

CURRENT TRENDS IN DEVELOPMENT OF LIME BASED COMPOSITES

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Summary: Prior to the beginning of this century, lime dominance as a building material particularly, lime mortar was incontrovertible. Reminiscence of this is reflected in many buildings of historic references which stand till date as their durability features are predominantly attributed to lime's inherent properties of flexibility, plasticity and breathability, among others. However, lime's characteristic long 'setting and hardening' periods, low mechanical strength and poor internal cohesion coupled with subsequent discovery of Portland cement put its use into decline. In this paper, new approaches involving lime based composites aimed at maximising lime's sterling features while improving its identified shortcomings are highlighted. The focus is particularly on lime based mortars blended with cement and 'Ground Granulated Blast Furnace Slag' (slag) in varying compositions individually, for improved performances. As this effort attempts to evolve lime revival for new constructions, it will also serve as a befitting response to the phenomena climate change with a view to minimising construction impacts on the environment.

Keywords: lime mortar, slag (GGBS), carbonation, performance indicators

1. INTRODUCTION

Lime mortar, an age-long proportional mixture of lime, sand and water is a plastic material that is slow to harden but allows movements within the mortar joints while maintaining its structural stability. Any movement experienced is taken up by minute adjustments within the flexible mortar beds over many courses of masonry units and the hairline cracks that may occur are subsequently resealed by the so-called 'autogenous healing'. Further to this are its greater environmental advantages of relatively low carbon dioxide emissions during manufacture and the adsorption of carbon dioxide during carbonation [1], [2].

However, lime mortar is associated with exaggeratedly long setting and hardening periods, low internal cohesion, relatively low mechanical strengths and a high water absorption capacity through capillarity among others [3]. These, coupled with

absence of rigorous studies about its characteristics and properties resulted in its relative disuse, thereby paving way for overwhelming acceptance of cement based mortars at about the second half of the 19th century [4], [5]. In other words, Cement-based mortars displaced lime-based mortars because of the former's faster setting, higher mechanical strength and advanced industrial development.

The current trend in lime based composite is to integrate individual beneficial features of lime and cement by designing lime based blended mortars with varying proportions of cement as an addition in each case. The resulting composite mortar would be improved in its physical, micro-structural, mechanical and thermal performances as it would be characterized by faster 'setting and hardening' than lime, and better flexibility and plasticity than cement among others [6]. Similarly, recent advancements in Slag utilisation, an industrial by-product from iron ore extraction [7], as an alternative binding material in concrete production prompts interests for its possible blend with lime for improved lime mortar performance.

The underlying purpose of these efforts is to facilitate protection of the environment and conservation of energy resources, while improving mortar performances. This will also facilitate advent of a sizable market for renewed interests in the use of lime as a building material [9], [14]. In this case, the focus is on the performance of lime based mortars (lime composite) in which a portion of the lime is substituted by cement or slag for modern construction works.

2. LIME-CEMENT COMPOSITE FUNDAMENTALS: PREVIOUS AND CURRENT TRENDS

Strength developments in lime (particularly, Natural Hydraulic Lime in this context) is due to the hydration of several hydraulic compounds that form hydrated calcium silicates (commonly C-S-H phases) as the main compounds. Three phases of hardening involving tri-calcium silicates (C_3S), di-calcium silicates (C_2S) and carbonation process have been established as a function of the chemical composition. While C_3S (which could be practically

finished because of its presence in small amount) contributes to the strength at early ages, C_2S gives its strength at long term as the major part of the contribution occurs from 28 days onwards, with maxima values at long-term ages. Lime carbonation is a very slow process (that can take many years in their total carbonation) and its strength contribution is lower than the hydraulic components [8], [9]. Similarly, in cement-based mortars, the setting is a consequence among others, of the hydration of the calcium silicates, which starts quickly owing to the hydration of the C_3S and continues more slowly because of the hydration of the C_2S . The hydration of both compounds gives strength to the mortar. The carbonation process of cementitious materials also takes place slowly. This is from reactions of the basic compounds of hydrated cement (essentially $Ca(OH)_2$ and CSH) with carbonic acid [9].

