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An assessment of different alkali-activated cements as stabilisers of sulphate-bearing soils

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Abstract: The stabilization of sulphate-bearing soils with traditional calcium-based stabilisers is not recommended, as reactions between the calcium and sulphates in the presence of water could lead to soil heave. Alternative stabilization methods are therefore required, and this paper proposes innovative alkali-activated cements (AAC), whose use for soil stabilisation and especially sulphate-bearing soils is little researched. To fill this knowledge gap, AAC systems with ground granulated blastfurnace slag precursor and different alkaline activators including commercial lime, wastepaper sludge ash (PSA), potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) were used to treat an artificial sulphate-bearing clay. AAC-treated clay specimens cured for 7 and 28 days respectively were soaked in water for 45 days; their one-dimensional swelling, unconfined compressive strength, pH, and ultrasonic pulse velocity were measured and compared to those of specimens not exposed to water. Material characterisation (SEM-EDS, Raman spectroscopy and FTIR) was performed to attest cementation and detect ettringite. In AAC systems, $CaO/Ca(OH)_2$ did not lead to specimen heave and damage and developed the highest strengths. Potassium-based activators performed less well but combined PSA- K_2CO_3 led to strength gain in time. Overall AAC led to higher strengths than lime only or lime and admixtures and show promise as sulphate-bearing soil stabilisers.

Introduction

Chemical ground improvement with cement or lime is a commonly used technique to improve the properties of unsuitable for construction soils, avoiding their replacement and landfilling. Unfortunately, not all soils are suitable for treatment with these stabilisers. One type of soils where calcium-based stabilisers would potentially cause long-term problems are sulphate-bearing soils, containing natural salts such as calcium sulphate occurring as gypsum or selenite ($CaSO_4 \cdot 2H_2O$), sodium sulphate occurring as

thenardite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), magnesium sulphate occurring as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or potassium sulphate occurring as arcanite (K_2SO_4), which are commonly encountered in many countries worldwide. Their distribution and type depend primarily on the climate; they usually tend to occur predominantly in arid and semi-arid environments, such as parts of the US, South America, India, Africa, and Australia, the Gulf region and other Middle East (Iraq, Iran) or Mediterranean countries (e.g. Spain). However, they are not absent from wetter parts of the world, for example Russia, Armenia or the UK, where gypsum or selenite are known to be abundant in Oxford and Kimmeridge clay formation and can also occur in London clay layers (Boyadgiev and Verheye, 1996; Kinuthia, 1997; Casby-Horton et al, 2015; Alsafi et al, 2017). Further sulphates to those already contained in a soil can be formed by oxidation of sulphides, which is commonly done by groundwater.

Due to their widespread occurrence, sulphate bearing soils are extensively encountered in ground engineering and infrastructure construction applications. If these soils require stabilisation due to poor engineering properties and behaviour (e.g., they are of low bearing capacity, shrinking-swelling, dispersive or collapsible etc), calcium-based stabilisers such as cement or lime could become problematic, as calcium can react with the sulphates (or sulphides), to form expansive crystals of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) and/or thaumasite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$). The formation of these crystals would then damage the achieved soil cementation and lightweight structures such as roads and pavements founded on the stabilised soils, as it can lead to substantial heave. Numerous publications, in particular from the USA, report on repair and rehabilitation costs caused by sulphate-induced heave, which amount to millions of dollars annually (e.g., Little et al., 2010; Bheemasetti et al, 2017; Talluri et al, 2020; Chakraborty et al., 2022). Soils stabilised with calcium-based stabilisers can also suffer from similar problems if sulphates enter the stabilised soil after stabilisation, e.g., through water. Water is in fact a decisive factor for sulphate-induced heaving, therefore the time of water ingress into the soil is of major importance for the initiation of heaving. Additionally, cement and lime stabilisation of sulphate-rich soils

is ineffective in increasing the soil strength to the required levels, as calcium is consumed to form ettringite rather than calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H) or calcium alumino-silicate hydrates (C-A-S-H) through pozzolanic reactions; the latter are the reactions predominantly linked to the strength gain of these soils upon stabilisation, even if in the short term ettringite can contribute to some strength gain (Chakraborty et al., 2022).

The problem has attracted a lot of research effort for the past three decades due to its severity in terms of damages (e.g., Dermatas, 1995; Kota et al, 1996; Wild et al, 1999; Sivapullaiah et al, 2000; Berger et al, 2001; Harris et al, 2004; Ouhadi and Yong, 2008; Little et al, 2010 amongst many other). However, the reactions, mineral formation and crystal growth mechanisms are very complex; therefore, ongoing research has been dedicated to the subject (e.g. Chrysochoou et al, 2012; Tallouri et al, 2013; Puppala et al, 2014; Knopp and Moormann, 2016; Singhi et al, 2017; Chakraborty et al., 2022 amongst many others). Recommendations are to set a sulphate content limit beyond which calcium-based stabiliser treatment is not deemed suitable; 2,000 ppm or 0.2% of soluble sulphate content is deemed to be a safe limit, whereas calcium-based stabilisers would not be recommended for soils of sulphate content above 7,000 ppm (Harris et al, 2004). When cement or lime stabilisers are used, a number of precautions were proposed e.g., the use of sulphate-resistant cements, containing a low content of tricalcium aluminate (C3A) (Puppala et al, 2004) and a number of treatment implementation and compaction recommendations to alleviate the potential problem (see e.g., Harris et al, 2004; Berger et al, 2001; Little et al, 2010; Talluri et al, 2013; Quiñónez-Samaniego et al, 2022 amongst other). The use of admixtures was also proposed, i.e., slags and pozzolanic materials e.g., silica fume, pulverised fuel ash (PFA), or ground granulated blastfurnace slag (GGBS) in the lime/cement mix (Wild et al, 1999; McCarthy et al., 2012; Chesomi et al, 2017). Using such waste/industrial by-product materials has the added advantage of offering waste management solutions (Bach et al, 2020; Mavroulidou et al, 2022). In line with the recommendation to use pozzolanic admixtures, Mavroulidou et al (2021a) studied the potential of various industrial

byproducts including GGBS, PFA, and waste materials such as Paper Sludge Ash (PSA) as admixtures to partially or fully replace lime, as well as the use of reactive magnesia (instead of calcium-based cements) to circumvent the engineering problem caused by the lime and Portland cement in the presence of sulphates in soil. It was found that when providing most favourable conditions for the formation of expansive crystals and for potential resulting damage, no combination of binder was fully successful in preventing the damage of the specimens and suppressing swelling. The authors have therefore identified the need of conducting further research towards the development of adequate stabilisers for sulphate bearing soils, so that their use in industrial applications can be proposed with confidence.

To address this research need, this paper follows on from Mavroulidou et al (2021a) and instead of using supplementary cementitious material as admixtures partially replacing lime or PSA (as in Mavroulidou et al, 2021), it focuses alternatively on the feasibility of using such materials to produce a different type of stabiliser, i.e., alkali-activated cements (AAC) as an alternative to Portland cement or lime for sulphate-bearing soils. In Mavroulidou et al (2021a) there was no attempt to create AAC systems as soil stabilisers using such materials, unlike in the presented study, and this is a novel contribution of this paper.

AAC are binder systems produced by the reaction of an alkali metal source (solid or dissolved) with a solid (alumino-)silicate powder. They have increasingly drawn the attention of researchers worldwide, especially as cements in mortars and concrete (see e.g. García-Lodeiro et al., 2013; Provis et al, 2019; Gluth et al, 2020; Procházka and Boháčová 2020; Hoang, 2021; Sanam and Mavroulidou 2021; Krivenko et al, 2022; Mavroulidou et al, 2023 amongst many other), because they have been proposed as greener and more sustainable cements compared to Ordinary Portland Cement (see e.g., Davidovits, 2013 or Provis, 2018). Conversely for soils, AAC are an emerging field of research (see e.g., Phetchuay et al, 2014; Vitale et al., 2017, 2019; Jafer et al., 2018; Rios et al, 2019; Coudert et al, 2019; Chen et al, 2020; Syed et al., 2020; Gokul et al., 2021; Mavroulidou et al, 2021b, amongst some of the most recent papers).

Therefore, the literature on AAC for ground improvement is relatively limited, especially for their use in sulphate-rich soils. Few recent exceptions include: Zhang et al (2015), who used metakaolin-based AAC to stabilise a lean clay mixed with gypsum to enhance its sulphate content; the authors confirmed that no ettringite crystals formed in the stabilized clay samples, after water-soaking; Jang et al (2021), corroborating Zhang et al's (2015) results by confirming that metakaolin-based AAC (geopolymer) could result in significant reductions in shrinkage and a greater strength gain compared to lime treatment for sulphate-rich soils. Alsafi et al (2017), who assessed the collapsibility potential of a natural gypseous soil from Iraq stabilized with AAC binder based on KOH-activated fly ash and observed an increased sulphate resistance compared to Portland cement treatment and a reduction in soil collapsibility, and Li et al. (2019), who used successfully AAC consisting of GGBS activated by carbide slag (CS) to treat a gypsum-bearing soil, and mitigated delayed calcium-sulphate reaction induced heaving. The number of studies on the topic is insufficient for the use of AAC in commercial applications and further research is needed; this is especially important, as different AAC systems require a case-by-case study, due to the very high diversity of materials that can be used as precursors (e.g. natural aluminosilicates such as volcanic ash, calcined clays etc., various by-product/waste materials from various industrial or mining processes, various municipal, agricultural or construction and demolition waste) and the variety of alkaline activators (e.g. sodium silicate, sodium, potassium or calcium hydroxide, sodium carbonate, etc) (Mavroulidou et al, 2021b; Li et al., 2019). It is therefore necessary to fill this knowledge gap by investigating how these innovative AAC stabilisers perform when treating sulphate-bearing soils and whether they could be used without causing sulphate-induced reactions hazards. A further reason for using AAC for ground improvement instead of lime or Portland cement is that these could potentially have the dual advantage of offering a solution to both the calcium-sulphate reactions problems in the stabilised soil (because lime or Portland cement are not directly used as the sole stabilisers of the soil), as well as the environmental impact of cement and lime in terms of CO₂ emissions and the use of natural resources to produce them,

since AAC can incorporate waste materials in their composition, which also reduces costs of treatment (see Mavroulidou et al 2021b).

The specific novelties of this paper are therefore as follows:

- (a) the feasibility study of using a range of different AAC systems for ground improvement and in particular for stabilising sulphate-rich soils for which there is paucity of information;
- (b) the use of waste-based activators such as PSA (containing CaO) or potassium-based activators such as K_2CO_3 and combinations of these to create AAC systems, whose use as stabilisers for sulphate-bearing soils has not been explored to the Authors' knowledge;
- (c) the extensive material analysis of the above innovative soil-AAC systems, which has not been done for the proposed application;
- (d) the comparative assessment of AAC performance against that of supplementary cementitious material admixtures (which are more commonly used to address stabilised sulphate-bearing soil heave);
- (e) the use of AAC to treat a soil rich in sulphates other than gypsum.

The success of the proposed AAC stabilisers is assessed in terms of swelling strain reduction, unconfined compressive strength (UCS) and stiffness evolution (based on ultrasonic pulse velocity (UPV) measurements (p-wave velocity) using a Portable Ultrasonic Non-destructive Digital Indicating Tester (PUNDIT)). The hypothesis guiding this study was that, if following treatment with AAC, the stabilised soil specimens could still maintain their strength and stiffness, and show little expansion and no damage although exposed to the most favourable conditions for ettringite formation, then the AAC stabilisers were successful in treating the soil. To support the interpretation of the findings, material characterisation of the treated soils (scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR)) was also performed.

