Technical Paper

Novel Binder of APC Residues and PFA for Road Aggregate Stabilisation – Petrographic Interpretation for Bonding

Behrooz Saghafi and Tetsuya Katayama

Abstract: Adding limestone quarry dust to Type 1 Unbound Mixture (a standard material for road foundation applications in the UK) reduced its stiffness significantly. Application of PFA-APC residues binder (a blend of pulverised fuel ash and air pollution control residues), as a novel, zero-energy binder, could successfully stabilise the material and improve its mechanical properties. Compressive strength of the stabilised material has been an indication of its performance over time, illustrating achievement of high compressive strengths. This paper presents new findings on the microstructure of the PFA-APC residues binder to explain the mechanism of developing such high strength. X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis revealed that the hardening is more due to formation of C-S-H gel, rather than the formation of crystalline hydrates. Also, it demonstrates share of each component in developing binding.

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Introduction

A government-sponsored research project on accommodating limestone quarry waste dust (LQWD) in road structure discovered a potential in placing it within UK pavement foundations. Incorporating LQWD to form 10 to 30% of the modified Type 1 Unbound Mixture (governed by Specification for Highway Works, Clause 803 [1]) reduced the significance of the effect of water content on the resilient modulus of the material; however, adding 10% reduced the resilient modulus of the new material for 33% although quantity of LQWD in the range of 10 to 30% did not create big differences in the results [2].

The 33% drop in Type 1 Unbound Mixture quality had to be claimed in order to secure the ground for the LQWD to enter into the modified system and eventually, construction industry. Stabilisation was found the best way to overcome the lost mechanical property [3]. Performances of several stabilisers were studied and PFA-lime was found the most suitable. PFA (pulverised fuel ash) is a waste by-product and very low amounts of CO₂ emissions are attributed to it [4] while lime is a major CO₂ emitter, as its production process not only requires heat but releases a significant volume of CO₂ due to the production’s chemical process [5]. Therefore, lime was sought to be replaced with a cheaper and greener PFA activator. Since the 1940’s when the steam power plants were common in the UK, their residues have created waste disposal problems [4]. The latest report stated that three million tonnes of PFA were sent to landfill every year with an additional 53 million tonnes left in stock [6]. PFA was initially introduced as a waste material; however, with the progress of discovering benefits in its use in construction material industry, it is now being introduced as a by-product.

Four different wastes (steel slag dust, air pollution control (APC) residues, paper recycling waste and sodium sulphate mixture) out of 12 candidates were found more likely to activate PFA; however, APC residues performed outstandingly. Based on neutralising value test results, one unit of APC residues was sufficient to activate one unit of PFA to develop cementitious characteristics.

Energy-from-waste plants burn the municipal wastes to create energy. The effluent steam must be prevented from entering into air and thus, is collected in the form of APC residues (as an ultimate waste) through a physical process. According to the statistics in 2006, APC residues have been produced in the UK at a rate of 128,000 tonnes per annum and it was predicted the rate would increase by a further 40,000 tonnes per year before 2013 [7].

A pleasant characteristic of PFA-based stabilised materials is that, due to their slow cementitious reactions, development of structural cracks in their body is rare. Such characteristic helps the road base to maintain its stiffness and do not originate reflective cracking on the asphalt concrete surfacing, the distress very common to the Portland cement-stabilised bases. Therefore, longer life span (due to having a stiffer foundation), lower price (due to reducing pavement layer thicknesses and maintenance cost) and further sustainability (due to replacing primary aggregate with waste materials of higher quality) are predicted for the pavements with PFA-based foundations.

The paper demonstrates the reasoning behind the successful performance of the PFA-APC residues binder in conjunction with the three-month mechanical behaviour of a pavement foundation mix containing LQWD stabilised with PFA and APC residues. Unconfined compressive strength (UCS) of the designed mix will also be compared with its PFA-lime counterpart to illustrate the depth of the achievement. Petrographic interpretation of the
PFA-APC residues has not yet been studied. Scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and quantitative energy dispersive X-ray spectroscopy (EDS) analysis are the tools used to study the binder microstructure and the outcomes are linked to the UCS of the mix in which PFA-APC residues performed as a binder. SEM is a device to magnify the surface of the material for detailed viewing. Scanning the material surface, XRD technique literally helps record the intensity of the material crystalline and amorphous sectors. EDS microanalysis can provide information on the chemical composition of a sample.

