Reclaimed Calcined Clay for Low Carbon Cements (Re-C3)

Summary Report

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3. Executive Summary

This report presents the findings of a technical study aimed at enhancing the circular economy in the UK's construction industry through the utilization of calcined reclaimed clays and finely ground bricks as supplementary cementitious materials (SCMs) in cement and concrete production.

The project aimed to address the key barriers to production and use of reclaimed calcined clays. This was achieved through the completion of the following work:

- Sourcing/processing/characterisation of reclaimed UK clays for use as SCMs (waste bricks) or as feedstock materials for the production of SCMs (interburden/overburden raw clays)
- Laboratory testing and analytical studies on: heating parameters (interburden/overburden raw clays only), pozzolanic reactivity, reactivity in cements and characterisation of calcined materials and hydrated cements containing calcined clays.
- Pilot production of calcined clays using two heating technologies:
  - Rotary kiln – a commonly available technology in the UK
  - Flash calcination – a new and innovative heating technique not yet trialled in the UK.
- Conformity testing of:
  - Calcined clays (from pilot production) and brick powders against appropriate standards (BS 8615:2019 Specification for pozzolanic materials for use with Portland cement - Natural pozzolana and natural calcined pozzolana)
  - Binary (BS EN 197:2011 Cement - Composition, specifications and conformity criteria for common cements) and ternary (BS EN 197-5:2021 Cement - Portland-composite cement CEM II/C-M and Composite cement CEM VI) calcined clay cements
  - Standard concrete mixes (BS 8500:2023 Concrete. Complementary British Standard to BS EN 206 Specification for constituent materials and concrete) containing formulated binary and ternary cements
- Demonstration of the pilot calcined clays for use as an SCM for precast concrete panels

3.1. Key Findings

- Reclaimed clays from operating quarries and finely ground bricks demonstrate significant potential as SCMs, contributing to the advancement of the UK's circular economy.
- Optimal performance of calcined clays requires tailored optimization for specific characteristics such as calcination temperature, particle size distribution and surface area.
- Both rotary and flash kilns can effectively produce calcined clays, with no discernible difference in compressive strength of blended cements observed between production methods.
- Recommendations for minor revisions to BS 8615:2019 have been proposed, which include: removal of the 90-day activity index requirement and relaxation of the water requirement.

- All seven of the calcined clays produced using pilot facilities performed exceptionally well in both standard and self-compacting concrete mixes. This provides the industry with the necessary confidence that calcined clays perform similarly to mainstream SCMs and in some cases, better.
- Also clays with less than 40% kaolinite content exhibit promising reactivity and are BS 8615 complaint.
- Achieving a cement strength class of 42.5 N is feasible through both binary (CEM I + calcined clay) and ternary (CEM I + calcined clay + limestone fines) blends with calcined clay as a component, with modest continued strength gain beyond 28 days.
- Additional sulfate or limestone incorporation in cements containing calcined clay does not appear to be necessary in terms of contribution to compressive strength, and the synergy between limestone powder and calcined clay (multi-component cements) is minimal.
- Workability issues in mortars and concretes can be addressed with appropriate superplasticizers, while strength development remains comparable to or superior to reference materials.
- In terms of durability, excellent chloride resistance is noted, and no issues are anticipated in relation to freeze/thaw, alkali silica reaction (ASR), or external sulfate attack.
- Carbonation levels in calcined clay concrete are marginally higher compared to reference concretes. This reduces with higher strength concretes.
- Long term durability tests (i.e. 2 year: carbonation, sulfate and ASR) are ongoing.

In conclusion, the findings of this study underscore the significant potential of calcined reclaimed clays and finely ground bricks as SCMs, offering sustainable solutions for the construction industry while contributing to the circular economy objectives of the UK. Implementation of the recommendations outlined in this report has the potential to drive positive environmental and economic outcomes in the sector.

4. Introduction

4.1. Background to Cement Manufacture

Cement is the essential ingredient in concrete, which is the world's second most consumed substance after water. Portland cement was first patented in Britain by a bricklayer, Joseph Aspdin, from Leeds in 1824 and to this day is one of society's most useful materials; no modern school, house, road, hospital or bridge could be built without it.

Cement is a manufactured powder that, when mixed with water and aggregates, produces concrete. The cement-making process can be summarised in 3 basic steps:

1. Raw material preparation: Calcium carbonate from chalk or limestone plus smaller amounts of clay and other materials containing silica, alumina and iron are quarried, crushed, ground and blended to the correct specification.
2. Clinker production: The raw meal is heated in a kiln at temperatures around 1,450°C, this is a highly CO2 intensive process with CO2 formed in the decarbonisation of the calcium carbonate, from the fuels required and the electrical energy used. The product is then cooled to produce an intermediate component known as clinker.
3. Cement production: The clinker is ground with other minerals including gypsum to produce cement.

Considerable progress has already been made in reducing emissions in UK cement manufacture (See *Figure 1*) through investment in newer more efficient plant and fuel switching from coal to biomass fuels.
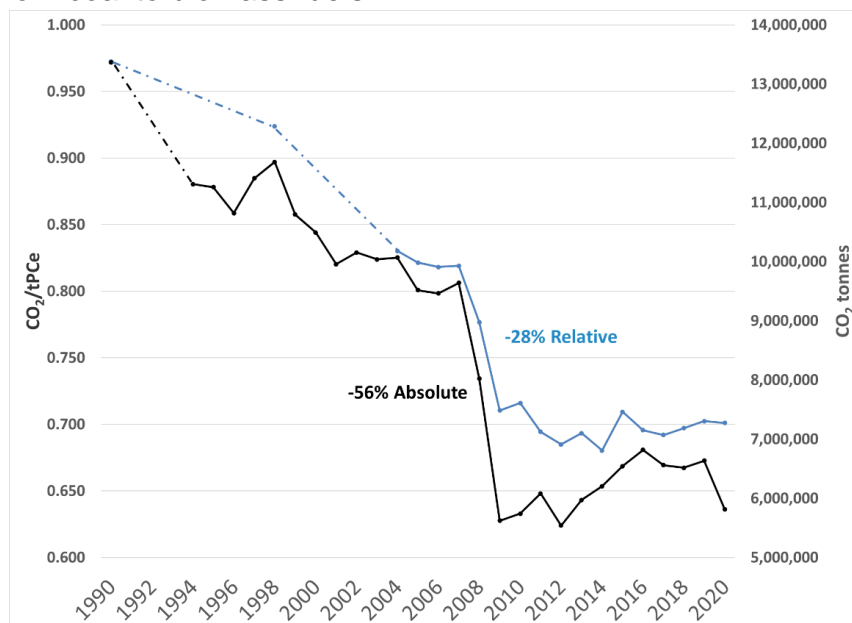
Figure 1: Reduction in absolute and relative emissions from UK cement manufacture 1990-2020

One of the main levers to further reduce CO_2 emissions from cement manufacture is reducing clinker content in cement by partial replacement with supplementary

cementitious materials (SCMs) such as fly ash, GGBS and/or limestone, reducing the CO_2/t (CO_2 per tonne of cement).

4.2.   Supplementary Cementitious Materials (SCMs)

SCMs generally contribute to the properties of hardened concrete mainly through their hydraulic or pozzolanic reactivity. Today these are primarily ground granulated blast furnace slag (GGBS) a by-product in the generation of steel from Iron ore; fly ash (FA) a waste by-product from the combustion of coal in power plants and ground limestone. These can be used individually with Portland cement CEM I to produce a binary cement or in specific combinations to produce a ternary cement. Ground limestone is mostly inert and its use in cements is restricted to lower quantities than GGBS or FA. The problem with the use of GGBS and FA in the UK is one of supply. These materials are no longer produced in the UK. Although both FA and GGBS is available on the international market, preference should be to source domestically produced materials ahead of imports as the most sustainable, lowest CO_2 solution. Therefore, other reactive SCMs need to be investigated.

There is already a small but developing global market and supply chain for calcined clay cement. However calcined clay is not currently manufactured or used in the UK.

4.3.   Project Aim and Methodology

In this project, reclaimed clays from several different UK sources were characterised, calcined and tested for the properties useful for cement and concrete production. The clays chosen are from a number of different sites with differing clay species. This is different from other projects analysing clays that have mainly tested materials with high kaolinite content. The project clays are a mixture of over/inter-burden, washings from kaolinite production and clays that are available but not currently used in existing quarries.

A number of these clays were calcined at pilot scale (1 tonne of each material) using two different heating methods to enable comparisons of the resulting properties. The two methods trialled were:

1. Rotary kiln – a commonly available technology in the UK
2. Flash calcination – a new and innovative heating technique not yet trialled in the UK. This technology has a lower heat consumption when calcining clays compared to the use of a rotary kiln.

In addition, a pre-calcined material, in the form of waste fired clay brick, was also evaluated. The prepared materials were expertly formulated into cement compositions and tested for conformity to EU/UK standards. Both fresh and hardened properties were examined to maximise the market potential of the new cements. The information from the testing and pilot work is being presented to the national standards body to modify the national concrete standards to remove a barrier to market for these new cements.

Deployment of these new cements on the UK market could reduce waste by 1.4 million tonnes and reduce the embodied CO_2 of cement by around 10-30% compared to the market leading CEM I cement.

This report summarises the output from key project work packages. Full reports for each section have been produced and are given in the attached appendices. The list below details the planned and additional work packages, indicates the work completed in these sections, and where applicable the sections of the report these work packages relate to:

WORK PACKAGE A: Project management – Project management was led by MPA with support from all partners. Over the course of the project over 100 technical and steering group meetings were held.

WORK PACKAGE B: Technical dossier on activated clay cements – MPA with the support of the UCL produced a technical dossier on calcined clays. This document was used to advance the project partners knowledge and update project plans. The dossier is available in **Appendix 1**.

WORK PACKAGE C: Activation of clays – Imerys characterized the 10 initial raw clay samples, activated them by laboratory furnace calcination and characterized the resultant calcined clays in preparation for Work Package E. See **section 5**.

WORKPACKAGE D: Waste fired clay bricks - Forterra prepared two samples of brick powder. These materials are reclaimed from Brick manufacturing and ground to produce a pozzolanic cement replacement. See **section 6**.

WORK PACKAGE E: Cement study (without admixtures) – For this report Work Packages E and G were combined. UCL carried out a set of experiments to understand the optimal heating parameters for the ten raw clays. Following this, all calcined materials including the two brick powders were characterised using a combination of physical and chemical methods. In addition, a range of binary and ternary cements were formulated from each of the calcined materials and studies on their fresh properties (with/without admixtures), hardened properties , hydration process and phase assemblage. See **section 7**.

WORK PACKAGE F: Admixture formulation – Prior to the project commencement it was unclear whether new admixtures would need to be formulated. The project worked with members of the Cement Admixtures Association (CAA) throughout, and it became clear that current admixtures could be used and that developing a specific formulation would be unlikely to satisfy the requirement of all the different clays investigated.

WORK PACKAGE G: Cement study (with admixtures) – See Work Package E

WORK PACKAGE H: Selection of clays for pilot production – After discussions between project partners, it was decided that the four clays to be taken through pilot scale production would not necessarily have the highest reactivity but would give a good variance of the available clay mineralogy and be readily available in project partners quarries in sufficient quantities.

WORK PACKAGE I: Pilot industry scale activation (rotary/flash) + grinding – The four clays were calcined to provide 1 tonne of material for each clay to be used in the cement and concrete testing, and for the concrete application demonstration. To allow the comparison of calcination methods, 3 clays were produced by each method with two clays manufactured using both methods.

Additional WORK PACKAGE: Characterisation of pilot calcined clays – Imerys characterised the clays produced to confirm complete calcination of the pilot scale manufactured clays and to inform technical discussions. This work is summarised in **section 8.**

Additional WORK PACKAGE: Refined mineralogical analysis of the raw clays by X-ray Diffraction (XRD) – The mineralogical composition of the 10 raw clays was

analysed by X-ray diffraction (XRD) as part of Work Package C early on in the project. Later results suggested that this initial XRD analysis was not accurate. Forterra, with support from Imerys and UCL produced an analytical methodology to determine the kaolinite content. See **section 9.**

WORK PACKAGE J: Validation of commercial cements – MPA cement members Tarmac Cement and Heidelberg Materials UK characterised the four clays calcined at pilot scale and one brick powder and tested performance of binary and ternary blended cements made with these powders in accordance with EN 197-1. The work included checking compliance with BS 8615. See **section 10.**

WORK PACKAGE K: Concrete study – The University of Dundee (UoD) completed a thorough suite of testing including strengths and durability in binary and ternary concretes, containing various levels of cement replacement up to 40%. See **section 11**.

WORK PACKAGE L: Demonstration project – Forterra held a demonstration of calcined clay cements at their site in Somercotes Derbyshire. Forterra assessed the suitability of the calcined clays used in the project for self-compacting concretes and conducted the factory production of pre-cast retaining wall elements. **See section 12.**

5. Activation of Reclaimed Clays: Characterisation of Raw and Lab Calcined Clay

Section Authors: Barbara Benevenuti, Deeba Ansari, Tony Newton
Detailed report available in: Appendix 2 - Characterization of raw and lab calcined clays

5.1. Introduction

The goal of this section was to characterise the 10 raw clay samples, to activate them by laboratory furnace calcination, to characterise the lab calcined clays and to prepare them to be further evaluated by UCL. In this summary report will be presented the main characteristics of the raw and lab calcined clays, which were considered, together with the UCL results, in the selection of the 4 clays to be calcined at pilot scale.

5.2. Materials and Methods

The tested raw clays (RC) and the companies providing them are presented in *Table 1* below. After laboratory calcination the samples are designated as CC (calcined clays).

Supplier	Raw clay ID		Calcined clay ID
Imerys	RC1		CC1-800-3
Imerys	RC2		CC2-800-3
Imerys	RC3		CC3-800-3
Imerys	RC4	Laboratory oven calcination at 800°C or 850°C for 3h	CC4-800-3
Imerys	RC5		CC5-800-3
Heidelberg	RC6		CC6-850-3
Heidelberg	RC7		CC7-850-3
Tarmac	RC8		CC8-850-3
Tarmac	RC9		CC9-850-3
Aggregates Industry	RC10		CC10-850-3

Table 1: Raw and lab calcined clays nomenclature

The raw and lab calcined clays had their chemical composition quantified by X-ray fluorescence (XRF), using a Panalytical Zetium and the SuperQ 6.3 software, using glass beads samples; their mineralogical composition semi-quantified by X-ray diffraction (XRD), using a Panalytical X'Pert Pro and the Highscore software and their colour evaluated by a X-Rite Ci4200 colorimeter. Furthermore, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), using an ATG/DSC NETZSCH STA449F3, were carried out to quantify their mass loss and to help identifying the dehydroxylation and other reactions taking place when the clays are exposed to high temperatures.

5.3. Main Results

The chemical composition of the raw clays was quantified by XRF and is presented

together with the loss on ignition (LOI) values in *Table 2*. As the chemical composition is not significantly modified after calcination, that of the calcined clays is not presented here, but can be seen in the appendix 2 report describing the work package C (WPC) full results.

The main parameter to be considered is the Al_2O_3 content, as it is an indication of the amount of clay minerals (potentially active phases) present in the material. Among the existing clay minerals, kaolinite is the most reactive, and its amount is usually the parameter considered to evaluate the reactivity (the pozzolanic activity) of a clay. *Table 2* indicates the maximum possible amount of kaolinite in the clays, calculated by stoichiometry from their Al_2O_3 content.

The iron content is related to the colour of the clay, especially after calcination. *Table 2* also presented the colour of each clay after calcination.

Sample	LOI	Al_2O_3	SiO_2	K_2O	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	P_2O_5	Max. kaolinite content from Al2O3	Colour of the lab calcined clay
RC1	2,5	16	73,3	5,3	1,6	0,1	0,1	0,3	0,6	0,1	40	
RC2	8,7	31,9	52,7	4,2	1,5	0,1	0,1	0,4	0,3	0,1	81	
RC3	10,5	34,5	50	3	1,2	0	0,1	0,4	0,2	0,1	87	
RC4	10,9	35,1	49,4	2,9	1	0,1	0,1	0,4	0,2	0,1	89	
RC5	54,7	18,3	23,6	0,8	1,4	0,4	0,4	0,2	0,1	0,0	46	
RC6	14,2	11,6	47,8	2,6	5	0,7	15,3	2,4	0,3	0,1	29	
RC7	10,9	21,7	52,5	2,8	7,3	1	1,3	1,8	0,3	0,3	55	
RC8	10	20,9	55,3	2,4	6,7	1,2	1,7	1,3	0,3	0,2	53	
RC9	9,2	23,9	53,5	1,2	8	1,1	1,7	1,1	0,3	0,1	61	
RC10	11,9	22,1	48,9	1,7	7,8	0,9	4	1,9	0,4	0,3	56	

Table 2: LOI, Chemical composition by XRF and calculated maximum kaolinite content of the raw clays and colour of calcined clays

The kaolinite content of the clays was quantified by XRD and by calculation from TGA, the results from both methods were not always in agreement. Furthermore, in some cases the kaolinite content as measured by semi-quantitative XRD was above the maximum value calculated by the Al_2O_3 content, as indicated in red in *Table 3*.

Samples	Max. kaolinite content from Al_2O_3 amount on XRF	Kaolinite content calculated from water loss in the range 400-700°C in TGA	Kaolinite content from XRD
RC1	40	15	8
RC2	81	59	58
RC3	87	69	71
RC4	89	73	78
RC5	46	41	49*
RC6	29	26	42
RC7	55	43	60
RC8	53	43	66
RC9	61	56	89
RC10	56	59	78

Table 3: Kaolinite content calculated from XRF, TGA and XRD

The XRD measures 89% of kaolinite in the RC5, but it doesn't consider the 54.7% of organic matter in the material. When taking it into account, the kaolinite content corresponds to 49%.

It is important to note that the XRD used for these measurements is calibrated to high kaolinite clays, being less accurate for materials containing more diverse compositions.

The complete XRD results can be found in appendix 2. Besides the kaolinite and other clay minerals content, they indicate the amount of impurities in the clays. One major impurity is quartz, which will have a negative impact on the grinding of the calcined material. Clays richer in quartz should be harder to grind, and for such clays the optimal fineness must be investigated, as there is no advantage in spend energy to reduce the grain size of the quartz particles.

The kaolinite content estimated by TGA seems to be more coherent with the chemistry of the clays than by XRD, but they are certainly not precise. By observing the TGA and DSC profiles (not presented here, they can be found in the appendix 2) it is clear that most clays contain not only kaolinite and inert phases, but also some other phases that undergo changes under high temperatures. These other phases interfere with the quantification of kaolinite by TGA, leading to the overestimation of this phase.

These results put into evidence the difficulty of precisely quantify the kaolinite content of a clay, which is very relevant, as it is the main parameter considered to qualify a clay. This topic is explored in a **section 9** of this report, where the best estimate of material mineralogy is given.

Nevertheless, by analysing the whole set of results, it is possible to classify the 10 candidate clays in two groups: the kaolinitic clays, which contains mostly kaolinite, along with inert impurities such as quartz, and the mixed clays, which also contains other clays minerals, such as illite or montmorillonite. The Imerys clays (RC 1 to 5) and Tarmac's RC9 belong to the first group, while the remaining clays belong to the second.

From the literature results, which usually correlate the reactivity of the clay solely to the amount of kaolinite it contains, one could expect the clays from the kaolinitic group to present better reactivity than the ones from the mixed group. It is however necessary to evaluate if the other clays phases present in these samples also contribute to the reactivity.

5.4. Conclusions and Recommendations

The main conclusions drawn from the results obtained in work package C are as follows:

- The candidate clays cover a wide range of chemical compositions. Their alumina content, an indicator of the total clay mineral contents, range from 11% to 35%.
- The quantification of their kaolinite content was made by XRD and TGA, but the results are not always concordant, and seem to be overestimated. The TGA, which seems to be the most reliable method in our case, indicated that the clays

have kaolinite contents going from 15% to 73%. However, the quantification of kaolinite is complex.

- The quantification of kaolinite is a complex matter, even if in the literature this aspect is not frequently mentioned. Most articles rely on the TGA to quantify the kaolinite, but from the results obtained in this study, we observe that many other phases can be confounded with kaolinite when using this method. Further investigation is needed to define the most precise way of quantifying kaolinite and other clay minerals.

- Despite the lack of accuracy on the kaolinite quantification, it is still possible to classify the clays in two groups: kaolinitic clays and mixed clays. Further investigation in the other work packages is needed to evaluate the reactivity (pozzolanic activity) of the clays from the different groups.

- The optimal calcination temperature for each clay will depend on its nature. Finding it for the kaolinitic clays should be straight forward, but for mixed clays the determination is more complex, as the different minerals present respond in different ways to the temperature.

- Besides the reactivity, the composition of the clay will also impact on the colour and on the ease of grinding of the clays. Materials richer in iron will have a darker and reddish tone, and those richer in silica will be harder to grind.

6. Waste Fired Clay Bricks – Brick Powder

Section Authors: Lisa Wachter (Forterra) & Andrew Smith (Forterra)
Detailed report available in: Appendix 3 - Activation of waste fired bricks

6.1. Introduction

In addition to the raw clays identified and provided by the Project Partners in this programme of work, Forterra proposed the potential of using waste fired clay brick as an alternative source of "calcined clay".

Unlike the work undertaken on the raw clays, the firing conditions, (calcination) for the bricks is dictated by the desired properties of the bricks in service, therefore typically fired up to temperatures that fall between 950°C and 1150°C, depending upon the brick type and the raw materials used.

As part of this project, Forterra proposed looking at 2 vastly different waste brick materials, a "London Brick Fletton" brick waste from Forterra's Kings Dyke brickworks and a "Stock" buff soft mud brick from Measham brickworks. Both have very different primary raw materials, manufacturing process and ultimately different firing temperatures, indicative of potentially very different "calcined clay properties".

Waste brick arisings typically come from the sorting process, prior to packaging, and can be a result of mechanical damage to the bricks, breakages, cracking or chipping, irregular or out of specification colour and texture. Such arisings are typically processed, where they are put through a primary crusher and potentially screened to give coarse aggregate and 0-4mm dust/sand.

Use of the part processed crushed brick waste as a calcined clay type Supplementary Cementitious Material (SCM), offers a "higher value" alternative use for these arisings, and ultimately provides an indication that finely milled clay brick construction and demolition waste could be utilised as a source of SCM.

The chemistry and mineralogy of the fired brick waste is presented in this report along with details of the assessment of reactive silica content and the ball milling process and specification of the final milled brick waste powder for each brick type.

6.2. Brick Waste Materials

Forterra evaluated 2 brick waste streams for the project, the KDBP (Kings Dyke Brick Powder) and the MBB (Measham Buff Brick). These 2 brick waste streams represent very different primary brick making raw materials, the KDBP is a Jurassic, Lower Oxford Clay, whilst the MBB is a Carboniferous Fireclay. Both have very distinctive mineralogy's and chemistries.

The chemistry of both the raw clays and the fired brick materials reflects the fundamental composition of the original raw material and the loss of volatiles during the high temperature firing process the bricks go through.

The key differences between the 2 clay types, in terms of chemistry, are the SiO_2 and Al_2O_3 content, and the CaO content, in terms of the oxides and the carbon and sulphur

content. The fireclay is by far the simplest in terms of chemistry, which is subsequently reflected in the raw clay mineralogy discussed later. The fireclay is dominated by Al_2O_3 and SiO_2, with relatively high alumina:silica ratio. This is indicative of clay rich raw materials, which is borne out by the typical fireclay mineralogy being dominated by kaolinite and illite, along with quartz.

The Lower Oxford Clay (LOC) is a more complex raw material, higher CaO content, higher MgO content, total alkalis are higher (Na_2O, K_2O, MgO and CaO), as are the carbon and sulphur content and associated LOI. The LOC contains a number of minerals and organic carbon that decompose during the firing process and thus are lost in the fired brick. The CaO relates to fossiliferous and finely disseminated calcite and dolomite within the clay. The high carbon content relates to carbon in both organic and inorganic phases, the inorganic being in the form of carbonate (calcite and dolomite) and finely disseminated organic carbon throughout the deposit. The high sulphur content relates to pyritic iron sulphide and traces of gypsum within the clay body.

Fireclays in the raw state are relatively simple clay deposits, predominantly (>90%) made up of kaolinite, illite and fine-grained quartz. The Lower Oxford Clay on the other hand is a more complex mix of illite, kaolinite and chlorite clay minerals with variable amounts of quartz, calcite, gypsum pyrite and feldspars, reflecting the very anoxic deposition conditions during the Upper Jurassic Period. In addition, the clay also contains approximately 6-7% organic carbon.

In addition to the determination of chemistry and mineralogy of the brick powders, the "Reactive Silica" content was also assessed, to the test method described in EN 196-2. The results showed that despite the MBB containing a higher kaolinite content, and higher silica, typically a measure of the reactivity of the clay type, the lower firing temperature of the KDBP resulted in more of the silica being available for reaction as a pozzolana, as can be seen in *Table 4*.

	KDBP	MBB
Total SiO$_2$ (by XRF)	54.16%	71.40%
Reactive SiO$_2$ (by EN 196-2)	39.74%	43.23%
% Reactive	73.4%	60.5%

Table 4: Reactive SiO$_2$ content of the 2 brick waste powders

6.3.   Waste Brick Processing

Brick waste arising from the sites ranges in size from the standard brick (215 x 102.5 x 65mm) through to fragments of broken bricks, the first process is a mobile plant jaw crusher on site which reduces the bricks down to 0-20mm.

The crushed brick waste was dried at 105°C for 48 hours before being allowed to cool and then loaded into the ball mill. Each milling process used approximately 70kg ± 4kg and was milled for 180 minutes (KDBP) or 210 minutes (MBB), producing the particle size distributions suitable for use as an SCM.

