

# Historic Concrete Science: *Opus Caementicium* to “Natural Cements”

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**The history of mineral components in cementitious materials begins with clays and bitumen in the most ancient mortars, followed by gypsum- and lime-based plasters, mortars, and concretes. Romans perfected the fabrication of extremely durable mortars that form the basis of audacious architectural monuments in Rome, massive harbor constructions, and water-proofed cisterns in the Mediterranean region. During the industrial revolution, “natural cements” were developed through the burning of impure limestone or Si- and Al-bearing materials blended with pure limestone. Delving into the past of concrete science and the composition, durability, and resilience of historic binders, mortars, and concretes can inspire the development of modern environmentally friendly cementitious materials.**

**KEYWORDS:** ancient Roman concrete; lime mortars; hydraulic binders; carbonation; pozzolans

## ANCIENT AND HISTORIC CEMENTITIOUS MATERIALS

A variety of geologic binding materials have been used in ancient and historic plasters, mortars, and concretes (FIG. 1). The oldest types, clays and bitumen, were readily available in some geologic environments. Others required heating and subsequent mixing with water before application. The use of gypsum-based binders (hemihydrate:  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) has some advantages over lime-based plaster in that they are much cheaper to process because of the lower calcining temperature and the much shorter burn time. Both gypsum and lime binders and mortars harden in air. A next step was the manufacture of “hydraulic binders” through the mixing of hydrated lime with pozzolans. In modern concrete terminology, a pozzolan is a material that reacts with lime in the presence of moisture to produce durable cementing hydrates (Massazza 1998). “Hydraulic” refers to the ability of the cementitious material to harden in water, but not all lime-pozzolan mortars were used in hydrologic settings. The hydrated lime–volcanic pozzolan mortars of Roman concrete were commonly known as *opus caementicium* or “aggregate work” (Brandon et al. 2014). More recent hydraulic binders are produced through the burning of impure limestone, or through the mixing of Si- and Al-bearing materials with pure, high-calcium limestone that are then burnt together. Here, mineralogical

and chemical processes in the lime cycle are reviewed and an overview is given of the methods used to identify and measure the “hydraulicity” of ancient and historic mortars.

## Historical Development of (Hydraulic) Lime Mortars

Mortars with geologic binder materials have been used since ancient times in diverse applications. These have surprisingly large compositional variations with great differences arising geographically and over time (FIG. 1). The deliberate incorporation of reactive volcanic

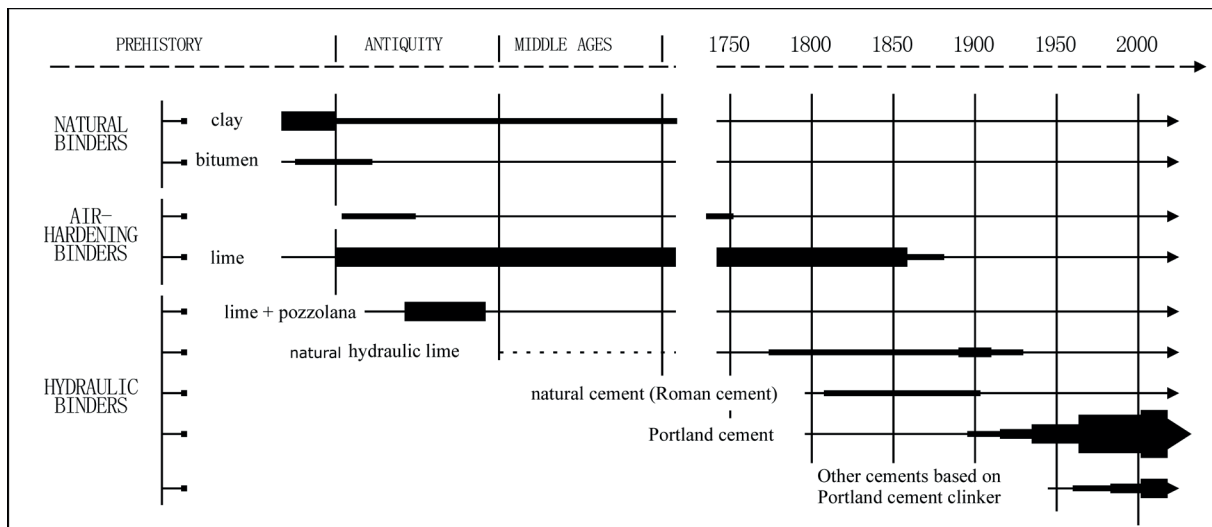
tephra (and tuff) with hydrated lime (composed mainly of portlandite,  $\text{Ca}(\text{OH})_2$ ) produced pozzolanic binding phases and resilient cementitious materials, often with hydraulic properties. Greeks used tephra and tuff from the island of Thera, also known as Santorini (Moropoulou et al. 2005). Romans used reactive tephra from the central Italian volcanic districts in the mortars of late Republican and Imperial era conglomeratic concretes. Some of these materials were designed to have hydraulic properties, as marine harbor structures (Brandon et al. 2014) and water-proofing coatings of cisterns and aqueducts (Secco et al. 2020); others were designed for mechanical resilience in the supporting walls and vaulted ceilings of architectural monuments (Jackson et al. 2014).