Research Programme

Strength and chemical properties of PFA-APC residues binder-based aggregate materials are studied. PFA-APC residues binder is used to stabilise Type 1 Unbound Mixture which contains high volume of LQWD. In order to compare performance of PFA-APC residues binder with a more renowned PFA-based binder, another mix with the same aggregate materials but stabilised with PFA-lime binder has been designed. UCS values of the mixes will be the comparison base. 15 cm Cubes are manufactured and the samples are tested at their ages of 3, 7, 14, 28 and 90 days to observe early and medium-term life performance of the study mixes.

Sampling from the cubes did not suit micro-structure study of the binder, because the mixes contained huge amount of limestone fines which could deviate the results and prevent coming into conclusion on the micro-structure of PFA-APC residues binder. Therefore, further procedure was carried out to sample solely PFA-APC residues binder. Study on the binder petrography has been completed at Kawasaki Geological Engineering Co. Ltd, Tokyo, Japan, where analytical investigation has been done on fresh and aged PFA and APC residues to conclude the share of every part of the binder in developing strength over time. Compressive strength of PFA-APC mix samples is the evidence of the ability of the PFA-APC residues binder in developing strength and petrography works as the micro-structural evidence of the development.

Research Materials

Strength-developing characteristics of the PFA-APC residues binder has been examined on the base/subbase mix and have been compared with a PFA-lime bound base/subbase material with identical amount of aggregate and binder. Therefore, two mixes have been designed:

- PFA-lime: 70% Type 1 Unbound Mixture + 20% LQWD + 8% PFA + 2% lime
- PFA-APC: 70% Type 1 Unbound Mixture + 20% LQWD + 5% PFA + 5% APC residues

Contents of the PFA-APC residues binder and PFA-lime binder have been proportioned after [3]. Type 1 Unbound Mixture and LQWD have been provided from a single quarry. Optimum moisture content (OMC), in accordance with [8], has been used both to ease material compaction and to provide necessary water for chemical reactions. OMC was found 6.6% for PFA-APC mix and 7.0% for PFA-lime one. Study on the density of the samples showed that the samples have been similar due to their very close densities.

To study the petrographic properties of the PFA-APC residues binder six types of samples have been considered:
1. PFA in its as-collected form,
2. PFA mixed with water to a thick paste and stored in sealed bag to harden for a year,
3. APC residues in its as-collected form,
4. APC residues stored in laboratory and exposed freely to its environment,
5. APC residues mixed with water to a thick paste and stored in sealed bag to harden for a year.
6. PFA-APC residues binder mixed with their OMC (24.3%) and stored in sealed bag to harden for a year.

These materials have been mixed and sampled separately. In order to resemble the binder used in PFA-APC mix the latter contained 50% PFA and 50% APC residues. However, no LQWD dust could be found in the mix number 6 and thus, petrography outcomes could represent the real activity of PFA and APC residues.

PFA has some cementitious components such as SiO₂, Al₂O₃ and Fe₂O₃. It is a very slow-rate binding material due to its lack of sufficient content of free lime. To speed up the chemical process, lime or cement is introduced to PFA. PFA was first used in concrete but lime or cement-activated PFA was later taken into soil stabilisation business which has been experienced for construction of road foundation in the UK. The PFA used in this study was not rich in free lime but it did contain considerable amounts of silicates and aluminates. Its particles were uniformly distributed between 1 to 0.001 mm in diameter.

APC residue is a pale grey-to-white, fine-grained, free flowing powder containing small black particles of activated carbon. It is composed of calcium compounds, predominantly calcium oxide and calcium hydroxide with smaller quantities of other compounds such as carbonate, sulphate and chloride complexes as a result of the lime neutralisation of acid flue gas. Being very alkaline with typical pH in the range of 11.5 to 13, it contains a high lime content varying between 25% and 40%, as revealed by neutralising value test. With 20% smaller than 0.001 mm and the largest particle being 0.5 mm in size, APC residues particles are naturally finer than PFA particles are.

