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5 Role of hydrotalcite-type layered double hydroxides in delayed pozzolanic reactions and their bearing on mortar dating

Abstract: Double-layer hydroxide minerals are part of a very interesting group of natural and synthetic compounds with trigonal or hexagonal symmetry and a flexible layered crystal structure. They are formed extremely frequently in geologic, industrial, and synthetic processes. The ease of formation is related to the possibility of accommodating divalent and trivalent cations in the structure, together with a range of anionic species. Some compounds of the group, namely those based on hydrotalcite chemistry, are invariably found as products of the pozzolanic reaction between lime and clays in ancient mortars and modern binders that serve as alternatives to Portland clinker. The present review wishes to relate the structural properties of hydrotalcite-type compounds to the crystal-chemical mechanisms taking place during long-term pozzolanic processes. The kinetics of CO₂ exchange between the hydroxide and the atmosphere has important negative consequences for the radiocarbon dating of ancient mortars.

Keywords: layered double hydroxides, LDH, hydrotalcite, ancient mortars, pozzolanic reaction

5.1 Introduction

A large number of layered double hydroxides (LDH) share common crystal-chemical and structural features, based on simple di- and tri-octahedral layers, commonly referred to in the mineralogical literature as gibbsite- and brucite-type octahedral layers. Their importance is related to their frequency of formation and widespread occurrence, derived from the possibility of incorporating a rich combination of cation and anion chemistry into the structure. Double layered hydroxides are therefore important in a number of diverse technical applications, such as cements and binders, paper formulation, metal corrosion, catalysis, and environmental applications, among others

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[1, 2]. In the field of catalysis and intercalation compounds, LDHs are defined as anionic clays.

Of all the known double hydroxide compounds, we are here interested in those occurring in binder systems, both ancient and modern. As a matter of fact, (Mg,Al) LDHs of the hydrotalcite group or (Ca,Al) LDHs of the hydrocalumite group are almost ubiquitously formed during long-term pozzolanic reactions in ancient hydraulic mortars [3], in modern pozzolanic cements [4], in slag cement systems [5–7], and in alternative binder materials based on calcined clays [8]. The Al-rich LDH phases forming in the portlandite and sulphate saturated system of cement are commonly called AFm (i.e. $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$) phases, including monosulphoaluminate, monocarbonate, and their solid solutions [9–12]. The AFt phases, including ettringite [13–15], are first crystallized during cement hydration, and then they convert with time into AFm phases.

The interest in LDH-type as products of pozzolanic reactions is therefore related on the one hand to the need of understanding the long-term behavior of the pozzolanic materials employed in ancient times, especially concerning their contribution to the methodologies proposed for the radiocarbon dating of ancient mortars [16]. On the other hand, the present drive towards clinker-free cements [17] faces the challenging use of alternative pozzolanic materials, mostly based on calcined clays, which invariably yield LDH-type AFm phases as reaction products. Furthermore, the ability of the LDH structure to intercalate a variety of inorganic and organic molecules makes them reference compounds in intercalation chemistry [1, 2, 18, 19], and potentially important players in the control of the superplasticizing effect during cement hydration [20].

5.2 Crystal structural features

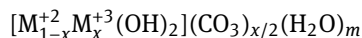
The crystal structures of trigonal LDH have been mainly investigated in mineral members of the pyroaurite [21, 22] and hydrotalcite [23] groups (Tab. 5.1 and Mills et al. (2011) [24]). The crystal structure is based on the $\cdot\text{ABC}\cdot\text{ABC}\cdot$ sequence of the basic brucite layer (Fig. 5.1) [13, 25]. The stacking yields a threefold periodicity with respect to the basal layer thickness (cell parameters: $a \approx 3.1 \text{ \AA}$, $c \approx 23.4 \text{ \AA}$) and a rhombohedral space group symmetry (R-3m or R-3).