If impure limestone (e.g., containing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ) is calcined without any additions, the resulting product is called a natural hydraulic binder. If the limestone is blended with other components before firing, the product is called an artificial binder. Romans advised using pure limestone for the production of lime (*de Architectura* 2.6.3) to further activate reactions with pozzolanic aggregates that produce calcium-aluminum-silicate-hydrate (C-A-S-H) binding phases. Investigations of geologic binding materials by John Smeaton in 1756 led to the discovery that lime calcined from impure limestone produced the best results in cement-based mortars. By dissolving limestone in nitric acid, he obtained an insoluble residue of quartz and clay-rich material to which he attributed hydraulicity, the property of limes and cements to set and harden underwater. The French engineer Collet Descotils in 1813 related these properties to the presence of silica. He stated that an intimate combination of silica with lime is produced when these limes are slaked, or hydrated. The first attempt to classify hydraulic binders was made by Louis Vicat in 1818, who introduced the hydraulicity index (HI).

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**FIGURE 1** Evolution since prehistorical times of the different types of binders and their relative importance. MODIFIED FROM FURLAN AND BISSEGER (1975).

$$HI = \frac{SiO_2 + Al_2O_3}{CaO} \quad (1)$$

In this formula, Vicat directly related hydraulicity to the  $SiO_2$  and  $Al_2O_3$  contents. However, equal importance was incorrectly attributed to these two constituents;  $Fe_2O_3$  and  $MgO$  were later found to also influence hydraulicity. An adapted formula for the cementation index (CI) was therefore developed about a century later by Edwin Eckel (2005).

$$CI = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{CaO + 1.4 \times MgO} \quad (2)$$

The cementation index was conceived to be a direct expression of the quantity of  $CaO$  that combines with the other constituents to form hydraulic minerals. Eckel emphasized that the properties of hydraulic binders depend not only on their composition (CI) but also on the conditions of their manufacture. These are indirectly related to burning temperature and time, which influence the mineral assemblage of the resulting product (Mertens et al. 2009).

**Natural cement.** In the late 18<sup>th</sup>-century, James Parker discovered that the calcination of clay deposits with septaria (nodules or concretions containing both clay and carbonate minerals) on the Isle of Sheppey, UK, produces an effective hydraulic binder. He called this “Roman cement” and obtained a patent in 1796. The name Roman cement is misleading, however, and was erroneously used to claim the rediscovery of ancient Roman “secrets” of lime production (Artioli et al. 2019 and references therein). In 1802, septaria were also found in clay deposits near Boulogne-sur-Mer in France. Elsewhere in France, analogous hydraulic binders were produced in Pouilly-en-Auxois and Vassy-les-Avallon beginning in 1827 and in the Bourgogne region beginning in 1835. Soon after, a natural cement production site arose near Grenoble in 1842 using a homogeneous layer of argillaceous limestone called the Filon de Porte de France.

In the 19<sup>th</sup> century, chemical analyses revealed the composition of cements in terms of their major element components; however, there were no means to identify the constituent minerals. Knowledge of cement mineralogy was gradually refined through studies with petrographic microscopy. In the beginning of the 20<sup>th</sup> century, it was observed that at lower temperatures, alumina combines with decarbonated lime to form  $C_3A$ , while at higher

temperatures, alumino-ferrites of lime ( $C_4AF$ ) and  $C_2S$  form. In current quick-setting cements, the main silicate is  $C_2S$  and the main aluminates are  $C_3A$  and  $C_4AF$ . Other components are  $C_3S$ , calcite, and spurrite ( $Ca_5(SiO_4)_2CO_3$ ), as well as  $C_{12}A_7$  and  $C_2AS$ . Slow-setting natural cement binders are produced by calcining naturally occurring argillaceous/siliceous limestone that is subsequently ground to a fine powder.

**Hydraulic lime.** Hydraulic limes contain enough free  $CaO$  to be slaked with water; they can set underwater. By contrast, “air lime” is the general term for calcium oxide ( $CaO$ ), or quicklime, that is slaked with water but sets through re-absorption of  $CO_2$  from the atmosphere. The combination of free lime with water induces an expansion that leads to the disintegration of the freshly burnt limestone. A minimum amount of free lime must be present in the calcined product to reduce the entire mass to a powder when slaked (Eckel 2005). A large range of products complies with this definition. These products are most commonly classified according to their chemical composition and more specifically their CI (Eq. 2) or HI values (Eq. 1). Nowadays, the mechanical strength of the hardened product is also used for classification. The advantage of hydraulic lime as compared with Portland cement is its low cost. However, the slow hardening and lower tensile strength of the resulting mortars and concretes have reduced production at the expense of Portland cement.