Unconfined Compressive Strength (UCS) of PFA-APC and PFA-lime Mixes

The compressive strength of the stabilised materials was tested as a guide to follow up the reactivity of binders of PFA-lime and PFA-APC residues, and suitability of the mixtures as base material. The cubes were manufactured in five layers based on [9]. The cubes were manufactured according to Clause 4.2 of BS 1924-2:1990. The materials were compacted in cubes using an electric hammer. The maximum mass the compactor device could manage controls the number of layers during the manufacturing process. It was important to finish the top surface of the sample at a tangent to the top edge of the mould. As the material was not wet enough to shear or trowel the top surface of the sample (as it is normally done in the case of ordinary concrete), any manual finish could significantly harm the sample shape and stability. In order to have an identical
amount of material in each sample and a constant sample height, the total mass for every sample was calculated using Clause 4.2.3.3 of the above standard. Using plastic wrapping, the samples were sealed immediately after manufacture to prevent water ingress and egress. Curing was done at laboratory temperature within the range of 18°C to 21°C.

An ordinary concrete mixer was used to blend the mixture of materials. As they contain two types of fly ash, which could easily fly away if mixed dry, the binders were turned into grout before adding to the aggregates, using a part of the mixtures water content. This prevented binder lumps and material segregation. It also helped the fluid binder to reach almost every part of the aggregate although the mixtures were left for a few hours after blending in sealed bags to make sure the binder and water had spread within the mixture.

Guides given in BS EN 12390-3:2009 [10] were used for accomplishing UCS tests. Cubes were loaded at a slow rate of 12 kN/min so that the young samples would not crush under fast loading. The crushing styles of the samples satisfied the requirements in BS EN 12390-3:2009.

O’Flaherty [11], based on an Australian document, declares that, for reasonably well-graded base materials, 0.8 MPa for 7 day moist-cured UCS can be used as a transition guide from an unbound state into a bound one. It gives a fair indication for grouping the mixture based on its UCS. O’Flaherty proposes another clue; cement-bound well-graded crushed rock aggregates may present 4 MPa at 28 day UCS while fly ash-based materials are very like in nature to cement-bound materials.

Fig. 1 includes histograms of the growth in the compressive stability of the PFA-lime and PFA-APC samples. Having started with 1.5 MPa of compressive strength after three days, the strength of 7 day PFA-APC samples (not moist cured) was much higher than the criterion of 0.8 MPa, giving an indication that the mixture would have cement bound-like performance. The 28 day UCS value for this material (5.18 MPa) has been well over 4 MPa, which qualifies them to be classified as bound material based on O’Flaherty [11]. An impressive point with PFA-APC mixture is its 3 month compressive strength of about 10.6 MPa which clearly indicates that the material is an absolute bound material after three months.

PFA-APC samples looked more stable than PFA-lime ones did; a comparison which illustrates the superiority of the APC residues in activating PFA. The 7 day PFA-APC samples have as high strength as was seen from 28 day PFA-lime samples, which suggests that PFA-APC samples have had three to four times higher strength growth rate during the first seven days. The magnitude of 28 day UCS test for PFA-APC mixture has been 2.5 times larger than that for PFA-lime mixture, which is another indicator of better bonding ability of PFA-APC binder. This ratio is maintained for three months at which PFA-APC samples were three times stronger in comparison to PFA-lime mixtures.

The high strength received from PFA-APC mixture is a direct effect of the chemical reaction of PFA-APC binder. Furthermore, it specifies the effectiveness of APC residues in successfully activating PFA for its cementitious properties, and the effect of such properties is seen in the strength of its samples. What increases the value of PFA-APC binder and proves its efficiency is the good stabilisation of aggregate systems containing high amounts of dust. Previous research of Ashtiani [12] had experienced that when a

![Unconfined Compressive Strength Values for PFA-lime and PFA-APC Samples at Their Testing Ages.](chart.png)

higher quantity of fines existed in the mixture, although high cement content was necessary to provide strength, the mixture became highly sensitive to its binder content. Therefore, there is a good potential in PFA-APC binder to well replace cement in such cases.

In comparison to what is seen from PFA-lime samples, the PFA-APC mixture has started with slightly higher compressive strength at its early life but with higher rate of reaction. The dominance of PFA-APC samples is further seen at increased ages of the samples, i.e. 28 days and three months. This confirms the results of preliminary compressive strength tests on PFA-APC residues and PFA-lime pastes when a replacement was being found for lime. PFA-APC residue paste had nearly three times bigger compressive strength in comparison to that from PFA-lime paste, which was the first ignition to continue the research based on APC residues.