	KDBP	MBB	Target
Milling Time @ 33rpm (minutes)	180	210	
Dx90 (µm)	95.7	87.7	< 115
Dx50 (µm)	14.7	13.8	< 15
Dx10 (µm)	1.49	1.42	< 1.5
Specific Surface Area (SSA) m²/kg	1402	1484	> 1400

Table 5: Resulting particle size distribution and specific surface area for the brick waste materials ball milled at 33rpm for 180 minutes

6.4.   Brick Powder as a SCM

Investigations into new raw materials, cements and admixtures were carried out on a Standard Lab Concrete (SLC) to maintain continuity in all assessments. This SLC is based on a "Concrete Wall Panel" mix design.
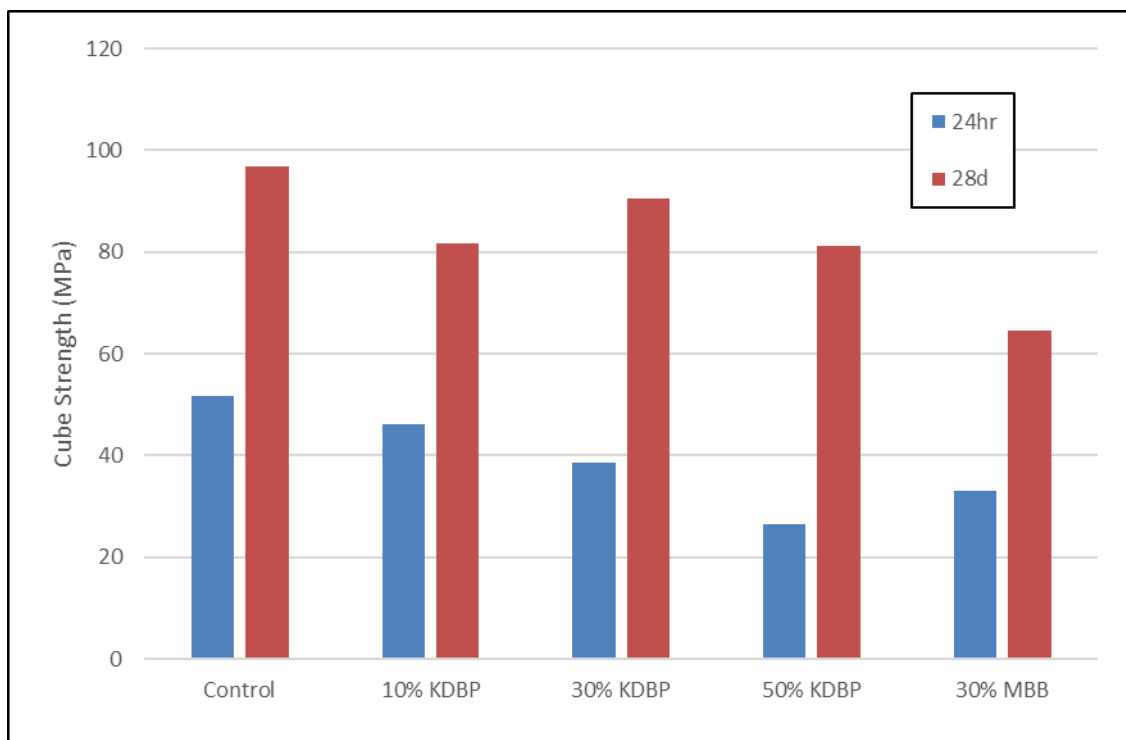
Figure 2: 24hr and 28d compressive strengths for the standard laboratory SCC C60/70 mix design with different brick powder replacements

Of particular interest to Forterra is the impact calcined clay cements has on the early-stage strength development of concrete, especially when using a Self Compacting Concrete (SCC) which is designed to achieve at least 15N/mm² compressive strength at 15 hours to enable safe demoulding and lifting of concrete units cast the previous day. The mix design is therefore over designed (via a higher cement content) to achieve the production requirements, i.e. demoulding at 15hrs, rather than the product/unit requirements.

6.5.   Conclusions

The main conclusions drawn from the work carried out in Work Package D are as follows:

- It appears that the KDBP brick powder is acting as a SCM even at replacement levels of CEM I up to 50%.
- Whilst 24hr strength are significantly compromised, the 28days strengths are approximately 80% of the Control sample concrete, indicating that the KDBP is acting during the latter stages of strength development rather than during the early strength gain period.

7. Cement Study Without or With Admixtures

Section Authors: Yun Bai (UCL), Yubin Cao (UCL), Yanru Wang (UCL), Tongbo Sui (UCL) & Shi Shi (UCL)

Detailed reports available in:
1. Appendix 4 - Characterisation, calcination temperature optimization and pozzolanic reactivity evaluation of UK reclaimed clays
2. Appendix 5 - Calcined clay blended binary and ternary cement study without admixtures
3. Appendix 6 - Calcined clay blended binary and ternary cement study with admixtures
4. Appendix 7 - Effect of sulphates on the performance of low-carbon cement formulated with different calcined clays

7.1. Introduction

Four Work packages of the project were conducted at UCL, including Work packages E and G, as well as two Extra Work packages. In total, ten raw clays and two brick powders were characterised by TGA test first and the ten raw clays were then calcined at different temperatures based on the TGA results. Followed by this, the pozzolanic reactivity of calcined clays was evaluated by the R3 method [1]. However, considering the low-reactivity nature of some of the calcined clays investigated in this project, the R3 method was slightly modified by reducing the ratio between calcium hydroxide and calcined clay from three to two.

Using the clays calcined at the established optimum temperature, the fresh properties, hydration kinetics, compressive strength and hydration products of calcined clay blended binary and ternary cement systems with or without superplasticiser were then studied. To further optimise the performance of the calcined clay blended binary and ternary cement systems, the effect of sulphate content on the fresh and hardened properties of blends was also studied and the optimum sulphate content was then recommended primarily based on the strength and hydration kinetics property.

7.2. Constituent Material Characteristics

The materials used in this study include ten raw clays, four calcined clays, two brick powders, fly ash, CEM I, limestone powder, ground granulated blastfurnace slag, metakaolin, gypsum and superplasticiser. The properties of all materials and admixture can be found in appendices 4-7. The physical and chemical characteristics of the calcined clays and brick powder can be found in Work Packages C and J. It should be noted that three calcination techniques (i.e., **furnace calcination**, **rotary calcination** and **flash calcination**) were adopted at the different stages of the study in order to transfer and scale up the systematic and small-scale laboratory studies to industrial practice. Specifically, the small-scale furnace calcined clays were used in Work Packages E & G, whilst the flash and rotary calcined clays were used in sulphate optimization. A list of the materials and their nomenclatures are given in *Table 6* below.

Material ID	Description	Material ID	Description
RC1	LP637 Imerys (Raw clay)	CC2F	RC2 Flash Calcined
RC2	LP638 Imerys (Raw clay)	CC2R	RC2 Rotary Calcined
RC3	LP639 Imerys (Raw clay)	CC3R	RC3 Rotary Calcined
RC4	LP640 Imerys (Raw clay)	CC7F	RC7 Flash Calcined
RC5	LP641 Imerys (Raw clay)	CC9F	RC9 Flash Calcined
RC6	21 GHS 284 Heidelberg Mixed Clay (Raw clay)	CC9R	RC9 Rotary Calcined
RC7	21 GHS 285 Heidelberg Upper Lias Clay (Raw clay)	KDBP	KD-Brick Powder
RC8	21 GHS 286 Maxey Clay Sample Tarmac (Raw clay)	BUBP	Buff-Brick powder
RC9	21 GHS 287 Keele Clay Sample Tarmac (Raw clay)	PC	Portland Cement
RC10	21 GHS 290 Clay Aggregate Industry (Raw clay)	L	Limestone powder
PC	Portland Cement	FA	Category N Fly Ash
MK	Commercial Metakaolin	GGBS	Ground Granulated Blastfurnace Slag

Table 6: Nomenclature for constituent materials used in this study

*Note: In addition to the flash and rotary calcined clays, the calcined clay used in Work Package E and G was furnace calcined clay provided by Imerys, which is named CC2, CC3, CC7 and CC9.

The particle size distribution (tested by University of Dundee using laser diffraction) and the morphology (investigated by University College London) of flash and rotary calcined clays are shown in Figure 3 and Figure 4, respectively. In general, the rotary calcined clays possess finer particles, ranging from 0.3-20µm, than that of flash calcined clays. It should be noted that the production processes of flash and rotary calcination were different in this study. The former consists of drying → pulverising → calcination → grinding, whilst the latter involves crushing → calcination → grinding.
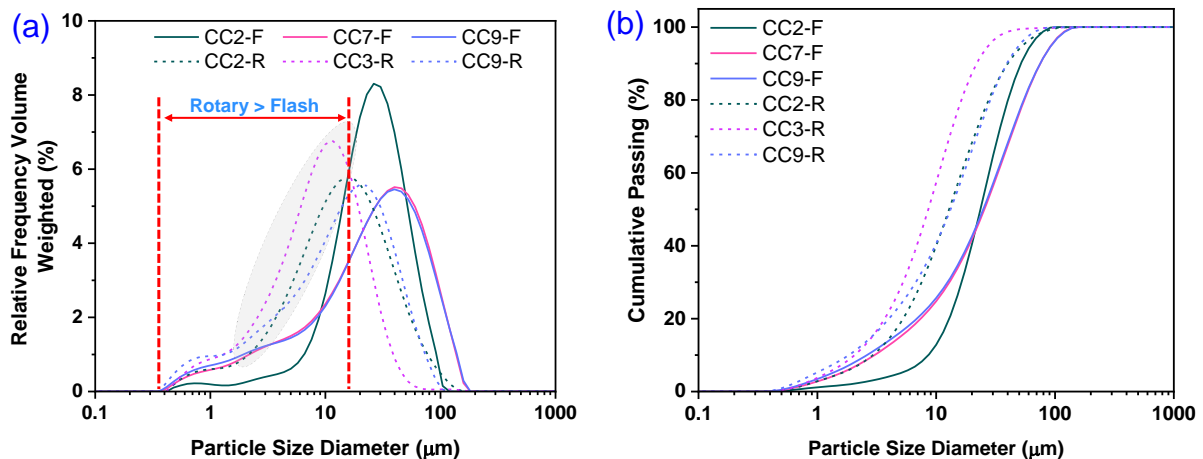
Figure 3: Particle size characteristics of flash and rotary calcined clays (a) particle size distribution; (b) cumulative passing

Figure 4 shows the morphology of flash calcined clay two. It can be seen that after flash calcination, two main features can be observed, i.e., layered structure and spherical morphology. Although the spherical particles are anticipated to increase the workability (or reduce the water demand), the quantity of the spherical particles are considered to be insignificant.

Elem	Wt %	At %	K-Ratio	Z	A
O K	45.47	62.57	0.1559	1.0439	0.3282
AlK	21.55	17.59	0.1455	0.9719	0.6899
SiK	21.73	17.03	0.1316	1.0002	0.6053
K K	1.49	0.84	0.0120	0.9504	0.8465
CaK	0.41	0.23	0.0035	0.9725	0.8822
FeK	2.48	0.98	0.0219	0.8852	0.9913
AuL	6.85	0.77	0.0463	0.6537	1.0329
Total	100.00	100.00			
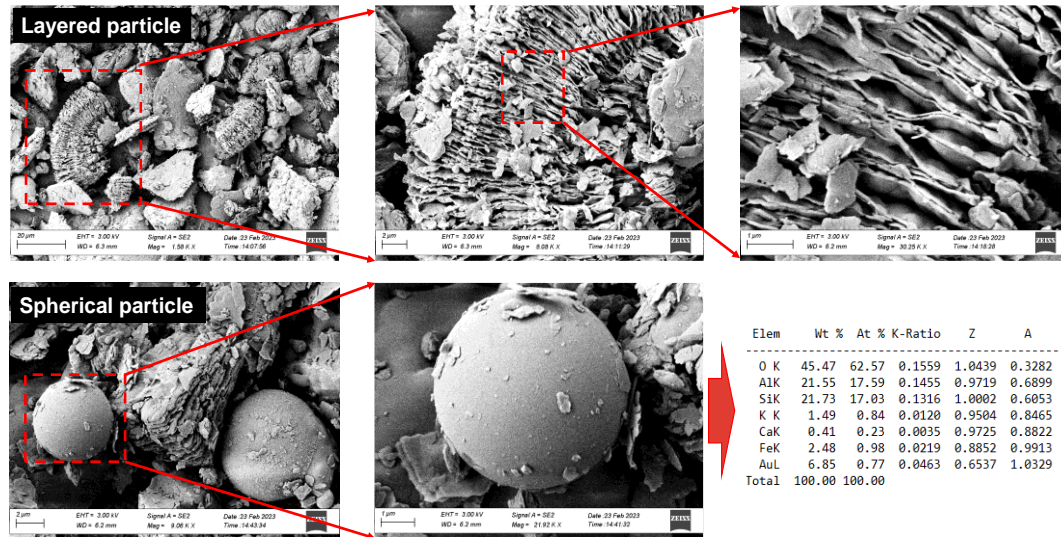
Figure 4: Morphology of calcined clay mineral in CC2F generated by flash calcination process

7.3.   The Formulations of Binary and Ternary Cement Systems

The formulations of the calcined clay blends investigated in this project are given in *Table 7* below. A fixed water to binder ratio of 0.35 was established through trial mixes and then adopted in the following studies. As the water demand of calcined clays varies, different dosages of superplasticiser were added to achieve the same flowability as that of the fly ash blended cement paste without adding superplasticiser which was adopted as the reference. The flowability of calcined clay blended cement paste was tested as per ASTM C1437-20, and the results are shown under section 7.5.1.

Cement system	w/c ratio	PC	Calcined clay/brick powder	Limestone powder
Binary	0.35	70%	30%	-
Ternary	0.35	55%	30%	15%

Table 7: Summary of blended cement paste mix proportions

7.4.   Characterisation, Thermal Activation and Pozzolanic Reactivity Evaluation

Ten raw clays were ground and sieved first (part of the calcined clays are shown in *Figure 5*), and then calcined in a lab furnace at different temperatures established from TGA tests (as shown in Table 8). The reddish colour of the CC9 (i.e., after RC9 being calcined) could be attributed to the changes in iron oxides [2, 3]. However, the transformation of iron oxides could be controlled by adjusting inert atmosphere, as described in section 10.3.

Figure 5: Visual comparison of colour and particle size of the raw clays, ground clays and calcined clays

The calcined clays were firstly characterised by XRD and TGA. This was then followed by a pozzolanic evaluation using a modified R3 method (details can be found in Appendix 4) in an attempt to understand the dehydration and clay minerals evolution after being calcined at different temperatures (as shown in *Table 8*) in order to establish the optimum calcination temperature for each raw clay.

RC1	RC2	RC3	RC4	RC5	RC6	RC7	RC8	RC9	RC10
850 °C	900 °C	850 °C	850 °C	900 °C	940 °C	940 °C	850 °C	940 °C	940 °C
800 °C	850 °C	800 °C	800 °C	850 °C	850 °C	900 °C	800 °C	900 °C	900 °C
525 °C	525 °C	525 °C	525 °C	525 °C	800 °C	850 °C	500 °C	850 °C	850 °C
					750 °C	750 °C		750 °C	750 °C
						500 °C		500 °C	500 °C

Table 8: Calcination temperatures of different raw clays determined by TG-DTG curves

The main findings from these tests are shown in Figure 6. By comparing Figure 6(a) and (b), it can be seen that after being calcined at the optimum temperature, the main crystalline clay minerals, such as kaolinite, disappeared, which was transformed to amorphous phases through the dehydroxylation process [2]. This transformation is considered to be the main source of pozzolanic reactivity in calcined clays [4, 5]. However, some clay minerals, such as illite and mica, can still be detected after calcination at the identified optimum temperature (as shown in table 9). Figure 6(c) and (d) show the TGA curves of raw clays and calcined clays at optimum temperature. After proper calcination, it can be found from Figure 6(d) that all calcined clays show good dehydroxylation ratio at the optimum temperature. On the other hand, if the clay was calcined at a temperature higher than the optimum temperature, the pozzolanic reactivity could also be reduced, due to the recrystallization process, such as the formation of spinel at 950°C [6].

A general order of pozzolanic reactivity for different kinds of calcined clays could be established by cumulative heat (as shown in Table 9) as well from lowest to highest:
CC4 > CC3 > CC2 > CC5 > CC9 > CC10 > CC7 > CC8 ≈ CC6 > CC1

The details on the temperature selection of each calcined clay based on TG-DTG results and the pozzolanic reactivity based on modified R3 method of each calcined clay at different temperatures can be found in Appendix 4.
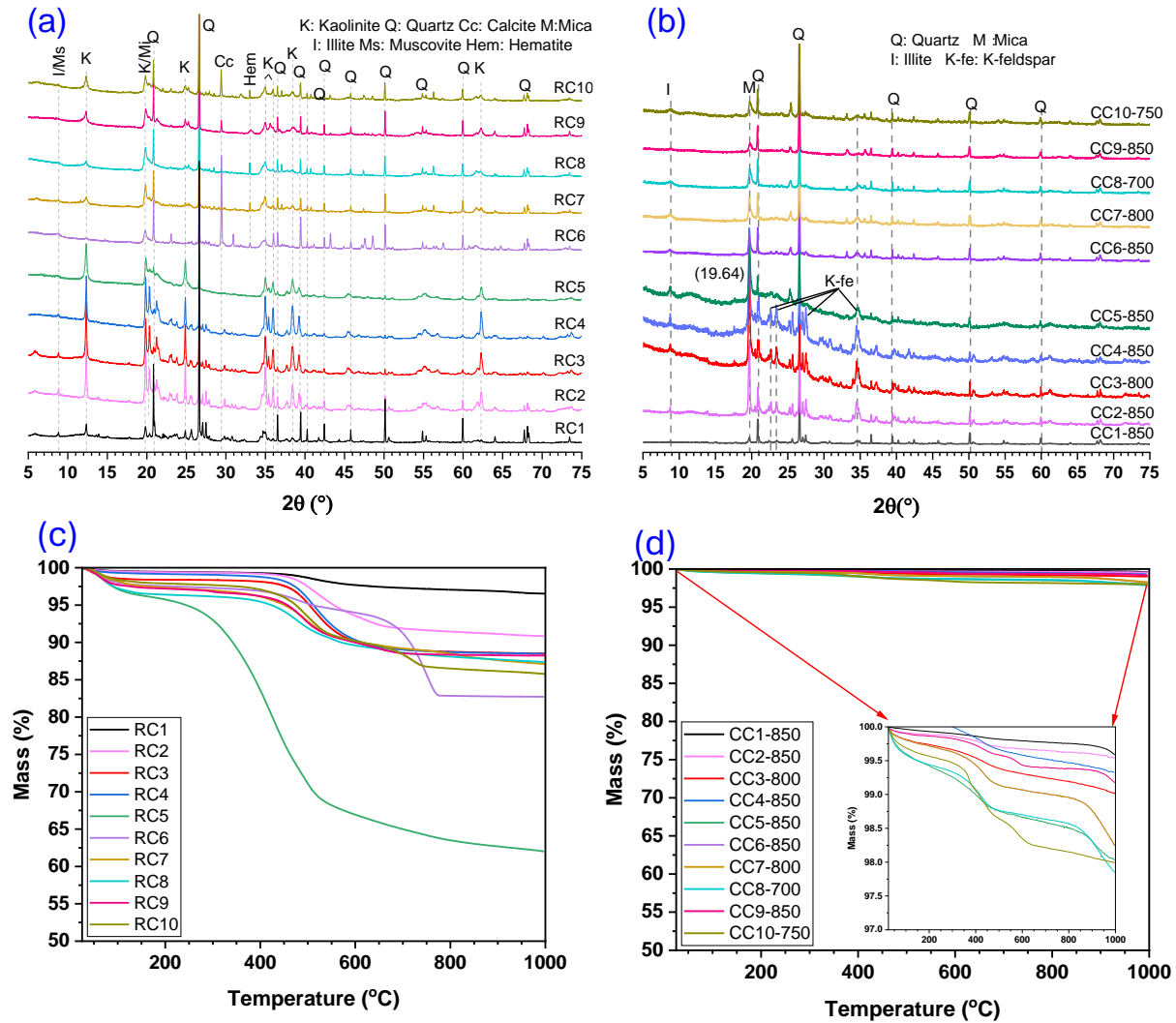
Figure 6: Characterisation and pozzolanic reactivity evaluation of calcined clays (a) XRD of raw clays, (b) XRD of calcined clays, (c) TG-DTG curves of raw clays, (d) TGA curves of calcined clays at optimised temperature

Calcined clay ID	Optimized temperature	Cumulative heat
CC1	850 °C	178.8 J/g
CC2	850 °C	538.1 J/g
CC3	800 ≈ 850 °C	574.1 J/g
CC4	850 °C	606.1 J/g
CC5	850 °C	506.1 J/g
CC6	850 °C	290.8 J/g
CC7	800 °C	318.0 J/g
CC8	700 °C	290.9 J/g
CC9	850 °C	460.5 J/g
CC10	750 °C	441.5 J/g

Table 9: Optimized temperatures and corresponding cumulative heat of different calcined clays

7.5.   Cement Study Without and With Superplasticiser

7.5.1. Fresh Properties

Different calcined clay shows different water demand which could be attributed to the presence of different clay minerals and varying clay mineral content. At fixed 0.35 w/b ratio, the flow diameters of different calcined clay formulated binary cement paste are different, which can be ranked as:

PC> FA > GGBS > CC3 > CC7 ≈ CC2 > CC9 > KDBP > BUBP

It should be noted that calcined clays/KD brick powders show higher water demand than fly ash and GGBS, whilst BUBP shows comparable water demand as that of PC, as shown in Figure 5(a). In the case of calcined clay/brick powder blended ternary cement systems, the substitution of PC by 15% limestone powder, however, as shown in Figure 5(b), shows little effect on the flowability.

In the absence of superplasticiser, to achieve comparable flowability as the reference (30% FA substitution, 166±10 mm), CC3 blended binary cement needs the highest w/b ratio, showing the highest water demand, which is followed by CC7, CC2, CC9, KDBP and BUBP. This trend corresponds nicely with the flowability results in Figure 5(a).

In the presence of superplasticiser, to achieve comparable flowability as the reference whilst the w/b is maintained at 0.35, CC7 blended binary and ternary cements need the highest superplasticiser dosage, which is 0.7% and 0.6%, respectively, whilst KD brick powder blended binary and ternary cements show the lowest dosage, with both at 0.2%. The lower water or superplasticiser demands of brick powder-based systems may be attributed to the fact that the brick production requires a temperature over 900°C which could change the layered structure of clay minerals, leading to the reduction in SSA and hence reducing the water demand.
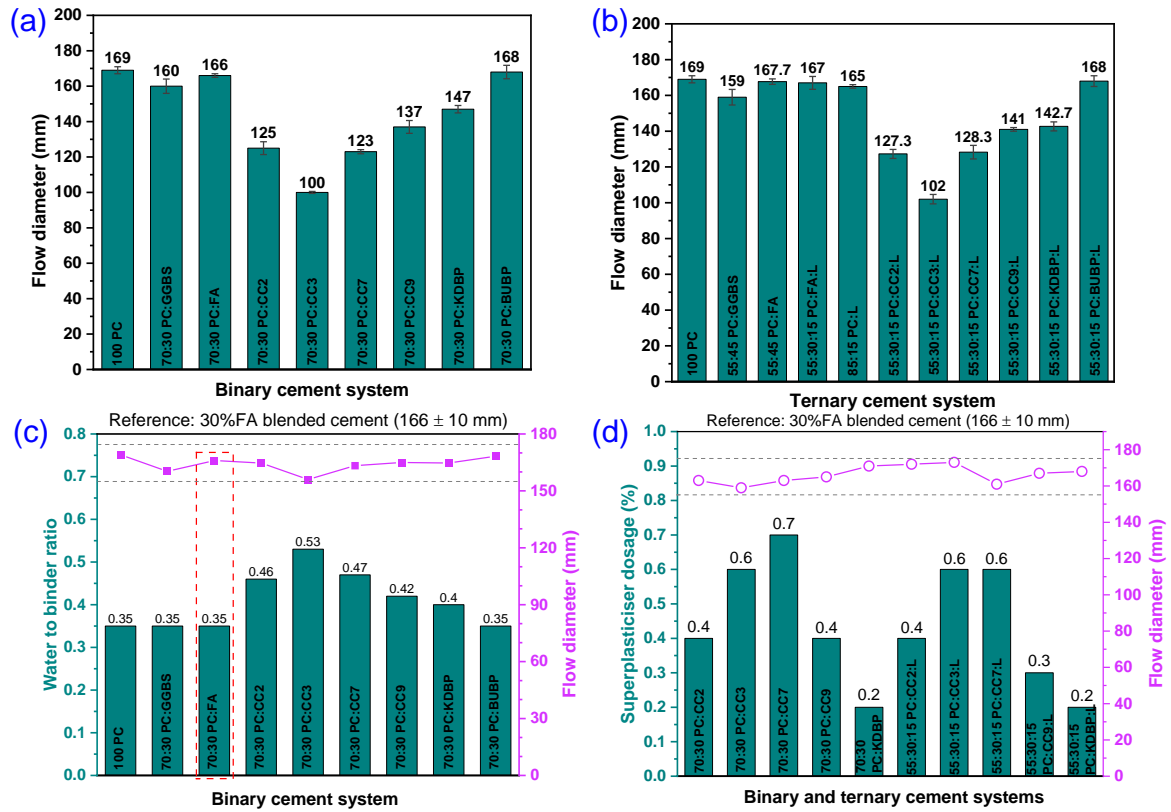
Figure 7: Fresh properties - (a)flowability binary cement without superplasticiser, (b)flowability ternary cement without superplasticiser, (c)w/b ratios binary cement comparable flowability, (d) superplasticiser dosages blended cement comparable flowability

7.5.2. Hydration Kinetics

The heat flow and cumulative heat of calcined clay/brick powder blended binary cement system without superplasticiser (a and b) or with superplasticiser (c and d) are shown in Figure 8. The substitution of calcined clay can reduce the heat flow of silicate hydration [8], but some calcined clays can enhance the aluminate hydration and delay the AFm phase formation, as shown in Figure 8(a). This is due to the fact that calcined clay is rich in aluminate phases compared to other traditional SCMs. Nonetheless, due to the reduction of CEM I, the total heat release of calcined clay blended binary cement is lower than that of CEM I. It must also be noted that only CC2 and CC3 blended binary systems produced higher total heat release than that of the fly ash blended cement after 120 hours. In general, the pozzolanic reactivity of brick powders is lower than calcined clays, with the pozzolanic reactivity of KDBP higher than BUBP.

The hydration kinetics results clearly show that the addition of superplasticiser not only can improve the workability but can also affect the hydration process [9]. Compared with its counterpart in Figure 8(a), the heat flow of the peaks of silicate and aluminate of each blended binary system reduces significantly after adding SP, especially for aluminate, as shown in Figure 8(c).

