Characteristics, Preparation Routes and Metallurgical Applications of LDHs: An Overview

Maria Richetta*
Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133, Rome, Italy

Abstract
The peculiar properties of layered Double Hydroxides (LDH) have progressively drawn the attention of the scientific community. The main characteristic of LDH is the ability to capture anionic species (organic and inorganic) to build different composites. This is made possible by the sandwich structure of the LDH, similar to the brucite architecture, made up of positive charged lamellas interspersed by anions. Several distant fields, ranging from medicine to physics and engineering, exhibit interest in LDH applications. To satisfy all those requirements, energy was spent to sculpt LDHs physical and chemical properties and for designing layered double hydroxides "ad hoc" for different needs and employments. Notably, among the many applications, those related to metallurgical processes and products are of particular interest. This paper presents the characteristics, the main preparation routes and reviews the applications of LDH to metallurgy with some examples taken from the experimental research of the author.

Keywords: LDH; Nanomaterials; Alumina refinement; Anticorrosion film; Surface functionalization; Catalysis; VOCs remediation; Heavy metal removal

Introduction
Layered Double Hydroxides belong to the hydrotalcite family and are also known as anionic clays. They exhibit a sandwich structure, similar to the brucite architecture, made up of positive charged lamellas, containing either divalent M2+ or trivalent M3+ metal cations, interspersed by six counterbalancing OH hydroxyl groups [1,2].

When divalent (M2+) cations are substituted by trivalent (M3+) ones, an imbalance of charges arises. Positive hydroxide layers are therefore alternated by negative ions (A-), intercalated between lamellas, thus forming an almost continuous repetition (Figure 1). The ratio x=M3+/ (M3++M2+), known as molar ratio, varies within the range (0.2 ÷ 0.4).

Several papers appeared in scientific literature regarding different fields of applications of LDHs, thanks to their peculiar morphology and growing mechanism. Foremost, by virtue of the widespread range of metal cation options, structures with different physical and chemical properties have been realized; in addition the considerable surface/volume ratio linked to the repetitive LDHs organization can be exploited to design high-performance solids; last but not least, the power of interwoven in interlayer space different species, such as: metal ions of mixed valences, water and even more complex organic molecules, has made them attractive for top applications in the most varied fields, from engineering to medicine. Just to recall only some of the possible utilizations we can cite: surfaces design with super hydrophobic properties [1], anticorrosion coatings [2,3], flame-retardants [4], waste water treatments [5,6], biomedical applications [7,8], gas sensors [7], nanostructured-modified textiles [8]. Furthermore, the possibility of substituting transition metals cations to divalent cations made LDHs very interesting in energy conversion and harvesting [9].

Among such various applications of particular interest are those regarding metallurgy. Since ‘60 they have been used in the Bayer process of alumina refinement, as demonstrated by the wide number of industrial patents. Other applications regard: Volatile Organic Compounds (VOCs) remediation in exhaust fumes emitted by industrial plants, ii) anticorrosion coatings, iii) catalysis, iv) metal surface functionalization, v) heavy metal capture in liquid wastes of industrial plants.

This work briefly describes the LDH characteristics and synthesis routes, and discusses the metallurgical applications. Some experimental results obtained by the author will be also reported.

Characteristics
The basic structure of a LDH is similar to the brucite [Mg(OH)6] one, in which the Mg cation is enveloped by OH- anions thus resulting...
in an nearly octahedral shape. The octahedral arrays build up a layered three-dimensional structure, in which each single sheet is positively charged. The charge is linked to the substitution of a "x" fraction of divalent cations M"2+ with a trivalent ones M"3+, as shown in Figure I [3-7].

Within the interlamellar space an assortment of commutable anions and water molecules can be intercalated to guarantee charge balance. The general formula describing this hydrotalcite-like structure can be expressed by the following general formula:

\[
[[\text{M}^{2+}]_{x-1}\text{M}^{3+}x(\text{OH})_{2}]^{x-} (\text{A}^y)^{x/n} \text{mH}_2\text{O}.
\]

The lattice stability imposes that the molar ratio \(\text{M}^{2+}/(\text{M}^{3+}+\text{M}^{2+})\) may vary within the interval (0.2-0.4). The electrostatic repulsion between adjacent cations and Pauling’s law are responsible of the upper limiting value. The lower one is instead related to the requisite of maintaining separate layers together with a 3D configuration.

Disparate metallic anions, either divalent (Zn, Mg, Mn, Fe, Co, Ni, Cu, Ca) or trivalent (Al, Mn, Cr, Fe, Co, Ni, La), have been adopted to compound LDHs. Even more than two different metal cations have been used to obtain additional physical/chemical properties. Jung et al. [8] investigated the effects of substituting Zn"+ in relation to structural results are still controversial.