Many of the trigonal mineral phases have the corresponding hexagonal polytype [26], based on the $\cdot\text{AB}\cdot\text{AB}\cdot$ sequence of layers. They all share the doubling of the interlayer basal spacing (cell parameters: $a \approx 3.1 \text{ \AA}$, $c \approx 15.6 \text{ \AA}$) and a hexagonal space group (P6₃/mmc). The hexagonal phases (such as sjögrenite, manasseite, barbertonite) are not discussed here.

Synthetic LDHs prepared by co-precipitation frequently show extensive stacking faults as the result of the intimate random intergrowth of the rhombohedral and hexagonal polytypes. The layer stacking arrangement is a function of the extent of Coulombic layer-interlayer interactions, as opposed to hydrogen bonding and the

nature of the interlayer anion [27]. High temperature hydrothermal treatment does not affect the stacking fault density, for entropic reasons, while low temperature treatments favor the rhombohedral polytype [28].

The general formula of the double hydroxides with 2(OH) and carbonate as the interlayer anion can be defined as:



The flexibility of the LDH structure derives from the ample substitution of divalent and trivalent cations in the brucite-type layer. The cations are homogeneously distributed in the structure without segregation, both in cases of disordered distributions or ordering patterns, which are frequent for the $M^{+2} : M^{+3}$ ratio of 2. The recurring ratio of $M^{+2} : M^{+3} = 0.75 : 0.25$ (i.e. $x = 0.25$, Tab. 5.1) is the one ensuring an optimal distribution of Al^{+3} cations in the brucite sheet, so that there are no neighboring Al atoms and repulsive forces are minimized [29]. In the (Mg,Al) system (hydrotalcite), higher concentrations of Mg produce areas with higher density of Mg and the nucleation of brucite, whereas higher concentrations of Al should cause the precipitation of gibbsite or bayerite. Similarly, in the Fe-rich system, higher concentrations of Fe or variations in the oxidation state of iron cause the precipitation of Fe hydroxides. In the latter case, the stability of so-called green rust is also related to the stabilizing effect of the

Tab. 5.1: Mineral members of the group of trigonal LDHs (space group R-3m or R-3). Cation and anion contents are referred to the general formula based on $(\text{OH})_2$ (see text). For a more complete list of mineral species see Mills et al. (2012) [24].

Mineral name	M^{+2}	M^{+3}	A^{-n}	H_2O
Hydrotalcite	$\text{Mg}_{0.75}$	$\text{Al}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Meixnerite	$\text{Mg}_{0.75}$	$\text{Al}_{0.25}$	$(\text{OH})_{0.25}$	$(\text{H}_2\text{O})_{0.5}$
Motukoreaite	$\text{Mg}_{0.67}$	$\text{Al}_{0.33}$	$\text{Na}_{0.11}, (\text{SO}_4)_{0.22}$	$(\text{H}_2\text{O})_{1.33}$
Pyroaurite	$\text{Mg}_{0.75}$	$\text{Fe}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Coalingite	$\text{Mg}_{0.83}$	$\text{Fe}_{0.17}$	$(\text{CO}_3)_{0.08}$	$(\text{H}_2\text{O})_{0.17}$
Iowaite	Mg	$\text{Fe}_{0.25}$	(O,Cl)	$(\text{H}_2\text{O})_{0.5}$
Desaultesite	$\text{Mg}_{0.75}$	$\text{Mn}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Stichtite	$\text{Mg}_{0.75}$	$\text{Cr}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Woodallite	$\text{Mg}_{0.75}$	$\text{Cr}_{0.25}$	(Cl) $_{0.25}$	$(\text{H}_2\text{O})_{0.5}$
Mössbauerite		$\text{Fe}_{0.25}$	$\text{O}, (\text{CO}_3)_{0.25}$	$(\text{H}_2\text{O})_{0.75}$
Trébeurdenite	$\text{Fe}_{0.4}$	$\text{Fe}_{0.8}$	$\text{O}_{0.4}, (\text{CO}_3)_{0.2}$	$(\text{H}_2\text{O})_{0.6}$
Reevesite	$\text{Ni}_{0.75}$	$\text{Fe}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Honessite	$\text{Ni}_{0.75}$	$\text{Fe}_{0.25}$	$(\text{SO}_4)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Takovite	$\text{Ni}_{0.75}$	$\text{Al}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Comblainite	$\text{Ni}_{0.75}$	$\text{Co}_{0.25}$	$(\text{CO}_3)_{0.125}$	$(\text{H}_2\text{O})_{0.5}$
Woodwardite	$\text{Cu}_{0.67}$	$\text{Al}_{0.33}$	$(\text{SO}_4)_{0.17}$	$(\text{H}_2\text{O})_{0.67}$
Caresite	$\text{Fe}_{0.67}$	$\text{Al}_{0.33}$	$(\text{CO}_3)_{0.17}$	$(\text{H}_2\text{O})_{0.5}$
Shigaite	$\text{Mn}_{0.64}$	$\text{Al}_{0.36}$	$(\text{SO}_4)_{0.18}$	$(\text{H}_2\text{O})_{0.72}$
Nikischerite	$\text{Na}_{0.11}\text{Fe}_{0.67}$	$\text{Al}_{0.33}$	$(\text{SO}_4)_{0.22}$	$(\text{H}_2\text{O})_{1.23}$