Materials and methods

Materials

The control (untreated) sulphate bearing soil and methods used in this study were kept the same as in Mavroulidou et al (2021a) so that consistent comparisons are made with these papers. Namely, kaolin clay in dry powder form was mixed with 4% per soil mass analytical grade sodium sulphate Na_2SO_4 powder supplied by Fisher Scientific, to create an artificial sulphate-rich soil (referred to as the 'untreated soil'). Kaolin was chosen for this research as this consists mostly of the non-swelling mineral kaolinite; swelling of the samples would therefore be linked to ettringite/thaumasite formation and not to the swelling nature of the clay minerals. The original kaolin clay did not contain sulphates as evidenced by gravimetric tests of total and water-soluble sulphate content according to BS 1377-3:1990 (BSI, 1990). Sodium sulphate was chosen due to its high solubility to create favourable conditions for ettringite formation.

For the AAC mixes GGBS from Hanson-Regen was used as a precursor. As noted in Mavroulidou and Martynková (2018) this slag is suitable for alkali activation as it has a high vitreous content (98%), a large specific surface ($450\text{-}550\text{ m}^2/\text{kg}$), an adequate activity modulus ($K_q=1.65$) and is pH-basic ($\text{pH}>10$). Alkaline activators included: (a) potassium hydroxide KOH pellets ($\geq 99\%$ purity) and anhydrous potassium carbonate pellets ($\geq 99\%$ purity) supplied by Fisher Scientific; (b) commercial hydrated lime (providing $\text{Ca}(\text{OH})_2$); (c) a high lime content PSA as a source of CaO ($\text{Ca}(\text{OH})_2$ upon hydration) from a newspaper recycling company in the South-East of England (Mavroulidou 2018; Mavroulidou and Awoliyi; 2018). PSA is a waste material originating from the incineration of non-hazardous sludge from secondary paper treatment stage. It is a calcium aluminosilicate, and as such it could be contributing in aluminosilicates in the AAC system, although it is not a pozzolan, as the total combined SiO_2 and Al_2O_3 and Fe_2O_3 content is $<50\%$; however, attempts in Mavroulidou and Martynková (2018) to activate this PSA for structural concrete were not successful; this is why here PSA was used mostly as an alkaline activator rather than as a source of aluminosilicates. Table 1 shows the chemical composition of the GGBS, lime and PSA.

Mix design

Dosages of lime or PSA used in Mavroulidou et al (2021a) were kept as the baseline for the amount of different activators to use, so that the efficiency of AAC to prevent sulphate-induced swelling can be compared directly to that of the blended admixtures used in Mavroulidou et al (2021a). Note that in the latter paper, the minimum dosages of lime and PSA used as the sole stabiliser of this soil were determined as 4% and 6% respectively, based on Initial Consumption of Lime (ICL) testing (Eades and Grim, 1966). Following on these dosages, Mavroulidou et al (2021a) then also replaced half of the minimum required lime and PSA respectively by GGBS, functioning as an admixture (in this case the relative ratios of lime:GGBS or PSA:GGBS were not ideal to create AAC systems).

Here, the proportions used in the mix design aimed instead to create appropriate AAC systems; for this, suitable activator dosages and proportions of alkali:precursor according to the literature (e.g., Haris et al, 2004; Du et al, 2016; Singhi et al, 2017; Mavroulidou et al, 2021b) were consulted. In particular the mix design was directly informed by the parametric study and outcomes of the 2^k factorial design analysis in Mavroulidou et al (2021b) where different and sulphate-free soils (a silt and an expansive clay consisting of kaolin-bentonite mix) were treated with AAC containing the same GGBS as here, and a number of alkali activators of which the same PSA and KOH. The factorial design analysis also identified the significant factors to consider in the mix design (molarity, activator dosage and activator:precursor ratio) affecting the UCS of the soils for the design of future tests so that the number of required tests is reduced. Thus, the parametric study and factorial design findings in Mavroulidou et al (2021b) were directly used for this feasibility study, to determine the levels of activator and precursor to be used for the PSA- and KOH-containing AAC systems as well as a suitable KOH solution molarity (4M) which was also found to be a significant factor; this molarity was also found to work well in other studies of the Authors (Mavroulidou et al 2021c). From Mavroulidou et al (2021b) it was found that activator:precursor ratio was highly

significant for the AAC design and that a ratio of 0.6 worked well for both PSA and KOH activator systems; in particular a dosage (also a significant factor) of 6% KOH and 10% GGBS and similarly for PSA, a dosage of 6% PSA and 10% GGBS had a very good performance in terms of strength for the different soils. This dosage of 6% was considered suitable for the presented study here, as it could then further be directly compared against the performance of 6% PSA used as the sole stabiliser in Mavroulidou et al (2021a). Moreover, by using the same dosage for both PSA and KOH activators a consistent comparison could be made between the two activators. Then, keeping the same activator:GGBS ratio of 0.6, and the same total activator dosage of 6%, 3% of PSA was replaced by 3% K_2CO_3 ; finally, a mix of 3% PSA and 10% GGBS was made, halving the activator:GGBS ratio and the PSA dosage, to assess the contribution of K_2CO_3 in the 3%PSA-3% K_2CO_3 activator mix, while also checking if halving the required amount of PSA would also be successful; this could then perhaps further reduce the probability of ettringite developing, due to the reduced amount of calcium-containing material used. For lime, literature suggested an optimal lime:GGBS ratio of 0.2 (i.e., Harris et al, 2004 reported an optimal 1%:5% lime:GGBS dosage). Keeping this ratio, the amount of lime and GGBS was increased to 2% and 10% respectively, so that direct comparisons can be made with the mix containing 2% lime and 2% GGBS in Mavroulidou et al (2021a), where 2% GGBS was partially replacing the required amount of lime; AAC systems with higher percentages of commercial lime were avoided to cut down treatment costs but also, in particular, to cut down the commercial lime usage, thus reducing environmental impact, which is precisely a major motivation for introducing AAC for ground improvement. An additional reason was to further reduce the probability of ettringite developing due to the reduced amount of calcium-based material used (i.e., same reasoning as when halving PSA dosage). Commercial lime amounts were thus kept low, and the AAC mix with commercial lime AAC was mostly used for benchmarking.

Table 2 shows the different alkali-activated stabilised-soil mixes, together with their respective plasticity characteristics at 1 h of mellowing. These were determined first, so that compacted specimens for further

testing be made at the same liquidity index of $IL = -0.05$. This was done to ensure a uniform consistency across the different soil mixes, thus excluding water content effects on the strength and stiffness of the specimens. For comparison purposes Table 2 includes some of the mixes studied in Mavroulidou et al (2021a) using similar mix components at different proportions implemented as admixtures to partially replace lime or PSA (without attempting to create AAC systems with these materials for soil stabilisation).

Specimen preparation and curing

In the preparation of the specimens all conditions were chosen so that the formation and deleterious effects of ettringite are encouraged, by doing exactly the opposite of what is recommended for sulphate-bearing soil chemical treatment. Namely:

a) a low compaction water content was used, below the Proctor optimum –which is around the plastic limit of the soil-, by adopting a constant liquidity index of $IL = -0.05$ for all soil mixes. Low water contents are more critical for expansion due to sulphates (Harris et al, 2004), therefore the recommendation is to use as much compaction water as practically possible (Little et al, 2010). For example, the National Lime Association (NLA) recommends moisture contents of 3-5% above the optimum moisture content to give abundant water for the sulphate to react, but Harris et al (2004) suggested 2% above optimum as the maximum practical moisture content to use.

b) the soil was compacted at a high compaction density of 1.43 g/cm^3 instead of the recommended low dry density which would give expansive crystals the required space to grow without disrupting the soil matrix (Harris et al, 2004);

c) a short mellowing period of 1h only was used instead of the extended mellowing periods recommended by literature or guidelines (see e.g. Berger et al, 2001; Talluri et al, 2013; Quiñónez-Samaniego et al, 2022);

d) the stabiliser was applied in one dose/stage rather than the recommended two stages (see e.g. Berger et al, 2001);

e) furthermore, the treated specimens were subjected to water ingress after the curing period was completed, to ensure ettringite formation is delayed and hence damaging to the cemented soils (early ettringite formation can instead contribute to some strength gain of the soil).

As in Mavroulidou et al (2021a), cylindrical UCS specimens (50 mm in diameter and 100mm in height) were statically compacted after 1 h of mellowing in 5 equal layers, using a monotonic displacement rate of 1mm/min. The specimens were cured at a constant moisture (referred to as 'air-curing' although the specimens were wrapped in several layers of cling film and stored at controlled temperature and humidity) for two different curing periods (7 and 28 days), to assess the effect of curing length on the UCS and sulphate resistance of the AAC. After each curing period, a set of duplicate specimens of each mix were subjected to UCS testing without soaking, whereas a second set of duplicate specimens of each mix cured for 7 and 28 days respectively (kept in their moulds) were placed for a further 1½ months on grids in water trays containing a layer of distilled water to cause a delayed migration of water into the specimen by capillary action through the bottom of the specimens. The trays with the specimens were kept in an environmental cabinet at 95% humidity and 25 (± 2)°C until testing; measurements of the specimen swelling were taken using dial gauges.

UCS and UPV testing

Before unconfined compressive strength testing, UCS specimens subjected to 45-day soaking provided information on the swelling strain, as well as UPV using a Portable Ultrasonic Non-destructive Digital Indicating Tester (PUNDIT) as a means to assess the soil stiffness evolution through p-wave velocity measurements at the end of the required constant moisture content curing periods and subsequent the 1 ½ months of water soaking. The dimensions and the mass of the specimens after curing and soaking

were measured; Unconfined Compressive Strength (UCS) testing was then performed at a constant rate of strain of 1mm/min. UCS tests were performed at a constant rate of strain of 1mm/min with different mixes. As a minimum, duplicate specimens were prepared. After unconfined compressive strength testing, the pH of the UCS specimens was also measured (see Table 3).

Material characterisation

Material characterisation in terms of Raman spectroscopy, Scanning Electron Microscopy (SEM)- Energy dispersive spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FTIR) was performed on the UCS specimens that had been subjected to water ingress for 45 days. An ARAMIS confocal Raman microscope (Horiba UK LTD) with a 633nm laser, 50X objective, 600 l/mm grating, 100 μ m pinhole and 80-2060 cm^{-1} Raman shift range was used. The sample was illuminated in reflection mode using a tungsten light. For SEM analysis images were taken using FEG-SEM (Phenom Pharos, scanning electron microscope) after a small aliquot was placed on aluminium stubs and double-sided carbon tape (Ted Pella), 15KV and backscattered detector. EDS elemental analysis was also done on the same samples using a Silicon drift detector (SDD) and 30s integration time. Infrared spectra of the samples were taken using a Bruker alpha Fourier Transform Infrared spectrometer with a diamond attenuated total reflectance probe (ATR). The background signal was collected for each sample and infrared spectra (40 times) acquired from 400-4000 cm^{-1} were analysed using Omnic 7.0 (Thermo Scientific) software.