The above reported stoichiometric formula for LDHs has to be regard as a "rationale" since LDHs are not stoichiometric, even from a microscope point of view. De facto metals cations are customarily presumed to be haphazardly distributed, on a hexagonal texture, within the layers. Also the lattice constant "a" results in a linear combination of ionic radii and molar fraction x. Nevertheless, some local cations order has been documented, and some authors have highlighted long-range cation ordering of organized superstructures [4,9,10]. Anyway results are still controversial.

As it was already underlined before, the LDHs interlayers’ host, besides water molecules, also charged or neutral species, both organic and inorganic. These moieties are usually faintly bound to the lamellas. Therefore they can be settled during the three dimensional formation stages or subsequently substituted by anions exchange. The anions can be gather as follows:

- Halides: Cl"-, F-, Br-, I-, etc.
- Non-metal oxoanions: carbonate, nitrate, sulfate, etc.
- Oxometallate anions: COO"- , MnO"4 , VO"4 , CrO"4 , WO"4 , etc.
- Anionic complexes of transition metals: Fe(CN)"6 , anionic metal porphyrins, Eu complexes, etc.
- Organic anions: -COO"-, -SO"4 , -PO"4 , etc.
- Anionic biomolecules: aminoacids, enzymes, proteins, DNA, TPA, etc.
- Anionic polymers: poly(styrene sulphonate), PMMA, etc.

To realize devices capable to control conductivity, or to be applied in water splitting, Zheng et al. [11] intercalated also neutral molecules, together with anions. After intercalation they suffered dissociation into the water content of the interlayer domain.

The disordered state of the interlamellar domain is demonstrated also by structural characterization, through XRD and/or EXAFS analysis, or by some physical properties of layered double hydroxides as electrical conductivity behaviour and hydration properties. All these peculiarities have driven some authors to consider this state a "quasi-liquid" one [12]. Needless to say, all these singularity are heavily tied to the significant interlayer water content. Two types of water can be recognized in LDHs [13]. First: the crystallite water, bounded to the interlayers and to the external surface. It is always present, also in dry conditions. Second: the adsorbed water that, depending on temperature, water vapour pressure and humidity, is alternately adsorbed and desorbed. It is evident that this is the most influential contribution not only to the previously described "architectural disorder" but also to one of the most significant phenomena occurring within the LDH: the anionic exchange. It is surprisingly easy to replace a large number of "old" ions with other "new" ones simply by immersing the LDH in a solution with an excess of new anions. This property is also adopted to prepare LDHs.

The fact that the ion exchange reaction has occurred is revealed by the variation in the distance between the lamellas, which is tightly linked to shape and density of the intercalated anions. This interlamellar space "d" is defined as the thickness of one hydroxide sheet plus one interlayer distance, and is normally determined by X-ray diffraction (XRD). The capability of intercalating even large and complex molecules is a direct consequence of the above-described adaptability of layered double hydroxides.

**Preparation Routes**

There are several procedures to synthetized LDHs. The option grounds on what types of cations form the layers, which are the intercalated anions and, particularly, which are the properties requested to the LDH, such as: crystallinity, porosity, morphology, etc. [3-7].

Two main groups distinguish the different synthesizing methods: direct and indirect.

Among the direct procedures we can enumerate: co-precipitation, salt-oxide method, sol-gel and electrochemical synthesis, in situ film growth. For what concerns indirect processes, it must be stressed that they consist essentially in modifications of pre-synthesized LDHs, such as: anion exchange, LDH reconstruction and delamination.

**Co-precipitation**

Co-precipitation was the first approach for preparing mixed double hydroxides [14], and it is still the simplest and most commonly used. In this method a low temperature chemical reaction develops inside an aqueous solutions of M"2+ and M"3+ salts in appropriate proportions, together with the specific anion "A" to be intercalated and in the attendance of an alkali metal base. Generally there are two conditions for co-precipitation; namely at low supersaturation (constant pH) and at high supersaturation (variable pH). During the process the pH behaviour must be kept under control, as well as the operating temperature. The alkali metal base causes the precipitation of the diveral and trivalent cations in hydroxide forms:

\[
(1-x)\text{M}^{2+}x\text{A}^{x-} + x\text{M}^{3+} + 2\text{NaOH} + n\text{H}_2\text{O} \rightarrow M_{1-x}^{2+}M_{x}^{3+}(\text{OH})_n\text{A}^{x-} + n\text{H}_2\text{O} + 2\text{Na}^{+}.
\]

To enhance crystallinity and size of the material, after precipitation a hydrothermal treatment is performed [15-17], followed by an aging process (from few hours to several days). Vigorous stirring and ultrapure water are used to ensure the purity of the LDH.

