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Roman cements — Belite cements calcined at low temperature

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ABSTRACT

Roman cement was a major material used in the architecture of the nineteenth and early twentieth century across Europe, until it was displaced by Portland cement, and is absent from the palette of materials from which conservationists may now select. Calcination of cement-stones and marls from six sites in Poland, Austria and the UK has been conducted. The resulting mineralogy is dependant upon the characteristics of the original feedstock and the calcination temperatures. The principal hydraulic components are belites and amorphous aluminates. The stable belites in cements calcined at lower temperatures are largely α' C_2S while β C_2S is stabilised as the calcination temperature is increased. Other components include uncalcined remnants, lime, brownmillerite and gehlenite. Optimum cements, assessed by compressive strength, were produced at relatively low temperatures, typically in the region of 750 °C. Two strength development profiles have been observed.

1. Introduction

Having been patented in 1796 by James Parker, Roman cement became established as a key material for both engineering and architectural works. Its use flourished in the UK until the middle of the nineteenth century, becoming challenged by the improvements to the properties of Portland cement resulting from developments in kiln technologies. An account of the development of Roman cement in the UK may be found in Francis [1]. The continental market for Roman cement was more extensive and prolonged. Tarnawski [2] reports the production of Roman cement in the Austro-Hungarian Empire of the late nineteenth century as being some five times that of Portland cement; the cement was used for renders and cast decorative elements throughout the periods of European Historicism and Art Noveau (Fig. 1). Its decline came after World War 1 with a change to modern functional architecture and an almost complete lack of decoration. Weber et al [3] describe the exploitation and properties of Roman cement mortars across Europe.

Unlike Portland cement, Roman cement was produced by calcining a single rock source (septaria or marl — a calcareous rock of some 25% or more clay content) at a low temperature with the only pre-calcination processing being to reduce the feedstock to small fragments [4–6]. In this respect it is similar to the production of natural hydraulic limes; however, the calcined clinker has to be ground to a powder as it does not contain sufficient free lime to slake. The use of un-modified raw material meant that each source yielded a cement with particular characteristics; hence, the term Roman cement covers the genre rather than a unique material. Roman cements were characterised by a brown colour and a rapid setting, typically 10–15 min although the Dictionary of Architecture [7] cites the best cements having a setting time of only 6 min. The most rapid setting was a particular asset in hydraulic engineering.

Conservation of the architecture of the late nineteenth and early twentieth centuries has not received the same considerations as other periods and it is only recently that interest in the materials of the period has revived [e.g., 3,8–13]. One of the fundamental principles of modern conservation is that historic buildings should be repaired by using materials which closely match those of the original structure. However, there only remains a single natural cement produced in Europe, that being Prompt as supplied by the Vicat Company [14]. In the US, Edison Coatings, Inc., re-launched Rosendale cement in 2004 to that market; Rosendale had previously been a major source of natural cement. The American cements frequently had a higher dolomitic content than European materials and produced slower setting times; descriptions of American Natural cements may be found in [15,16].

Although this research has been primarily motivated by the re-establishment of Roman cements into the conservation arena, it also forms part of the developing literature on belite cements produced by various synthesis techniques such as low temperature calcination, sol–gel and spray drying, and the Pechini Process [e.g., 17–19].

As part of its 5th Framework Programme, the European Commission has supported the ROCEM Project to investigate both the properties of the historic materials and their associated technologies together with the means to re-introduce Roman cement to the market [20]. Contemporary accounts of the calcination process are generally poorly specified. Whilst the original patent describes the use of “a

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Fig. 1. Example of the use of Roman cement as a stucco and cast ornament.

heat stronger than that used for burning lime" "nearly sufficient to vitrify them" [21], other descriptions suggest a lower temperature. A frequent comment was that an inferior cement would be the result of calcination in which all of the limestone is decarbonated [e.g. 5]. Eckel [16] developed a Cementation Index (CI) and suggested that raw material with a higher CI, Eq. (1) should be calcined at a lower temperature; a temperature of 900 °C or a little higher being suitable for an Index of 2.0.

$$CI = (2.8{*}SiO_2 + 1.1{*}Al_2O_3 + 0.7{*}Fe_2O_3)/(CaO + 1.4{*}MgO) \quad (1)$$

Although novel at the time and based upon assumptions which would now be challenged, the CI bears similarity to the modern Lime Saturation Factor, LSF, Eq. (2).

$$LSF = (CaO + 0.75{*}MgO)/(2.85{*}SiO_2 + 1.18{*}Al_2O_3 + 0.65{*}Fe_2O_3) \quad (2)$$

The CI assumes that all reactions have gone to completion. However, the contemporary view that the best cements were those containing a residual amount of calcite would cast doubt on this assumption and the CI should be viewed as being a potential rather than absolute indicator.

Eckel's CI is the only quantitative indicator available in the historic literature that provides guidelines to the chemical composition of raw materials suitable for the production of natural cements. The two existing standard specifications for natural cements – the Austrian Norme of 1878 [2] and the ASTM C 10 Standard of 1974 – stipulate generally that such cements are produced by calcining naturally occurring argillaceous limestones at a temperature below the sintering point. They contain a range of performance requirements of the calcined cements rather than describe specific composition of the raw materials and the conditions of the production process.

This paper reports an intensive programme of calcination of two marls from Poland and Austria together with more limited calcinations of septaria from various UK locations. A pilot study of calcination of septaria (CI = 1.4) from Whitby, North Yorkshire has shown that optimum cements may be produced at temperatures of approximately 900 °C [13] and this was used to guide the programme (note: this was the temperature set on the kiln control panel and no measurement was made of temperature within the charge). The opportunity is also taken to represent an updated mineralogical analysis of the Whitby cements from the pilot study. A principal aim of the study was to identify general criteria for optimum calcinations which would produce the required hydraulic nature and appearance of the final burnt cements. Such criteria will facilitate the future identification of optimum calcination conditions for each given geological material. They require constant modification when the composition and characteristics of the raw material change, which is an inherent feature of natural geological sources.

2. Experimental details

Two European marls have been used; one was sourced from Lilienfeld in Austria (AT-L) which was a site of historic cement production in the nineteenth century and the other originated from separate beds in an active quarry in Folwark, Poland (PL-F). Septaria were collected from UK beach sources at Whitby (WLB), Speeton (SP), Sheppey (SH) and Cobbolds Point (CP) which was part of the Harwich cement supplies.

Table 1 indicates the range of geological periods from which material has been sourced.

The identification of the clay minerals in the marls was carried out according to Brindley and Brown [22] and Moore and Reynolds [23]. The mineral content was evaluated semi-quantitatively according to Schultz [24]. Total porosity of each marl was analyzed by mercury intrusion porosimetry in the range 440–0.0035 µm. The BET surface area was measured by nitrogen adsorption at 77.5 °K.

Each source has been calcined over a range of peak temperatures and residence time at this temperature. The combination of temperature and time is used to classify each cement (e.g. 920/300); the temperature cited is the temperature set on the kiln control unit rather than one measured at a specific location within the kiln. The calcination of the Whitby septaria in the pilot study has been described elsewhere [13]. An improved kiln and refined conditions were used for the remainder of the calcinations. An electric kiln (Carbolyte GPC12/36) was used through which an airflow of 21 l/min was maintained to ensure a minimum oxygen content of at least 12% during the decarbonation phase of calcination. All feedstock was reduced to a fragment size of approximately 7–10 mm thickness to homogenise its bulk composition and minimise any temperature gradients within the pieces during calcination.

AT-L was calcined in 10 kg batches and the thermal history monitored at several locations within the charge (Fig. 2). The temperature was increased at 1 °C/min in a two-step sequence. A soaking period of 600 min at 300 °C was included, to reduce the potential for explosive failure of the fragments within the kiln, before the temperature was increased at 1 °C/min until the desired temperature was attained. The thermal history of AT-L (920/300) is shown in Fig. 3 where a large temperature difference is apparent across the charge at any instance resulting from the ambient laboratory air being injected into the kiln.

