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Electrokinetic and thermodynamic characterization of lime-water interface: Physical and rheological properties of lime mortar

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HIGHLIGHTS

- The calcination process of limestone modifies the surface free energy of the lime.
- Quicklime is more hydrophilic when produced in a traditional kiln between 850–900 °C.
- ξ potential of traditional quicklime were much larger than industrial quicklime.
- The traditional process generates products with more plasticity.

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ABSTRACT

The surface properties of the portlandite are very important in the behavior of the suspensions of lime used as binders, plasters, mortars and paint, for use in the architecture heritage conservation. These rheological properties depend heavily on surface thermodynamic properties, surface tension-surface free energy and load the lime present in aqueous medium. It selected two types of quicklime, originating from the same rock but made in two types of kilns: traditional and industrial Kiln. It has determined values of the surface free energy of the lime in the form of CaO and $Ca(OH)_2$ as well as the rock used in its preparation. In addition, it conducted an electrokinetic study to determine electrophoretic mobility in a water/lime system. It analyzed various types of oxides after laboratory slaking and periods during which the portlandite remained in water. This study revealed that quicklime is monopolar and has a hydrophilic nature. Tradition quicklime, γ^{Total} values decrease as temperature increases the calcination of limestone. This has greater hydrophilicity than that of industrial quicklime. Moreover, traditional lime, introduces more charges than that fabricated by industrial processes, with larger values of ξ Potential. ξ Potential data confirm the optimal plasticity properties of the traditional lime, and that this quality is maintained.

1. Introduction

Lime has been used since ancient times as a material to improve cohesion used in construction materials [1]. The recoveries of traditional construction activities currently constitute an area of interest for product design, regarding its application in restoration [2]. Traditional and semi-industrialized products based on lime constitute a proposal that has been growing in recent years.

Lime is a binder obtained through a group of processes that are encompassed within the term *lime cycle*. This cycle includes a first stage of calcination of limestone between 850 and 900 °C to obtain quicklime (CaO). The dissociation temperature of $CaCO_3$ occurs at 898 °C when pCO_2 is 1 atm. This temperature is reduced by decreasing the pCO_2, and increases with its increase [3]. The end result is collapse of the crystal structure of $CaCO_3$ [4].

In the calcination process, the type of kiln, burning time, size of carbonate particles, density, and limestone purity are important in their properties [5–8]. Quicklime from traditional manufacturing (longer calcination and variable temperature inside kiln) has a slow hydration and lower slaking temperature (850–900 °C) than the industrial quicklime process (faster calcination in the kiln) [9] Lime formed during a relatively short period of calcination has a more porous structure and is highly reactive [3]. It appears

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that the thermal decomposition and chemical reaction control the process, influenced by the speed of calcination [10].

The process of slaking has been extensively studied in recent years [3,11–17]. The type of slaking has a significant impact on the resulting product. A supply of excess water during hydration favors the dispersion of particles, reducing their tendency to agglomerate [18]. The primary and aggregated crystals generated during and just after slaking, control the evolution of the portlandite microstructure [11,18], and improve its rheological properties while it remains in suspension in water. These crystals constitute the largest particle size because of agglomeration orientation, characteristics that most strongly affect the loss of plasticity [2,17].

The zeta (ξ) potential is one of the fundamental parameters controlling the interaction of the particles in suspension. Colloidal particles dispersed in a solution are electrically charged because of their ionic characteristics and bipolarity. According to extended DLVO (Derjaguin-Landau-Verwey-Overbeek) theory [19,20] three types of interfacial interactions should be considered, i.e., Lifshitz-van der Waals (LW), electrostatic (EL), and acid-base (AB). Their contributions depend on the nature of the interfaces involved (i.e., the ξ potential and surface free energy components).

The rheological behavior of putty lime depends on the aggregation or dispersion of portlandite nanoparticles in aqueous suspension [11] and is a function of many factors that can be classified into four groups. These are the distribution and sizes of particles, the shape and surface area of the particles, concentration and ξ potential of the dispersion [11,12,21,22].

In the present paper, the properties of surface free energy and ξ potential are determined. The objective is to understand how they affect production technology in the surface properties of the lime and the effect on them the time that this material remains in water (aging of lime putty). In terms of these parameters, it can explain better the properties of slaking lime and its rheological behavior. These properties are of interest in the advancement of knowledge of this high-value construction material.

It used for this study lime from the *Moron de la Frontera* City (Seville, Spain), which currently has two forms of quicklime production, traditional and industrial. This unique case allows greater control of variables involved in the production process such as the nature of the limestone, as reflected in previous works [6], kiln type and its technological implications; such as the effect of calcination temperature and heating rate [3,8,18,23,24].