The same is also true for the total heat release, as shown in Figure 8(d).
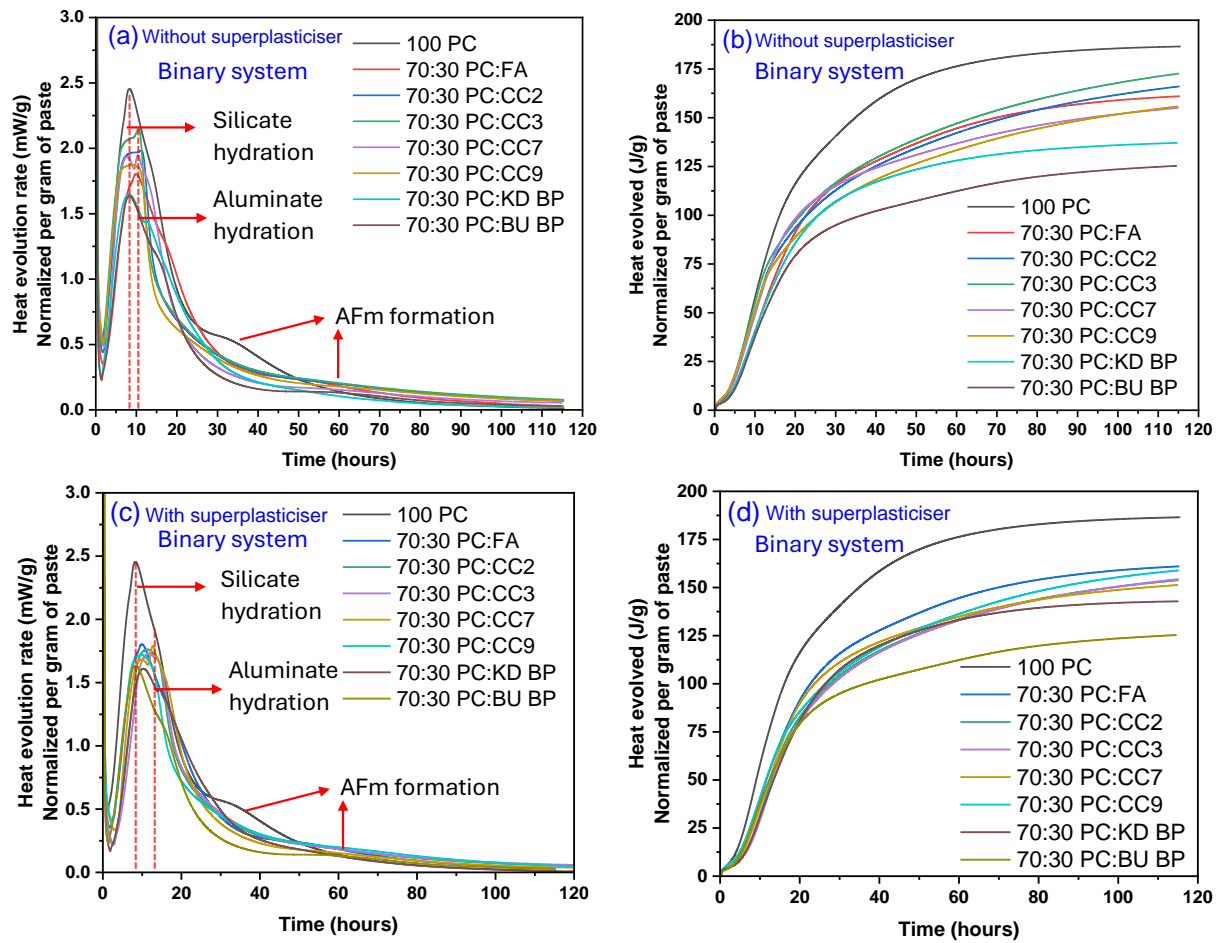
Figure 8: Heat flow and cumulative heat of calcined clay/brick powder blended binary cement system without superplasticiser (a and b) or with superplasticiser (c and d)

In calcined clay blended ternary cements, the substitution of 15% PC with limestone enhances the aluminate reaction compared with calcined clay blended binary cements, as shown in Figure 9(a). The substitution of limestone powder also enhanced and accelerated the formation of AFm phases. Compared with the binary cement system, the cumulative heat of ternary cement is slightly reduced, as shown in Figure 9(b). For ternary cements, the addition of superplasticiser reduces both the heat flow and the cumulative heat release, Figure 9(c and d).
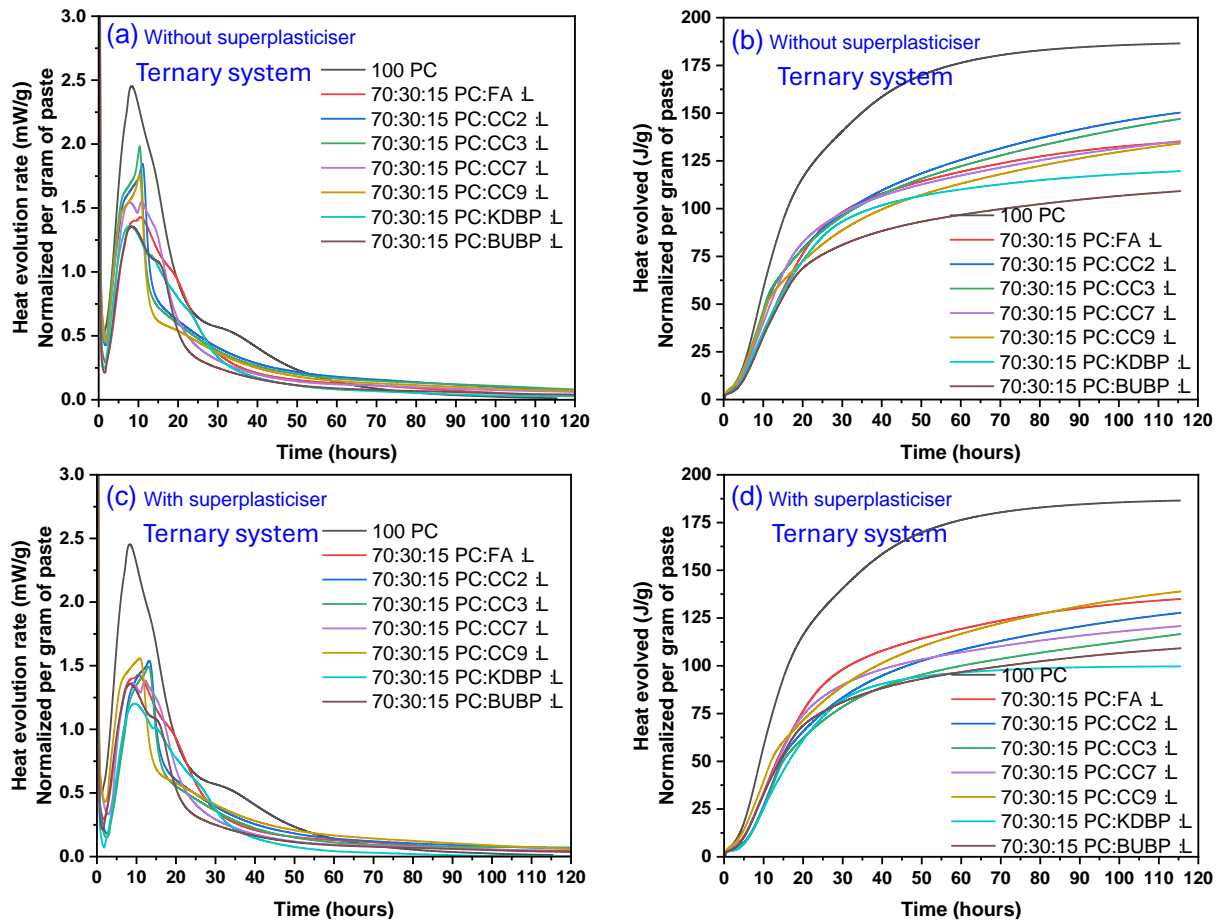
Figure 9: Heat flow and cumulative heat of calcined clay/brick powder blended ternary cement system without superplasticiser (a and b) or with superplasticiser (c and d)

7.5.3. Compressive Strength

As shown in *Figure 10*, when calcined clay is used as a supplementary cementitious material to replace CEM I, it can affect the compressive strength of cement pastes. At fixed w/b ratio of 0.35, calcined clay/brick powder blended binary cements show comparable or even higher compressive strength than that of the reference (i.e., 30% fly ash blended binary cement). Compared with the reference, calcined clay blended cement shows better performance both at early stage (3 days) and long-term stage (28 days). However, the early compressive strength or long-term compressive strength of calcined clay/brick powder blended cement are all lower than CEM I.

In the calcined clay blended ternary cement systems, due to the further reduction of CEM I content, the compressive strength of calcined clay blended ternary cement is lower than that of calcined clay blended binary cement. However, except BUBP, the compressive strength of calcined clay or KDBP blended ternary cement is all higher than that of the reference (i.e., FA blended ternary cement). It should be noted that the compressive strength of calcined clay or KDBP blended ternary cement shows slower strength development from 14 days to 28 days, and higher development from 28 days to 91 days.
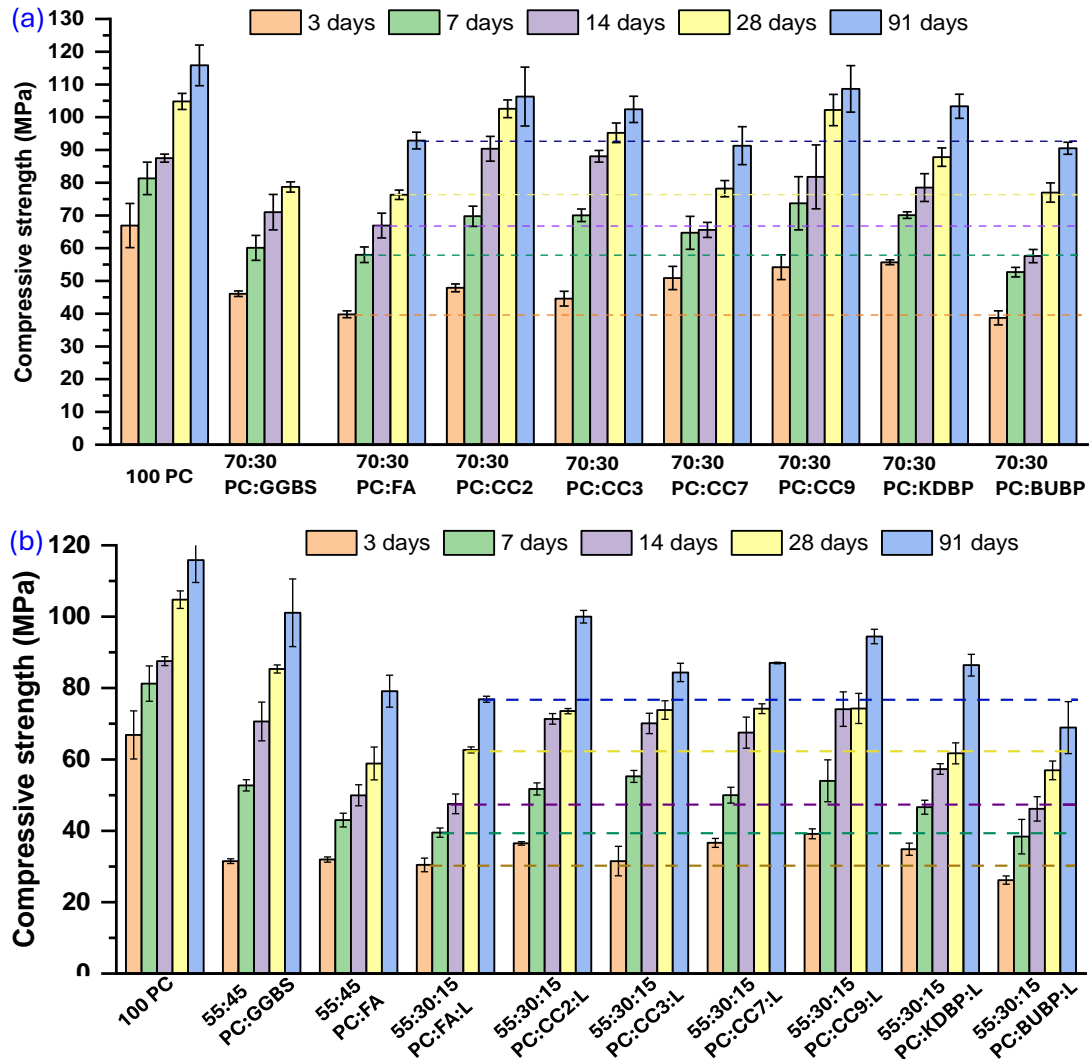
Figure 10: Compressive strength of calcined clay/brick powder blended binary (a) and ternary (b) cement systems without superplasticiser

As mentioned in the previous section, increasing w/b ratio and adding superplasticiser are the two commonly adopted methods to improve the workability of fresh cement products. However, the exact effect of these two methods on the compressive strength of calcined clay/brick powder blended cement is unclear. Figure 11 shows the compressive strength results of binary cement with comparable flowability modified by different methods. Due to the presence of layered minerals in calcined clay, to achieve comparable flowability without using superplasticiser, the addition of more water is required. As a result, the compressive strength is significantly reduced compared to that of the reference and those modified by superplasticiser, as shown in Figure 11(a). It should also be noted that, in the absence of superplasticiser, the higher-grade calcined clay shows lower compressive strength, presumably due to the much higher w/b ratio needed to achieve the same flowability.

It is a common practice to use superplasticiser either as a plasticiser or a water reducer. The former can improve workability, whereas the latter can increase strength. As shown in Figure 12, when used as plasticiser, the compressive strength of calcined clay blended cement was slightly reduced, especially for CC2, CC3 and CC7, as shown in Figure 11(b). However, it significantly enhanced compressive of the CC9 blended binary cement, showing higher strength than CEM I.
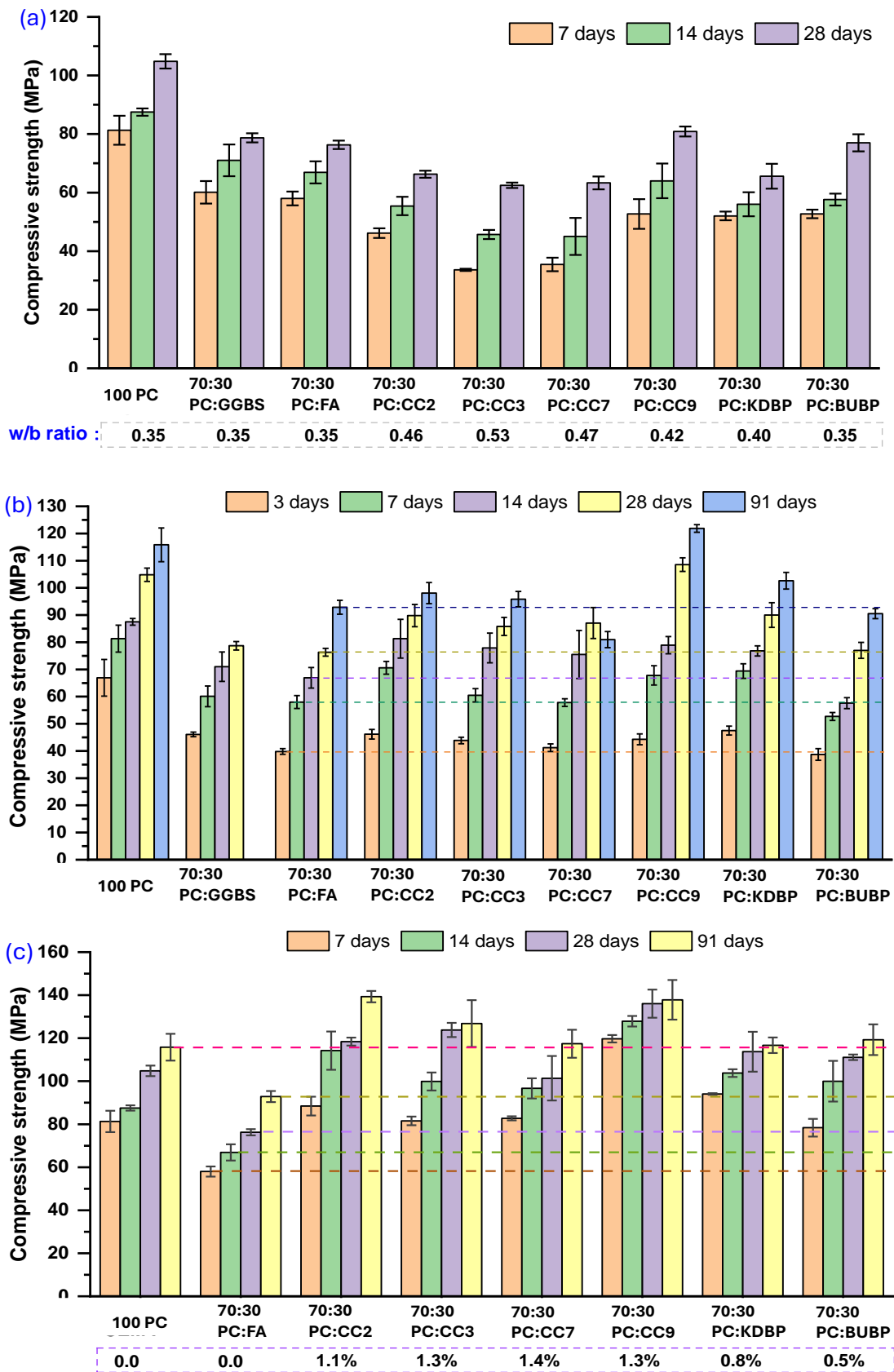
Figure 11: Compressive strength of calcined clay/brick powder blended binary cement system with comparable flowability modified by different methods, (a) increasing w/b ratio, (b) adding lower dosage of superplasticiser at fixed 0.35 w/b ratio, (c) adding higher

Figure 12: Two different usages of superplasticiser and the details on w/b ratio and dosage content of superplasticiser

When the superplasticiser was used as a water reducer, it was found that the compressive strength of calcined clay or brick powder blended cement is significantly increased. In particular, as shown in Figure 11(c), the compressive strength of CC2, CC3 and CC9 blended binary cement is not only higher than that of the reference, but even higher than that of CEM I. On the other hand, CC7 and brick powders blended binary cement systems show comparable compressive strength with that of CEM I, but higher than that of the reference. To understand how the calcined clays can influence the compressive strength, the hydration products were also characterised by TGA, FTIR and XRD tests at different hydration ages. The details can be found in Appendices 2 and 3.

7.6.   Effect of Sulphate on the Properties of Blended Cements

In this section the effect of sulphate addition on the calcined clay/brick powder blended cement systems were investigated with to in this report. Detailed information can be found in Appendix 7. Two methods were adopted to optimize the SO_3 content, namely, isothermal conduction calorimetry (ICC) test for identifying sulphate depletion point and obtaining the cumulative heat, and compressive strength test.

7.6.1. Hydration Kinetics – ICC Test

Calcium sulphate can react with aluminates both from C_3A and calcined clay minerals, which could affect the setting time and compressive strength [10]. In addition, the phase assemblage of the hydration products could also be affected which may potentially influence some durability performance of cementitious materials. Figure 13 shows the heat flow and cumulative heat of CC9F blended binary cement after different SO3 adjustment. Compared to the reference without adding any extra SO3, the addition of calcium sulfate can shorten the induction period of hydration reaction by up to 3 hours, as shown in Figure 13(a). The addition of sulphate can also significantly enhance and accelerate the silicate reaction. For the cumulative heat results, with the increase of SO_3 content, the cumulative heat increases first and then

decreases after 72 hours, as shown in Figure 13(b). This phenomenon could help to optimize the sulphate content which can further improve the performance of calcined clay/brick powder blended cement.
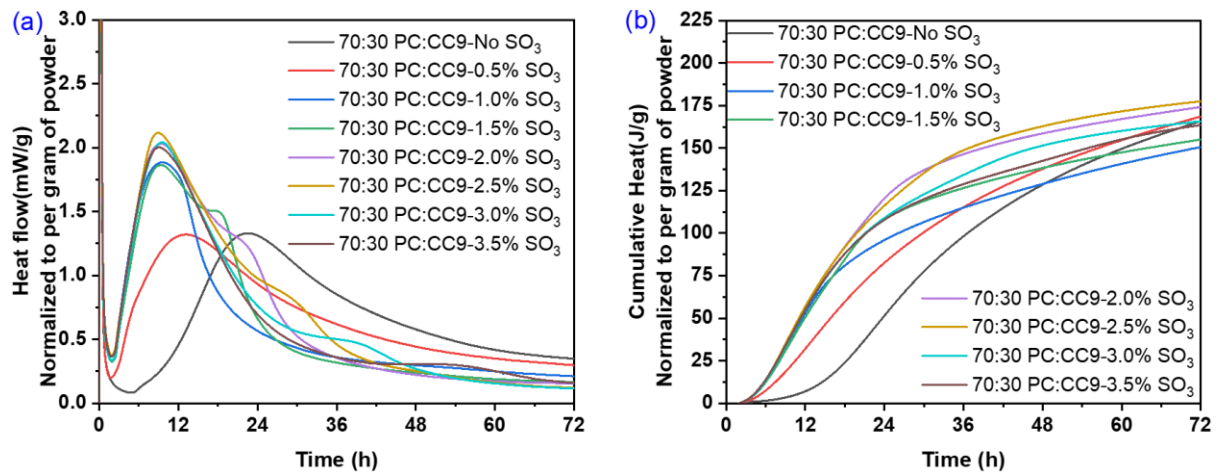
Figure 13: Heat flow and cumulative heat of CC9 blended binary cement with different sulphate contents

Based on the sulphate depletion point and cumulative heat, the optimum sulphate content for each binary cement is determined according to ASTM C563, as shown in Figure 14. The details for each calcined clay and brick powder can be found in Table 10.
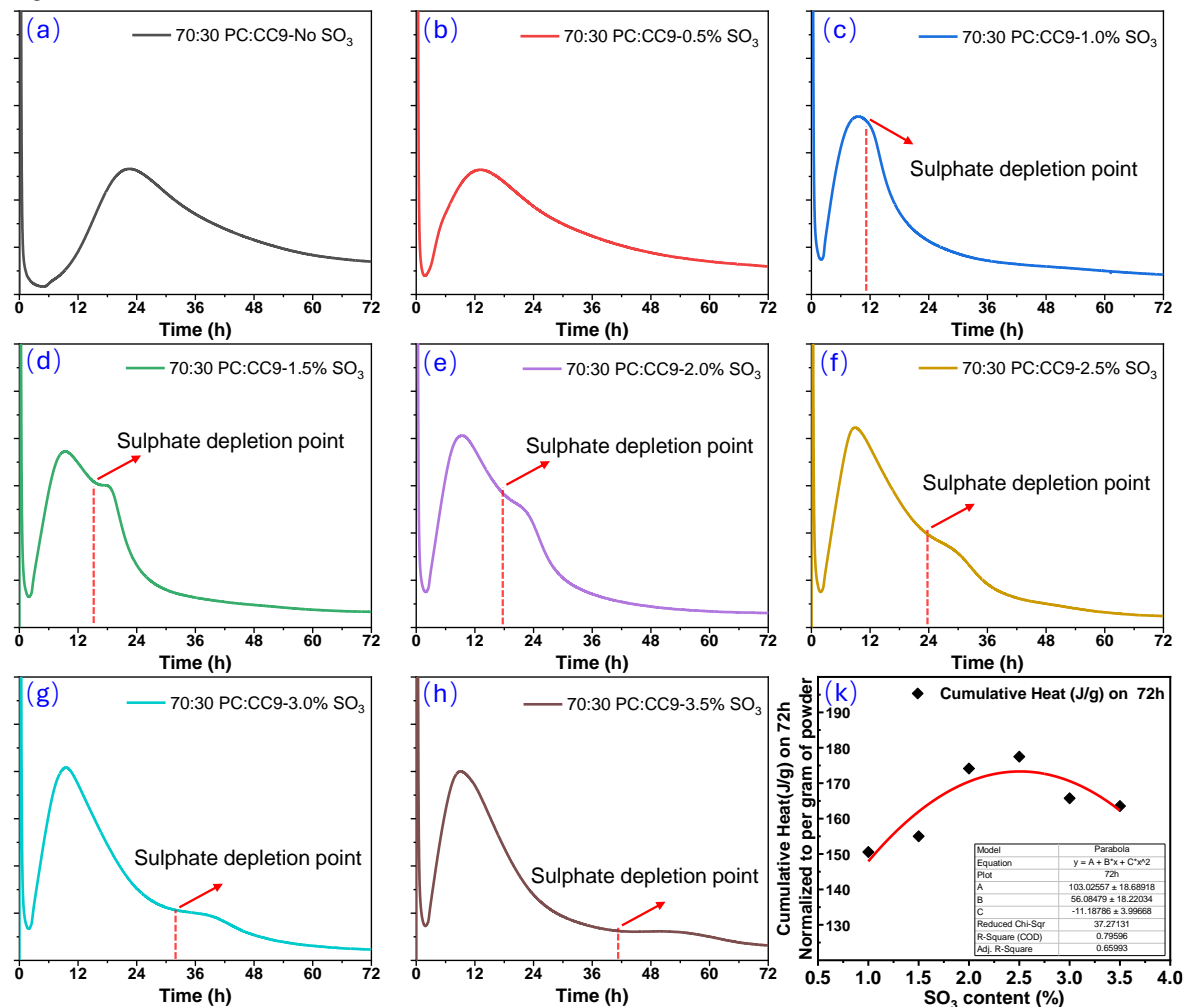
Figure 14: SO₃ optimization based on sulphate depletion point and cumulative heat

Blended Cement	Optimum SO₃ content	SO₃ for 70% clinker	SO3 for 30% CC/BP
70:30 PC:CC2F	~ 2.5%	2.1%	~ 0.4%
70:30 PC:CC7F	~ 2.0%	2.1%	0
70:30 PC:CC9F	~ 2.5%	2.1%	~ 0.4%
70:30 PC:CC9R	~ 2.5%	2.1%	~ 0.4%
70:30 PC:KDBP	1.0~1.5%	2.1%	-1.0~-0.5%

Table 10: Summary of SO₃ content for each calcined clay and brick powder

Note: 2.1% is calculated by sulphate optimization of pure clinker, where clinker needs 3.0% of SO_3 to achieve the highest cumulative heat and proper sulphate depletion point position.