## ROMAN ARCHITECTURAL AND MARINE CONCRETES PREPARED WITH HYDRATED LIME AND VOLCANIC POZZOLANS

Ancient Roman concretes (*opus caementicium*) are composed of conglomeratic rock (*caementa*) bound by a complex binding material (*materia*) fabricated with hydrated lime and reactive aggregate, as described by the Roman architect, Vitruvius, in 27–30 BCE (*de Architectura* 2.4.1). The binding material is commonly known as a “pozzolanic mortar,” referring to the Bay of Pozzuoli source region for pumiceous tephra aggregate (*pulvis puteolanus*) quarried for marine concrete structures (*de Architectura* 2.6.6). The mortars for architectural concrete structures used excavated sands (*harenae fossicae*) as scoriaceous tephra aggregate, quarried from volcanic districts near Rome (*de Architectura* 2.4.1). Vitruvius described the intensive activating potential of quicklime using analogies with pyroclastic volcanic eruptions: “through violent fire, moisture is snatched from the tuff and the earth in the same way in which in the furnace liquid is snatched from the lime” (*de Architectura* 2.6.3). When the lime, tephra, and *caementa* “come into

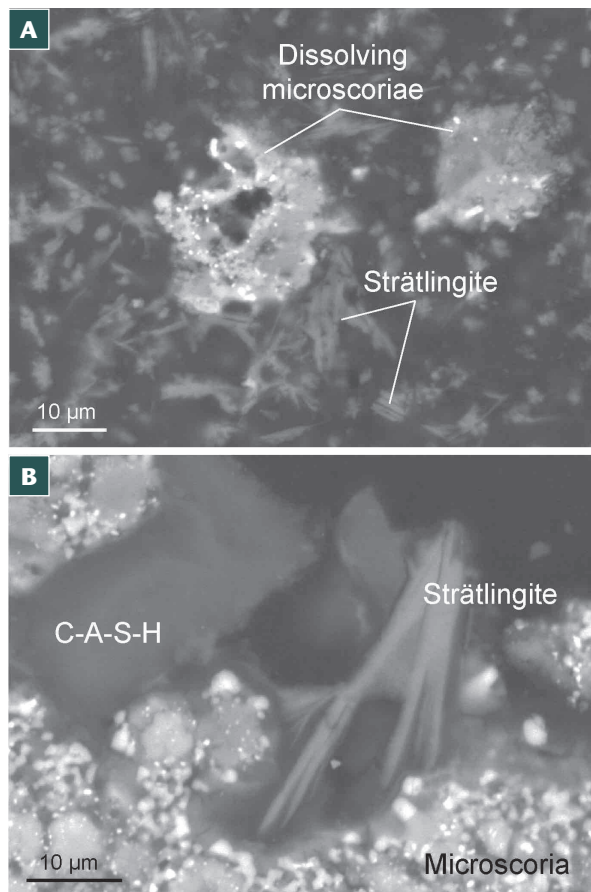


one mixture, they suddenly cohere into one [substance] by accepting liquid and quickly solidify" (*de Architectura* 2.6.1).

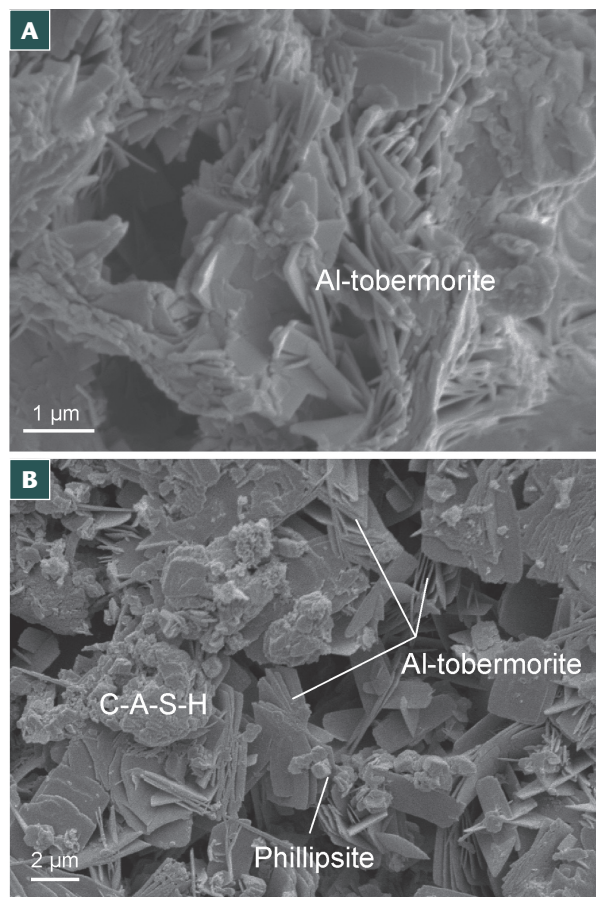
A recent replica of the mortar of the wall concrete of the Markets of Trajan (110 CE) uses reactive tephra aggregate from the mid-Pleistocene Pozzolane Rosse (and Tufo Lionato) pyroclastic flows (Jackson et al. 2014) and high-calcium quicklime similar to that of the Monte Soratte region northeast of Rome (*de Architectura* 2.5.1; Fichera et al. 2015). A pozzolanic, poorly crystalline C-A-S-H binding phase and hydrotalcite mineral cements formed at 28 days of hydration. By 90 days of hydration, however, the hydrated lime (portlandite) was fully consumed. The cementing system had transitioned to post-pozzolanic processes that produced hydrogarnet (katoite) and strätlingite ( $\text{Ca}_2\text{Al}_2(\text{SiO}_2)(\text{OH})_{10} \cdot 2.25(\text{H}_2\text{O})$ ), a durable, layered crystal with acicular and platy morphologies. The strätlingite crystals toughen interfacial zones and create obstacles to the propagation of microcracks (FIG. 2), increasing the energy required to fracture the mortar (Jackson et al. 2014).

