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Original article

Hydroxyapatite-based consolidant and the acceleration of hydrolysis of silicate-based consolidants



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ABSTRACT

Limestone, composed of the mineral calcite, is susceptible to environmental weathering processes that cause weakening from disintegration at grain boundaries. This paper discusses the effectiveness of hydroxyapatite (HAP) as an inorganic consolidant for physically weathered Indiana Limestone compared to a commercially available silicate-based consolidant (Conservare[®] OH-100). A double application is also investigated, in which samples are coated with HAP followed by Conservare[®] OH-100. Finally, a technique to accelerate the hydrolysis reaction of the initially hydrophobic Conservare[®] OH-100 is also developed. The motivation for using HAP is its low dissolution rate and crystal and lattice compatibility with calcite. To artificially weather limestone, so that the damage found in nature could be mimicked in the lab, a reproducible thermal degradation technique was utilized. Then, a mild wet chemical synthesis route, in which diammonium hydrogen phosphate (DAP) salt was reacted with limestone, alone and with cationic precursors, was used to produce HAP microfilms to consolidate the grains. The effectiveness of Conservare[®] OH-100 is investigated by applying it alone, and by following up with an ethanol-water rinse to accelerate the hydrolysis reaction. Samples that were to be rinsed were left to hydrolyze naturally over two and seven weeks before being reacted in the ethanol-water mixture. The dynamic elastic modulus (a measure of stiffness) and water sorptivity of the treated stones were evaluated. HAP was found to be an effective consolidant for weathered Indiana Limestone, as it restored the modulus of damaged stones to their original values and exhibited superior performance to Conservare[®] OH-100. Rinsing the Conservare[®] OH-100-treated stones increased stone hydrophilicity significantly, although not to the level of DAP-treated stones, as determined by water sorptivity. The formation of the consolidants in the pores and at grain boundaries was confirmed by scanning electron microscopy (SEM) and energy-dispersive X-Ray spectroscopy (EDX).

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1. Research aims

The first aim of this study was to develop an inorganic consolidant treatment for weathered limestone based on the mineral hydroxyapatite, as an alternative to conventional silicate and polymeric consolidants. The second aim was to investigate the ability of hydroxyapatite to act as a coupling agent for a silicate-based consolidant. Lastly, a technique to accelerate the reaction of the silicate-based consolidant was developed and the efficacy of the three treatments were investigated and compared, in an effort to find the most effective consolidant for weathered limestone.

2. Introduction

Limestone, a calcite-based sedimentary stone with chemical formula CaCO_3 , has been used for millennia in the construction of various monuments, buildings and sculptures around the world. Unfortunately, due to its porosity and chemical properties, it is vulnerable to various forms of weathering, such as salt crystallisation, freeze/thaw cycles, clay-induced swelling and acid dissolution [1,2]. Over the years, such weathering can lead to severe structural damage. Due to the historical and archaeological value of these structures, preventive and curative measures to preserve and restore limestone are of utmost importance.

A consolidant is intended to restore the mechanical integrity of deteriorated stones by binding the grain boundaries and fracture surfaces, either physically or chemically [3]. The ideal consolidant should retain the stone's water transport properties and aesthetics, and the treatment should be reversible, or at least not hamper further treatment. There are various classes of

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consolidants, including polymeric, lime-based and silicate-based materials.

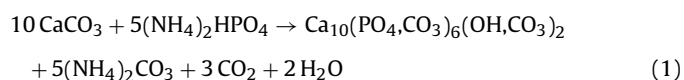
Polymeric consolidants, which include epoxy resins, polyacrylates, polymethacrylates, polyesters and polyvinyls, can be divided into two categories: thermoplastic polymers and thermosetting polymers [4,5]. Thermoplastic polymers stiffen as the solvent evaporates, but the chains are not crosslinked; thermosetting polymers are formed via cross-linking of chains to form a three-dimensional insoluble network. In both cases, the polymer solidifies inside the stone and holds the grains together. The main disadvantages of polymer-based consolidants are their limited penetration depth, sensitivity to ultraviolet rays and susceptibility to microbial attack [6,7].

Lime-based consolidation consists of applying limewater, $\text{Ca}(\text{OH})_2$, to the stone which in the presence of atmospheric carbon dioxide, CO_2 , converts to calcium carbonate, CaCO_3 . The treatment is chemically compatible with calcite, but is plagued by its slow reaction rate, limited penetration depth and induced changes to the stone's appearance [4]. To address some of these issues, recent work on lime-based consolidants has focused on the development of nanolimes, but penetration is still limited to about one millimetre [8].