inter-layer cations [30–32]. The amount and distribution of anions and water in the interlayer are affected by the ordered distribution of the cations in the brucite layer [27, 33].

The phase hydrocalumite $\text{Ca}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{OH},\text{CO}_3,\text{Cl})(\text{H}_2\text{O})$ is the corresponding structure in the (Ca,Al) system. It can be described as a stacking of distorted portlandite layers, with additional water and anions in the interlayer [13, 34]. Several members of the hydrocalumite series are formed during the reaction of Portland cement with water, having a complex relationship with monosulfate in the SO_4 loaded system [9, 11, 36–38]. The (Ca,Al) LDH structure can reach high hydration states, up to a full additional layer of water, and also incorporate a substantial amount of organic molecules [18, 19, 39, 40], so that the structure has been proposed for metal immobilization [41].

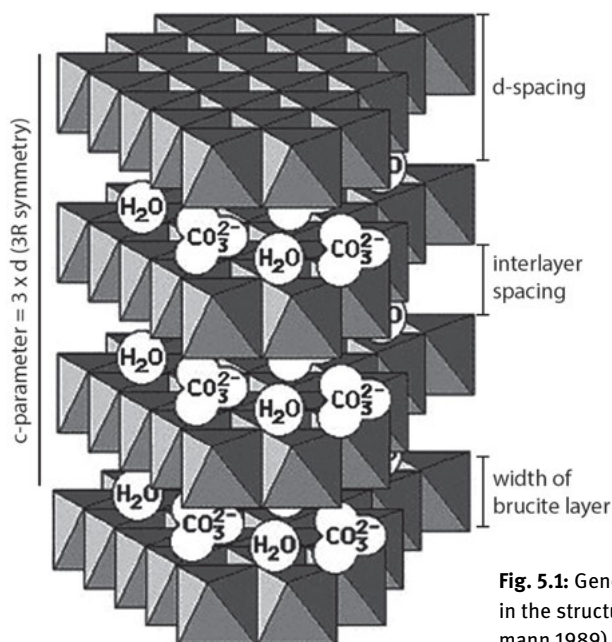


Fig. 5.1: General stacking of brucite layers in the structure of LDH (modified after Pöllmann 1989) [19].