In order to reduce this influence, the kiln conditions were changed for all calcinations of the remaining marls. The charge size was

Table 1
Source of raw feedstock

Marl or septaria	Geological formation
WLB	Upper Lias, Lower Jurassic
AT-L	Gosau Group, Upper Cretaceous
PL-F	Upper Cretaceous
SH	London Clay, Lower Eocene
CP	London Clay, Lower Eocene
SP	Speeton Clay, Lower Cretaceous

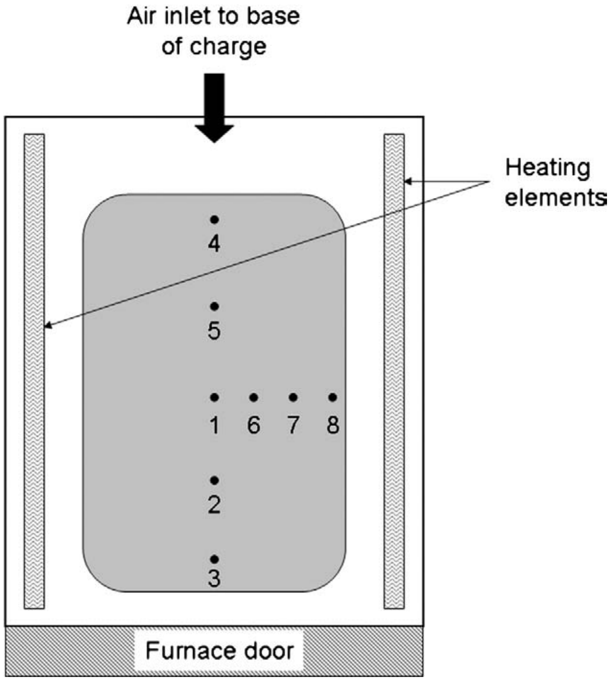

Fig. 2. Location of thermocouples within feedstock charge.

reduced to 5 kg and a ceramic brick was placed between the charge and the air inlet and between the kiln door and the charge. This greatly reduced the temperature differences as seen in Fig. 4; thermocouples 1, 2, 4, 5 and 6 exhibited a temperature spread of less than 15 °C during the residence period. Additionally, the lag between the kiln temperature and the temperature within the charge was reduced such that the temperatures were more constant during the residence period.

It is apparent that the temperature within the charge did not attain the same peak value as that set on the kiln control. The peak temperature in the centre of the AT-L (920/300) charge was 819 °C whereas that in the centre of the PL-F (800/1000) was 760 °C. Such differences should be accounted for when conducting pre-production trials in larger kilns, as well as attempting to make direct comparisons between cements reported in this paper. However, since the purpose of this work was to reveal trends within the characteristics of the differently calcined cements rather than assign these to specific calcination conditions each cement has been described by the kiln settings rather than ascribing measured peak temperatures and residence times from an average of an arbitrarily determined typical element within the charge. It is also recognised that each batch will contain samples of cement having undergone slightly different calcination regimes. This is not considered significant when it is also acknowledged that there is a within batch variation in the mineralogical composition of each feedstock due to natural variability.

The calcination parameters for each feedstock are summarised in Table 2.

All clinkers were ground using a Retch BB200 MANGAN crusher and sieved and recombined, as shown in Table 3, to meet the requirements of the nineteenth century Austrian Norme [2].

Samples of each cement were analyzed by traditional wet chemical techniques to determine their oxide composition (with the exception of WLB used in the pilot study) and X-ray diffraction to determine their mineralogy. XRD patterns were collected using a Siemens D5005 diffractometer CuKα radiation, 40 kV, 40 mA equipped with a diffracted-beam graphite monochromator. Silicon powder, 325 mesh from Aldrich, was added as an internal standard to quantify the amorphous phase content. The measurements were performed between 2 and 70° of 2θ with step size 0.04°, 4 s/step. Contents of phases were calculated by the Rietveld method using the TOPAS software [25]. During refinement the fundamental parameter approach was applied [26] and the following parameters were refined: zero correction, sample displacement, background, overall atom displacement, and, for each phase, scale from which the content is calculated. The content of the amorphous phase was calculated following a correction made to yield the correct proportion of the included standard from the XRD analysis.

Paste samples for both strength and setting time determination were produced at a w/c ratio of 0.65. This was selected to yield a paste

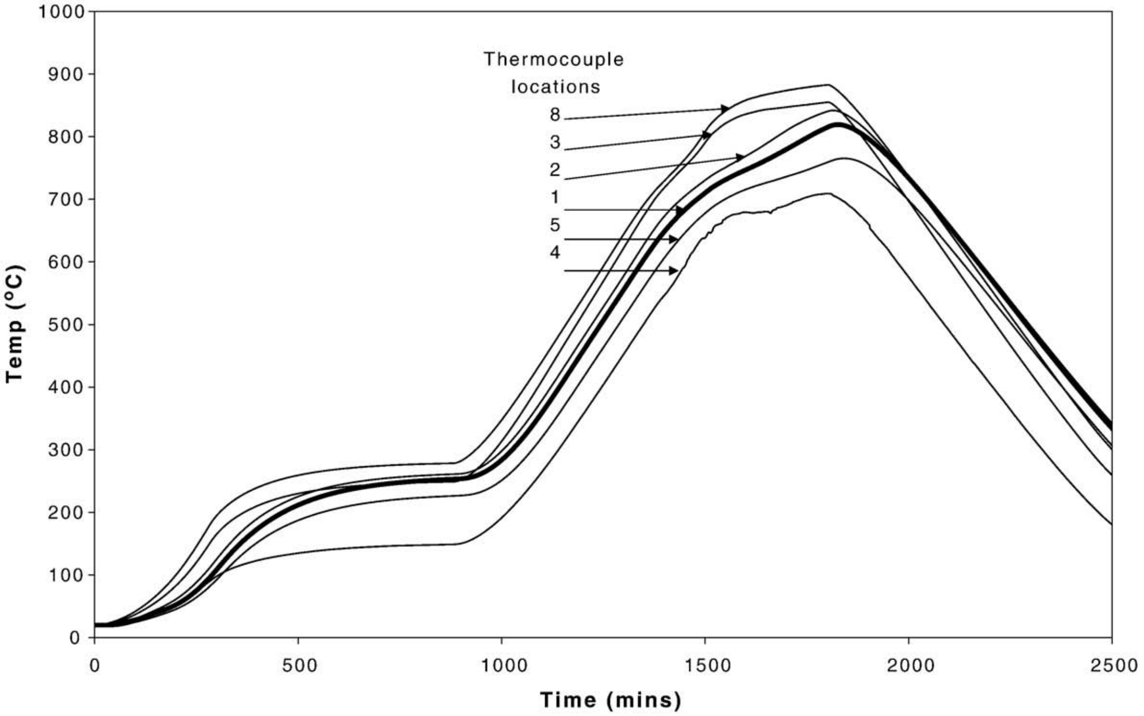

Fig. 3. Temperature profiles of AT-L (920/300) during calcination. Profiles of thermocouples 6 & 7 are coincident with that of thermocouple 2.

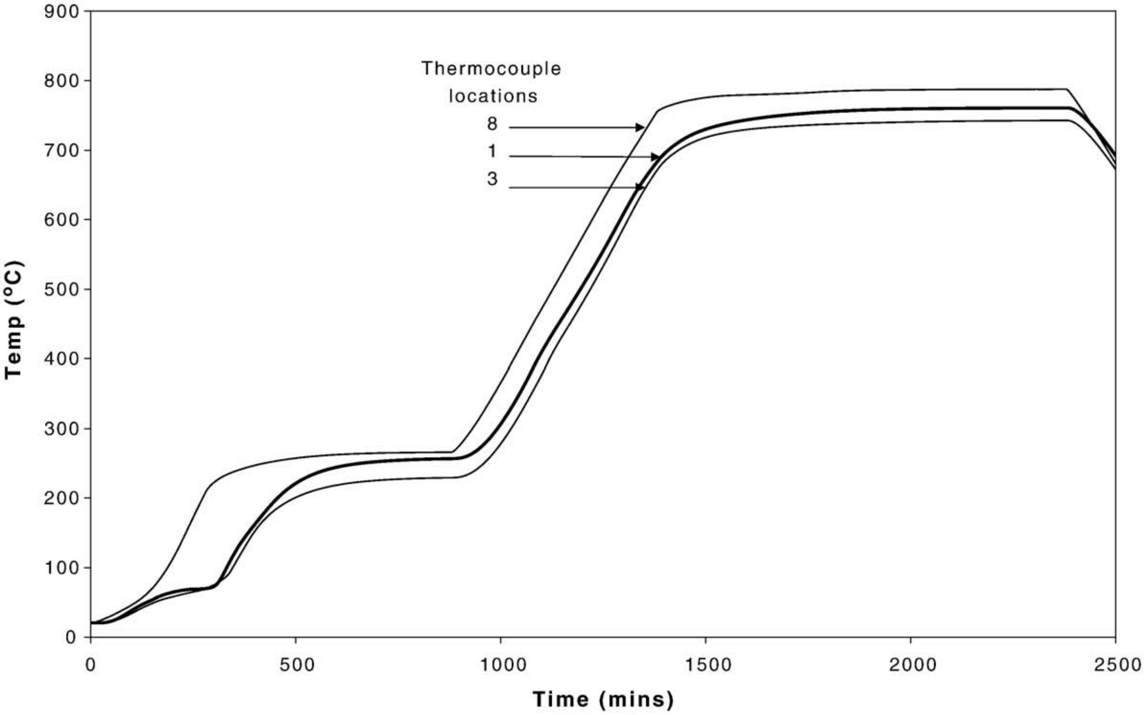

Fig. 4. Temperature profiles of PL-F (800/1000) following modification to kiln conditions. Profiles of thermocouples 1, 2, 4, 5 and 6 are within 15 °C of the profile of thermocouple 1. The profiles of thermocouples 7 and 8 are identical.

of sufficient fluidity to allow the formation of the samples before the onset of the setting process. Setting time was determined using pastes cast in 35 mm film canisters (30 mm×48 mm tall); the procedure specified in BS EN 196-3 is not applicable to cements with a very short initial setting time. The compressive strength was determined from pastes, cast into 120 mm×22 mm diameter cylinders, which were subsequently sawn to a height of 22 mm before the first age of testing. Such strength samples have been used in previous investigations of cement pastes and grouts [e.g., 27,28] although the final sample height was 44 mm rather than 22 mm used here. The decision to use this configuration was influenced by the need to conserve material supplies, since a 5 kg kiln charge would only yield some 2.5 kg of cement following calcination and grinding. Additionally, the extensive use of mortars would have encountered production difficulties when using the fastest setting cements; it being impossible to satisfactorily mix and compact mortars which set within 1 min. Since the objective of this element of the programme was a comparative assessment of the cement properties following different calcinations rather than to compare mortar properties with those sampled from historic objects, the use of pastes is appropriate.