Roman marine concretes, fabricated with reactive pumiceous aggregate from the Bay of Pozzuoli and hydrated lime (Brandon et al. 2014), also began with pozzolanic activation, which produced a C-A-S-H binding phase and an unusual layered crystal, Al-tobermorite, of similar composition ( $\text{Ca}/(\text{Si} + \text{Al}) = 0.79$ ) in relict lime clasts (Jackson et al. 2013). Post-pozzolanic interactions of the tephra with alkaline fluids in the massive harbor structures then produced zeolite (phillipsite) and Al-tobermorite

crystals that refine pore space in the cementing matrix of the concrete (Jackson et al. 2017) (FIG. 3). The post-pozzolanic Al-tobermorite has more siliceous compositions ( $\text{Ca}/(\text{Si} + \text{Al}) = 0.45\text{--}0.69$ ), similar to crystals in young basalt at Surtsey Volcano, Iceland. Romans mainly selected high-calcium lime for the pozzolanic activation of the marine concretes (Brandon et al. 2014). They relied on the beneficial reactivity of tephri-phonolitic pumiceous aggregate with zeolite surface coatings from the Gulf of Naples (de'Gennaro et al. 2000) and transported this throughout the eastern Mediterranean region (Brandon et al. 2014) to produce long-term beneficial reactivity and post-pozzolanic mineral cements.



**FIGURE 2** Scanning electron microscopy images of the mortar of a concrete substructure of the Markets of Trajan (~110 CE). (A) Strätlingite crystals and microscoriae in the cementing matrix of the mortar. (B) Partially dissolved calcium-aluminum-silicate-hydrate (C-A-S-H) binding phase and strätlingite crystals in the reactive interfacial zones of the scoria aggregate.



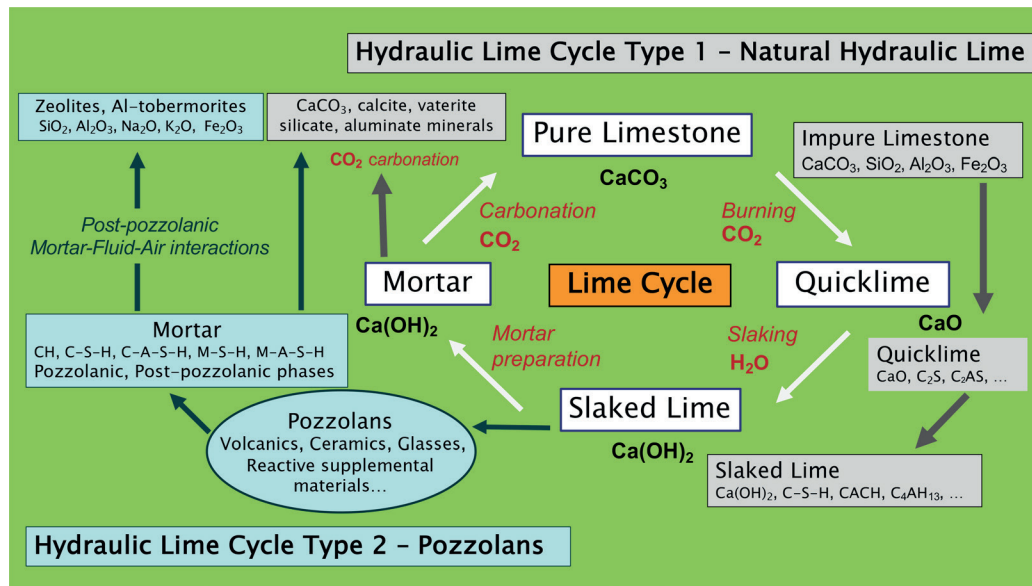
**FIGURE 3** Scanning electron microscopy images of a Roman marine mortar, *Baianus Sinus* breakwater (late 1<sup>st</sup> century BCE). (A) Pozzolanic Al-tobermorite in a relict lime clast. (B) Post-pozzolanic Al-tobermorite and phillipsite in the cementing matrix along with poorly crystalline pozzolanic C-A-S-H binder.

