

Extended Abstract

Layered Double Hydroxides as Consolidants and Anion Absorbents for Heritage Conservation [†]

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Knowledge from materials science can be used to design systems that target specific issues in the conservation of cultural heritage, such as cleaning, consolidation, and anion removal. Layered double hydroxides are a group of anionic clays that have several properties of interest in the field of heritage conservations, one of them being the property to absorb different anions (sulphate, chloride, phosphate, and so on) responsible for the building materials degradation process. In this work, some layered double hydroxides with compositions of $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{Cl})_{0.25}$, $[\text{Mg}_{0.375}\text{Ca}_{0.375}\text{Al}_{0.25}(\text{OH})_2](\text{Cl})_{0.25}$ and $[\text{Ca}_{0.70}\text{Al}_{0.3}(\text{OH})_2](\text{Cl})_{0.30}$ were prepared, characterized, and tested as consolidants [1–3]. The prepared materials will be further referred as MgAl-LDH, CaAl-LDH and CaMgAl-LDH, respectively.

The layered double hydroxides were prepared using the co-precipitation method, starting from metallic salts [1]. Fourier-transform infrared spectrometry (FTIR) and Raman spectroscopy were used to identify the respective functional groups of the prepared materials, while diffusion light scattering (DLS) was used to analyze the particle size. The relative kinetic stability of the consolidant particles, dispersed in various solvents (ethanol and water), was also determined. The relative kinetic stability (KS) of the suspension was determined from the variation of absorbance over time via UV-VIS spectrometry. KS was calculated using Formula (1):

$$\text{KS\%} = 1 - [(A_0 - A_t)/A_0] \times 100 \quad (1)$$

where A_0 represents absorbance at 0 min, and A_t is absorbance at time t .

Cubic test bricks measuring $4 \times 4 \times 4$ cm were made using gypsum, sand, and water at a ratio of 1:2:0.75 w/w . First, the consolidation effect of the LDH was studied by dispersing the solids in water (0.5 g/L) and applying the dispersion on test bricks with a brush (3 times on every side).

Second, test bricks were made by incorporating 5% (w/w) of every consolidant into the slurry. The differences in color, mechanical strength, and porosity versus the control samples, were studied.

The effect of adding 5% (*w/w*) of a calcined LDH (600 °C, 4 h) on the anion concentration was also investigated.

The color of the treated sample was measured using a Konica Minolta-Chroma Meter CR-410 colorimeter. The mechanical properties (compressive strength) were determined in accordance with ASTM C805 using a Proceq-SilverSchmidt Concrete Test Hammer Type L. The peeling test was carried out using the Drdáký method with a 2 × 2 cm flex tape. The last water absorption capacity and the apparent porosity were determined based on STAS 6200/12-73 and STAS 6200/12-80.

FTIR and the Raman spectrum of the synthesized LDH present several peaks comparable to those in the literature [4]. FTIR: The broadband located at ~3450 cm⁻¹ arises from the stretching vibration of the layers hydroxyl groups, as well as the interlayer water molecules. The bands at ~1630 cm⁻¹ are attributed to the bending vibration of water (νH–O–H); bands at 1380 cm⁻¹ confirm the presence of interlayer CO₃²⁻. Bands lower than 1000 cm⁻¹ are assigned to the vibration mode of M–O, M–O–M, O–M–O, and metal hydrogen bond vibration modes. Raman: The LDH lattice vibrations in the Raman spectra of the samples appear mostly below 600 cm⁻¹. Three bands appeared at ~510, ~440 and ~210 cm⁻¹ for the MgAl-LDH, respectively, at 530 and 410 cm⁻¹, followed by the band at 1080 cm⁻¹—assigned to CO₃²⁻ vibrations of calcite, in the case of CaAl-LDH. All the LDH dispersions in water and water/ethanol present good kinetic stability, higher than 60% in the case of CaAl-LDH dispersed in mixtures of water/ethanol. DLS analysis showed that the average particle size varied between 150 and 300 nm; the kinetic studies on the particles' dispersion stability in solvent confirmed that all consolidants' dispersions present good stability in water and ethanol/water.

Consolidant testing:

- I. Brushed samples: The treated samples showed small ($\Delta E^* < 5$) differences in color versus the test specimens. The consolidants did not significantly improve the mechanical properties (compressive strength) of the samples; however, the peeling tests showed that the sample surface is notably (approximately 30% for MgAl-LDH) more stable after treatment with the consolidant dispersion. The water absorption capacity and the porosity of the treated bricks showed few differences compared to test bricks, showing that the consolidants applied via brushing did not modify the porosity and water absorption capacities.
- II. Samples with 5% incorporated LDH: The addition of LDH in the slurry showed little effect on the final color ($\Delta E \leq 5$) or mechanical properties of the samples; however, the porosity and water absorption capacity of the test specimens increased, probably due the high specific surface and mesopores of the consolidants. In order to study the anion absorption capability of the prepared materials, the LDH were calcined and added into the slurry; the addition of 5% calcined Mg-Al-LDH showed a good absorption capacity of sulphate anions, absorbing approximately 15% of the sulphate anions.

The consolidants applied via brushing did not alter the color of the test bricks and showed a promising effect in the peeling test. Incorporating the LDH 5% *w/w* into the bricks led to an increase of 6% in water absorption capability and an increase of porosity of about 10%. The incorporation of calcined LDH into the bricks lowered the anion content by about 15%.

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References

1. Iftekhhar, S.; Küçük, M.E.; Srivastava, V.; Repo, E.; Sillanpää, M. Application of zinc-aluminium layered double hydroxides for adsorptive removal of phosphate and sulfate: Equilibrium, kinetic and thermodynamic. *Chemosphere* **2018**, *209*, 470–479, doi:10.1016/j.chemosphere.2018.06.115.
2. Shui, Z.; Yu, R.; Chen, Y.; Duan, P.; Ma, J.; Wang, X. Improvement of concrete carbonation resistance based on a structure modified Layered Double Hydroxides (LDHs): Experiments and mechanism analysis. *Construct. Build. Mater.* **2018**, *176*, 228–240, doi:10.1016/j.conbuildmat.2018.04.222.

3. Guo, L.; Wu, Y.; Duan, P.; Zhang, Z. Improving sulfate attack resistance of concrete by using calcined Mg-Al-CO₃ LDHs: Adsorption behavior and mechanism. *Construct. Build. Mater.* **2020**, *232*, 117256, doi:10.1016/j.conbuildmat.2019.117256.
4. Yang, Q.; Wang, S.; Chen, F.; Luo, K.; Sun, J.; Gong, C.; Yao, F.; Wang, X.; Wu, J.; Li, X. Enhanced visible-light-driven photocatalytic removal of refractory pollutants by Zn/Fe mixed metal oxide derived from layered double hydroxide. *Catal. Commun.* **2017**, *99*, 15–19, doi:10.1016/j.catcom.2017.05.010.

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