Archaeometry and Cultural Heritage: the Contribution of Mineralogy

Luis Ortega

Seminarios de la Sociedad Española de Mineralogía
09

XXXII Reunión de la Sociedad Española de Mineralogía

International Seminar on Archaeometry and Cultural Heritage: the contribution of Mineralogy

Bilbao, 27 de Junio 2012

Editores:
José Miguel Herrero
Marius Vendrell

SEM
Sociedad Española de Mineralogía
www.ehu.es/sem

Seminarios de la Sociedad Española de Mineralogía

Volumen 09

Archaeometry and Cultural Heritage: the Contribution of Mineralogy

Seminario celebrado en
Bilbao, 27 de Junio de 2012

Editores:
José Miguel Herrero
Marius Vendrell

Cover photo
French faience test pieces from the Le Bois d'Épense (Les Islettes, NE France) factory, early 19th century. Width of the clay balls 2-3 cm. *Photo M. Maggetti (pers. coll.).*

Seminarios de la Sociedad de Española
de Mineralogía

Museo Geominero del Instituto Geológico y
Minero de España
c/ Calle de Ríos Rosas, 23
28003 Madrid

http://www.ehu.es/sem
sem@ehu.es

Editores
José Miguel Herrero
Marius Vendrell

Diseño y maquetación
Soma Dixital, S.L.

Impresión
Lugami Artes Gráficas, S.L.

Depósito legal
CA-602-2004

ISSN
1698-5478

Impreso en España - Printed in Spain

2012

Binders in historical buildings: Traditional lime in conservation

/ Carlos Rodríguez-Navarro

Dpto. Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n, 18002 Granada

Abstract

Mankind has used many types of binders throughout history: from mud in vernacular earthen architecture to current high-performance cement. However, gypsum and lime have been by far the most common and important binders in historical buildings. Their use expands several millennia and is represented in the architectural feats of all kind of civilizations. Here, the history, technology and uses of gypsum- and lime-based binders are reviewed. We focus on the study of the different steps of the gypsum and lime cycles as a conceptual framework to underline past applications and performance of these binders, and their current use in architectural conservation. Special emphasis is paid to the technology and uses of lime as a versatile and compatible conservation material.

Resumen

La humanidad ha usado muchos tipos de ligantes a lo largo de la historia: desde el barro en la arquitectura vernácula de tierra a los actuales cementos de altas prestaciones. Sin embargo, el yeso y la cal han sido, con diferencia, los ligantes más comunes en edificaciones históricas. Su uso se extiende durante varios milenios y está presente en los hitos arquitectónicos de todo tipo de civilizaciones. Se revisan aquí la historia, tecnología y usos de los ligantes basados en el yeso y la cal. Nos centramos en el estudio de las diferentes etapas en los ciclos del yeso y la cal, como un entramado conceptual para destacar las aplicaciones y comportamientos de estos ligantes en el pasado y su actual uso en la restauración arquitectónica. Se hace un especial énfasis en la tecnología y los usos de la cal como un material de restauración versátil y compatible.

Key-words: *Binders, lime, portlandite, gypsum, calcite, mortars, plasters, historical buildings, carbonation, hydration, topotactic.*

1. Introduction

A binder is defined as a material which acts as a glue or cement when mixed with an aggregate (e.g., sand) and water to form a fresh plaster, render, mortar or concrete. Following setting and hardening, such composite materials play a structural and/or decorative role in a building *(Lea 1970)*. Since the advent of sedentism and building technology, which could be traced back to the Pre-Pottery Neolithic A in South-West Asia (e.g., Jordan river valley), ca. 11,700 to 10,500 years ago *(Finlayson et al. 2011)*, mankind has used many different binders. Mud (clay-rich earth) was among the first binders used *(Houben and Guillaud 1994)* as exemplified by the adobe walls of Jericho (Israel) dated to 8300 BC *(Allen and Tallon 2011)* or the earthen structures (rammed earth) in Çatalhöyük (Anatolia, Turkey) dated to 6000-7500 BC *(Mellaart 1967)*.

However, the use of this type of binder does not involve pyrotechnology (i.e., no heat treatment was required). As a result, earthen structures display a low strength and are prone to weathering and damage. With the advent of pyrotechnology ca. 12000 years ago *(Kingery et al. 1988)*, a new class of binders emerged with superior properties in terms of strength and durability, as well as versatility and applicability. Among them, gypsum and lime have played an outstanding role in building history from the Neolithic until nowadays.

Here, the history, technology and uses of gypsum and lime binders will be reviewed. Special emphasis will be paid to the case of lime, as this has been the binder most profusely and ubiquitously used by mankind. Furthermore, lime has recently emerged as the binder of choice for architectural conservation. Therefore, its current use in heritage conservation will also be outlined.

2. Gypsum binders

2.1. Gypsum as a building and decorative material

Gypsum-based mortars and plasters have been used since ancient times, especially to cover masonry, as decorations, or as a support for mural paintings *(Elsen 2006)*. Due to their setting upon addition of water, gypsum-based binders could be considered the first "hydraulic binder" used by mankind since ca. 9000 years before present *(Gartner 2009)*.

Gypsum was the most common binder in Ancient Egypt both for masonry and decorative purposes since Pharaonic times *(Lea 1970; Lucas and Harris 1962).* Lucas and Harris (1962) report the use of gypsum in several tombs and as mortar and plaster in the Giza pyramid. Other studies have confirmed its presence in mortars from the pyramids of Medium (2600 BC), Cheops (2500 BC) and Unas (2250 BC) *(Regourd et al. 1988)*.

Gypsum plasters were commonly used in the Middle East and in countries around the Mediterranean basin, especially during the Middle Ages (e.g., Islamic Architecture) (Elsen 2006). In the area around Paris, gypsum mortars were thoroughly used in gothic buildings such as the Cathedrals of Chartres and Bourgues *(Adams et al. 1992)*, which may explain why gypsum-based binders are known as *"Plaster of Paris"*. Despite its low strength and poor durability in humid environments, examples of gypsum mortar applications in northern Europe are numerous. For instance,

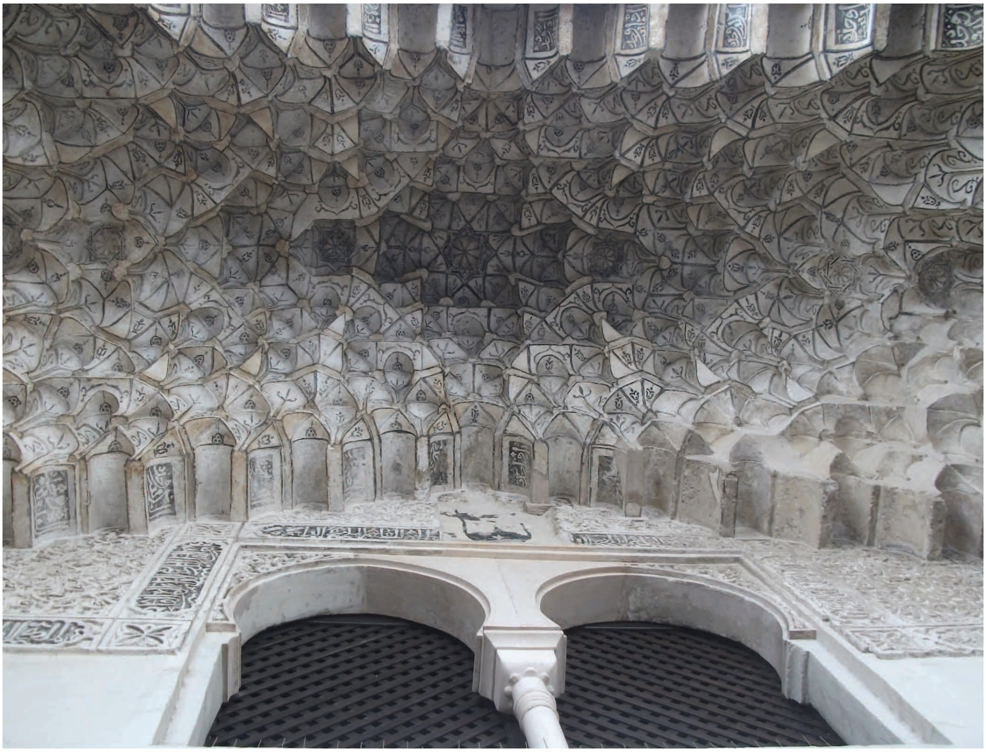

Fig. 1. Gypsum-based "mocárabes" in the Corral del Carbón, a XIV c. Islamic building in Granada (Spain).

Kawiak (1991) describes the use of gypsum mortars in a XII c. church in Wislica, Poland.

Up until nowadays gypsum has been applied either as mortar and plaster for surface finishing, or as cast and/or carved decorations *(Arredondo 1991 Luxán et al. 1995)*. A significant example of this latter application is the case of the *"mocárabes"* and decorated plasters *("yeserías")* from the Alhambra and other Islamic buildings in Granada (Spain) *(Fig. 1)*.

At the Alhambra (and by extension in most Medieval Islamic architecture) two main gypsum-types were used:

- "black gypsum" *(yeso negro)*, made of highly impure hemihydrate (50-60 wt %) containing significant amounts of ashes produced during calcination, and
- "white gypsum" *(yeso blanco)* a purer material made of > 66 wt % hemihydrate *(Rubio-Domene 2006)*.

Gypsum renderings were extensively applied as a base for mural painting. In all these cases the major component after setting was gypsum, although in some ancient mortars and plasters, anhydrite has been also found *(Regourd et al. 1988)* along with calcite *(Kawiak 1991)*. The presence of anhydrite poses the question about the possible origin of anhydrous calcium sulfate after dehydration of gypsum at relatively low T (< 30 °C) and RH (<< 70 %) *(Charola et al. 2008)*. Conversely, it could be argued that anhydrite crystals are unhydrated relicts of the original binder prepared following calcination at high T (> 350 °C) of gypsum mixed with calcite, what is known as *"Keene's cement"* or "Estrich Gips" *(Sayre 1976; Kawiak 1991)*.