Recent investigations of the renders, or waterproofing coatings, of cisterns at the archaeological site of Nora, Sardinia (3<sup>rd</sup>–1<sup>st</sup> centuries BCE) (Secco et al. 2020), and at Amaiur Castle, Navarre (13<sup>th</sup>–17<sup>th</sup> centuries CE) (Ponce-Antón et al. 2020), provide new insights into the role of magnesium in ancient pozzolanic systems. The renders of the Nora cisterns contain organic matter combustion residues as charcoal frustules of the cell walls of wood and as bone residues with hydroxyapatite. X-ray diffraction analyses of renders containing magnesium-rich ground ceramic (cocciopesto) and combustion residues show broad reflections indicative of a nanocrystalline disordered magnesium-silicate-hydrate (M-S-H) and/or magnesium-aluminum-silicate-hydrate (M-A-S-H) binding phase that accompanies calcium-rich pozzolanic reaction products (Secco et al. 2020). The mortar and plaster coatings of the

Amaïur Castle cistern contain hydrotalcite, a magnesium–aluminum carbonate ( $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$ ), which formed during pozzolanic reactions with lime produced from impure or partially dolomitized limestone. Amesite, a magnesium aluminosilicate ( $\text{Mg}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$ ), formed during alkali–silica reactions in mortars containing siliceous aggregates, schists, and volcanic rocks (Ponce-Antón et al. 2020). The magnesium-rich binding phases presumably decrease the porosity and increase the chemical resilience in the waterproofing systems of the ancient cisterns.

## MINERALOGICAL UNDERSTANDING OF THE LIME CYCLE

The mineralogical and chemical processes of lime hydration and carbonation that take place over time are described by the lime cycle (FIG. 4), which illustrates the intriguing concept of starting and ending with carbonate minerals ( $\text{CaCO}_3$ ), or limestone. Two distinct types of reaction processes occur in the more complex hydraulic lime cycle.



**FIGURE 4** Conceptual drawing of the lime cycle showing slaking and aerial carbonation of lime from pure limestone (white), slaking and hydration of impure limestone to form a natural hydraulic binder (gray), and slaking and hydration of lime mixed with pozzolans to produce pozzolanic and post-pozzolanic binding phases (blue).

### Limestone Calcination and Hydraulicity

The first step of the lime cycle involves the thermal decomposition of carbonates into oxide(s) with the release of  $\text{CO}_2$  (Rodríguez-Navarro et al. 2009, 2012). Thermal decomposition of calcite is known to be homogeneous and topotactic (a chemical solid-state reaction within a crystal lattice in which the structure of the products is related to that of the reactants by crystallographic relationship(s)) (FIG. 5A), producing a transformation within the crystal lattice that involves the displacement or exchange of atoms (Rodríguez-Navarro et al. 2009). The decomposition of dolomite is also a topotactic reaction. The reaction occurs with the initial formation of a face-centered cubic, mixed oxide ( $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}$ ), which undergoes demixing into oriented, Mg-poor CaO and Ca-poor MgO crystals. Subsequently, pure CaO and MgO crystals form during coarsening via oriented aggregation and sintering. CaO nanocrystals react with  $\text{CO}_2$  present in the air and/or released upon further

dolomite decomposition, resulting in the formation of Mg-calcite (Rodríguez-Navarro et al. 2012).

In the case of hydraulic lime binders, a second set of processes occurs simultaneously. Clay minerals contained in the limestone first lose interlayer or adsorbed water at 100–250 °C and then dehydroxylate at temperatures >300–400 °C. Above about 900 °C, they transform into new crystalline phases, typically Al–Si spinel, cristobalite, or mullite. Quartz experiences a polymorphic transition to beta-quartz at 573 °C, which is unstable relative to tridymite at 867–1470 °C, and to cristobalite above 1470 °C (Taylor 1997). The Si and Al oxides that form upon heating react with calcium (and magnesium) oxides, leading to the formation of silicates and aluminates that confer hydraulicity to the cementitious binding phases. Beta-dicalcium silicate ( $\beta\text{-C}_2\text{S}$ ) is the main hydraulic phase component. Tricalcium silicate ( $\text{C}_3\text{S}$ ) occurs as a minor phase because its formation requires higher temperatures (Taylor 1997). The first aluminate phase that forms is monocalcium aluminate (CA). The aluminate,  $\text{C}_{12}\text{A}_7$ , begins to appear at 800–1000 °C and then transforms into  $\text{C}_3\text{A}$ . Such  $\text{C}_3\text{A}$

may form at >850 °C but appears more frequently at 1000–1200 °C. Some authors have reported the formation of gehlenite ( $\text{C}_2\text{AS}$ ) as an intermediate phase at 800–1200 °C. Provided enough iron is present in the raw materials, ferrite ( $\text{C}_4\text{AF}$ ) phases form at 950–1000 °C, initially with low Al/Fe ratios (Taylor 1997). Large differences in the temperature of occurrence of the individual phases are reported, mainly related to the numerous factors that may influence these heterogeneous reactions, including grain size, homogenization degree of the raw material, or the presence of other impurities.

