REVIEW PAPERS

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Hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$): A Potentially Useful Raw Material for Refractories

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ABSTRACT

Hydrotalcite also known as aluminum-magnesium layered double hydroxide, was broadly investigated in the past decade due to its many applications in catalysis, adsorptive flotation and flame retardant in polymers. In refractory castables, hydrotalcite was observed to be a by-product of the hydroxylation reaction between magnesia sinter and hydratable alumina or calcium aluminate cement. It can be synthesized using coprecipitation reactions from Al-Mg soluble salts. Novel methodologies were recently developed to produce large quantities of hydrotalcite starting from caustic magnesia and aluminum hydroxide under controlled temperature. Considering its chemical composition ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$), which is roughly 60 mass-% MgO and 40 mass-% Al_2O_3, and the many advances made in its synthesis, hydrotalcite has great potential for use in refractories, especially those involving in situ generation of spinel ($MgAl_2O_4$). This paper critically reviews the occurrence of hydrotalcite in refractories, the most effective synthesis methods, and presents some potential uses in refractory applications.

KEYWORDS

1 Introduction

The term "anionic clays" is used to designate natural or synthetic layered double hydroxides (LDHs) containing anionic species in their interlayer domain [1–3]. This denomination arose in parallel with the expression "cationic clays" used for materials that are comprised of negatively charged layers, such as $Al_2Si_2O_9H_4$ (with Al^{3+} cations occupying the sites of silicon or divalent cations such as Mg^{2+}, or Ca^{2+} taking the place of aluminum) which have interlayer cations to neutralize the aluminosilicate charges [4–6]. Synthesis of LDHs began around 1930, using precipitation reactions of dilute metal salt solutions in alkaline media. After the Second World War, many researchers studied aspects related to their structure, synthesis and properties [7]. Currently, several types of LDHs are used in various applications depending on their composition, crystallinity, thermal stability and other physicochemical properties. Some examples of

applications are: oil adsorbents, supports for catalysts, sorption agents for industrial wastewater containing anionic surfactants, colourings and acid herbicides, sensors in electrochemistry, and flame retardant in polymer nanocomposites [5, 8, 9].

The LDHs can be represented by the general formula:

$$[M^{2+}_{(1-x)} M^{3+}_{x} (OH)_2]^{x+} \cdot (A^{m-}_{x/m}) \cdot nH_2O \qquad (1)$$

where M^{2+} is a divalent metallic cation (for example, Mg^{2+} or Ca^{2+}), M^{3+} is a trivalent metallic cation (such as Al^{3+}, Cr^{3+} or Fe^{3+}), A^{m-} is an intercalated anion with charge m– (usually $(CO_3)^{2-}$) and $0.20 \leq \times \leq 0.33$. The crystal structure of an LDH is often described by reference to the structure of brucite ($Mg(OH)_2$). In brucite, magnesium cations are located at the center of octahedra, which have hydroxyl anions on their vertices. These octahedra share their edges forming flat and neutral layers, which are held together by hydrogen bonds. In this type of structure, when divalent cations are isomorphically substituted by trivalent ones, the layers generate a positive residual charge. Electroneutrality of the system requires the

presence of anions and water molecules between the lamellae, which leads to stacking of the double hydroxide layers with a slightly ordered interlayer domain. In the LDH case, the lamellae are not only held together by hydrogen bonds, as is the case for brucite, but by electrostatic attraction between the positively charged layers and the interlayer anions. A schematic representation of the structure of an LDH is shown in Fig. 1.

Among the many LDHs, those known as Mg-Alhydrotalcites ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$) are the most studied and employed in technological applications due to their easy synthesis and wide range of properties [1, 2, 5]. Recent studies have found that this type of hydrotalcite also has great potential for application in refractories [10–15]. In refractory castables, hydrotalcite was discovered to be a by-product of the hydroxylation reaction between magnesia sinter and hydratable alumina or calcium aluminate cement. The small amount of hydrotalcite formed at the surface of the magnesia particles behaves as a protective layer minimizing the deleterious effects of the hydroxylation [12,13]. Hydrotalcite can also be used in manufacturing porous ceramics due to ex-

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tensive weight loss [14] and the formation of highly refractory phases (in particular, spinel $MgAl_2O_4$) [15] which accompanies its thermal decomposition.

