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In Honour of Professor R.N.Swamy*

**ALKALI ACTIVATED LIME AN ENVIRONMENTAL FRIENDLY BINDER
MATERIAL FOR BUILDING INDUSTRY**

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ABSTRACT

Since Traditional Portland cement manufacturing requires high energy consumption along the production of CaO and CO₂ due to the decomposition of CaCO₃, a “Green Chemistry” as well as the production of low energy binder materials are urgently required.

Slaked lime was worldwide used as an inorganic binder material. However, the paste obtained is mainly CaCO₃ which is characterized for having low mechanical strength, high permeability to water and low resistance to the freeze-thaw cycles.

This paper reports how by using “Green Technology” a stronger and environmental friendly binder was obtained for building industry applications. Hence, the mechanical behavior and microstructure of an alkali activated lime is shown. Sodium carbonate was used as an alkaline activator, while metakaolin was used as a pozzolan. It was observed that the compressive strength increased up to 400% more than slaked lime and by XRD several crystalline phases were detected such as: Gehlenite, Portlandite, calcite, and calcium aluminum oxide carbonate hydrate.

Keywords: lime, alkali-activated lime, compressive strength, microstructure.

I. INTRODUCTION

Mortars of lime and lime-pozzolans have been used as a binder material around the world since ancient times from Egyptian, Roman, Mayan civilizations up to date [1]. Building limes can be classified into two groups: 1) Air lime, it contains calcium oxide and calcium hydroxide and 2) Hydraulic lime, which is mainly composed for a mixture of calcium hydroxide, calcium aluminates and calcium silicates. The setting process in the air lime takes place for the reaction of calcium hydroxide ($\text{Ca}(\text{OH})_2$) with carbon dioxide (CO_2) producing calcium carbonate (CaCO_3). Therefore, the carbonation process should be divided into a carbon dioxide diffusion process followed by a chemical reaction in which calcium carbonate crystals are formed [2]. These calcium carbonate crystals are the main chemical product and they provide to lime binders its physical, mechanical and chemical properties. By this reason a low mechanical strength, high porosity and low durability to the freeze-thaw cycles, long setting times, etc. are characteristics of these air lime mortars. In hydraulic-lime binders a more complex chemical reaction takes place: silicates and aluminates (SiO_2 and Al_2O_3 or $\text{SiO}_2 + \text{Al}_2\text{O}_3$) combine with calcium hydroxide and water forming the corresponding calcium silicate hydrates, calcium aluminates compounds or calcium aluminum silicates hydrates in this case a stronger and more stable binder is developed [3]. Other authors have been working with pozzolan-lime mixtures to improve physical, mechanical and chemical properties of mortars [4,5,6,7,8]. The reactivity of these mortars as well as final properties depend on its particle size, surface area and on its mineralogical constituents [4].

On the other hand, alkali activated lime binders, this new “old” technology is becoming popular in recent time due to the mechanical properties obtained at low cost, low greenhouse gas emissions. However, the developments of alkali-activated lime dates back to Egyptian civilization through Imhotep’s formula to make limestone blocks for pyramids construction [9]. Imhotep had two different chemical formulas: a very simple one for the casting of limestone core blocks and another one to produce high quality stones for exterior layer. This formula includes three main materials: 1) Soft limestone and lime, 2) Natron salt (sodium carbonate), and 3) clay. Almost all clay materials are aluminosilicates and they can chemically react with metal oxides and hydroxides forming the corresponding chemical compounds.

In the present work, lime (calcium hydroxide) was alkaline activated by sodium carbonate and highly reactive metakaolin was used as silicon and aluminum source for the inorganic polymerization. As a result a three-dimensional inorganic polymer formation was developed into the lime matrix and excellent compressive strength behavior was obtained at room temperature. As an added bonus, the process is environmentally friendly.

II. EXPERIMENTAL.

II.1 Raw materials and mixtures design.

A commercial metakaolin from Engelgard Corporation (METAMAX) was used as a source of silicon and aluminum for the inorganic polymerization.