Results and discussion

UCS specimen testing

Figure 1 (a)-(c) shows the UCS results of the tested specimens, while indicative photos of the specimens after soaking are shown in Figure 2; indicative stress-strain curves of 28-day cured samples after water exposure are shown in Figure 3. Swelling strains and UPV measurements after 45-day soaking are shown

respectively in Figures 4(a) and 4(b). Furthermore, the pH of the UCS specimens after UCS testing are shown in Table 3. From the UCS results in Figures 1 and 3 the following observations were made:

- a) The 7 day-treated UCS specimens gave inconsistent strength results after soaking throughout the AAC mixes and especially for mixes 1 (2L_10G) and 4 (6P_10G). Conversely, the results of the respective 7 day cured samples that were not exposed to water ingress (referred to here as 'air' cured) were very consistent throughout the AAC mixes. Similarly, the 28-day cured specimens both before, and after soaking gave very consistent results throughout the AAC mixes. The reason for the discrepancies between the 7 day cured specimens when subjected to soaking would be either incomplete cementation and/or damage due to expansive crystals of ettringite as the presence of sulphate in soils is known to reduce the shear strength considerably and to alter the behaviour of the calcium-based stabiliser treated sulphate-rich soil from that of an initially cemented soil behaviour to that of a normally consolidated soil after long curing periods. Thus, strength increases initially with curing and then decreases with further curing; this has been attributed to the prevention of cementation of soil particles by sulphate and the formation of ettringite. However, for short curing periods the effect of sulphate was reported to be marginal (Sivapullaiah et al, 2000). To verify this, the material characterisation results will be used. It should be noted that in Mavroulidou et al (2021a), the opposite was observed i.e., that the 28-day cured soaked specimens had higher differences than the 7-day cured ones after soaking. The authors attributed this to the greater damage of the cemented soil matrix, as longer curing periods could cause a greater rigidity and a denser matrix after pozzolanic reactions, making crystal expansion effects more harmful as there is limited space in the soil voids for the crystals to grow (Little et al, 2010). Conversely, for the AAC systems shown here, it is possible that shorter curing times were insufficient for activation, therefore there could be a substantial quantity of unreacted components of the AAC system which would act mostly as a filler rather than as a binding agent

(Pourakbar et al, 2015), corroborating the assumption that the great differences were due to lack of sufficient cementation.

- b) A difference with Mavroulidou et al (2021a) paper mixes, was that the AAC mixes showed no crystal formation on the surface of the specimens whereas specimens presented in the Mavroulidou et al (2021a) had a visible layer of white crystals forming on the top of the specimens during soaking (see Fig 2(a) vs Fig 2(b)). It can therefore be hypothesised that no (or little) ettringite formed in the AAC mixes; this hypothesis will be verified by the material characterisation results.
- c) Mixes 1-4 showed a clear improvement in the soil strength, the best being Mix 1 (2L_10G) with lime activating GGBS for both curing times. It was followed by Mix 4 (6P_10G) for both curing times but then, interestingly, at later times, mix 3 with a lower PSA content kept developing in strength whereas mix 4 strength development had stopped (and slightly reversed). This is difficult to explain; in some instances, unreacted components (if one mix ingredient is supplied in excess) would potentially not help in strength gain as they would act as fillers only, and not as components of the cementing binder. It is unclear however if this was the case here. The worse AAC mix was mix 5 with KOH activator. This was not expected, as KOH is one of the most common activators used in AAC for concrete (see e.g., RILEM, 2014; Mavroulidou and Martynková, 2018; Mavroulidou and Shah, 2021). KOH used as activator of GGBS in similar concentration and an activator:GGBS ratio, was found to be effective for an expansive clay in Mavroulidou et al (2019) and (2021b) (admittedly the latter papers adopted a shorter period of water immersion, i.e., 21 days and a much higher compaction water content, which could have facilitated the reactions). Furthermore, other researchers also successfully used KOH in AAC. For example, Pourakbar et al (2015) and (2016) treated a high-plasticity clay using KOH solutions of different molarities to

activate palm oil fuel ash (POFA); it is notable however that their UCS tests were performed on specimens cured at constant humidity i.e., not subjected to water soaking, which appears to be a critical condition to assess cementation. Moreover, in Pourakbar et al (2015) it was demonstrated that strength gain occurred over a long curing time (90 and 180 days of curing); however, in field conditions it would be difficult to control the ingress of water into the stabilised soil (e.g., from the water table) and it would be difficult to wait for so long periods for practical (construction) purposes.

- d) It is interesting that the 7-day cured mix 1 and 28-day air-cured specimens of mix 1,3 and 6 had a lower strength than the respective ones submerged in water, and this happened despite the higher degree of saturation. This shows that the specimens of these mixes not only had cemented before exposure to water but also, being cemented already, they continued curing and gaining strength over time during their exposure in water. The UCS of mix 4 both at 7 and 28 day curing reduced somehow upon water ingress; on the other hand the differences in strength are small (especially considering the accuracy level of UCS testing). This indicates that soil 4 must have cemented already at 7 days of curing (presumably due to the relatively high content of PSA which was found to lead to early strength gains in concrete in Mavroulidou and Shah, 2021 and Mengasini et al., 2021) and that there was no clear deleterious effect from sulphate attack to the cement. Conversely mix 5 softened almost fully. Thus, it becomes clear that mix 5 did not cement and its strength was due to suction effects which got gradually lost once the soil was exposed to water and the material softened as expected for an uncemented clay soil. As for mix 2 from Mavroulidou et al (2021a), where lime (of a content equal to the ICL) was partially replaced by GGBS, the strength upon constant moisture curing especially at 28 days of curing had increased sufficiently to point at cementation, however the specimen strength reduced 4 times upon exposure to water indicating some possible sulphate-induced effects.

- e) The indicative stress-strain curves of the AAC specimens (Fig 3) show a clear brittle behaviour for the highest strength achieving specimens, with peak strengths achieved within 1.5-2.5% of axial strain. Mix 6 may not have achieved strengths as high as the other AAC-soil mixes but it shows a less abrupt loss in strength, which would be advantageous for practical applications, whereas this modest strength gain could still be sufficient depending on the applications considered.

Consistently with the UCS results, the swelling strains (Fig 4a) show a clear improvement for AAC mixes 1,3,4,6 after 28 days of curing, whereas mix 5 (6K_10G) with KOH only, exhibited a higher swelling than Mix 9 (lime treatment only), which also showed very high swelling strains. As for the 7-day treatment both mix 5 and mix 6 showed very high strains (the latter higher than mix 9 -lime treatment only -), consistently with the UCS results that indicated that these specimens had not cemented. Otherwise, AAC treatment was successful in reducing swelling compared to mixes in Mavroulidou et al (2021a) where admixtures were used to replace lime (or PSA). Note that the swelling strains shown in Fig 4(a) were those after the specimens had been extracted from the moulds at the end of the soaking period. This was done consistently with Mavroulidou et al (2021a) although one-dimensional swelling measurements obtained from dial gauges before specimen extraction were also available for all mixes.

Generally consistent with the UCS are also the ultrasonic pulse velocity UPV (p-wave velocity) PUNDIT measurements (see Fig 4b). The p-wave velocity equals the square root of the stiffness/density ratio; thus, for a constant density, the higher the UPV, the higher would be the stiffness. Therefore, consistently with the UCS results, mix 1 shows the highest UPV. Mixes 3 and 4 also show a high UPV and mix 3 (3P_10G) has a slightly higher UPV indicating a higher density; this is consistent with its higher strength at 28 days of curing compared to mix 4 (6P_10G). As for the UPV of mix 3 of 7 day cured specimens subject to soaking it is interesting that this is higher (on average) than the UPV of the respective specimens of mix 4 indicating a denser structure although mix 3 strength was clearly lower (but also very consistent between the two

specimens); these combined observations of strength and UPV indicate that mix 4 could have been potentially affected by the formation of ettringite as opposed to mix 3.

Finally, inspecting the pH of the soil it is seen that it is dropping (but not considerably) between 7 and 28 days of curing in most cases due to pozzolanic/long-term reactions. The pH stays however high enough for ettringite to form (requiring a pH \approx 10-12, to form according to Harris et al, 2004, whereas Ghorab et al, 2018 show that by lowering the pH to 9.5 the ettringite phase in Portland limestone cement disappears, and an amorphous phase forms instead). The pH remains also high enough to sustain pozzolanic reactions in mixes with Ca(OH)₂ content by maintaining solubility of the silica and alumina, even beyond the 2 ½ month period of curing (first under constant moisture conditions and then during exposure to water ingress) as long as sufficient lime and water is available (Al-Mukhtar et al., 2010).

Material characterisation

Figure 5 shows selected SEM-EDS analysis results of the AAC mixes after 45 days of exposure in water. Some elongated crystals were visible in many of the samples; EDS analysis of all samples, where such crystals formed, showed only up to about 5-6% S; this is low compared to 40-50% in Chakraborty et al (2022), who presented SEM-EDS evidence of ettringite development in lime-treated sulphate-rich soils. Some elemental imaging of a number of samples (not shown here for brevity) also indicated that the concentration of S was correlated with Na and Mg, rather than Al or Si as would be expected for ettringite crystals (see e.g., Mix4). It should be noted however that a limitation of SEM for the characterisation of ettringite is that ettringite crystals may become unstable in the dry high vacuum conditions of the SEM. Using FESEM or micro-XRF could be recommended as a further investigation. Other observations are the presence of considerable amounts of C together with O in some of the mixes (e.g., mix 1 -7 day or mix 6 -7 day cured) indicating possible carbonation. Mix 5 showed no evidence of potential cementitious gels incorporating Ca on any of the sites inspected based on chemical composition and/or morphology

(only one site is shown here for brevity); on the other hand, some indication of sulphates (possibly unreacted Na_2SO_4) is found in the 28-day sample of Mix5. No evidence of sulphates was found on the sample of mix 6 -7 days, but likely carbonation was noted as mentioned above, also in the 28-day SEM with some calcite shaped crystals. Some evidence of possible pozzolanic reaction products was found for mix 6, 28-day sample, and this could support the higher strength observed at 28 days of curing. Possible formation of C-S-H is shown in most mixes (except 5) spectra with Ca, Si and O peaks. Some Mg peaks were also seen (see e.g. mix 4 -7 day and mix 6- 7day amongst other not shown here for brevity) with possible integration of Mg into the C-S-H structure due to the composition of PSA and GGBS.

FTIR analysis (Fig 6(a)-(d)) further supports the findings on carbonate formation and the lack of clear evidence of ettringite forming. Namely there are some C-O stretching vibrations in the range 1400–1600 cm^{-1} , indicating CO_3^{2-} formation in all mixes, in particular mix 4, and an increase as the time passes for most mixes (except 5) in particular mixes 4 and 6; note that peaks at 1420-1450 and 870 cm^{-1} are both present in calcite; this indicates that some CaCO_3 has formed, partly due to GGBS carbonation (Tashima et al, 2017). As for the sulphates, one band that is to be noted is the 1120 cm^{-1} band. Inorganic sulphates have two bands, one at around 1125 cm^{-1} and one at 630 cm^{-1} . Here only some variations on the samples for the band at 1125 cm^{-1} are observed, as the other band is much weaker. It seems that Mix 4 and 5 at 7 days, have stronger absorption for sulphate than the rest of the samples -however, interestingly, mix 5 is the KOH-activated mix. Also Mix 4 and 6 at 28 days have stronger absorption for sulphate than the rest of the samples. For ettringite there is a characteristic band at 1675 cm^{-1} and 3633 cm^{-1} (3633–3433). Looking into this part of the spectrum further (see zoom in Fig 5(c)), there is some difference in that area in the samples. Namely, at 7 days, Mix 1 appears to have the most ettringite formation, followed by Mix 3 and 5; then at 28 days, Mix 1 and 3 kept this increased crystal formation in a much clearer way. As for C-S-H there is evidence in the literature that the silicate bands in C-S-H correspond to oligomeric (1110 cm^{-1}) and dimeric (1018 and 946 cm^{-1}) mineralogic species (John and Stephan, 2021); therefore, in the FTIR results,

there is evidence of polymerisation in all samples. Furthermore, there was a different degree of dimeric formation in some samples, most notably for mix 4 at 7 days as well as the same mix and mix 6 at 28 days. Other observations are that the OH band at approximately 3650 cm^{-1} is also visible for all samples. Also, all samples appear to show a characteristic strong asymmetric stretching vibration band in the region of $990\text{--}1100\text{ cm}^{-1}$, typical for inorganic silicate and alumino-silicate spectra (Si-O-Si or Al-O-Si).