Because Mg-Al hydrotalcite does not exist in significant quantities in nature [1], it must be produced for applications in refractories at competitive costs and with controlled characteristics (mainly, particle size distribution, specific surface area and crystallinity). For the production of Mg-Al hydrotalcite, several factors must be considered, including the degree of substitution of divalent cations for trivalent ones, the nature of the interlayer anion, the pH of the synthesis medium and, in some cases, the reaction atmosphere [3]. Furthermore, to obtain abundant crystalline material, parameters such as the concentration of the reactants, their rate of addition, degree of agitation, the pH of the resulting suspension and the mixture temperature must be controlled. In order to understand the many production possibilities, the following section presents a critical view of the recent literature about hydrotalcite synthesis.

2 Methods of synthesis and modification

2.1 Coprecipitation methods

Coprecipitation based methods are the most used routines for preparation of hydrotalcite (Table 1) [1, 4, 7, 8]. Numerous studies employing this method can be found in the literature. They take two different forms: coprecipitation at variable pH and at constant pH. In the variable pH method, a solution
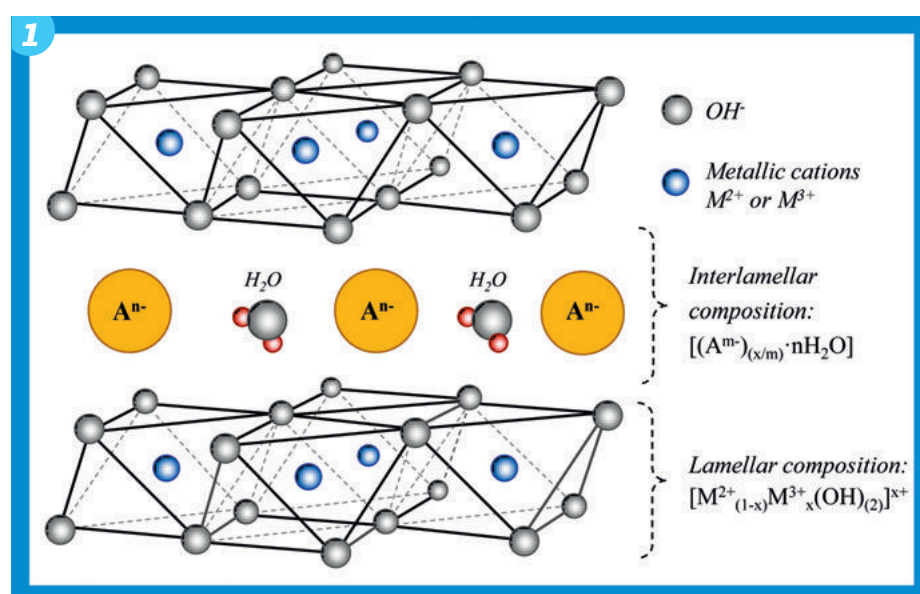

Fig. 1 • General structure of hydrotalcite [2, 4]

containing salts of the divalent and trivalent cations ($MgCl_2$ and $AlCl_3$, for instance) is added to an alkaline solution containing the anion that will be interleaved ($NaHCO_3$, for instance) (Table 1, a–b) [16]. In the coprecipitation at constant pH approach, the dissolved di- and trivalent cations, the interlayer anion, and alkaline solution are all combined at the same time. This second method requires the use of a more sophisticated experimental apparatus, but it results in particles with greater uniformity [17]. As pH is increased, the Mg^{2+} and Al^{3+} ions react with OH^- and $(CO_3)^{2-}$ generating hydrotalcite, which has very low solubility and

therefore precipitates (Table 1, c–e). These reactions are performed under strong stirring and require a further purification step to remove any remaining counter ions (Table 1, f–g). In addition to the reactants' concentrations, the speed of addition, the final pH of the suspension, the degree of agitation (usually vigorous) and the mixture temperature must be carefully controlled. Coprecipitation is usually carried out at relatively low temperatures (up to only 35 °C) to prevent the formation of other phases such as simple hydroxides.

One of the inconveniencies of the coprecipitation method is that the instantaneous