7.6.2. Compressive Strength

Sulphate not only can react with aluminate, but can also affect the reaction rate of silicate, thereby affecting the hydration process and hydration products, which is related to the compressive strength development. Hence, as shown in Figure 15, the compressive strength of calcined clay/brick powder blended binary cement was also tested to help determine the optimum sulphate content. The optimum SO_3 contents determined by compressive strength results show good correlation with the results determined by the ICC test. The details for each calcined clay and brick powder can be found in Appendix 7.
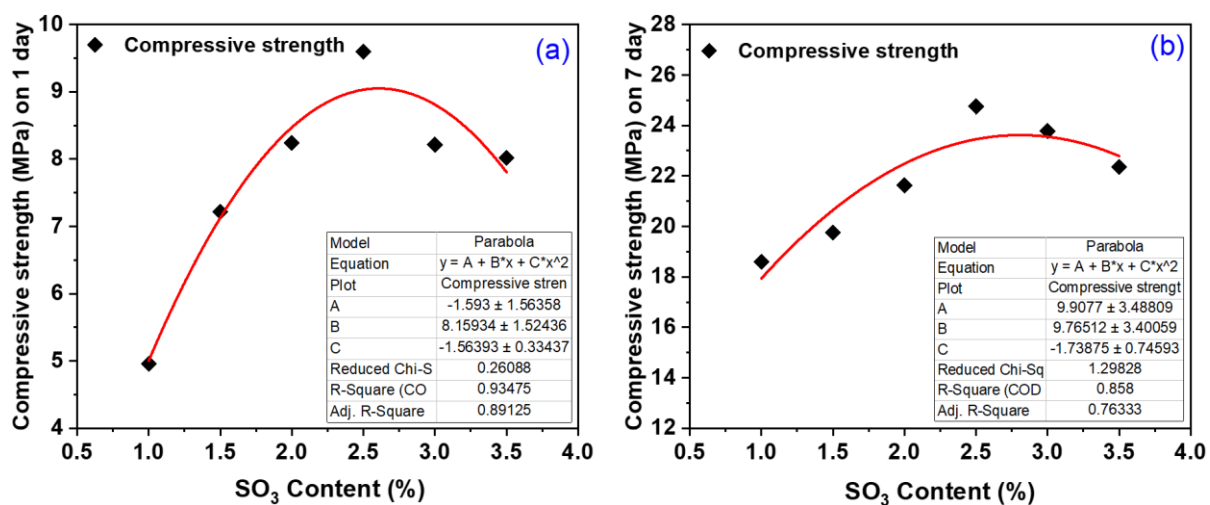
Figure 15: Proper SO₃ content for CC9F blended cement determination based on compressive strength results at 7 days.

7.7.   Conclusions

The characterisation of ten raw clays, ten calcined clays and two brick powders, fresh and hardened calcined clay/brick powder blended binary or ternary cements and sulphate optimization works were completed at UCL. The main conclusions from the cement study Work packages E, G and two Extra Works are below:

- The kaolinite content of nine clays (excluding RC5) can be sorted as RC4 > RC3 > RC10 > RC9 > RC2 > RC7 > RC8 > RC6 > RC1. However, the tested UK clays are not pure with different proportions of companion minerals such as quartz and carbonates.

- The pozzolanic reactivity of calcined clays with proper calcination is: CC4 > CC3 > CC2 > CC5 > CC9 > CC10 > CC7 > CC8 $\approx$ RC6 > RC1. The calcined clays at different temperatures show different cumulative heat and pozzolanic reactivity.

- Due to the presence of different clay minerals, the optimal calcination temperature for each raw clay is different based on the modified R3 method, and the calcination temperature is mainly focusing on 800 °C to 850 °C.

- In binary and ternary cement systems, the water demand of calcined clay blended cement is higher than that of fly ash blended cement, which significantly reduces the flowability of blended cement paste.

- In the binary and ternary systems, the compressive strength of calcined clay blended cement in early ages is comparable to that of FA blended cement, but the calcined clay blended cement has better compressive strength than that of FA blended cement after 28 days. The compressive strength of BU brick powder blended cement is comparable to that of FA blended cement, while KD brick powder blended cement is better than FA blended cement.

- The addition of superplasticiser significantly improves the workability of calcined clay/brick powder blended binary and ternary cement. Different grades of calcined clay need different dosage of superplasticiser to achieve comparable flowability.

- The usage of superplasticiser will affect the reaction of aluminate thereby delaying the compressive strength development of early stage, but shows little effect on long term compressive strength, which also could be proved from ICC results.

- Different grades of calcined clay/brick powder blended binary cement needs different optimal sulphate contents to achieve the highest cumulative heat and compressive strength performance. The addition of alkaline sulphate could promote the early hydration of calcined clay blended cement.

- This study shows that the use of UK calcined clay and brick powder to replace FA in binary and ternary systems is technically feasible and has great potential. The low-grade clays are more suitable for binary system, while the high-grade clays are more suitable for ternary system to achieve better performance.

7.7.1. References

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8. Characterization of Pilot Calcined Clays

Section Authors: Barbara Benevenuti, Deeba Ansari, Tony Newton
Detailed report available in: Appendix 8 - Characterization of the pilot calcined clays

8.1. Introduction

The work presented in this report was carried out by Imerys in addition to the initially planned work packages C and I. This extra work consisted in characterizing the clays calcined at pilot scale, with the goal of contributing to the interpretation of the results obtained in the other work packages, where the performance of the calcined clays was evaluated in mortars and concretes.

8.2. Materials and Methods

The six pilot calcined clays and their respective description are presented in *Table 11*.

Samples	Description
CC2-F	Imerys' RC2 calcined in a flash kiln
CC2-R	Imerys' RC2 calcined in a rotary kiln
CC3-R	Imerys' RC3 calcined in a rotary kiln
CC7-F	Heidelberg's RC7 calcined in a flash kiln
CC9-F	Tarmac's RC9 calcined in a flash kiln
CC9-R	Tarmac's RC9 calcined in a rotary kiln

Table 11: Pilot calcined clays

The pilot calcined clays had their chemical composition quantified by X-ray fluorescence (XRF), using a Panalytical Zetium and the SuperQ 6.3 software, using glass beads; their mineralogical composition semi-quantified by X-ray diffraction (XRD), using a Panalytical X'Pert Pro and the Highscore software and their colour evaluated by a X-Rite Ci4200 colorimeter. Furthermore, the particle size distribution (PSD) was measured by laser granulometry and the specific surface by BET.

8.3. Main Results

The chemistry measured by XRF are well in line with that expected from the raw calcined clays chemistry, so they are not presented here (see report section 9).

The mineralogy, measured by XRD using the internal standard method, which allows quantification of amorphous phases, is presented in Table 12. It shows that the amount of amorphous phase likely corresponds to the metakaolin content (and perhaps other meta-clays?).

Except for CC3R, all the clays have similar amounts of amorphous phases. As the alumina content of CC2 is superior to that of CC7 and CC9, it is expected that CC2 contains more metakaolin, and CC7 and CC9 probably contain other meta-clays and perhaps other amorphous minerals. No residual raw clays are observed, indicating that they were fully calcined.

CC2 (F and R) have high amounts of muscovite/illite, a clay phase that can increase the water demand of the material. The other clays have lower amounts. CC7 and CC9 have high amounts of quartz, a hard mineral that can impact on the grindability of these clays, and thus to their particle size distribution after milling. The feldspar, present in most of the samples, can have a similar effect on the grindability.

Finally, all the clays have iron containing phases. The two flash calcined clays that underwent the colour control process, CC7F and CC9F, have the higher magnetite contents. This observation is coherent with the working principle of the colour control method, which consists in controlling the cooling atmosphere to prevent the conversion of magnetite to hematite, ensuring the clay has a more greyish tone, as shown in Figure 16.

%	CC2F	CC2R	CC3R	CC7F	CC9F	CC9R
Amorphous phases	46	46	70	47	50	46
Muscovite/ illite	26	31	13	14	12	13
Quartz	11	8	3	26	35	34
Feldspar	14	14	13	9	0	1
Anatase + Rutile	0	0	0	1	1	2
Hematite	1	1	0	2	1	4
Magnetite	0	<0.1	<0.1	1	1	0
Mullite	2	nd	nd	nd	nd	nd
Anhydrite-II	nd	nd	nd	1	nd	nd

Table 12: Mineralogy by XRD of the pilot calcined clays

Figure 16: CC9 calcined in flash (left) and rotary kiln (right)

The particle size distribution (PSD) and the BET specific surface of the clays is presented in Figure 17. The rotary calcined clays were milled in Imerys' Lixhe plant, and the flash calcined clays were milled at FLS facilities, except for CC2F, which was considered fine enough not to require further milling. The PSD results show that the rotary clays are a little finer than the flash clays, and that CC2F is coarser than the other flash clay, with a fraction of the particles having a grain size above 100µm (likely agglomerates of smaller particles).

The specific surface of the pilot calcined clays seems to depend more on the nature of the clay than on the process of calcination. The CC2F, CC2R and CC3R have relatively low surface area, the remaining clays have higher.

For the CC9, the rotary material has a significantly larger surface than the flash one. It could be related to the grinding process which led to a higher fineness of the CC9R, but also to the phases formed during the calcination, which are not exactly the same, as observed by XRD.

Both PSD and specific surface can affect the reactivity and water demand of the clays, which was evaluated in the mortar and concrete tests (see report section 10).

	SS BET (m2/g)
CC2F	6,9
CC2R	6
CC3R	7
CC7F	17,7
CC9F	11,8
CC9R	17,7
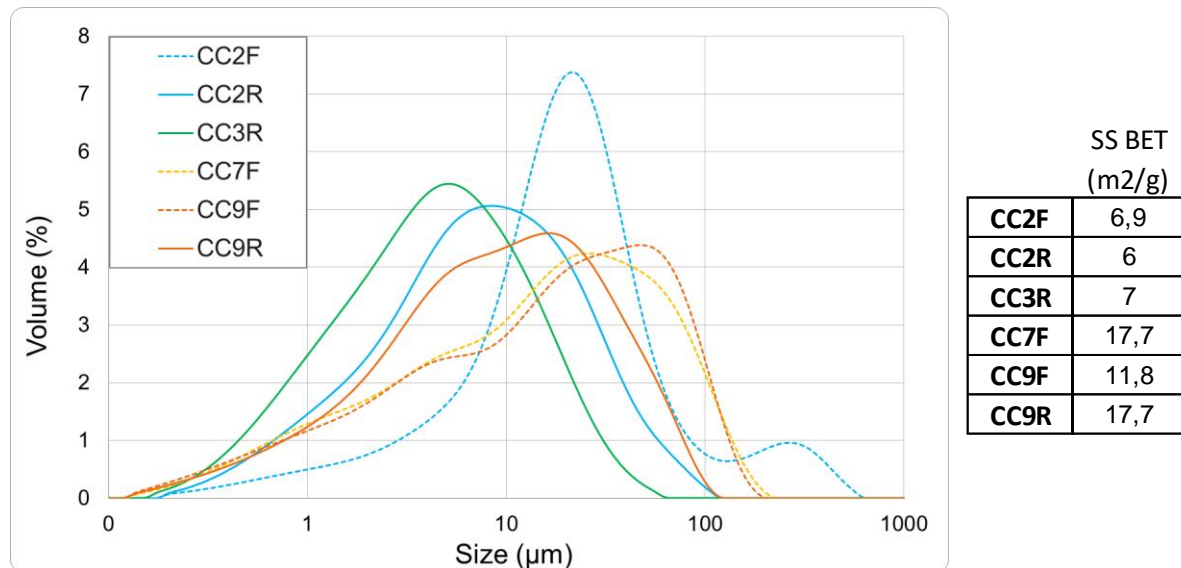
Figure 17: PSD and BET of the pilot calcined clays

8.4.   Conclusions and Recommendations

The main conclusions drawn from the results obtained in this study are as follows:

- The calcination in both rotary and flash pilot kilns appear to be adequate, with no residual raw clay and no or very little over-calcined phases being detected by XRD.
- Using the internal standard method with the XRD, it was possible to quantify the amorphous phase in the clays, which are usually considered to be metakaolin. Their amounts were similar for all pilot calcined clays, except for CC3R, which was higher. From results obtained elsewhere in the project, we know that CC2 must have higher metakaolin amounts, so CC7 and CC9 likely contain other meta-clays. The XRD method does not allow differentiation of metakaolin and other meta-clays, but these phases have different reactivities (pozzolanic activities). The reactivity of the clays must be assessed in cement and concrete tests, as this work has indicated that it cannot be reliably estimated by their composition alone.
- The PSD of the pilot calcined clays are not all equal, and this characteristic may affect both the reactivity and the water demand of the clays. This aspect was further investigated in the concrete trials presented in section 11.
- The colourimetry results indicate that the clays with lower iron content have lighter colours, but also that the colour control process, used in the flash

calcination, can convert the reddish colour of iron rich clays into a more habitual grey tone.

The properties of the pilot calcined clays determined in the present study are in line with those of the laboratory calcined clays prepared by Imerys in Work Package C, indicating that a screening study at laboratory scale is pertinent to assess the potential of the clay samples.

9. Refined Mineralogical analysis of the Raw Clays by X-ray Diffraction (XRD)

Section Authors: Barbara Benevenuti (Imerys), Deeba Ansari (Imerys), Tony Newton (Imerys), Andrew Smith (Forterra)
Associated Appendix: Appendix 9 - Determination of Kaolinite Content of Raw Clays

9.1. Introduction

The mineralogical composition of the 10 raw candidate clays have been estimated by X-ray diffraction (XRD) in the Work Package C, in the beginning of the project. Later results obtained in the project suggested that these initial XRD results were not accurate.

As the quantification of the clay minerals, particularly that of kaolinite, is the most commonly used parameter to evaluate the quality of a given clay, it was decided to rerun the XRD for the raw clays, using a modified method, allowing to better identify and quantify the mineralogical phases present in the samples.

9.2. Materials and Methods

The ten raw clay samples evaluated in the first stage of the project were tested by using a Bruker D8 Advance diffractometer and the TOPAS V6 software, to quantify their mineralogical composition. The internal standard method (20% of ZnO standard) was used to quantify the amorphous or poorly crystalline phases.

9.3. Results

The mineralogy measured by XRD is presented in *Table 13* below.

Thanks to the internal standard method it was possible to quantify the amorphous, microcrystalline or poorly crystallised phases, that are otherwise "invisible" to XRD.

The results indicate that these "amorphous" phases account for a significant percentage of the phases present in most of the clays. By ignoring them, which is the case in XRD measurements not using internal or external standards, the quantification of the phases is overestimated proportionally to the amount of "amorphous" present in the material.

It is important to highlight that in the raw clays tested, it is unlikely that the materials contain truly amorphous (vitreous) phases. The phases not being detected by the XRD are probably poorly organised crystalline structures, which is often the case for kaolinite.

In the last line of *Table 13*, provides the sums of the kaolinite and "amorphous" content for each clay. It is assumed that this value could better correspond to the real kaolinite content on the samples, unless other clay minerals (such as illite) are also present in a poorly crystallised state.

The presence of these poorly crystallised phases that cannot be identified by XRD, and that can be composed of different minerals, make the quantification of kaolinite by this technique more complex and less precise.

Finally, it is necessary to specify that raw clay RC5, by its nature, contains significant amounts of organic matter, invisible to the XRD. This explains the very high "amorphous" content for this sample, which can certainly not be attributed only to poorly crystallised clay minerals.

The tested clays have very variable levels of kaolinite and other potentially active clay minerals (illite and muscovite being the most relevant ones), even if we consider the limited precision of the measurements. RC1, RC6 and RC8 have the lower clay minerals contents, and RC2, RC3, RC4 have the higher ones.

Family	Phase Name	RC1	RC2	RC3	RC4	RC5	RC6	RC7	RC8	RC9	RC10
Clay - 1:1	**Kaolinite**	**11.7**	**47.7**	**62**	**52.5**	**23.7**	**5**	**23.6**	**8.2**	**36.9**	**26.4**
Clay - 1:1	Halloysite	0	0.8	0.4	0	0	0.6	0.9	1	0.8	0
Clay - 2:1	Vermiculite	0	0	0	0	0	0	0.2	0	0	0
Clay - Chlorite	Clinochlore	0	0.5	0	0	0	0	0.7	0	0	0,4
Mica & Illite	Illite / Muscovite / Phengite	16.7	26.7	18.9	16.1	4.6	23.1	24.5	23.3	13.3	17.2
Crystalline silica	Quartz / cristobalite	36.2	9.5	4.6	3.1	2.1	21.8	19.3	19.4	23.3	15.7
Feldspar	Albite/Anorthite/Anorthoclase/ Microcline/Orthoclase/Sanidine	28.2	9.8	5.9	7.7	0	8.2	1.3	3.8	1.7	3.4
Iron oxides	Fe2O3/FeO/Fe3O4	0.6	0.5	0.6	0.6	0	0.4	0.2	0.6	3.4	0.4
Iron sulfide	FeS2 Pyrite	0	0	0	0.5	0	0.9	2.3	2.5	0.1	1.4
Pyroxene	Aegirine / Pigeonite	0.8	0	1.8	1.3	0	0	0.8	0.4	0	0
TiO2	Rutile + Anatase	0	0	0.8	0.6	0	0.5	1.3	1.3	2.1	0.9
Tourmaline	Schorl	5.9	4.5	4.5	2.1	0	2.0	2.8	1.2	0	2.8
Calcium sulfate	Bassanite / Gypsum	0	0	0	0	0	0.5	2.1	0	0	0
Carbonates	Calcite/Dolomite/Siderite	0	0	0.6	0.3	0	24.6	0.1	0.8	1.9	7.7
Amorphous	Amorphous/ Poorly crystallized phases	0	0	0	15.4	69.6	12.5	20.0	37.4	16.3	23.8
	Kaolinite + Amorphous	**11.7**	**47.7**	**62**	**67.9**	**NA**	**17.5**	**43.6**	**45.6**	**53.2**	**50.2**

Table 13: Clay Phase Analysis

As mentioned, RC5 has very high amounts of organic matter (as shown by the amorphous results), and RC6 has significant amounts of calcite, which upon calcination may convert to free lime and CO_2 which are both undesirables. The quartz (and for some clays the feldspar) contents are relatively high for most clays. These minerals are on the whole inert, however as these minerals are generally harder than the calcined clay it will impact on the grindability of the clays. The relatively high iron content of the clays RC5 to R10 explain their darker colour. The different forms of iron oxide/sulphide have different colours: Fe_2O_3 is reddish/brown, FeO and Fe_3O_4 are black, and pyrite is golden.

Finally, all the clays contain relatively low titanium oxide contents, which is positive as this material is suspected of being carcinogenic when in a very fine form.

9.4.   Normative Mineralogy

Despite the greater accuracy of the quantitative XRD undertaken by Imerys, especially of the Imerys materials, RC1-RC5, there were still reservations in respect of the values presented in *Table 13*, for RC6-RC10. These are known to be more complex and have mixed clay mineralogy's as well as a significant suites of non-clay minerals. Coupled with the anomalies in respect of the mineralogy not fitting with the chemistry, it was decided to undertake a more in-depth investigation into the methodology for quantifying more accurately the mineralogical, and specifically the clay mineralogy of raw clays, so that the conventional metric of using kaolinite content as a surrogate for "potential reactivity" could be assessed.

A full description of the rationale and methodology used to create a Normative Mineralogy for this project is presented in Appendix 9.

It is clear that by only using one technique, be that Q-XRD or DSC/TGA it is possible to use assumptions that result in inaccuracies in the interpretation of the results. In order to establish a more robust and thus more accurate measure of the mineralogy of the clay raw materials it was agreed that by using X-ray Diffraction and X-ray Fluorescence in combination, it is possible to generate a "Normative Mineralogy", which is an approximation to quantitative X-ray Diffraction. It uses the chemistry as building blocks of chemical elements to logically build the known minerals present, as determined by the XRD. The result of that process is presented within this report and has been successfully deployed to make sense of complex mixed clay mineral assemblages.

As a sense check, the results from the TGA have been used to correlate the measured weight losses between 400-650°C with that of the Normative Mineralogy. The results show that within a range of ±10% weight loss it is possible to get a reliable value for the clay mineral contents of the raw clays, and thus validates the values for clay mineral content, especially kaolinite, used in this project.

Unlike XRD, which can be "subjective", and the results open to interpretation, XRF provides an absolute, in analytical terms. XRF analysis was undertaken by Imerys, and the results reported in *Table 14*. The major element oxide chemistry of the raw clays, as is to be expected, is dominated by alumina and silica, reflecting the dominant alumino-silicate minerals present in the materials. The primary alkali is predominantly potassium, which is typically associated with illite, muscovite mica and potassic feldspars. RC6, RC10 and KDRC all have elevated levels of calcium which is commonly associated with calcite and dolomite (carbonates) as well as present in some feldspars and in calcium montmorillonite. The only other major elemental oxide is that of iron, and although low in the RC1-5 samples, ranges from 4.5% to 8% in the other materials. Iron is present in many mixed clay deposits, typically as iron oxides or hydroxides, but can also be present in chlorite clay minerals, as well as in pyrite, and iron sulphide, especially in "black anoxic" type clay deposits such as RC6-8 and KDRC.

The starting point for the Normative Mineralogy is the chemistry of the raw clays, which is presented in *Table 14*. Using this, along with the known minerals present as detected by qualitative XRD (as opposed to quantitative XRD) it is possible to build the Normative Mineralogy by apportioning the available elemental oxide composition to

the mineralogy. This is done by using a standardised chemical composition for each of the identified minerals, along with the value for LOI which includes volatiles lost during the calcination process, therefore compounds such as water in the form of OH and H_2O, carbon dioxide (CO_2) from the decomposition of both carbonate minerals such as calcite and dolomite, but also from the "combustion" of any organic matter present. These too can be used to validate the calculated Normative Mineralogy.

Samples	LOI	Al₂O₃	SiO₂	K₂O	Fe₂O₃	TiO₂	CaO	MgO	Na₂O	P₂O₅
RC1	2.50	16.00	73.30	5.30	1.60	0.10	0.10	0.30	0.60	0.13
RC2	8.70	31.90	52.70	4.20	1.50	0.10	0.10	0.40	0.30	0.10
RC3	10.50	34.50	50.00	3.00	1.20	0.00	0.10	0.40	0.20	0.13
RC4	10.90	35.10	49.40	2.90	1.00	0.10	0.10	0.40	0.20	0.11
RC5	54.70	18.30	23.60	0.80	1.40	0.40	0.40	0.20	0.10	0.03
RC6	14.20	11.60	47.80	2.60	5.00	0.70	15.30	2.40	0.30	0.12
RC7	10.90	21.70	52.50	2.80	7.30	1.00	1.30	1.80	0.30	0.31
RC8	10.00	20.90	55.30	2.40	6.70	1.20	1.70	1.30	0.30	0.20
RC9	9.20	23.90	53.50	1.20	8.00	1.10	1.70	1.10	0.30	0.08
RC10	11.90	22.10	48.90	1.70	7.80	0.90	4.00	1.90	0.40	0.26
KDRC	18.14	16.14	47.80	2.63	4.61	0.84	7.67	1.46	0.49	0.17

Table 14: XRF major element oxides for the raw clays as reported by Imerys

Samples	Kaolinite	Illite	Montmorillonite	Chlorite	Quartz	Feldspar	Carbonates (Calcite/Dolomite)	Fe Compounds (Hematite & Pyrite)	Muscovite	Schorl (Tourmaline)
RC1	4				46	20		2	28	
RC2	54				8	16			17	5
RC3	69				4	13			10	4
RC4	75				1	17		1	3	3
RC5[2]	38	10			1			1		
RC6	6	24[1]			29	7	29	4		
RC7	12	31[1]	9	9	20	10		4		
RC8	16	24[1]	24	1	19	5	1	10		
RC9	49	13		2	19	7		7		
RC10	28	21		13	20	3	7	3		
KDRC	7	29		9	23	8	10	6		

Table 15: Normative Mineralogy based on modelling the chemistry (XRF) with the mineralogy (XRD)

1 Mixed layer illite/montmorillonite is common in these clay types, so the absolute values stated are likely to be aggregated.
2 Low total due to high organic carbon (lignite) content contributing to the LOI

Using these principles, _Table 15_, shows the calculated "Normative Mineralogy" of the 10 raw clays in the study, plus the raw clay used to manufacture the fired clay bricks used to create the brick powder (KDBP).

Whilst the Normative Mineralogy results shown in _Table 15_ are the best fit, based on mineralogy and chemistry, it is worth considering a "sense check" to see how these relate to the TGA weight losses measured. By converting the expected weight loss from the mineral assemblages calculated in the Normative Mineralogy exercise, again using standard mineral compositions, it is possible to back calculate the expected weight loss from each mineral based on the percentage in the sample. The results of this exercise are presented in _Table 16_.

Sample	TGA Weight Loss (400-650°C) (%)	Normative Mineralogy Calculated Total Weight Loss (%)	Calculated % Weight loss based on Normative Mineralogy						
			Kaolinite	Illite	Montmorillonite	Chlorite	Calcite	Muscovite	Organic[1]
RC1	**2.1**	**1.7**	0.56					1.12	
RC2	**8.3**	**8.5**	7.86					0.68	
RC3	**9.7**	**10.0**	9.66					0.40	
RC4	**10.2**	**10.6**	10.50					0.12	
RC5	**16.0[2]**	**17.3**	5.32	1.20					10.80
RC6	**11.0**	**16.4**	0.84	2.88			12.70		
RC7	**8.2**	**9.8**	1.68	3.72	3.29	1.08			
RC8	**5.4**	**5.7**	2.28	2.88	0.12		0.40		
RC9	**8.0**	**8.7**	6.86	1.56		0.24			
RC10	**8.7**	**9.1**	0.98	3.48		1.56	3.08		
KDRC	**16.2**	**17.6**	0.98	3.43		1.08	4.40		7.70

Table 16: Calculated weight loss based on the Normative Mineralogy mineral % contents in Table 15

Notes
[1] These are estimates as organic carbon thermal decomposition takes place over a wide temperature range.
[2] Uncertainty of actual temperature range weight loss due to very high organic carbon content. Value is the best estimate from the TGA curve.

On the whole the total weight loss based on the Normative Mineralogy values for the clay, and none clay minerals in each sample, are reasonably close, within ±10% variance. There are 3 samples with high weight losses within the 400-650°C temperature range, RC5, RC6 and KDRC, that fall within the 10% variance value, but none the less are at the upper level of this. This is most likely due to the high levels of none clay mineral content that are also highly likely to be thermally decomposing within the target temperature range, RC5 and KDRC due to high organic carbon contents, and RC6 due to a very high calcite (carbonate) content.

The resulting calculated weight loss for each of the clay sources can therefore be regarded as being representative of the actual mineralogical assemblages and

provides confidence that the values are as close as possible to reality and fall within the variability of the analytical accuracy of the techniques utilised in this project.

9.5. Conclusions

The results from these refined XRD measurements confirm the difficulty of properly quantifying kaolinite and other clay minerals, due to the presence of poorly crystallised phases that cannot be identified by XRD, and when dealing with clays that are not routinely run within a specific laboratory, interpretations are often based on judgments by the operator, and are therefore subjective rather than objective.

However, they do give sufficient indications to identify which clays are more likely to be reactive (the ones containing the higher amounts of clay minerals such as kaolinite and illite). The information about the impurities present is also useful, helping to estimate some properties such as grindability and colour.

Despite the difficulty of determining the amount of kaolinite and other clay minerals, these results show that the 10 clays tested in the project cover a large range of compositions. Evaluating the performances of significantly different clays is one of the main interests of the Re-C3 project, and it is confirmed that the clay candidates were well selected.