A variation of plaster of Paris is the so-called *"scagliola"* which is a composite material prepared by mixing soft-burned gypsum (hemihydrate or bassanite, see section 2.2), glue and pigments with water. Such a composite material has been used as an imitation of marble, thereby its name *"stucco marble"*. To some authors, however, *scagliola* is a gypsum-based plaster made of purer and finer hemihydrate particles, which typically makes the set material whiter than normal gypsum plasters *(Rubio-Domene 2006)*. *Rubio-Domene (2006)* indicates that the so-

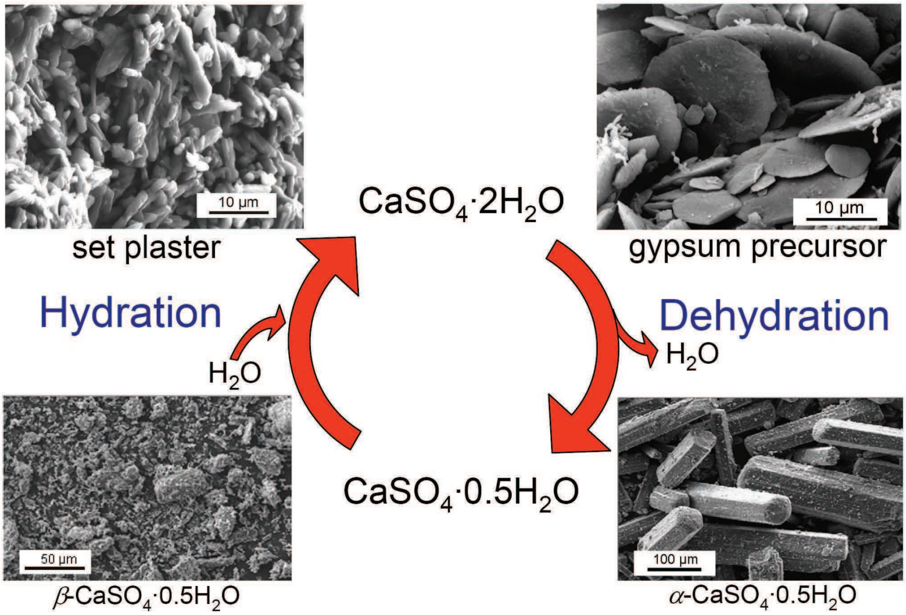

Fig. 2. The gypsum cycle. Scanning electron microscopy (SEM) images show examples of lens-shaped gypsum prior to dehydration, bassanite phases formed after dehydration (modified from Singh and Middendorf, 2007) and gypsum in a set plaster.

called *"stucco"* is made by mixing inert anhydrite with glue.

2.2. Calcium sulfate phases

The common calcium sulfate minerals are gypsum ($CaSO_4 \bullet 2H_2O$, monoclinic, $I2/c$), bassanite ($CaSO_4 \bullet 0.5H_2O$, trigonal, $P3_12$), and anhydrite ($CaSO_4$, orthorhombic, $Amma$). Here we report the space groups compiled in Hawthorne et al. (2000); note however that hemihydrate and anhydrite form different polymorphs (see below).

Gypsum is the most abundant sulfate mineral on the Earth surface and has a very widespread occurrence in evaporite deposits and other sediments, in fumaroles, and in ore deposits *(Vaniman and Chipera 2006)*. Evaporation of sea water initially leads to gypsum precipitation, followed by the crystallization of anhydrite (CaSO4) in the residual brine due to a reduction in water activity. Anhydrite and bassanite also occur in situations where thermal activity has naturally dehydrated precursor gypsum, or in acid alteration environments (see review by *Charola et al. 2007).*

2.3. The gypsum cycle

The use of calcium sulfate as a binder involves a series of steps which form the so-called "gypsum cycle" or "calcium sulfate cycle" *(Fig. 2)*.

The first step consists in the thermal dehydration of gypsum to form a hemihydrate (the mineral bassanite). The second and final step of this cycle involves the hydration and setting of bassanite to form gypsum which acts as a binder. Below we will study these two steps separately.

2.3.1. The dehydration of gypsum

The use of gypsum as a binder involves its thermal treatment to form the hemihydrate ("plaster of Paris"), according to the dehydration reaction:

$$CaSO_4 \bullet 2H_2O \rightarrow CaSO_4 \bullet 0.5H_2O + 1.5H_2O \quad (1)$$

This reaction starts at 42°C (315 K) (i.e., equilibrium transition T between bassanite and gypsum) at standard atmospheric pressure *(Charola et al. 2007).* Because at this T the reaction is extremely slow, $T > 373$ K is normally required in order to accelerate the dehydration kinetics. Industrial plaster of Paris is produced under humid conditions at ca. 413 K *(Charola et al. 2007)*. Depending on the dehydration procedure, two hemihydrate varieties are obtained, α- or β-$CaSO_4 \bullet 0.5H_2O$. Heating gypsum in a humid atmosphere produces the first variety, while heating in a dry atmosphere results in the second variety *(Freyer and Voigt 2003; Singh and Middendorf 2007)*.

Under near-equilibrium conditions, heating to ~373-473 K (dehydration T depends on the type of precursor bassanite: *Freyer and Voigt 2003)* produces γ-$CaSO_4$ (also known as $CaSO_4$(I)), according to:

$$CaSO_4 \bullet 0.5H_2O \rightarrow CaSO_4 + 0.5\ H_2O \quad (2)$$

The anhydrous product is called soluble anhydrite, a metastable phase which rapidly rehydrates under normal atmospheric conditions. As in the previous step, some overstepping (T higher than the equilibrium decomposition T) is required to speed up the reaction.

Further heating at 633 K leads to the formation of anhydrite (β–$CaSO_4$ or $CaSO_4$(II)) which does not react with water *(Prasad et al. 2005)*. Heating of anhydrite at 1453 K results in the formation of α–$CaSO_4$ ($CaSO_4$(I)) *(Charola et al. 2008)*.

Le Chatelier (1887) was the first to show the two steps dehydration of gypsum. Since his pioneering work, much has been published on the mechanisms and kinetics of gypsum thermal decomposition (see reviews by *Freyer and Voigt 2003; Charola et al. 2008*).

There is however no consensus on the actual mechanism of thermal decomposition of gypsum. For instance, the two-step dehydration process has been challenged by Prasad et al. (2005) that reported direct dehydration of gypsum to form γ–$CaSO_4$, followed by its rapid hydration to yield bassanite. There is also a persisting controversy regarding the existence of several hydrated (metastable) phases with formula $CaSO_4 \bullet nH_2O$, where the actual value of n is not well established for some of these phases (see *Adam 2003*).

Crystallographic studies (using XRD and/or neutron diffraction) show that the thermal decomposition of gypsum crystals most probably follows a topotactic mechanism *(Abriel et al. 1990)*. Topotaxy can be defined as a solid-state chemical change in which the reactant provides a template for product phase generation *(Galwey 2000).* This means that there is a clear structural relationship between precursor and product phases due to a good matching between their crystallographic structures. In situ TEM-SEAD analyses have confirmed that the dehydration reaction is in fact topotactic *(Sipple et al. 2001)*.

2.3.2. The hydration of bassanite

The setting and hardening of plaster of Paris has been the subject of extensive research over the last 100 years, although it is a process not fully understood *(Singh and Middendorf 2007)*. Hemihydrate hydration follows the overall (exothermic) reaction:

$$CaSO_4 \bullet 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \bullet 2H_2O \quad (3)$$

Both the kinetics and properties of set gypsum are dependent on the type of bassanite precursor phase (α– or β–$CaSO_4 \bullet 0.5H_2O$). The α–phase shows a shorter induction period and produces a set plaster with higher strength than the β–phase *(Singh and Middendorf 2007)*.

Most researchers agree that the hydration of bassanite is a solution mediated process *(Singh and Middledorf 2007)*. In contact with water, bassanite crystals start to dissolve generating a saturated solution with respect to this phase. Bassanite is more soluble than gypsum: 0.65 wt % calcium sulfate hemihydrate dissolves in water at room T, against 0.2 wt % in the case of gypsum. The resulting solution rapidly reaches supersaturated with respect to gypsum leading to its crystallization.

Precipitation of gypsum reduces the activity of both Ca^{2+} and SO_4^{2-} in solution, which further promotes the dissolution of the remaining bassanite and the precipitation of more gypsum. Typically, newly formed gypsum appears as µm-sized acicular crystals which form a highly porous, yet strong, 3D-mesh structure *(Singh and Middlendorf 2007)*. Both the morphology/size of gypsum crystals and the kinetic of the hydration reaction can be modified by the addition of different inorganic and organic compounds *(Solberg and Hansen 2001)*. For instance, addition of $Ca(OH)_2$ accelerates setting *(Ridge and King 1976)* whereas addition of carboxylic acids (and their salts) have been shown to delay hemihydrate setting, leading to the formation of larger equant gypsum crystals as opposed to the fibrous interlocking crystals in additive-free set pastes (*Singh and Middlendorf 2007; Gartner 2009)*. As a result, the flexural and compressive strength of gypsum plaster is significantly reduced *(Lanzón and García-Ruiz 2012).*

In addition to precipitation in solution, Melikhov et al. (1991) indicate that a topochemical reaction is responsible for the formation of gypsum pseudomorphs after bassanite. This is consistent with the reported pseudomorphic transformation of hemihydrate into gypsum in a water vapor atmosphere *(Triollier and Guilhot 1976),* a process which appears to be topotactic. Note however that a tightly interface-coupled dissolution-precipitation reaction could also explain the formation of gypsum after a pseudomorphic replacement of bassanite. For details on such a replacement process see the recent review by *Putnis (2009)*. Overall, these observations suggest that the mechanical properties of the set material may strongly depend on the textural properties of the precursor bassanite (in addition to the curing and setting conditions, as well as the absence/presence of additives and impurities).

2.4. Deterioration and conservation of gypsum mortars and plasters

Gypsum plasters and mortars are prone to decay *(Cotrim et al. 2008)*. This is primarily due to the low strength of gypsum, which has a hardness of 2 in the Mohs scale, and its relatively high solubility (2.1 g/L at 20°C). Gypsum plasters and mortars are therefore highly susceptible to chemical weathering (dissolution) and loss of structural stability, particularly in humid environments and outdoors exposure. Although they undergo very similar decay problems as those of lime mortars, they are however less sensitive to air pollutants *(Sayre 1976).*

Gypsum can undergo deliquescence and reprecipitation under fluctuating relative humidity (RH) conditions. Its equilibrium relative humidity (RHeq) at 25°C is 99.9 %, so when the RH is higher than its RHeq, gypsum crystals dissolve. When the RH drops, crystals reprecipitate as a non-coherent powder, and may even induce crystallization damage (salt weathering) when they grow within the pores of adjacent building materials (mortar, bricks or stone) *(Charola et al. 2007)*. At $T > 42°C$, transition to anhydrite can take place, thereby resulting in a significant weakening of the material. Such a transition can also occur at lower T if $RH < RHeq$ *(Charola et al. 2007)*.

Little has been published on the conservation of gypsum plasters and mortars. In general, lost material tends to be replaced with new gypsum-based materials. Consolidation and protection of this type of building and decorative material has been performed using the same approaches used for other materials such as stone or lime mortars *(Sayre 1976; Ashthur 1990; Cotrim et al. 2008)*. Much research is needed to develop and apply specific conservation treatments for gypsum-based materials. *Van Driessche et al. (2012)* recently reported the direct precipitation of nanosized bassanite which eventually transforms into gypsum at room T. This technology offers a new, potentially effective way to consolidate gypsum-based building materials via the application of a suspension of nanosized bassanite. When transformed into gypsum, it could act as a consolidant in a similar manner as nanolimes applied on porous building materials (see section 3.5).