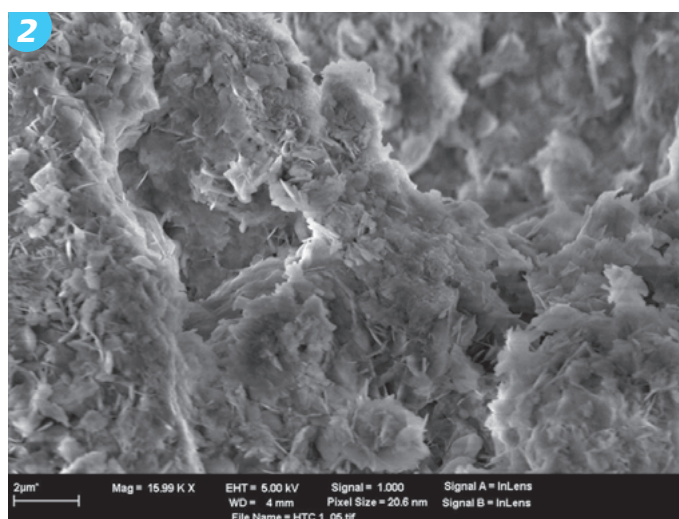| Table 1 • Compilation of the coprecipitation methods	
Steps	**Observations**
a) Acid (pH ~ 4-6) aqueous solution of bivalent ($6MgCl_2 \rightarrow 6Mg^{2+} + 12Cl^-$) and trivalent ($2AlCl_3 \rightarrow 2Al^{3+} + 6Cl^-$) cations (Mg:Al ratio of (3-2):1) ↓	Excess of Mg^{2+} or Al^{3+} ions: precipitation of hydrotalcite plus $Mg(OH)_2$ or $Al(OH)_3$, respectively
b) $6Mg^{2+}_{(aq.)} + 2Al^{3+}_{(aq.)} + 18Cl^-_{(aq.)} + nH_2O$ ↓	pH ≤ 7: stable solution
c) pH increase (by addition of $NaHCO_3$, NaOH or NH_4OH) ↓	$(CO_3)^{2-}$ ions can also be supplied by CO_2 dissolution in water during the mixing
d) $6Mg^{2+}_{(aq.)} + 2Al^{3+}_{(aq.)} + 18Cl^-_{(aq.)} + mNa^+_{(aq.)} + m(CO^{2-}_3)_{(aq.)}) + mOH^-$ ↓	pH ~ 10–12: metastable solution
e) $Mg_6Al_2(OH)_{16}(CO_3)\cdot4H_2O_{(precipitated)} + 18NaCl_{(dissolved)}$ ↓	pH ~ 10–12: hydrotalcite suspension
f) Purification (by centrifugation or dialysis) ↓	Withdrawal of dissolved NaCl from the suspension
g) $Mg_6Al_2(OH)_{16}(CO_3)\cdot4H_2O_{(aqueous\ suspension)}$ ↓	Particles: small, irregular and with low crystallinity
h) Hydrothermal treatment (autoclave) and controlled drying (lyophilization) ↓	Increase crystallinity, narrow particle size distribution and avoid agglomerates formation
i) $Mg_6Al_2(OH)_{16}(CO_3)\cdot4H_2O_{(dried)}$	Dried hydrotalcite particles

value of pH may vary at different locations within the suspension, no matter how fast the agitation. Because of this, the method often results in large agglomerations of primary particles in stable aggregates with wide particle size distribution. This morphology generally has very low specific surface area and almost no porosity. Moreover, once aggregates are formed, they are very stable and resist attempts at disintegration even under ultrasonic treatment. As an alternative route for better coprecipitation, urea (CH_4N_2O) added to the initial system can form a homogeneous and stable solution with the metal salts at low temperatures. When the temperature is raised to approximately 90 °C, the urea decomposes slowly as pH is increased homogeneously. This process shifts the pH of each part of the solution equally, avoiding the hydrotalcite particle agglomeration [19].

Coprecipitated Mg-Al hydrotalcites and other LDHs have numerous possible applications. These include use as agents for adsorption of chemical species (phosphate ions, sulfate and sulfide diluted in water, carbon dioxide, carboxyl groups, hydroxyl, phenyl, carbonyl and phosphorus), in catalysis (hydrotalcite composed of Mg and Al can be used as catalysts in the transesterification reaction of sunflower oil and oil used in the presence of methanol), and many other possibilities [5, 6, 9].

2.2 Modification by hydrothermal reaction
Hydrothermal treatments using autoclaves expose a suspension of hydrotalcite particles to an elevated temperature for a given time under the action of water vapour pressure and heating. This mechanism improves the crystallinity of the synthesized samples, refines their geometry and narrows their size distribution. Some papers in the literature have studied the effects of different hydrothermal treatment conditions on the structural properties of synthetic hydrotalcite [13, 18], After synthesis by coprecipitation, samples were subjected to different hydrothermal treatment conditions in a stainless steel autoclave coated with PTFE (Table 1, h–i). The hydrotalcite crystallization was significantly affected by variations in hydrothermal treatment temperature between 70 °C and 140 °C for 0 to 11 hours.