### Lime Hydration and Formation of Portlandite

The next step of the lime cycle involves a slaking process in which water is added to the lime, whose hydration leads to the formation of portlandite. Two different mechanisms have been proposed for this reaction. One involves direct precipitation of portlandite from the solution formed during slaking of the lime (Ruiz-Agudo and Rodríguez-Navarro 2010). A second hydration pathway occurs as a solid-state reaction between solid CaO and water, which vaporizes under heat released during reaction and subsequently reacts with solid CaO. Beruto et al. (1981) hypothesized that vapor-phase hydration of lime is a pseudomorphic reaction that leads to the topotactic formation of portlandite. This was experimentally demonstrated by Kudlacz and Rodríguez-Navarro (2014), who showed that this reaction progresses via an intermediate disordered phase prior to the final formation of oriented portlandite nanocrystals (FIG. 5B).

If the stoichiometric amount of water is mixed with lime oxide, the product is a dry powder (a dry hydrate). If an excess of water is added, an aqueous dispersion of hydroxide particles (a lime paste or lime putty) is formed. Lime prepared by this last process is traditionally called “slaked lime” (FIG. 4).



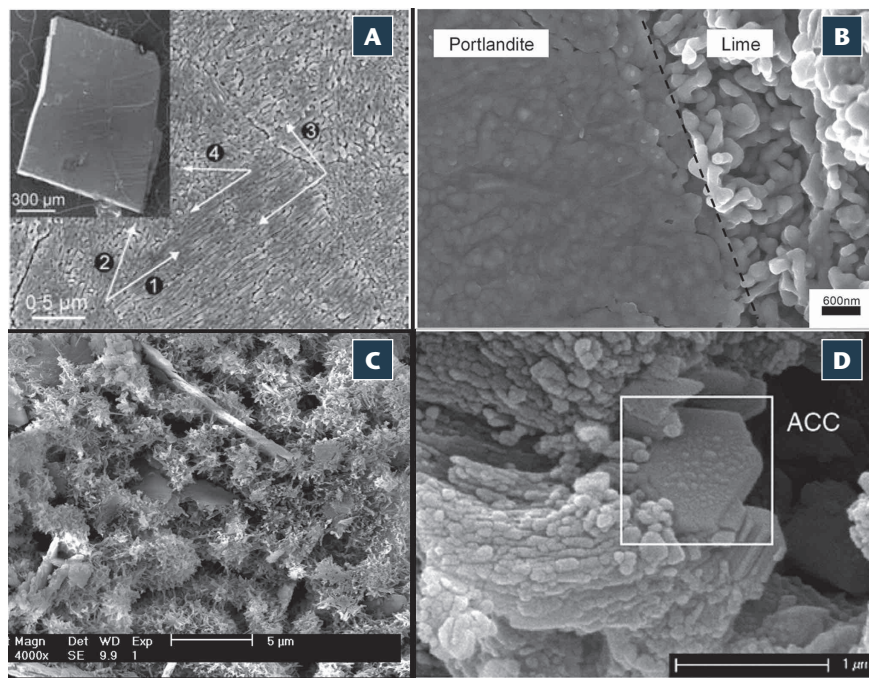
Rodriguez-Navarro et al. (2005) showed that in the case of a dry hydrate, oriented aggregation is responsible for the significant reduction of surface area and reactivity, which also results in degradation of the rheological properties (Ruiz-Agudo and Rodriguez-Navarro 2010). By contrast, an excess of water present during traditional lime slaking hinders the irreversible aggregation of particles in lime putties. This explains why lime putties tend to show better rheological properties and are the preferred choice for conservation purposes. The properties of slaked lime can be improved when lime putties are kept underwater. This process of aging has been in practice since Roman times (*de Architectura* 7.2.1-2), although the mechanisms at play were not demonstrated until recently. Rodriguez-Navarro et al. (1998) reported higher amounts of smaller plate-like portlandite particles in lime putties aged several months compared with freshly slaked pastes. This results in an increase in the surface area, reactivity, viscosity, and plasticity of the putty. The microstructural characteristics of the lime oxide precursor also have a significant effect on the rheological evolution of slaked lime putties (Ruiz-Agudo and Rodriguez-Navarro 2010).

For hydraulic lime, the addition of water results in hydration to produce calcium silicate and aluminate phases. This represents the first hardening phase of hydraulic lime binders driven by  $\beta$ -C<sub>2</sub>S. Similar to the hydration of C<sub>3</sub>S, it produces portlandite and a poorly crystalline calcium-silicate-hydrate (C-S-H) phase that has a layered structure (FIG. 5C) with pores from nanometer to macroscopic dimensions (Taylor 1997). Although the rate of  $\beta$ -C<sub>2</sub>S hydration is substantially lower than that of C<sub>3</sub>S, there is consensus that both reactions share a common mechanism.