In conclusion, APC residues are known as a replacement to lime in activating PFA and developing a hard fly ash-based material from the material mechanical properties point of view. The UCS of the PFA-APC mix delivers this idea that it can be introduced as a base/subbase material for road construction purposes based on the time-dependent, cement-like performance of the novel binder, PFA-APC residues. Although this statement can be witnessed according to the UCS results, still further study is necessary to clear the main shares in developing such strength. Microstructure of the binder can unveil the extent each material component has had in building up the strength.

**Petrographic Study of the PFA-APC Binder**

Polished thin sections (thickness 15-20 µm) were prepared using non-polar solvent following the method after [13], except that powder specimens were embedded within epoxy resin before cutting. After completing polarizing microscopy (magnifications 25-200x) and powder X-ray diffraction analysis (XRD: 2-60°2θCuKα) for bulk mineralogy, polished thin sections were
subjected to scanning electron microscopy (SEM: 500-2000x), then
to quantitative energy-dispersive spectroscopy (EDS: accelerating
voltage 15 kV, beam current 0.12 nA, measurement 100 s, dead
time 30%, ZAF correction) to analyse chemical compositions of the
constituents contained (glass, hydrates) based on mineral standards
for calibration.

Under the polarising microscope equipped with reflected light
apparatus, PFA abounded in dark-coloured spherical glass particles,
both solid minute particles and large hollow cenospheres, along
with opaque materials comprising of carbon and iron oxides. APC
residues contained light coloured spherical glasses, occasionally
presenting hollow cenospheres like that of PFA.

**XRD Analysis**

PFA contained quartz and mullite 3Al₂O₃·2SiO₂, and presented a
broad halo of the background due to the abundance of the glass
phase that is amorphous to XRD (Table 1, Fig. 2(a), Fig. 2(b)). Fresh APC residues presented diffraction peaks of portlandite
Ca(OH)₂, calcium chloride hydroxide CaClO₂H, halite NaCl, sylvite
KCl, and anhydrite CaSO₄, but some of which were overlapping.
Gehlenite 2CaO·Al₂O₃·SiO₂ was possible but was not positively
identified.

**C-S-H Gel**

In general, this hydrate is only poorly crystalline in the hydrating
system of Portland cement at ambient temperature. Because major
diffraction peaks of C-S-H (II) (9.0°, 29.1°, 31.9°2θCaKα) were
overlapping with other constituents present in the specimens (ettringite 9.1°, calcite 29.4°, halite 31.7°), positive identification
was not obtained by XRD only. Hence, SEM-EDS analysis was
performed for confirmation.

**AFm and AFt Phases**

APC residues were found chemically active: they formed Kuzel’s
salt 3CaO·Al₂O₃·Ca[(SO₄)₃·(2Cl)·11H₂O (basal reflection: 10.5°2θ) in the powder specimen when stored in a sealed glass
bottle (1 year) (Fig. 2(c)). APC residues mixed with water were
solidified by hydration (1 year) even without adding external source
of calcium (CaO, Ca(OH)₂, CaCO₃) (Fig. 2(d)). In this hardened
specimen, secondary calcite CaCO₃ had formed through
atmospheric carbonation, but a traceable amount of mono-
sulfate 3CaO·Al₂O₃·2CaSO₄·12H₂O (9.8°2θ) was also detected. By contrast, solidified APC-PFA binder specimen (1 year) contained Friedel’s
salt 3CaO·Al₂O₃·CaCl₂·10H₂O (11.3°2θ) as the sole AFm phase,
along with ettringite 3CaO·Al₂O₃·3CaSO₄·32H₂O (9.1°2θ).

**SEM Observations**

Both APC residues and PFA contained spherical glass particles,
ranging from small solid globules to large hollow cenospheres (Fig.
3). Occasionally, dendritic magnetite was present in the PFA glass.
Hardened APC-PFA binder specimen (1 year) uniformly contained
C-S-H gel, a hydration product of the glass particles, occupying a
paste-like matrix. By contrast, Friedel’s salt and Kuzel’s salt
appeared locally as minute flakes in areas that had originated from
APC residues (Fig. 4). In the powdery specimen of APC residues
(stored 1 year), ettringite already formed presenting a fibrous to
reticular network.