According to the above, co-precipitation represent a direct procedure, which ensures a high control of growth parameters, such as pH, temperature, solution concentration, cations ratio, aging time,
providing a direct procedure to synthesize Layered Double Hydroxides with well-defined composition, well-crystallized phases, and good tuning of the cation ratio.

**Salt-oxide method**

This approach was introduced to synthesize Zn-Cr-Cl LDHs [18], to be later extended to Zn-Al-Cl and Cu-Cr-Cl [5,6]. It consists in a solid-liquid reaction between an aqueous solution of the trivalent metal chloride and the aqueous solution of the divalent metal chloride in excess. Several attempts were done to synthesize LDHs with composition different from Zn-Cr-Cl, Zn-Al-Cl, and Cu-Cr-Cl but without success. The reason relies on the fact that salt oxide synthesis permits a high degree of crystallinity, but does not allow varying and determining the stoichiometry as co-precipitation does.

**Sol-gel method**

The synthesis involves formation of a colloidal suspension (sol) followed by gel formation, as a consequence of internal crosslinking. The precursor of the sol-gel transition, are metal-based-alkoxides and/or acetylacetonides that suffer strong hydrolysis and polymerization with HCl and HNO₃. The sol-gel approach was introduced by Lopez et al. [19] to increase the cation ratio. It was further extended to include transition metals Ni, Cr, and CO [20-22] thanks to the demonstrated properties of homogeneity, thermal stability, quite good control of stoichiometry, high porosity [23].

**Electrochemical deposition**

In 1994 the first films of Ni-Al, Ni-Mn, Ni-Cr and Ni-Fe LDH were electro-deposited on the working electrode of a conventional battery containing a metal-nitrate bath [24]. The principle bases on the electrically induced reduction of nitrate ions to produce hydroxide ions on the working electrode. This implies a local enhancement of the pH and a subsequent precipitation of the LDH film. It is essentially a one-step technique that permits direct deposition with good adhesion, control of film density, morphology and thickness, advantages that the conventional methods do not provide. In those cases, in fact, first we have to recover the LDH powder, treat it, and only after these passages, deposit it onto substrate by means of physical procedures with not the same reproducibility and morphology. Recently sol-gel technique attracted much interest not only to involve other metals, but also to produce modified electrodes for applications in several different fields of electrochemical sensing [25-29].

**In situ film growth**

It can be consider a sort of modified version of the co-precipitation technique. It is still a one-step recipe that guarantees quite a good adhesion and morphology [30-32]. Instead of adopting dissolved metal salts, one of the two metals is provided as a substrate, which behaves either as a sacrificing element for the film growing on it, or a reacting source of one of the corresponding metal. Differently from electrochemical deposition, in this case there is only the need to submerge the metal substrate into the aqueous solution of the other metal salt and the base. Apparently it could be possible to deposit LDH films on any substrate. The only thing to do is to deposit on a surface appropriate sacrificial metal films that react in solution. Moreover, and very important, is the fact that the surface can be patterned to form a circuit with a thin layer of the sacrificial metal to support the growth of LDH. Integrated sensors and devices could take great advantage from this technique [33].

Nevertheless, it is still far to be reached a good control of the deposited LDH morphology and composition. In a previous work of Richetta et al. [34] (Zn-Al) LDH nanostructures were grown on Al foils. A nutrient solution composed of a 1:1 ratio of zinc chloride ZnCl₂ and hexamethylenetetramine (C₆H₁₂N₄) at 5 mM concentration was employed for the hydrothermal growth of LDH. The same concentration of Zn(NO₃)₂ was used for samples intercalated with NO₃ anions. Hexamethylenetetramine acted as a pH regulator for the solution basicity, through the hydrolyzation and release of ammonia.

The XRD spectrum displayed in Figure 2 evidenced that (Zn, Al) LDH crystal structure is hexagonal. For all the samples (intercalated with Cl and NO₃ anions) the lattice parameter a=3.065 Å represents the distance between two metal cations. The lattice parameter c, namely the spacing between basal planes of hexagonal cell exhibited some differences depending on the intercalated anions ranging from 7.55 to 7.57 Å. Figure 3a and 3b shows the structures obtained by operating at 80°C with different time and different intercalated anions. The samples exhibit a similar petal-like morphology and it was observed that longer time of growth gives rise to a coarser structure.

X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) results demonstrated a correlation between the Al content and the LDH morphology. In particular, a high available content of Al is connected to a small dimension of petals, as it could favour the nucleation by increasing the number of nucleation sites.