### Carbonation of (Hydraulic) Lime Mortars

The final stage of the lime cycle is carbonation, which involves the reaction of hydroxide(s) with CO<sub>2</sub> from the atmosphere in the presence of an aqueous phase. Carbonation is an exothermic process that proceeds from the surface into the pore system at a rate controlled by drying, CO<sub>2</sub> diffusion, CO<sub>2</sub> and calcium hydroxide dissolution in the pore water, and nucleation and growth of calcium carbonate, thus completing the cycle. The setting and hardening of lime mortars start with drying and shrinkage, followed by the precipitation of calcium carbonate, which acts as a binding mineral phase. Calcium-silicate-hydrate (C-S-H) binding phases may also eventually react with CO<sub>2</sub> or CO<sub>3</sub><sup>2-</sup> ions, producing CaCO<sub>3</sub> and hydrous silica (Taylor 1997). The CaCO<sub>3</sub> mineral phase, morphology, and microstructural features, and its evolution as carbonation progresses, are all key parameters influencing the physico-mechanical properties and performance of lime mortars (Cizer et al. 2012a and references therein).

Carbonation of lime mortars begins with the formation of amorphous calcium carbonate on portlandite crystals, followed by its dissolution and re-precipitation as scalenohedral calcite (FIG. 5D). With longer exposure time, calcite



**FIGURE 5** Scanning electron microscopy images of mineral changes during the lime cycle. (A) Porous CaO crystals formed after calcite (see pseudomorph in inset); preferred orientations indicated with arrows. REPRODUCED FROM RODRIGUEZ-NAVARRO ET AL. (2009) WITH PERMISSION FROM AMERICAN MINERALOGIST. (B) Partially hydrated calcite pseudomorph (calcined at 900 °C) showing the lime and portlandite interface (dashed black line). REPRODUCED FROM KUDLACZ AND RODRIGUEZ-NAVARRO (2014) WITH PERMISSION FROM THE AMERICAN CHEMICAL SOCIETY. (C) Calcium-silicate-hydrate (C-S-H) matrix formed through hydration of hydraulic lime binder. REPRODUCED FROM CIZER ET AL. (2006) WITH PERMISSION FROM RILEM. (D) Lime paste after carbonation in air showing amorphous calcium carbonate (ACC) precipitated on the basal face of the portlandite crystals. REPRODUCED FROM CIZER ET AL. (2012A) WITH PERMISSION FROM SPRINGER NATURE.

at the exposed surface evolves to scalenohedra with cracks and dissolution features along the carbonation profile and to scalenohedra with smooth faces farther from the surface. Scalenohedra transform to rhombohedra via dissolution-precipitation reactions resulting from the pH drop occurring upon Ca(OH)<sub>2</sub> consumption and further CO<sub>2</sub> dissolution into the pore water (Cizer et al. 2012a).

The CaCO<sub>3</sub> polymorphs (calcite, aragonite, or vaterite) formed during carbonation, as well as their morphology, size, and phase evolution, are governed by the properties of the portlandite crystals and the carbonation conditions. These include the relative humidity, which controls the pore water content and drying rate, and pCO<sub>2</sub>, which determines the pH and solution speciation. In this sense, lime putties carbonate faster than dry hydrates because of the differences in the morphology of the portlandite crystals. High relative humidity and pCO<sub>2</sub> conditions favor carbonation and the scalenohedral-to-rhombohedral transformation (Cizer et al. 2012b).

### Hydration of Pozzolan-Lime Mortars

Mortars and concretes fabricated from lime and sand-to gravel-sized reactive aggregates—such as volcanic rocks, waste ceramics, artificial tephra with tailored glass compositions, and/or diverse supplemental admixtures and organic materials—hydrate through the pozzolanic reactions among lime, silica, alumina, and alkali cations that produce durable binding hydrates (Massazza 1998); magnesium may also participate in these reactions (Ponce-

Antón et al. 2020; Secco et al. 2020) (FIG. 4). After calcium hydroxide is fully consumed, the pH of the system decreases. Alkali-activated dissolution–precipitation reactions may ensue, which produce post-pozzolanic mineral cements. These are zeolites, strätlingite, and siliceous Al-tobermorite in ancient Roman concretes (Jackson et al. 2014, 2017) and amesite, for example, in historic waterproofing mortars (Ponce-Antón et al. 2020). The reactive aggregate becomes a reservoir for the long-term beneficial production of silicate mineral cements, rather than the damaging alkali–silica gel of Portland cement concretes (Taylor 1997).