3. Lime binders

3.1. Lime-based building materials: definitions, history and uses

The term lime s.l. refers both to calcium oxide (CaO) or quicklime, the product of the calcination of calcium carbonate (calcite or aragonite: $CaCO_3$), and to the compound obtained after the hydration of the oxide, i.e. calcium hydroxide ($Ca(OH)_2$), the mineral portlandite, also known as slaked lime or hydrated lime *(Boynton 1980; Gárate Rojas 1994)*. This term also applies to the products of the hydration of Ca and Mg oxides formed after the calcination of magnesium limestone and, in particular, dolomite ($CaMg(CO_3)_2$). Calcitic lime is commonly known as fat lime, while dolomitic or magnesian limes are commonly called magre limes *(Cowper 1927; Gárate Rojas 1994)*.

Archaeological evidence shows that lime was used in the construction of some of the floors and paving of the ruins excavated in Çatalhüyück *(Mellaart 1967)*, dated between 10000 and 5000 BC *(Von Landsberg 1992; Kingery et al. 1998)*. These archaeological findings, along with the remains of 4500 years old lime kilns found in Khafaje, Mesopotamia, confirm that lime was a common building material in the Levant during the Neolithic *(Davey 1961)*.

The Egyptians also used lime as a binder. Some coatings of lime in different pyramids have been dated ca. 4000 BC *(Boynton 1980)*. However this is challenged by *Lucas and Harris (1962)* and *Ghorab et al. (1986)* who indicate that the Egyptians did not use lime in construction (they used gypsum) until Roman times. Other ancient civilizations, like India, China and the different cultures of pre-Columbian America (e.g., Mayans and Aztecs) systematically used lime as a building material *(Gárate Rojas 1994)*.

The type of lime first used hardened when exposed to air, and was called air lime. The Greek and Roman civilizations discovered that calcination of marly limestones, i.e., with a concentration of aluminosilicates (clays) > 10 wt %, yielded a binding material that hardened underwater (hydraulic setting) and had improved mechanical properties *(Malinowski 1981)*.

Upon calcination of impure limestones, clays dehydroxylate at 400 to 600°C. The resulting silica and alumina combine with CaO formed after the decomposition of $CaCO_3$ at 950 to 1250º C, to produce calcium aluminates and silicates (Callebaut et al. 2001). These limes are called *natural hydraulic limes*. Dicalcium silicate (C_2S) is the main phase that reacts with water causing their hydraulic setting, unlike in the case of cement where tricalcium silicate (C_3S) is the main hydraulic phase *(Callebout et al., 2001)*.

In addition to natural hydraulic lime, the so-called *artificial hydraulic limes* have been also used. They were discovered by the Phoenicians and perfected by the Greeks and the Romans. Artificial hydraulic limes were obtained by mixing lime with a pozzolanic material, name taken from the town of Puzzoli, located nearby the Vesuvius in Italy, where a tuff with high hydraulic capacity was extracted. A pozzolanic material contains highly reactive silica and alumina. When combined with $Ca(OH)_2$ in the presence of water generates new products, mainly hydrated calcium silicates and aluminates, with superior binding or cementing properties *(Mertens et al. 2009)*.

The Greeks used the so-called *"Santorini earth"*, a tuff, as a puzolanic additive mixed with lime for the manufacture of hydraulic lime mortars as those found in Thera (Santorini, Greece) *(Alejandre Sánchez 2002)*. The Greeks also used a technique called "polishing" consisting in the application of coatings made of lime and crushed limestone mixed with pozzolana *(Malinowski 1981; Alejandre Sánchez 2002)*. The Romans used lime in construction since the last two centuries of the Republic (200-100 BC). In addition to air lime, they routinely used lime mixed with either natural (pozzolana s.s.) or artificial (brick powder) pozzolanic materials, thus obtaining the well-known *opus ceamentitious* and the *cocciopesto* described by Vitruvius (30 BC).

After the fall of the Roman Empire, natural and artificial hydraulic limes, including Roman cement, together with traditional air lime were the most common binders in construction since Byzantine time, though the Middle ages, Renaissance and Baroque, until the discovery of Portland cement in the early 19th century by Aspdin (Lea 1970).

However, since mid-18th century, traditional limes began to be replaced by high performance artificial hydraulic limes, made by researchers such as *Smeaton (1791) or Vicat (1837)*. In 1824 Aspdin patented a process for obtaining a cement which hardened under water (hydraulic setting) and acquired the strength of Portland limestone, one of the most resistant stoned used in British architecture, hence the name *"Portland cement"*. See details on such pioneering works in the report by Haswell (1865). The homogeneity and uniform properties, easy of application and high mechanical strength after a rapid setting explains the immediate success and massive use of Portland cement until present day.

However, in recent decades, lime has re-emerged as the optimal material for the conservation of historic structures and buildings *(Teutonico et al. 1994)*, replacing cement in such interventions. There are several reasons for the revival of lime *(Elert et al. 2002)*. Compared with cement, lime is more compatible from a mechanical, physical and chemical point of view when applied in historical structures (brickworks and/or stone) *(Elert et al. 2002; Lanas and Alvarez 2003; Hansen et*

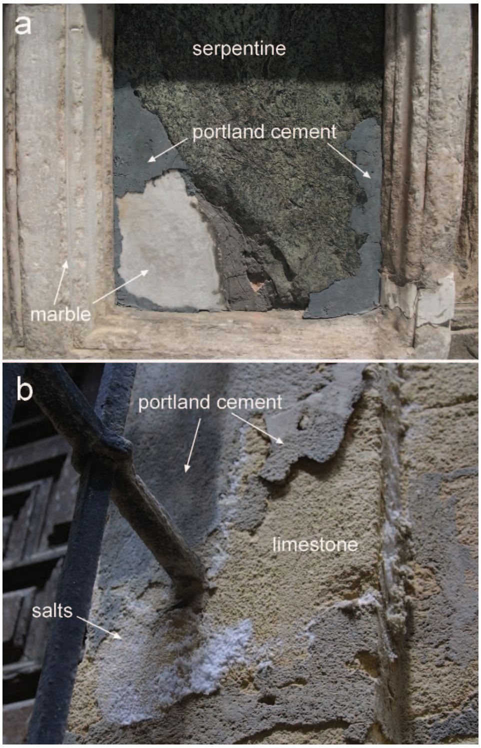

Fig. 3. Examples of the high incompatibility between Portland cement and historic structures: a) Portland cement applied on serpentine and marble at the Chancilleria (Granada, Spain); b) salt efflorescence and detachments associated to Portland cement applied on limestone ashlars (Granada Cathedral, Spain).

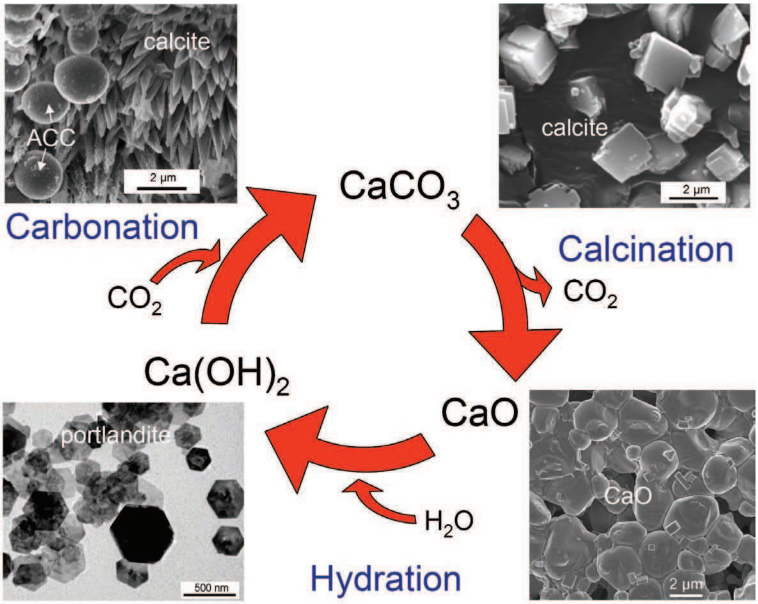

Fig. 4. The lime cycle: Electron microscopy images show reactant and products of the different stages of the cycle. ACC: Amorphous Calcium Carbonate.

al. 2008). For instance, the absence of alkalis and sulfates in lime prevents salt weathering due to the formation of deleterious carbonates and sulfates of Na/Ca or Mg, as can be seen after the application of Portland cement *(i.e., Rodríguez-Navarro et al. 1998; Maravelaki-Kalitzaki et al. 2003; Hansen et al. 2008)*. Crystallization of such salts causes extensive damage in both new construction and historic structures *(Fig. 3)*.

In successive sections recent advances in the study of air limes are presented. We will focus on the case of high calcium or calcitic limes as these have been the most profusely used by mankind and tend to be preferably applied in architectural conservation *(Hansen et al. 2008).*

The most important aspects that determine lime properties, reactivity, applicability and suitability as a binder in conservation will be studied within the framework of the "lime cycle". Finally we will discuss aspects related to recent studies on the characteristics of historic lime mortars, and the design and testing of conservation mortars as well as methods for their actual consolidation and protection.

3.2. The lime cycle

The lime cycle consists of three stages *(Fig. 4)*:

- calcination;
- hydration or slaking; and
- carbonation (or air setting).

Below we will present a detailed description of each stage of this cycle.

3.2.1. Calcination

The first stage of the lime cycle involves the calcination of limestone at a sufficiently high temperature as to cause the decomposition of calcite according to the reaction:

$CaCO_3 \rightarrow CaO + CO_2\uparrow$ *(4)*

This reaction is strongly endothermic, so the production of calcium oxide requires high energy consumption and the use of suitable kilns. Traditional lime kilns involved the firing of wood or coal along with limestone blocks, resulting in lime mortars with a high content of ash *(Luxán and Dorrego 1996)*. Kilns used since the industrial revolution placed the fuel and the limestone in separate compartments (Boynton 1980). Thus, the resulting limes do not present any ashes and have homogeneous characteristics, something difficult to achieve through the use of traditional kilns.

The temperature of dissociation of $CaCO_3$ is 898°C at pCO_2 = 1 atm. This T is reduced the lower the $pCO2$ is, and increases as pCO_2 increases (Boynton 1980). CO_2 released by carbonate decomposition (plus CO_2 generated by the combustion of wood or coal in traditional kilns) must be evacuated to avoid the re-carbonation of CaO, or to hinder carbonate decarbonation.

The presence of other gases, e.g. water vapor released during the combustion of wood in traditional lime kilns, may speed up the decomposition process and reduce calcination T *(Beruto et al. 2003)*. The characteristics of the oxide product are strongly dependent on T and duration of the calcination process *(Boynton 1980)*. CaO crystals formed a low T, and/or after a relatively short period of calcination, are nanosized, show a very porous structure and are highly reactive *(Fig. 5a)*.