Calcium hydroxide (lime) and Sodium Carbonate (alkaline activator) were analytical commercial grade with 95% of purity.

De-ionized water was used to obtain these pastes.

All mixes were manufactured without aggregates and using a constant water/binder ratio fixed at 0.8 to avoid compressive strength variations.

A lime-water paste was used as a reference and four alkaline activated pastes were elaborated as shown:

- 1) Alkali-activated paste 1: 20% of Na_2CO_3 – 100% of $\text{Ca}(\text{OH})_2$ – 20% $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (weight percentage).
- 2) Alkali-activated paste 2: 20% of Na_2CO_3 – 100% of $\text{Ca}(\text{OH})_2$ – 10% $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
- 3) Alkali activated paste 3: 10% of Na_2CO_3 – 100% of $\text{Ca}(\text{OH})_2$ – 10% $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
- 4) Alkali activated paste 4: 20% of Na_2CO_3 – 100% of $\text{Ca}(\text{OH})_2$ – 5% $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
And 100% $\text{Ca}(\text{OH})_2$ as standard lime paste.

II.2 Mechanical characterization

Compressive strength of hydraulic cement mortars was performed using the test method ASTM C109 so that 2-inch (50 mm) cube specimens were used [9]. In this way, a series of 30 samples for compressive strength were prepared for different aging times (3, 7, 14, 28 and 45 days).

II.3 Morphology and microstructure characterization

A PHILIPS environmental scanning electron microscope model XL 30 was used to observe the morphology of the hydration products as well as the microstructure of the bulk material.

An X-ray diffractometer, RIGAKU model DMAX 2100, was used to identify the phases present in the lime and alkali activated lime. Diffraction patterns were collected using Cu Kalfa (1.5406 Å) radiation with Ni filter. The scans were conducted with the Rigaku goniometer over a 2 - 80 degrees 2-theta range with 0.02 degrees as sampling interval and 4.8 as scan speed (deg/min).

III. RESULTS AND DISCUSSION.

III.1 Compressive strength and microstructure of test results of four different alkali-activated lime series.

Compressive strength of standard lime (used as reference) is shown in Figure 1. It can be appreciated the low compressive strength developed (nearly to 0.17 MPa). This poor compressive strength is directly related to its microstructure. Figure 2, shows a “weak” lime paste microstructure with high porosity. This kind of microstructure is generally present in all lime mortars due to the setting process (carbonatation process) already mentioned it.

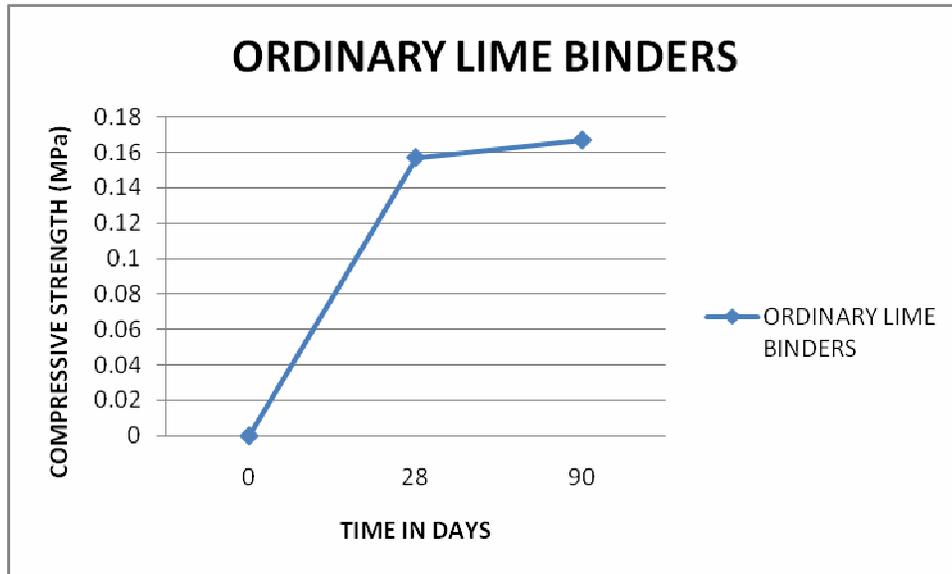


Figure 1 Compressive strength of lime paste (Reference material).