The project on the whole, based on the clays that were taken forward for full assessment, shows that clay resources with less than the commonly reported 40% minimum kaolinite content, can be successfully converted into reactive calcined clays. Whilst kaolinite is known to have reactive properties when converted to metakaolin, little work has been undertaken on the mixed clay deposits where kaolinite and illite, and in some cases montmorillonites and chlorites as secondary clay minerals, perform well as calcined clay replacements for Portland Cement.

These results suggest that when it comes to standards for assessment of clay resources as potential calcined clay feedstock, the criteria used shouldn't be prescriptive in terms of the minimum level of kaolinite present in the deposit, or for that matter a limit on the total clay content. The assessment criteria should use a performance-based assessment technique, that measures reactivity, either in test mortar prisms, or in concrete cubes . By doing this, there is a much wider scope for the utilisation of currently under-utilised raw material sources, and therefore a much wider opportunity to capitalise on the use of clays to create calcined clays for cement replacement.

10. Validation of Commercial Cements

Section Authors: Nina Cardinal (Heidelberg Materials UK) & Simon Chudley (Tarmac Cement)
Detailed report available in: Appendix 10 - Validation of commercial cements

10.1.　Introduction

Work package J of the Re-C3 project dealt with the characterisation of four clays calcined at a pilot scale and one brick powder and with the performance of binary and ternary blended cements made with these powders. The testing in work package J was carried out at the cement testing laboratories of Heidelberg Materials UK and Tarmac Cement.

10.2.　Materials and Nomenclature

The four clays and one brick powder taken to the pilot phase are listed below. RC2 and RC9 were both flashed and rotary calcined at FLSmidth and IBU-tech respectively to provide a comparison of the effect of the different calcination processes on the clay properties.

Clay Designation		Clay Provider	Calcination Process
Raw	Calcined		
RC2	CC2R	Imerys	Rotary
RC2	CC2F	Imerys	Flash
RC3	CC3R	Imerys	Rotary
RC9	CC9F	Tarmac	Flash
RC9	CC9R	Tarmac	Rotary
RC7	CC7F	Heidelberg Materials UK	Flash
BP1	BP1	Forterra KDBP	Not applicable

Table 17: Clay nomenclature

The mineralogical composition of the raw clays, established by applying a normative mineralogy approach to the XRF data, is shown in *Table 18* below. It highlights RC1 and RC2 to be high in kaolinite, RC7 to be low in kaolinite and RC9 representing an intermediate kaolinite content.

	RC2	RC3	RC7	RC9
Quartz	8	4	20	19
Feldspar	16	13	10	7
Fe Oxides	-	-	4	7
Kaolinite	54	69	12	49
Illite	-	-	31	13
Chlorite	-	-	9	2
Smectite	-	-	9	0
Muscovite	17	10	-	-

	5	4	-	-
Schorl	5	4	-	-
Montmorillonite	-	-	9	-

Table 18: Raw clay mineralogical composition

The reference cements and constituents and the limestone for blending with the clays are listed in *Table 19* below.

Material	Designation
CEM I - 52,5N	PC1
	PC2
	PC3
Limestone Powder	L1
	L2
	L3
CEM II/A-LL – 52,5N	N/A
GGBS	GGBS
Fly Ash	FA

Table 19: Reference material nomenclature

The naming convention used through this report for the blended calcined clay cements is illustrated below.

Cement Group	Cement Detail	Designation
CEM II/B-Q	75% Source 1 PC + 25% Imerys Source 2 clay flash calcined	75:25 PC1:CC2F
	70% Source 2 PC + 30% Forterra KDBP	70:30 PC2:BP1
CEM II/C-M	55% Source 1 PC + 30% Heidelberg clay flash calcined + 15% Source 2 limestone	55:30:15 PC1:CC7F:L2
	50% Source 1 PC + 40% Tarmac clay rotary calcined + 10% Source 1 Limestone	50:40:10 PC1:CC9:L1

Table 20: Blended cements nomenclature

A total of 30 cements falling into three groups were blended and tested: CEM II/B-Q, CEM II/C-M and reference cements. The binary CEM II/B-Q cements covered calcined clay levels of 25, 30 and 35 %. In the ternary CEM II/C-M group, clinker replacements levels (with calcined clay and ground limestone) of 45% and 50% were investigated with 55:30:15 and 50:40:10 cements. The reference cements comprised CEM I, CEM II/A-LL, 25% and 40% fly ash cements and 36% and 45% GGBS cements.

An extensive comparison programme for all test methods was carried out between Tarmac Cement and Heidelberg Materials UK on the reference cements. It confirmed good reproducibility of test results between the two laboratories.

10.3.   Calcined Clay Characterisation

The particle size distributions of the calcined clays are shown in *Figure 18* below.
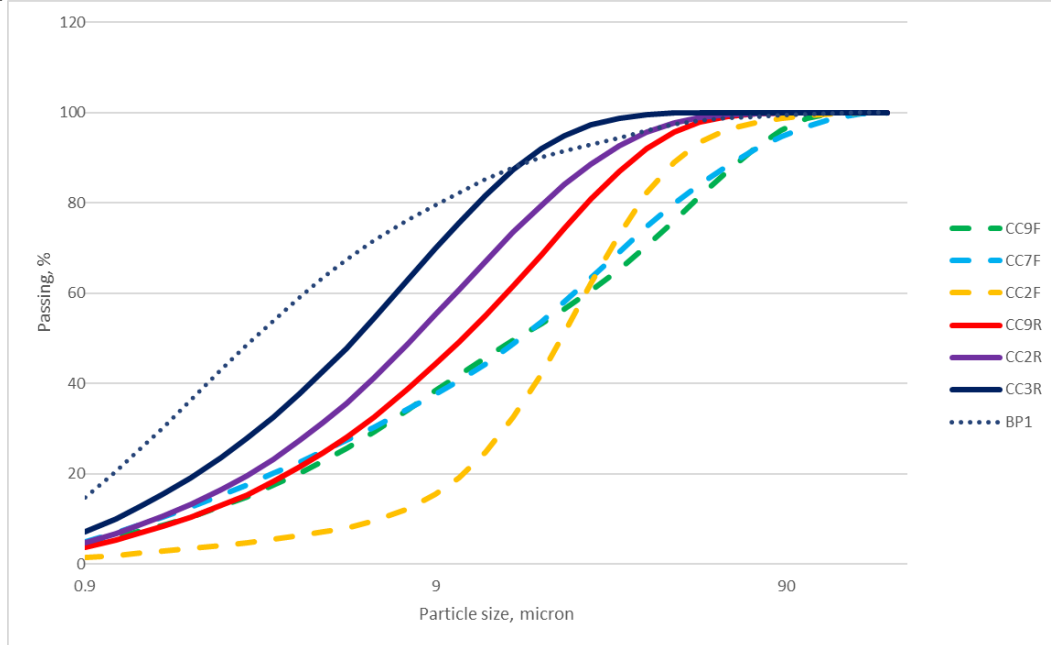
Figure 18: Calcined clay particle size distribution

CC9F and CC7F have almost identical PSDs as they were ground to the same target fineness following calcination. CC2F was deemed fine enough following flash calcination and was therefore not ground. This has resulted in a slightly coarser material with a different shape to the particle size distribution. The three rotary calcined clays were all ground post calcination, resulting in very similarly shaped distributions, all three slightly finer than the ground flash calcined clays, with CC2R being the finest. The brick powder stands out for being the finest material.

The calcined clays were assessed against the requirements of Part 1 of BS 8615. *Table 21* below shows the results against the chemical requirements of BS 8615-1. DTS stands for 'deemed to satisfy' as BS 8615 states that if the CaO content is below 10%, the requirement for reactive CaO is satisfied. The results in *Table 21*, from testing completed by Tarmac cement, demonstrate that all clays meet the requirements of the standard except for BP1 being just above the upper limit for CaO.

		BP1	CC2F	CC2R	CC3R	CC7F	CC9F	CC9R	BS 8615-1
LOI	EN 196-2	2.9	1.1	0.6	1.0	1.6	0.3	0.8	≤ 7.0%
Chloride	EN 196-2	0.07	0.00	0.00	0.00	0.00	0.00	0.00	≤ 0.1%
SO_3	EN 196-2	2.83	0.00	0.00	0.08	0.84	0.09	0.19	≤ 3.0%
Free CaO	EN 451-1	0.1	0.1	0.0	0.0	0.2	0.7	0.7	≤ 1.5%
CaO	EN 196-2	**10.6**	0.2	0.1	0.0	2.3	2.1	2.3	≤ 10.0%
Reactive CaO	EN 196-2	**10.4**	DTS	DTS	DTS	DTS	DTS	DTS	≤ 10.0%
Reactive SiO_2	EN 196-2	48.0	43.4	37.5	52.0	57.6	51.3	56.7	≥ 25.0%
$SiO_2 + Al_2O_3 + Fe_2O_3$	EN 196-2	79.0	91.9	93.5	95.0	90.4	93.4	91.8	≥ 70.0%
Na_2Oeq	EN 196-2	2.5	3.4	2.9	2.4	2.3	0.8	1.1	≤ 5.0%
MgO	EN 196-2	1.8	0.4	0.4	0.3	1.7	0.9	1.1	≤ 4.0%
P_2O_5	ISO 29581-2	0.001	0.003	0.001	0.001	0.002	0.003	0.003	≤ 5.0%
Clay Content	EN 933-9	0.1	0.2	0.3	0.5	0.4	0.2	0.5	≤ 1.5g / 100g
TOC	EN 13639	0.1	0.0	0.0	0.0	0.2	0.1	0.0	≤ 0.5%

Table 21: Calcined clay assessment against BS 8615-1 chemical requirements

The physical properties are shown below. All clays meet the requirements for the 28-day and 90-day activity index of BS 8615-1 except for BP1, CC2F, CC2R and CC9R at 90days when tested with the highest strength reference cement, PC2. All clays also comfortably satisfy the initial setting time requirement but the water requirement of CC2F, CC2R, CC3R and CC7F is higher than BS 8615-1 allows.

		Reference Cement	BP1	CC2F	CC2R	CC3R	CC7F	CC9F	CC9R	BS 8615-1
45micron residue (%)	EN 933-10	-	8.3	8.5	0.9	0.1	17.5	23.5	4.5	≤ 40.0%
43micron residue (%)	PSD	-	9.7	12.6	4.3	1.2	20.2	24.0	7.6	-
28d AI (75:25%)	EN 196-1	PC1	82	94	111	111	99	94	95	≥ 75%
		PC2	75	85	89	89	90	88	86	
90d AI (75:25%)		PC1	89	89	97	108	98	96	91	≥ 85%
		PC2	**82**	**79**	**84**	88	92	88	**84**	
Soundness (70:30%)	EN 196-3	PC1	0	0	0	0	0	0	1	≤ 10mm
		PC2	0	1	0	0	0.5	0	0	
Initial Set (75:25%)	EN 196-3	PC1	1.4	1.4	1.3	1.5	1.2	1.4	1.3	≤ 2x TC
		PC2	1.3	1.3	1.2	1.4	1.3	1.4	1.3	
Water requirement (%)	EN 450-1	PC1	109	**122**	**118**	**127**	**118**	107	111	≤ 115%

Table 22: Calcined clay assessment against BS 8615-1 physical property requirements

A visual comparison of the colour of the reference materials and the calcined clays is shown below. The flash calcination at FLSmidth was carried out with a reducing zone after the calciner where the higher Fe_2O_3 (hematite) content present in RC7 and RC9, which is red in colour, is reduced to Fe_3O_4 (Magnetite), the latter being grey in colour.
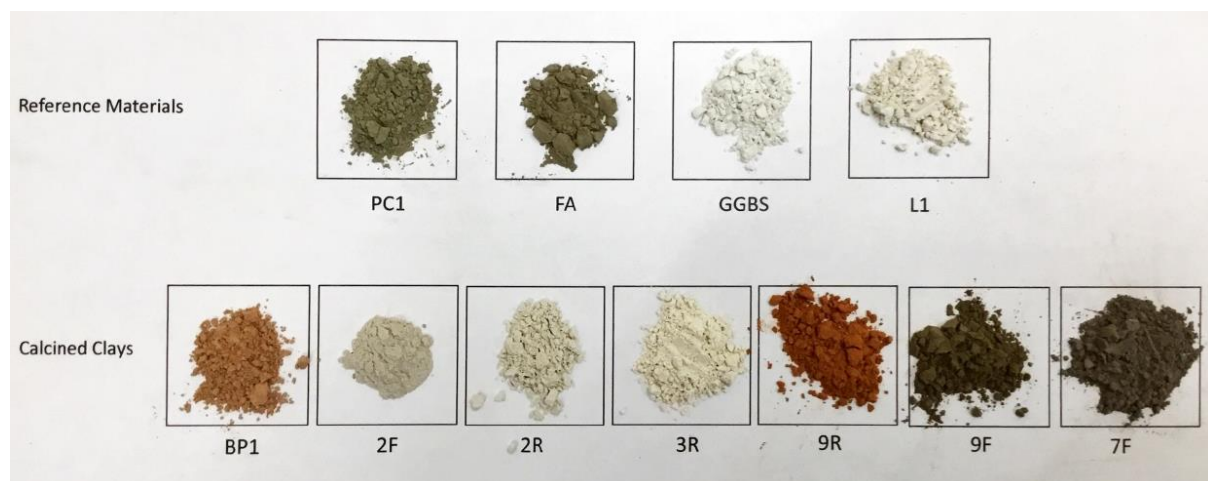

Figure 19: Visual comparison of material colours

10.4.   Calcined Clay Cement Properties
All cements were assessed against the requirements of BS EN 197-1.
The initial setting time results of the calcined clay cements are compared with the reference cements below.
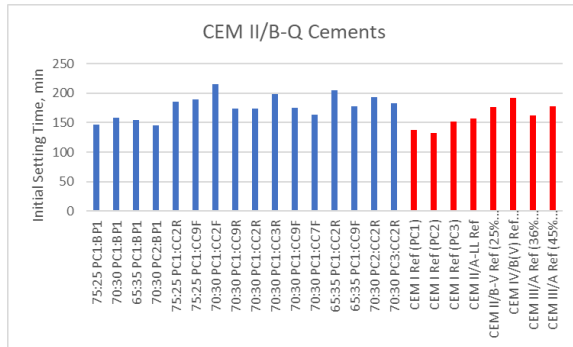
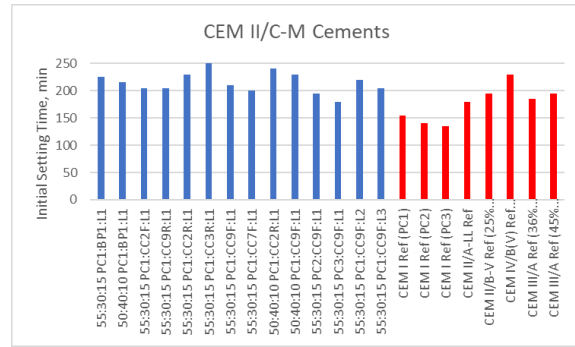*Figure 20: Initial setting times of CEM II/B-Q cements*

Figure 21: Initial setting times of CEM II/C-M cements

For both, the CEM II/B-Q and CEM II/C-M cements, the setting times are higher than those of the CEM I reference cements and closest to the setting time of the fly ash reference cements.

The water demand results below highlight that most of the calcined clay cements have a higher water demand than any of the reference cements and that the CC2R, CC2F and CC3R clays, which have a higher kaolinite content, result in higher water demand than the BP1, CC7F, CC9R and CC9F clays. In addition to the higher kaolinite content, higher fineness may also play a role, as CC2R and CC3R also exhibit higher fineness.
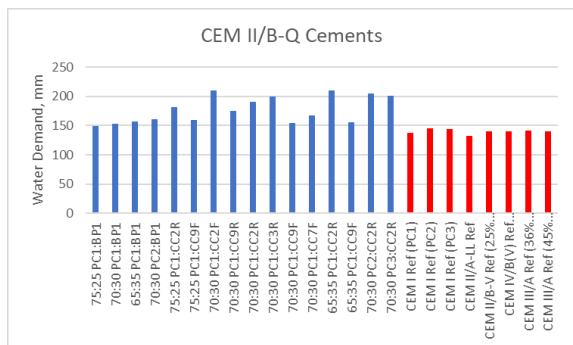

Figure 22: Water demand of CEM II/B-Q cements
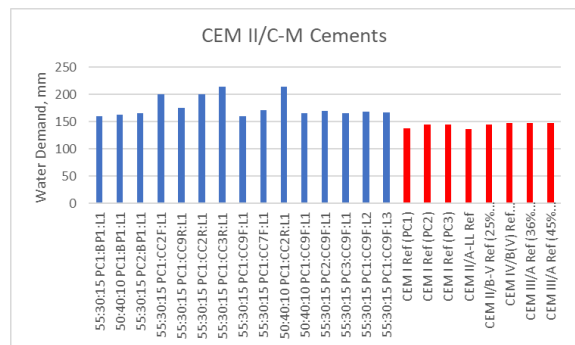
Figure 23: Water demand of CEM II/C-M cements

Mortar flow testing has confirmed these findings. The effect of increasing calcined clay content on flow was most pronounced for the CC2R clay. Increasing the calcined clay content by 10% from 30% to 40% in the CEM II/C-M cements results in a higher loss of flow than the increase by 10% from 25% to 35% in the CEM II/B-Q cements. A comparison of the 70:30% and 55:30:15% cements showed that the difference in flow at the same calcined clay level is small between the two groups of cements, the CEM II/C-M cements giving only slightly lower flow results than the CEM II/B-Q cements.

Figure 24: Mortar flow results for binary, ternary and reference cements

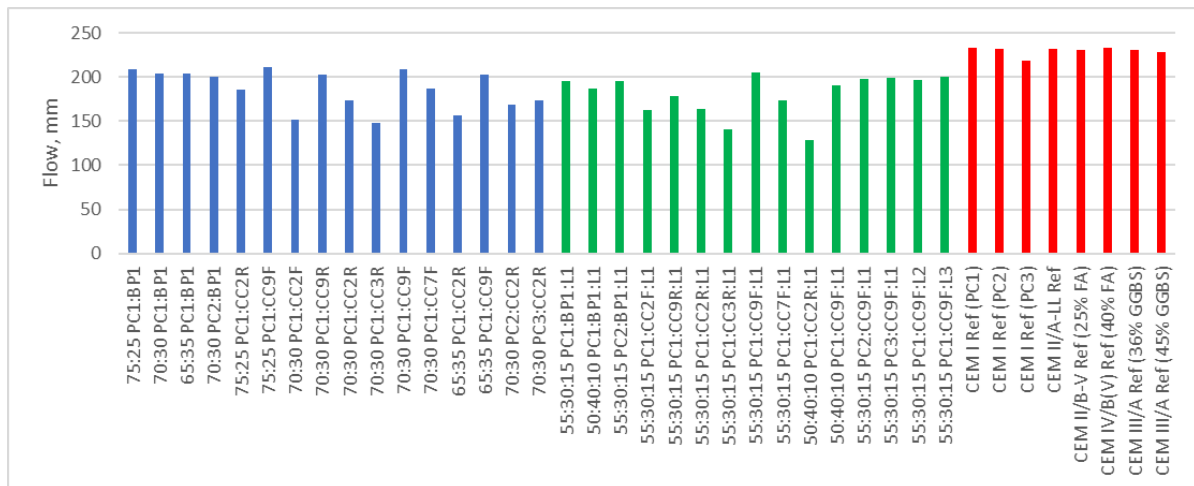When comparing the flow and water demand for flash calcined and rotatory calcined clays, there is no consistent difference between rotary and flash calcined clays. Cements with the CC9 clay exhibit a slightly lower flow with rotary calcination, whereas cements with CC2 clays show no difference in the CEM II/C-M cement but a decrease in flow for the flash calcined materials in the CEM II/B-Q cement.

The expansion results, a measure of soundness, of all calcined clay cements were mostly 0 mm and a maximum of 2 mm, meeting comfortably the requirement of ≤10 mm of EN 197-1. Compressive strength testing was carried out at 1, 2, 7, 28, 56 and 90 days for all cements.

Figure 25 below shows the strength development up to 90 days for all CEM II/B-Q cements made with the PC1 reference cement.
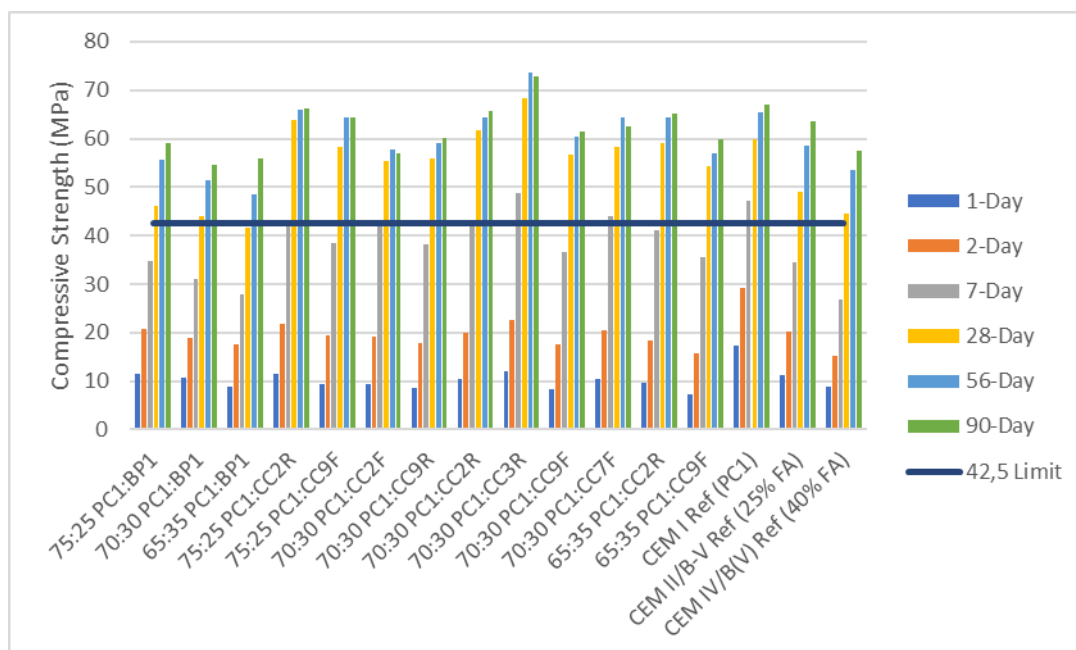

Figure 25: Mortar prism compressive strength results for binary CEM II/B-Q cements

While the 1-day and 2-day strengths are lower than that of the PC1 reference cements they are generally comparable to the CEM IV/B-V cement with 25% fly ash and higher than the reference cement with 40% fly ash. All cements meet the 2-day 10 MPa 42,5N strength minimum requirement of EN 197-1 comfortably. At 28-days, all CEM II/B-Q cements exhibit significantly higher strength levels than both fly ash reference cements and exceed the EN 197-1 42,5N limit by a significant margin except for the cements with BP1. In fact, all cements, except the BP1 cements, would meet the BS EN 197-1 52,5L strength requirement. The highest strength is exhibited by the cements made containing CC2R and CC3R, the higher kaolinitic clays, whereas CC2F, which was not ground after calcination, exhibits strength levels similar to those of CC7F and CC9F.

The increasing clinker replacement levels of 25%, 30% and 35%, studied on BP1, CC2R and CC9F, result in a small reduction in early and later strength, the only exception being the 56-day and 90-day strength of the cements containing CC2R. The 28-day strength loss with increasing calcined clay content for CC2R is surprising given that it had a 28-day activity index >100%.

The strength development for all CEM II/C-M cements made with the PC1 reference cement and source L1 limestone fines are shown below.
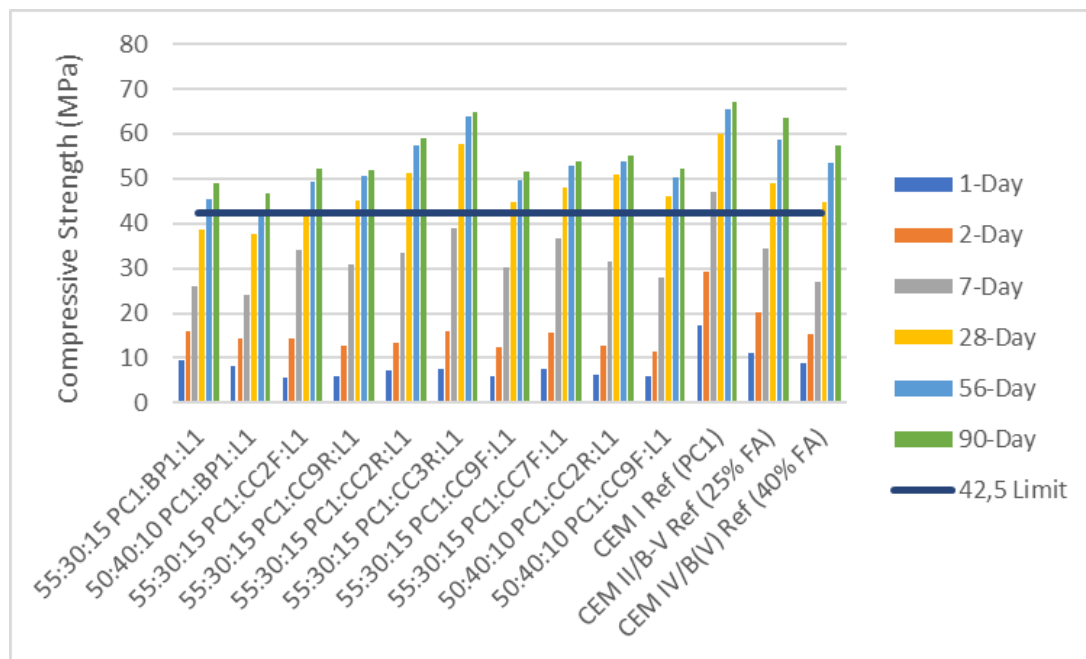
Figure 26: Mortar prism compressive strength results ternary for CEM II/C-M cement

The 1-day strengths are mostly lower not only than the PC1 reference cement strength but also compared to the two fly ash reference cements. At 2-days the strengths are comparable to the 40% fly ash reference cements. While meeting the 2-day 10 MPa 42,5N strength minimum requirement of EN 197-1, it is borderline in many of the cases. At 28-days, with the exception of the BP1 cements, all CEM II/C-M cements exhibit either similar or higher strength levels than both fly ash reference cements. They also meet the 42,5 N limit albeit borderline except for the CC2R, CC3R and CC7F cements. As for the CEM II/B-Q cements, the highest strength is exhibited by the cements made with the CC2R and CC3R clays, the higher kaolinitic clays. Only

the 55:30:15% cement made with CC3R closely matches the 28-day strength of the reference PC1, but exbibits lower 1-day, 2-day and 7-day strength than PC1.