Raman analyses (see Fig 7) showed that spectra were dominated by silica plus some carbonates; note that the match with quartz is shown as indicative of the spectra obtained which were dominated by quartz-like signals indicating silica content -but not necessarily quartz. This was followed by calcium carbonate (calcite)- like signals. As for ettringite/thaumasite formation there is some possible match in Mix 3 and Mix 6. For mix 3 this is consistent with the FTIR results, but for mix 6, Raman does not corroborate the FTIR results, but it is interesting, as it provides some backup information as to the validity of the FTIR interpretation. It should be noted that given the very specific and random localisation of the crystals, it is practically very difficult to find such crystals and get good spectra, while performing the Raman analysis.

Note that due to practical reasons the material characterisation was performed 45 days after the end of soaking/UCS testing. During this period, the samples were carefully wrapped and stored; however further curing and chemical reactions would have taken place but the results can still elucidate the differences across the AAC mixes.

Discussion

The study showed promise for the development of suitable AAC binders for stabilising sulphate-rich soils. This is unlike the results in Mavroulidou et al (2021a) with calcium lime- replacing supplementary cementitious material admixtures, where it was concluded that no combination of binder was fully successful in suppressing swelling and preventing the sulphate-induced damage of the specimens. However a number of points need to be highlighted: first of all the adoption of very unfavourable

conditions, going against recommendations, to test the mixes to the limits. It is possible that if some of the recommendations to mitigate sulphate-induced effects were adopted, mixes containing supplementary cementitious material admixtures in Mavroulidou et al (2021a) would have given better results. In both Mavroulidou et al (2021a) and in this paper, the choice was made to have a compaction water content below the plastic limit to exacerbate the effects of sulphates (swelling/expansive crystal development). This may have resulted in some mixes being too dry. For calcium-based mixes this would have been unfavourable for the continuing development of pozzolanic reactions. The water content was in particular very low in mixes with potassium activators, whose plasticity index was the lowest of all other mixes; furthermore, the exothermic reaction during the preparation of solutions using distilled water to dissolve the pellets may have lowered further the water content. The low water content may have resulted in unfavourable conditions for stabilisation (although note that Pourakbar et al, 2015 argue that by lowering water content activator concentration increases and polycondensation and hardening are favoured). In previous studies of the authors where KOH AAC mixes were successful with other soils (Mavroulidou et al (2019) and Mavroulidou et al, 2021b) the KOH solution was prepared the day before the mixing to avoid exothermic reaction effects; this practice should be re-introduced in future work and comparisons with the presented results made. Moreover, in Mavroulidou et al (2019) and Mavroulidou et al (2021b) a higher compaction water content was used. Therefore, it is recommended that the mixes with potassium are revisited (e.g., through a parametric study) using a different treatment protocol.

Regarding the success of calcium based stabilisers note that Sivapullaiah et al (2000) discuss that in the presence of $\text{Ca}(\text{OH})_2$ as in hydrated lime and PSA (after hydration), sodium sulphate would lead to the formation of sodium hydroxide (see reaction (1)) a strong base which is a commonly used alkali-activator in AAC for concrete or soil, and that this could then lead to C-S-H formation before conversion to ettringite.



If proven successful, AAC for the stabilisation of sulphate-rich soils would offer several environmental advantages as discussed in Mavroulidou et al (2021b): AAC offer the possibility to include a wide variety of waste materials in the binder mix, either as activators or precursors (here a waste material of the paper recycling industry, PSA, was used); this can reduce AAC costs, save in non-renewable natural resources, contribute to solid waste management and potentially promote sustainable soil stabilisation practices using locally available suitable waste materials, thus potentially minimising material transport. Although here lime activator was shown to give the most successful overall AAC mix, commercial lime replacements in AAC activator systems (such as carbide lime in Li et al, 2019 or PSA, proposed here and showing good promise), could also contribute to using alternative stabilisers other than commercial lime and Portland cement, linked to high CO₂ emissions for their production.

Conclusions

Engineers need alternative materials to Portland cement and commercially-produced lime to overcome the challenges posed by the stabilization of sulphate-bearing soils. To address this need, this paper assessed the feasibility of using AAC, whose application for soil stabilisation and especially sulphate-bearing soils is little researched. To fill this knowledge gap, innovative AAC systems with a GGBS precursor and a range of alkaline activators of different types, i.e., commercial lime, wastepaper sludge ash (PSA), potassium hydroxide (KOH) and potassium carbonate (K₂CO₃) were used to treat an artificial sulphate-bearing clay, under conditions that would favour the development of deleterious expansive crystals had lime or Portland cement been used as the sole stabiliser. The rationale was that, if the AAC stabilised soil specimens could maintain their strength and stiffness, and show little expansion and no damage after being exposed to most favourable conditions for expansive crystal formation, then the AAC stabilisers could be deemed successful in treating the sulphate-bearing soil. To assess this, one-dimensional swelling, UCS and UPV tests were performed. Furthermore, comprehensive material analysis was used to attest

cementation and the development (or otherwise) of expansive crystals. Based on these tests the findings and conclusions can be summarised as follows:

- (a) AAC treatments were successful in achieving higher strength gains than lime-treated only sulphate-rich soil or soil treated with supplementary cementitious material admixtures in previous studies by the Authors.
- (b) As opposed to supplementary cementitious material admixtures subjected to the same harsh conditions, favouring the development of deleterious expansive crystals, AAC-treated specimens showed no damage or evidence of such crystal formation after prolonged curing; this was corroborated by material characterisation results, which showed little evidence of ettringite formation.
- (c) In this study AAC systems with $\text{CaO}/\text{Ca}(\text{OH})_2$ activator (i.e. lime and PSA) showed the best performance in terms of engineering properties and durability to sulphate attack. Interestingly, neither lime or PSA resulted into problems in the presence of sulphates when used in AAC systems, unlike in cases where they are used as soil stabilisers on their own.
- (d) In terms of swelling strains, strength and stiffness, PSA used in AAC mixes had a similar performance as lime used in AAC activator mixes, with the added advantage of being a waste material whose use for ground improvement could divert its landfilling and reduce industry CO_2 emissions due to the production of commercial lime;
- (e) Potassium-based AAC activators had an inferior performance and require further research and a modified treatment protocol. However, potassium carbonate combined with PSA AAC activator was found to lead to strength gains in time and shows potential for an improved performance upon further mix optimization;
- (f) Overall, the feasibility study showed promise for the development of suitable AAC systems, which would be able to both maintain high soil strengths and mitigate sulphate induced damage.

The rationale of this feasibility study was to assess a range of different activators as potentially adequate sulphate-bearing soil stabilizers and exclude AAC binders that do not show promise. For this, mix design was guided by previous studies by the Authors on different and sulphate-free soils; no attempt was made to optimize each AAC system. Future studies are therefore recommended for further mix optimization for each type of AAC system; such studies could also investigate amendments in the treatment protocol that could further improve the performance of these systems. Furthermore, the required chemicals for the successful AAC could be further sourced from various waste sources and the consistency in the results checked. Moreover, the novel stabilisers should ideally be tested for different sulphates, sulphate contents and soil types and further hydromechanical property testing performed. Such studies are of importance so that comprehensive practical recommendations can be made for these novel stabilisers and confidence is built towards standardisation and commercial uptake of these stabilisers in the future, with the combined advantage of tackling the sulphate-bearing soil stabilization challenge, while developing innovative soil stabilisers of potentially lower environmental impact than common stabilisers such as Portland cement and commercially-produced lime.

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Author contributions

Mavroulidou: Conceptualization, Methodology, Supervision, Data analysis, Visualization, Writing – original draft, Writing– review & editing. Gray: Experimental methodology & investigation (geotechnical soil testing). Pantoja-Muñoz: Experimental methodology and investigation (material analysis), Writing (material analysis). Gunn: Conceptualization, Writing –review& editing.

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Data availability

The raw data are available from the corresponding author on reasonable request.

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Tables**Table 1 Typical oxide composition (reported as oxide wt.%) of GGBS, PSA and lime**

Chemical composition	PSA	GGBS	Hydrated Calcium lime
SiO ₂	19.20	34.68	0.70-1.00
TiO ₂	0.20		
Al ₂ O ₃	8.70	14.16	0.10-0.20
Fe ₂ O ₃	0.50	0.05	0.06-0.10
MnO	0.02		
MgO	2.80	7.74	1.40-0.50
CaO	60.70	38.74	95.00-97.00
Na ₂ O	0.15	0.46	
K ₂ O	0.20	0.55	
P ₂ O ₅	0.17		
SO ₃	0.48	0.21	
SrO	0.09		
BaO	0.04		
Li ₂ O	0.01		

Table 2. Plasticity characteristics of the untreated soil and the different treated soil mixes

Mix #	Mix ID	Mix type	LL (%)	PL(%)	PI (%)
Control	Untreated soil	Untreated soil	52	25	27
Mix 1	(2L_10G)	2% lime-10% GGBS	69	37	32
Mix 2*	(2L_2G)	2% Lime-2% GGBS	58	32	26
Mix 3	(3P_10G)	3% PSA-10%GGBS	71	37	34
Mix 4	(6P_10G)	6% PSA-10% GGBS	72	38	34
Mix 5	(6K_10G)	6% KOH-10% GGBS	59	32	27
Mix 6	(3P_3KC_10G)	3% PSA-3%K ₂ CO ₃ -10%GGBS	58	36	23
Mix 7*	(3P_3G)	3% PSA-3% GGBS	63	37	26
Mix 8*	(6P)	6% PSA	69	39	29
Mix 9*	(4L)	4% lime	61	27	34

*Mixes studied in Mavroulidou et al (2021 a) are shown here for comparison purposes.