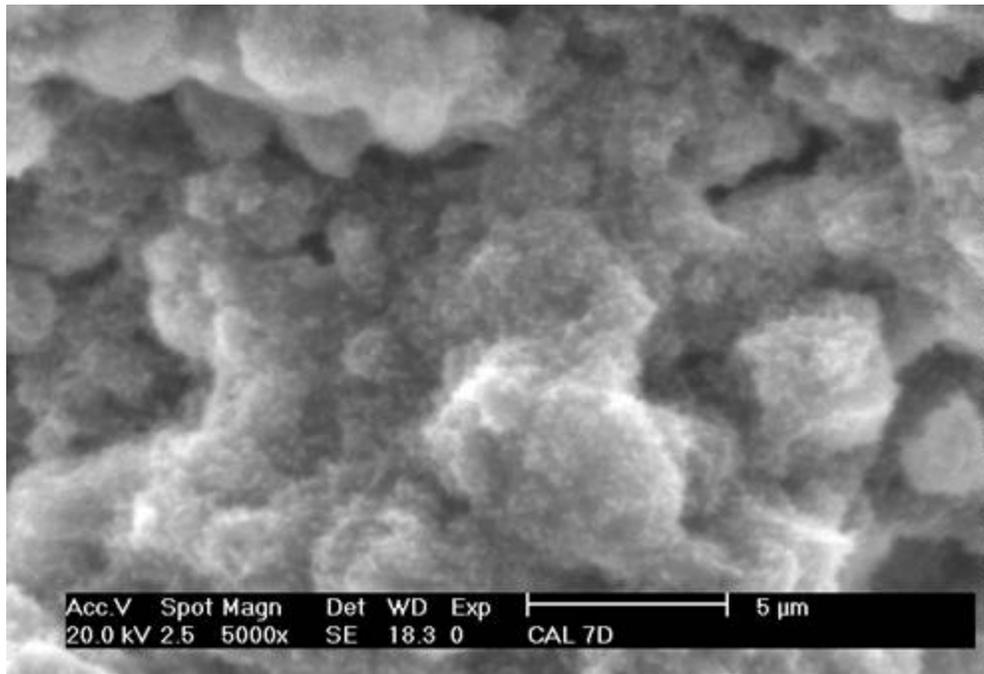


Figure 2 ESEM microstructure of calcium hydroxide – water paste.

Additionally, to the low compressive strength of lime mortars durability problems are common in these building materials. Matrix with high porosity is affected by different agents such as: water, acids, sulphate ions and biological materials. Figure 3 shows the fractures on the lime mortar cube caused by the expansive sulphate-ion.