Calcination in air at T above 900°C and/or during long periods of time favors the oriented aggregation of CaO nanocrystals and the subsequent sintering and densification *(Rodríguez-Navarro et al. 2009)*. These phenomena can lead to the formation of completely inert or "dead burnt" CaO at T ca. 1400°C. In

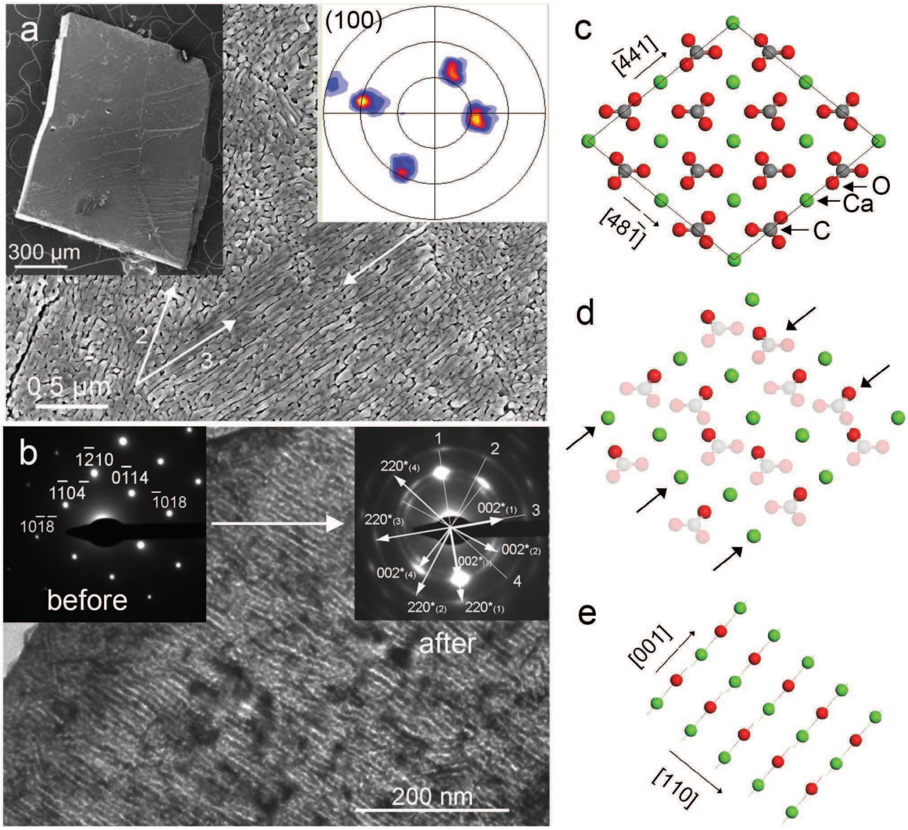

Fig. 5. The thermal decomposition of calcte: a) SEM image of the porous structure of CaO crystals formed after calcite (see pseudomorph in inset). Preferred orientations of CaO crystals are indicated with arrows. The left inset shows the (100) pole figure of CaO crystals with a preferred orientation with respect to the parent calcite (the projection plane is parallel to the cleavage plane of calcite); b) TEM photomicrographs of oriented CaO nanocrystals formed upon calcite decomposition following e-beam irradiation in the TEM chamber. Insets show the corresponding SAED pattern of precursor (calcite) and product (CaO) phases. Four sets of product CaO crystals with preferred crystallographic orientation are identified in the SAED as shown by the orientation of their reciprocal lattice vectors (1 to 4); c) projection of the calcite structure on the cleavage plane; d) loss of CO_2 from former CO_3^{2-} groups in the calcite (10.4) planes; and e) final transformation (via a topotactic mechanism) into oriented CaO crystals. Modified from Rodríguez-Navarro et al. (2009).

general, the most reactive limes are those subjected to a relatively *"soft"* calcination process ("soft burning") *(Boynton 1980)*.

An adequate knowledge of the mechanism of $CaCO_3$ calcination is crucial to optimize this process and to obtain oxides with desired properties. Despite many studies, there is no consensus on how such a reaction occurs *(Rodríguez-Navarro et al. 2009)*. We recently investigated the thermal decomposition of calcite, both studying the kinetics of the reaction and its textural and microstructural aspects *(Rodríguez-Navarro et al. 2009)*. X-ray diffraction (XRD), two-dimensional XRD (2D-XRD), scanning (FESEM) and transmission electron microscopy (TEM-SAED) allowed us to determine that the calcination of calcite is pseudomorphic and topotactic *(Figure 5b).*

The release of CO_2 from CO_3^{2-} groups existing along the (10.4) planes of calcite, results in a realignment of oxygen and Ca atoms to form CaO nanocrystals that preserve a close crystallographic relationship with the parent calcite crystal *(Figure 5c-e)*. Pseudomorphs are highly porous (up to 54% porosity) due to the molar volume difference between calcite and calcium oxide. CaO nanocrystals (initially with size ca. 5 nm and with surface area of up to 80 m^2/g) show the following crystallographic relationships with the precursor calcite: $\{10.4\}_{calcite}//\{110\}_{CaO}$ and $\langle\bar{4}41\rangle_{calcite}//\langle 110\rangle_{CaO}$. These results enabled us to propose a new model for the thermal decomposition of calcite, which is schematically shown in *Fig. 5.*

The nanosized character of CaO crystals formed topotactically pre-determines the kinetics of the following stage of the lime cycle, namely, the hydration step, as well as the properties of the resulting hydroxides. On the other hand, the close textural and crystallographic relationship between carbonate and oxide crystals means that the textural and microstructural characteristics of the carbonate will largely determine the properties of the resulting oxides. This assertion is corroborated by various studies showing that the surface area, porosity, pore size and crystal size distribution of the carbonate rock, in addition to the presence of impurities, determine the properties, in particular the reactivity, of product calcium oxide *(Elert et al. 2002)*.

Depending on the composition and textural characteristics of carbonate rocks, it will be therefore necessary to establish the optimal parameters for calcination (temperature and duration) *(Boynton 1980)*.

3.2.2. Hydration

In contact with water calcium oxide reacts forming calcium hydroxide ($Ca(OH)_2$), the mineral portlandite, according to the reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (5)$$

Reaction (5) is highly exothermic. Thus, safety precautions have to be taken during traditional lime slaking, both due to possible burns and to the corrosive effect of splashes (pH 12.4). If the hydration occurs with the stoichiometric amount of water, a dry powdered precipitate is formed. Dry hydrate is the standard industrial product nowadays. If excess water is added, the final product is an aqueous dispersion of hydroxide crystals. This way a lime paste (or lime putty) is formed.

There are numerous studies on the effect of oxide/water ratio, oxide grain size, temperature of water, presence of alcohol or additives in the slaking water, and agitation in the properties of the hydroxide formed after slaking (see review by *Elert et al. 2002)*.

Various mechanisms for the transformation of calcium oxide into portlandite have been proposed *(Ramachandran et al. 1964; Beruto et al. 1981; Wolter et al. 2004; Sato et al. 2007)*. It appears that a part of $Ca(OH)_2$ directly precipitates from the supersaturated solution formed upon dissolution of CaO in the slaking water. However, there is evidence suggesting that the hydration of a considerable amount of CaO occurs as a solid state reaction between the oxide and water vapor generated as a result of the increase in temperature experienced during hydration *(Wolter et al. 2004)*.

Yet, it is not clear how these two processes occur and what their relative merit is in the overall slaking process. Beruto et al. (1981) propose that vapor phase hydration of CaO is controlled by the structure of the reactant and product, being a pseudomorphic reaction that generates nanometric $Ca(OH)_2$ crystals. It could be hypothesized that given the structural similarity between $(111)_{CaO}$ and $(001)_{Ca(OH)_2}$ planes, the replacement of $O^=$ in the oxide by OH^- groups could easily result in the topotactic formation of portlandite. This would imply that the microstructural characteristics of the oxide would be (at least partially) inherited by the hydroxide.

This mechanism could help to explain why depending on the characteristics of the oxide (e.g., surface area, porosity and particle size) hydrated limes with different properties are generated, even when slaking is performed under identical conditions *(Elert et al. 2002).*

Rodríguez-Navarro et al. (2005) have shown that there are significant microtextural differences between traditional slaked limes (lime putties) and commercial (powder) hydrated limes. The formers have a greater proportion of particles with size < 1 μm. Apparently, the drying process undergone by dry hydrated limes results in both reversible (non-oriented) and irreversible (oriented) aggregation of portlandite crystals. Oriented aggregation results in an increase of the effective size of $Ca(OH)_2$ particles (aggregates), which results in a significant reduction of surface area and reactivity, and a worsening of rheological properties (viscosity, plasticity and workability) *(Ruiz-Agudo and Rodríguez-Navarro 2010)*. This is consistent with studies carried out at the beginning of the 20th century which concluded that slaked lime behaved as an irreversible colloid once dried *(Ray and Mathers 1928)*.

In the case of lime putties, there is a range of phenomena that occur after slaking if the paste is kept underwater during long periods of time (months or years). This is the so-called *"ageing"*, which was used since Roman times to improve the properties of slaked lime *(Cowper 1927; Ashurst 1990).* Pliny indicates that there was a law in ancient Rome which established that lime putties should be *"aged"* for at least three years prior to their application *(Rodríguez-Navarro et al. 1998).*

This tradition, based on empirical observations, has survived to our day. However, until relatively recently, there were doubts about whether or not ageing produced any improvement in the properties of lime paste, and if this was the case, it was not known which was the cause and/or mechanism of such improvement. *Rodríguez-Navarro et al. (1998)* showed that after ageing of lime pastes for 2 to 10 months, there was a reduction in the size of portlandite crystals and an increase in their surface area. Planar (hexagonal platelets) with overdeveloped {0001} forms appeared in parallel with the disappearance of larger prismatic crystals. Preferential dissolution of the prism faces along (0001) planes resulted in an overall increase in the amount of plate-like portlandite crystals. In addition, secondary precipitation of sub-micrometric, planar portlandite crystals also occurred during ageing. All these smaller planar crystals led to an overall increase in surface area, reactivity, dynamic viscosity and plasticity *(Rodríguez-Navarro et al. 2009; Atzeni et al. 2004; Ruiz-Agudo and Rodríguez-Navarro 2010).*

However, Ruiz-Agudo and Rodríguez-Navarro (2010) indicate that depending on the characteristics of the oxide (hard vs. soft burnt lime), the rheological evolution of slaked lime putties was different, although in all studied cases a general improvement was observed after long periods (several months) of ageing.

3.2.3. Carbonation

Carbonation of calcium hydroxide in the presence of atmospheric CO_2 occurs according to the overall reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (6)$$

The resulting $CaCO_3$ crystals act as a binder or cement due to their interconnected microstructure *(Beruto et al. 2005)* joining the rest of the elements in the mix (aggregate).

