SUPPORTING INFORMATION

LAYERED DOUBLE HYDROXIDE AND ZIRCONIUM PHOSPHATE AS ION EXCHANGERS FOR THE REMOVAL OF ‘BLACK CRUSTS’ FROM THE SURFACE OF ANCIENT MONUMENTS

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Experimental

Preparation of MgAlCl/SO$_4$ samples

The studies on the Cl^-/SO_4^{2-} exchange were performed equilibrating weighed amount of MgAlCl with calculated volumes of 0.1M Na_2SO_4 solution, in order to have an amount of sulphate anions equal to 50%, 25%, 10% and 5% with respect the IEC (hereafter MgAlSO$_4$_x where x is the percentage of SO_4^{2-} intercalated). The dispersions were left stirring for 90 minutes, then centrifuged and washed three times. The solids were dried in an oven at 40°C.

Sulphate release from MgAlSO$_4$ in the presence of NaCl or CaCl$_2$

833 mg of wet paste MgAlSO$_4$ (corresponding to 200 mg of dry solid) were mixed with the 50 mg of NaCl or 46 mg of $CaCl_2$ (Cl^-/Al^{3+} molar ratio = 1). The XRD of the mixtures were collected immediately after the contact and when they were completely dried in air.

ZrPNaH and MgAlCl mixed with gypsum and CaCO$_3$

Weighted amounts of MgAlCl and ZrPNaH, in the form of wet paste, were gently mixed with an amount of gypsum and $CaCO_3$ so that the Cl^-/SO_4^{2-} and Cl^-/CO_3^{2-}equivalent ratio was 1:1.

Results and Discussion

Ion exchange Cl^-/SO_4^{2-} in the MgAlCl

LDH with increasing sulphate content were prepared by Cl^-/SO_4^{2-} ion exchange in order to obtain information on the exchange mechanism. The wet and dry solids were characterized by XRD (Figure S1) and for their chemical composition by EDX (Table S1). The XRD patterns of the samples at different SO_4^{2-} content show that the ion exchange process is quite complex and a separate discussion for the wet and dry solids is necessary. In the range of the investigated exchange percentages, the wet samples (Figure S1 (a)), show both the chloride and the sulphate phase suggesting that the exchange goes on by a first order phase transition. However, assuming that the *(003)* relative reflection intensities are proportional to the relative amount of phases, it is possible to note that the intensity ratio between the sulphate and chloride phase is always higher than expected (Table S1) and the intensity of sulphate becomes absolutely prevailing at 41.4% of IEC. In light of these findings it is reasonable to suggest the formation of a solid solution of chloride into the sulphate phase beside the residual chloride phase. The XRD of the dry samples (Figure S1 (b)) show for $MgAlSO_4$_25 and $MgAlSO_4$_50 that the reflection of the sulphate phase loses in intensity and become very broad. The dry samples with low sulphate content ($MgAlSO_4$_10 and $MgAlSO_4$_5 of Table S1) show only the chloride phase probably implying the solubilisation of sulphate anions into chloride phase.

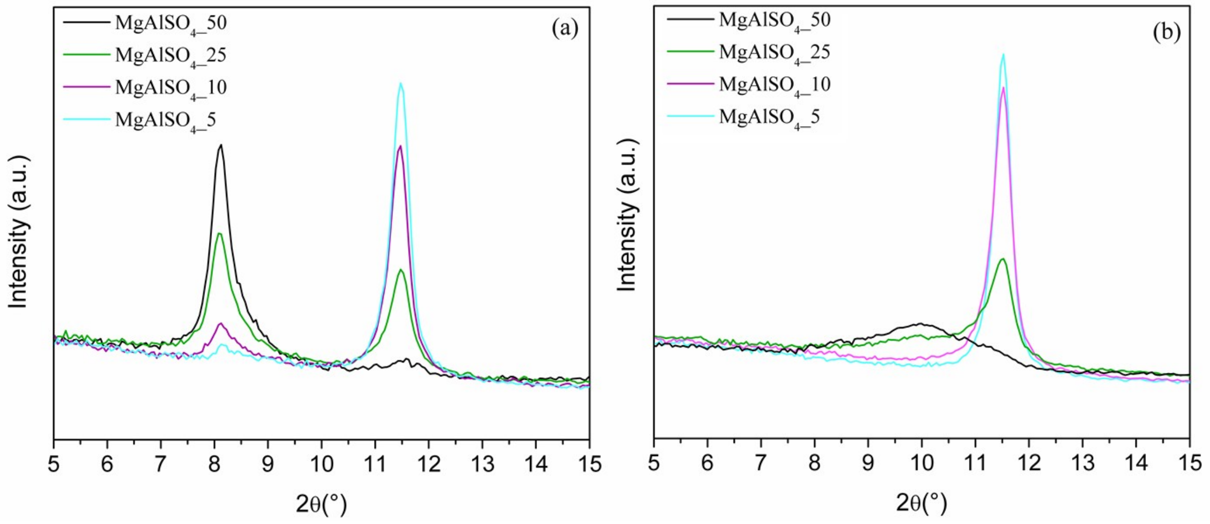

Figure S1 *(003)* reflections of the XRD of wet (a) and dry (b) $MgAlSO_4$ at the indicated percentage of exchange.