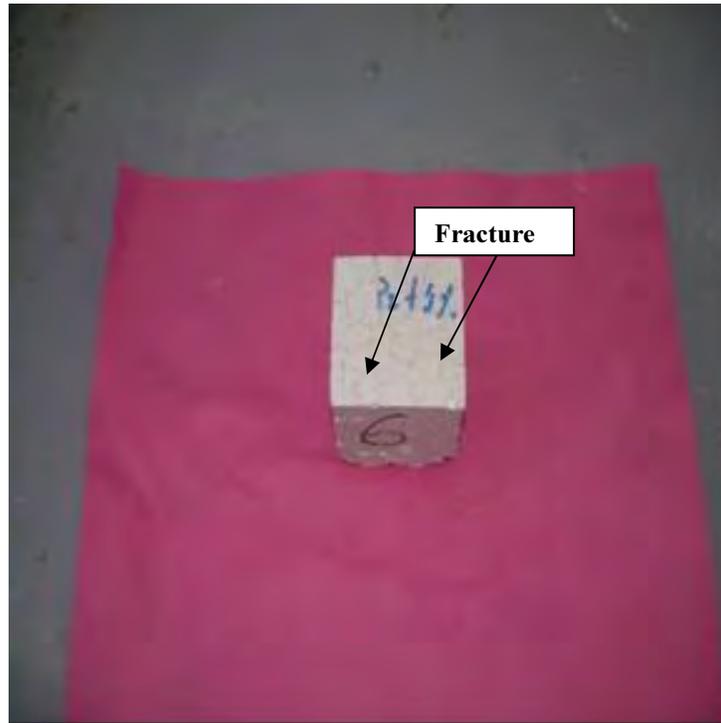


Figure 3 Lime mortar damaged by the expansive sulphate-ion.

Figure 4, shows the compressive strength behavior of Alkali-activated limes (pastes 1, 2, 3 and 4). Paste 1 had the best behavior of all pastes (alkali activated limes and standard lime) due to its high alkali and meta-kaolin content. This material showed the highest reactivity due to a strong ion-interchange between sodium carbonate, calcium hydroxide, metakaolin and water. This can be confirmed by the XRD results (Figures 5 and 6). Different crystalline phases were detected such as: Gehlenite, Calcium aluminum oxide oxalate hydroxide hydrate, calcite, portlandite, and free aluminum silicate. In all these curves, compressive strength increases with time due to the setting process involved it and in all cases, the strength is higher than compressive strength obtained it by standard lime.

For the set of alkali-activated lime pastes (paste 1, 2, 3, 4), the compressive strength behavior is also similar to ordinary portland cement pastes. In OPC pastes, the calcium silicate phases (beta-di-calcium silicate and tricalcium silicate) are stronger with time and reached almost its maximum resistance at 90 days.

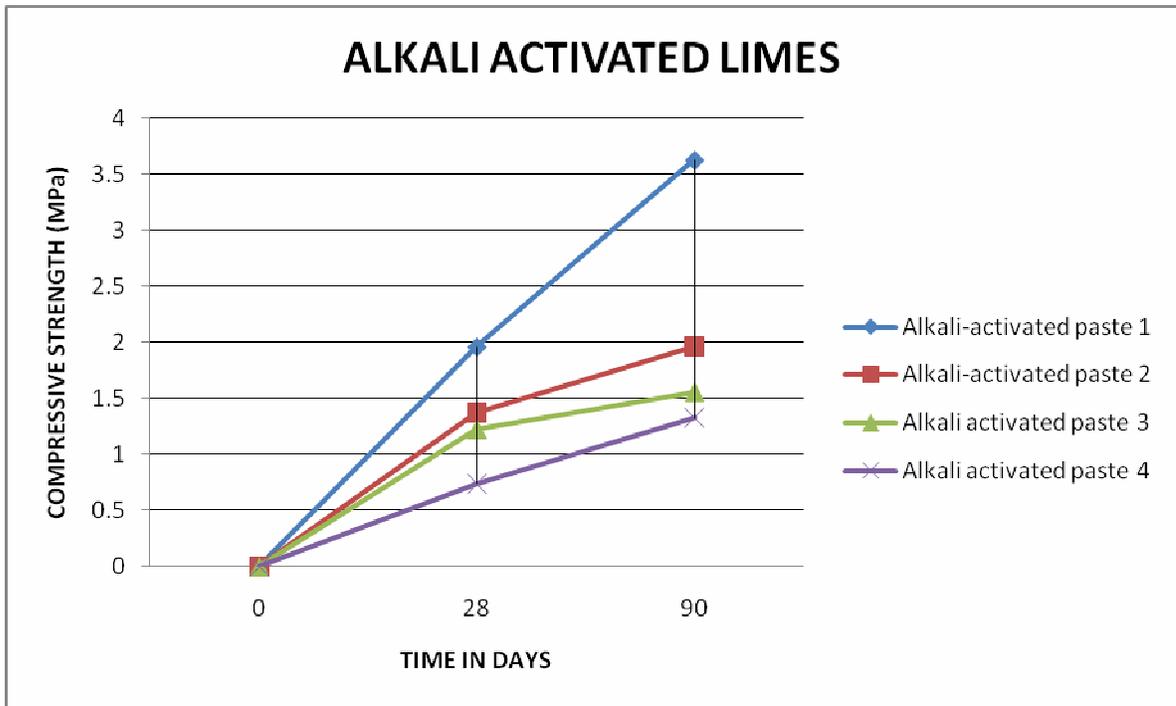


Figure 4 Alkali-activated limes.

