Mechanical properties of lime-cement masonry mortars in their early ages

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Abstract: Lime-cement mortars are often used in restoration of existing buildings (especially twentieth century onward) as well as new constructions, in order to combine the individual strengths of either type of binder. Despite the knowledge that mortars have a significant impact on the non-linear mechanical behaviour of masonry from the earliest moments of construction, literature that systematically quantifies the impact of adding lime to cement mortars, or vice versa is scarce and scattered. This work is therefore focussed on bridging the research gap that exists in lime-cement masonry mortars with regard to their mechanical properties in the early ages (up to 7 days of curing). Five different mix compositions have been studied with 1:3 binder-aggregate ratio and 10% to 75% lime content in the binder, both by volume. Changes in properties like mechanical strength and stiffness along with ultrasound pulse velocity have been quantified, correlated and associated with change in quantity of lime in the binder (by volume) of the mortar. It was found that every 10% increase in the quantity of lime in the binder led to a 14% decrease in mechanical strength and a corresponding 12% decrease in stiffness, at 7 days of curing age. E-modulus was found to evolve faster than flexural strength, which in turn was found to evolve faster than compressive strength. Impact of curing temperature and the concept of activation energy has been addressed for the mix 1:1:6 (Cement: Lime: Sand).

Keywords: lime-cement masonry mortars, mechanical strength, stiffness, early-ages, ultrasound pulse velocity (UPV), curing temperature and activation energy

1. Introduction

With regard to use in masonry, mortars generally comprise of cement and lime in varying proportions, mixed with aggregates (sand) and, in some cases admixtures, in order to obtain certain requisite properties for different applications. Typically, the addition of air lime in the binder of mortar is carried out with the aim of obtaining better workability, more plastic deformation in masonry, increased bond, protection from moisture penetration and reduction of excessive stiffness [1]. Various research works have been identified, focusing their studies on properties of masonry mortars, such as changes in mineralogy and basic mechanical characteristics at different curing ages from 7 to 365 days [2-12]. However, it is difficult to make direct comparisons due to differences in the composition of materials in the binder as well as binder-aggregate and water-binder ratios of the mixes tested. With regard to addition of air lime, these groups have established some reasonably well accepted trends, such as extent of deformation prior to reaching maximum stresses, ability to withstand loads post failure and decrease in mechanical strength and stiffness of mortars. Different experimental campaigns reported trends and values that were not found to be unanimous. While corresponding drop in strength of mortar with increase in quantity of lime in the binder (2% drop in strength for 1% increase in lime in binder), is reported by both Macharia [13] and Arandigoyen *et al.* [2], the former observes it to be a linear trend, while the latter has not established a clear, linear correlation. These observations make room for development of an experimental campaign, which may systematically link the quantity of lime or cement in the binder with the mechanical strength of a masonry mortar. Similarly, difference in values of other mechanical characteristics, such as porosity and stiffness were found in the literature. Arandigoyen *et al.* [2] have shown open porosity to be independent of lime content in binder, with values of the same ranging between (20-23) %. Cizer *et al.* [3] state this range of open porosity to be (18-28) %, with porosity in the mortar increasing with lime content in the binder. Further, Macharia [13] reported an increase in open porosity of mortars, from 0 to 45% followed by a subsequent decrease, with increase in lime content of the binder. Values of Young's modulus found in the literature (reported mostly at 28 days of age) were found to be significantly different, ranging from 3 GPa up to 24 GPa [14-16].

It may be noticed, that the literature available on this topic is scattered, and that therefore there is not much consensus with regard to the effect of lime in masonry mortars with respect to basic mechanical properties. More importantly, these studies have been almost universally focussed on behaviour of mortars, which have gained adequate maturity, generally accepted as 28 days for cement based materials and at least 90-180 days for lime based materials [17-18]. However, based on the literature review conducted, no research focused on the behaviour of lime-cement mortars specifically between 0-7 days of curing age, which could be of relevance for crack development. This knowledge is also important to bridge the research gap with regard to gain of mechanical strength and stiffness in masonry and consequently stresses developed, in early ages. It may be observed from existing literature, that by the age of 7 days cement-lime mortars gain more than 75% of their total strength [2,3], though it is not explicitly quantified. Such observations open windows for quantifying the rate of gain of strength and stiffness, with respect to time and composition of binder. Further, it also provides grounds to attempt correlation of different properties, which were found to be scarce in literature [7].

Another approach to understanding the evolution of mechanical properties is through studying the microstructure and mineralogical characterization and consequently degree of hydration. While there is a notable amount of work focussed on the early ages, all these studies have been performed at the paste level, which poses a problem of representativeness [3,6,11-12,19]. It is difficult to upscale these results directly from paste to mortar due to a difference in the pore structure, porosity, capillarity and consequently the humidity flux in the materials involved [19-20]. Furthermore, in most cases, carbonation and hydration are studied separately to reduce the complexity of the problem. This implies that the curing conditions adopted for pastes are most often significantly different from what are used for mortars and in-situ conditions.

Regardless of the scale of study, paste or mortar, it is interesting to note that the effects of temperature have not been taken into account, while studying lime and cement together. Temperature dependent studies are found in abundance for cement based pastes, cement based mortars, and concrete, and are used to obtain varying information like activation energy, kinetics of the reaction and impact on mechanical strength in the short and long term [21-24]. This data is missing for lime-cement mortars and needs to be studied, in order to interpret the implication of masonry construction in different climates around the world.

This paper therefore, aims at discussing mechanical properties of lime-cement masonry mortars at early ages, i.e. between 0-7 days of curing. Different properties like mechanical strength, ultrasound pulse velocity, density and evolution of stiffness are presented for five different lime-cement mixes. Subsequently, one masonry mortar, with

50% lime in the binder (by volume) which is often used on field, was studied further to understand the effects of curing temperature.