Pastes were mixed using a Silverson RBXL high shear mixer in which the cement was added to the water to ensure the most rapid thorough mixing. The moulds, blocks of 6 cylinders, were attached to a VB table and the paste vibrated into the cylinders by placing the mixing container on top of the block. A similar process was used for the setting time samples. The strength samples were left in the moulds for approximately 5 h before stripping and sawing into the 22 mm specimens for testing. They were water cured at 20 °C before testing, at ages between 6 h and 1 year. Immediately prior to testing the ends of the samples were lightly sanded using fine wet-and-dry paper. An Instron 4206 was used at a crosshead speed of 0.5 mm/min; four samples being tested at each age. A ball-joint was placed between the sample and the Instron anvil to account for any lack of parallelism between the test surfaces of the samples. The coefficient of variation in measured strengths of pastes produced in the pilot programme referred to in [13] was typically in the range 1.5%–8.0% with only the exceptional set yielding a variation greater than 10%; this was taken to validate the experimental method.

Final setting was assessed using the Vicat needle specified by BS-EN 196-3:2005 undertaken in a room controlled at 20 °C and 50% rh.

3. Marl composition

Oxide composition, LSF and CI for all of the calcined cements are shown in Table 4. The principal differences are variations in the SiO_2, CaO and SO_3 contents. Further discussion of the cement composition may be found later. The cement analyses have been obtained as an average of some 150 kg of raw material so they are taken as representative of each marl source and more reliable than measurements on small marl fragments.

It is apparent that these marls are different to the combined raw materials used in the production of Portland cement. Their LSF values are much lower than those of approximately 1.0 for Rapid Hardening

Table 2
Calcination parameters for all source materials

Marl or septaria	Residence time (min)	Peak temp (°C)
WLB (pilot study)	90–330	825–1100
AT-L	100–600	870–1100
PL-F	150–1250	750–1150
WLB	500	810–890
SH	500	810–890
CP	500	810–890
SP	500	810–930

Table 3
Particle size distribution of all cements

Sieve size (μm)	Proportion passing (%)
212–425	16.6
106–212	16.6
<106	66.7

Table 4
Average oxide composition from calcined cements after correction for the Loss on Ignition of each cement

	AT-L	PL-F	SH	CP	WLB	SP
SiO_2	32.05	31.39	20.87	25.75	24.40	18.13
Fe_2O_3	3.99	2.68	6.13	8.02	4.33	7.39
Al_2O_3	10.15	7.86	7.13	7.46	8.23	7.35
TiO_2	0.48	0.48	0.48	1.16	0.48	0.40
CaO	48.72	53.25	55.87	47.91	54.10	57.53
MgO	1.81	1.64	2.77	2.73	1.50	1.10
SO_3	0.08	0.76	2.60	0.97	3.94	5.44
K_2O	1.96	1.48	1.29	1.05	1.05	0.98
Na_2O	0.69	0.28	0.50	0.90	0.36	0.44
Na_2O eq	1.98	1.26	1.35	1.59	1.05	1.08
LSF	0.47	0.54	0.8	0.57	0.67	0.89
CI	2.02	1.77	1.18	1.66	1.43	1.08

Portland Cement cited by Lea [29], reflecting their typically higher clay contents. Hence, if all reactions were taken to completion the presence of free lime would not be expected. Additionally, their values of Na_2O equivalent alkali contents place them in excess of the limit of 0.6% for consideration as a low alkali cement.

The mineralogy of the marls and septaria are shown in Table 5. It is apparent that silica is present in both the clay minerals and as quartz, with the latter content varying considerably between the sources. Additionally, the clay type varies between sources. A detailed petrographic analysis of AT-L and PL-F [30] also reveals differences in the microfabric of the marls. Whilst both marls contain calcitic micro-fossils, their pre-ponderance is much greater in PL-F. This will result in a less homogeneous amalgamation of the calcareous and argillaceous components. The porosities of the two marls is different with PL-F being more porous than AT-L reflecting a weaker diagenesis [30]. Analysis of the UK marls shows that the porosity and associated surface area of SH, CP and WLB are similar to AT-L whilst the surface area of SP is approximately 1 order of magnitude lower still. A further feature of the Sheppey septaria is the presence of large calcite filled septarian cracks. The calcined lime is likely to remain as free lime since the efficient combination of lime with silica and alumina relies upon the intimate mixture of all components.

Thus, key features to be considered in future investigations of potential sources of feedstock include both oxide and mineralogical composition, porosity and the uniformity of distribution of the individual components both on the micro- and macroscopic scales. It is apparent that a simple reliance on the Cementation Index is not appropriate for understanding the potential of a marl.

4. Strength development

A principal aim of this research was to identify the optimum calcination conditions. A kriging algorithm was used to generate field maps to illustrate the variation of strength with calcination. The package EasyKrig V3.0 from Woods Hole Oceanographic Institution was used: Variogram – general exponential-Bessel; Kriging – Ordinary Kriging model, Point to Point scheme, Search radius 0.3, Relative variance 2.5. These maps are a convenient means to show strength as a function of calcination conditions at any particular age (Fig. 5).

A rapid setting time was characteristic of historic Roman cements. In this study the quickest setting was found to coincide with the higher early age strengths and to be slower at both low and high calcination temperatures [31]. The shortest setting time for all cements lies in the range 1–3 min. The exception was CP which varied 5–9 min over the temperature range investigated. In the early nineteenth century, the UK practice was to assess the strength of Roman cement by building a brick cantilever. Consequently, the strength would be assessed at early ages, the precise age being a function of the time interval between the addition of each brick but likely to be a matter of a few hours or days. It was not until later in the century that the age of test in mechanical machines was specified. Given the historical experience and the results from this study we have classified 3 zones of calcination: optimal which coincides with highest 4 week strength and the most rapid setting; sub-optimal at lower temperatures and super-optimal at higher temperatures. These are shown in Fig. 5a.

All marls yield the highest early age strengths (4 weeks) when calcined at low temperatures; approximately 820 °C for PL-F, approximately 870 °C for AT-L and approximately 900 °C for WLB. Analysis of the thermocouple data for the particular PL-F and AT-L cements indicates an average temperature, within either charge during the residence time, of 755 °C; it should be acknowledged that the temperature of the AT-L charge is not certain given the variable and unstable temperatures within and between locations in the charge (see Fig. 3) and the maximum temperature was measured at 780 °C. It is acknowledged that the calcination parameters of batch size and air-flow through the kiln were not identical for each marl. At an age of 1 year, maximum strengths are observed for the same temperatures for PL-F and AT-L. The relative strength of cement (strength of a cement produced at a given temperature / strength of optimal cement) increases as the calcination temperature increases such that cements with a low 4 week strength exhibit 1 year strengths approaching those cements which possessed high 4 week strengths, thus expanding the region of superior performance. By way of example; cement PL-F 820/400 yielded a 4 week strength of 14.4 MPa and a 1 year strength of 23.2 MPa whilst PL-F 940/850 yielded strengths of 3.4 MPa and 18.4 MPa respectively. Thus, whilst the latter super-optimal cement exhibited a strength of only 24% of the optimal cement at 4 weeks, at 1 year this proportion had raised to 79%. A practical interpretation of this is that if performance at 1 year were to be the preferred criterion then there is a greater leeway in the specification of calcination conditions than if the criterion were to be the performance at an age of 4 weeks. By way of contrast, WLB exhibits highest 1 year strengths for cements calcined at approximately 1010 °C although the optimum cement, based on the criterion of strength at an age of 4 weeks, was calcined at approximately 920 °C. However, this may be a reflection of the previously reported [13] loss of strength of some WLB cements after curing periods greater than 26 weeks; this was observed particularly in the cements which had shown the higher early age strengths. The reduction in strength was not accompanied by any visible signs of distress nor after 9 years of water storage. The maximum strength of WLB pastes was in the range 20–22 MPa which occurred at an age of 6 months for the optimum cement and at later ages for the super-optimum cements. Thus, both cements exhibited similar maximum strengths; the mechanism associated with the strength loss requires further investigation.