Table S1 Amount of sulphate anions in the equilibrating solution and in the solids. The relative intensity of the (003) reflection of the sulphate phase is also reported.

Sample	SO_4^{2-} added (% IEC)	SO_4^{2-} uptake (% IEC) [(a)]	*(003)* Relative Intensity[(b)]
$MgAlSO_4$_5	5	4.4%	20%
$MgAlSO_4$_10	10	10%	27%
$MgAlSO_4$_25	25	25%	55%
$MgAlSO_4$_50	50	41.4%	80%

[(a)]Determined by EDX; [(b)]*(003)* relative intensity = $\frac{I_{SO_4^{2-}}}{I_{SO_4^{2-}} + I_{Cl^-}} \times 100$

Reaction of $MgAlSO_4$ wet paste with NaCl and $CaCl_2$ in powder form

To confirm and to get further insight about the role of the chloride and calcium ions in the effects mentioned above, the reaction of $MgAlSO_4$ with two different salts, NaCl and $CaCl_2$, was investigated by mixing the wet paste $MgAlSO_4$ with NaCl or $CaCl_2$ powder (see experimental section). The XRD patterns of the wet and dry mixtures were then collected. The XRD pattern of the wet $MgAlSO_4$-NaCl system is shown in Figure S2 (a): the $MgAlSO_4$ phase was solely observed, suggesting that the chloride concentration in the paste is not high enough to form the MgAlCl phase. This confirms the higher affinity of sulphate ions toward LDH other than that of chloride ions.[1] Differently, the XRD pattern of the dry system (Figure S2 (b)) shows the presence of several crystalline phases that are: MgAlCl, Na_2SO_4, residual NaCl and traces of dry $MgAlSO_4$, confirming hypothesis that the increase of the free chloride ion concentration in the mixture acts as driving force for the release of sulphate ions from the interlayer region of LDH to the paste. However, the presence of residual NaCl together with dry $MgAlSO_4$ traces clearly indicates that the only increase of chloride ions concentration is not enough to achieve complete regeneration of the MgAlCl phase.

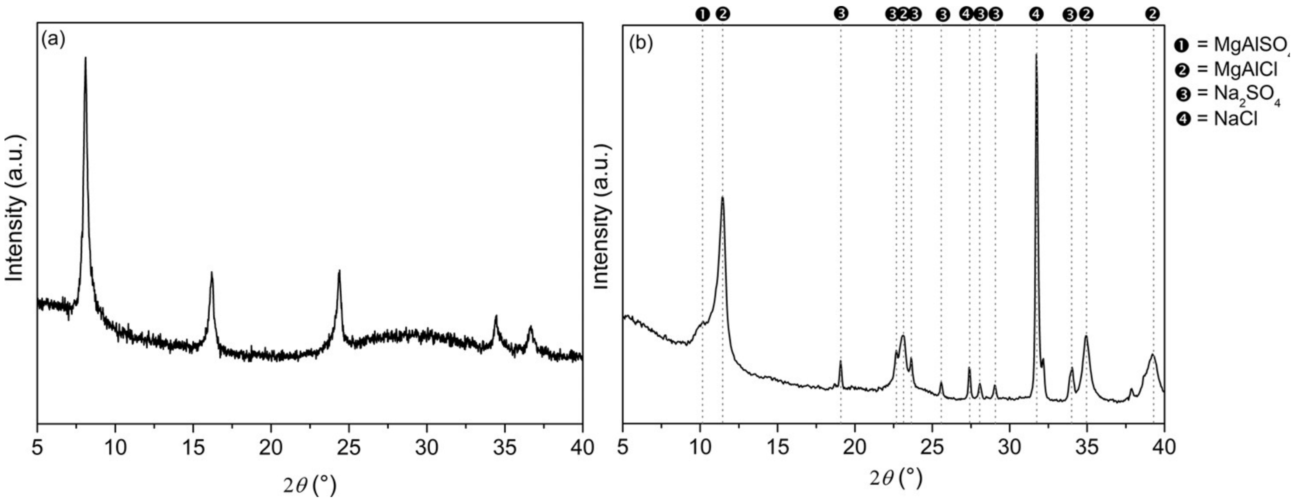

Figure S2 XRD patterns of $MgAlSO_4$-NaCl: hydrated mixture (a); dry mixture (b).