5.3 Formation of hydrotalcite during pozzolanic reaction

The complex crystal chemistry and the extreme flexibility of the LDH structure makes their nucleation very frequent during the water solid-reactions taking place in mortars, cements, and binding materials. LDH phases are often observed as products of the pozzolanic reactions occurring in ancient hydraulic mortars [3, 42, 43]. The pozzolanic reaction is based on the success of Roman *opus caementitium*, which indeed

revolutionized the architecture of the ancient world in the beginning of the second century BC. The pozzolanic reaction in ancient times was consciously triggered by mixing lime with natural volcanic materials containing reactive glass [3, 4], although, when volcanic material was not locally available the mortar formulation included fragmented or ground pottery (*cocciopesto*) as ubiquitously available reactive silica source. Sometimes the hydraulic reaction was stimulated by the addition of reactive silica of plant origin, and even unusual clays with high reactivity were employed, especially in late Roman times [44].

Concerning the properties of the LDH phases formed by pozzolanic reaction, their crystal-chemistry is generally controlled by the chemical composition of the employed pozzolanic additive, as showed by the XRD patterns of several representative mortars reported in Fig. 5.2. When the Vitruvian tradition of employing acid (i.e. high silica) pyroclastic products is respected, the chemistry of the pozzolanic products is controlled by the dominant $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ composition, and thus the precipitation of hydrocalumite-type LDH's like Ca-hemicarbonate is favored (d-spacing of the basal peak $\approx 8.0 \text{ \AA}$). On the other hand, the presence of Mg,Al-containing materials such as natural clays, fired pottery, or more basic pyroclastic products shifts the reaction equilibria from a pure portlandite/limestone system to a more complex chemical en-

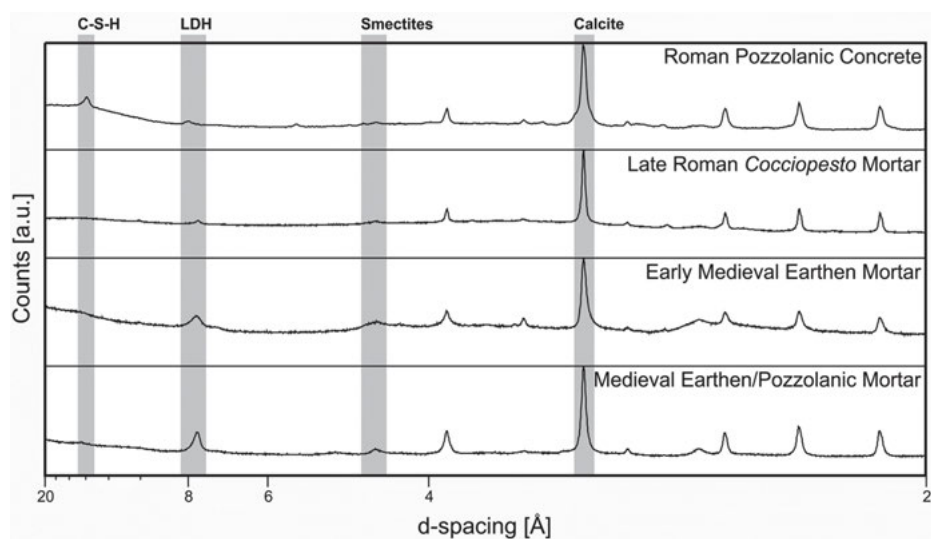


Fig. 5.2: XRPD patterns of ancient mortars formulated with different pozzolanic materials, showing the ubiquitous formation of AFm phases. From top to bottom: Roman pozzolan concrete from the Republican city walls of Aquileia (North-Eastern Italy); late Roman *cocciopesto* mortar from the baptismal font of the San Giovanni Baptistery in Lomello (Pavia, North-Western Italy); early Medieval earthen mortar based on pure saponite clays from the Torba monastery (Castelseprio, Varese, North-Western Italy); Medieval mortar based on smectite clays and basic pyroclastic hyaloclastites from the ruins of the Sarchidic castle (Forni di Sopra, North-Eastern Italy).

vironment, where hydrotalcite-type LDH phases are stabilized (d-spacing of the basal peak $\approx 7.7 \text{ \AA}$). Hydrotalcite is the most common LDH phase found in ancient mortars (Fig. 5.2), as it is the phase likely to be formed from fully hydrolized cations [45, 46].