2. Experimental program

2.1 Materials and sample preparation

In order to ensure constant properties and repeatability in the testing programme, binder of all the mixes was composed of air lime, type CL-90 S, along with Portland cement, type CEM I – 42.5 R. The lime used had a density of 2.24 g/cm^3, bulk density of 0.36 g/cm^3, blaine specific surface area 150000 cm^2/g and the mean value of its particle size distribution was between 5.5-6.5 μm. For lime, the chemical composition information in percentage was as follows {LOI (Loss on Ignition) - 25%; CaO - 74.35%; SiO_2 - 0.12%; MgO - 0.68%; Al_2O_3 - 0.06%; Fe_2O_3 - 0.05%; SO_3 - 0.197%; K_2O - 0.013%}. The density and blaine specific surface of the cement used was 3.12 g/cm^3 and 3508 cm^2/g respectively, with a clinker composition of 62.2% C_3S and 12.6% C_2S and bulk density of 0.93 g/cm^3. For cement, the chemical composition information in percentage was as follows {LOI - 2.05%; CaO - 63.4%; SiO_2 - 20.55%; MgO - 1.75%; Al_2O_3 - 4.27%; Fe_2O_3 - 3.2%; SO_3 - 3.05%; K_2O - 0.77%}. The properties of raw materials have been measured specifically for the corresponding batches of lime and cement used in this experimental campaign, as certified by the suppliers. Lime was supplied by Lhoist (Control number 90000998782) and cement by Secil (ACM-049/2016). Despite the knowledge that CEM II is more often employed in field applications, CEM I was chosen for the sake of maximizing scientific control over the variables involved, in terms of repeatability of results and possibility of replication by other authors. According to EN 197-1 [25], while CEM I and CEM II may both constitute of (0-5) % minor additional constituents apart from clinker; CEM II permits further (6-35) % variation in constituents by mass. These constituents include blast furnace slag, silica fume, natural and calcined Pozzolana, fly ash, burnt shale and limestone, very few of which have non-variable composition themselves. Based on the location of production and raw materials available, variation in chemical composition of CEM II was considered much more likely than that of CEM I. And therefore CEM I was chosen in an attempt to reduce the number of potential variables in the mortar mixes, increase chances of replication by other authors as well as better the reproducibility of results within this experimental campaign.

The aggregate consisted of sand with a particle size range of 0/4 mm [Figure 1], in accordance with the standard BS 1200-1976 [26]. The sand used was of siliceous nature (Chemical composition: SiO_2 - 98.92%; Fe_2O_3 - 0.04%; Al_2O_3 - 0.56%; TiO_2 - 0.03%; CaO - 0.13%) and had a bulk density of 1.6 g/cm^3. For the sake of consistency with regard to moisture content in the mixes, prior to each casting, the aggregates were heated at 105°C and subsequently cooled down to room temperature. The materials comprising the binder were pre-conditioned in an environment of 20°C temperature and 65% relative humidity for up to 7 days before casting of each mix.

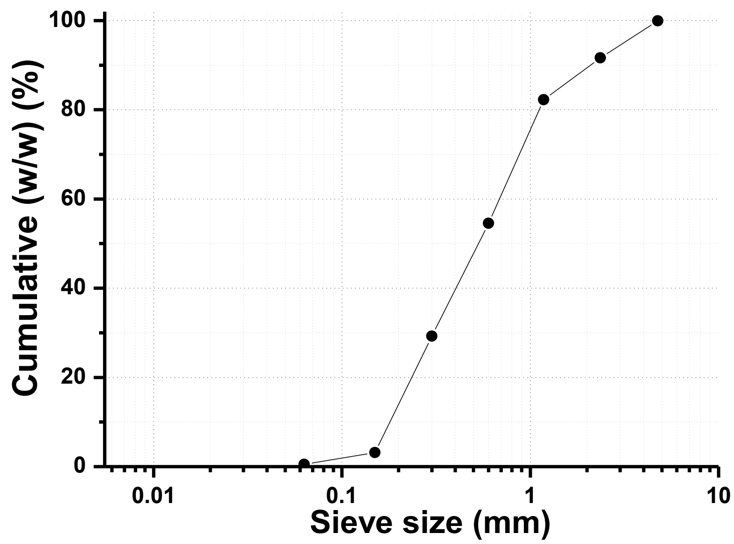

Figure 1: Particle size distribution of aggregate [0.063, 4] mm

Table 1: Composition of blended lime-cement mortars (For every 1 m^3 of mortar produced)

Nomenclature of mixes		Cement: Lime: Sand (Ratio by volume)	Cement (kg)	Lime (kg)	Water (kg)	Water-Binder ratio	
Notation	**Lime in binder (Volume %)**					**(By weight)**	**(By volume)**
9C1L30S	10	9:1:30	315.2	13.4	295.6	0.90	0.79
2C1L9S	33.3	2:1:9	233.5	44.5	303.1	1.09	0.81

1C1L6S	50	1:1:6	175.1	66.8	303.1	1.25	0.81
1C2L9S	66.7	1:2:9	116.8	89.0	325.0	1.58	0.87
1C3L12S	75	1:3:12	87.6	100.1	331.3	1.76	0.88

Five different mix compositions were chosen with a binder-aggregate ratio of 1:3 by volume, and quantity of lime in the binder varying from 10% to 75% by volume [Table 1]. Design proportions of these compositions were chosen based on mortars commonly used on field and studied by other authors for masonry structures [2,19,27]. The notations employed denote the proportion of different constituents of the mix by volume; 1C3L12S for instance, represents a mix ratio 1:3:12 in the order of cement, lime and sand. Further, all graphs have been supplemented with the quantity of lime in the binder (by volume) in order to facilitate comprehension. For consistency in quantities of raw materials measured, all proportions were converted to mass by employing the apparent densities of air lime, cement and sand. From the point of view of industrial application, ensuring adequate workability for the mixes was a concern [28]. Consequently, a mortar flow of 175±10 mm was targeted for all mixes, according to EN 1015-3 [29]. Apart from Elasticity Modulus Measurement through Ambient Response Method (EMM-ARM) [30], and unconfined cyclic compression test [31], all experiments conducted involved prismatic specimens of size 40×40×160 mm, which were cast according to standard EN 196-1 [32]. The curing conditions were based on standard EN 1015-11 [33], which requires the specimens to be kept in an environment with 95±5% relative humidity and 20±2°C temperature for the first seven days of curing. Demoulding of the specimens was carried out two days after casting as per standard EN 1015-11, because of the lime content in the binder being less 50% by mass, except for the mix 1C3L12S (75%) which had greater than 50% lime by mass and was consequently demoulded after 5 days [33].

2.2 Mechanical tests

Table 2: Summary of mechanical tests: Specimens (Type and quantity), curing conditions, standards, age of testing

Name of test	**Curing conditions**	**Specimens (Type and quantity)**	**Comments**

Compressive strength, Flexural strength, Ultrasound pulse velocity (UPV), Hardened density	20±1°C {95±5% RH till demoulding, 65±5% after demoulding}	Prism (40*40*160) mm^3; Average values obtained from 3 specimens in flexural strength, UPV, density; 6 samples from 3 specimens in compressive strength;	EN 1015-11 [33]; Tested at ages 1, 2, 3, 4 and 7 days for strength; At 7 days for density and UPV;
E-modulus – cyclic compression	20±1°C, sealed;	Cylinder (60 mm dia, 120 mm height); Average values obtained from 3 specimens;	EN 12390:13 [31]; Tested at 7 days;
EMM-ARM (Continuous measurement)	20±1°C, sealed; 30±1°C, sealed; 40±1°C, sealed;	Cylinder (Length 550 mm, inner dia 44 mm, outer dia 50 mm); Average values obtained from 2 specimens;	EMM-ARM user manual [34]; Tested from 0 to 7 days;

All mechanical tests performed in this work have been summarised in [Table 2], and described in more details in Section 2.2.1 (Discrete measurements) and Section 2.2.2 (Continuous measurements).