Fig. 6 shows examples of the three categories of calcination for both AT-L and PL-F. It is apparent that two distinct strength development profiles may be observed. The first is displayed by sub-optimal and optimal PL-F in which the classic early rapid rise in

Table 5
Mineralogy of feedstock material

	Quartz (%)	Feldspar (%)	Calcite (%)	Dolomite (%)	Pyrites (%)	Clay minerals	SSA (m^2/kg)	Porosity (%)
AT-L	9	2	63	3	–	(16% illite+ 7% chlorite)	7	7
PL-F	4	–	71	1	–	(24% smectite)	33	23
SH	19	1	61	–	2	(16% illite+ 1% kaolinite)	11	9
CP	9	2	61	–	2	(16% smectite+ 7% illite+ 3% kaolinite)	7	9
SP	–	–	–	–	–	–	0.8	4
WLB	10	0	64	–	2	(7% illite+ 18% kaolinite)	11	7

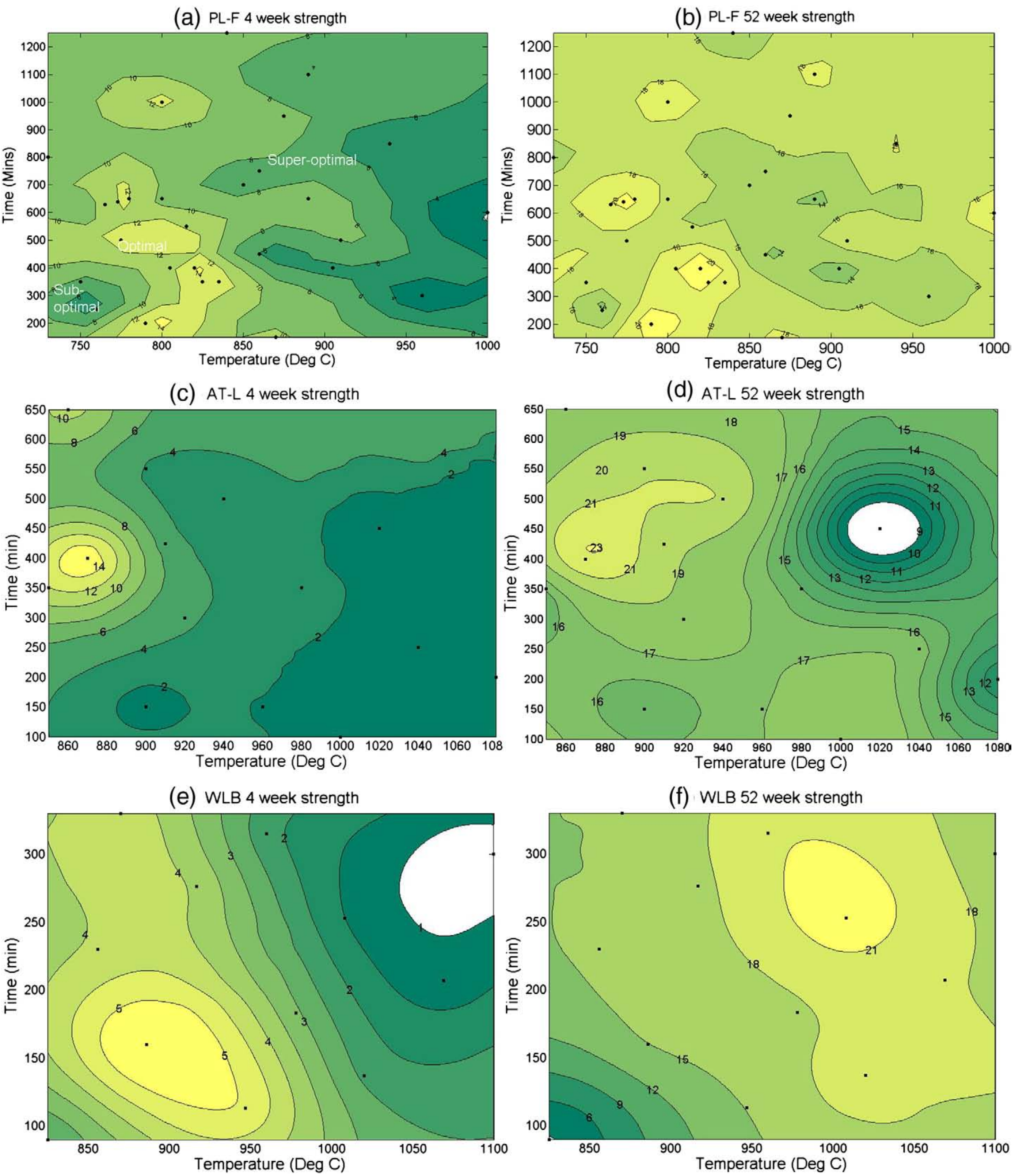

Fig. 5. Strength of PL-F, AT-L and WLB pastes at two ages: (a, c, e) 4 weeks, (b, d, f) 52 weeks. The classification of calcination conditions is shown in Fig. 5(a).

strength is followed by a declining rate after a few weeks. The second, as previously observed for WLB [13], may be characterised by:

- A substantial strength achieved within 6 h of mixing, up to 4.2 MPa has been measured;
- followed by a dormant period of varying length of up 26 weeks;
- followed by a period of accelerated strength development.

The second profile is not confined to particular marls but may also occur under certain calcination conditions for a given source. Thus,

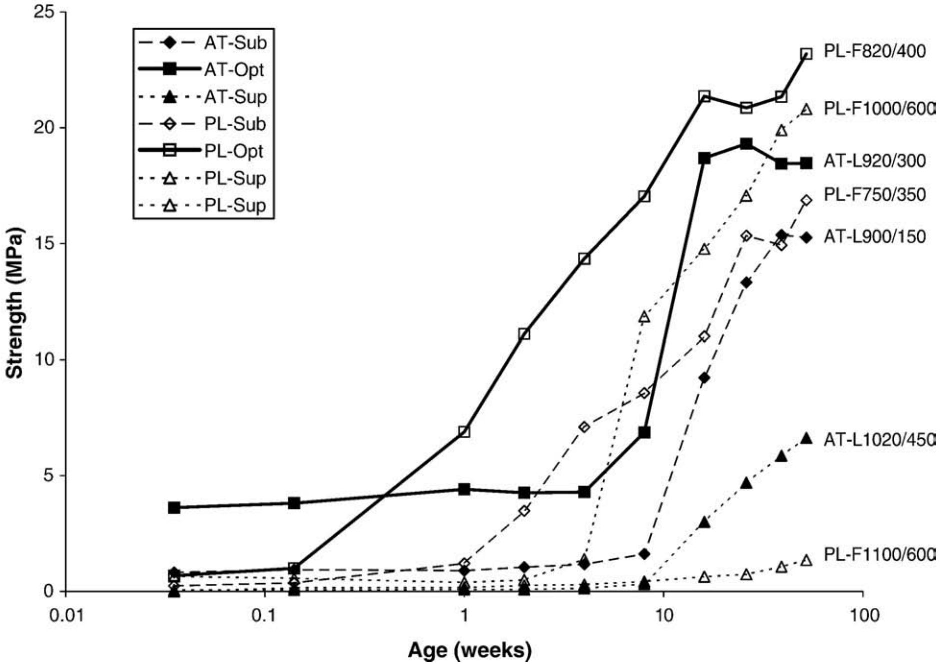

Fig. 6. Strength development profiles of sub-optimal, optimal and super-optimal PL-F and AT-L cements.

super-optimal PL-F (e.g. see PL-F 1000/600 on Fig. 6) demonstrates this profile which in the extreme case shown (PL-F 1100/600) exhibits a prolonged dormant period. XRD analysis of this particular cement shows complete reaction of the quartz and calcite with the production of 43.6% beta-belite; it is not clear whether this cement is exhibiting a genuine dormant period or is a particularly unreactive cement despite the high belite content. All of the UK cements exhibited the second profile for the range of calcination conditions considered as can be seen in Fig. 7, which shows the strengths of pastes produced from cements calcined at 890 °C.