The kinetics of petals growth has been investigated by measuring the petal thickness vs. temperature and time of treatment. Under the assumption that the diffusion of Al atoms controls the speed of LDH growth process, the present author calculated an activation energy Q=0.73 eV. Such value is quite lower than the self-diffusion energy of Al (Qδ=1.31 eV [35]) thus it seems that the petal growth strongly depends on the specific microstructural features of aluminium
substrate. On these grounds the calculated Q value has been compared with pipe diffusion activation energy (Qp=0.85 eV [36]), i.e. the diffusion along dislocations, and grain boundaries diffusion activation energy (Qgb=0.55 eV [37]). Since Qgb Qp the value of 0.73 eV is an apparent activation energy because it does not depend on a single physical phenomenon but on the diffusion along both types of defects, i.e. grain boundaries and dislocations. In other words the growth is substantially controlled by the lattice defects present in the Al substrate. Similar conclusion were drawn by Porteau et al. [38] who pointed out that the commonly observed nanoflower morphology could be the result of uncontrolled overgrowth from discrete dislocation-driven nanoplates and/or partial detachment of spiral layers that are tied by the dislocation core and suggested that the growth of nanostructures of LDHs are likely to be dislocation-driven. Of course, the controlled crystal growth can lead great benefits to the preparation of LDHs with well-defined nanostructures and potentially improved properties. Further work is underway to assess the achieved results and control LDH growth kinetics by changing the microstructure of the aluminum substrate through mechanical and heat treatments.

**Anion-exchange**

When it is not possible to produce the desired anion to be intercalated within the LDH by co-precipitation, the desired ion, by ion exchange, replace the anion present in a previously prepared LDH. The reaction is possible thanks to the peculiarities of LDHs. This indirect method has been widely applied to synthesize new LDH phases by anionic exchange reactions, described by:

The reaction equilibrium constant favours the ion of higher charge density in such a way that it permits to define a comparative list of ion selectivity [5,6], which for monovalent ions reads: \( OH^- \), \( F^- \), \( Cl^- \), \( Br^- \), \( NO_3^- \), \( I^- \). In other words we have the reaction is carried out by stirring a water suspension of a LDH precursor or of a pre-synthesized LDH.

**Reconstruction by rehydration after thermal treatment**

When we take LDHs at temperature within the range 500-800°C, it calcinated and transforms into a mixture of metal oxides. If they are rehydrated with an aqueous solution containing anions, they transform into new LDHs, as was demonstrated by Miyata [39] with Mg-Al-CO₃. Also organic anions have been recently intercalated by this procedure [40].

**Delamination/restacking method**

The delamination process consists in a complete separation of the brucite-like sheets of a layered double hydroxide, which leads to a stable colloidal solution of monodispersed lamellas. Gradually drying this colloidal compound, well-ordered LDHs can be retrieved, with the potentiality of intercalating changed anionic species. Delamination can be achieved by several different mechanisms, in particular if we use organically modified LDHs [3,41]. To give some examples, organic intercalated anions like acetate, formate, or lactate abet delamination in water [42]. Alternatively, in formamide it is possible to delamate nitrate-based [43] or amino-acid intercalated [44]. A subsequent drying process permits to recover well-ordered LDHs and LDH-polymer complexes [42].

**Metallurgical Applications**

The number of LDHs applications is very high and makes impossible a comprehensive description, therefore the attention will be focused on the most relevant ones: i) Bayer process, ii) volatile organic compounds (VOCs) remediation in exhaust fumes of industrial plants, iii) heavy metal capture in liquid wastes of industrial plants, iv) anticorrosion coatings.

**Bayer process**

Aluminium is extracted from bauxite and an intermediate step is the production of alumina from bauxite through the Bayer process. Aluminium production stands at 90% on alumina stockpiles. The Bayer process is the fundamental and most economical method for obtaining aluminium oxide from bauxite.

Alumina extraction and processing derive by a series of operations, mostly independent one with respect to the other, that takes place in different plants. To describe how LDHs are employed in Bayer process, which is quite complex, it is worth to summarise its main steps.

a) **Extraction:** To form what is generally called "pregnant liquor", i.e. a supersaturated solution of sodium aluminate, bauxite (gibbsite, böhmite, diaspora) is stepped into a hot caustic soda (NaOH) solution to dissolve the aluminium bearing minerals. The chemical reactions are:

\[
Al(OH)_3 + Na^+ + OH^- \rightarrow Al(OH)_4^- + Na^+
\]

\[
Al(OH)_3 + Na^+ + H_2O \rightarrow Al(OH)_4^- + Na^+
\]

where the first one refers to gibbsite, and the second one to böhmite and diaspora.