Addition of cement to the lime mortar mix has a significant effect on its pore distribution as porosity, pore size and vapour diffusion coefficient are progressively reduced with increase in cement content. This also correspondingly increases the mortar strength [5]. Also, during individual drying process, cement and lime shrink, and in particular, cement tends to crack. With mixture of lime and cement as a mortar, a relatively weak mortar is produced (depending on the mix proportions) and any cracking occurs as hair cracks which are distributed throughout the joint. Excessively strong mortar with a high cement content however, tends to concentrate the effects of any movement into fewer but relatively wider cracks. These which may extend through both masonry units and mortar, are unsightly and may admit water [10].

However, effect of cement on porosity and pore size of lime mortars is crucial since changes in texture can substantially modify key properties of the mortars particularly, its breathability [11]. In conservation works especially, cement is considered chemically incompatible with lime based mortars as it has low permeability, responsible for the introduction of soluble salts and characterised with a high modulus of elasticity that is unfit for accommodation of masonry deformations. It is also established that Portland cement reacts with carbonic acid to form alkali carbonate or bicarbonate salts which are undesirable. However if Portland cement is used in a small amount, this will remain a minor problem as previous works show that an increase in cement content increases the amount of soluble salts (even though not in a proportional manner) [5], [11].

Several studies have investigated some aspects of lime–cement mortars. Viscosity of a cement–lime paste is observed to be more heavily influenced by the morphology of the lime than by its chemical composition [12]. Using fractal geometry and capillary sorption (as a relevant hygrometric property), microstructural characteristics (such as porosity, morphology of the pores, pore size distribution and surface fractal dimension) of blended pastes of lime and cement reveals an increment of complexity of the microstructure (i.e. more complex pore size distribution and amorphous morphology) with increase in cement percentages, due to the gel nature of the hydrated calcium silicates. The capillary water absorption is however characterised with higher capillary coefficients values for the pastes with higher amounts of lime as shown in figure 1 [6].

Microstructural properties of cement and lime binders are also modified by carbonation as the porosity and surface fractal dimensions decrease. In this case, carbonation is observed to be a

function of the binder composition but independent of the water/binder (w/b) ratio [13].

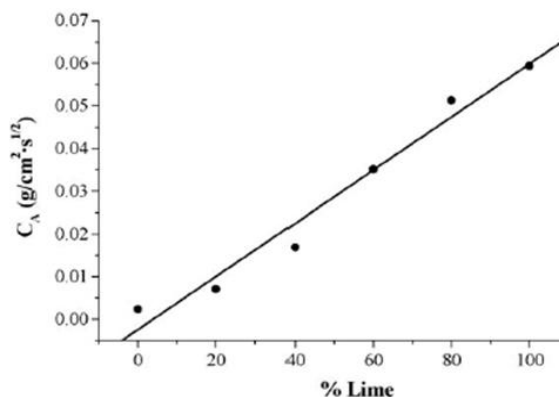


Fig. 1. Capillary coefficient (C_A) vs. percentage of lime in the pastes.

Blended mortar with a high percentage of lime presents a large plastic zone, which could be useful in its service-life as a result of its ability to absorb strains caused by wall movements as graphically demonstrated in figure 2 [9]. Conversely, evaluations of the Young's moduli of compressive and flexural strengths at the 365th curing day (Figures 3a & 3b) [9] indicate modulus increase with increase in the percentage of cement in the binder and with increase in the binder/aggregate (B/Ag) ratio in each case. This which translates to progressive rigidity could put the material under strain, giving rise to cracks, and causing the breakage of the material during its service life.

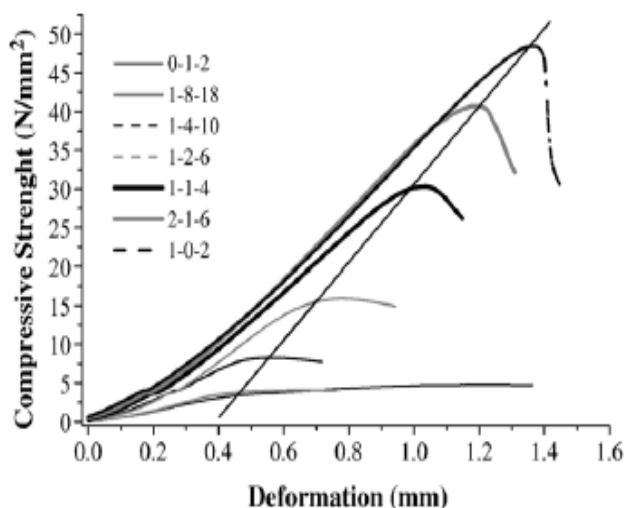


Fig. 2. Compressive strength (N/mm^2) vs. deformation (mm). (Note: Stated Mix ratios correspondingly indicate: Cement/lime/aggregate ratios (by volume))

It is necessary however to have a high lime substitution percentage to influence the microstructure of cement-lime blended mortar, except in the case of a lime containing magnesium hydroxide or calcic lime featuring sizeable specific surface area [14], among others.