As a general rule, after increasing the hydrothermal treatment temperature, there was an increase in the average particle size of hydrotalcite and a decrease in the specific surface area. This behaviour can be understood from the fact that, at high pressure, water can be heated beyond its normal boil-
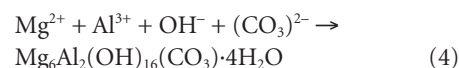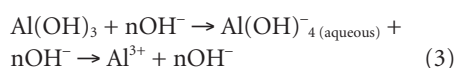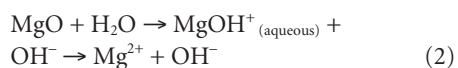
ing point, which increases ion solubility. In this condition, ions can diffuse over long distances and choose more favourable crystal planes and positions for precipitation and growth. The kinetics of nucleation and crystal growth is modified; fewer crystallization cores are formed (because dissolution is preferred over precipitation) and they tend to grow more expressively, since there are few sites for precipitation.

2.3 Cohydroxilation of MgO and $Al(OH)_3$
The residual presence of counter ions is an important drawback of coprecipitation methods. After precipitation of hydrotalcite, salt anions and cations (Cl^-, $(NO_3)^-$, Na^+, K^+, for example) remain dissolved in the suspension. If the hydrotalcite will be used in refractory applications, further purification steps (centrifugation or ultrafiltration) would be required, reducing the output of the process significantly and increasing its cost (Table 1, e–f). Due to this difficulty, recent works have investigated cleaner and more effective alternative routes to produce hydrotalcite [13, 20].

As an alternative to coprecipitation, in the method known as cohydroxylation, formation of hydrotalcite occurs without the presence of counter ions. Hydrotalcite normally occurs in refractory castables as a by-product of the reaction between Mg^{2+} (from the hydroxylation-dissolution reaction of MgO sinter), Al^{3+} (from hydratable alumina hydration) and $(CO_3)^{2-}$ (from CO_2 dissolved in water during mixing) ions, according to the general cohydroxylation expressions:

$$MgO + H_2O \rightarrow MgOH^+_{(aqueous)} +$$
$$OH^- \rightarrow Mg^{2+} + OH^- \qquad (2)$$

$$Al(OH)_3 + nOH^- \rightarrow Al(OH)^-_{4\,(aqueous)} +$$
$$nOH^- \rightarrow Al^{3+} + nOH^- \qquad (3)$$

$$Mg^{2+} + Al^{3+} + OH^- + (CO_3)^{2-} \rightarrow$$
$$Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O \qquad (4)$$

In this system, two important benefits related to the combination of MgO and hydratable alumina can be observed:

1) a thin hydrotalcite layer forms over the surface of the MgO sinter particles that hinders its hydroxylation, and
2) after reacting with hydratable alumina, significantly stronger structures are attained.

Exploiting this behaviour, a recent work describes a novel method to produce large quantities of hydrotalcite from caustic MgO and $Al(OH)_3$. Caustic MgO is a high surface area reactive form of MgO that reacts easily with water, releasing a large quantity of Mg^{2+} ions while increasing the pH of the suspension above 11 [21, 22, 23]. $Al(OH)_3$, on the other hand, is an amphoteric compound that has great solubility in water, forming $Al(OH)_4^-$ ions in pH above 9. Combining these raw materials in suitable temperature conditions (above 50 °C and up to hydrothermal conditions of 150 °C) causes formation of hydrotalcite nanoparticles ($D_{50}\sim 200$ nm) without need of further purification steps [13]. Figure 2 shows hydrotalcite nanoparticles formed by this technique.

As will be seen in the next section, hydrotalcite synthesized by this method is suitable for use in refractory formulations. The process provides:

1) high output and competitive cost,
2) purity level compatible with the requirements of the refractory industry, and
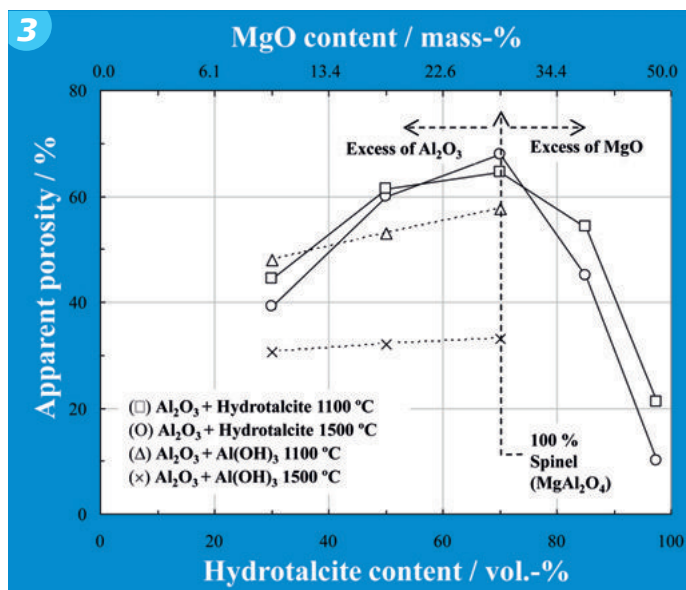3) stable suspension of very thin particles.