Optimal PL-F cements yield strengths at 1 week which are similar to those of AT-L and WLB at 1 day. However, the latter display substantial dormant periods such that they are overtaken by an age of 4 weeks. The best early age strengths (1 day) for SH and SP are approximately 2 MPa whilst those of CP are similar to PL-F; CP exhibits a dormant period whereas this feature is absent in PL-F. The ranking of

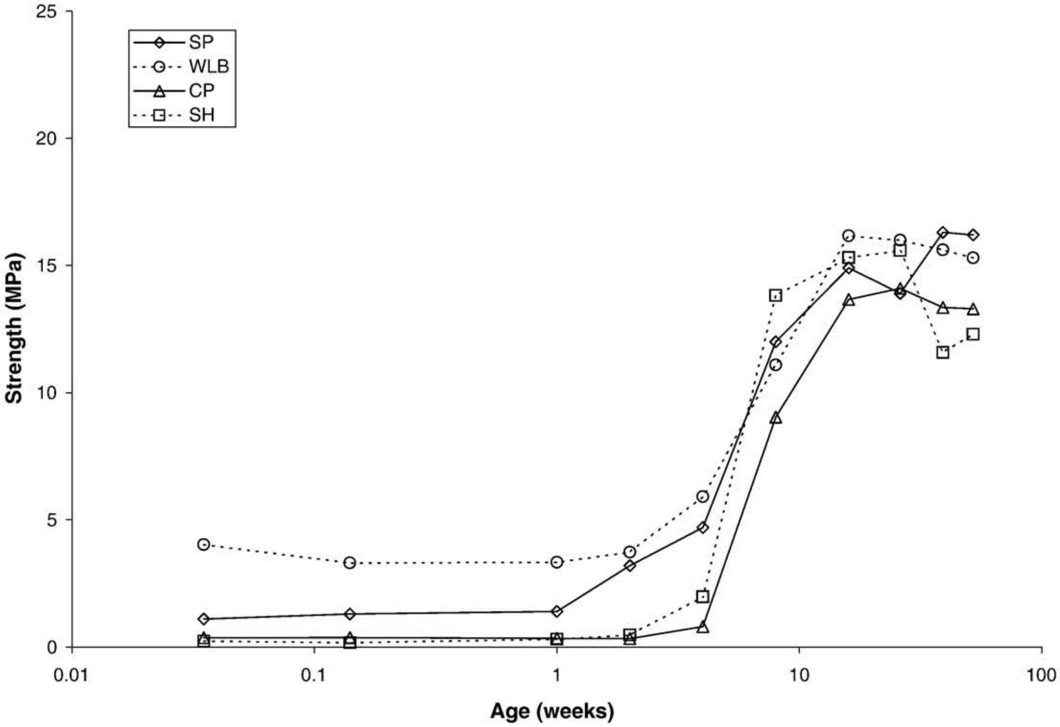

Fig. 7. Strength development profiles of UK cements calcined at 890 °C for 500 min.

the UK cements at this early age correlates with similar comments found in the historic literature.

5. Cement composition

The kriging algorithm has also been used to generate field maps to illustrate the development of mineralogical species as calcination conditions vary. The data for some of the cements have been previously published in the form of two-dimensional contour maps [13,31]. In this paper a one-dimensional presentation is used to present data for all cements at a specific residence time (AT-L, 405 min; PL-F, 394 min; WLB, 143 min) being in the region of the optimal conditions. The previously reported data for WLB (pilot study) has been re-analysed to include determination of the amorphous phases. Mineralogy of the SH, CP, WLB and SP cements is shown in Bar Chart form. All data may be seen in Figs. 8 and 9.

At the lower temperatures there are identifiable remnants of uncalcined material, i.e. calcite and quartz and the content of these

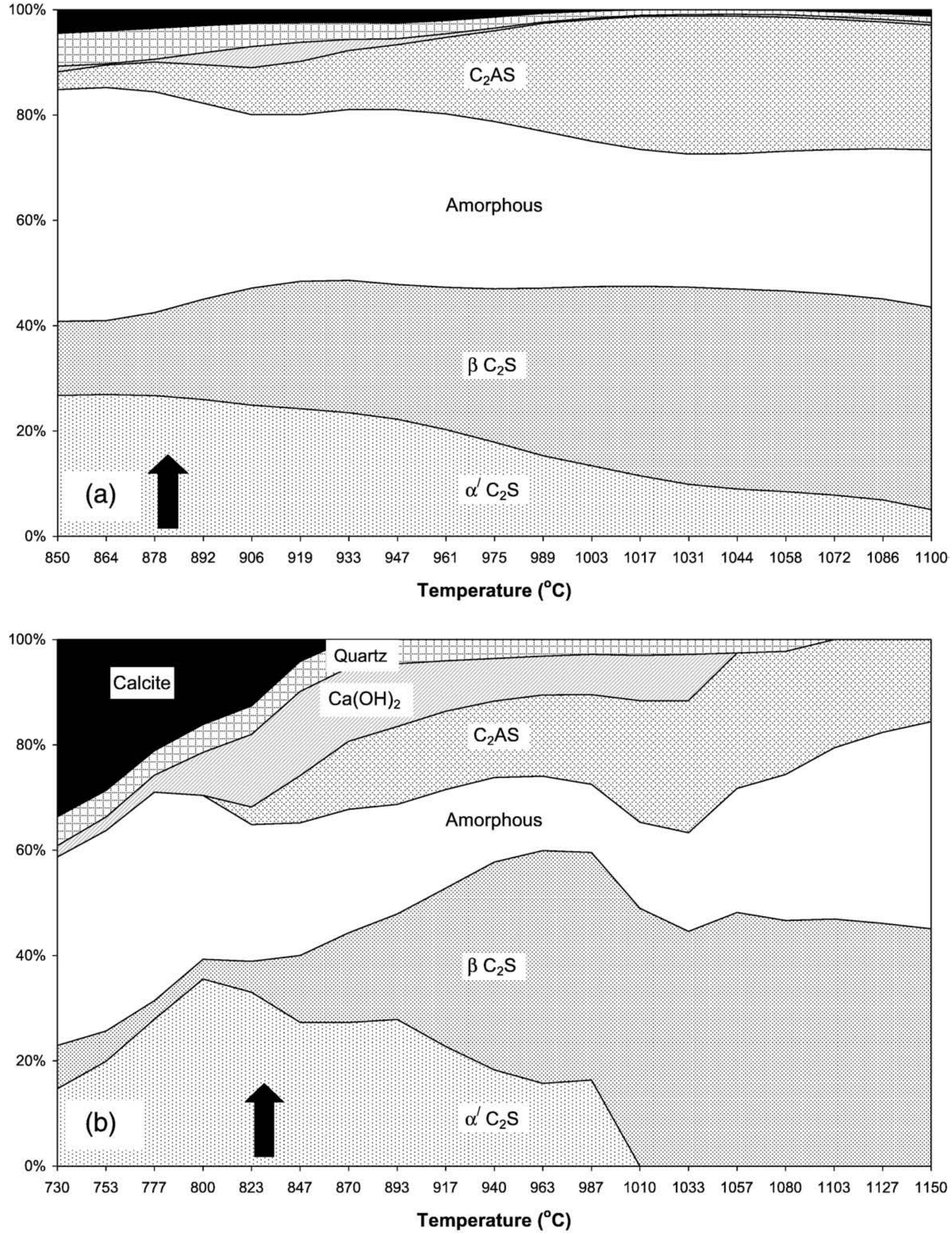

Fig. 8. Mineralogy of cements at different calcination temperatures: (a) AT-L, (b) PL-F, (c) WLB (pilot). The arrows indicate the optimum zone of calcination.

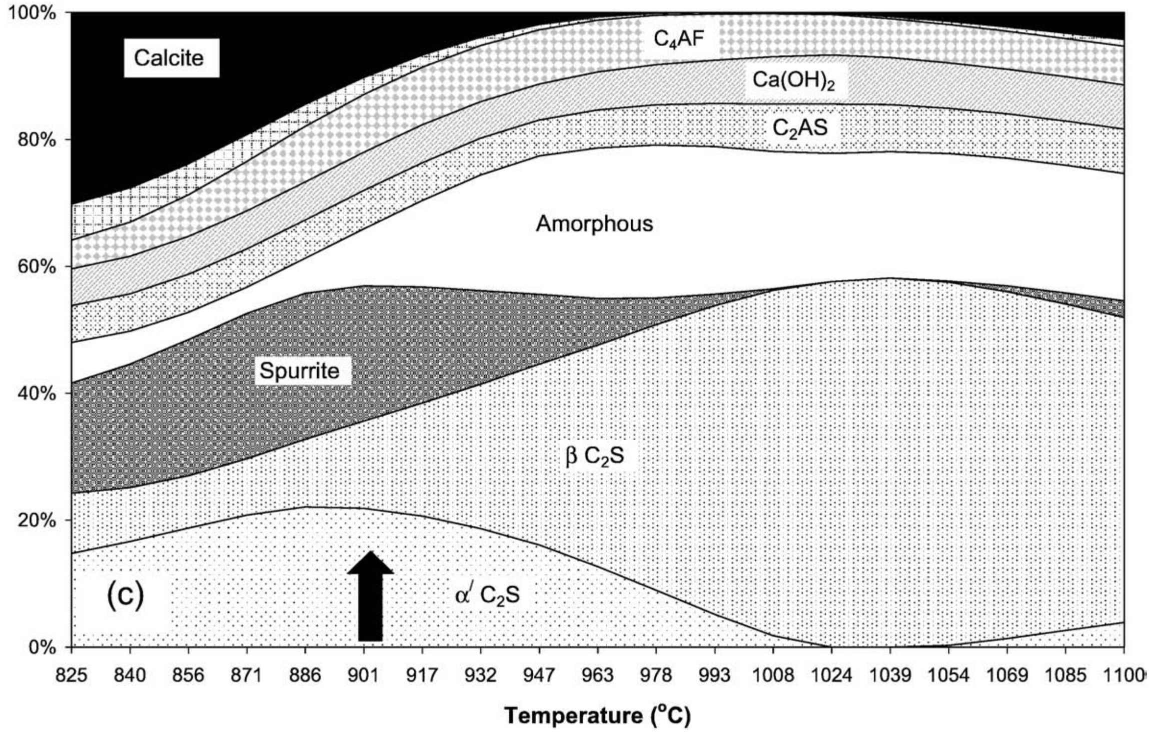

Fig. 8 (*continued*).