Depending on the bauxite ore the suitable caustic concentration, temperature, and pressure of the digester are chosen. Several flash tanks at atmospheric pressure and at about 106°C cool down the slurry, together with steam flashing.

b) **Clarification/settling:** Sedimentation is the first stage of clarification. During this stage the solids (bauxite residue) is separated from the pregnant liquor (sodium aluminate in solution). To assist the sedimentation you need to adjoin some chemical additives. Residue of bauxite sinks in the settling tanks. These residues are then removed and transferred into washing tanks to go through several washing stages. Along this line the caustic soda is recovered to be reused in the digestion process. The pregnant liquor is further taken out of the bauxite residue by means of security filters. Therefore the final product is not polluted by impurities.

c) **Precipitation:** The pregnant liquor is progressively cooled down. During this stage crystallization process starts, forming small crystals of aluminium trihydroxide Al(OH)₃ that grow and agglomerate in larger structures.

d) **Evaporation:** A chain of heat exchangers heats the spent liquor, which is successively cooled in flash tanks. Inside the heaters a condensate is formed and rehashed, for example to wash bauxite residue or as boiler feed water.

e) **Classification:** It consists in classifying into size range the precipitated gibbsite crystals. Normally cyclones, or gravity classification tanks carry it out. Coarse crystals, after being separated from the spent liquor by vacuum filtration, are doomed to calcination, while the fine crystals, after being purified from organic impurities, return to precipitation step to be agglomerated.

f) **Calcination:** Calciners roast at temperature up to 1100°C the filtered cakes. This step is necessary to drive off free moisture and chemically connected water. Therefore alumina solids are achieved.
Calcination is described by the following reaction:

$$2\text{Al}(	ext{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$

Alumina is the product of this last stage.

The liquid part of the slurry is highly alkaline and requires neutralization to render it environmentally benign. A common practice is neutralization using Mg reach seawater. This treatment results in the formation of LDH hydrotalcite [45].

$$\text{Mg}_{n}\text{Al}_m(\text{OH})_{n+m}\text{CO}_3\cdot 4\text{H}_2\text{O}$$

LDHs can be used for removing several species (both organic and inorganic) in the Bayer process and several methods have been patented. The removal mechanism couples intercalation of small anions with adsorption of larger organic molecules on the external surfaces [46-50]. Two LDHs, hydrotalcite and hydrocalumite, have received particular attention for removing impurity in the liquors. Hydrotalcite has been adopted to remove the organic humate present in Bayer liquor. The outcome of adding Mg compounds to contaminated Bayer liquors is a precipitate containing Mg/Al hydroxides [50]. The precipitate consists in an impure hydrotalcite, derived by the reaction of the Mg salt with the aluminate anion. It seems that is the surface adsorption rather then intercalation of anions that reduce the humate concentration in the Bayer liquor, because the large humate molecules do not fit between the hydrotalcite layers.

Nigro and O’Neill [48] have patented a method to remove coloured impurities, such as ferrate. They used calcined hydrotalcite in the temperature range 450-650°C with their re-hydration in Bayer liquor. Reduction of oxalate in spent liquor was observed by Perrotta and Williams [51] following the formation of hydrocalumite at 60°C.

An alumina producing process was patented by O’Hare, et al. [52]. During this process bauxite was treated with an alkali to form a mixture of a solution of alumina trihydrate and aluminated-ions. The solution was treated before or after the precipitation phases, with a layered double hydroxide to remove impurities by intercalation into the LDH layers made of [LiAl₂(OH)₆].

In the Bayer process, the main purpose is to extract as much bauxite as possible. Many investigators proposed novel processes to get back the alumina from liquor [48-51]. Most of those procedures relies on the following steps: ii) form an Al-bearing LDH (Al-LDH) by operating on the first liquor with a metal hydroxide (being the metal different from aluminium), and recovering a treated stream of first liquor that carries an aluminate concentration lower than the first one; iii) separate the Al-LDH from the first liquor; iii) sand back the first liquor treated stream to an initial location inside the alumina refinery. The separate Al-LDH can be stored, sold or reprocessed within the same plant to extract its alumina content. It is sometimes contacted with a solution containing carbonate ions to give rise to both slurry containing an insoluble salt of aluminate ions released by the Al-LDH. Several different types of Al-LDH can be employed. Among them: hydroxilate, hydrocalcite, Li/Al and Mg/Al LDHs, just to give some examples. A model is represented by the process studied by Rosenberg [53].

**VOCs remediation in exhaust fumes of industrial plants**

One of the main drawbacks of some industrial activities is the trace of Volatile Organic Compounds (VOCs) that represent a serious environmental problem. This is the case of various solvents, required in a number of technological processes. Some of those solvents escape into the atmosphere and contribute to air pollution.

Types of common VOCs that need treatment when present in an air stream are: (i) aliphatic carbon; (ii) aromatic hydrocarbons; (iii) chlorinated hydrocarbons; (iv) alcohols, ethers, and phenols; (v) ketones and aldehydes. In Table 1 vapour treatment technologies to the above contaminants are reported.