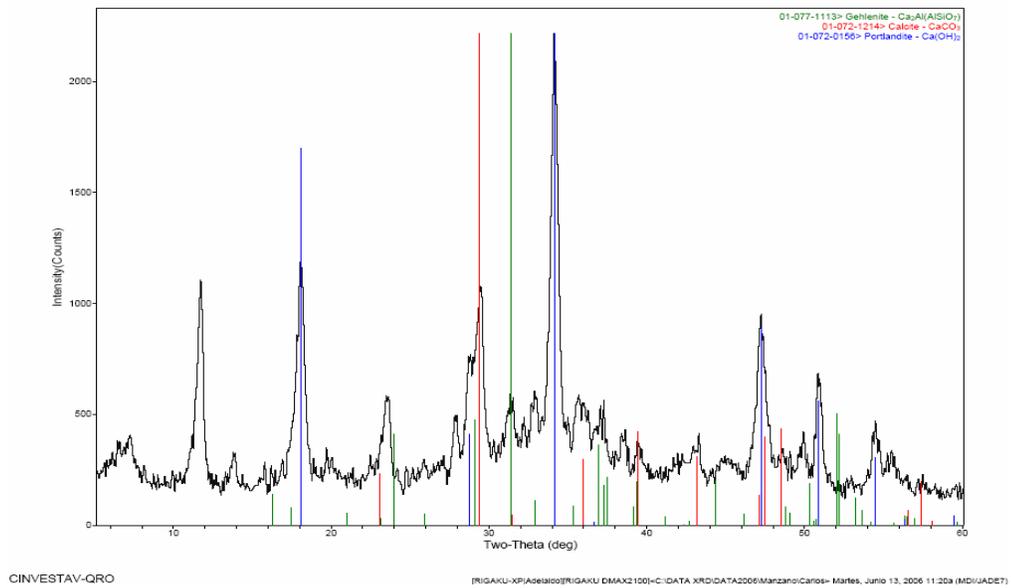


Figure 5 XRD pattern (part 1) of alkali activated lime with 20% of Na_2CO_3 – 100% of $\text{Ca}(\text{OH})_2$ – 20% $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (weight percentage).