decreases with subsequent increases in calcination temperature. Optimal cements are seen to contain small quantities of calcite, in line with historic comments that the best cements were not completely de-carbonated [e.g. 5]. Further remnants of the marl may well be decomposed clays which have yet to be re-combined with lime to form crystalline minerals and would be

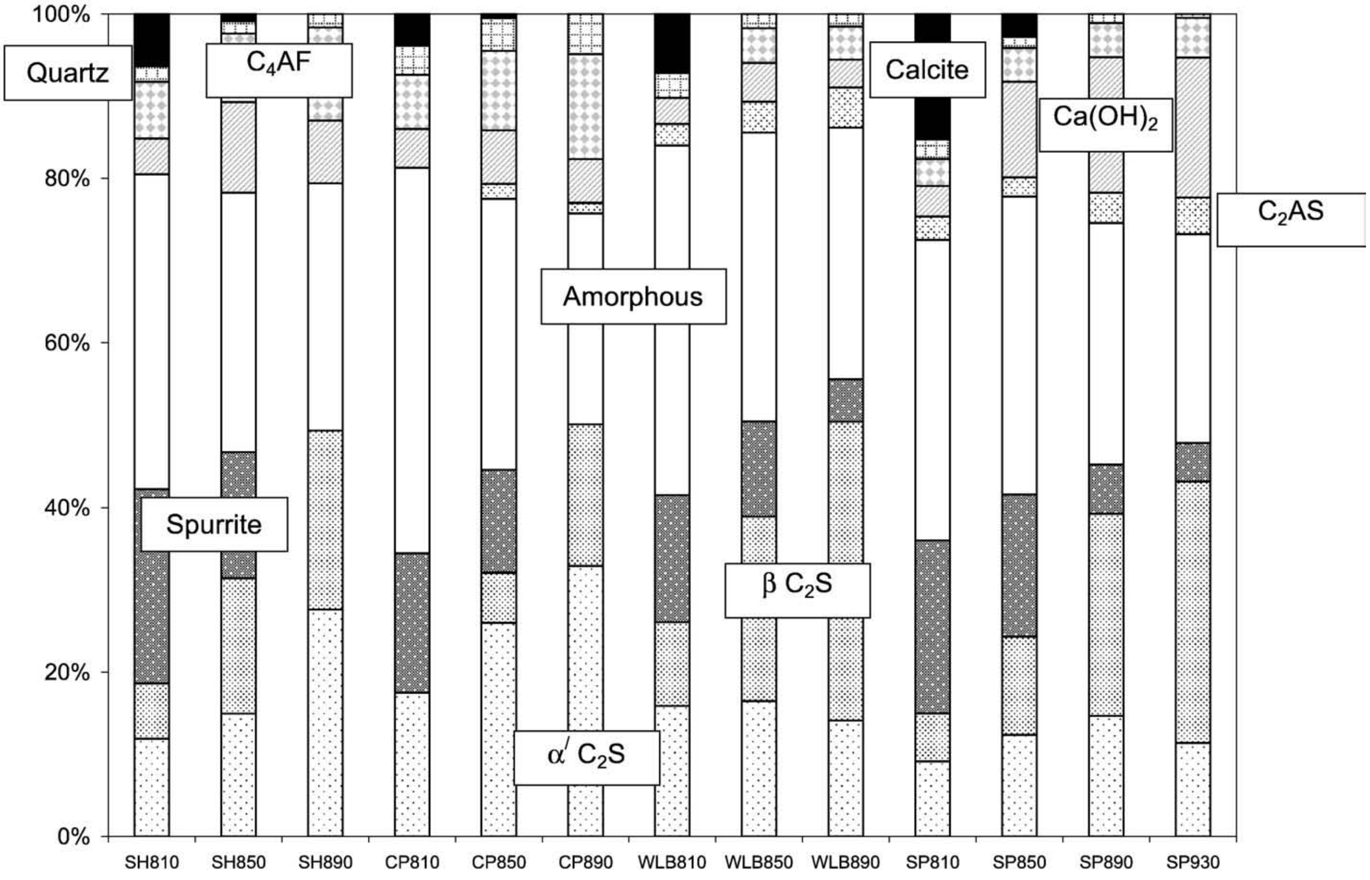

Fig. 9. Mineralogy of UK cements — SH, CP, SP and WLB.

accounted for within the amorphous material. We will return to this later.

A key feature in the success of the calcination of Roman cement marls and septaria is the natural intimate mixing of all of the oxides in the raw material and is important because there is only limited evidence of melt formation [30] with most re-combination being by solid state reaction. It has previously been shown that PL-F marl contains substantial calcium in the form of micro-fossils as well as the highest total calcite content. Without a ready supply of intimately mixed silica the de-carbonation of the lime will yield large quantities of free lime which will require higher temperatures to combine with the silica. Fig. 10 shows that PL-F generally possesses the highest free lime content which peaks at approximately 850 °C. WLB, AT-L and CP have much lower free lime contents indicating a more efficient production of belites. Unfortunately, a systematic study of the micro-fabric of the UK septaria and cements is not available. Hence, an explanation for the high free lime contents of SP and SH is speculative; however, that of SH may reflect the presence of calcite filled septarian cracks. XRD analysis shows that this lime is essentially present as $Ca(OH)_2$ indicating a very reactive CaO produced at these relatively low temperatures which has slaked during grinding and storage.

The principal crystalline silicates are belite and gehlenite and both are dependent on the calcination temperature, although not in a consistent manner across the range of cements and calcination temperatures studied. Whilst AT-L shows an essentially constant total belite composition, except at the lowest temperatures, that of PL-F and WLB increases with temperature until a maximum is reached. This may be a function of two factors; the temporary presence of other silicate complexes and the ability of the de-carbonated lime to react with the silicates.

The mineralogy of WLB is more complex than that of AT-L and PL-F as substantial spurrite, the carbonated form of belite, is observed, and if this is accounted for within the total belites then this cement responds in a similar manner to AT-L. Spurrite is found in all of the UK cements and decreases with increasing calcination temperature, disappearing at moderate temperatures. The presence of spurrite in the UK cements but not AT-L or PL-F is not yet fully accounted for but may be a function of two parameters, i.e. chemical and physical. Glasser [32] has proposed that fluoride, chloride and sulphate may facilitate more rapid formation of spurrite. Illitic clays are a possible source of chloride; however, AT-L also contains illite but no spurrite. An analysis of the UK cements revealed small quantities of chloride (0.08% SH; 0.12% CP; and 0.02% WLB) and it is probable that the explanation lies elsewhere. The marls with the highest sulphate contents are SH, WLB and SP (Table 4). The remaining UK marl, CP, has a moderate sulphate content comparable to that of PL-F. Glasser reported a reduction in the spurrite decomposition temperature from 912 °C to 790 °C as the CO_2 pressure was reduced from 1 to 0.08 atmospheres. In contrast to CP, the PL-F marl has a much higher surface area and porosity which may yield a lower CO_2 partial pressure and more dynamic atmosphere within the marl fragments. It is possible that any spurrite formed in PL-F cements was decomposed within the range of calcination temperatures considered and thus not observed upon cooling. In a later study, Bolio-Arceo and Glasser [33] suggested that melt formation is a necessary pre-cursor to spurrite formation. Whilst evidence of limited melt formation has been observed in PL-F and AT-L cements, often associated with a potassium alumino-silicate [30], a similar comprehensive study of all of the UK cements has yet to be undertaken. In a recent study, Mertens et al. [34] studied the composition of Vicat's Prompt Natural cement. It is known that the temperature range in the kiln encompasses similar temperatures at which spurrite has been identified in the UK cements. They report the presence of spurrite as well as sulphate in the form of anhydrite and Ye'elimite. More work is required to fully appreciate the presence of spurrite within the UK cements; however, the association with sulphate should be investigated.