Table 3. pH after 45 days of soaking (brackets show differences in the duplicate where applicable)

Mix ID	pH (average)	
	7-day cured	28-day cured
Mix1 (2L_10G)	11.1 (+/-0.05)	11.1
Mix 2 (2L_2G)	10.85 (+/-0.05)	10.75 (+/-0.05)
Mix 3 (3P_10G)	11.05 (+/-0.05)	10.75 (+/-0.05)
Mix 4 (6P_10G)	11.5	11.3
Mix 5 (6K_10G)	10.35 (+/-0.05)	10.05 (+/-0.05)
Mix 6 (3P_3KC_10 G)	10.55 (+/-0.05)	10.15 (+/-0.05)
Mix 7 (3P_3G)	10.75 (+/-0.05)	10.7
Mix 8 (6P)	11.35 (+/-0.05)	11.3

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Figure captions

Figure 1 UCS results in terms of average q_u (error bars show minimum and maximum values): (a) AAC mixes compared to mixes tested in Mavroulidou et al (2021a); (b) 7-day air cured mixes before and after water soaking; (c) 28-day air cured mixes before and after water soaking

Figure 2 (a) Indicative photo of layer of crystal forming in mixes tested in Mavroulidou et al (2021a); (b) No visible crystal layer in AAC mixes

Figure 3 Indicative stress-strain curves of 28-day cured samples (after water exposure)

Figure 4 Measurements on specimens after 45-day soaking: (a) Average swelling strains; (b) UPV (error bars show minimum and maximum values)

Figure 5 Indicative SEM-EDS results: (a) Mix 1 2L-10G (7-day curing); (b) Mix 1 2L-10G (28-day curing); (c) Mix 3 3P-10G (7-day curing); (d) Mix 3 3P-10G (28-day curing); (e) Mix 4 6P-10G (7-day curing); (f) Mix 4 6P-10G (28-day curing); (g) Mix 5 6K-10G (7-day curing); (h) Mix 5 6K-10G (28-day curing); (i) Mix 6 3P-3KC-10G (7-day curing); (j) Mix 6 3P-10G (28-day curing)

Figure 6 FTIR results (a) 7 day cured mixes; (b) 28-day cured mixes; (c) zoomed focus on the ettringite 3365 cm^{-1} band area; (d) zoomed focus on silicate bands in C-S-H

Figure 7 Indicative Raman spectroscopy results

Figure 1

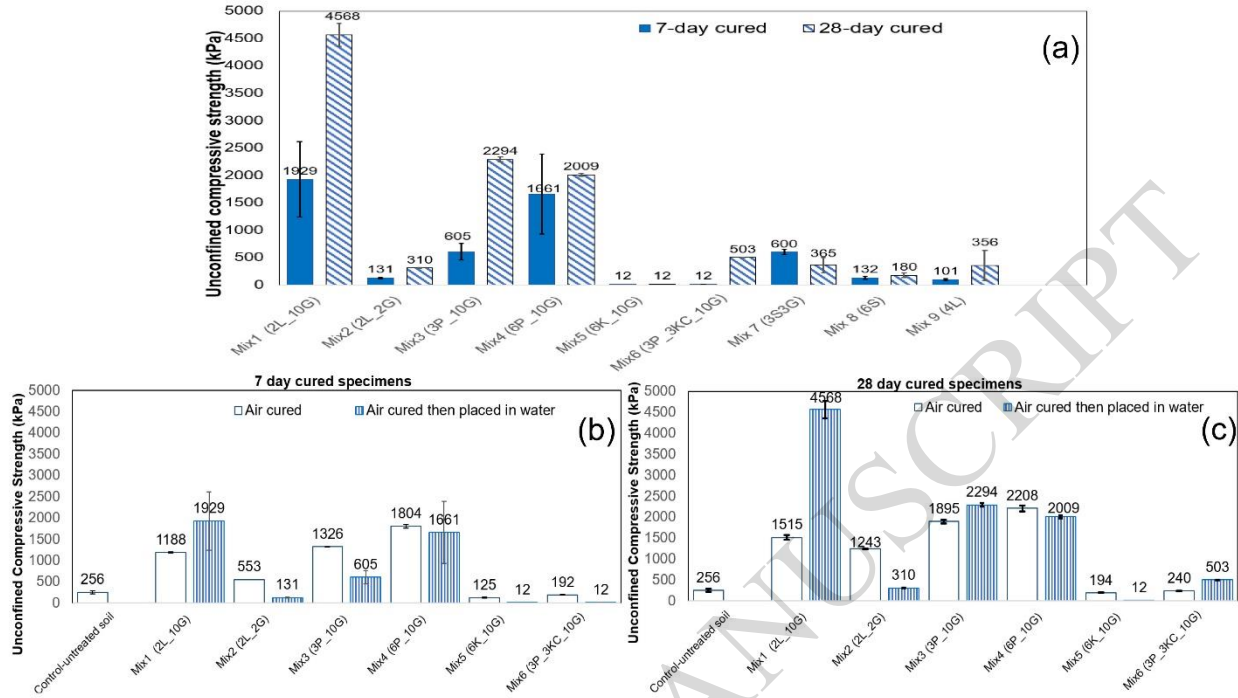


Figure 2



(a)



(b)

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Figure 3

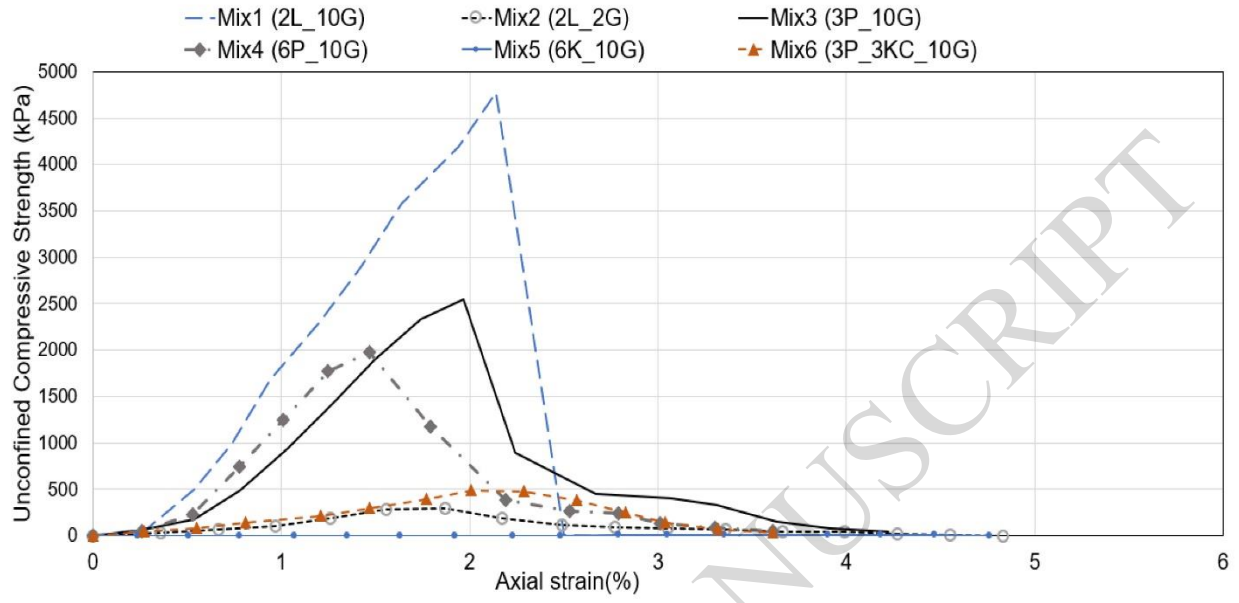
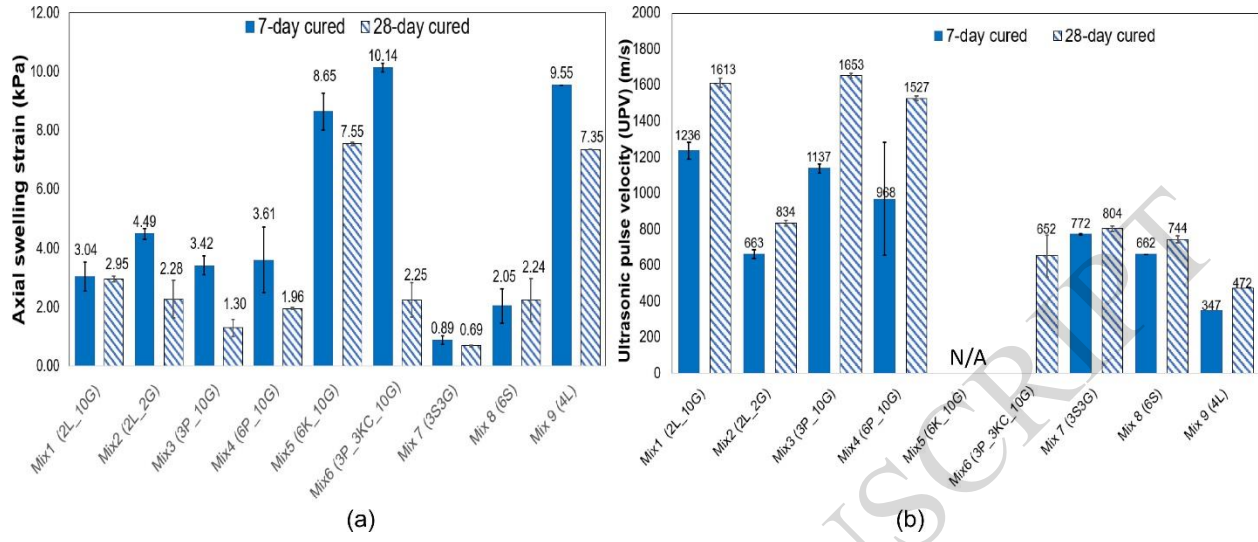