2.2.1 Discrete measurements

Based on the recommendation of standard EN 1015-11 [33], the three-point bending (flexural strength) test was carried out at curing ages of 7 days, for three specimens of each mix, employing displacement control at the rate of 0.006 mm/s, with a preload of 150 N. Displacement control method was chosen for flexural strength because of low absolute values obtained in the early ages i.e. less than 7 days. The resulting halves from the flexural tests were then subjected to uniaxial compression at a rate of 50 N/s, and each value of compressive strength was obtained by averaging results from six tests, from three specimens [33]. The evolution of ultrasound pulse velocity was measured in the same set of specimens for each mix at 7 days of curing age. The measurements were carried out along the length (160 mm) of the specimens using waves of 150 kHz frequency to transmit and receive P-waves. Ultrasound pulse velocity was calculated by dividing the length of the specimen (160 mm) by the time that passed between transmission and reception of P-waves through the specimen. Time taken by the P-waves ranged between (50-110) μs, for the specimens tested in this work. In addition to this, the loss or gain in weight of the specimens was also monitored, in order to record the density.

To deepen existing knowledge on behaviour of blended mortars at early ages, a representative mix namely 1C1L6S with 50% lime in the binder by volume was chosen to be studied additionally at 1, 2, 3 and 4 days of curing age. The choice of this mix resulted from similar patterns observed in mechanical behaviour of all mixes tested; leading to the conclusion that selection of a mix with equal volumes of lime and cement would be a representative choice. Furthermore, it was found in literature that this proportion has been extensively studied by different researchers [2,19]. It is also one of the most commonly used masonry mix proportions on field for general purposes in interior and exterior conditions [35]. For the same mix 1C1L6S, Young's modulus was measured at the age of day 7, using the conventional method of cyclic compression according to EN 12390-13 [31]. For this test, three cylindrical specimens with 120 mm height and 60 mm diameter were used. Due to insufficient gain of mechanical strength in the early ages as well as the presence of significant lime in the binder, top and bottom surfaces of the specimens could not be rectified using a cylinder end grinding machine, as that could damage the specimens. Therefore, epoxy resin was used to cap the specimens, in order to ensure even application of load during the test. Four continuous loading/unloading cycles were applied with an axial pre-load of 50 N and loading rate of 45 N/s, with the help of a 25 kN hydraulic actuator. The loading rate was based on constant duration of each branch of loading cycle, pre-defined at 60 s. Maximum load equalled approximately one-third of the maximum compressive strength of the mortar at that age. The setup of the LVDTs adopted was similar to that used by Silva [36] for testing soil specimens stabilized by cement.

2.2.2 Continuous measurements

EMM-ARM (Elasticity Modulus Measurement through Ambient Response Method) is a method, which was introduced in 2009 by Azenha [30], to measure the development of stiffness of cement pastes and concrete. With regard to mortars, and taking into account the most recent developments of the method [37], a PVC mould was used, filled with the mortar to be tested. The mould was placed horizontally in simply supported conditions and subjected to forced vibrations at mid-span. The acquisition sampling rate used was 1250 Hz, acquisition time per sample was 300 seconds and time between two sampling events was 720 seconds. Additionally, the expected start frequency was set as 60 Hz. The corresponding response was then monitored using accelerometers to perform modal identification. Subsequently, evolution of the first flexural resonant frequency of the composite mould was assessed, as a result of the increasing stiffness of mortar cast inside it. Continuous estimations of Young's modulus were obtained employing the dynamic equation of motion, according to the principles set forward in [37,38]. This method was used for all mortar mixes, to study the evolution of Young's modulus from the time of casting up to the age of day 7, with curing temperature of 20±2°C. Since the specimens are completely sealed in this test, relative humidity may be considered comparable with the curing conditions specified in EN 1015-11, i.e. 95±5% [33]. Additionally, EMM-ARM was performed at ambient temperatures of 30±2°C and 40±2°C for the mix 1C1L6S in order to obtain values for rate of hydration and activation energy. The moulds had the dimensions: 550 mm in length, 44mm internal and 50 mm external diameter. Two steel rods of 6mm diameter and 85 mm length were required to be drilled into the PVC tube to act as supports for a span of 500mm. After the mortar was cast into the mould, the specimen was sealed from both ends using 20 mm thick polystyrene cylinder caps [34].

3. Results

3.1 Discrete measurements

Table 3: Mechanical properties of blended lime-cement mortars at 7 days of curing age

Mix	Density (g/cm^3)	CV (%)	Compressive strength (MPa)	CV (%)	Flexural strength (MPa)	CV (%)	UPV (m/s)	CV (%)
9C1L30S (10%)	2.11	0.5	8.94	3.6	2.67	9.8	3290	1.0
2C1L9S (33%)	1.99	0.5	6.09	2.8	1.52	5.6	2811	0.5
1C1L6S (50%)	2.01	0.3	4.12	5.5	1.23	4.8	2542	0.7
1C2L9S (67%)	1.91	0.4	1.48	6.7	0.41	7.7	1822	0.4

1C3L12S (75%)	1.94	0.7	0.63	8.9	0.28	4.5	1434	2.1

Results obtained from tests carried out at 7 days of curing age, namely compressive strength, flexural strength, ultrasound pulse velocity and density are presented for all mixes with their corresponding coefficients of variation (CV) [Table 3]. It may be observed that mechanical strength of the mortar tends to decrease with increase in content of lime in the binder (by volume). Therefore, linear regression analyses were performed for the experimental data of mechanical strength with quantity of lime in the binder (by volume) [Figure 2]. Apart from high R^2 values which indicate good fitting of the data with respect to the equations proposed, p-values obtained were also really low. A p-value < 0.05, enables rejection of a null hypothesis i.e., data is unrelated or that the trends obtained were by chance. Similarly, a high F value has the same significance. In the case of F-value however, there is no fixed limit to surpass and the value may be arbitrarily large. And thus due to high R^2 and F values and p-values < 0.05, the regression analyses were considered acceptable [Figure 2]. The values of the mix 9C1L10S (10% lime in the binder) were considered as a reference for both cases. It was found that for every 10% increase in lime content of the binder (by volume), compressive strength and flexural strength decrease by 14.3% and 14.2% respectively, with respect to the reference mix. This implies that if the quantity of lime in the binder is increased from 10% to 40%, the mechanical strength will reduce by approximately 40%.