A common feature of all cements is the presence of belite in two polymorphs, namely in the β and α' forms. The latter form is stable in cements calcined at the lower temperatures and the β form is predominantly stabilised as the calcination temperature is increased; α' C_2S is at a maximum in the region of optimal cements. Indeed, only β C_2S was observed in PL-F and WLB (pilot study) cements produced at temperatures of 1000 °C and greater, the α' form appears to be present in AT-L calcined to slightly higher temperatures although this may be a function of the slightly different calcination conditions described

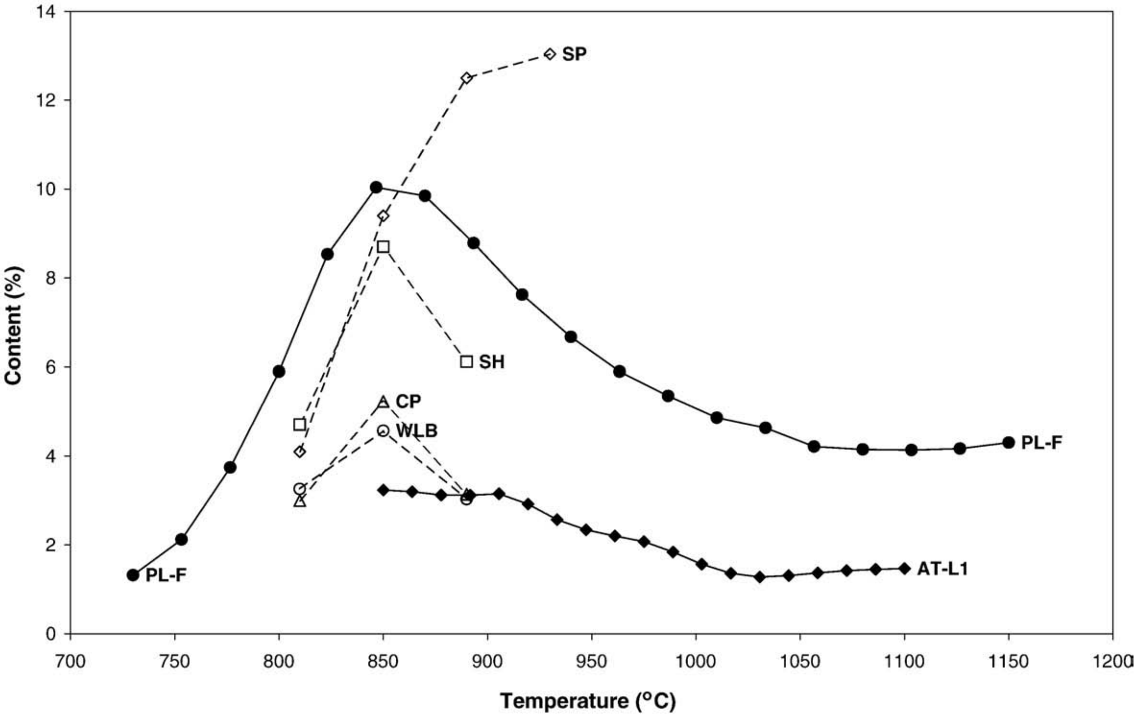

Fig. 10. Free lime as a function of calcination temperature.

Table 6
Sample calculation of the composition of the principal oxides in the amorphous phase (PL-F 820/400)

Mineralogical composition by XRD (%)		Oxide composition by chemical analysis (%)	
Quartz	5	SiO_2	28.07
Calcite	16	Fe_2O_3	2.33
Gehlenite	0	Al_2O_3	6.96
beta-belite	4	TiO_2	0.56
Portlandite	10	CaO	47.95
alpha'-belite	36	MgO	1.43
Total crystalline	71	SO_3	0.57
Amorphous	29	Na_2O	0.24
Free lime	7.94	K_2O	1.46
		LOI	10.27
Silica in crystalline phases	19.50	*Silica in amorphous phases*	8.57
Alumina in crystalline phases	0.00	*Alumina in amorphous phases*	6.96
Lime in crystalline phases	43.01	*Lime in amorphous phases*	4.94

earlier. Lea [29] states that the α' polymorph converts to the β form upon cooling through the temperature range 650–670 °C with α' C_2S being stable at the higher temperatures. One explanation for the stabilisation sequence observed in this study may be that of a small crystal size which increases as the calcination conditions become more intense. A constraint in the XRD analysis is to fix the crystal size; however, if this is left as a variable, the size of the α' C_2S increases to a maximum of 35 nm. Similar observations have been previously reported by Hong and Young [18] in their study of highly reactive belites and the stabilisation of various polymorphs was attributed to the fine particle size of the α' C_2S with an equivalent-sphere particle size of 40 nm.

Aluminate is observed in two crystalline phases, gehlenite and brownmillerite. The latter was only observed in the UK cements and may be a reflection of their generally higher iron contents.

Reference has been previously made to the presence of amorphous phases. It is likely that these are not solely genuinely amorphous but also contain poorly crystalline phases as well as decomposed clay remnants. Observation of the hydration of these cements has shown that setting is accompanied by the production of calcium aluminate hydrates; however, no crystalline aluminate phase was observed in AT-L and PL-F despite selective dissolution of silicates and free lime in salicylic acid and methanol [35]. Hence, the source of aluminates is believed to be within the amorphous phase, whose composition may be estimated by accounting for the difference between the total oxide composition of a cement and the oxides within the crystalline phases, assuming stoichiometric combination (see Table 6 for a sample calculation). Of particular note is the reduction in the alumina content of the amorphous phase due to the crystallisation of gehlenite at the more intense calcination conditions (Fig. 11). A correlation between either the quantity of calcium aluminate hydrates [35] and amorphous alumina or setting time and amorphous alumina would not be expected as this phase will comprise minerals from both the decomposed clay as well as various reacted calcium aluminates. However, at the highest calcination an increase in setting time and reduction in amorphous alumina was observed.

For the sake of clarity some minor components have been omitted from the presentations in Figs. 8 and 9. Wollastonite was observed in some PL-F cements produced at intense calcination conditions. Periclase was present in SH cements. Sulphate in the form of anhydrite and ye'elimite was recorded in both Yorkshire cements WLB (pilot), WLB and SP with ye'elimite being the preferred phase following more intense calcination. Hematite was present in SP but not CP, both cements with a high iron content. However, the latter cement contained approximately twice the brownmillerite content of the former indicating a higher degree of reaction.

It has not been possible to determine a link between cement composition and the dormant period before the period of accelerated strength development. Further fundamental work on hydration studies is required to develop a better understanding of this phenomenon.

6. Comparison of Roman cements and Prompt

Table 7 shows a comparison of the oxide and mineralogical compositions of cements AT-L, PL-F, SH, CP, WLB, SP and a sample of Prompt which has been previously investigated [35]. The first two cements represent marls calcined at optimal conditions whilst the UK cements were all calcined at 890 °C for 500 min for which strength developments are shown in Fig. 7.

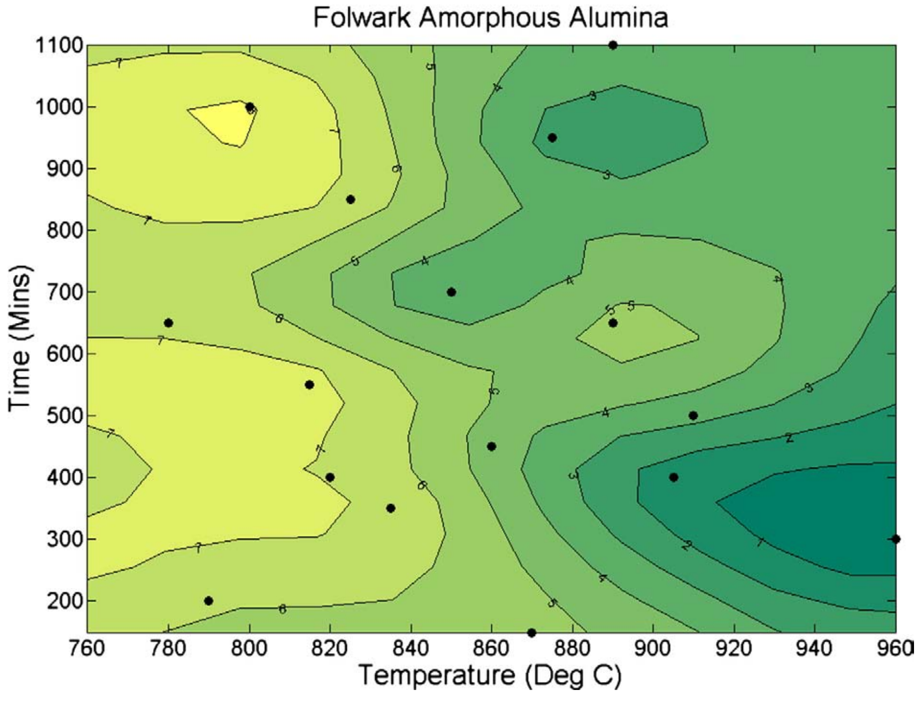

Fig. 11. Al_2O_3 content in the amorphous phase of PL-F.