**Quantitative EDS Analysis**

**Glass Phases**

APC residues are characterized by high-Ca glass, resembling
high-Ca fly ash, but is rich in phosphorous (mainly CaO 18-38%,
SiO₂ 35-45%, P₂O₅>1%) inherent to the municipal waste originally
containing animal bones, whereas PFA by low-Ca glass with low
phosphorous (mostly CaO < 2%, SiO₂ 57-75%) (see Table 2).

<table>
<thead>
<tr>
<th>Crystalline Phase</th>
<th>Nominal Composition</th>
<th>PFA (a)</th>
<th>Hardened PFA* (b)</th>
<th>Fresh APC (c)</th>
<th>APC Stored** (d)</th>
<th>Hardened APC* (e)</th>
<th>PFA-APC* (f)</th>
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<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>++</td>
<td>+</td>
<td>(+)</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Mullite</td>
<td>3Al₂O₃·2SiO₂</td>
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<td>Gehlenite</td>
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<td>Magnetite</td>
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<td>Calcite</td>
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<td>Anhydrite</td>
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<td>Sylvinite</td>
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<td>Portlandite</td>
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<td>Chloride Hydroxide</td>
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<td>C-S-H(II)</td>
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<td>Monosulfate</td>
<td>3CaO·Al₂O₃·CaSO₄·12H₂O</td>
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<tr>
<td>Kuzel’s Salt</td>
<td>3CaO·Al₂O₃·Ca[(SO₄)₃·(2Cl)·11H₂O</td>
<td>+</td>
<td></td>
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<tr>
<td>Friedel’s Salt</td>
<td>3CaO·Al₂O₃·CaCl₂·10H₂O</td>
<td>+</td>
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<tr>
<td>Ettringite</td>
<td>3CaO·Al₂O₃·3CaSO₄·32H₂O</td>
<td>(+)</td>
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++ abundant, + common, (+) trace, * hardened with water (1 year), ** stored in air, powdery (1 year)
Analysis points by EDS were shown in the SEM images (Figs. 3 and 4). On the CaO-Al₂O₃-SiO₂ diagram (Fig. 5), glass phases of the APC residues have more calcic compositions occupying the pseudowollastonite-gehlenite-anorthite and silica-pseudowollastonite-anorthite triangles than the PFA glasses which occupy the silica-anorthite-mullite triangle. This is because hydraulic lime is added during combustion of municipal wastes to form APC residues. Hence, APC glasses can be distinguished from PFA glasses even in the hardened PFA-APC binder specimen, based on higher Ca content. PFA glasses have broadly similar compositions to those reported for Japanese PFA [14].
In the hardened PFA-APC binder, glass phases hydrated to C-S-H gels that are more calcic (Ca/Si=1.9-2.1) around the APC glass than the C-S-H gel (Ca/Si=0.6-1.7) around the PFA glass (Table 2). This reflects the difference in the original Ca/Si ratios of these glasses. C-S-H gel from the APC glass roughly corresponds to so-called C-S-H (II) (Ca/Si>1.5) after [15], while C-S-H gel from the PFA glass to C-S-H (I) (Ca/Si<1.5). Chloride ion, detected up to 3wt% in the C-S-H gels, came from water-soluble halite and sylvite originally contained in the APC residues. Such a concentration of chloride ion is similar to that found in field concretes exposed to de-icing salts or marine environments.

**AFm and Aft Phases**

From the APC residues stored in the bottle, both Kuzel’s salt and ettringite contained by P2O5 were identified (Table 3). Of the AFm phase in the hardened PFA-APC binder specimen, Friedel’s salt was predominant with a composition of (Ca152, Mg30.16, Na0.04, K0.07)3.30 (Al1.05, Fe0.48, Si0.45, P2O7, Ti0.01, Mn0.01)2.04O6.00[(2Cl)1.29, (SO4)1.28, X0.99]1.00 nH2O (X=2OH or CO3)2, and Kuzel’s salt (Ca3.42, Mg0.06, Na0.08, K0.02)3.56 (Al1.99, Fe0.04, Si0.65, Ti0.81, Mn0.01)2.04O6.00[(2Cl)0.33, (SO4)0.36, X0.33]1.00 nH2O was subordinate. This suggests...
that chloride ions in the specimen were replacing sulfate ions in the Kuzel’s salt, transforming into more stable Friedel’s salt.