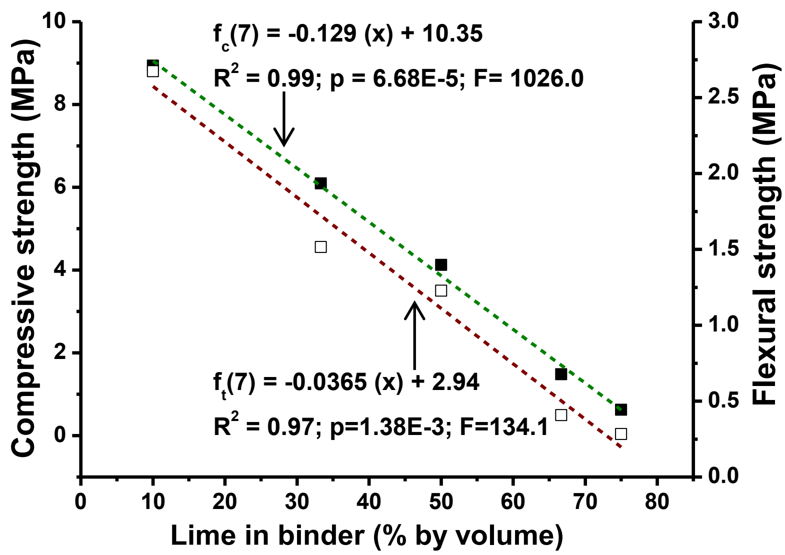

Figure 2: Change in mechanical strength as a function of lime content in binder (% by volume)

Ultrasound pulse velocity seemed to decrease with increasing lime content in the mix. Despite performing a linear regression analysis (R^2=0.95) no meaningful interpretation could be obtained from correlating the two parameters. Density of the mortars on the other hand, seems to exhibit no pattern, at all, either with regard to quantity of lime in the mortar or with ultrasound pulse velocity.

From the behavioural knowledge of concrete, it is known that E-modulus (E) is often expressed as a function of density (ρ) and compressive strength (f_c) i.e. ($\rho^a f_c^b$) with varying values of exponents (a and b) [39,40]. The exponent usually used for compressive strength is 0.5, whereas the exponent used for density may vary. In this work, in order to fit data for lime-cement mortars, the product ($\rho^{1.5} f_c^{0.5}$) was chosen. Furthermore, because E-modulus is known to be directly proportional to the square of ultrasound pulse velocity [41], instead of using E-modulus, UPV^2 was expressed as a function of ($\rho^{1.5} f_c^{0.5}$), i.e. UPV^2 was found to be directly proportional to ($\rho^{1.5} f_c^{0.5}$). A fixed value of constant of proportionality has not been proposed since ultrasound pulse velocity depends on a lot of variables such as air content, water content and so on. Additionally, in case different materials are employed or if measurements of properties are carried out at a different curing age, the constant of proportionality may be expected to change and must be re-calculated. The plot of [Figure 3] was created for different lime-cement mixes with the X axis corresponding to the product $X(t) = \rho(t)^{1.5}f_c(t)^{0.5}$ (ρ is density of the mortar in kg/m^3; f_c is the compressive strength in MPa) while the Y axis corresponds to squared ultrasound pulse velocity i.e. $Y(t)= UPV(t)^2$ (m/s) as measured in the longitudinal direction of the prismatic specimens. All properties obtained for this graph were measured at 7 days of curing age, and therefore t=7, otherwise t would correspond to the curing age at which the different properties are measured. The R^2 value obtained for this linear regression was 0.99, which makes it conceptually possible to estimate the value of compressive strength of different lime-cement mixes (on the raw materials used herein) as a function of lime content in the binder, simply by measuring the corresponding density and ultrasound pulse velocity, within an error range of ±5%.

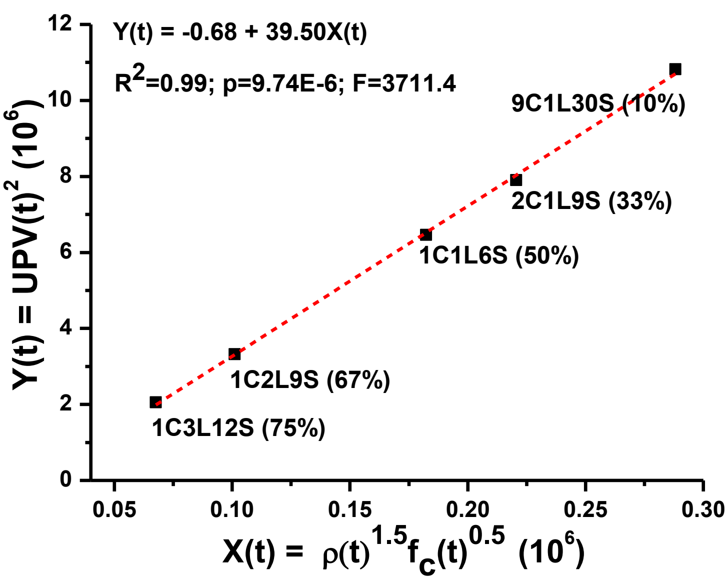

Figure 3: Relationship between compressive strength, ultrasound pulse velocity and density; where t=7 days (curing age)

3.2 Continuous measurements

3.2.1 Evolution of E-modulus

It is possible to observe the evolution of stiffness (as measured by EMM-ARM) of the different lime-cement blended mixes in Figure 4.

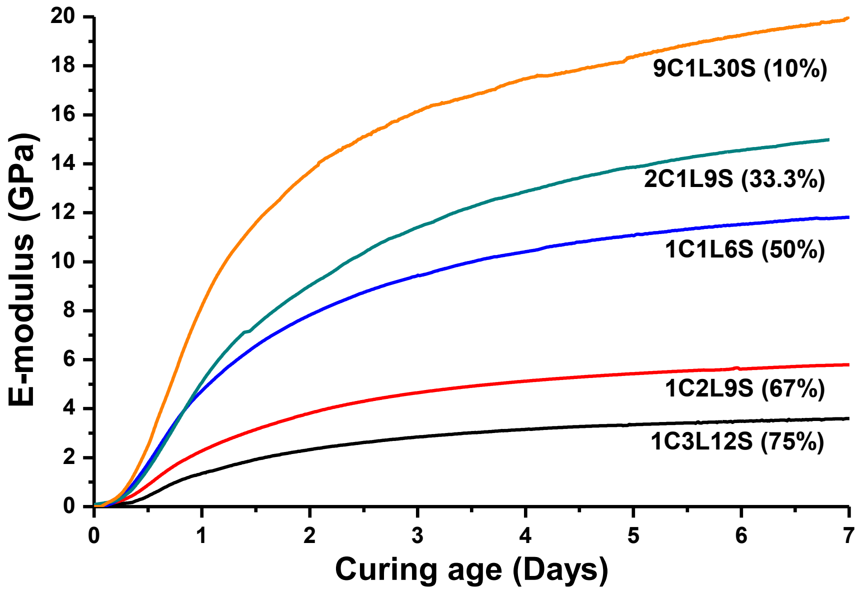

Figure 4: Evolution of Young's modulus from time 0 to 7 days of curing age for lime-cement blended mortars

The global trend observed in mechanical strength in the quantity of lime in the binder, was found true for stiffness as well. Increase in lime, leads to a decrease in the stiffness of the mortar. This observation was found to be consistent with literature [15], since as the quantity of cement increases in the mix, more products of cement hydration are formed. One of the most abundant products of the reaction is C-S-H (calcium silicate hydrate) crystals, which along with its internal system of pores, has significantly greater volume than the C_3S and C_2S minerals it replaces. This network of C-S-H crystals then forms strong connections with the solid phase, binding discrete compounds into a cohesive whole and consequently contributing to the overall strength and stiffness of hydrated cement [42]. In the early ages, only cement hydration is considered as relevant, since competition between hydration and carbonation is almost non-existent under atmospheric conditions: hydration is much faster and takes place before carbonation initiates [19].