The exceptional production conditions of such lime has made it an object of study for application in restoration works of Cultural Heritage [11,12,25–27] demonstrating its quality as a building material. In November 2011, declared Intangible Heritage of Humanity, in the category of Best Practices by UNESCO [28].

2. Material and experimental methods

2.1. Production process lime and limestone source

Traditional Kilns lime of the arabic type, to produce lime (Fig. 1) fed by combustible vegetation of olive and pine. These kilns operate with a volume of stone around 70 tons; with calcination times from 10 to 20 days (depending on environmental conditions and kiln size), with continuous feed every 15 min and a substantial daily consumption of wood. Temperatures reached inside the kiln vary from 1100 °C, at the heat source, to 750 °C, in outer areas. Smoke color, from black to white, and change in color of the stone, from reddish orange to yellow-gold observed in the upper recesses of the kiln (*caños o troneras*), facilitate the determination of the exact burning of the stone [28].

The kiln assembly is critical to the quality of the lime produced, because it is designed so that the temperature to which the stone is subjected in its interior is as homogeneous as possible. The assembly of vaults of the kiln and its structure (*Ahornado* process) is done via the method of *dry stone*, built with *armaderas* (larger stones) in a concentric arrangement. These stones are fit with other smaller stones called *matacanes* and, finally, the gaps are filled with other small stones called *ripios* [29]. This design allows that temperature inside the kiln to be as homogeneous as possible. Slaking lime is done by *spraying* (powder Lime) and traditional procedure by *fusion* (putty lime) with mechanical agitation in large amounts of oxide over 30 days. This initiates a slow increase in temperature, not exceeding 100 °C.

Fig. 1. Traditional lime kiln, Morón de la Frontera, Seville (Spain).

In industrial lime production used discontinuous vertical kilns fed with combustible natural gas, coke, fuel and oil. Limestone is subjected to temperatures between 900 and 1000 °C, over short periods of time, obtaining quicklime that is then sieved, crushed or ground and finally hydrated to obtain a very fine dry powder (powder lime).

Limestone used from the geological *Unit of the Sierra de Estepa* (External Areas of the Baetic Chain, Spain). They are constituted by micritic, oncolitic and oolitic limestone of age lower and mid-Jurassic [30].

The limestones, although having textural variations, have high purity (>90% CaO with <1% SiO_2) and very similar levels of major and trace elements. Generally, these correspond to very compact limestone with porosities 5–10%. From the standpoint of pore size distribution, two types can be distinguished. These are a variety with micropore sizes largely <2 mm and a more porous type with the presence of micropores and macropores [31].

3. Samples

It carried out a comparative study of three types of quicklime (CaO) (see Table 1). Two of these were obtained from the same limestone, but with different manufacturing technologies. These were traditional continuous vertical kilns (***TL***) (Fig. 2a), industrial continuous vertical kilns (***IL***) (Fig. 2b), and commercial lime, supplied by Panréac with analytical purity (ref: 211234.1211; lot: 0000534420 M = 56.08 g/mol; ***PL***).

Traditional Kilns are characterized by heterogeneous burning. Thus, for the *TL* lime it analyzed three varieties, located in different areas of the kiln with different calcination temperatures. These were TL (1) (1100 °C), TL (2) (900 °C) and TL (3) (850 °C). This was done to see if temperature changes affected the surface free energy properties and ξ potential of lime.

In the laboratory, it prepared lime putty from the quicklime (CaO) obtained by two calcination processes, traditional (SPL_{TL}) and industrial (SPL_{IL}). The slaking was done in distilled water in a lime/water ratio of 1:3, without stirring. The hydrates were also made from quicklime of analytical purity (SPL_{PL}).

Table 1
CaO Samples and corresponding $Ca(OH)_2$ obtained of hydrations at 0 and 6 months.

Samples	Burning temperatures	Corresponding Ca $(OH)_2$ (0-6 month)
TL(CaO) Traditional method. Francisco Gordillo's lime	**TL(1)** 1100 °C	$\mathbf{SPL}_{TL}(\mathbf{1})$
	TL(2) 900 °C	$\mathbf{SPL_{TL}(2)}$
	TL(3) 850 °C	$\mathbf{SPL_{TL}(3)}$
IL(CaO) Industrial method. Calcinor, Andalusian of Limes	1000 °C	$\mathbf{SPL_{IL}}$
PL(CaO) Analytical purity. PANREAC AppliChem	¿?	$\mathbf{SPL_{PL}}$