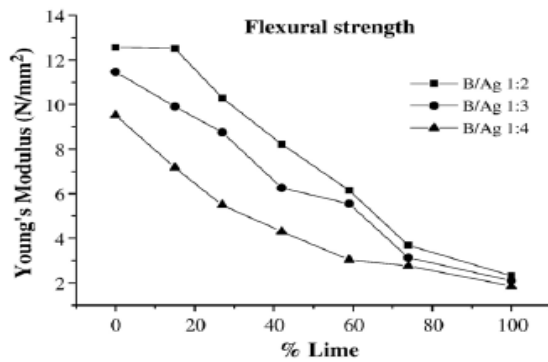


Fig. 3a. Young's modulus (N/mm²) at 365 days of flexural strength

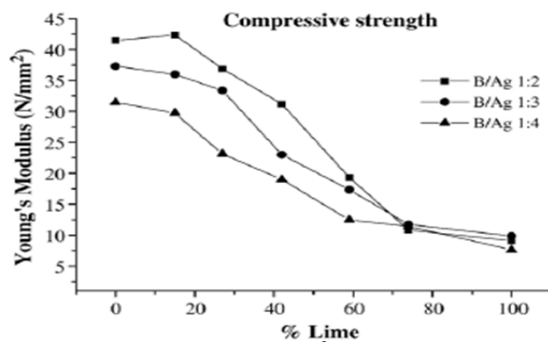


Fig. 3b. Young's modulus (N/mm²) at 365 days of compressive strength.

It is noteworthy to state here that many of the studies were directed at physico-chemical characteristics of the composite materials aimed at comparative behavioural studies between new formulations and specific old historic mortar samples initially characterised by mineralogical and chemical analyses using FT-IR Spectrometry, X-Ray Diffractometry, SEM-EDAX analyses, etc. [15], [16]. Such efforts were limited at conservation/restoration of old historic buildings. In some other cases, attention was on replacing minimal percentages of cement by lime to evolve cement-based mortar with microstructural improvements [14].

As a consequence, current research trends focus on evolving sustainable performance synergies between lime and cement by maximising the advantageous features of each of the materials as highlighted, at the expense of their identified drawbacks. In effect, this has a potential of evolving blended lime/cement mortars for improved mortar performances in new constructions with attendant reduction on environmental impacts from construction industry.

3. LIME-SLAG COMPOSITE FUNDAMENTALS: PREVIOUS AND CURRENT TRENDS

Ground Granulated Blast Furnace Slag (Slag) is a granular glassy amorphous waste material formed as a by-product from production of steel and iron.

It is introduced as a new eco- friendly alternative binding material in response to the current ecological-economical,

climate change related challenges [19]. It belongs to the quaternary system, CaO-MgO-Al₂O₃-SiO₂ which varies significantly, depending on the iron ore. It is essentially of silicates and aluminosilicates of calcium and other oxides with main inorganic constituents such as silica (30–35%), calcium oxide (28–35%), magnesium oxide (1–6%), and Al₂O₃/Fe₂O₃ (18–25%) [17]. Anhydrous calcium silicates and aluminates of the slag are compounds potentially reactive with water, and consequently, with the wet environment [18]. It has been widely used as a successful replacement material for Portland cement, thereby improving some properties, thus, bringing environmental and economic benefits such as low heat of hydration, long term strength, resistance to acid, better durability and general cost saving measure to the cement industries [19], [20], [21]. It has also been used as a supplementary cementing material for production of blended cement and slag cement [22].