The setting of air lime mortars and plasters begins with an initial period of drying and shrinkage and is followed by the carbonation reaction. The reaction interface advances through the porous system from the surface towards the unreacted core. This process consists of several steps:

- (i) diffusion of CO_2 (gas) through the open pores,
- (ii) dissolution of $Ca(OH)_2$ in the pore water,
- (iii) absorption and dissolution of CO_2 in the alkaline pore water forming carbonic acid H_2CO_3;
- (iv) its immediate dissociation into bicarbonate and carbonate ions,
- (v) reaction between Ca^{2+} and $CO_3{}^{2-}$ ions forming $CaCO_3$ through nucleation and growth.

All these processes are interrelated and altering the kinetics of one process influences the others *(Van Balen and Van Gemert 1994; Cultrone et al. 2005; Cizer et al. 2012).*

The volume, geometry and size of the pores, as well as the water content, play an important role in the progress of carbonation. This is primarily due to the fact that water largely controls the rate of CO_2 diffusion, which along with CO_2 dissolution (forming carbonic acid) are rate determining steps for carbonation. As water evaporates during drying, an effect which is promoted by the exothermic nature of carbonation (Moorehead, 1986) and the less hydrophilic character of newly-formed $CaCO_3$ if compared with $Ca(OH)_2$ (*Beruto and Botter 2000; Beruto et al. 2005*), pores tend to stay open. This accelerates CO_2 diffusion towards the interior of the material which is carbonating.

However, the porosity is slightly reduced due to the precipitation of $CaCO_3$ crystals, which have a molar volume 11.7% higher than that of $Ca(OH)_2$ *(Moorehead 1986)*. Overall the kinetics of carbonation is very slow, an the reduction in pore size (*Lawrence et al. 2007)* could further contribute to a reduction in carbonation rate over time. This may help explaining why uncarbonated portlandite has been found in lime mortars several centuries old *(Marchese 1980)*, although this is a matter of controversy *(Adams et al. 1998).*

$CaCO_3$ formed after carbonation may appear as three anhydrous polymorphs, calcite, aragonite and vaterite, depending on the conditions of the reaction, (i.e. pH, T, supersaturation) and the presence of impurities or additives. Calcium carbonate may also precipitate as an amorphous phase (Amorphous Calcium Carbonate, ACC), which is hydrated and metastable. ACC, which usually precipitates as small spheres of less than 1µm in diameter, turns into calcite as the reaction progresses. As we will see later, this phase seems to play a key role in the process of carbonation of $Ca(OH)_2$ *(Cizer et al. 2012)*.

The textural characteristics of $CaCO_3$, as well as the cementing structure formed after carbonation, appear to depend on the properties and characteristics of precursor portlandite crystals and on the conditions of carbonation (i.e., water content, T and RH, pCO_2, pH, and ionic activity). There are studies on the effects of the size, surface area, and habit of portlandite crystal on the kinetics of carbonation. In general, the smaller the portlandite crystals are, the higher their reactivity during carbonation is *(Van Balen 2005)*. In turn, the textural features of the portlandite precursor and the kinetics of carbonation determine the physical and mechanical properties of lime-based materials (*Cizer et al. 2012)*.

Regarding the mechanisms of $Ca(OH)_2$ carbonation, two possible routes exist: a) precipitation in solution and b) replacement of portlandite by calcium carbonate. The latter can occur either via a solid state reaction *(Gillott 1967; Matsuda and Yamada 1973; Moorehead 1986)* or through a tightly coupled process of dissolution/precipitation *(Putnis 2009)*.

Carbonation in solution has been thoroughly studied because it is important in the industrial precipitation of calcium carbonate used in paper, paint, plastic and pharmaceutical industries *(see overview by Cizer et al. 2012).*

This reaction takes place according to the Ostwald rule of stages following the precipitation sequence:

ACC → vaterite → (aragonite) → calcite

(Ogino et al. 1987). Some studies show the initial precipitation of ACC nanoparticles in lime mortars subjected to carbonation *(Rodríguez-Navarro et al. 2002; Cizer et al. 2012)*, which is followed by the formation of scalenohedral and, finally, rhombohedral calcite crystals *(Cultrone et al. 2005; Cizer et al. 2012) (Fig. 4)*.

Occasionally, the formation of aragonite or vaterite has been observed *(Zanco 1994)*. It should be noted that the use of a calcitic aggregate may promote the direct epitaxial (homoepitaxial) precipitation of calcite, i.e., not following the Ostwald's rule. Such a regrowth should generate a coherent interface between the aggregate and the binder. This could help to explain why conservation lime mortars prepared with calcitic aggregates tend to show a higher strength than those prepared using dolomitic or siliceous aggregates *(Lanas and Alvarez 2003).*

With respect to the second mode of carbonation, that is, the transformation in solid state or via coupled dissolution/precipitation, there is no consensus on what is the actual mechanism of reaction. *Gillott (1967) and Matsuda and Yamada (1973)* indicate that in the presence of low amounts of water, portlandite crystals transform into calcite through a solid state reaction controlled by the structure, i.e., topotactic transformation. In his classic study, Moorehead (1986) indicates that in addition to the precipitation of calcium carbonate in solution, which he considered a secondary process, carbonation occurred following a solid state replacement. Nonetheless, he noted that water was necessary for the reaction to progress. This casts some doubts about the solid state nature of the carbonation process. *Beruto and Botter (2000) and Beruto et al. (2005)* show that carbonation was significantly accelerated for RH values > 75%, when more than 4 H_2O monolayers were adsorbed onto portlandite crystals. $Ca(OH)_2$ dissolution into the adsorbed water enabled the carbonation to progress at a sufficiently high speed. This implies a pseudomorphic replacement via coupled dissolution/precipitation, which should be much faster than a solid state reaction *(Putnis, 2009)*.

Beruto et al. (2005) called attention to the fact that the direct precipitation of calcite from a saturated $Ca(OH)_2$ solution generates dispersed particles, without any degree of cohesion or mechanical resistance, while through a mechanism of pseudomorphic replacement, as described above, a very cohesive and mechanically resistant paste of calcium carbonate is obtained.

Although the mechanism of carbonation via this pseudomorphic replacement is not yet fully understood, it has very important implications. Amongst them are the following: the size, morphology and level/type of aggregation of calcium hydroxide crystals determine how it will be the texture and microstructure of calcite crystals formed after carbonation. This may help explaining why depending on the type of calcitic slaked lime, mortars with different properties and durability are obtained after carbonation.

For instance, mortars prepared with aged lime putties show faster carbonation and a higher mechanical strength than mortars prepared with fresh lime putties or with dry hydrate (Cazalla et al., 2000). Rodríguez-Navarro et al. (2002) show that mortars prepared using aged lime putty (16 y old) display a carbonated structure which resembles Liesegang patterns, which is also observed in historical buildings *(Fig. 6)*. The authors linked the formation of the Liesegang pattern with the microtextural characteristics of aged portlandite crystals.

3.3. Historic lime mortars and plasters

The study of lime mortars and plaster collec-

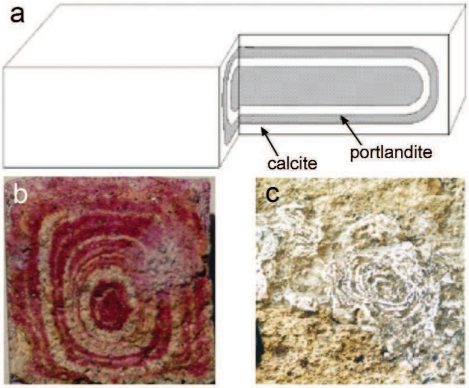

Fig. 6. Formation of a Liesegang pattern in carbonated lime mortars prepared with 16 y old lime putty: a) scheme of a mortar prism; b) section of the prism after 1 y carbonation following phenolphthalein impregnation. The red rings correspond to uncarbonated parts, while the whiter rings are fully carbonated (modified from Rodríguez-Navarro et al., 2002); c) example of Liesegang pattern following differential weathering in lime plasters in a historical building (Saint Maria Church, Utrera, Spain) (modified from Hansen et al., 2008).

ted from historical buildings has been a constant in recent decades, highlighting their tremendous compositional variety, both depending on location and age *(Elsen 2006).*

The study of such materials, which in many cases present major alteration problems, is justified for several reasons. First, the study of lime-based materials with different age, provenance and uses is of importance from a historical and architectural point of view. On the other hand, their analysis can help identify what components were historically used in the production of lime mortars and plasters, and shed light on the manufacturing technology.

This information is critical if we are to reproduce such materials with a view to their application in architectural conservation interventions. In this respect, the Venice Charter (1964) recommends the use of materials and technologies the closest to those originally used in the making of the element to be conserved.

The number of published studies on lime-based materials, mostly mortars, used in historical buildings from prehistory to practically our days, is large, and has steadily increased over the last two decades.

Analytical techniques such as polarized light microscopy (see an example in *Fig. 7*), scanning and transmission electron microscopy, x-ray diffraction, termogravimetry, differential thermal analysis, infrared (FTIR) and Raman spectroscopy, x-ray fluorescence, atomic absorption spectrometry, and calcimetry, among others, have been used to study the composition and microstructure of old lime mortars *(Moropoulou et al. 1995; Bakolas et al. 1995a,b, 1998; Riccardi et al. 1998; Franzini et al. 1999; Maravelaki-Kalaitzaki et al. 2003; Elsen 2006; Edwards and Farwell 2008).*

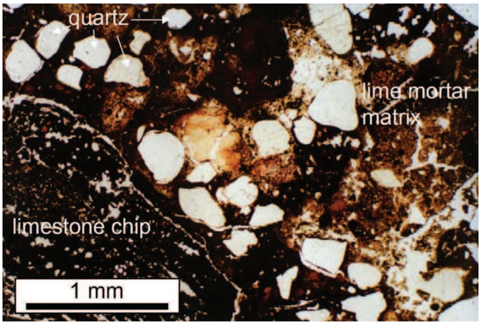

Fig. 7. Optical microscopy photomicrograph of a lime mortar from the walls of the IX c. Castle of Cañete la Real (Malaga, Spain). Plane light.

Goins (2000) proposed a complete analytical protocol for the study of both modern and ancient lime mortars. It is not our intention to make an extensive review of these publications. The interested reader is refereed to the Getty Conservation Project Bibliography Series “Preservation of Lime mortars and plaster” (http://www.getty.edu/conservation/publications_resources) and the review by Elsen (2006). Here, however, a few aspects of the study of old lime mortars will be reviewed to get an insight into the importance of this field.

An interesting aspect of ancient lime technology refers to the slaking of quicklime mixed with the aggregate before adding water. This is the so-called *"hot lime"* technology *(Moropoulou et al. 1996)*. A variation is called “dry” slaking, which involved the mixing of quicklime with a wet aggregate *(Elsen 2006)*. Apparently it was a common slaking method and generated mortars of excellent quality and durability *(Moropoulou et al. 1996)*. Such a slaking process could have produced alkali-aggregate reactions between lime and siliceous sand *(Armelao et al. 2000)*, favored by the high temperature reached. *Margalha et al (2011)* have carried out laboratory studies on the potential benefits "hot lime" technology can have in the case of air lime mortar mixed with siliceous sand. Their results, however, do not show that this technology impart any clear advantage to these mortars. In contrast, Malinovski and Hansen (2011) conclude recommending the use of hot lime technology for conservation lime mortars.