Figure 4



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Figure 5a

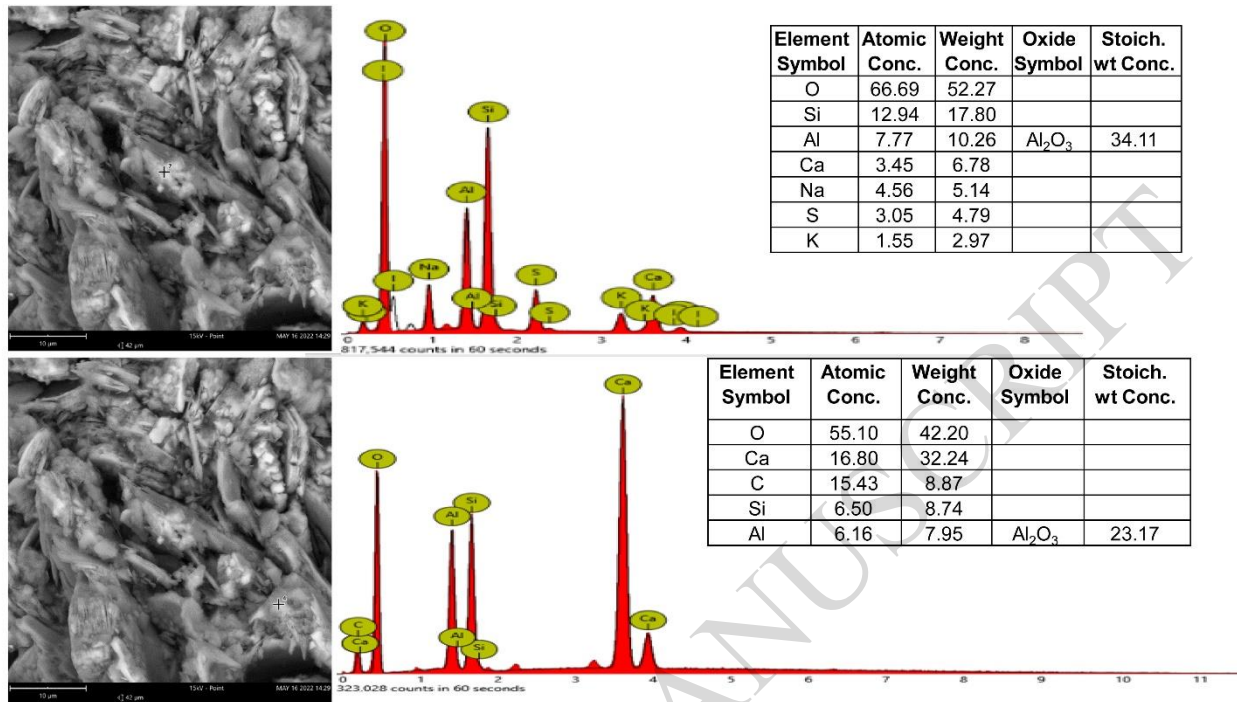


Figure 5b

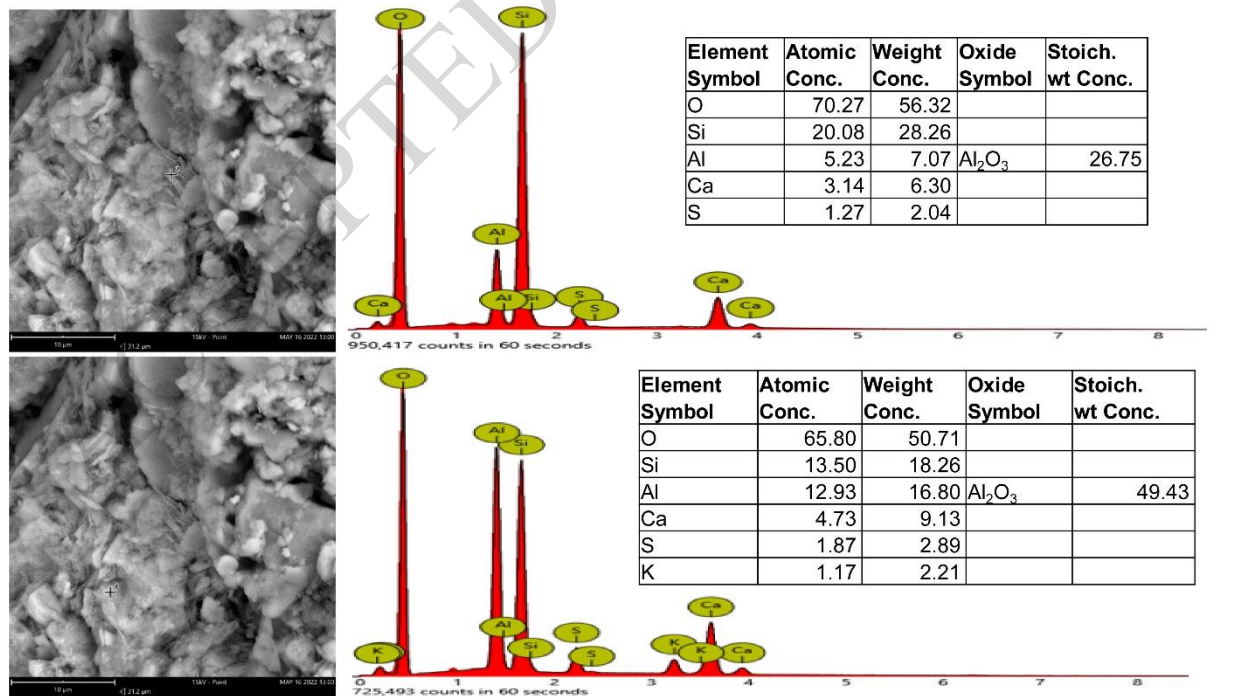


Figure 5c

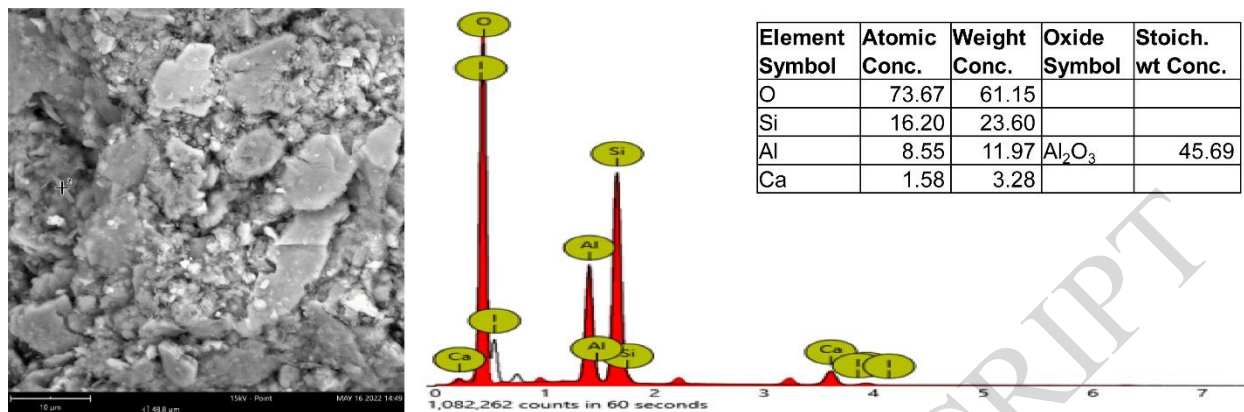


Figure 5d

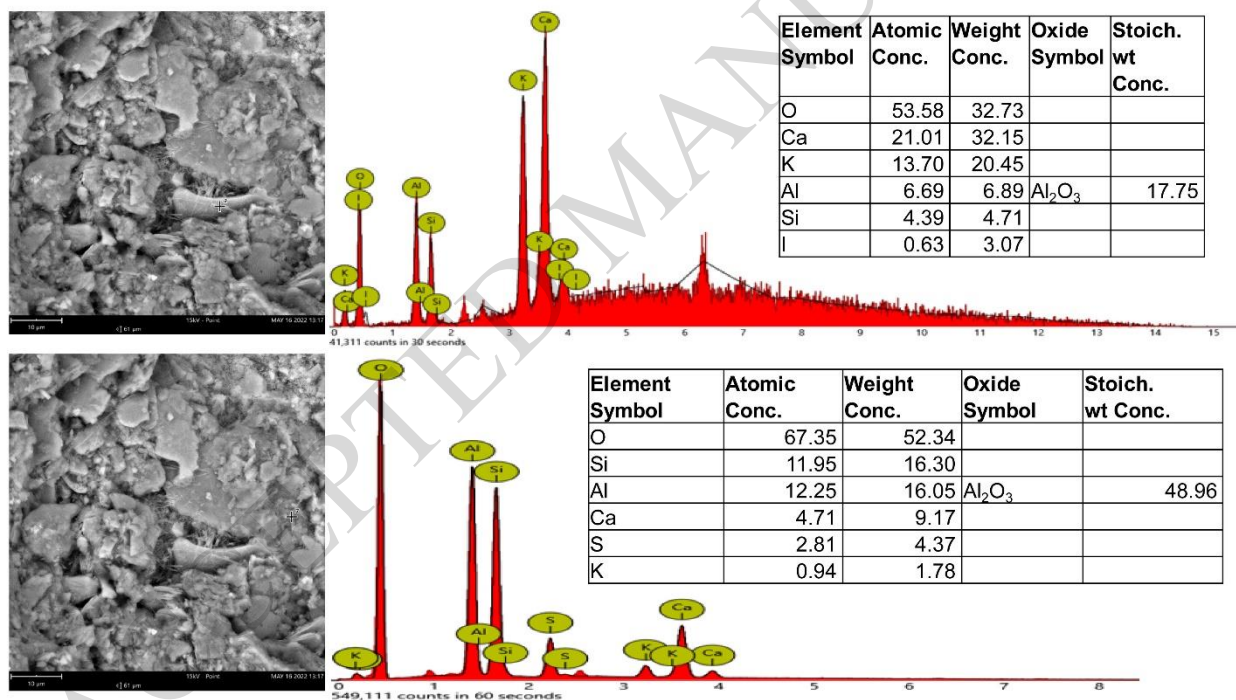


Figure 5e

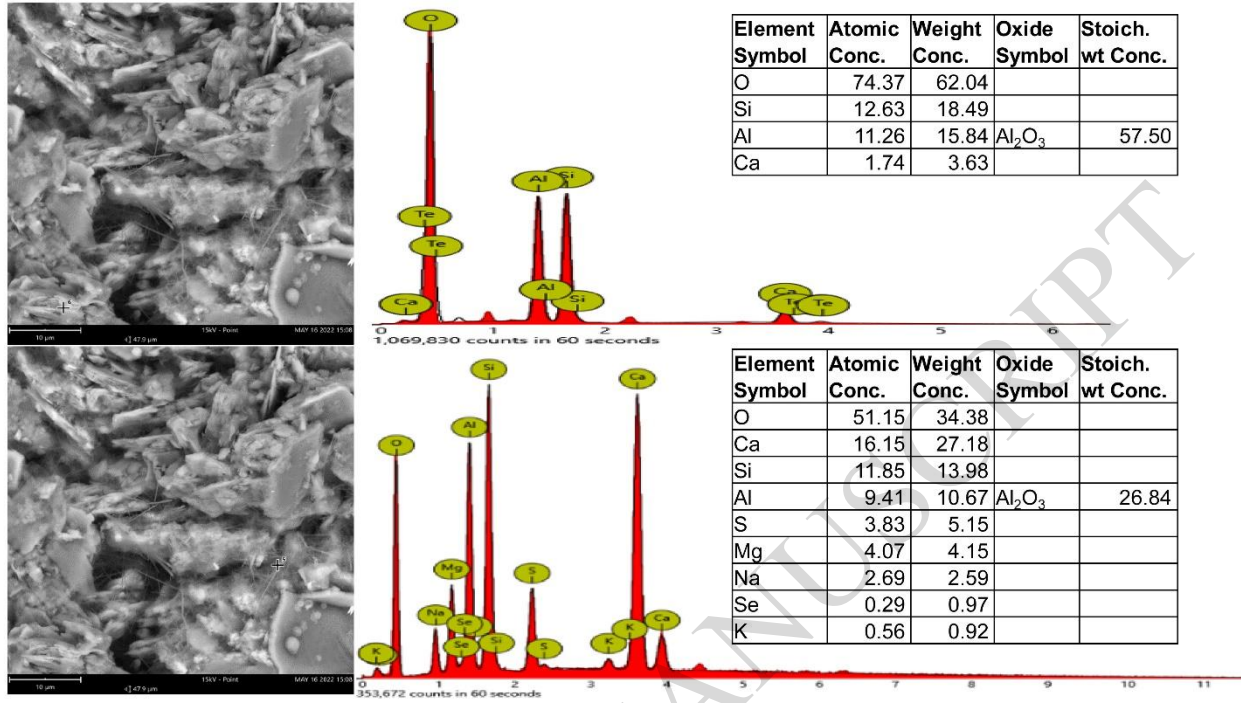