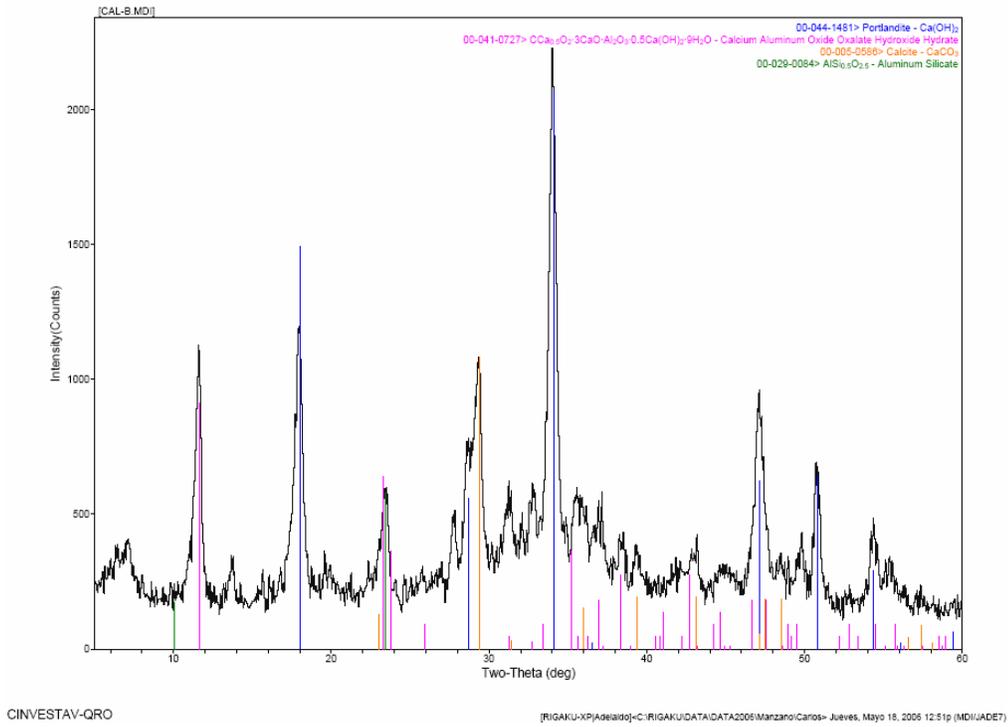


Figure 6 XRD pattern (part 2) of alkali activated lime with 20% of Na_2CO_3 – 100% of $Ca(OH)_2$ – 20% $Al_2O_3 \cdot 2SiO_2$ (weight percentage).

In Figure 7 shows a dense and strong microstructure for this alkali activated lime mortars, a lowest porosity is clearly appreciated when is compared with standard lime mortars. This microphotograph additionally shows a polymer inorganic network mixed into the lime matrix.

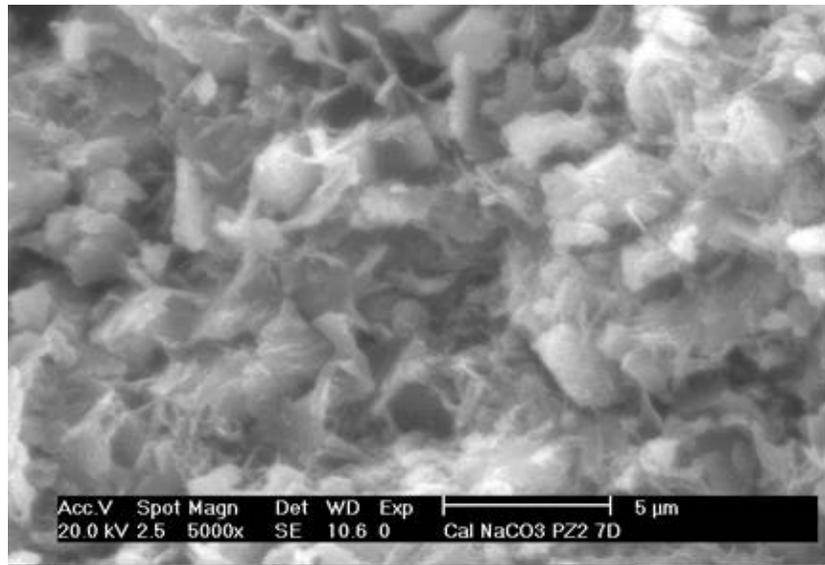


Figure 7 ESEM Microstructure of an Alkali-Activated Lime.

Alkali-activated lime may have applications as a Mortar for joining bricks and concrete products, Ceramic building products such as: Alkali-activated lime bricks, fiber reinforced panels (non-structural) Plasters for walls, etc.

IV CONCLUSION

The addition of sodium carbonate and metakaolin to calcium hydroxide develop additional crystalline phases, such as: Gehlenite and calcium aluminum oxide oxalate hydroxide hydrate, due to these phases the mechanical strength increase by the formation of inorganic polymers into the matrix of portlandite and calcite.

The Compressive strength of the lime and alkali activated lime changes dramatically from 0.17 MPa to 3.6 MPa. This Alkali activated lime can be used for novel materials applications at low cost and environmental friendly with low CO₂ emissions.

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