Several investigations to maximise integration of slag for improved building materials including its hydration process, mechanisms and kinetics, particularly, its blend with Portland cements have been extensively explored by various authors [17],[23]. However, there is research paucity on the influence of slag on lime performance with regard to lime based mortars. Nevertheless, some previous studies are highlighted. Investigations into specific surface areas and pore structure on autoclaved slag-lime and slag-quartz-lime pastes were carried out by measuring their water and nitrogen adsorption isotherms at Autoclaving temperatures of 181 and 213°C respectively [24]. While the specific surface areas measured by water were appreciably higher than the nitrogen surface areas, the total pore volumes measured by water were found to be smaller (as reflected in Table I) [24]. This was attributed to a probable interaction between the polar water molecule and the ionic surface, which takes place in a pore structure with narrower entrance way than inside pore size. This interaction gives a possibility of interference with the further adsorption, blocking the entrances to further capillary condensation of water vapour, an outcome which requires further investigations and net implications.

Also, in determining physical and engineering properties, through morphological and microstructural characteristics of hydrothermally treated hardened pastes of slag-lime alone and in the presence of silica sand (i.e. mortar), both hydrogarnet crystals and the C-S-H (calcium-silicates hydrates) phase were displayed in slag-lime alone. However, the hydration of slag-lime-sand mixture (an optimum composition) was associated with formation of ill-crystallized tobermorite and crystalline 11A tobermorite as the main products [25]. Thus, the change in the microstructure and the physical state of the formed hydration products was established to be responsible for the strength changes in the hydrothermally treated specimens which is dependent of autoclaving time as shown in figure 4 [5].

Table 1: Some Surface Characteristics of Autoclaved Specimens

Auto-claving Time (hrs)	Degree of hydration	From Nitrogen Adsorption					From Water Vapour Adsorption				
		S_{BET} (m ² /g)	S_t (m ² /g)	V_p (ml/g)	S^{cor} (m ² /g)	V^{cor} (ml/g)	S_{BET} (m ² /g)	S_t (m ² /g)	V_p (ml/g)	S^{cor} (m ² /g)	V^{cor} (ml/g)
Slag-lime pastes at 10 atm.											
0.5	26.7	10.9	10.8	0.0621	40.8	0.2325	31.9	30.8	0.0513	119.3	0.1922
2	30.2	15.7	15.3	0.0900	52.0	0.2981	38.1	38.7	0.0444	126.1	0.1470
6	44.8	14.0	13.8	0.0620	34.3	0.1384	33.5	33.7	0.0599	74.7	0.1323
12	64.5	16.6	16.4	0.0771	25.7	0.1196	36.5	36.3	0.0498	56.6	0.0772
24	75.6	17.4	17.4	0.0858	23.0	0.1133	34.4	35.4	0.0378	45.4	0.0500
Slag-quartz-lime pastes at 10 atm.											
0.5	19.8	14.0	14.2	0.0714	70.9	0.3615	36.9	36.4	0.0401	186.8	0.2032
2	27.1	20.6	20.5	0.1443	76.1	0.5327	41.4	41.1	0.0448	152.9	0.1654
6	46.5	27.3	27.3	0.1474	58.6	0.3171	57.5	58.0	0.0980	123.6	0.2108
12	65.3	29.5	29.4	0.1633	45.2	0.2500	74.5	72.8	0.1247	114.0	0.1908
24	72.3	28.8	27.9	0.1474	39.9	0.2040	67.4	63.9	0.0791	93.3	0.1094

(Note: S_{BET} : BET surface area (calculated on ignited weight bases); S_t : specific surface area; V_p : total pore volumes)

Development of bricks from a slag-lime mixture (with 15% of lime and 4% of gypsum) and sand using bricks of size 19x9x9 cm shows a promising possibility [26]. Bricks made in a hydraulic machine at a pressure of 50kg/cm², cured at 95% humidity and 27±1°C temperature over a period of 28 days resulted into bricks of wet compressive strength (80-150 kg/cm² range), bulk density and water absorption values comparable with that of conventional bricks. Overall manufacturing process is simple and devoid of any firing or autoclaving, specialized plant or machinery, with much less energy consumption, compared with conventional burnt clay bricks and calcium silicate bricks.