**Discussion**

It is widely accepted that APC residues contain chlorides (NaCl, KCl, CaClOH) and Ca-bearing substances (calcite, portlandite and anhydrite), although they present several overlapping XRD peak patterns. Of these, the Ca-rich group originates from the hydraulic lime injected during the combustion process (e.g. [17]), which remains as 15-20% of free-lime in the residues [18]. When APC residues are kept in moist condition, AFt phase (ettringite, [19]) may form, and when washed by water, AFm phase (Friedel’s salt, [20]) may occur.

**Significance of Glass Phases and C-S-H Gel**

Previous workers in characterising the APC residues relied mostly upon powder XRD analysis and identified only crystalline phases, without using polarising microscopy. As a result, amorphous phases constituting the substantial part of the APC residues have long been missed from discussion.

Present study, however, for the first time revealed common occurrence of the amorphous phases (glass and C-S-H gel) contained in the APC residues and in their hydration products, as discussed in the previous sections.

**Table 3. Compositions of the Hydration Products AFm and AFt Phases in APC Residues and in PFA-APC Binder, Analysed by EDS on Polished Thin Sections. (Numbers in Fig. 4)**

<table>
<thead>
<tr>
<th></th>
<th>APC Residues (Stored 1 Year)</th>
<th>PFA-APC Binder (Solidified 1 Year)</th>
<th>APC Residues (Stored 1 Year)</th>
<th>PFA-APC Binder (Solidified 1 Year)</th>
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<tr>
<td></td>
<td>11</td>
<td>8</td>
<td>12</td>
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<tr>
<td></td>
<td>Kuzel’s Salt</td>
<td>Ettringite</td>
<td>Friedel’s Salt</td>
<td>Kuzel’s Salt</td>
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<tr>
<td>SiO₂</td>
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<td>1.12</td>
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<td>P₂O₅</td>
<td>7.78</td>
<td>3.82</td>
<td>0.47</td>
<td>0.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.89</td>
<td>5.43</td>
<td>0.52</td>
<td>5.74</td>
</tr>
<tr>
<td>Cl</td>
<td>5.80</td>
<td>2.09</td>
<td>7.26</td>
<td>4.87</td>
</tr>
</tbody>
</table>

**Note:**
- O=0.226Cl, ** not included in the compositional formula because of a higher content of P₂O₅.
- *** total cation numbers for normalised O=6 were calculated, using O=7 (AFm phases) or O=9 (AFt phases).
- **** normalised to 1.00 (AFm phases) or 3.00 (AFt phases).

AFm phases: 3CaO·Al₂O₃·Ca[2Cl, SO₄ X]·nH₂O, where X= 2OH, CO₃ (not detected by EDS)
AFt phases: 3CaO·Al₂O₃·3Ca[2Cl, SO₄ X]·nH₂O, where X= 2OH, CO₃ (not detected by EDS).

Fig. 5. Compositions of Glass Phases in APC Residues and PFA, as Analysed by EDS on Polished thin Sections. Phase diagram after [16].
well as chemical compositions by quantitative EDS analysis on polished thin sections. It was made possible to distinguish glass particles with C-S-H gel of APC residues from those of PFA, even in the solidified mix of the PFA-APC binder.

With the APC residues, glass particles correspond in composition to high-Ca fly ash (CaO > 20 wt%), and their hydration product C-S-H gels in the Ca/Si ratio roughly fall into the range of C-S-H (II) (Ca/Si > 1.5). In contrast, with the PFA examined, most of glass particles represent compositions of low-Ca fly ash (CaO < 8 wt%), and their C-S-H gels correspondingly fall into the range of C-S-H (I) (Ca/Si < 1.5).

The predominance of the low-Ca glass in the PFA suggests a good pozzolanic activity of this glass with OH ions to form C-S-H gel, when Ca(OH)\(_2\) is supplied, whereas high-Ca glass in the APC residues suggests subordinate hydraulic activity. It is reasonable to assume that the mechanism of solidification of the PFA-APC binder is due to the pozzolanic reaction of these glass phases which form abundant C-S-H gel (basically amorphous to XRD) as a cementing paste material in the matrix.

The observed range of the chloride content (<3 wt%) in the C-S-H gels in the PFA-APC binder is in the same order to that reported from the C-S-H gels, formed by hydration of cement minerals alite and belite in field concretes that contain chloride ions supplied from the de-icing salt (halite) applied in winter [13]. This means that an excess amount of the chloride ions, which could not enter the Friedel’s salt, are adsorbed by the C-S-H gels that form by hydration of the glass phases. It will be helpful to assess the long-term durability of the chloride-bearing hydrates derived from the APC residues in light of petrography and chemistry.