A well effective technology for VOCs control is oxidation, either thermal or catalytic. Oxidation units can destroy nearly 75% of VOCs and toxic emissions. Heating a VOC to an adequately high temperature, in presence of oxygen, will convert the VOC to an harmless end product. During thermal oxidation, the air polluted by VOC is captured by a ventilation system, preheated and combusted at high temperature to form carbon dioxide and water. In addition to combustion temperature, also residence times are parameters that influence VOC reduction efficiency [54].

Catalytic oxidation, similar to the thermal one, combines a conventional heat exchanger with a catalyst. It employs a bed of active materials (catalyst) that facilitates the overall combustion reaction. A catalyst inside the combustion unit lowers the activation energy for combustion, which occurs at lower temperature (320-540°C) avoiding formation of NOx by-products [55]. These processes have been demonstrated to be very up-and-coming to get rid of VOCs at low concentration. As a result, fuel costs for catalytic oxidation are lower. Typical catalyst materials include platinum, palladium, and metal oxides such as chrome-alumina, cobalt-oxide, copper-oxide, and manganese-oxide. Catalytic materials may be inserted into the combustion unit in either a monolithic or beaded configuration.

The control of the micro kinetics, consisting of micro pore diffusion, chemisorption, surface reaction, and desorption, is the task of the catalyst developer. The efficiency of catalytic oxidation process is highly affected by the catalyst material and its physic-chemical properties. In many catalytic oxidation procedures noble and transition metals are applied. Catalysts made with noble metals degrade VOCs easily. However, they are not suitable for large-scale applications due to high cost and rapid deactivation, determined by poisoning of sulphur and chlorine.

For these reasons a great effort has been made to find new metallic oxide catalysts capable of having the same or even better performance.

| VOC                                | Thermal Oxidation | Catalytic Oxidation | Adsorption | Condensation | Biofiltration | Membrane Filtration |
|------------------------------------|-------------------|---------------------|------------|--------------|--------------|--------------------|
| Aliphatic carbon                   | X                 | X                   | X          | X            | X            | X                  |
| Aromatic carbon                    | X                 | X                   | X          | X            | X            | X                  |
| Chlorinated hydrocarbon            | X                 | X                   | X          | X            | X            | X                  |
| Alcohols/Ethers/Phenols            | X                 | X                   | X          | X            | X            | X                  |
| Ketones/Aldehydes                  | X                 | X                   | X          | X            | X            | X                  |

Table 1: Technologies used for treating vapour contaminants.
most difficult and expensive part of an adsorption technology. It may adsorbed anion and regeneration of the adsorbent LDH. This is the its maximum. The steps following adsorption are desorption of the oxyanions for exchange process, the ion exchange would reach ionic radius of these oxyanions falls in the range of 0.19-0.26 nm. perrhenates, pertechnetates, iodates, molybdates and vanadate. The chromates, phosphates, selenites, selenates, borates, nitrates, the total oxidation of VOCs [65]) mixed oxides, obtained after the calcination phase, have been able to act as catalysts [59,62], or as catalyst support [63-65]. Thanks to their activity and robust stability for VOCs combustion, LDHs can be catalyst or catalyst precursor. The activity of a catalyst or its physic-chemical characteristics is deeply depending on synthesis routes, calcination temperature, precursors and promoters. Nano-sized structures show higher activity because of higher specific surface area and also superficial chemisorbed oxygen. Therefore, research is addressing new synthesis methods that lead to the synthesis of new thermally stable systems with even smaller crystallite dimensions (~10 nm).

**Heave metal capture in liquid waste**

The presence of various environmental pollutants in water has raised worldwide concerns. Toxic contaminants include organic and inorganic compounds such as paraholic compounds, pesticides, dyes, oxyanions, heavy metals, which are originating from the wastewaters of different industries such as steel, electropolishing, plastics, battery manufacturing, mining etc. [66]. Heavy metal, principally, but also the other by-products, are not biodegradable. They use to gather in living structures, inducing severe risks to the human beings and to the environment [67,68]. Also in this case LDHs represent a suitable solution for contaminants uptake, since they posses: a) large surface area; b) anion exchange capacity; flexible interlayer region, accessible to polar molecules and anions. Three different mechanisms are responsible of the pollutants removal from aqueous media. Namely: anion exchange, surface adsorption, and memory effect. The charge balance between layer charge density and intercalated anions influences the anion exchange, while, for what concerns surface adsorption the involved mechanism is the adhesion of pollutants to the LDH surface. The memory effect is one of their most attractive features as an adsorbent. When LDHs are thermally decomposed around 500°C, they can be calcined and can lose the layer structure, forming highly active composite metal oxides with high thermal stability, large surface area, basic properties, small crystal size, and high stability against sintering even under extreme conditions [69]. Rehydration or sorption of different anions permits the reconstruction of these calcined products.