## CHARACTERIZING HISTORIC BINDERS

There are conflicting ideas and perceptions about the technological knowledge and practices in the Middle Ages concerning the deliberate use of natural hydraulic lime. Studies of a 16<sup>th</sup>-century dockyard in Venice (Italy) indicate the deliberate use of a hydraulic lime binder for foundations but not for indoor masonry (Biscontin et al. 2002). Mortars were apparently deliberately made with natural hydraulic lime in Ottoman baths in Budapest (Hungary) during the same period (Pinter et al. 2009). During the Renaissance, ancient techniques of mortar manufacture and raw material choice were reassessed (Moropoulou et al. 2005), indicating an intentional selection of hydraulic limes prepared from impure limestones.

Research challenges involve the characterization of the hydraulicity of ancient and historic mortars and the provenance identification of the source limestone. Chemical analysis of the mortar is useful to determine the hydraulicity, which can be deduced from microscopic observations only in rare cases. However, the main difficulty resides in separating the binding phase(s) from the other mortar constituents (Arizzi and Cultrone 2021). Generally, this is achieved by dissolving a part of the mortar, or a previously disaggregated fraction of the mortar, in dilute acid. Middendorf et al. (2004) introduced a standardized methodology in an attempt to establish uniformity in the procedure for the chemical analysis of binders. The HI (Eq. 1) and CI (Eq. 2) values are calculated from the abundances of major elements in the bulk mortar composition. This method should correctly assess the bulk chemistry of the binding phase(s), while microprobe analyses provide fine-scale information about points or areas in the binding phase or cementing matrix, including information about cementing mineral phases. The main limitation is that volatile components, such as CO<sub>2</sub> and H<sub>2</sub>O, cannot be measured. Additional information can be obtained through powder X-ray diffraction analyses of specific mortar fractions, data that complement the results of petrographic studies and chemical analyses. The presence of hydrated calcium silicates or aluminates point toward the use of hydraulic lime. Thermogravimetric analyses appear to be useful for calcareous binders (Arizzi and Cultrone 2021) to distinguish between hygroscopic water, water from hydrated salts, loss of water bound to hydraulic compounds, and loss of CO<sub>2</sub> (>600 °C). Samples with high amounts of water bound to hydraulic compounds and proportionally low amounts of CO<sub>2</sub> are considered to have hydraulic properties. It is difficult, however, to determine whether the hydraulicity of a cementitious material is induced by the addition of supplementary materials and/or reactive aggregates or by the use of natural hydraulic lime. Finally, analyses of relicts of lime particles—underburned or overburned lime fragments and lime lumps *sensu stricto*—have proved to be a powerful method to determine the hydraulicity and provenance of limestone (Elsen 2006) because the chemistry of these particles is expected to be identical to that of the limestone used to

prepare the lime (Fichera et al. 2015). Other binder-related particles are considered to be partly sintered particles formed in traditional kilns where temperatures in hot zones were sufficient to initiate fusing or sintering of the lime. Mineralogical analyses of overburnt fragments can provide information about maximum burning temperatures. The most commonly observed binder-related particles, the lime lumps *sensu stricto*, are often distinct, rounded, porous structures in the matrix of the cementitious material, indicating that the lime was dry-slaked with the minimum amount of water needed to convert all of the CaO into Ca(OH)<sub>2</sub>.

## CONCLUSIONS

Ancient and historic mortars and concretes used a wide range of geologic binding materials, giving rise to broad compositional variations over diverse geographical and chronological domains. Binders derived from burning limestone show many variations in the lime cycle. These are the processes through which quicklime is hydrated and reacts with impurities in the lime, with pozzolans, interstitial fluids in the cementitious materials, and carbon dioxide in the atmosphere, to produce a range of silicate and aluminate phases, as well as the calcium carbonate phases of limestone rocks. Calcination of limestone is a solid-state reaction that follows a topotactic mechanism, or structural change in the calcium carbonate mineral lattice, to produce crystallographically equivalent, orientational relationships in the resulting lime (CaO). Hardening and setting involve hydration in the case of hydraulic “impure” limes and/or carbonation in the case of aerial “pure” limes. Mechanistically, this may involve the precipitation of silicate or carbonate minerals from solution, a solid-state reaction, or pseudomorphic coupled dissolution–precipitation processes. By contrast, the interactions of hydrated pure (or impure lime) with reactive aggregates produces pozzolanic calcium-(aluminum)-silicate-hydrate phases and post-pozzolanic mineral cements, as in ancient Roman concretes. The properties of the original geologic binding materials determine the properties of the reaction products and, thus, influence the performance of ancient, historic, and conservation lime mortars; each step of the lime cycle influences the properties of the final material. The chemical and mineralogical characterization of lime particles in ancient and historic mortars provides information on the hydraulic character, nature, and provenance of geologic binding materials, as well as the technologies used in lime production and mortar preparation. A plethora of recent research projects are bringing new insight into the composition and durability of historic binders, mortars, and concretes, showing how delving into the past of concrete science can inspire the development of modern environmentally friendly cementitious materials.

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