A significant reduction in strength is found when comparing the 70:30% with the 55:30:15% cements. This indicates that at these replacement levels there is no synergetic effect of the limestone fines with the calcined clay, in fact, in all but one cases the percentage reduction in strength is higher than the 15% limestone fine addition.

When comparing the strength development for the two different replacement levels, i.e. 55:30:15% vs 50:40:10%, of the CEM II/C-M cements, only small differences are observed. This indicates that the reduced clinker content in the 50:40:10% cements can be compensated for by reducing the limestone content and increasing the calcined clay content.

The effect of the fineness on strength was studied in blends made with unground calcined clay, ground calcined clay and the filter dust from the flash calcination process. The activity index was determined for all three clay processing stages for both CC9F and CC7F.

Clay	Condition	Activity Index with Reference PC1 (%)		Activity Index with Reference PC2 (%)	
		28-day	90-day	28-day	90-day
CC9F	Ground	94	96	88	88
	Pre-Grinding	78	83	81	81
	Filter Dust	96	96	86	87
CC7F	Ground	99	98	90	92
	Pre-Grinding	82	87	79	80
	Filter Dust	99	98	84	88

Table 23: The effects of fineness on Activity Index

The higher values obtained for the activity indices with PC1 compared to PC2 are purely a reflection of the lower strength of PC1 compared to PC2. The requirements of BS 8615-1 are for the 28-day index to be at least 75% and the 90-day index 85%. The results demonstrate that without grinding, the clays do not consistently meet these minimum requirements but that once ground to a fineness similar to that of the CEM I and fly ash, both clays comfortably meet the requirements. There are no further strength gains from the even finer filter dust compared to the ground clays.

When comparing the strength development of CC2R with CC2F and CC9R with CC9F in the 70:30% CEM II/B-Q and the 55:30:15% CEM II/C-M cements no consistent effect of the calcination process on the strength development is found.

BP1, CC2R and CC9F were also tested in binary and/or ternary 70:30% and 55:30:15% cements blended with the three different reference CEM Is. The results do not show a consistent pattern related to the strength of the CEM Is, indicating that different clays may react differently with different CEM Is.

The three different limestone sources had no significant effect on the strength development of 55:30:15% cements made with CC9F.

Not orginally planned but later added to the programme were mixes produced with different sulfate levels through controlled gypsum additions. The effect of the increased SO_3 levels on the strength development is shown below as the difference in strength between the original cement and the re-sulfated cement.
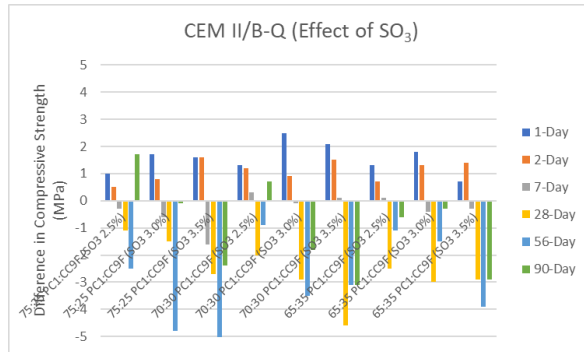

Figure 27: SO₃ effects on mortar prism strength for CEM II/B-Q Cements

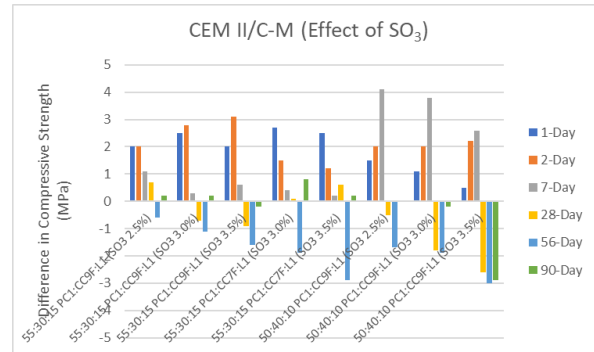Figure 28: SO₃ effects on mortar prism strength for CEM II/C-M Cements

In all cases the 1-day and 2-day strengths increase with the SO_3 addition. This early strength increase is more pronounced in the CEM II/C-M cements. The early strength gains typically peak at 3.0% SO_3 and then drop off at 3.5% SO_3. At 7 days, there is no consistent effect of SO_3 addition. The significant increase of 7-day strength of the 50:40:10% cement is notable but unexplained. At 28-days and beyond, the SO_3 addition results generally in a loss in strength which is more pronounced in the CEM II/B-Q cements than the CEM II/C-M cements.

10.5.   Conclusions and Recommendations

The main conclusions drawn from the work carried out in work package J are as follows:

- All clays, except for the high kaolinitic clay after flash calcination, required grinding after calcination to optimise the clay fineness and reactivity.
- There was no discernible effect of flash versus rotary calcination on compressive strength nor fresh mortar properties.
- While SO_3 additions increased the early strength of the calcined clay cements, they reduced the 28-day strength and beyond.
- All clays produced respectable strength results, most cements with up to 40% calcined clay content meeting the 42,5N strength class in EN 197-1. Also, the clays with lower kaolinite contents demonstrated good reactivity. Most of the calcined clay cements without limestone additions outperformed the 25% and 40% fly ash reference cements in terms of strength development.
- The clays met the requirements of BS 8615-1 except for the water requirement in some cases and the 90-day activity index when tested with a high strength reference cement.
- The calcined clay cements with and without limestone additions have a higher water demand and exhibit a lower mortar flow than any of the reference

cements and the water demand is highest and the flow lowest with the higher kaolinitic clays.

- The early strength of the CEM II/B-Q cements is comparable to that of the 25% fly ash reference cements, whereas that of the CEM II/C-M cements is closer to that of the 40% fly ash reference cement.
- An increase in clay content from 25 to 35% does generally lead to a small reduction in early and later strength.

Based on the work carried out in work package J, it is recommended that the water requirement and activity index limits in BS 8615-1 are reviewed.

The effect of different clinker sources on the strength development of calcined clay cements also warrants further investigation.

11. Durability of Calcined Clay Concrete

Section Authors: Thomas Hope (UoD), Roderick Jones (UoD), Moray Newlands (UoD), & Michael McCarthy (UoD).
Detailed report available in: Appendix 11 - Durability of calcined clay concrete

11.1.   Introduction

Work Package K of the Re-C3 project evaluated the performance of four UK clays, which were either rotary (R) or flash (F) calcined, in binary and ternary concretes, at various levels (up to 40% cement), and w/c ratios ranging from 0.4 to 0.6. The performance of calcined clay concretes was compared to a selection of reference concretes (CEM I, CEM II, etc) to evaluate the comparative performance.

11.2.   Constituent Material Characteristics

The properties of all cementitious materials, aggregates and admixtures used are available in appendix 11. A list of the materials and their nomenclatures are given in *Table 24*.

Material Name	Description	Material Name	Description
PC1	Portland Cement 1	**CC2F**	Clay 2 Flash Calcined
PC2	Portland Cement 2	**CC2R**	Clay 2 Rotary Calcined
PC3	Portland Cement 3	**CC3R**	Clay 3 Rotary Calcined
L1	Limestone 1	**CC7F**	Clay 7 Flash Calcined
L2	Limestone 2	**CC9F**	Clay 9 Flash Calcined
L3	Limestone 3	**CC9R**	Clay 9 Rotary Calcined
FA	Category N Fly Ash	**FBP**	Forterra KDBP
GGBS	Ground Granulated Blastfurnace slag		

Table 24: Nomenclature for constituent materials used

The properties of the six calcined clays (CC) and one brick powder (FBP) tested by the University of Dundee as part of Work Package K are given in *Table 25*.

It was noted that when compared with the fly ash used (6.19 m^2/g), most calcined clays had a higher specific surface area (5.28 m^2/g to 21.04 m^2/g), as measured by B.E.T., with only CC2R reporting a lower surface area (5.28 m^2/g), and both CC2F and FBP (7.09 and 6.49 m^2/g respectively) comparable to the fly ash. The rotary calcined clays had lower B.E.T. specific surface areas than the fly ash, however, the source of clay had a greater influence than calcination method. The specific surface areas of the GGBS (1.93 m^2/g) and the limestone (LS) sources ranged from 1.88 m^2/g to 2.21 m^2/g. A general hierarchy could be established, with surface area increasing in the following order: CC2, CC3, CC7, CC9.

The particle densities of the calcined clays were greater than that of the fly ash (2260 kg/m^3) and ranged from 2350 kg/m^3 to 2740 kg/m^3 but were lower than that of GGBS at 2900 kg/m^3.

Property	CC2F	CC2R	CC3R	CC7F	CC9F	CC9R	FBP
45µm sieve ret., %wt	11.5	3.4	1.7	30.4	29.7	7.8	5.3
Loss-on-Ignition, %wt	0.82	1.32	0.62	0.58	0.50	0.49	3.40
PSD*, d_{10}, µm	8.6	2.9	2.1	3.0	2.6	1.8	0.8
PSD*, d_{50}, , µm	23.6	12.8	8.6	25.4	24.9	13.2	3.8
PSD*, d_{90}, , µm	51.7	40	21.9	75.1	74.9	39.3	19
Particle density, kg/m³	2490	2582	2352	2601	2631	2740	2689
SSA, B.E.T., m²/g	7.09	5.28	10.40	15.36	21.04	14.48	6.49
SiO_2, % wt	53.4	51.7	55.3	54.5	59.1	58.9	50.9
Al_2O_3, % wt	33.1	33.6	37.8	23.3	22.6	24.4	19.4
Fe_2O_3, % wt	2.3	1.8	1.3	7.3	8.6	8.3	6.0
CaO, % wt	0.3	0.1	0.2	2.8	2.9	2.8	10.9
MgO, % wt	0.4	0.4	0.3	1.8	1.0	1.2	1.9
K_2O, % wt	4.6	4.0	3.4	3.0	1.2	1.6	3.0
Na_2O, % wt	0.2	0.2	0.2	0.3	0.1	0.3	0.5
P_2O_5, % wt	0.1	0.1	0.1	0.3	0.1	0.1	0.2
Cl^-, % wt	0.0	0.0	0.0	0.0	0.0	0.0	No data
SO_3, % wt	0.0	0.0	0.0	2.0	0.1	0.6	3.1
MnO, % wt	0.0	0.0	0.0	0.0	0.1	0.1	0.0
TiO_2, % wt	0.2	0.1	0.0	1.2	1.2	1.1	0.9

Table 25: Physical and chemical characteristics of calcined clays and brick powder as tested by University of Dundee

* Using laser diffraction

11.3.   Concrete mix designs

The concrete mix designs adopted for use in the project are given in Table 26. Trial mixing was carried out to identify these for the calcined clays and aggregate package. A fixed water content of 170 kg/m³ was used, allowing the cement combination content to vary with water / cement ratio. An admixture (containing a superplasticiser) was used to achieve a target consistence class of S3 (minimum slump of 100mm). The coarse aggregates were a crushed limestone and the fine aggregates a graded quartz from UK sources conforming to BS EN 12620 (BSI, 2002).

w/c ratio	Test combinations	Free water, l/m³	Total Cement (Combination), kg/m³	Aggregates, kg/m³		
				0/4	4/10	10/20
0.40	CEM II/B-Q, CEM II/C-M (Q-L), CEM II/B-V	170	425	750	369	686
0.50	CEM I, CEM II/A-L, CEM II/B-Q, CEM II/B-V, CEM II/C-M (Q-L), CEM III/A, CEM IVB(V)	170	340	760	374	756
0.60	CEM II/B-Q, CEM II/C-M (Q-L), CEM II/B-V,	170	283	756	373	818
0.55	CEM I, CEM II/B-Q, CEM II/B-V, CEM III/A	170	309	864	405	652

Table 26: Summary of concrete mix proportions

11.4.   Consistence and strength development

The admixture doses and corresponding slump for the binary (CEM II / B-Q) and ternary concretes (CEM II/C-M), at 30% calcined clay in replacement of cement and 0.5 w/c ratio, are shown in *Figure 29* and *Figure 30*.

Calcined clay binary and ternary concretes had higher admixture demand (0.46 % to 1.16%) than the fly ash (0.37% and 0.41%) and GGBS (0.35% and 0.52%) concretes. Compared to calcined clay, the FBP concretes had lower admixture requirements (0.35 % to 0.48 %) but generally remained higher than those of the FA and GGBS references. Within the calcined clays, no single clay type consistently had the lowest admixture demand, although a general order could be established from lowest to highest:

<center>CC9F<CC9R<CC3R<CC2R<CC7F<CC2F</center>

It appears that both the source of clay and the method of calcination influence the rheology of concrete, but the extent of this could not be established owing to the influence of multiple variables such as particle size, mineralogy, and surface areas of the calcined clays.

Using a suitable admixture broadly within the recommended dosage range of the manufacturer, allowed the calcined clay binary and ternary concretes to achieve the target consistence. With further optimisations of the concrete mix design and development of calcined clay specific admixtures, it is likely that higher slump classes could be attained.
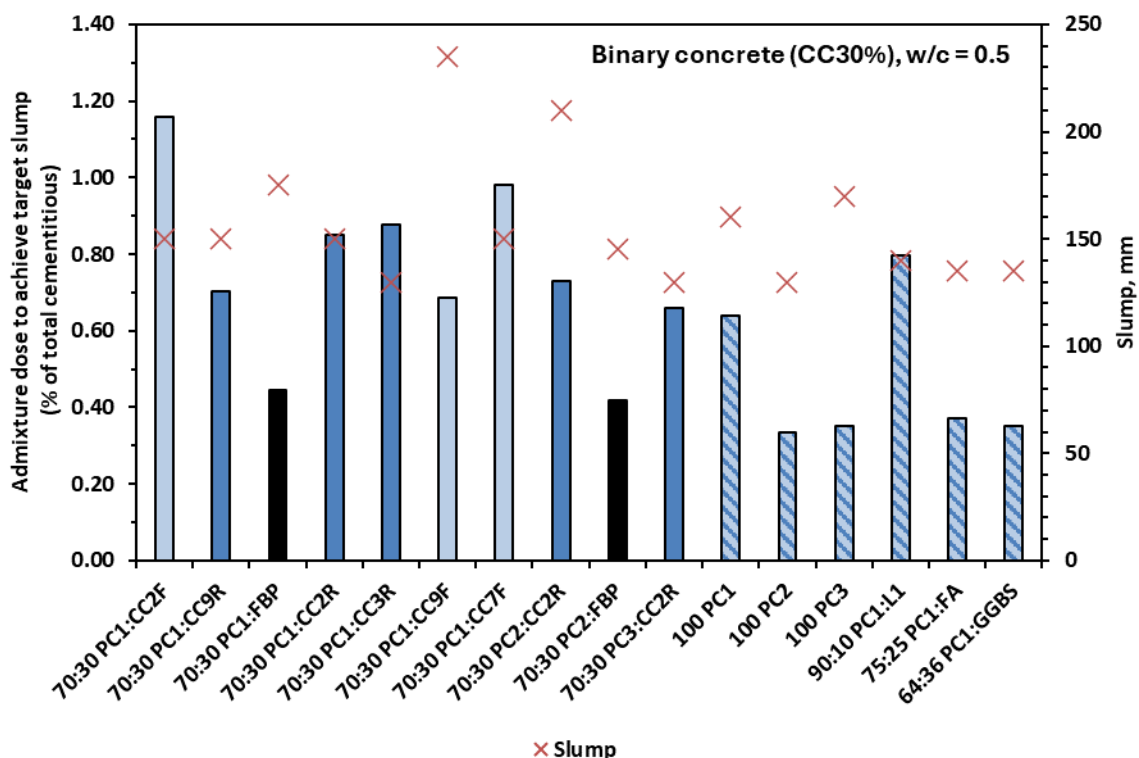

Figure 29: Admixture dose required to achieve target slump and the corresponding slump achieved for binary concretes at w/c = 0.5
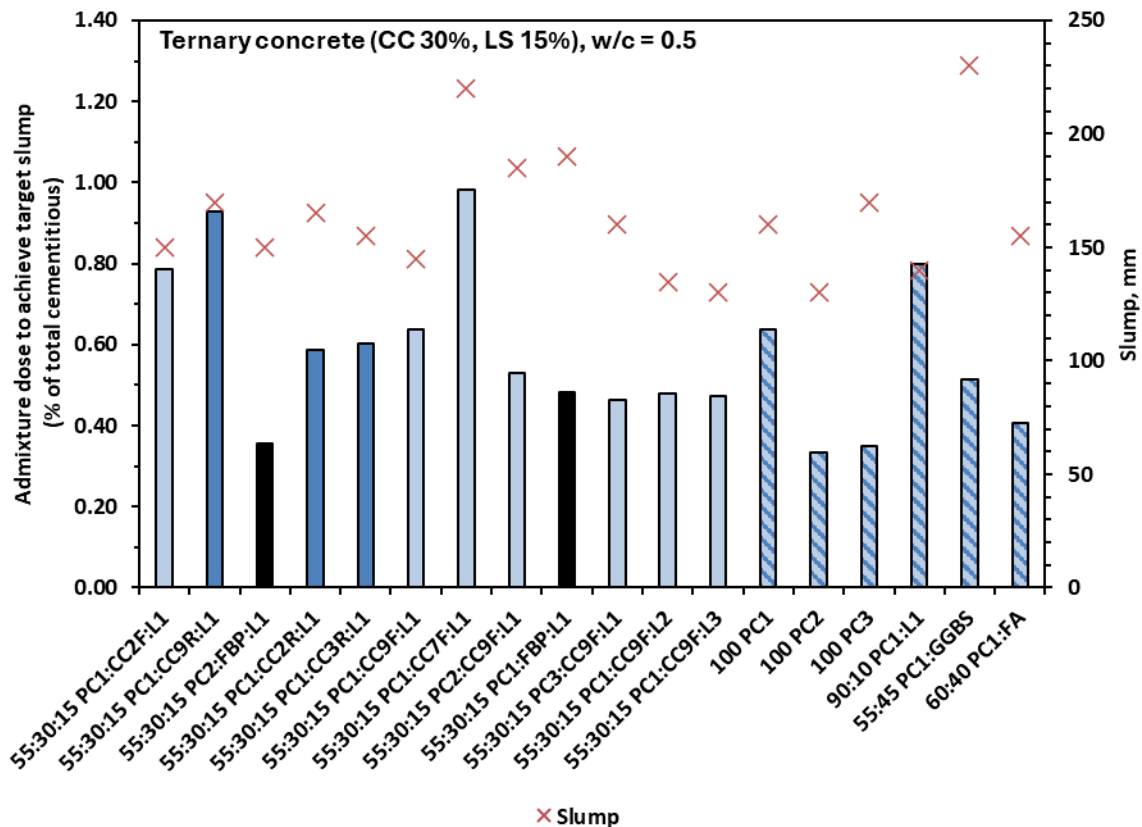
Figure 30: Admixture dose required to achieve target slump and the corresponding slump achieved for ternary concretes at w/c = 0.5

The cube strength development results for the CEM II/B-Q binary and CEM II/C-M ternary concretes at equivalent w/c ratios of 0.5, are given in *Figure 31* and *Figure 32* which also includes the CEM I, FA, GGBS and LS references.

The concrete strength development results show that the calcined clay concretes gain strength rapidly between the ages of 3 days and 14 days, with strength gains reducing thereafter. The 28-day strengths of the binary calcined clay concretes (54.5 MPa to 75.5 MPa) exceeded the 28-day strength of the 25% FA (49 MPa) and were comparable or greater than that of the 36% GGBS (57 MPa). The calcined clays, with the exception of CC9R, had comparable strengths to the 25% FA even at 56 and 180 days (61 MPa and 71 MPa respectively).

The 28-day strength of the ternary calcined clay concretes at a w/c ratio of 0.5 (46.5 MPa to 56.5 MPa), were comparable to or exceeded that of the 40% FA (47.5 MPa) concrete but were lower than that of the 45% GGBS (58.5 MPa). As observed in the binary concrete, at 180 days the 40% fly ash reference was similar to the calcined clay concretes and in many cases exceeded these ternary concretes. In both binary and ternary concrete, at a w/c ratio of 0.5, FBP gave lower strengths than those with calcined clay at 28 days but continued to gain strength from 28 days to 180 days. Comparatively, the calcined clays concrete strength did not increase significantly beyond 28 days. Although continuing to gain strength to 180 days, the ultimate strength of the FBP concretes were often lower than or had comparable strength to that of the 25% or 40% FA references in the binary or ternary concretes respectively.
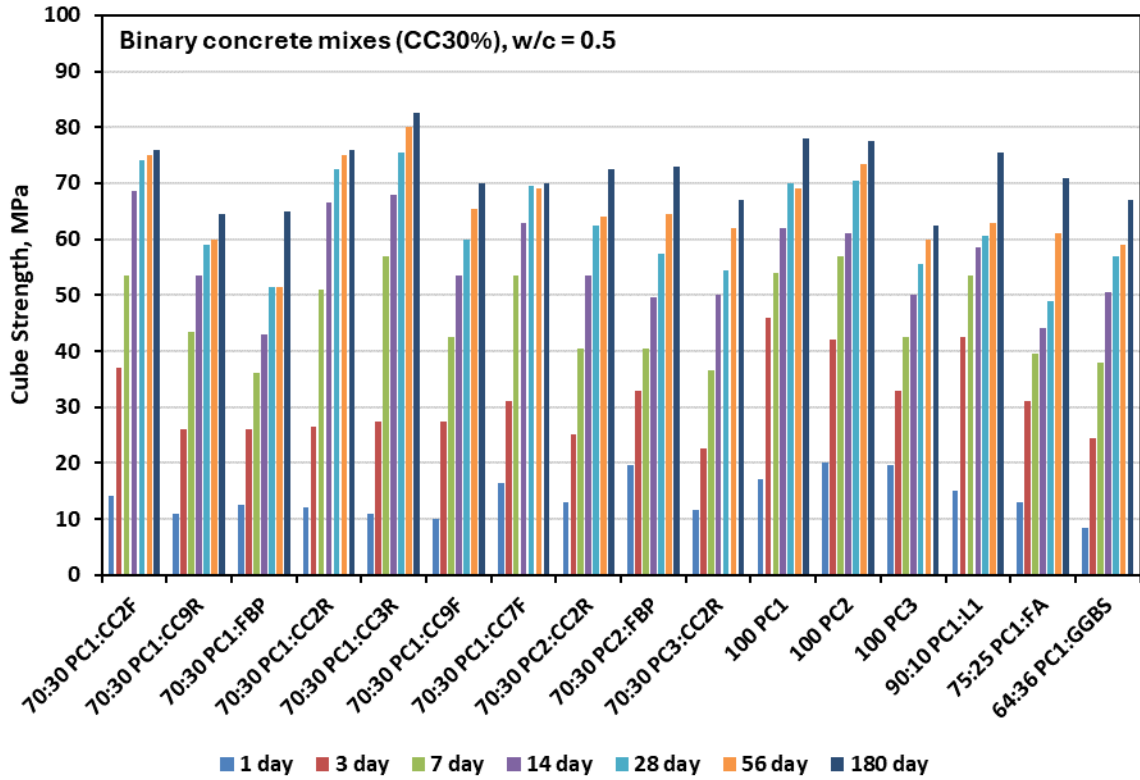
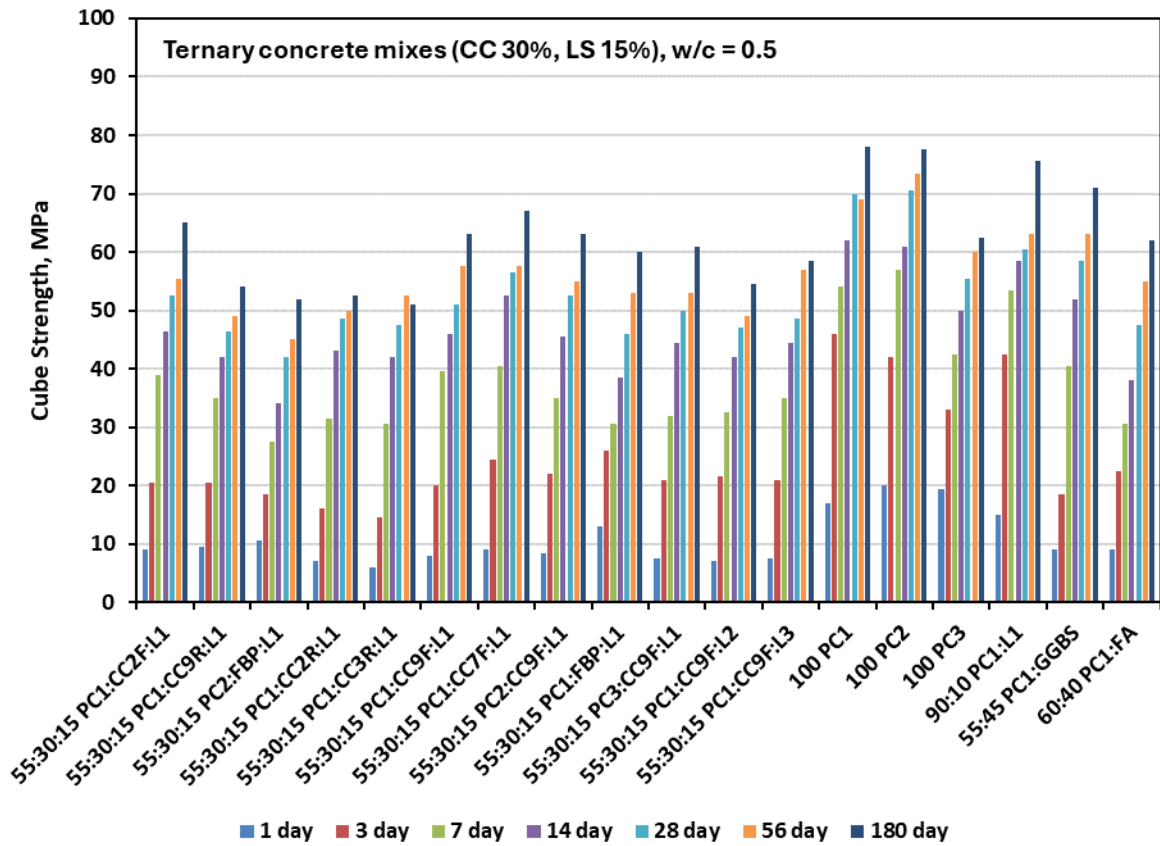*Figure 31: Concrete strength development of binary calcined clay and reference concretes at w/c = 0.5*

Figure 32: Concrete strength development of ternary calcined clay and reference concretes at w/c = 0.5

The strength results of the calcined clay binary and ternary concretes show that strengths comparable to or better than the FA, GGBS, and CEM I concretes can be obtained at the same w/c ratio. In ternary concretes, despite the replacement of 15% clinker with limestone giving reductions in strength of 15 % to 37%, when compared to the calcined clay binary concretes, a 28-day strength greater than 45 MPa was consistently attained.