Several papers appeared during the past few years discussing the potentiality of LDH for contaminants uptake. Those pollutants include: oxyanions [70-75], monoatomic anions [76-78] cations [79-81], organics [82-84], and gas [85,86]. For example, Kovalda et al. [87] demonstrated the capabilities of Co:Mn:Al LDH (calcined at 500°C) in the total oxidation of ethanol (Figure 4).

Thus far, the most investigated oxyanions are arsenites, arsenates, chromates, phosphates, selenites, selenates, borates, nitrates, perhenates, pertechnetates, iodates, molybdates and vanadate. The ionic radius of these oxyanions falls in the range of 0.19-0.26 nm. In the case in which the interlayer region is sufficient large to fit the oxyanions for exchange process, the ion exchange would reach its maximum. The steps following adsorption are desorption of the adsorbed anion and regeneration of the adsorbent LDH. This is the most difficult and expensive part of an adsorption technology. It may account for 70% of the total operating and maintenance cost for an adsorption system. A successful desorption/regeneration process should restore the adsorbent similar to its initial properties for effective reuse. Adsorbates can be recovered either for reuse or for proper disposal, depending on their market demand.

Various alkaline, salt and mixed solutions have been successfully used to desorb oxyanion-loaded LDHs. Uncalcined carbonate-LDHs adsorbs more than 85% of As(III) and Cr(VI) [88,89]. The desorption of As(V) and Se(IV) was dependent on the anion species and their concentrations in the desorbing solutions [90].

A number of studies also showed that oxyanion-loaded LDHs could be regenerated [91-96]. The adsorption capacity of the LDHs is gradually reduced after a few cycles of regeneration. Moreover, some research works appeared on the possible recovery of adsorbates, such as As(V), PO$_4^{3-}$ and Cr(VI) from spent LDHs [75,96,97]. Gillman [96] reported that the minute amount of As in the As-loaded LDHs could be easily recovered by saturating As-loaded LDHs with phosphate, while Kuzawa et al. [95] proposed a scheme whereby the desorbed PO$_4^{3-}$ in the spent desorption solution could be recovered as calcium phosphate precipitate by addition of CaCl$_2$, and the remaining spent desorption solution could also be reused after supplementing additional NaOH (Figure 5) [98,99].

LDH based novel nanocomposites originated by the hybridization of LDH with other materials, such as carbon nanotubes, graphene and carbon nanofibers [100]. The relevant importance of nanocomposites is determined by their high surface area and enhanced adsorption capacity with respect to their parental LDHs. The hybrids capacities derive from the mixed qualities of both parental materials and hence have better adsorption properties. Synthesis route and applications of these nanocomposites are described in detail [101,102].

Compared to LDH alone as an adsorbent, LDH-containing hybrids exhibit enhanced adsorption tendency of toxic pollutants due to their improvement in surface area [100-103], higher anion exchange tendency [104,105], better stability [106], increase in chelating and binding

![Figure 4: Oxidation of ethanol over catalysts obtained by calcinations of Co:Mn:Al - LDHs (redrawn from Kovanda et al. [87]).](image-url)
situations [107], excellent selectivity for different metal ions [108-110], low toxicity and ease in separation and reusability when hybridized with magnetic particles [111-113]. As a result, these superior properties, they are up-and-coming adsorbents for wastewater treatment.

**Anticorrosion coatings**

Many technological applications demand materials with well-defined surface properties. Recently, surface functionalization of metallic materials has become a very active research area. Surface functionalization aims at improving specific responses of the material when interacting with its environment. Advances in surface engineering, nanomaterials and nanotechnology allow material manipulation down to the molecular scale. Functional coatings have been widely studied for various applications, including that requiring corrosion protection. In this last case, coatings must behave as a physical barrier against the attack of aggressive species toward the metallic interface. Moreover, if the protective barrier is disrupted, coating might inhibit the corrosion process. Therefore, corrosion protection needs anticorrosion pigments or corrosion inhibitors to protect the metal underneath.

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Depending on the final application of the coated material, the thickness of the coating and the number of layers can range from few microns up to several hundreds of micrometres. During the past, effective systems relied on the use of chromate-rich surface treatments and/or primers and pigments based on chromates. However, nowadays the use of hexavalent chromium in almost all sectors is forbidden.