Figure 5f

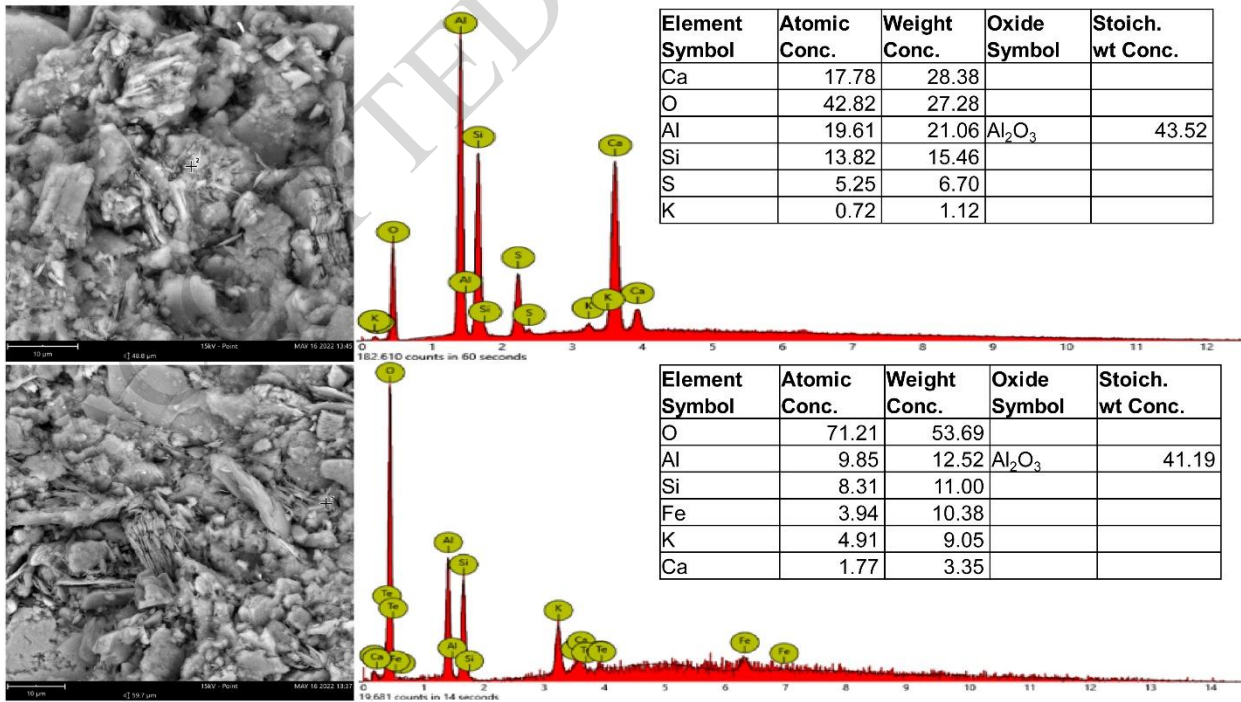


Figure 5g

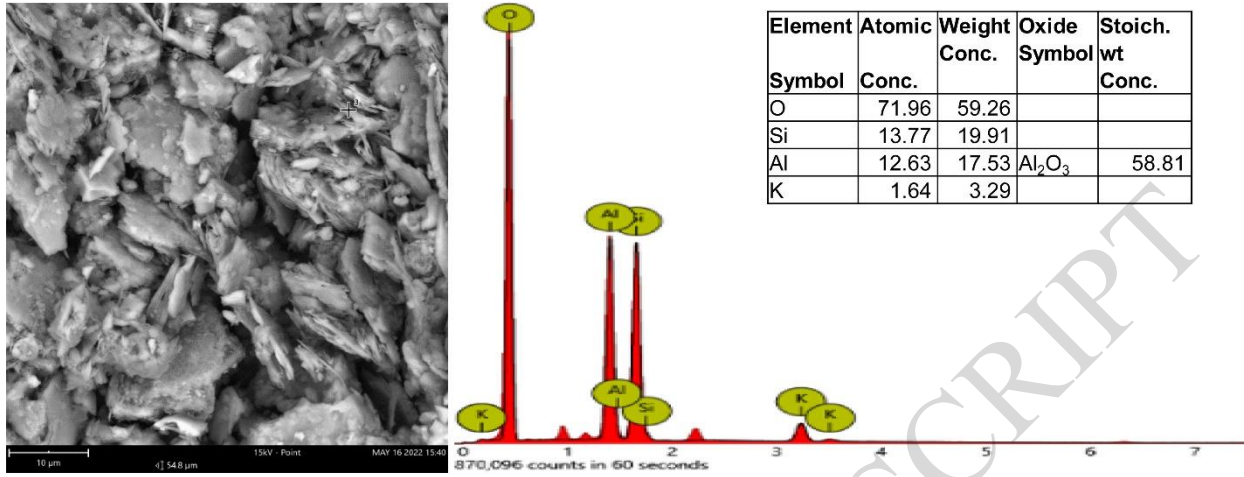


Figure 5h

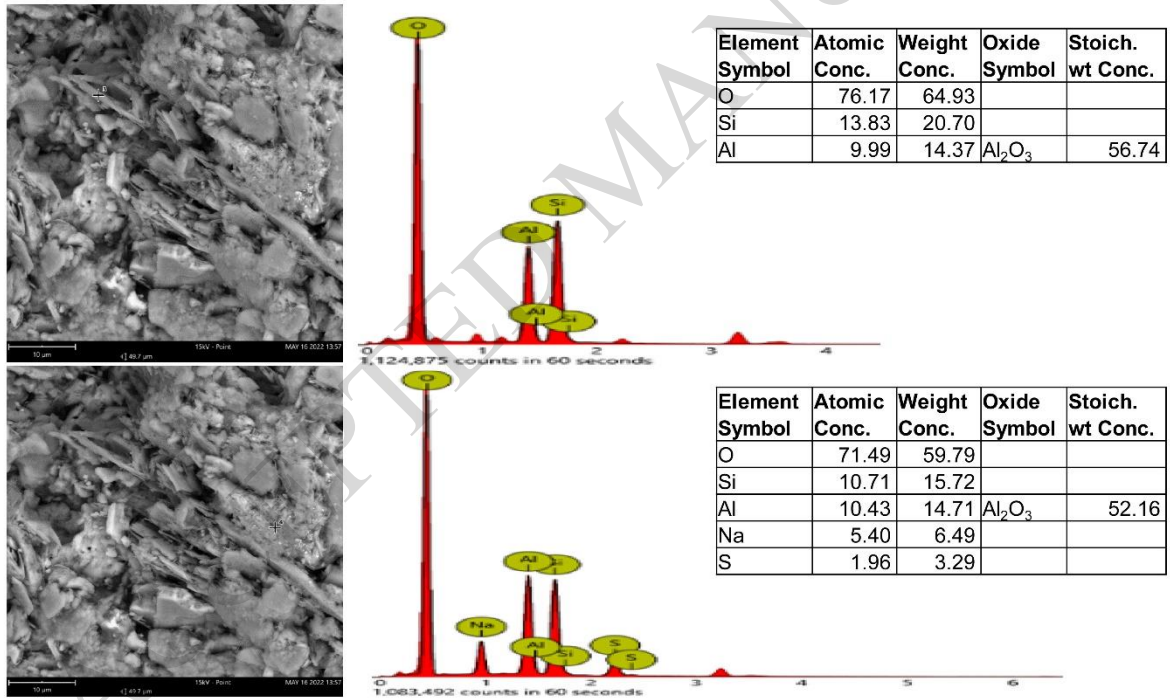


Figure 5i

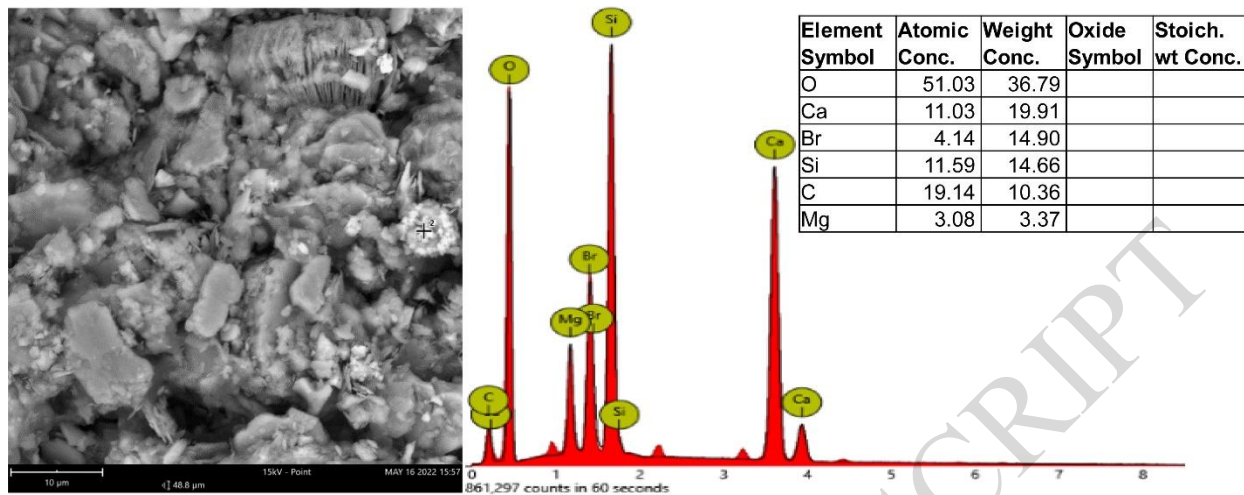


Figure 5j

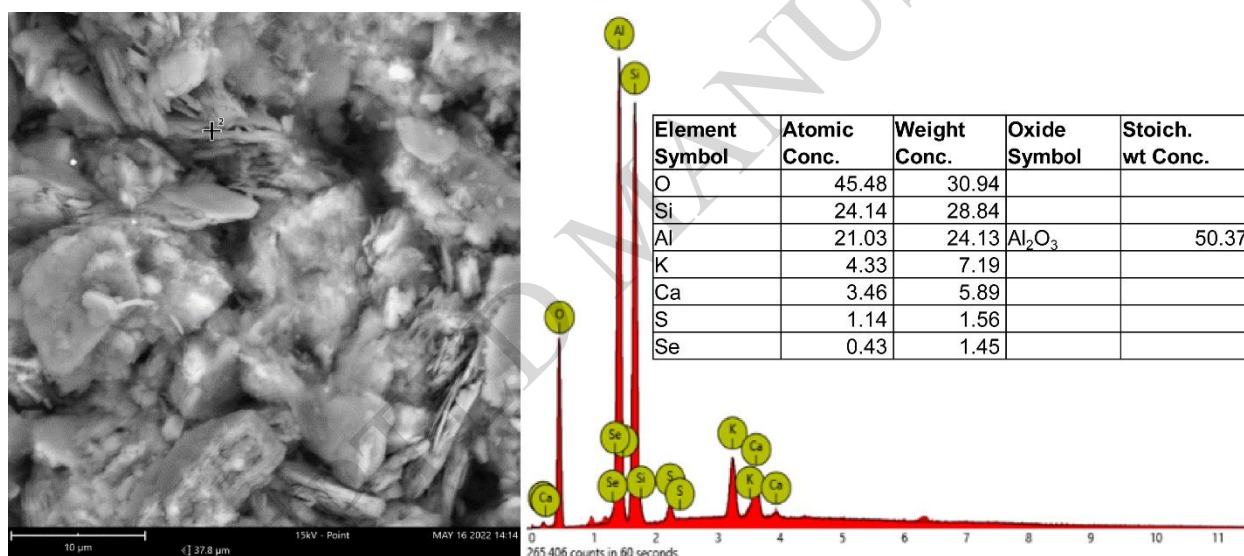


Figure 6a

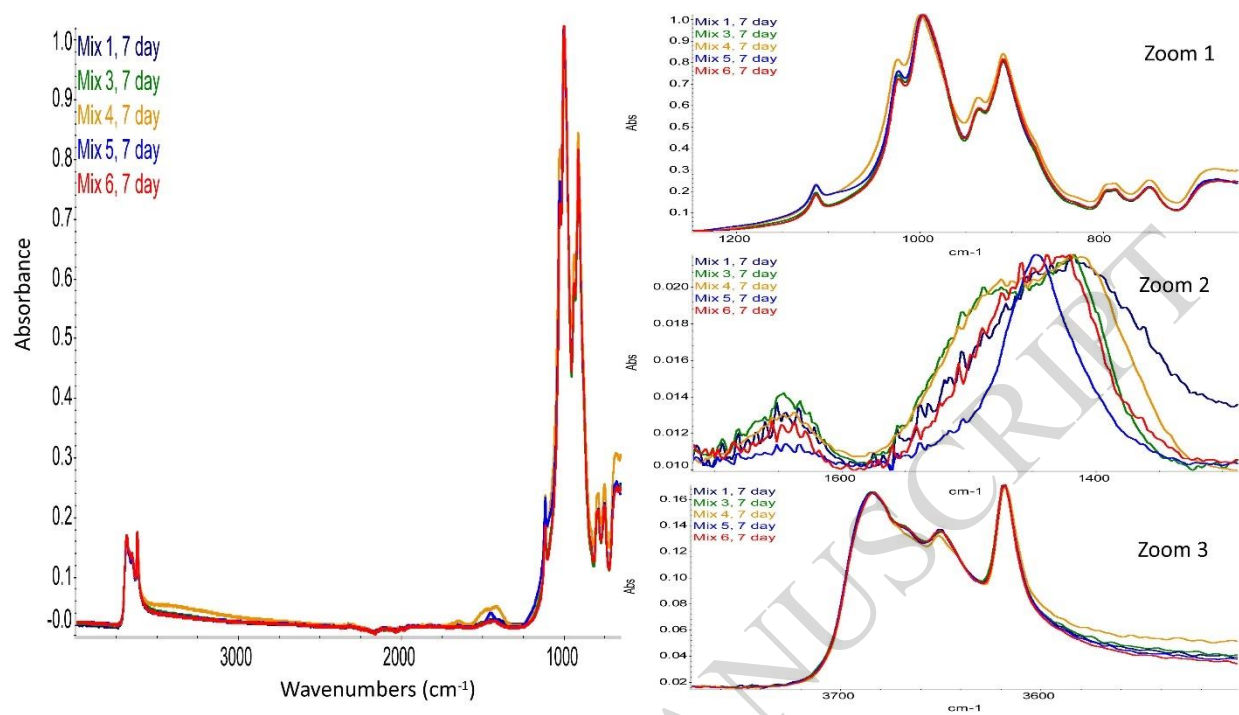