A large number of studies, such as those of *Bakolas et al. (1995a, 1995b, 1998)* on Byzantine and post-Bizantine lime mortars, or Moropoulou et al. (1996) show that, in addition to air lime mortar, many of the mortars of such times included lime mixed with ceramics, crushed or powdered. In general, it appears that the use of artificial hydraulic lime mortars was much more common after the fall of the Roman Empire than previously thought *(Elsen 2006)*.

Bakolas et al. (1995b) studied 14th to 18th c. Venetian mortars, and concluded that one of the most distinctive features in historic lime mortars is the presence of whitish nodules (lumps) with dimensions ranging between a few mm and 1 or 2 cm. These nodules are composed of calcite, so they could either correspond to fully carbonated slake lime lumps, or uncalcined limestone chips.

The presence of traces of silicates (hydraulic phases), a high porosity and numerous fractures suggest that these nodules correspond to slaked lime lumps that did not dissagregate upon mixing with sand and water *(Franzini et al. 1999)*, possibly due to the lack of aging of the original lime which displayed a low plasticity *(Tuncoku and Caner-Saltik 2006)*. Alternatively, they could be the result of the hot lime or dry slaking technology *(Bakolas et al. 1995a, 1998)*. Local overheating during dry slaking could provoke an agglomeration of the hydrated lime particles, causing the formation of such nodules.

Regarding the formulation of historical lime mortars, classic treaties such as those of Vitruvius (30 BC) and Alberti (1452), established that 1:3 was the optimal binder to aggregate ratio. However, many researchers have found that, in general, Roman and Greek lime mortars with considerable age difference had very similar textural and compositional characteristics, among which it is highlighted that the binder/aggregate ratio was higher than 1:3, typically 1:2 *(Foster 1934; Elsen 2006)*.

Another important aspect of old lime mortar technology refers to the use of additives (we do not consider here those imparting hydraulic character). Typically, organic additives were dosed in the lime mix to improve the mortar properties both in the fresh and hardened state. Examples of such additives are: egg white, blood of ox, juices of various fruits such as figs, keratin and casein, oils from plants (e.g, linseed oil), and animal fats, among others *(Moropoulou et al. 2005)*.

For instance, both Aztecs and Mayans used nopal juice *(Oppunctia ficus indica)*, which is very rich in pectin, as an additive in preparing lime mortars and plasters of high plasticity and capacity to avoid cracking during drying, tradition which is currently preserved in different parts of Mexico and the United States *(Cárdenas et al. 1998)*.

Researchers have attempted to reproduce traditional building practices using natural additives to improve the performance of lime used in architectural conservation. For example, *Yang et al. (2010)* used the ancient China vernacular sticky rice technology for improving the performance of new conservation lime-based mortars. The presence of amylopectin in the rice caused the formation of a matrix of calcite nanocrystals which granted an enormous strength and durability to such conservation mortars.

Modern, both natural and artificial, organic additives have been also tested for improving the performance and properties of lime-based conservation mortars. For instance, *Izaguirre et al (2010)* noted an increase in plasticity, adhesion, durability and mechanical strength of lime mortar dosed with potato starch, plasticizers, air-entraining agents and water repellents.

3.4. Lime-based conservation mortars

The study of old lime mortars have yielded a significant amount of information which has been applied for the design of new lime-based conservation mortars.

To be compatible with old masonry and to play a proper role, restoration mortars must meet a series of requirements, among which the following can be highlighted *(Maurenbrecher 2004)*:

- (a) the mortar should not have a higher strength than stone or brick: a conservation mortar is not "better" the stronger it is;
- (b) the water absorption and water vapor permeability of the mortar must be of the same order of magnitude or greater than that of the other masonry elements. This favors the accumulation of water (and salts) in the mortar which may act as a sacrificial material;

- (c) mortars must have a minimum retraction to prevent crack development;
- (d) should ensure a good contact with bricks or stone. This is favored by a high plasticity and workability;
- (e) in general, its physical properties (thermal expansion, color, etc) should ensure a high compatibility with the different elements in the old masonry structure, while ensuring that the mortars is sufficiently durable. This is particularly relevant in cases where loss of mortar is so general that the survival of the whole masonry structure is in jeopardy *(Fig. 8)*.

A consensus exists on the need of using conservation lime mortars with formulations and manufacturing / application techniques as similar as possible to the traditional ones. For example, it is generally recommended the use of calcitic lime pastes, especially those that have undergone aging. Faria et al. (2008) note that resistance to salt crystallization damage is significantly higher in mortars prepared with lime pastes aged for 10 to 16 months if compared with mortars prepared with commercial dry hydrate. There is however no consensus on what is the optimal aging time. The golden rule should be the longer the better. However, from a practical point of view, a period between 2 and 10 months aging brings about a significant improvement *(Rodríguez-Navarro et al. 1998). Ashurst (1980)* recommends a minimum of three months ageing period.

In addition to slaked lime, conservation mortars and plasters include water and aggregate. Unlike in the case of Portland cement, water content does not appear to appreciably affect the mechanical behavior of air lime mortars *(Lawrence and Walter 2008). Nonetheless, Arandigoyen et al. (2005)* show that increased water/lime ratios increase the mortars porosity, an effect which could be detrimental in the presence of ice or soluble salts. It seems that depending on the type of lime, water requirements vary. A method to overcome such an effect is to prepare mortars with a standard consistency *(Hansen et al. 2008)*. A precaution to consider is the purity of the water used. Vitruvius recommended the use of high purity sand without fines, discarding the use of sea water due to the harmful effect of salts.

Fig. 8. Ruins of the Castle of Cañete la Real (Malaga, Spain). The piece of wall shows extensive loss of joint mortar linking the stone blocks.

With regards to the most appropriate binder/aggregate ratio in conservation mortars and how it affects the mortar properties, there are mixed results. Classically, the use of a 1/3 (lime/sand) ratio was recommended as indicated by Vitruvius and Alberti. *However, Lanas and Alvarez (2003)* demonstrate that the best physical-mechanical properties are achieved when a binder/aggregate ratio of 1:1, or even 2:1, is used. However, other authors such as *Cazalla et al. (2002)* note that the best mortars (in terms of speed of carbonation and mechanical properties) are those with a 1:4 ratio. Note that Lanas and *Alvarez (2003)* used hydrated lime powder, while *Cazalla et al. (2002)* got the best mortars using lime putty aged for 14 years. It follows that depending on the type of lime used, and the final application of the conservation mortar (joint mortar, repointing, sacrificial layer, or plaster), the binder/aggregate ratio has to be gouged.

The aggregate is another important component of a conservation lime mortar. The aggregate is added to reduce costs, to minimize the formation of drying cracks, and to provide proper consistency in the fresh state, and adequate strength and permeability (porosity) after setting. The type of sand is highly variable. *Cowper (1927)* in his classic report provides some general rules for the selection of proper sand (see also *Elert et al. 2000*).

3.5. Decay and conservation of lime mortars and plasters

Lime mortars and plasters suffer different damaging processes when exposed both outdoors and indoors. These include chemical (dissolution, sulfation in polluted environments), physical (thermal changes, freeze/thaw, salt crystallization) and biological (mechanical action of roots, degradation by bacterial action) weathering processes *(Ashurst 1990; Furlan 1991; Doehne and Price 2010).* They cause loss of cohesion, increase in porosity, and granular disintegration, among other phenomena.

Such a damage often entails the loss of material, as it is shown in *Fig. 8*, so the more common type of conservation intervention is to reapply a new mortar or rendering prepared according to the guidelines referred to in the previous section.

However, there are situations in which it is necessary to consolidate the lime-based historical material. Studies dedicated to the consolidation and/or protection of lime mortars are fairly limited when compared with studies dedicated to the design and testing of restoration mortars. There are however some studies that compare various types of products for the consolidation of historic lime mortar following an approach very similar to that followed during the consolidation of stone.

For example, *Toniolo et al. (2011)* have studied the effectiveness of different consolidants applied on lime mortars. The tested consolidants were:

- polyethylmetacrylate-methylacrylate copolymer (Erabiliz B72);
- tetraethyl orthosilicate (RC 70 - TEOS);
- saturated barium hydroxide solution.

Changes in color and mechanical properties were evaluated after consolidation. With regard to the appearance of the treated materials, the best behavior was observed after the application of barium hydroxide. The highest increase in strength was observed after the application of TEOS, while the worst behavior was observed in the case of the barium hydroxide.

Inorganic consolidants such as lime water or barium hydroxide have been thoroughly applied on lime plasters. While the classic lime water treatment seems to be highly ineffective, the $Ba(OH)_2$ treatment appears to be very promising (Doehne and Price, 2010). Carbonation of this hydroxide leads to the precipitation of cementing $BaCO_3$. In the presence of sulfates, highly insoluble $BaSO_4$ is also formed which contributes to the strengthening of the lime-based material and limits salt damage.

Izaguirre et al. (2009) studied the effects of some protective treatments (water repellants) applied to air lime mortars, observing a significant improvement of the mortars resistance to freeze/thaw cycles.

Treatment based on the application of alcoholic dispersions of $Ca(OH)_2$ nanoparticles, the so-called *"nanolimes"*, show some promising results as a novel and effective consolidation method for lime-based mortars, renderings and plasters *(Baglioni and Giorgi 2006).* Yet, much research has to be dedicated to the study of novel, effective conservation treatments for the in situ consolidation and protection of lime-base building materials.

4. Concluding remarks

Mankind has used gypsum and lime binders for decorative and structural purposes in historical buildings since prehistory. Both binders share some interesting features in their processing and setting (e.g., the gypsum and the lime cycles). In particular, their "activation" and settings show some mechanistic similarities:

- (a) their calcinations/dehydration is a solid state process which follows a topotactic mechanism, and
- (b) their setting involves two different mechanisms, namely
  - (i) crystallization in solution, and
  - (ii) either a solid state reaction or a coupled dissolution/precipitation process.

Lime is somehow different in that its cycle shows an additional step of hydration, which from a mechanistic point of view also involves precipitation in solution and another process which may be either a solid state reaction or a pseudomorphic tightly coupled dissolution/precipitation.

Research should focus on elucidating which one of the process already mentioned, i.e., solid state or dissolution/precipitation, actually takes place, and how is the atomic scale mechanism involved in such a process.

It is shown that due to the structural relationships between parent and product phases in both gypsum and lime cycles, the properties of the parent phases predetermine the properties of the product phases. This has profound consequences on the performance of both ancient and modern (conservation) gypsum- and lime-based materials, and emphasizes the fact that each stage of the two cycles has an effect on the properties of the final set material.

An overview of the uses of both gypsum and lime as binders in historical buildings, their use in conservation interventions, and their actual decay and conservation, shows that despite the numerous research efforts that have taken place over the last few decades, much is still to be investigated. For instance, the development of novel effective conservation methods for in situ consolidation of both gypsum and lime building materials is still a challenge.