Silicate-based consolidants are very effective on silicate stones, such as quartzitic sandstone, due to their chemical compatibility [9,10]. One such consolidant is tetra-ethoxy-ortho-silicate (TEOS), $-(\text{Si}(\text{OC}_2\text{H}_5)_4)_n-$ [11] (commercially available in the U.S. as Conservare[®] OH-100) [12]. It is usually applied via brushing or spraying and penetrates via capillary suction. Over time, atmospheric water replaces the $-\text{OC}_2\text{H}_5$ groups with $-\text{OH}$ groups. This process is known as hydrolysis, and is very slow, taking six to eight weeks to complete [9]. Once TEOS has hydrolyzed, the oligomers condense with each other to form a silica gel. The gel can then form covalent bonds with the silanol groups on the surface of sandstone [13].

Unfortunately, TEOS is not as effective on carbonate stones, as it can only bond mechanically i.e. by filling in the irregularities in the stone [4]. This is due to the absence of $-\text{OH}$ groups in calcite that would allow chemical interaction to occur. A variety of chemical coupling agents has been tested with the goal of enhancing bonding between silicate consolidants and carbonate stones [9], but none is widely used. Exposure of carbonate stones to ammonium hydrogen tartrate results in formation of calcium tartrate [14], which is potentially useful as a coupling agent (owing to exposed OH groups) or as a consolidant itself. However, the occurrence of a condensation reaction between the tartrate and silicate species has not been directly demonstrated.

To address the lack of an effective consolidant for limestone, hydroxyapatite (HAP) was tested as a consolidant for limestone, using the precursor diammonium hydrogen phosphate (DAP) and based on the following mechanism [15]:



This reaction occurs via a dissolution/precipitation process at ambient temperature and pressure. As indicated in the formula, HAP is usually found carbonated due to its interaction with carbon dioxide from the atmosphere. There are a number of metastable calcium phosphate phases, such as dicalcium phosphate dihydrate and octacalcium phosphate, that may form first depending on reaction conditions [16,17]. However, HAP is the most stable calcium phosphate and the precursor phases eventually convert to HAP via dissolution and reprecipitation. The HAP formed through this reaction was found to be crystalline in nature [18].

As illustrated by Sassoni et al. [15], this treatment restores the mechanical integrity of deteriorated Indiana limestone, in certain

cases to its initial undamaged conditions. In addition, the benefits of this treatment are:

- structural compatibility (i.e., similarity in crystal symmetry and lattice spacing) between calcite and HAP [19];
- retention of water transport properties;
- no chromatic alteration;
- the inorganic and non-toxic nature of treatment.

Consolidation with HAP has been independently investigated by several groups [15,20,21].

The incorporation of a calcium-based precursor provides calcium ions for HAP formation externally, which increases the rate of the reaction significantly and prevents dissolution of calcite from within the stone as the calcium is provided at a concentration above the solubility limit of calcite [18]. Calcium chloride, CaCl_2 , was found to be the most effective calcium precursor for this purpose, among a number of calcium salts that were investigated by Naidu et al. [19].

The motivation for the present study is to evaluate the use of HAP as a coupling agent between calcite and a silicate consolidant. We therefore test the effectiveness of treatment with DAP followed by Conservare[®], in comparison with DAP or Conservare[®] alone. We also examine the availability of OH groups on the surface of HAP spectroscopically to rationalize the results of the consolidation tests.

3. Methodology

3.1. Materials

Indiana limestone (IL) is composed mainly of calcite (CaCO_3 , >97%) and minute amounts of MgCO_3 , Al_2O_3 and SiO_2 . Most of the calcite is in the form of calcite-cemented oolites, with trace amounts of sparry crystals. IL has a porosity of approximately 14% [22]. IL samples used in this study were core-drilled cylinders with a diameter of 2 cm and a height of 5 cm.

The DAP (puriss. p.a. >99%) and calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, assay >99.0%) were both purchased from Sigma-Aldrich, their concentrations made up with demineralised water. TEOS was obtained from PROSOCO, Inc. as Conservare[®] OH-100 and diluted in a 1:3 v/v ratio with ethanol (EtOH) before application. This was done as undiluted conservare was found to form cracks inside the stone [13].

For spectral analysis, commercial HAP nanopowder (<200 nm, >97% purity) was obtained from Sigma-Aldrich. Trimethylethoxysilane (TMES, >98%) was obtained from Sigma-Aldrich, sodium hydroxide (NaOH, ACS reagent grade >97%) from ACROS and hydrochloric acid (HCl) from EMD Chemicals. Deuterium oxide (D_2O , >99.9% purity) was purchased from Cambridge Isotope Laboratories, Inc.

Ethanol solvent (200 Proof) was manufactured by Decon Labs, Inc., decane (99.5% purity) from Fisher-Scientific and hexane (assay >98.5%) from EMD Chemicals.

3.2. Accelerated weathering

Subjecting limestone samples to heat induces accelerated degradation of the stone [15,23]. The higher the temperature, the greater the damage. Heating beyond an hour has minimal further effect, as once the cracks between the grains open, only a further increase in temperature can create further damage. It was found that subjecting IL samples to 300 °C for 1 hour decreases the stone's dynamic elastic modulus by 40%, comparable to the decrease in E_{dyn} due to natural weathering in the field of ~36% [24]. Hence, using

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