Additional calcined clay concretes evaluating the effect of replacement level of cement in binary and ternary concretes found 30% to be the optimum replacement level in binary (of 15 %, 25 %, 30 %, 35%) and 40% calcined clay and 10% limestone to be optimum for ternary (of 30:15 and 40:10). Calcined clays CC2R, CC9F, and the FBP were also evaluated at w/c ratios of 0.4, 0.5, and 0.6 in both binary and ternary concretes. The same trends observed at 0.5 w/c ratio were also broadly seen at 0.4 and 0.6 w/c ratios. A more detailed discussion of these results is available in appendix 11.

Generally, flash calcined clay gave higher strengths than the same source clay compared to rotary calcination, although the source clay had a greater influence on strength development than the method of calcination. The concrete strength results indicate the hierarchy for 28-day strength development was as follows: CC2>CC3>CC7>CC9 although the strength differences between CC2 and CC3 were relatively small.

11.5.   Carbonation

11.5.1.   Accelerated Carbonation

The rates of carbonation, K_{AC}, for both calcined clay and brick powder binary (CEM II/B-Q) and ternary (CEM II/C-M) concretes at 0.5 w/c ratio and 30% calcined clay in cement are given in *Figure 33* and *Figure 34*. These were derived from the BS EN 12390-12 accelerated carbonation test (BSI, 2020) carried out at 3.0 % CO_2. The rates given are the best fit final rate of carbonation at the end of the test (70 days) per root time.
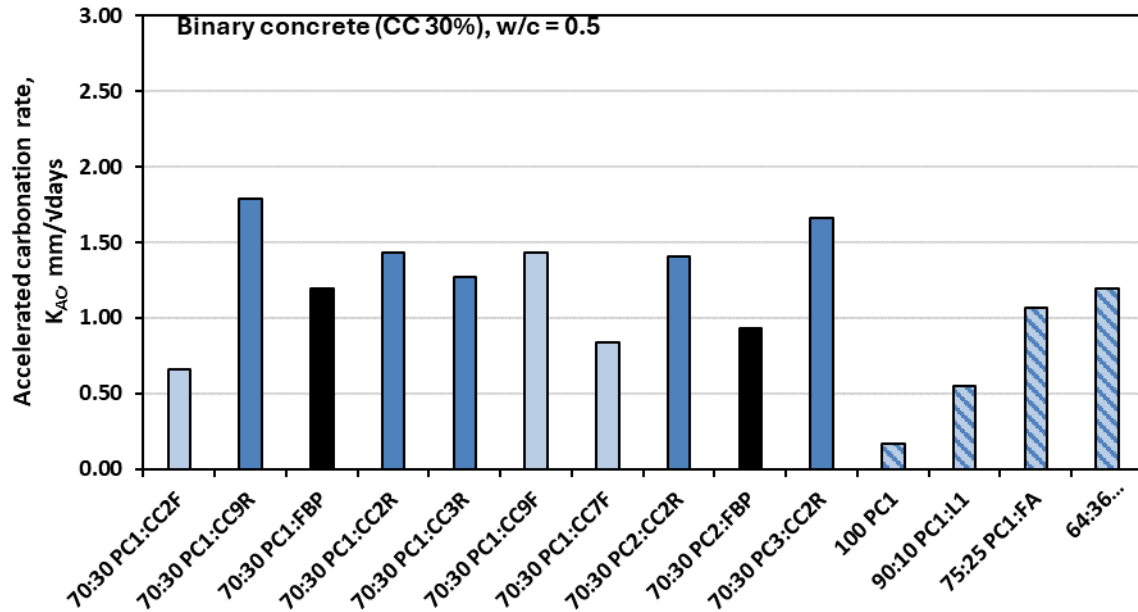
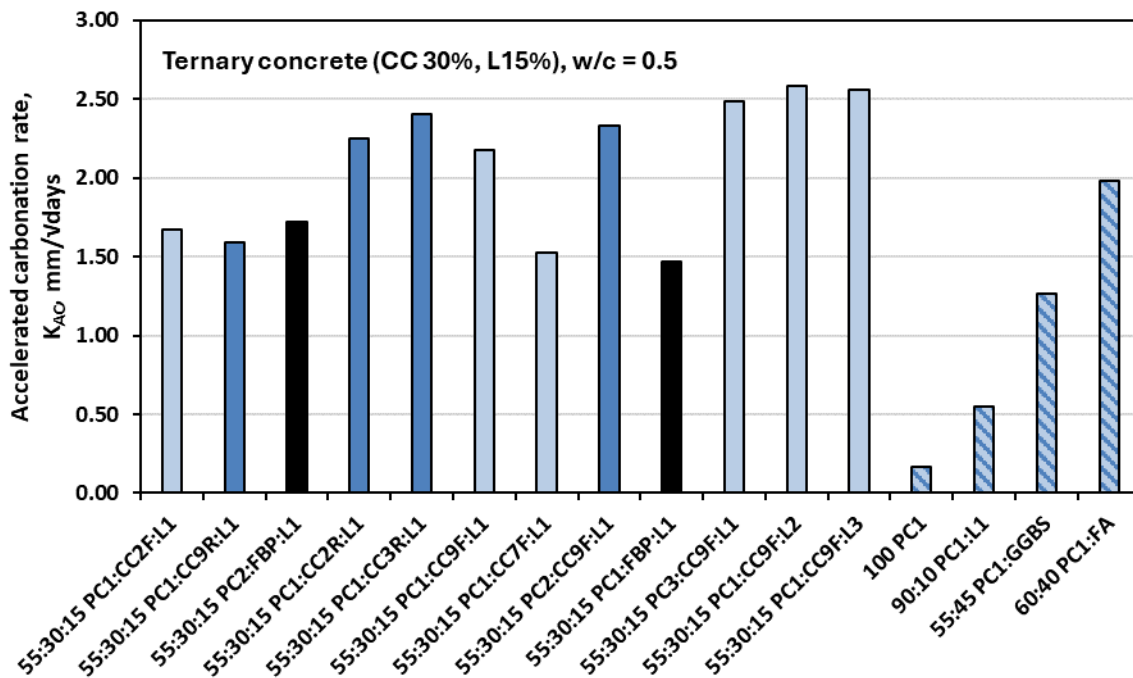*Figure 33: Rate of accelerated carbonation KAC at 3.0% CO2 for binary concretes at w/c = 0.5*

Figure 34: Rate of accelerated carbonation KAC at 3.0% CO2 for ternary concretes at w/c = 0.5

In the binary concretes, the calcined clays and brick powder generally had higher rates of carbonation (0.66 mm/√days to 1.79 mm/√days) than the 25% FA (1.06 mm/√days) and 36% GGBS (1.20 mm/√days) concretes, although CC2F and CC7F gave comparable rates. In general, the rotary calcined clays had higher rates of carbonation (1.27 mm/√days to 1.79 mm/√days) than the flash calcined clays (0.66 mm/√days to 1.43 mm/√days), but as previously observed for strength development, the source clay also appears to be more influential. Similar behaviour was observed in the ternary concretes, with the accelerated carbonation rates of the calcined clays and brick powder (2.49 mm/√days to 2.58 mm/√days) exceeding that of the 45% GGBS (1.27 mm/√days) concrete. CC2F, FBP, CC9R, and CC7F did exhibit lower rates of

carbonation than the 40% FA (1.98 mm/√days) concrete, whereas these were higher for CCR, CC3R, and CC9F.

It should be noted that while the rates of accelerated carbonation were not excessive in the calcined clays, these materials often had higher 28-day strengths (minimum of 54 MPa in binary and 46 MPa in ternary) than the FA and GGBS reference concretes. Consideration of carbonation performance should be considered however, when designing lower strength concretes, as the rate of carbonation will increase with reducing concrete strength. This behaviour is shown in *Figure 35*, comparing the FBP, CC2R, and CC9F in binary and ternary concretes at 0.4, 0.5, and 0.6 w/c ratios against a 25% FA concrete.
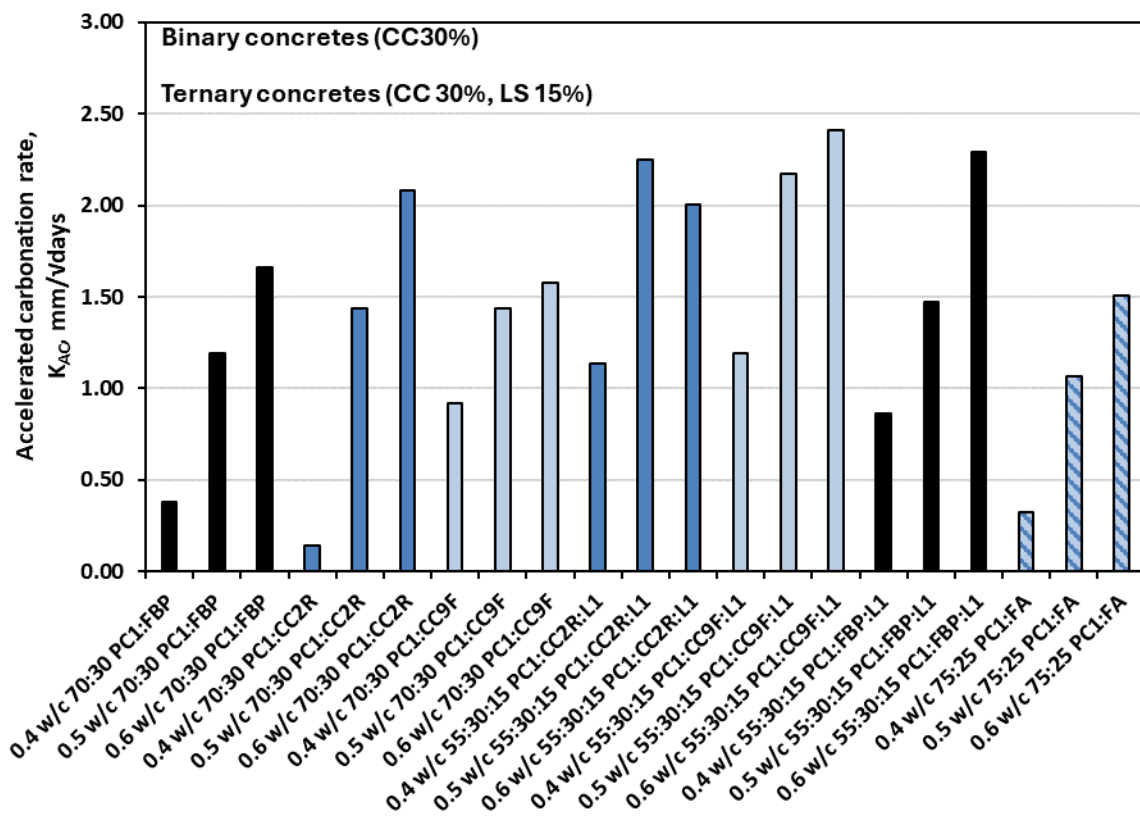

Figure 35: Rate of accelerated carbonation KAC at 3.0% CO2 for binary and ternary concretes (0.4, 0.5, and 0.6 w/c ratio)

11.5.2.   Natural Carbonation

The rate of natural carbonation to BS EN 12390-10 (BSI, 2018) was tested at 6 months exposure (outside, sheltered from direct rain), with further testing set to continue beyond the scope of this project. The 6 months natural carbonation depths for the binary (CEM II/B-Q) and ternary (CEM II/C-M) calcined clay concretes are shown in *Figure 36* and *Figure 37*.

In the binary concretes, the natural carbonation depths for calcined clays ranged from 0.2 mm to 1.4 mm. CC9R, CC2R, and CC3R had lower carbonation depths than the 25% FA (0.7mm) and 36% GGBS (0.4 mm) concretes, while these were higher for CC2F, CC9F, and CC7F. Higher depths of carbonation were observed in the ternary

concretes with limestone (0.5 mm to 2.5mm) with only CC9F using PC1 outperforming the 45% GGBS concrete (0.8mm). CC7F, CC9F using PC2 and PC3, and FBP had comparable depths to the 40% FA concrete (1.3mm). The carbonation depths of CC2F, CC9R, CC2R, and CC3R exceeded that of the 40% fly ash reference, with carbonation depths of over 2 mm after 6 months.

The change of PC appeared to influence the depth of carbonation, with CC2R concretes using PC2 and PC3 having higher carbonation depths (0.7 and 0.9 mm respectively) than CC2R using PC1 (0.2mm). This behaviour was mirrored in CC9F ternary concretes, with PC2 and PC3 giving higher carbonation depths (1.5 and 1.4 mm respectively) than PC1 (0.5mm).
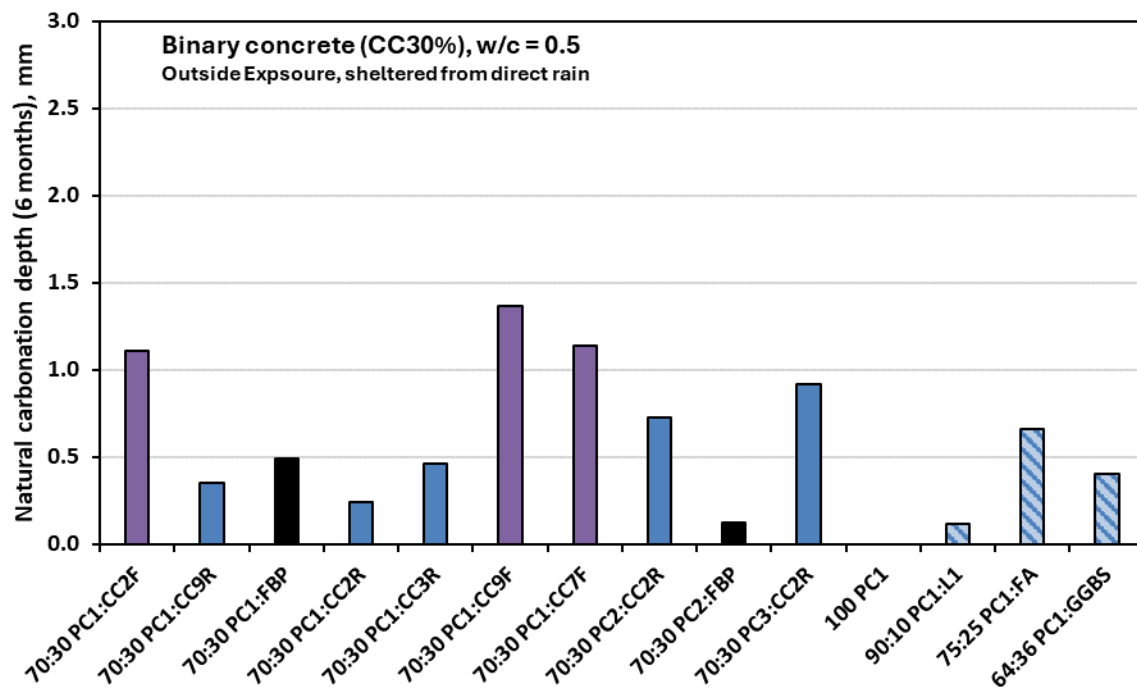

Figure 36: Natural carbonation depths after 6 months exposure for binary concretes at w/c = 0.5
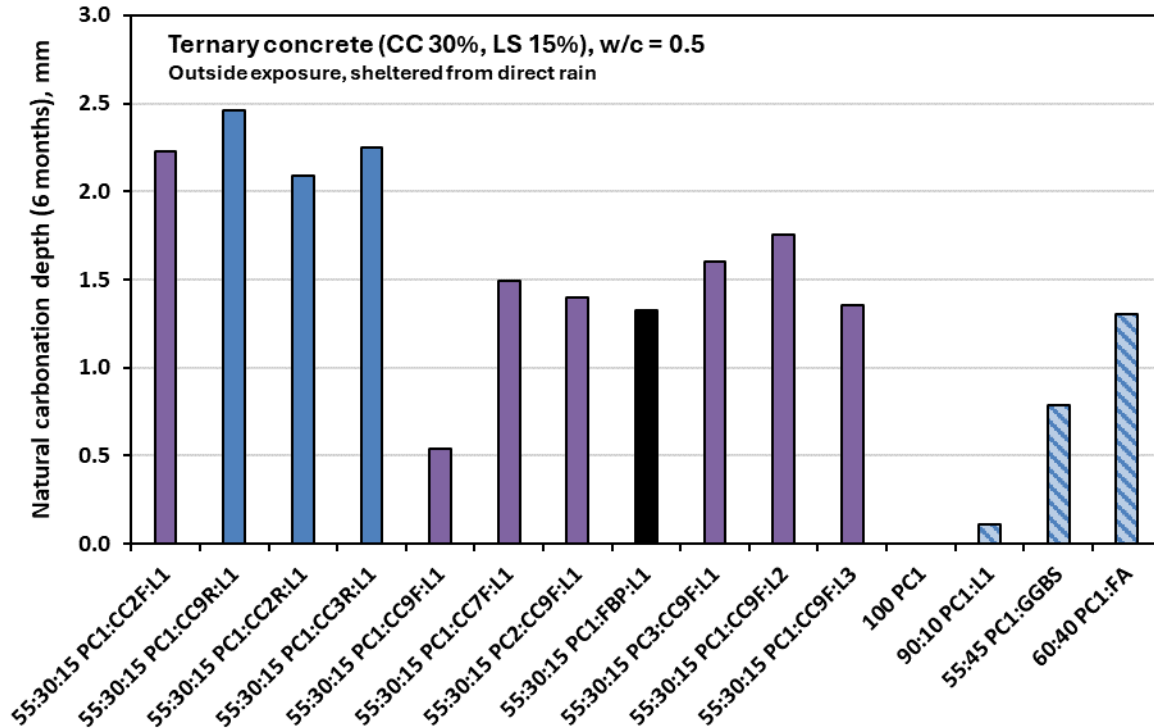
Figure 37: Natural carbonation depths after 6 months exposure for ternary concretes at w/c = 0.5

The ranking of the calcined clays was also not consistent between binary and ternary concretes, with the rotary outperforming the flash binary concretes, while the opposite was generally true for the ternary concretes.

Additional calcined clay concretes evaluating the effect of replacement of cement level in binary and ternary systems and at w/c ratios of 0.4, 0.5, and 0.6 are given in the full appendix 11. These results demonstrate increasing natural carbonation depth with increasing calcined clay level in both binary and ternary concretes. The trends at 0.4 w/c ratio were broadly mirrored at 0.4 and 0.6 w/c ratio.

11.6.   Chloride Migration

The non-steady state chloride migration coefficients for both the calcined clay and brick powder binary (CEM II/B-Q) and ternary (CEM II/C-M) concretes at 0.5 w/c ratio and 30% calcined clay in cement, plus 15% limestone in the ternary systems, are given in *Figure 38* and *Figure 39*. These were derived from the BS EN 12390-18 chloride migration test (BSI, 2021).

The figures show that the inclusion of calcined clay reduces the chloride migration coefficient in both binary and ternary systems. In the binary concretes, calcined clay (0.90×10^{-12} m²/s to 5.40×10^{-12} m²/s) outperformed the 25% FA (7.90×10^{-12} m²/s) and offered better or comparable performance to that of the 36% GGBS (4.94×10^{-12} m²/s) concretes. Similar behaviour was observed in the ternary concretes with all calcined clays (0.64×10^{-12} m²/s to 7.38×10^{-12} m²/s) giving comparable or better performance to that of the 40% FA (6.77×10^{-12} m²/s) concrete. Calcined clays CC2R, CC2F, CC3R, CC9R, and CC9F with PC3 demonstrated better or comparable performance to the 45% GGBS (4.16×10^{-12} m²/s) concrete.
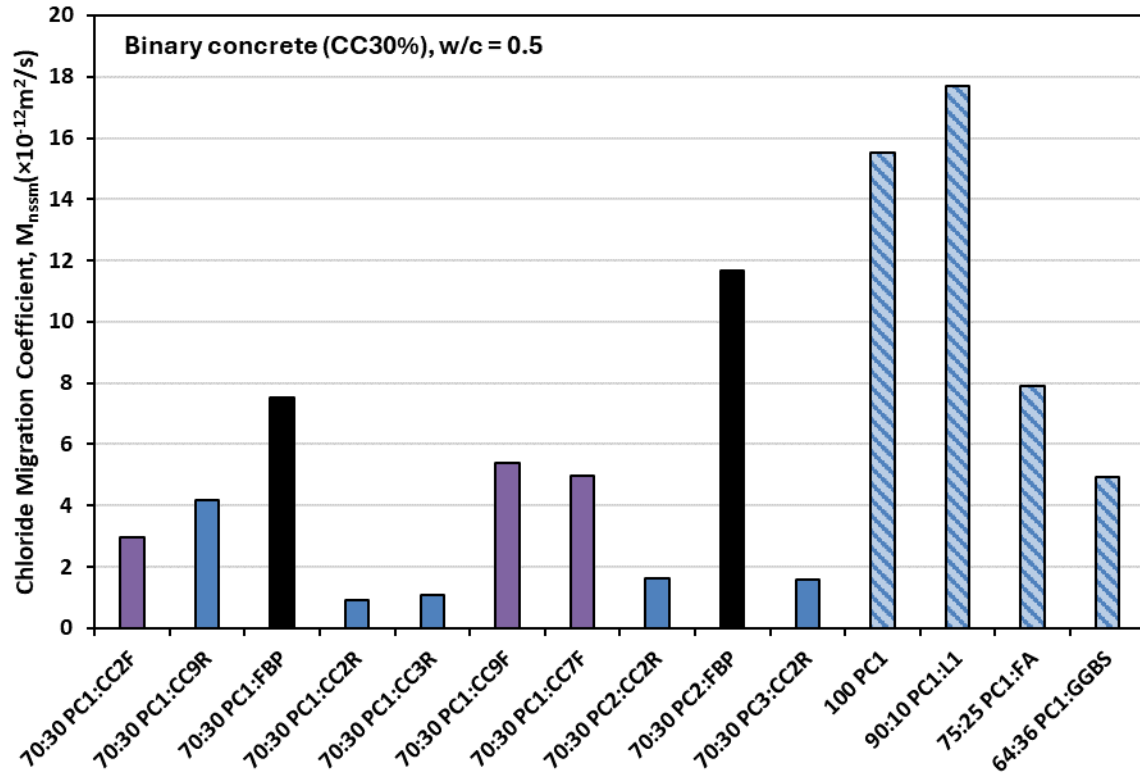
Figure 38: Non-steady state Chloride Migration Coefficient for binary concretes at w/c = 0.5

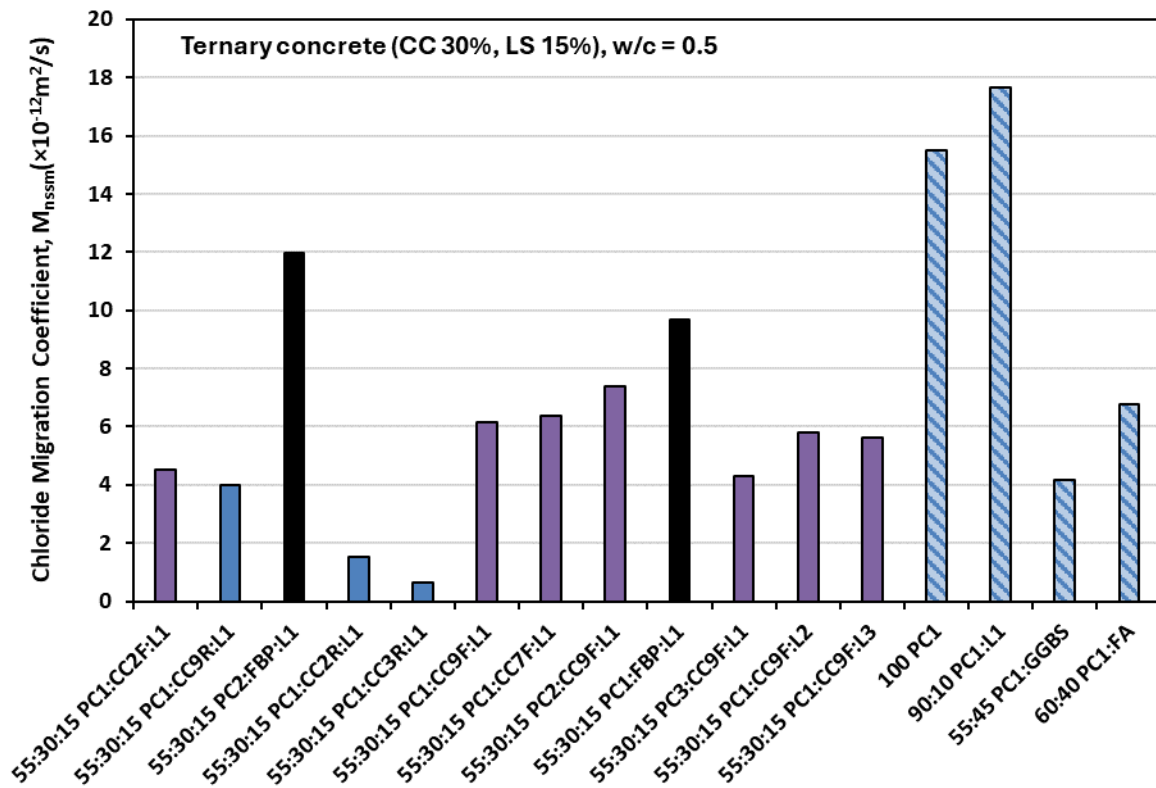*Figure 39: Non-steady state Chloride Migration Coefficient for ternary concretes at w/c = 0.5*

In both binary and ternary concretes, the FBP (7.53 x10^{-12} m²/s to 11.98 x10^{-12} m²/s) was outperformed by the calcined clays and the FA and GGBS concretes, although it

still offered better chloride resistance than the CEM I (15.52 x10^{-12} m^2/s) and CEM II/A-L (17.68 x10^{-12} m^2/s) concretes. The differences in performance between the binary and ternary calcined clay concretes was small, suggesting that the replacement of clinker with limestone has little effect on chloride resistance. This is likely to be due to the relationship between Al_2O_3 content and chloride resistance, and the comparatively low contribution of Al_2O_3 by PC compared to that of calcined clays. Further exploration of the relationship between Al_2O_3 and chloride ingress can be found in appendix 11.

All calcined clays gave good resistance to chloride ingress in concrete. Rotary calcination appeared to give the lowest chloride migration coefficients, although the source of clay still seemed to be influential with CC2R/CC2F and CC3R/CC2F giving the best chloride resistance. The generally hierarchy of chloride performance of the calcined clays and brick powder was as follows; CC2R/CC3R, CC2F, CC9R, CC7F, CC9F, FBP.