In order to quantify the effect of lime in the binder of the mortar, values of E-modulus were compared every 24 hours, from 1 to 7 days [Figure 5]. Based on the seven linear regression analyses performed for values from day 1 to day 7 (average R^2 of 0.97; p=1.51E-3; F=137.9), a statistical correlation could be established. Once again, in all the cases, the mix 9C1L30S (10% lime in the binder by volume) was used as a reference. It was found that at all curing ages, day 1 to day 7: every 10% increase in the quantity of lime in the binder led to a corresponding 12%

decrease in stiffness of the mortar. It is also possible to observe that all mortars, regardless of the quantity of lime in the binder, appear to gain approximately 40% of their total stiffness in the first 24 hours, and 80% in the first 72 hours. After the fourth day, the increase in stiffness of all the mortars was found to be less than 5%.

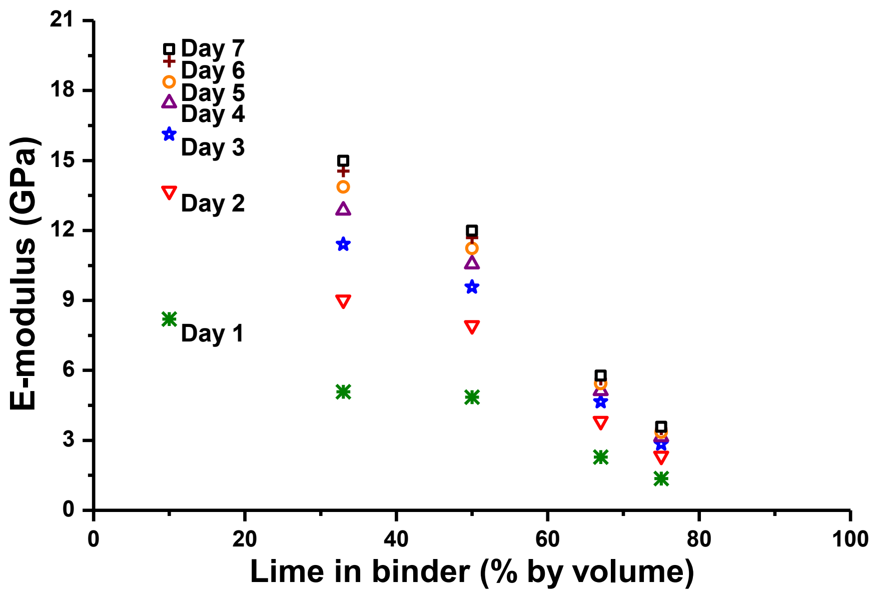

Figure 5: Growth in stiffness as a function of lime content in binder (% by volume) at different ages

Further, stiffness was normalized with respect to the value attained at day 7 for all mortars and plotted together [Figure 6]. The curves obtained, overlap in a remarkable manner, leading to the first conclusion that the dormant period of all the mortars is almost the same, between 3-4 hours [Figure 7].

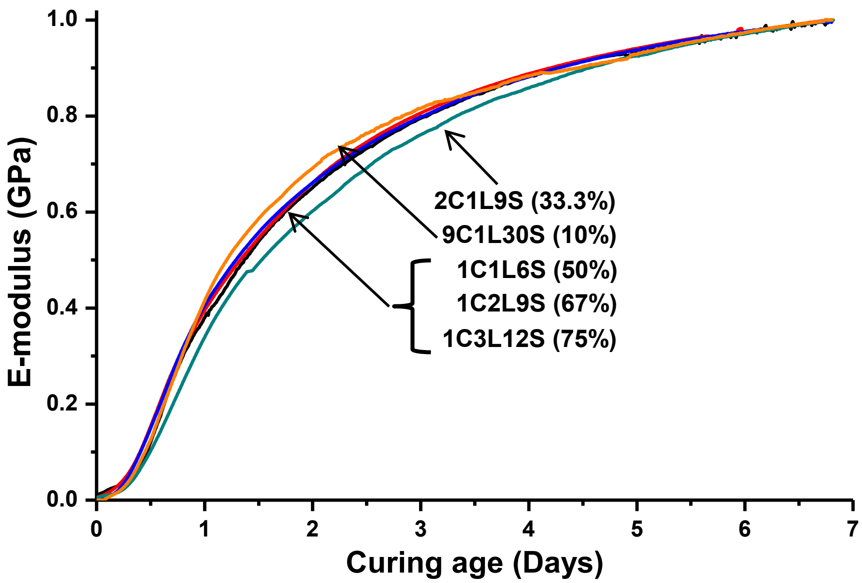

Figure 6: Evolution of normalized values of Young's modulus for lime-cement blended mortars

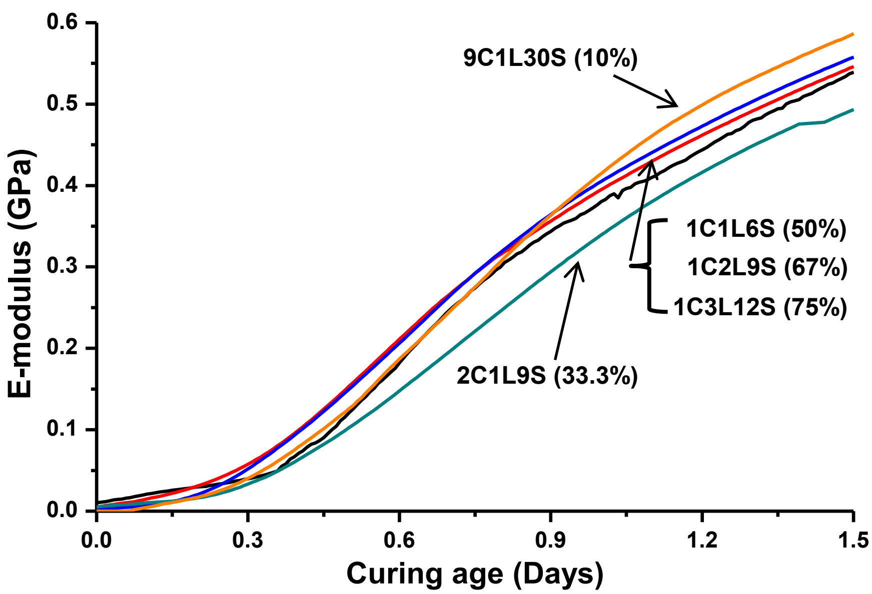

Figure 7: Evolution of normalized values of Young's modulus up to 1.5 days (Zoom-in of Figure 6)