**Role of AFm Phases**

AFm phases are represented by 3CaO-Al\(_2\)O\(_3\)-Ca[Cl, SO\(_4\), 2OH, CO\(_3\)]\(\cdot\)nH\(_2\)O and AFt phases by 3CaO-Al\(_2\)O\(_3\)-3Ca[Cl, SO\(_4\), 2OH, CO\(_3\)]\(\cdot\)2OH, 3CaO-2Al\(_2\)O\(_3\)-Ca[Cl, SO\(_4\), 2OH, CO\(_3\)]\(\cdot\)2H\(_2\)O\(_2\). In the presence of limestone powder or hydraulic lime, formation of the AFm phase in the cementitious materials has often been held to improve mechanical properties. For example, addition of limestone powder to Portland cement mortar forms an AFm phase monocalciumaluminate 3CaO-Al\(_2\)O\(_3\)-CaCl\(_2\)·11H\(_2\)O (basal reflection: 11.6°2θ), but there are arguments as to positive effect on the strength development of the binder. Some [21] admit this while others [22] do not. Likewise, hydraulic lime (containing calcite) added to the PFA produces another AFm phase hemicalciumaluminate 3CaO-Al\(_2\)O\(_3\)-Ca[Cl, SO\(_4\), 2OH]\(\cdot\)10.5H\(_2\)O (10.8°2θ). However, strength development of the PFA-lime binder system is attributed to densification of the microstructure of amorphous C-S-H gel that forms from PFA through a pozzolanic reaction (e.g. [23]).

Friedel’s salt is a stable AFm phase, having a solid solution with hydrocalcium 3CaO-Al\(_2\)O\(_3\)-Ca(OH)\(_2\)·12H\(_2\)O (11.0°2θ), which is formed through an intermediate metastable compound Kuzel’s salt from monosulfate after conversion from ettringite in the Portland cement mortar and concrete exposed to the chloride ingress. Because Friedel’s salt fixes chloride ions, the mechanism of formation of this hydrate has been utilised for desalination of water in recycling plant [24].

In the PFA-APC binder system studied here, the occurrence of crystalline hydrates of the AFm phases (Kuzel’s salt and Friedel’s salt) and AFt phase (ettringite) was rather local, surrounding the Ca-Al-rich particles which originally belonged to the APC residues. Hence, these AFm phases would not be a major contributing factor to the strength development of the binder. Kuzel’s salt was metastable and was replaced by more stable combination of ettringite and Friedel’s salt, and which latter fixed chloride ions that had originally been present as soluble NaCl and KCl in the APC residues.

**Conclusions**

Stabilisation was found to be effective in reclaiming the losses caused by importing limestone quarry waste dust into a qualified UK road foundation material, Type 1 Unbound Mixture. To appreciate sustainability and cost, a novel mixture of PFA and APC residues, creating a new binder for pavement material stabilisation purposes, was developed. Unconfined compressive strength of the Type 1 Unbound Mixture containing 20% extra limestone dust and stabilised by PFA-APC residues binder demonstrated the capability of the novel binder in enhancing new mixture’s mechanical properties in the course of time. Petrographic study of the novel binder explained the reasoning and what has actually caused the strength behind the scene. The following conclusions are drawn from this study as conclusion summaries:

1. PFA-APC binder could effectively stabilise the unbound material of high quantity of limestone quarry waste dust although binding has had a slow process.
2. In comparison to a well-known PFA activator, lime, APC residues had higher premium performance which meets further construction purposes by providing greater strength and contractor purposes by quicker stabilising reactions.
3. The binding process is attributed to the formation of X-ray amorphous C-S-H gel by the pozzolanic reaction, which took place between the lime of APC and the glass phases contained in both APC residues and PFA.
4. The mechanism of the binding in the PFA-APC residues is similar to that of the hardening process of the blended Portland cement, such as fly ash cement, as well as of the PFA-lime system, rather than the formation of crystalline hydrates such as AFm phases.
5. Chloride ions in the APC residues are fixed by the Friedel’s salt and trapped by the C-S-H gel, while metastable Kuzel’s salt decomposes into more stable combination of ettringite and Friedel’s salt.

**References**