Additional calcined clay concretes evaluating the effect of replacement level of cement in binary and ternary systems and at w/c ratios of 0.4, 0.5, and 0.6 are given in appendix 11. These results demonstrate similar chloride resistance performance between replacement level in both binary and ternary concretes, indicating that the level of calcined clay in cement is less influential than the source of the clay. The results of varying w/c ratio between 0.4, 0.5, and 0.6 at 30% calcined clay replacement are in line with expectations, with lower w/c ratios resulting in a lower chloride migration coefficient, although the performance of CC2R and CC9F at 0.6 w/c ratio was still good.

11.7.   Sulfate Resistance

The BR164 sulfate wear resistance test (BRE, 1992) is currently in progress, using $NaSO_4$ and $MgSO_4$ solutions at 20°C. This is a 1-year test with the images below representing interim results taken at 6 months sulfate exposure of CC2R, CC9F, and FBP binary concretes at 30% replacement of cement and 0.5 w/c ratio, along with a 0.5 w/c ratio CEM I reference.
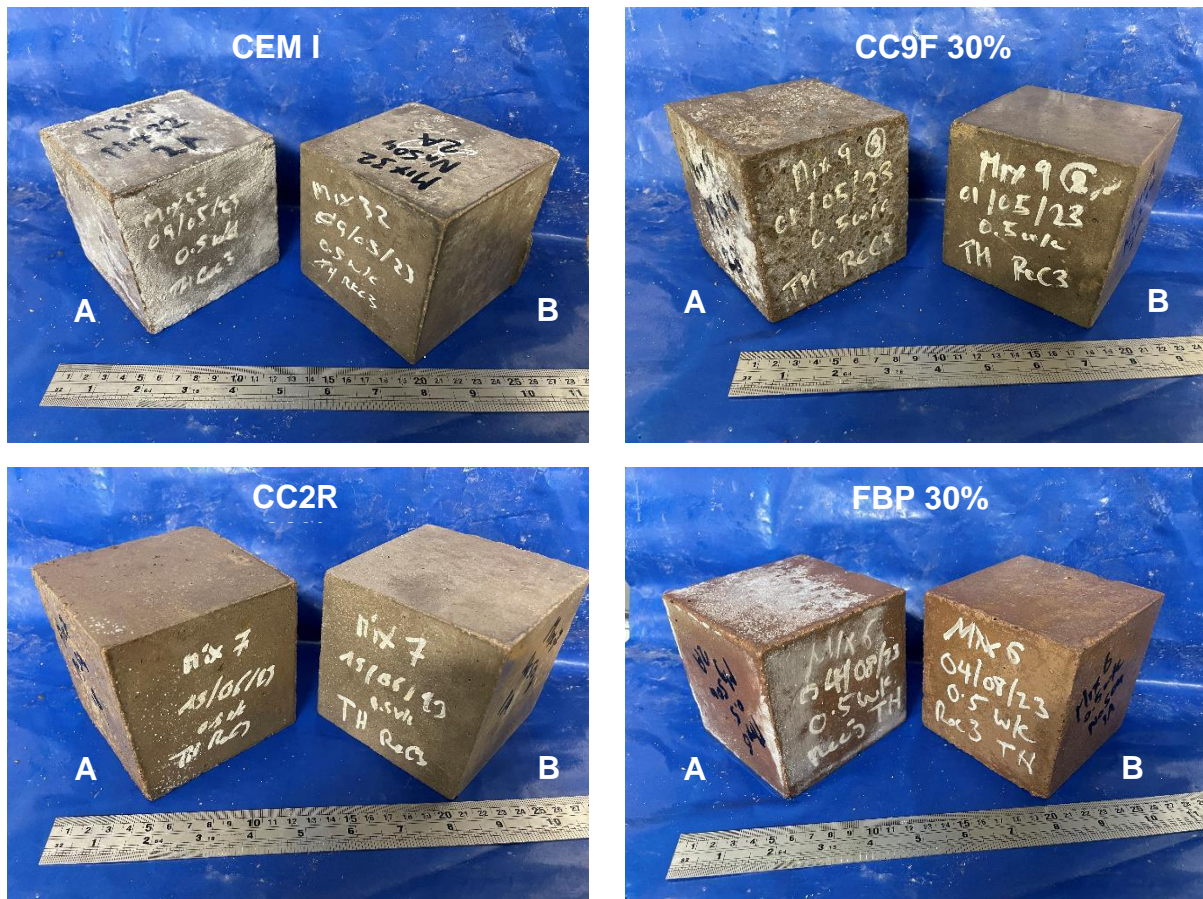
Figure 40: Binary concretes at 0.5 w/c ratio after 6 months exposure (A = MgSO4, B = NaSO4)

The most notable surface deterioration occurred in CC9F in the $MgSO_4$ exposure solution, with minor deterioration also observed in the CEM I concrete along the cube edges. Very little deterioration was observed for CC2R or the FBP concretes in $MgSO_4$, with similar observations for the four concretes after 6 months exposure to the $NaSO_4$ solution.

11.8. Freeze-thaw Scaling

The PD CEN/TS12390-9 (BSI, 2016) freeze-thaw scaling performance of CC2R and CC9F calcined clay binary concretes at 25% replacement of cement and 0.55 w/c ratio, along with FA, GGBS and CEM I concretes are currently under evaluation. The end of this testing programme falls out of the time scope for this project and will be reported later.

Preparation for the freeze-thaw testing involved determining the AEA dose required to achieve a fresh air content of 4.5 % ± 0.5%. Mixing with the calcined clays was found to entrap air and to negate this a defoamer was used for all air-entrained concretes. With the inclusion of the defoamer, no issues were identified with the concretes and the target air content could be achieved satisfactorily.

11.9. Alkali-Silica Reaction

The BS 812-123 alkali-silica reactivity concrete prism method (BSI, 2019) is currently in progress and will continue to run beyond the scope of this project and will evaluate CC2R and CC9F at 25% replacement of cement, a high-alkali CEM I and FA, and

GGBS references. The results of this testing programme will be reported once complete.

11.10. Conclusions

The main conclusions from the concrete study Work Package K below are based on concretes with equal w/c ratio (and thus do not necessarily have equal standard 28-day strengths):

- The calcined clays generally have higher specific surface areas measured by B.E.T., from 5.28 m^2/g to 21.04 m^2/g than the fly ash, GGBS, and limestone sources. The calcined clays had higher particle densities, ranging from 2350 kg/m^3 to 2740 kg/m^3 than the fly ash but generally lower than that of the GGBS and limestone sources.

- This high specific surface area results in calcined clay concrete mixes having increased cohesion and hence water demand, requiring larger doses of admixture than the fly ash, GGBS, and CEM I reference concretes to achieve the target consistency. The data indicates that the admixture can be further optimized for the particular clay characteristics.

- Calcined clay binary and ternary concretes were found to react (in terms of increasing compressive strength), from around 3 to 14 days, beyond which only small increases in strength occurred. In contrast, FBP was found to gain strength at a slower rate, but this continued up to 180 days.

- The use of calcined clay resulted in higher 28-day concrete strengths compared to the CEM I, fly ash, and GGBS concretes.

- Calcined clays, in particular CC2R and CC3R, demonstrate equal or higher resistance to chloride migration, in both binary and ternary concrete mixes, compared to fly ash or GGBS reference concretes.

- The rates of accelerated carbonation for calcined clay concretes were higher than those of the reference fly ash and GGBS and were more pronounced for the ternary concretes.

- Although the period of exposure was limited, the rotary calcined clays generally had lower or comparable natural carbonation depths to the 25% fly ash in the binary concretes, while those with the flash calcined clays were higher. In the ternary concretes, higher depths of carbonation were observed in the rotary calcined clay concretes, compared to those with flash calcined clay. Both resulted in higher carbonation depths than the 40% fly ash reference.

- Only initial (6 month) data was obtained on sulfate attack by the project completion and visually there was no significant deterioration for binary concretes in $MgSO_4$, or any concretes exposed to $NaSO_4$.

- At the time of project completion, the freeze-thaw scaling tests were still in progress and the test results will be reported at a later stage via professional journals. Similarly, long-term natural carbonation and ASR testing data will be reported as above.

- The results of Work Package K show that although the raw clay differ in characteristics, pre and post-processing methodology and calcination method control reactivity and the behaviour of calcined clays in concrete, all clays tested were highly reactive.

11.11. References

BRE. (1992). *Sulphate resistance of buried concrete.* Watford: Building Research Establishment Press.

BSI. (2002). *BS EN 12620 - Aggregates for concrete.* London: British Standards Institution.

BSI. (2016). *PD CEN/TS 12390-9: Testing hardened concrete - Freeze-thaw resistance with de-icing salts. Scaling.* London: British Standards Institution.

BSI. (2018). *BS EN 12390-10: Testing hardened concrete - Determination of the carbonation resistance of concrete at atmospheric levels of carbon dioxide.* London: British Standards Institution.

BSI. (2019). *BS 812-123: Testing Aggregates - Method for determination of alkali-silica reactivity - concrete prism method.* London: British Standards Institution.

BSI. (2020). *BS EN 12390-12: Testing hardened concrete - Determination of the carbonation resistance of concrete. Accelerated carbonation method.* London: British Standards Institution.

BSI. (2021). *BS EN 12390-18: Testing hardened concrete - Determination of the chloride migration coefficient.* London: British Standards Institution.

12. Demonstration Project

Section Authors: Lisa Wachter (Forterra) & Andrew Smith (Forterra)
Detailed report available in: Appendix 12 - Demonstration project

12.1.   Introduction

Work package L of the Re-C3 project assessed the suitability of the calcined clays used in the project for self-compacting concretes and conducted the factory production of retaining wall elements with each clay (See *Figure 41*). The testing and production of the demonstration elements in Work Package L was carried out at Forterra's bespoke precast site in Somercotes.

Figure 41: L-shaped retaining wall units produced as part of the Re-C3 project using the different calcined clays

12.2.   Self-Compacting Concrete Development

An extended study was conducted to optimise and assess the performance of the clays in self-compacting concrete (SCC). A frequently used production SCC mix from Forterra's bespoke precast plant was chosen as a base. The performance characteristics of the production SCC mix are shown in *Table 27* below.

	Stripping strength (16h)	28d characteristic strength	Slump class	Cement content	Aggregate size	w/b-ratio
Requirement	15MPa	C50/60	SF3 (760-850 mm)	Min. 380kg	Max. 10mm	Max. 0.45
Actual value	22MPa	64.1MPa	740mm	465kg	10mm	0.41

Table 27: performance characteristics of the production SCC mix

Taking this mix as a reference and base, different cement replacement levels for the CII/B-Qs (a site blended equivalent to a CEM II/B-Q) were defined as follows: 19% (1/1 replacement of the limestone in the cementitious material of the reference mix), 25%, 30%. All initial work was done with the brick powder (KDBP) for availability reasons. In addition, a ternary cement CII/C-M (Q-L) with the following replacement levels was set up and evaluated: 55% Portland Cement (PC4), 30% Clay, 15% Limestone (L1). (Note: PC4 is the current Porland Cement (CEM I) used at Forterra's Somercotes Precast Plant).

To assess the workability performance different superplasticisers were evaluated. A slump-flow test, assessed in accordance with EN 12350, was conducted, the retention over 30 minutes was measured and a visual inspection conducted to get additional information about tendency of segregation.

All tested admixtures were effective with the brick powder. As expected, their efficiency varies, as it would be with concrete with other replacements as well. Some of the admixtures needed a very high dosage to make a flowable concrete, as expected when choosing admixtures for a different target concrete.

Furthermore, compressive strength of all the different mixes was evaluated. For this a total of six cubes with the dimensions of 100mm*100mm*100mm were cast and stored in water tanks after demolding until testing after 1d, 7d and 28d.
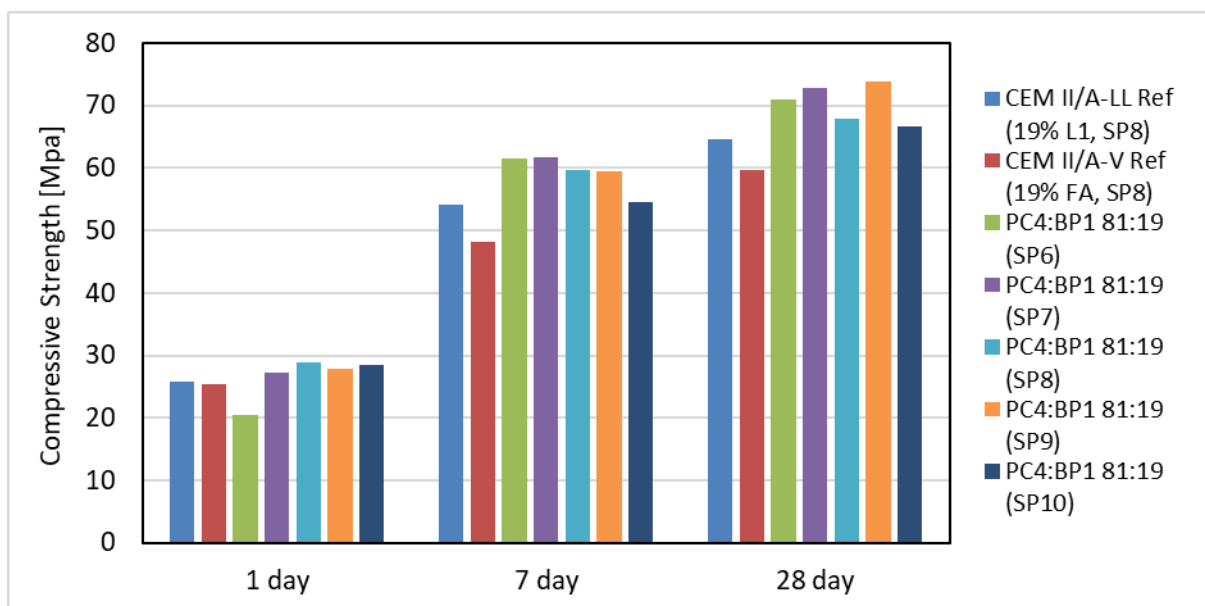

Figure 42: Compressive strength of SCCs with different superplasticisers

In the test series different cementitious replacement levels (19% (shown in *Figure 42*), 25% and 30%) were tested. *Figure 42* shows exemplary compressive strength results for the SCC with different admixtures. Only the SP6 1d result is slightly weaker than the reference mixes, all other results are exceeding the reference compressive strength. As expected, increasing the replacement level is weakening the compressive strength results. This becomes especially apparent in the 1d strength data. None of the 30% replacement mixes can keep up with the early strength of the reference mix. This changes with time, after 28d all mixes, also the 30% replacement, exceed the reference compressive strength.

For the precast sector in addition to workability and "easy casting" the priority is curing time and early age strength. For Forterra's sites an average stripping strength of 15MPa after 15h is needed. Hence, in addition to the standard test ages (1, 2, 7 and 28d) an early age study was conducted with brick powder mixes (*Figure 43*) that range from 13hrs through to 24hrs to show the development of early age strength
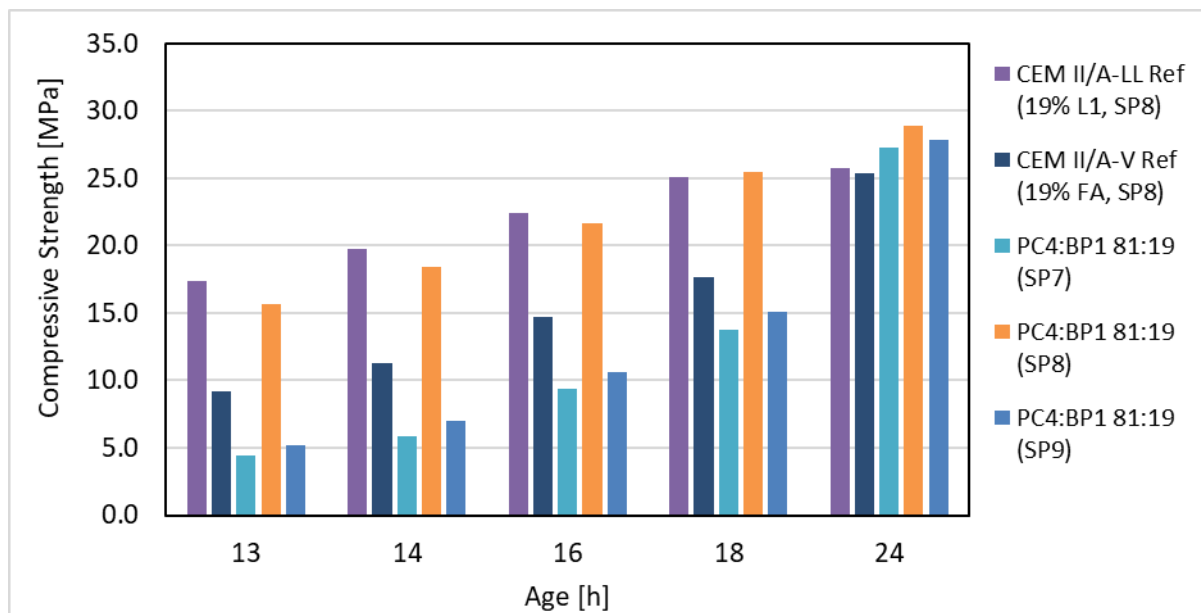
Figure 43: Impact of different admixtures on early age compressive strength development

Figure 43 shows the impact of the admixture on compressive strength development in the early stages. The brick powder mix with the SP8 has similar early age strength as the reference mix. The reference mix with fly ash (CEM II/A-V Ref) has significantly lower early strength development, especially in the first 18h. However, it does catch up with the CEM II/A-LL Ref after 24h. These early age strengths exemplify why an admixture study, and the early age testing is essential for precast, as the 24h result does not give a good enough indication of the actual strength development before 24h.

12.3.   Demonstration Production

After gathering and analysing all the information from the brick powder trials, a mix design for the demonstration project was agreed (*Table 28*). For sustainability reasons and to get the maximum performance of the calcined clays, a 30% cement replacement was chosen.

	Binary Mix (kg/m³)	Ternary Mix (kg/m³)
Cement (CEM I)	325	255
SCM (Calcined Clay)	140	140
SCM (Limestone Fines)	-	70
0/4mm Sand (Fine Agg)	870	870
10/20mm Limestone (C. Agg)	830	830
Filler (Limestone Fines)	60	60
W:B Ratio	0.41-0.43	0.41

Table 28: SCC mix design for the Binary and Ternary Production Trials

All seven clays were evaluated in the lab before using them in the production facilities. A different behaviour and appearance of the concrete with the different clays could be observed. In the workability study the slump-flow and the t500 time were measured to get information about thixotropy.

The graph below shows the flow in mm on the x-axis and the t500 time in seconds on the y-axis. The target workability was defined as a flow of 650-750mm with a t500 time of 2-8s (red window in *Figure 44*).
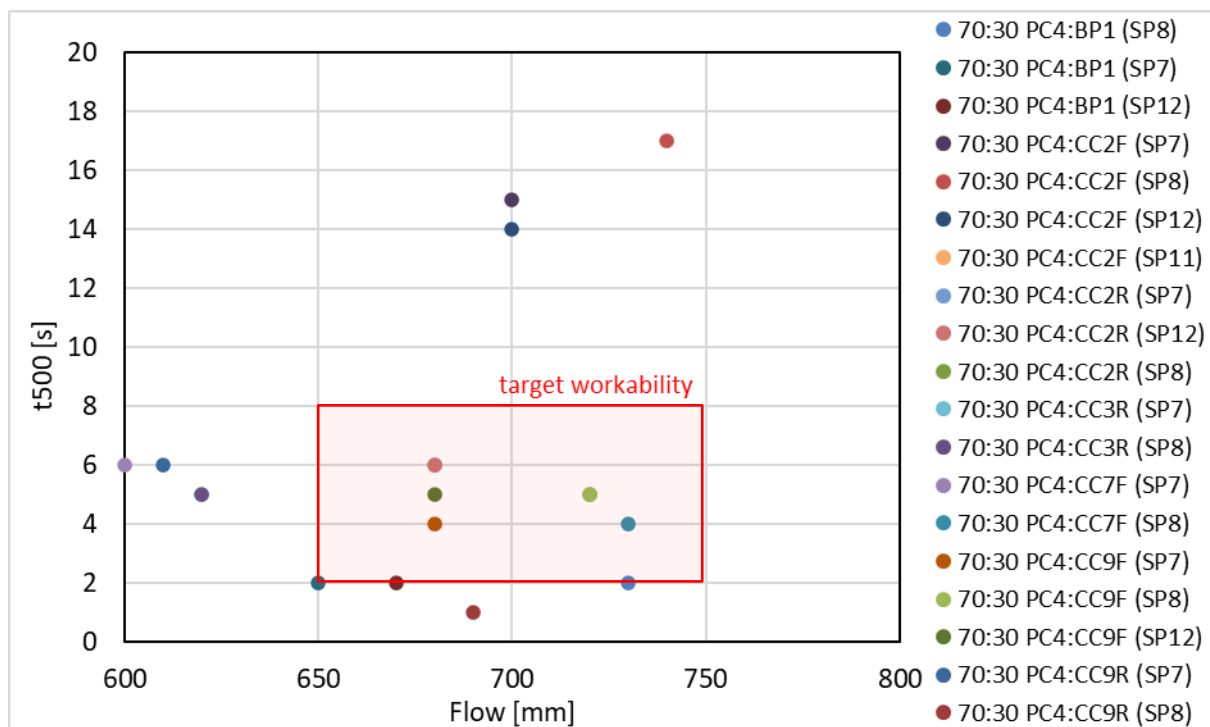
Figure 44: Impact of different admixtures on workability

The decision was made to use SP8 in the production trials for all mixes.

All seven binary mixes and three ternary mixes were cast from December 2023 to January 2024 in Forterra's Somercotes bespoke precast plant. For all mixes, retaining wall elements were cast and an assessment of the strength development was conducted, using batch mixed concrete and casting/storing cubes alongside the cast units.
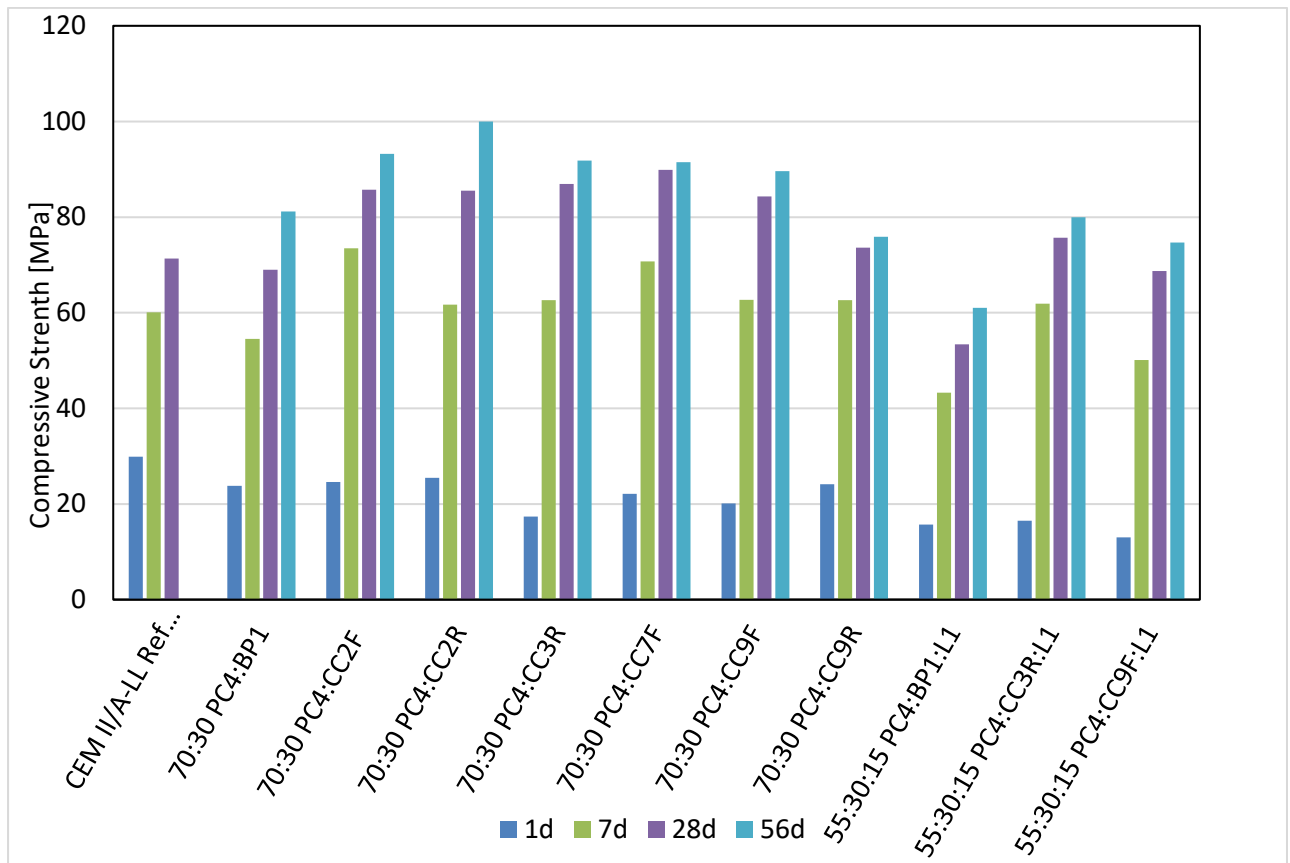
Figure 45: Plant trial compressive strength data

The strength data of the plant trial confirms the results obtained from the lab trials. All binary mixes are equal to or exceeding the reference mix (CEM II/A-LL Ref) in final strength (28d). The ternary mixes perform as expected. They are low in 1d strength and improving slightly at 7d. The CC3R and CC9F ternary mixes have high 28d strengths and are meeting (CC9F) or exceeding (CC3R) the 28d strength of the reference mix. This is with a reduction of the CEM I (PC4) content by 120kg/m^3.

12.4. Conclusions

The main conclusions drawn from the work carried out in Work Package L are as follows:

- All seven tested reclaimed calcined clay materials have made a cohesive, flowable self-compacting concrete with a high cement replacement level of 30%.
- The strength development for all mixes assessed in the demonstration project is looking promising, especially the final compressive strength is impressively high with up to 100MPa. All binary mixes were equivalent to or exceeding the reference mix.
- Ternary mixes are lacking early compressive strength, which is as expected. The additional limestone does not seem to contribute to the strength development. Final strength with the CC3R and CC9F is meeting or exceeding the reference mix. Considering the Portland cement reduction of about 30% this is promising for end-users.

- Overall, the calcined clays are a strong alternative for secondary cementitious replacements. No issues or extra effort can be anticipated for the use of calcined clay instead of other SCMs, despite normative rules and availability at this point in time.

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