The second observation, is the slight difference noticeable with regard to the mixes 2C1L9S (33%) and 9C1L30S (10%) i.e. the mixes with the least quantities of lime in the binder by volume. Both the mixes exhibit lower relative reactivity, up to the age of 15 hours and have slightly longer dormant periods compared to the other mixes [Figure

7]. This is consistent with results found in literature. Fourmentin *et al.* [43], state that the presence of lime accelerates the process of cement hydration, reducing its dormant period, but to a negligible extent. This phenomenon has been attributed to the high specific surface area of lime, which possibly provides larger surface area for precipitation of the C-S-H crystals. These authors further state that this accelerating effect of lime saturates after a certain quantity. This observation is to a large extent, coherent with the behaviour of different mixes in this campaign, as all mixes with or greater than 50% lime in the binder exhibit similar dormant periods and relative kinetics [Figure 6]. Another explanation is that lime causes destruction of Al-O bonds networks (corresponding to oxides of Aluminium) in Tri-calcium aluminates, which are formed as a product of cement hydration; resulting in an increase in alkalinity of the mix, consequently accelerating the reaction [19]. However, the mix 9C1L30S (10%) lime, does not appear to continue to conform to this expected behaviour of lower relative kinetics, mainly after 24 hours of curing age. It is interesting to observe that while the relative reactivity of this mix appears to be the low up to approximately 15 hours, it then becomes fastest (compared to all other mixes) by the end of 24 hours [Figure 7]. This behaviour may merit further investigation, as it could lead to more information on an optimum quantity of lime necessary to obtain desired properties from a blended mortar, especially in its early ages. Since, stiffness and strength may not necessarily evolve at the same rate, knowledge of such behaviour can possibly help optimize rules of thumb for speed of masonry construction and avoid cracking of mortar. Such data could also be used for numerical modelling. Seemingly inexplicable pathologies are often a result of insufficient knowledge of early residual stresses developed in load bearing structures. This field has hardly been explored in masonry constructions even though it is very important to know when the material starts bearing loads. Apart from evolution of stiffness and strength, setting of mortar and its shrinkage are two important phenomena that may occur in the very early ages [44]. Treatment of data from EMM-ARM can lead to quantification of the former parameter, as well as provide information in assisting microstructural studies, when performed at the paste level [24].

3.2.2 Comparison of results of EMM-ARM with cyclic compression test

The feasibility of E-modulus obtained from EMM-ARM was examined using the conventional method of unconfined cyclic compression test according to EN 12390-13 [31], for the mix 1C1L6S (50% lime in the binder). A detailed description of the set up may be found in reference [45]. In order to ensure similar curing conditions, the specimens used for cyclic compression were kept sealed up to the time of testing. This test was initially designed to test the elasticity modulus of concrete, and adapted subsequently for mortars. The comparison of results from the two methods has been carried out only at the 7th day of curing age due to practical reasons, namely lack of adequate strength in the mortar in earlier ages, which makes it challenging to demould the specimens without creating micro cracks in it. At the time of testing, E-modulus was obtained from EMM-ARM (average value) corresponding to 11.8 GPa and that from cyclic compression test corresponding to 10.9 GPa (Obtained from an average of three specimens with a coefficient of variation of 0.2%). The comparison has been presented at time 6.5 days, corresponding to the actual moment of demoulding and preparation of specimens that were used for the cyclic compression test. The difference of 7.4% in the results was considered acceptable from a statistical point of view. In fact, even if allowance is provided for differences obtained in results stemming from variations inherent to the cyclic compression test, up to 10% variation was found common in the measurement of static Young's modulus of mortars [10]. The results obtained from EMM-ARM have been observed as repeatable and have been validated by far weaker materials, such as stabilized soil [46].

3.2.3 Relative evolution of mechanical properties of mix 1C1L6S

Since, mechanical strength and stiffness of all blended mixes, exhibited a good linear correlation with respect to the quantity of lime in the binder of the mix, mortar 1C1L6S (with 50% lime in the binder by volume) was chosen as a representative for further investigation. For the said mix, evolution of compressive strength, flexural strength and Young's modulus have been normalized with respect to corresponding maximum values attained at day 7, and presented [Figure 8]. Additionally, the absolute values have been presented in Table 4.

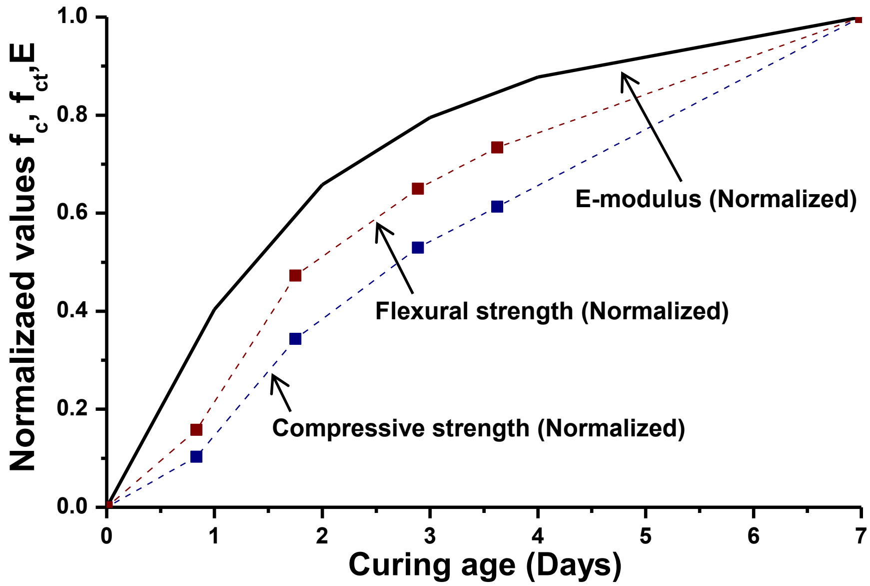

Figure 8: Relative evolution of mechanical properties – 1C1L6S lime-cement blended mortar (50% lime by volume)

Table 4: Absolute values of mechanical properties of blended lime-cement mortars from 0 to 7 days of age

Absolute values/ Curing age (Days)	**Compressive strength (MPa)**	**CV (%)**	**Flexural strength (MPa)**	**CV (%)**	**E-modulus (GPa)**	**CV (%)**
0.8	0.43	4.2	0.19	13.2	4.8	2.7
1.8	1.42	4.2	0.58	1.1	7.9	1.9
2.9	2.18	4.0	0.80	4.1	9.6	1.9
3.6	2.53	4.5	0.90	10.1	10.6	1.9
7	4.12	5.5	1.23	4.8	12.0	1.6