Many alternatives have been explored so far. In particular, two main strategies have been pursued: i) encapsulation/loading of functional active species in bearers; ii) handling of the coating matrix composition to incorporate functional groups of bulk and/or surface. LDHs have been able to store inorganic corrosion inhibitors, and to release them by ion exchange mechanisms [114-116]. Recently, attention has been given to LDH composition, ability to store different functional species and impact on the barrier properties of hybrid and organic coatings. For example, different ions (vanadates, organic inhibitors) were intercalated in LDH [117-119]. Localised impedance spectroscopy revealed the inhibiting effect of LDH loaded with mercaptobenzothiazole and added to epoxy coatings applied on AA2024. The corrosion inhibition efficiency was tested in artificial defects formed in the coated AA204. Snihirova et al. [119] demonstrated that LDH containers provide effective early-stage corrosion inhibition. LDHs evidenced an interesting property, i.e. they act as chloride ion trappers [119-121]. LDHs modified with nitrates are sensitive to the concentration of chlorides [121-123] and, based on this, nitrates can be released from the LDHs. This process is governed by an ion-exchange equilibrium mechanism, and allows the entrapment of chloride ions. Tedim et al. [120] highlights the capability of nitrate-containing LDH to trap chloride ions, which are diffusing through a coating, a process that can contribute to increase corrosion.

It is expected that LDH deliver the inhibitor into the corroding areas when the matrix is damaged. LDH dispersions in polymeric matrices may also result in better mechanical properties and stress dissipation ability. Moreover they do not damage the organic matrices barrier properties as proved in recent studies [123,124]. LDHs loaded with effective corrosion inhibitors seem to be a powerful option to design new smart organic coatings and present scale-up potential. For better compatibility with the organic matrices the key parameters to observe include surface functionalization of the LDH, its concentration and effective dispersion in the coating formulation as well as long-term stability.

Electrochemical and corrosion tests, integrated by physicochemical characterization, demonstrate inhibiting efficiency of various healing systems. However it is difficult to predict the healing efficiency and the response time of carriers embedded in coatings. Very few articles are published on this issue. Recently, Javierre et al. proposed some mathematical/analytical models, correlating the healing kinetics with the coating composition. The authors conclude that the healing process depends on: thickness of the layers present in the coating; elastic modulus of the coating; dimensions of the initial damaged area [125,126].

If necessary LDHs can be deposited with micrometric precision to form desired patterns and protect specific parts of a surface, as shown in the example of Figure 6 [127].

A very important application is to magnesium alloys. They have excellent mechanical properties thus are expected to be applied in automobile, aerospace and electronics industry; however they are vulnerable to the aggression by chlorine ions in a neutral or acidic environment due to their lower potentials. Corrosion of magnesium alloys is a critical issue for their industrial applications on a large scale. Very few coatings are characterized to be efficient for magnesium protection. However, new coatings with effective dispersion in the coating formulation as well as long-term stability are expected to be applied in automobile, aerospace and electronics industry; however they are vulnerable to the aggression by chlorine ions in a neutral or acidic environment due to their lower potentials. Corrosion of magnesium alloys is a critical issue for their industrial applications on a large scale.
scale. Zeng et al. [125] prepared nano-sized ZnAl-LDHs coating by co-precipitation and hydrothermal method on AZ31 Mg alloy, and in order to prolong the service life of the ZnAl-LDH coating, a polylactic acid (PLA) coating was sealed on the top layer of the coating using a vacuum freeze-drying method.

The ZnAl-LDH coating was synthesized by the combination of the co-precipitation and the hydrothermal process on AZ31 Mg alloy. It exhibits two layers, namely a compact inner layer and porous outer layer. A thick PLA coating was sealed on the porous outer layer of the LDH coating with a strong adhesion and the PLA coating can delay the penetration of aggressive ions to provide a longer protection effectively. The system provides a very good corrosion protection owing to the barrier function, ion exchange and self-healing ability.

The reported examination remarks late approaches introducing sharp anti-corrosion functionalities in protective coatings, by guest reservoirs carriers of corrosion inhibitors. LDHs, used as chloride trappers and corrosion inhibitor exchangers, provide effective corrosion inhibition, while contributing for good barrier effects. To enhance other coating properties, such as wear or abrasion resistance as reported elsewhere [127], addition of nanoparticles may contribute. This is undoubtedly an interesting area to explore in order to reach more efficient self-healing functionalities. Furthermore, the size and geometry of the defects to be healed, the number of defects and the area or volume to be protected as well the possibility of occurrence of multiple damaging events are still open questions for which very few answers exist.

Conclusions

A lot of papers are published today focusing different aspects of LDHs synthesis and/or applications in several and different fields. The present paper provided an overview of the characteristics and the main preparation routes of LDHs. Moreover, it reviews their applications to metallurgical routes and in some preparation routes metallurgy becomes of fundamental importance to control the process of LDHs growth and the final characteristics.

Finally, it is noteworthy to observe that the high frequency with which innovative applications appear is stimulated by the high versatility and low cost of LDHs and suggests that these nanomaterials could play an increasing role in metallurgy in the near future.

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