The study and testing of nanosized crystalline, or even amorphous, precursors (bassanite, nanolimes) for the consolidation of gypsum and lime mortars and plasters could be an interesting and potentially fruitful research path worth to explore.

5. Acknowledgement

This research was financed by the EU Initial Training Network Delta-Min (Mechanisms of Mineral Replacement Reactions) grant PITN-GA-2008-215360, the Spanish Government (grant MAT2009-11332) and the Junta de Andalucía (research group RNM-179).

Some of the results here presented were obtained during the development of the Lime Mortars and Plasters project, a joint collaboration between the Getty Conservation Institute, the Catholic University of Leuven and the University of Granada.

Contributions by K. Elert, E. Hansen, K. Van Balen, O. Cizer, E. Ruiz-Agudo, O. Cazalla, E. Sebastian Pardo and K. Kudlacz are acknowledged.

6. References

Abriel, W., Reisdorf, K. and Pannetier, J. (1990) Dehydration reactions of gypsum: A neutron and X-ray diffraction study. J. Solid State Chem. 85, 23-30.

Adam, C.D. (2003) Atomistic modelling of the hydration of $CaSO_4$*. J. Solid State Chem. 174, 141-151.*

Adams, J. Kneller, W. and Dollimore, D. (1992) Thermal analysis (TA) of lime- and gypsum-based medieval mortars. Thermochim. Acta 211, 93-106.

Adams J., Dollimore D., and Griffiths D.L. (1998) Thermal analytical investigation of unaltered $Ca(OH)_2$ *in dated mortars and plasters. Thermochim. Acta 324, 67-76.*

Alberti, J.B. (1452) On the Art of Building in Ten Books (De Re Aedificatoria). Translation by Leach, N., Rykwert, J., and Tavenor, R, 1988. MIT Press, Cambridge.

Alejandre Sánchez, F.J. (2002) Historia, Caracterización y Restauración de Morteros. Universidad de Sevilla, Sevilla.

Allen, E. and Thallon, R. (2011) Fundamentals of Residential Construction. Wiley, Hoboken, N.J.

Arandigoyen, M., Pérez Bernal, J.L. Bello López, M.A. and Alvarez J.I. (2005) Lime-pastes with different kneading water: Pore structure and capillary porosity. Appl. Surf. Sci. 252, 1449–1459.

Armelao, L., Bassan, A., Bertoncello, R., Biscontin, G., Daolio, S. and Glisenti, A. (2000) Silica glass with calcium hydroxide: a surface chemistry approach. J. Cultural Heritage 1, 375-384.

Arredondo, F. (1991) Yesos y Cales. Ed. E.T.S. Ing. Caminos, Madrid.

Ashurst, J. (1990) Mortars for stone buildings. In Conservation of Building and Decorative Arts, Vol. 2, J. Ashurst and F.G. Dimes, eds., p. 78-96. Butterworths, London.

Atzeni, C., Farci, A., Floris, D. and Meloni, P. (2004) Effect of aging on rheological properties of lime putty. J. Am. Ceram. Soc., 87, 1764-1766.

Baglioni, P. and Giorgi, R. (2006) Soft and hard nanomaterials for restoration and conservation of cultural heritage. Soft Matter 2, 293-303.

Bakolas, A., Biscontin, G., Moropoulou, A. and Zendri, E. (1995a) Characterization of the lumps in the mortars of historic masonry. Thermochim. Acta 269/270, 809-816.

Bakolas A, Biscontin G, Contardi V, Franceschi, E., Moropouolou, A., Palazzi, D. and Zendri, E. (1995b) Thermoanalytical research on traditional mortars in Venice. Thermochim. Acta 269/270, 817-828.

Bakolas, A., Biscontin, G., Moropoulou, A. and Zendri, E. (1998) Characterization of structural Byzantine mortars by thermogravimetric analysis. Thermochim. Acta 321, 151-160.

Beruto, D., Barco, L., Belleri, G. and Searcy, A.W. (1981) Vapor-phase hydration of submicrometer CaO particles. J. Am. Ceram. Soc. 64, 74-80.

Beruto, D.T. and Botter, R. (2000) Liquid-like H20 adsorption layers to catalyze the $Ca(OH)_2/CO_2$ *solid-gas reaction and to form a non-protective solid layer at 20°C. J. Eur. Ceram. Soc. 20, 497-503.*

Beruto, D.T., Vecchiattini, R and Giordani, M. (2003) Effect of mixtures of H_2O*(g) and* CO_2*(g) on the thermal half decomposition of dolomite natural stone in high* CO_2 *pressure regimes. Thermochim. Acta 405, 25-33.*

Beruto, D.T., Barberis, F. and Botter, R. (2005) Calcium carbonate binding mechanisms in the setting of calcium and calcium-magnesium putty-limes. J. Cultural Heritage, 6, 253-260

Boynton, R.S. (1980) Chemistry and Technology of Lime and Limestone, Wiley, New York.

Callebaut, K.; Elsen, J.; Van Balen, K.; and Viaene, W. (2001) Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium): Natural hydraulic lime or cement? Cement Concrete Res. 31, 397-403.

Cárdenas, A., Arguelles, W.M. and Goycoolea, F.M. (1998) On the possible role of Opuntia ficus-indica mucilage in lime mortar performance in the protection of historical buildings. J. Professional Assoc. Cactus Develop. 3, 1-7.

Cazalla, O., Rodríguez-Navarro, C., Sebastian E. and Cultrone, G. (2000) Aging of lime putty: effects on traditional lime mortar carbonation, J. Am. Ceram. Soc. 83, 1070– 1076.

Charola, A.E., Pühringer, J. and Steiger, M. (2007) Gypsum: a review of its role in the deterioration of building materials. Environm. Geology 52, 339–352.

Cizer, O., Rodríguez-Navarro, C., Ruiz-Agudo, E., Elsen, J., Van Gemert, D. and Van Balen, K. (2012) Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime. J. Mater. Sci. 47, 6151-6165.

Cotrim, H., Veiga, M.R. and Brito, J. (2008) Freixo palace: Rehabilitation of decorative gypsum plasters. Construction Building Mater. 22, 41-49.

Cowper, A.D. (1927). Lime and lime mortars. DSIR Special Report No. 9. Reprinted 1998 by Shaftesbury, Donhead Publishing.

Cultrone, G., Sebastian, E., and Ortega Huertas, M. (2005) Forced and natural carbonation of lime-based mortars with and without additives: Mineralogical and textural changes. Cement Concrete Res. 35, 2278-2289.

Davey, N. (1961) A History of Building Materials. London, Phoenix.

Doehne, E. and Price, C.A. (2010) Stone Conservation: An Overview of Current Research. Getty Conservation Institute, Los Angeles.

Edwards, H.G.M. and Farwell, D.W. (2008) The conservational heritage of wall paintings and buildings: an FT-Raman spectroscopic study of prehistoric, Roman, mediaeval and Renaissance lime substrates and mortars. J. Raman Spectrosc. 39, 985-992.

Elert, K., Rodríguez-Navarro, C., Sebastian, E., Hansen, E. and Cazalla, O. (2002) Lime mortars for the conservation of historic buildings. Studies Conservation 47, 62-75.

Elsen J. (2006) Microscopy of historic mortars — a review. Cement Concrete Res. 36, 1416–1424.

Faria, P., Henriques, F. and Rato, V. (2008) Comparative evaluation of lime mortars for architectural conservation. J. Cultural Heritage 9, 338-346.

Finlayson, B, Mithen, S.J., Najjar, M., Smith, S., Maricevic, D., Pankhurst, N. and Yeomans, L. (2011) Architecture, sedentism, and social complexity at Pre-Pottery Neolithic A WF16, Southern Jordan. PNAS 108, 8183–8188.

Foster, W. (1934) Grecian and Roman stucco, mortar, and glass. J. Chem. Edu. 11, 223-225.

Franzini, M., Leoni, L., Lezzerini, M. and Sartori, F. (1999) On the binder of some ancient mortars. Miner. Pretrology 67, 59-69

Freyer, D. and Voigt, W. (2003) Crystallization and phase stability of $CaSO_4$ and $CaSO_4$-based salts. Monatsh. Chem. 134, 693–719.

Furlan, V. (1991) Causes, mechanisms and measurement of damage to mortars, bricks and renderings. In Science, technology, and European cultural heritage. Proceedings of the European symposium. Bologna, Italy, 13-16 June 1989, 149-159.

Galwey, A.K. (2000) Structure and order in thermal dehydrations of crystalline solids. Thermochim. Acta 355, 181-238.

Gárate Rojas, I. (1994) Las Artes de la Cal (2ª Edición). Ministerio de Cultura-ICBRBC, Madrid.

Gartner, E.M. (2009) Cohesion and expansion in polycrystalline solids formed by hydration reactions - The case of gypsum plasters. Cement Concrete Res. 39, 289–295.

Ghorab, H.Y. Ragai J. and Antar A. (1986) Surface and bulk properties of ancient Egyptian mortars. Part I: X-ray diffraction studies. Cement Concrete Res. 16, 813-822.

Gillott, J.E. (1967) Carbonation of $Ca(OH)_2$ investigated by thermal and X-ray diffraction methods of analysis. J. Appl. Chem. 17, 185-189.

Goins, E.S. (2000) A new protocol for the analysis of historic cementitious materials: interim report. In International RILEM workshop on Historic Mortars: Characteristics and Tests, 71-79, RILEM, Cachan, France

Hansen, E.F., Rodríguez-Navarro, C. and Van Balen, K. (2008) Lime putties and mortars: Insights into fundamental properties. Studies Conservation 53, 9-23.

Haswell, C.H. (1865) Limes, cements, mortars and concretes. J. Franklin Institute 49, 361-367; 50, 171-175, 295-302.

Houben, H. and Guillaud, H. (1994) Earth Construction: A Comprehensive Guide. CRATerre-EAG, Intermediate Technology Publications, London.

Hawthorne, F.C., Krivovichev, S.V., and Burns, P.C. (2000), The crystal chemistry of sulfate minerals. Rev. Miner. Geochem. 40, 1-112.

Izaguirre, A., Lanas, J. and Alvarez, J.L. (2009) Effect of water-repellent admixtures on the behaviour of aerial lime mortars. Cement Concrete Res. 39, 1095-1104.

Izaguirre, A., Lanas, J. and Alvarez, J.L. (2010) Ageing of lime mortars with admixtures: durability and strength assessment. Cement Concrete Res. 40, 1081-1095.

Kawiak, T. (1991) Gypsum mortars from a twelfth-century church in Wislica, Poland. Studies Conservation 36, 142-150.

Kingery, W.D., Vandiver, P.B. and Prickett, M. (1988) The beginnings of pyrotechnology, part II: production and use of lime and gypsum plaster in the pre-pottery neolithic Near East. J. Field Archaeology 15, 219-244.