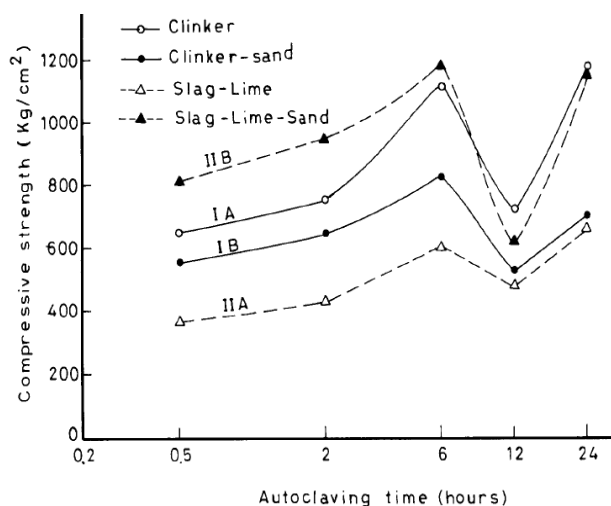


Fig. 4. Compressive strength as a function of autoclaving time

Influence of particle size on the early hydration of slag particle activated by Ca(OH)₂ solution is also found to be essentially attributed to the chemical compositions as higher Ca/Si ratio of slag is crucial for the reactivity of slag particles at least in the

early stage of hydration. However, the overall hydration degree of slag consisting of fine particles develops faster than that of coarse slag due to its large specific surface area [27], as illustrated in figure 5 [26].

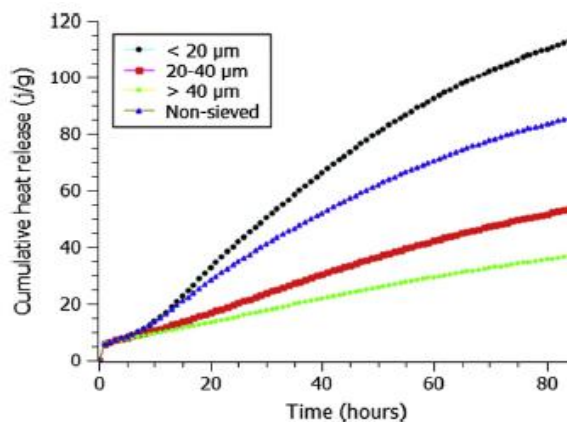


Figure 5: Hydration Heat evolution rate of slag with varying particle sizes.

The kinetics of the reaction between slag and calcium hydroxide (CH) were also investigated as CH consumptions for three different mass ratios of slag and CH over a temperature range of 15° to 50°C and 0 to 32 days hydration period were monitored through Thermo-gravimetric analyses [28]. The reaction rate constant (k) is found to be a function of the slag/CH ratio and increases as the content of CH increases (see Table II) [28]. The activation energy for slag hydration in the presence of Portland cement also agrees well with what obtains for slag/CH in the context.

Table 2: Rate Constants and Activation Energies for Various Slag/CH Ratios

Slag/CH	T (°C)	k	E_m (kJ/mol)	r^2
80/20	15	0.2006	14.5	0.93
	25	0.2926		
	35	0.3295		
	50	0.3979		
90/10	15	0.2953	17.9	0.94
	25	0.4306		
	35	0.5680		
	50	0.6633		
95/5	15	0.8048	22.6	0.95
	25	1.0105		
	35	1.6983		
	50	2.0974		

(Note: k : reaction rate constant; T : Absolute temperature (°C); E : Knudsen activation energies (kJ/mol) for respective slag/CH ratios; r : correlation coefficients)

Despite these advancements, there is a wide research gap on the influence of slag on lime performance with regard to lime based mortars. The current research attempts are therefore focused on evaluation of the performance effects of lime as a binding material when inter-mixed with slag in varying compositions with a view to recycling this industrial by-product for improved lime performance.

Arising from the outcomes of some of the related previous studies, enhanced individual integration of additions like cement and particularly slag with lime, is expected to facilitate improved physical, micro-structural, mechanical and thermal performances of emerging lime based composite mortars for overall satisfactory mortar performances in new constructions.

4. FINAL COMMENTS

This paper presents a review of related previous and current studies to arrive at a satisfactory lime based mortar performance synergy, involving lime, a major constituent on one hand, and additions like cement and particularly slag on the other. It signifies the current trend in advancement of lime based composites development of mixtures that would meet satisfactory levels of performance relative to conventional masonry mortars, but which use cement or slag (separately) as a partial replacement for lime. The research outcome is expected to have positive impacts on performance properties of lime mortars as well as sustainability of the environment.

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