Table 7
Oxide and mineralogical composition of selected cements

	AT-L	PL-F	SH	CP	WLB	SP	Prompt
Temperature (°C)	920	820	890	890	890	890	600–1200
Time (min)	300	400	500	500	500	500	
Loss on ignition	6.5	10.0	3.2	2.2	1.4	5.4	10.0
SiO_2	29.1	27.9	20.2	25.5	24.0	17.0	19.1
Fe_2O_3	3.6	2.5	6.3	7.1	4.3	7.6	2.4
Al_2O_3	9.2	6.9	7.4	6.3	8.2	6.8	7.1
TiO_2	0.4	0.4	0.5	0.9	0.5	0.4	0.4
CaO	46.8	48.2	54.2	49.5	53.2	54.6	52.8
MgO	1.5	1.6	2.7	2.4	1.5	0.8	3.5
SO_3	0.0	0.7	1.5	0.8	4.0	5.5	3.7
Na_2O	0.7	0.3	0.5	0.7	0.2	0.4	0.6
K_2O	2.1	1.5	1.3	1.0	1.0	0.9	1.6
Free CaO	0.2	6.4	6.1	3.1	3.0	12.5	
Quartz	4	5	2	5	1	1	1
Calcite	6	16	0	0	0	0	16
Anhydrite			0	0	0	2	
Brownmillerite			11	13	4	4	5
Gehlenite	4	0	0	1	5	3	4
beta-belite	20	4	21	17	35	23	20
alpha'-belite	30	36	27	33	14	14	13
Portlandite	0	10	7	5	3	15	3
Periclase			3	0	0	0	3
Spurrite			0	0	5	6	
Ye'elimite			0	0	3	1	2

It is apparent that, as expected, there is substantial variability in the composition of the cements. The silica content varies between 17 to 29% with both SP and Prompt showing low values. The periclase content varies between 0.8 to 3.5% with the previous cements being at the extreme ends of this range. It should be noted that these values are much lower than that found in typical North American Natural Cements, being approximately 20% [35]. The sulphate content ranges between 0 to 5.5% with WLB, SP and Prompt showing high values.

All cements show evidence of low temperature calcinations with the presence of both quartz (all cements) and calcite (AT-L, PL-F and Prompt). All cements contain both polymorphs of belite; the cements with the lowest silica content show the lowest total belite content. The UK marls were all produced at identical calcination conditions; it can be seen that the balance of the two polymorphs is not constant with two cements showing higher β belite and two higher $\alpha^{/}$ belite contents. Further study of the morphology and clay mineralogy of the original marls may yield an explanation of this difference. Unlike the laboratory cements, Prompt is calcined over a wide range of temperatures from 600–1200 °C [36]. It has been reported that C_3S may be formed in the hottest regions of the kiln [36]; however, none was detectable in the sample used in this study or in [34]. Those cements with the high sulphate contents contained small amounts of anhydrite or the calcium sulpho-aluminate, ye'elimite. Although spurrite has been previously reported in Prompt [34] it was not detected in the current sample; however, spurrite was observed in WLB and SP. Periclase was detected by XRD in only two cements, SH and Prompt.

This comparison shows that substantial variability within the Roman cement family of cements is to be expected and this is a consequence of the wide range of feedstock which can be used to prepare these cements.

7. Retardation of mortars

The rapid setting time necessitates the use of a retarder in the production of practical mortars. As part of the development process, an electric kiln was developed in the laboratory of the Polish authors which could calcine up to 250 kg of marl in a single batch. The calcination parameters were informed by those identified to yield optimum cements in the small-scale laboratory kiln. A cement calcined from PL-F marl was used to produce an un-retarded paste and mortars which were retarded by the addition of 0.4% citric acid or 0.6% of potassium citrate by weight of dry cement, all materials were produced at $w/c = 0.65$. These dosage levels retarded the setting and extended the workable time to at least 10 min. The mortar was produced to comply with EN196-1 with the exception that the water was added at the end of the mixing process. Samples were cured for periods up to 52 weeks subsequent to which the determination of strength followed the procedures of the same standard. Fig. 12 indicates that only minor differences in compressive strength are

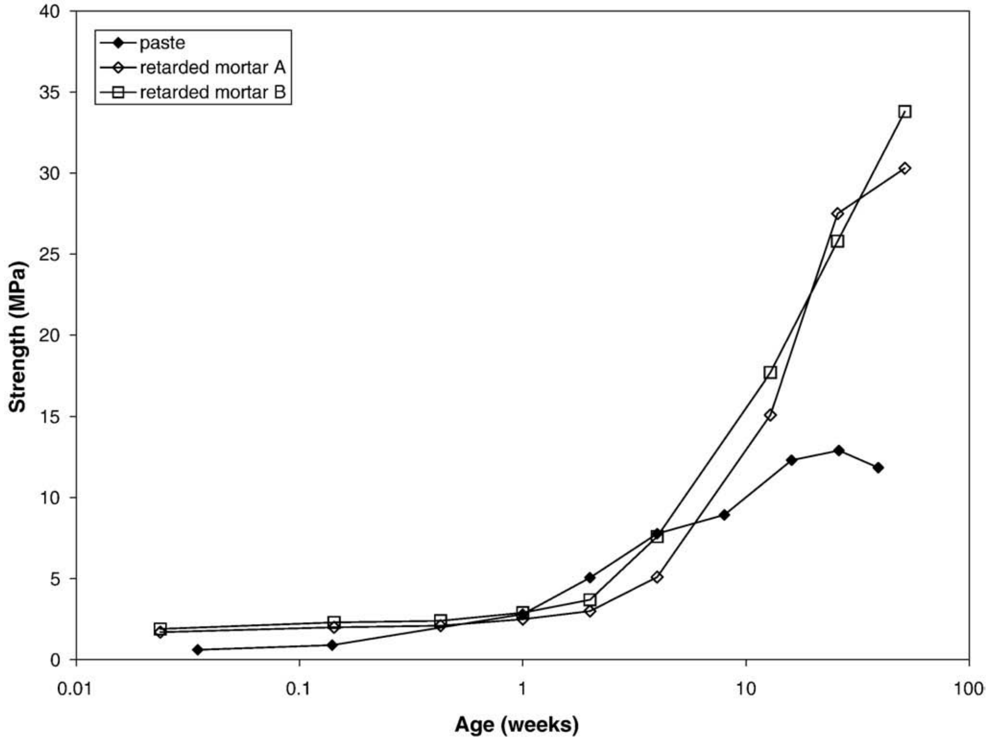

Fig. 12. Strength development profiles for PL-F with retarder; mortar A (citric acid), mortar B (potassium citrate).

apparent in the initial period up to an age of some 4 weeks although the use of citric acid yields the lowest strength in the period 2–4 weeks. However, the use of either retarder results in the substantially enhanced strengths at subsequent ages. This characteristic was also observed on un-retarded and retarded (0.38% citric acid) pastes of PL-F 805/400; the setting time was increased from 5 to 15 min.

It is apparent that the cement shown in Fig. 12 does not show the same paste strength profile as shown by the optimal PL-F cements in Fig. 6. A comparison of the mineralogy of the two cements reveals the trial cement from the electric kiln to be sub-optimal with low α' C_2S and total belite contents and a high calcite content. Fig. 5(a and b) indicates that such a cement would have a poorer performance than an optimal cement. Such use of mineralogy and strength data facilitated the process of scaling-up the production process from the laboratory bench study.

8. Conclusions

Cements which match the characteristics of nineteenth century Roman cement have been successfully calcined in batches of up to 250 kg. Their composition changes significantly as the intensity of the calcination conditions increases. The principal hydraulic phases are aluminates of unknown mineralogy occurring within an amorphous phase together with crystalline belite. For cements calcined at lower temperatures the dominant belite is α' C_2S whereas β C_2S is the stable form as the calcination temperature increases. The Cementation Index alone is insufficient to classify the reactivity of the marls and study of other parameters such as clay mineralogy, pore structure and micro- and macro-fabric is recommended. The strength development of the cements is strongly dependent upon calcination conditions, principally temperature. Two strength development profiles have been observed; one being the classic rapid early rise followed by a steady decline in the rate of strength increase whilst the second shows a three stage process including a significant dormant period. The hydration mechanisms responsible for the dormant period remain to be confirmed. Optimal cements are produced at low temperatures, approximately 750 °C from measurements within the charge, and contain evidence of incomplete calcination through the presence of quartz and calcite. The use of citric acid or potassium citrate suitably retards the rapid setting of the original cement and may yield strength enhancement following curing for 12–52 weeks.

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