Fig. 3 • Effect of Mg-Al hydrotalcite addition to the apparent porosity of a dense Al_2O_3 matrix, see [15] for further details

3 Hydrotalcite as a raw material for porous ceramics

Due to their unique combination of high refractoriness and low thermal conductivity, porous ceramics are appropriate for applications that involve contact with high temperature (above 600 °C) fluids, such as hot air and liquid metal filtering and thermal insulation. This technological importance motivated the development of many production methods. One of the most explored in literature is based on decomposition of $Al(OH)_3$ previously inserted into a dense Al_2O_3 matrix. Pore generation occurs during the material's initial heating and is caused by two factors: volume shrinkage accompanying dehydroxylation and the large quantity of defects and irregularities created by freshly decomposed material (alumina transition phases) [15, 24, 25, 26].

Compared to alternative methods that use foams and organic particles, using $Al(OH)_3$ as a porogenic agent does not release toxic volatiles, generates high refractoriness phases (alpha-alumina) and can easily be incorporated into various ceramic matrices, including insulating refractory concrete. Despite these advantages, an important difficulty can be introduced by the generated transition phases. They have a strong tendency to promote sintering with the dense phase of the matrix. During its decomposition at about 300–450 °C, aluminum hydroxide undergoes a volumetric contraction of about 60 %, generating pores with dimensions of 100 nm to 10 µm, depending on initial granulometry. Furthermore, after this reaction, defect-rich transition compounds are formed. This material is very porous (in the literature, internal pores on the order of 50 to 200 nm have been ob-

served) with high surface area greater than 100 m²/g. The combination of these two mechanisms generates structures with porosity of about 50–60 % after sintering at 1100–1200 °C. However, when the sintering temperature exceeds this range, a significant reduction in porosity is observed (Fig. 3) [15, 25, 26]. To avoid this densification and porosity loss, a recent work replaced the inserted $Al(OH)_3$ by an equivalent volume of Mg-Al hydrotalcite [15].

Comparing the two systems, at lower temperatures (up to 1100 °C), the porosity attained is similar (Fig. 3). However, as firing temperature increases to 1500 °C the samples with $Al(OH)_3$ undergo a significant reduction of porosity. With hydrotalcite, on the other hand, porosity remains practically the same as is observed at 1100 °C. The lower densification of samples containing hydrotalcite can be explained by the formation of Mg-Al spinel ($MgAl_2O_4$). Because spinel is an extensive solid solution, it typically forms a microstructure consisting of large grains, which naturally decreases the driving force for sintering and densification [27]. It should be noted, however, that improved high temperature porosity was obtained when the total sample composition reached the Al_2O_3:MgO ratio suitable for formation of stoichiometric spinel (1:1 mole or ~30 mass-% MgO or ~71 vol.-% of hydrotalcite). Lower porosity levels were observed for compositions with excess Al_2O_3 or MgO. This dependence of porosity on sample composition stems from the fact that up to 1500 °C, excesses of Al_2O_3 or MgO precipitate at grain boundaries, restricting their growth and favouring densification [15, 27]. Because of this, spinel solid solution forms under a narrow range of composition conditions.

4 Conclusions

Magnesium-aluminum hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$) is a potentially useful raw material for refractories. Its chemical composition (close to spinel, $MgAl_2O_4$) and the many possible synthesis methods favour its use in different applications in this field. In situ generation of hydrotalcite as a byproduct of the hydroxylation reaction of MgO and hydratable alumina is a well-known anti-hydration technique for castables containing MgO. It provides a protective coating on the surface of the MgO particles, halting hydroxylation and its deleterious effects. Preformed hydrotalcite can also be used as a porogenic agent in dense high alumina matrixes due to its large mass loss after decomposition and because of the formation of spinel. The high refractoriness of this phase allows high porosity to be achieved even at temperatures in the range of 1500 °C. Finally, considering its many technological applications in other fields (such as catalysis, water treatment and nanocomposites) and the extent of recent research about its synthesis and characterization, hydrotalcite is clearly an up-and-coming trend in materials science and engineering.

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