It may be observed that Young's modulus evolves faster than flexural strength, which in turn evolves faster compared to compressive strength. This behaviour is similar to what is observed in concrete and is usually expressed in the form of a single mathematical equation, with varying coefficients which are adapted based on the property being discussed or the type of cement involved [30]. In the current work, such an equation was established for mortar 1C1L6S (as an example) [Equation 1]. The function v(t) denotes the mechanical property being considered, normalized with respect to corresponding maximum value attained on day 7 (Compressive strength, flexural strength or Young's modulus) [Equation 1]. Normally for such equations in the case of concrete, normalization of the property is done with respect to value attained at 28 days of curing age. However, since this paper corresponds to early age studies, day 7 was chosen for normalization. The parameter t [Equation 1] corresponds to time (in days, up to 7) and the parameter n, is dependent on the mechanical property under consideration. In this work, n was found to be equal to 1.14 for compressive strength, 0.50 for E-modulus and 0.82 for flexural strength, with an average R^2 of 0.996.

$$v(t) = \left[e^{\left(1-\sqrt{\frac{7}{t}}\right)}\right]^{n} \tag{1}$$

The presented formulation [Equation 1] provides an opportunity for the correlation between strength and stiffness to be tested for other lime-cement proportions in masonry mortars, and if possible to be subsequently generalized. This relation is significant for primarily three reasons; the first is associated with cracking of the mortar, since its stiffness evolves much faster than its strength which can actually sustain the loads, it is important to have an idea of the absolute values that develop with time. The second is associated with feasibility of the experimental campaign itself. Tests of compressive strength are easier to perform than those of E-modulus at early ages and offer smaller scatter (statistically) in the experimental values obtained [47]. Finally, such relations could also prove useful for numerical simulation of the mechanical behaviour of mortar, as a function of time.

3.2.4 Effect of curing temperature on mix 1C1L6S

The effect of curing temperature was assessed by performing the EMM-ARM test for the mortar 1C1L6S (50% lime in the binder, by volume) at 20±2°C, 30±2°C and 40±2°C [Figure 9]. It may be noted that the data presented in [Figure 9], are from the mathematical expressions that fit the experimental data almost perfectly (R^2 value was found to be greater than 0.99 in all three cases), corresponding to [Equation 2].

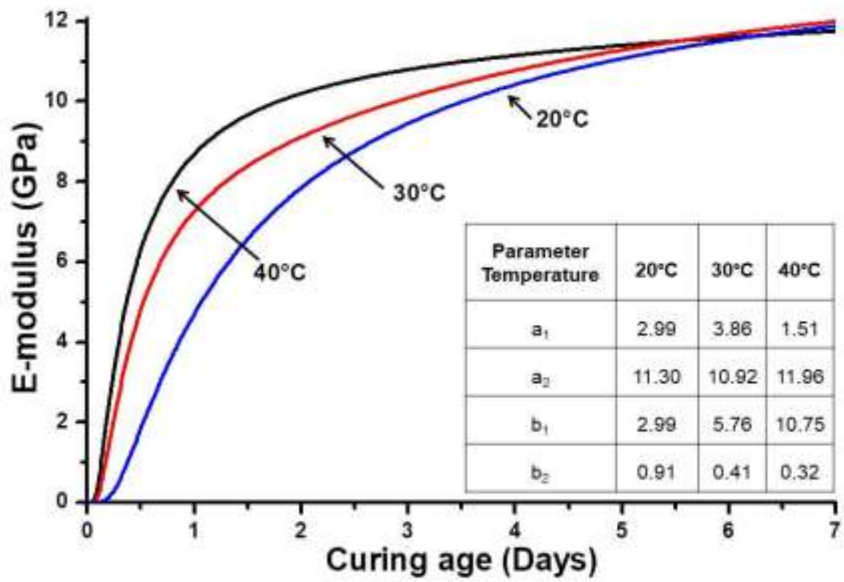

Figure 9: Evolution of Young's modulus – 1C1L6S lime-cement blended mortar (50% lime by volume) at 20, 30 and 40°C

The function E(t) corresponds to the evolution of E-modulus as a function of time, parameter t corresponds to time, and other variables in the equation are dependent on temperature [Figure 9]. After 7 days, similar values of stiffness were attained from all three curing temperatures, 12 GPa.

$$E(\mathrm{t}) = a_1 e^{\left(\frac{-b_1}{t}\right)} + a_2 e^{\left(\frac{-b_2}{t}\right)} \quad (2)$$

Two interesting phenomena were observed, which are surprisingly similar to what has been reported as occurring in concrete [24]. The first one, is evident from Figure 9; greater the curing temperature, faster is the reactivity kinetics, which is known to be true for cement mixes as well [48]. The effect of temperature comes into play right from the end of the 'dormant period' of cement hydration and may be noticed after around two hours from the time of casting. In fact, it is possible to note from the reaction kinetics, that as the curing temperature increases, the dormant period of the hydration process ends faster with respect to time. Thereafter, from around 4 hours to 4 days of curing, it is possible to observe a remarkable difference in reactivity kinetics of the same mix as a function of curing temperature, because this is the period in which cement hydration is more pronounced. For example, after 24 hours of curing, the mix cured at 40°C (8.7 GPa) is almost 50% more stiff compared to the mix cured at

20°C (4.7 GPa). This difference reduces to 20% at the end of 48 hours of curing, and continues to decrease, till similar values of stiffness are reached at the 7th day of curing. This significant difference in stiffness at the end of 24 hours of curing time is important, when combined with the knowledge of relative evolution of different mechanical parameters [Section 3.2.3]. Since stiffness was observed to evolve faster than strength, the material may invite stresses that it does not have the capacity to withstand. This information is crucial in the early ages to avoid cracking of the material and subsequent damage to the structure. The second phenomenon is associated with final values of stiffness attained at 7 days of curing age. While it is true that all three mixes tend to attain the same value by the end of 7 days of curing time, it may be observed that the mix that was cured at 40°C, gains the lowest mechanical stiffness at the end of this period. Nevertheless, this difference (less than 1%) does not appear to be significant. However, at temperature ranges higher than 80 degree Celsius, the products from the hydration reactions are expected to become denser, causing higher capillarity porosity, and may therefore cause a change in mechanical properties worth taking into account [28]. It seems reasonable to conclude that up to temperatures of 40 degree Celsius, lime-cement masonry mortars show no tendencies to attain smaller values (of any significance) of mechanical stiffness that may be a cause for concern. A word of caution here is that the results obtained in this work are only valid up to 7 days of age, and cannot be extrapolated to later ages without taking into account the phenomenon of carbonation. This is because carbonation is affected by a decrease in relative humidity that could be caused by increased curing temperature [19].

To calculate the rate of reaction, the derivative of rate of stiffness development $\left(\frac{d\alpha}{dt}\right)$ was plotted with respect to time, to graphically obtain the peak value of each curve [Figure 10]. The rate of stiffness development α was estimated by employing [Equation 3].

$$\alpha(\mathrm{t}) = \frac{E(t)}{E\ (ult)} \qquad (3)$$

The value of E(t) may be adopted from Equation 2, and the value of E(ult) may be obtained from time tending to infinity, i.e. an asymptotic value E(ult)= a_1+a_2. Further details with regard to this procedure may be found in [24].