Figure S3 (a) shows the XRD pattern of the wet $MgAlSO_4$-$CaCl_2$ mixture collected immediately after the contact and displaces the co-presence of the dry $MgAlSO_4$ and gypsum phases precipitated by reaction between the free calcium ions and the sulphate ions of the LDH. As no traces of MgAlCl are observed, it can be suggested that the Cl^- ions intercalated are solubilized in the sulphate phase, as previously discussed. Significant changes occurred when the mixture was entirely dehydrated (Figure S3 (b)): the Cl^-/SO_4^{2-} exchange is complete and all the sulphate ions are precipitated as gypsum, confirming that the presence of free calcium ions facilitates the replacement of SO_4^{2-} with Cl^- in the LDH interlayer space by removing SO_4^{2-} from the aqueous phase through the precipitation of $CaSO_4$.

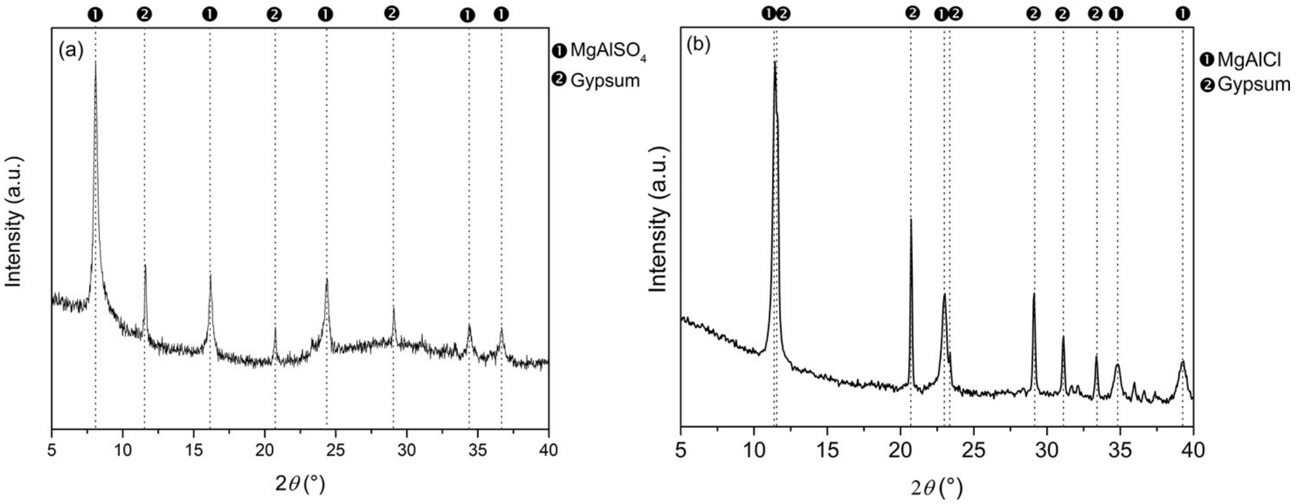

Figure S3 XRD pattern of $MgAlSO_4$-$CaCl_2$: hydrated mixture (a); dry mixture (b).

Reaction of MgAlCl/ZrPNaH wet paste with $CaCO_3$ and $CaSO_4$

In order to evaluate the selectivity towards gypsum rather than calcite a wet paste constituted by ZrPNaH, MgAlCl, Gy and $CaCO_3$ (see experimental) was examined by XRD (Figure S4). In the spectrum it possible to detect the following phases: residual ZrPNaH, $MgAlSO_4$, ZrPCaH, residual Gy and not dissolved $CaCO_3$. It is worthy to note the absence of carbonate form of LDH that proves the higher selectivity of LDH towards sulphate of Gy rather than the carbonate of $CaCO_3$, despite the well know affinity of LDH for carbonate anions. This makes the paste not harmful toward the marbles or other carbonate based stones.

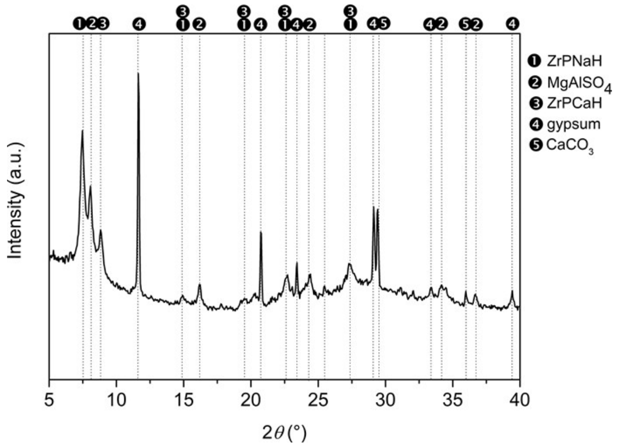

Figure S4 XRD pattern of ZrPNaH, MgAlCl, Gy and $CaCO_3$ wet paste.

References

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