It is interesting to note that, following the ancient tradition of pozzolanic reactions involving *cocciopesto*, there is at present a stream of active research towards using calcined clays as pozzolanic materials [8]. The drive for this is mainly sustainability [17, 47, 48], in order to move industrial cement production away from the present clinker technology, which is responsible for large CO_2 emissions [49]. The focus here is on understanding and optimizing clay reactivity [50, 51], in the attempt to employ natural clays in the formulation of alternative cements. At this stage, reasonable success has been obtained by the substitution of calcined clays in place of industrial supplementary cementitious materials (i.e. blastfurnace slags, fly-ash, etc.). In the future, thermally, chemically, or mechanically activated clays may be the core of alternative binder technology. Again, LDH phases are common products of alkali activated or geopolymeric formulations. Understanding the formation of hydrotalcite phases during the hydration of alternative binders is of course mandatory for the control of their rheological, chemical, and mechanical properties.

5.4 Critical role of hydrotalcite-type phases in mortar dating

Following a few pioneering applications of radiocarbon dating to historical mortars [52–55], a number of research groups embarked in the last 40 years on the systematic attempt to date ancient lime-based mortars using radiocarbon dating techniques. The principle is rather simple: lime-based mortars and plasters were and are produced through the carbonation of lime putty (i.e. slaked lime), and thus absorb atmospheric carbon dioxide (i.e. CO_2) during the process to convert calcium hydroxide (portlandite) into calcium carbonate (calcite). Conceptually, the process takes place rather quickly after the placement of the binder within or on the surface of the architectural component. The binder therefore should incorporate the carbon signature of the atmosphere at the time of preparation, and it represents a viable material for radiocarbon dating of the architectural structures [16, 56].

However, despite the straightforward simplicity of the theory, in practice the application of radiocarbon dating encounters a number of difficulties, mainly due to the mineralogical and chemical complexity of the real systems. First of all, the carbonate present in the sample may be contaminated by geologic carbonate (i.e. old carbonate or fossil carbonate) [57]. Even minute quantities of geologically old calcite can produce large errors in the resulting dates. Furthermore, the carbonation process after the emplacement may not be so rapid, so that the obtained dates are from calcite produced quite some time after the production (i.e. younger carbonate). Or else there might be subsequent “younger” generations of calcite contaminating the original carbonate, due to percolating water, organic impurities, or subsequent recrystallization in con-

tact with younger fluids. For this reason, when available some laboratories rely on the dates obtained on the “lime lumps” embedded in the mortar matrix, which are supposed to be relicts from the original slaking process [58]. It is however known that the carbonation of the lump material may take place quite some time after the original emplacement of the mortar, depending on the density of the portlandite nodule.

The real problem therefore lies in the careful extraction, separation, characterization, and processing of the carbonate fractions present in the matrix that correspond to the carbonation of the “original” lime putty of the binder. A number of research laboratories have developed different protocols to solve this problem [59–62]. The issue is far from being resolved, and at present each laboratory has different protocols for the extraction of the calcite fractions (thermal step treatments, acidification, cryo-fracturing, etc.). This may result in rather different dates from the same samples if using different protocols, and therefore a complex interpretation of the results. The major conceptual problem at present is that many laboratories tend to separately date the different extracted calcite fractions (thereby obtaining a wide range of dates), and then select the resulting dates that best fit the expectations based on rather subjective and arbitrary considerations.

