is PSA and this is interesting as an outlet for this waste material. To gain a better understanding of the phenomena further study is required with further soil tests but also in particular including material analysis (chemical and microstructural).

References

- Bernal SA, Provis JL, Myers RJ, San Nicolas R and Van Deventer JSJ 2015. Role of carbonates in the chemical evolution of sodium carbonate-activated slag binders. *Materials and Structures* 48(3), 517 – 529.
- 2. Cristelo, N., Glendinning, S., Fernandes, L., Pinto, A.T. 2013. Effects of alkaline-activated fl y ash and Portland cement on soft soil stabilisation. *Acta Geotechnica* **8**, 395 405.
- Du, Y-J, Yu, B-W, Liu, K, Jiang, N-J, Liu, M.D. 2016. Physical, Hydraulic, and Mechanical Properties of Clayey Soil Stabilized by Light-weight Alkali-Activated Slag Geopolymer *Journal of Materials in Civil Engineering*, DOI: 10.1061/(ASCE)MT.1943-5533.0001743
- 4. Frías M, García R, Vigil R & Ferreiro S (2008) Calcination of art paper sludge waste for the use as a supplementary cementing material. *Applied Clay Science* **42**, 189-193.
- 5. Gluth, G.J., Lehmann, C., Rübner, K., Kühne, H.C. 2014. Reaction products and strength development of wastepaper sludge ash and the influence of alkalis. *Cement and Concrete Composites* **45**, 82-88.
- Martynková, R., Mavroulidou, M. 2015. Properties of alkali-activated concrete based on industrial wastes or by-products, 14th Int. Conf. on Environmental Science and Technology, Rhodes, Greece, 3-5 September 2015

http://cest2015.gnest.org/papers/cest2015_00439_oral_paper.pdf [Accessed 08/09/2017]

- 7. Mavroulidou, M. 2018. Use of paper sludge ash as a calcium-based stabiliser for clay soils *Waste Management and Research*, **36**, 1066–1072
- 8. Mavroulidou, M, Martynková, R. 2018. A study of alkali-activated concrete mixes with ground granulated blast furnace slag *Journal of the Global Network For Environmental Science and Technology* **20**, 216-225
- 9. Mavroulidou M., Ziniatis A., Gray C, et al 2017. Alternative calcium-based chemical stabilisers for ground improvement: Paper Sludge Ash treatment of London Clay, 15th International

Conference on Environmental Science and Technology Rhodes, Greece, 31 August to 2 September 2017

- Mavroulidou M., Gray C., Gunn MJ, Mbey P., Nangyal H. 2019a. A laboratory study of innovative cementing agents, as alternatives to conventional soil stabilisers, XVII ECSMGE European Conference on Soil Mechanics and Geotechnical Engineering, Reykjavik, Iceland 1st-6th September 2019
- Mavroulidou M., Garelick J., Gray C., Gunn MJ, Youssef A., Hassan S. 2019b. A study on the use of paper recycling waste streams for geotechnical applications, *XVII ECSMGE European Conference on Soil Mechanics and Geotechnical Engineering*, Reykjavik, Iceland 1st- 6th September 2019
- 12. Provis JL 2014. Introduction and scope. In: Provis JL, van Deventer JSJ (eds) Alkali-activated materials: state-of-the-art report, RILEM TC 224-AAM. Dordrecht, Springer, 1–11
- 13. Sargent, P., Hughes, P. N., Rouainia, M. and White, M. 2013. The use of alkali activated waste binders in enhancing the mechanical properties and durability of soft alluvial soils. *Engineering Geology* **152**, 96–108.
- 14. Spathi, C. 2015. Novel applications for paper sludge ash. PhD thesis, Imperial College, London