Figure 6b

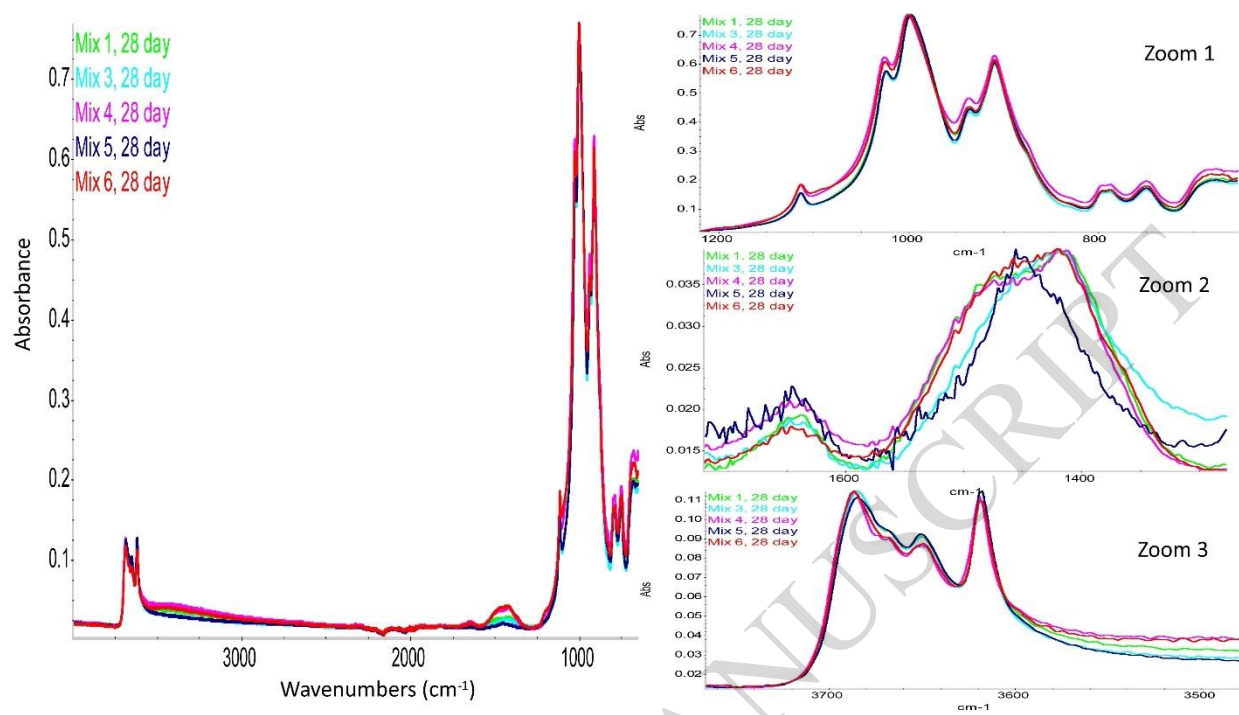


Figure 6c

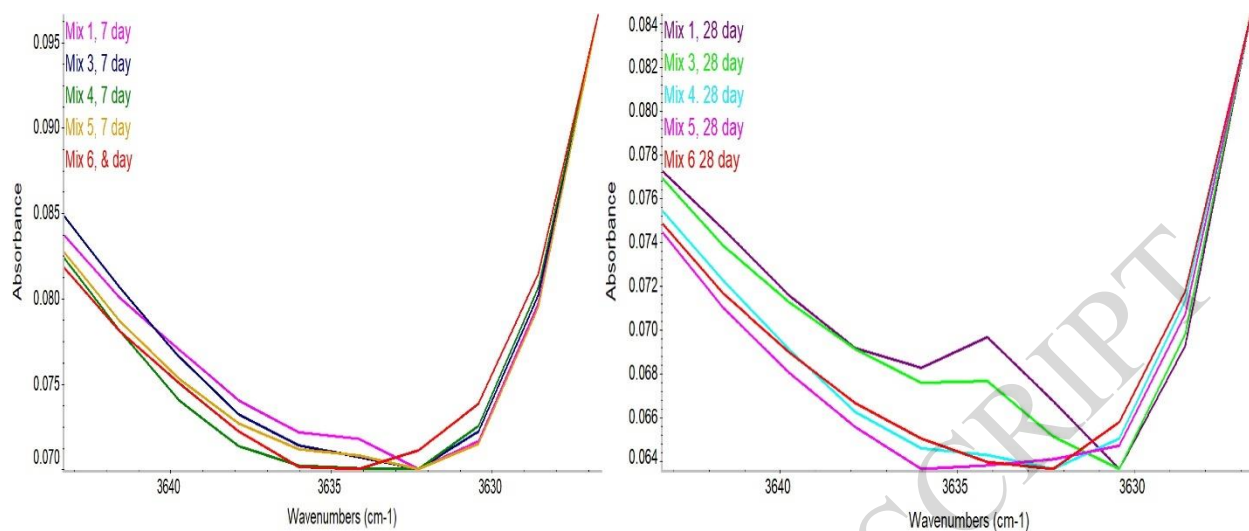
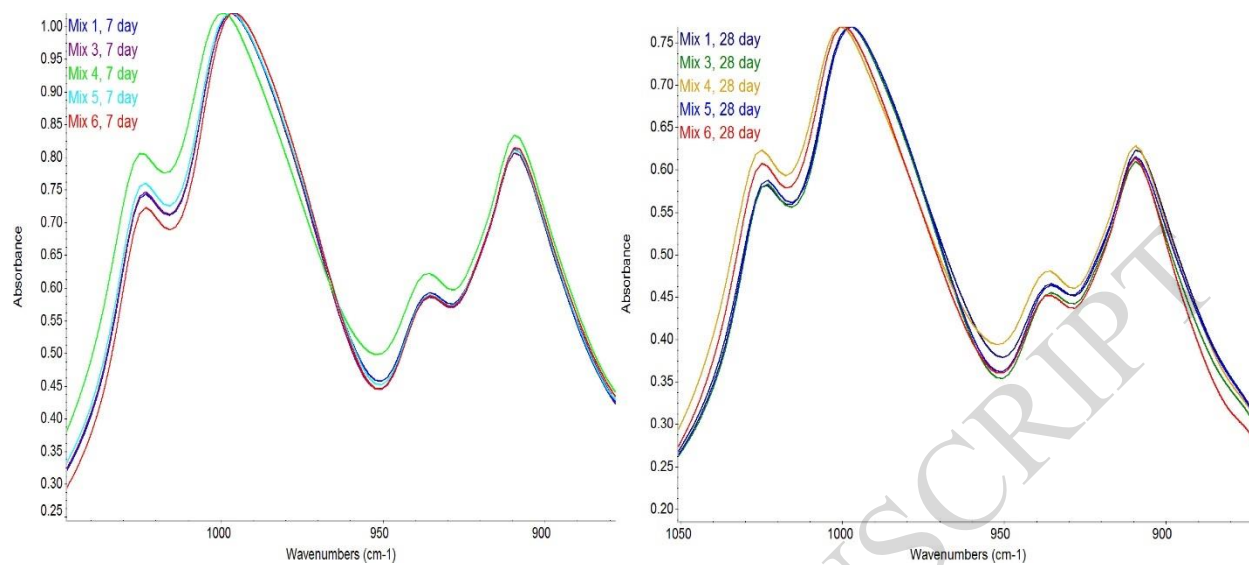
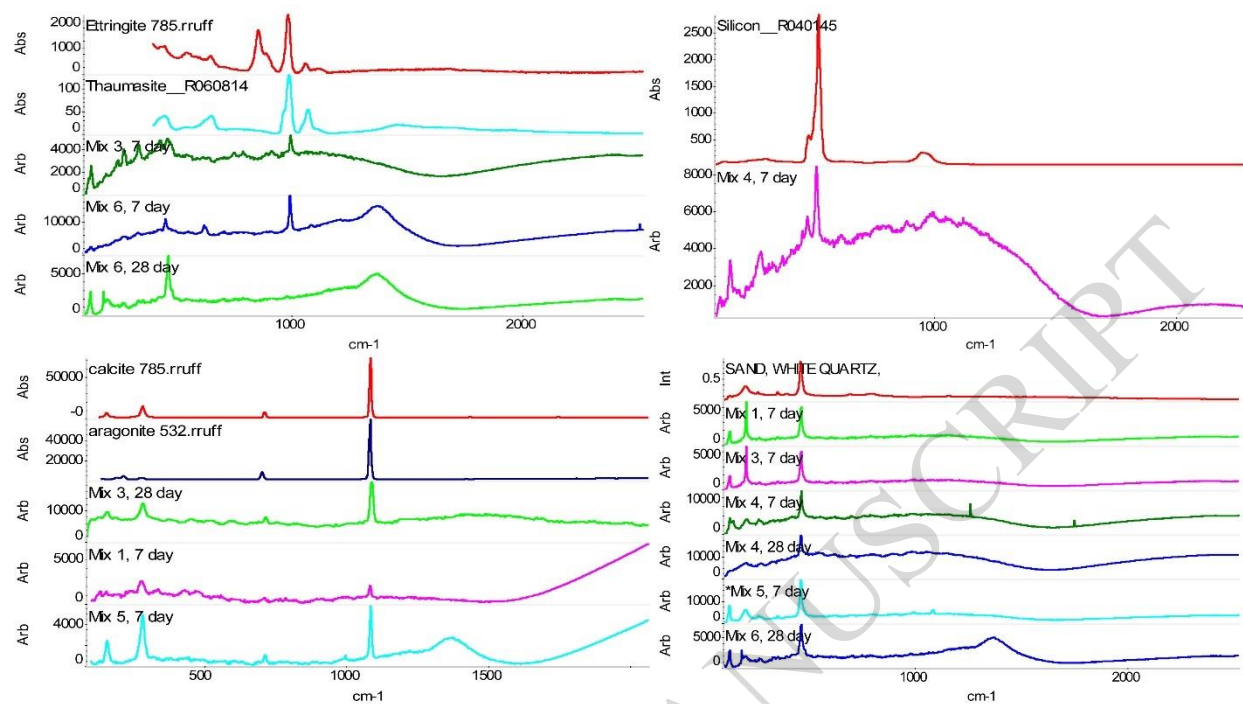


Figure 6d



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Figure 7



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