In our laboratories, we focus on the careful preparation and full mineralogical characterization of the calcite fractions extracted from the samples. The aim is to define the criteria and treatments able to separate (physically and chemically) the different generations of calcite in the mortar samples. Then each fraction is carefully checked by mineralogical and spectroscopic characterization in order to decide before hand (i.e. before the dating protocol) whether the sample is suitable for dating or contaminated by older or younger carbon. At this stage, contamination by old carbon can be safely detected by cathodoluminescence-induced spectroscopy (Fig. 5.3). The protocol is very efficient and it has been tested on samples from different environments and chronological periods. We may safely state that fossil carbonate can be efficiently detected, although sometimes it is too fine-grained to allow a complete removal. However, the protocol may at least justify the exclusion of the sample on physical basis.

The contamination of younger carbon is more difficult to detect. Sometimes, delayed carbonation or slow pozzolanic reactions occur at much later times, so that younger calcite is formed, and carbonate anions are exchanged into the interlayer of hydrotalcite-type phases. Interaction with percolating fluids may also dissolve some of the originally formed calcite and re-precipitate the carbonate in younger secondary calcite. This later calcite can sometimes be removed by physical sieving or light acidation of the binder fraction, although there are not yet appropriate tests to evaluate the process.

A common problem when extracting the finer fraction of the original calcite binder of ancient hydraulic mortars for dating purposes is that it is frequently contaminated by hydrotalcite or hydrocalumite phases, depending on the type of pozzolanic material and the extent of the pozzolanic reaction. The binder fraction to be dated is therefore intimately mixed with LDH compounds with the same grain size. The ther-

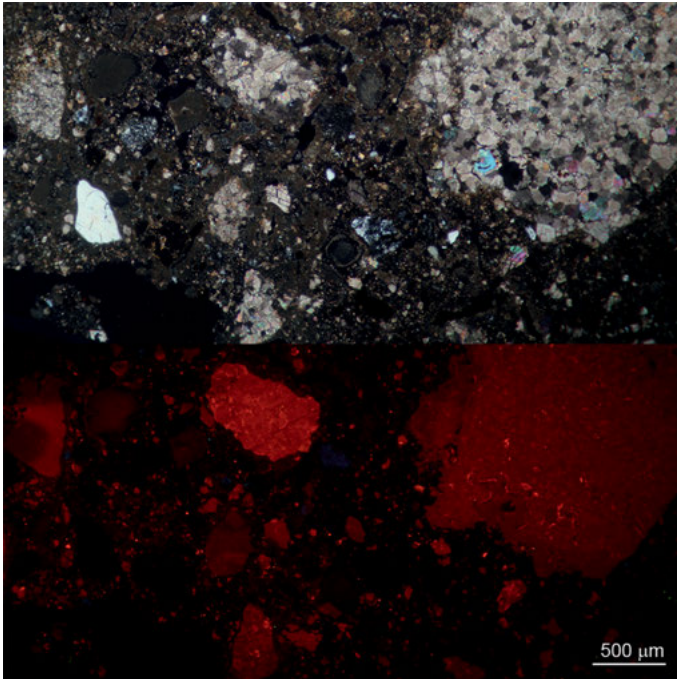


Fig. 5.3: Above: polarized optical microphotograph of a thin section of an historical mortar (crossed Nicols), clearly showing polycrystalline geologic carbonate embedded in the mortar matrix. Below: the same area measured in cathodoluminescence spectroscopy. The orange luminescence clearly shows that geologic carbonate is present both in large fragments as aggregate and as fine particles intermixed with the mortar binder.

mal decomposition of hydrotalcite [63–66] is tentatively being exploited to separate the two contributions: the younger CO_2 released during the decomposition of hydrotalcite (at about 350–400 °C) is eliminated by heating in vacuum conditions; then the sample is brought to a higher temperature and the CO_2 released by the calcite decarbonation is reduced to graphite and radiocarbon measured. This improved protocol seems to be a very promising method for the reliable dating of ancient mortars that have undergone pozzolanic reactions to some degree.

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