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A new use of hydroxyapatite-based consolidant: cleaning and consolidation of stones in one step by reaction with gypsum crust

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The reaction between diammonium hydrogen phosphate (DAP) and calcite in the stone to form hydroxyapatite (HAP) had provided a new product to consolidate limestone or Ca-rich stones, for example sandstones with carbonatic cement. However, what does it happen with the stones without Ca-bearing compounds? Obviously, HAP cannot form. In the other hand, recent research about consolidation with DAP show a good interaction between carbonatic stones and HAP, improving their mechanical properties. For these reasons, we propose a new method for the consolidation of building stone capable of cleaning the gypsum crust and consolidating stones at the same time, based in the Ferroni-Dini method [1] and using DAP. Based on this method, we aim at obtaining a consolidating component reacting DAP (instead of ammonium carbonate) and the gypsum contained in the crust of weathered stones in polluted environments. As an advantage, we do not need to use barium hydroxide (the second step required in the Ferroni-Dini method), thereby reducing the time necessary to carry out the consolidation. Here, we report different tests to evaluate this new procedure. In a first set of experiments, a DAP solution was poured on a gypsum (dihydrate calcium sulphate) saturated solution and by monitoring the free calcium content of the solution using an ion-selective electrode we have evaluated the fluctuations in the content in calcium of the solution and the speed of the reaction. Once the reaction finished, we analyzed the solids formed to verify the formation of hydroxyapatite by FTIR and microRAMAN. The second test consisted in the alteration of limestone blocks with sulfuric acid to obtain a crust of gypsum and, after that, the samples were consolidated by means of cellulose compress soaked in DAP 3M during different reaction times (30 minutes, 1 hour and 4 hours, at controlled temperature -20 ºC- and relative humidity -40% HR-). The samples were then analyzed by XRD, FTIR, microRAMAN and SEM-EDX to verify the formation of hydroxyapatite and the elimination of gypsum by transformation into ammonium sulphate (highly soluble). Our preliminary results show that the reaction occurs at room temperature in a short period of time. The amount of gypsum decreases with reaction time, while the amount of HAP significantly increases, with the gypsum being almost completely removed after 4 hours of reaction. We can conclude that this procedure is an optimal solution to remove the gypsum contained in the crust of the weathered stones and to consolidate them, independently of the mineralogical composition of the stone.

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[1] M. Matteini, "In review: An assessment of Florentine Methods of Wall Painting Conservation Based on the Use of Mineral Treatments", in "The Conservation of Wall Paintings: Proceedings of a Symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute", London, 1987, pp. 137-146.