Lanas, J. and Alvarez J.I. (2003) Masonry repair lime-based mortars: Factors affecting the mechanical behavior. Cement Concrete Res. 33, 1867-1876.

Lanzón, M. and García-Ruiz, P.A. (2012) Effect of citric acid on setting inhibition and mechanical properties of gypsum building plasters. Construction Building Mater. 28, 506–511.

Lawrence, R.M., Mays, T.J., Rigby, S.P., Walker, P. and D'Ayala, D. (2007) Effects of carbonation on the pore structure of non-hydraulic lime mortars. Cement Concrete Res. 37, 1059-1069.

Lawrence, R.M. and Walker, P. (2008) The impact of the water/lime ratio on the structural characteristics of air lime mortars. In: D´Ayala & Fodde (eds), Structural Analysis of Historic Construction. Taylor & Francis Group, London, 885-889.

Lea, F.M. (1970) The Chemistry of Cement and Concrete, 3rd edn. Edward Arnold Ltd., London.

Le Chatelier, H (1887) Recherches expérimentales sur la constitution des mortier hydrauliques. Dunod, Paris.

Lucas, A. and Harris, J.R. (1962) Ancient Egyptian Materials and Industries. Edward Arnold, London.

Luxán, M.P. Dorrego, F. and Laborde, A. (1995) Ancient gypsum mortars from St. Engracia (Zaragoza, Spain): Characterization. Identification of additives and treatments. Cement Concrete Res. 25, 1765-1775.

Luxán, M.P. and Dorrego, F. (1996) Ancient XVI century mortar from the Dominican Republic: Its characteristics, microstructure and additives. Cement Concrete Res. 26, 841-849.

Malinowski, R. (1981) Ancient mortars and concretes. Durability aspects. Proceedings ICCROM Symposium. Rome, ICCROM, p. 341-349.

Malinowski, E. S. and Hansen T. S. (2011) Hot lime mortar in conservation - Repair and replastering of the facades of Lacko Castle. J. Architec. Conservation 17, 95-118.

Marchese, B. (1980) Non-crystalline calcium hydroxide in ancient non-hydraulic lime mortars. Cement Concrete Res. 10, 861-864.

Margalha, G., Viega, R., Silva, A.S, and Brito, J. (2011) Traditional methods of mortar preparation: The hot lime mix method. Cement Concrete Composit. 33, 796-804.

Maravelaki-Kalaitzaki, P., Bakolas, A. and Moropoulou, A. (2003) Physico-mechanical study of Cretan ancient mortars. Cement Concrete Res. 33, 651-661.

Maurenbrecher, A.H.P. (2004) Mortars for repair of traditional masonry. Practice Periodical Struct. Design Construct. 9, 62-65.

Matsuda, O. and Yamada, H. (1973) Investigation of the manufacture of building materials by carbonation hardening of slaked lime. Sekko to Sekkai 125, 170-179.

Melikhov I.V., Rudin V.N. and Vorob'eva L.I. (1991) Non-diffusive topochemical transformation of calcium sulphate hemihydrate into the dehydrate. Mendeleev Commun. 1, 33-34.

Mellaart, J. (1967) Çatal Hüyük: A Neolithic town in Anatolia. Thames & Hudson, London.

Mertens, G., Snellings R., Van Balen K., Bicer-Simsir B., Verlooy P. and Elsen J. (2009) Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity. Cement Concrete Res. 39, 233–240.

Moorehead, D.R. (1986) Cementation by the carbonation of Hydrated Lime, Cement Concrete Res. 16, 700–708.

Moropoulou A., Bakolas A. and Bisbikou, K. (1995) Characterization of ancient Byzantine and later historic mortars by thermal and X-ray diffraction techniques. Thermochim. Acta 269/270, 779–795.

Moropoulou, A., Tsiourva, T., Bisbikou, K., Bakolas, A. and Zendri, E. (1996) Hot lime technology imparting high strength to historic mortars. Construction Building Mater. 18, 151-159.

Moropoulou, A. Bakolas, A. and Anagnostopoulou, S. (2005) Composite materials in ancient structures. Cement Concrete Compos. 27, 295–300.

Ogino, T., Suzuli, T. and Kawada, K. (1987) The formation and transformation mechanism of calcium carbonate in water. Geochim. Cosmochim. Acta 51, 2757-2767.

Prasad, P.S.R., Chaintanya, V.K. Prasad, K.S. and Rao, N. (2005) Direct formation of the γ-CaSO4 phase in dehydration process of gypsum: In situ FTIR study. Am. Miner. 90, 672-678.

Putnis, A. (2009) Mineral replacement reactions. Rev. Miner. Geochem. 70, 87-124.

Ramachandran, V.S., Sereda, P.J. and Feldman, R.F. (1964) Mechanism of hydration of calcium oxide. Nature 201, 288-289.

Ray, K.W. and Mathers, F.C. (1928) The colloidal behaviour of lime. Ind. Eng. Chem. 20, 475-477.

Ridge, M.J. and King, G.A. (1976) A problem with hydrated lime. J. Appl. Chem. Biotechnol. 26, 742-746.

Regourd, M., Kerisel, J., Deletie, P., and Haguenauer, B. (1988) Microstructure of mortars from three Egyptian pyramids. Cement Concrete Res. 18, 81-90.

Riccardi, M.P., Duminuco, P., Tomasi, C. and Ferloni, P. (1998) Thermal, microscopic and X-ray diffraction studies on some ancient mortars. Thermochim. Acta 321, 207-214.

Rodríguez-Navarro, C. Hansen, E. and Ginell, W.S. (1998) Calcium hydroxide crystal evolution upon aging of lime putty, J. Am. Ceram. Soc. 81, 3032–3034.

Rodríguez-Navarro, C., Cazalla, O., Elert, K. and Sebastian, E. (2002) Liesegang pattern development in carbonating traditional lime mortars. Proc. R. Soc. Lond. A 458, 2261-2273.

Rodríguez-Navarro, C., Ruiz-Agudo, E., Ortega-Huertas, M., and Hansen, E. (2005) Nanostructure and irreversible colloidal behavior of $Ca(OH)_2$*: Implications in cultural* *heritage conservation. Langmuir 21, 10948-10957.*

Rodríguez-Navarro, C., Ruiz-Agudo, E., Luque, A., Rodríguez-Navarro, A. B. and Ortega-Huertas, M. (2009) Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals. Am. Mineral. 94, 578-593.

Rubio-Domene, R.F. (2006) El material de yeso: comportamiento y conservación. Cuadernos Restauración 6, 57-68.

Ruiz-Agudo, E. and Rodríguez-Navarro, C. (2010) Microstructure and rheology of lime putty. Langmuir 16, 3868-3677.

Sato, T., Beaudoin, J.J., Ramachandran, V.S., Mitchell, L.D. and Tumidajski, P.J. (2007) Thermal decomposition of nanoparticulate $Ca(OH)_2$ *– Anomalous effects. Adv. Cement Res. 19, 1-7.*

Sayre, E.V. (1976) Deterioration and restoration of plaster, concrete and mortar. In Preservation and Conservation: Principles and Practices, S. Timmons, ed., 191-201, Preservation Press, Washington, D.C.

Singh, N.B. and Middendorf, B. (2007) Calcium sulphate hemihydrate hydration leading to gypsum crystallization. Progr. Crystal Growth Charact. Mater. 53, 57-77.

Sipple, E,M., Bracconi, P., Dufour, P. and Mutin, J.C. (2001) Electronic microdiffraction study of structural modifications resulting from the dehydration of gypsum. Prediction of the microstructure of resulting pseudomorphs. Solid State Ionics 141–142, 455–461.

Smeaton, J. (1791) Narrative of the building and a description of the construction of the Eddystone Lighthouse. London.

Solberg, A. and Hansen, S. (2001) Dissolution of $CaSO_4{\bullet}1/2H_2O$ *and precipitation of* $CaSO_4{\bullet}2H_2O$*: A kinetic study by synchrotron X-ray powder diffraction. Cement Concrete Res. 31, 641-646.*

Teutonico, J.M., McCaig, I., Burns, C. and Ashurst, J. (1994) The Smeaton project: Factors affecting the properties of lime-based mortars. APT Bull. 25, 32-49.

Toniolo, L., Paradisi, A., Goidanich, S. and Pannati, G. (2011) Mechanical behaviour of lime based mortars after surface consolidation. Contruct. Building Mater. 25, 1553-1559.
Triollier, M. and Guilhot B. (1976) The hydration of calcium sulphate hemihydrate. Cement Concrete Res. 6, 507-514.

Tuncoku, S.S. and Caner-Saltik, E.N. (2006) Opal-A rich additives in ancient lime mortars. Cement Concrete Res. 36, 1836-1893

Van Balen, K. and Van Gemert, D. (1994) Modeling lime mortar carbonation. Mater. Struct. 27, 393-398.

Van Balen, K. (2005) Carbonation reaction of lime, kinetics at ambient temperature. Cement Concrete Res. 35, 647-657.

Van Driessche, A.E.S., Benning, L.G., Rodríguez-Blanco, J.D., Ossorio, M., Bots, P. and García-Ruiz, J.M. (2012) The role and implications of bassanite as a stable precursor phase to gypsum precipitation. Science 336, 69-72.

Vaniman, D.T. and Chipera, S.J. (2006) Transformations of Mg- and Ca-sulfate hydrates in Mars regolith. Am. Miner. 91, 1628-1642.

Venice Charter (1964) International Charter for the conservation and restoration of monuments and sites, Venice, 1964,http://www.icomos.org/docs/venice_charter.html).

Vicat, L.J. (1837) A practical and scientific treatise on calcareous mortars and cements, artificial and natural. John Weale, London.

Vitruvius, P. (30 BC), The Ten Books on Architecture (Traslation by M.H.Morgan 1960). Dover Publications, New York.

Von Landsberg, D. (1992) The history of lime production and use from early times to the Industrial Revolution. ZKG 45, 199-203.

Wolter, A., Luger, S. and Schaefer, G. (2004) The kinetics of the hydration of quicklime. ZKG Int. 57, 60-68.

Yang, F., Zhang, B. and Ma, Q. (2010) Study of sticky rice_lime mortar technology for the restoration of historical masonry construction. Acc. Chem. Res. 43, 936–944.

Zanco, A. (1994) Identification of vaterite, metastable $CaCO_3$ *phase, inside the Eremitani Church, in Padua. Sci. Technol. Cultural Heritage 3, 135-137.*

Seminarios 09. SEM

Archaeometry and Cultural Heritage: the contribution of Mineralogy

Sociedad Española de Mineralogía

SEM

Sociedad Española de Mineralogía
Museo Geominero del Instituto Geológico y Minero de España
c/ Calle de Ríos Rosas, 23
28003 Madrid

patrocinadores y entidades colaboradoras:

SEM

eman ta zabal zazu
UPV EHU

EUSKO JAURLARITZA
GOBIERNO VASCO

Thermo SCIENTIFIC

EVE Ente Vasco de la Energía

ZTF-FCT
Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

BilbaoTurismo