From the graph in [Figure 10], it is easy to observe that the mix cured at the highest curing temperature, namely 40°C, exhibits the fastest kinetics, followed by the mix cured at 30 and subsequently 20°C. The maximum values of each of the curves in time were observed to be 11.2, 5 and 3.8 hours, for 20, 30 and 40°C, respectively.

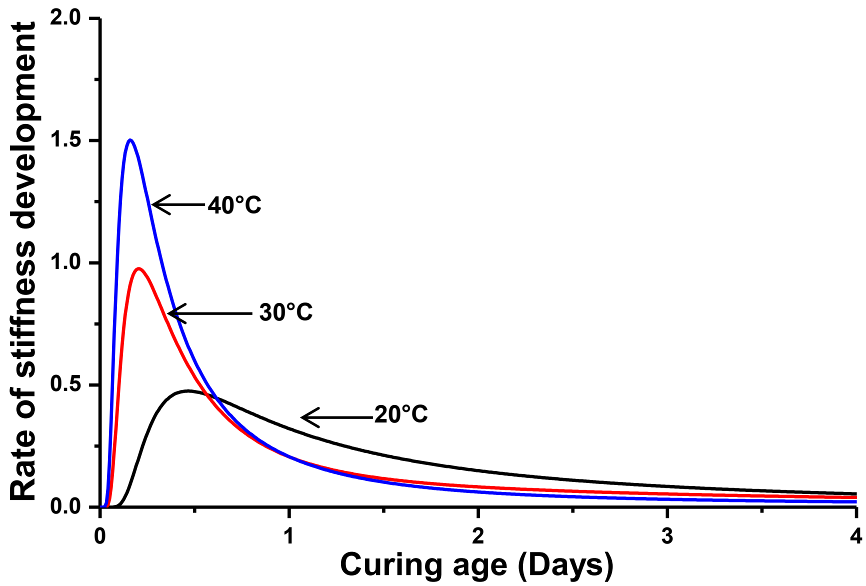

Figure 10: Reaction rate – 1C1L6S lime-cement blended mortar (50% lime by volume) at 20, 30 and 40°C

Subsequently, each of the maximum values of rate of hydration k(T) was plotted in the logarithmic scale on the y-axis with the inverse of temperature (T) (in Kelvin) on the x-axis to obtain the value of slope and intercept [Figure 11].

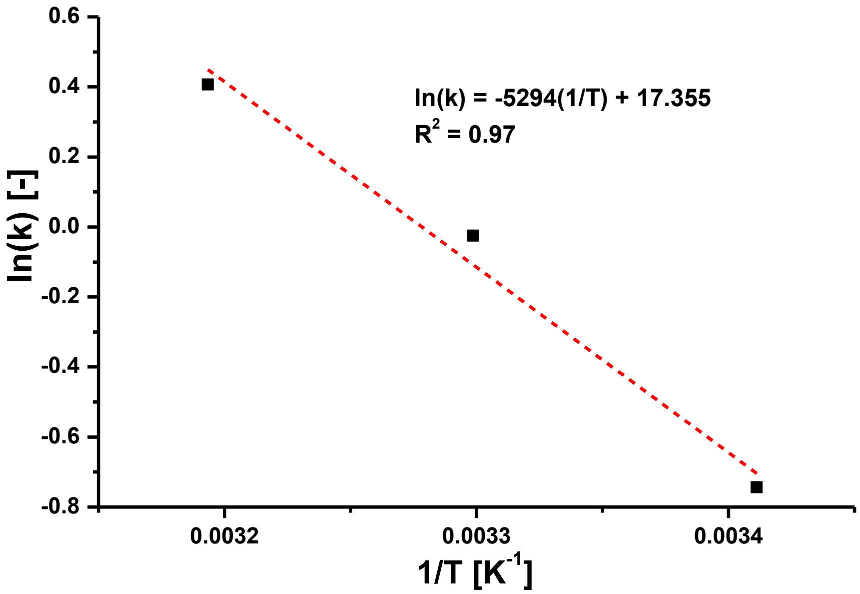

Figure 11: Arrhenius plot of rate coefficient, activation energy – 1C1L6S lime-cement blended mortar (50% lime by volume). Here, *k* if the rate of hydration and *T* is the temperature

If [Equation 4] is adopted to express this relation, it is possible to obtain the value of activation energy (E_{act}) from the slope and the proportionality constant (A_t) of the Arrhenius equation from the intercept, where R is the universal gas constant.

$$\ln\big(k(T)\big) = \ln(A_t) - \frac{E_{act}}{R}\left[\frac{1}{T}\right] \tag{4}$$

The value of activation energy obtained corresponded to 44.01 kJ/mol. On referring to literature, it was found that these values seemed to be in the same range as those obtained for cement paste and concrete [24]. However, since for masonry mortars, such information was not found from the literature review conducted, a direct comparison of values was not possible. Such information is crucial to better understand the kinetics and thermodynamics of cement hydration in the presence of lime and may be used in numerical modelling of multi-physical phenomena.

4. Conclusions

Unprecedented information with regard to masonry mortars has been presented and discussed in this paper, focusing on the early age behaviour of said lime-cement mixes, i.e. up to the age of 7 days, from the time of casting. The following information can be summarized to highlight the main findings of the paper.

1) Using a mortar with 10% (by volume) lime in the binder as reference, every 10% increase in lime content (by volume) was found to result in a corresponding 14% decrease in compressive and flexural strength, at 7 days of curing age. With the same reference, every 10% increase in lime content (by volume) exhibited 12% loss in E-modulus at curing ages of 1 to 7 days.
2) It was possible to estimate values of compressive strength of the mixes tested in this program, simply by measuring the corresponding density and ultrasound pulse velocity, at 7 days of curing age. The error range of estimation was found to be ±5%.
3) Evolution of E-modulus of five different masonry mortars has been presented from the time of casting up to 7 days of curing age, at 20±2°C. All mortars were observed to gain 40% of their total stiffness (normalized with respect to value at day 7) within a day and 80% of their stiffness within 3 days. After this period, the increase in stiffness was found to be less than 5%.
4) Choosing the mix 1C1L6S (50% by volume, lime in the binder) as representative, further studies were carried out. Evolution of E-modulus, compressive strength and flexural strength has been presented using a single mathematical formulation, with one parameter that needs to be adapted for each property. It was found that an increase in curing temperature led to faster kinetics of reaction and shortened the dormant period corresponding to cement hydration. However, the maximum curing temperature, causing the fastest evolution of stiffness, led to a slight deterioration in the final value of stiffness of the mortar. Finally, the rate of reaction and activation energy for has also been presented for the said mortar.

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6. Compliance with ethical standards

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Conflict of interest

The authors declare that they have no conflicts of interest.

Ethical standards

The research project completely complies with ethical standards required by the European community for research work. No research was performed on any human beings or animals.

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