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## Chemical consolidants for cultural heritage preservation: does crystal engineering have a role to play?

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Cultural heritage refers to intangible traditions and tangible artifacts. The latter have been at the epicenter of several scientific disciplines, mainly in the framework of preservation. An important and integral part of the preservation of cultural heritage objects (large or small) is the application of chemical consolidants. These are chemical compounds (inorganic, organic, or hybrid) that are used to stabilize and strengthen deteriorating artifacts, structures, or artworks. Important attributes of a consolidant for managing stone deterioration include high penetration depth, chemical compatibility with the stone, and the ability to improve mechanical properties, while minimizing the risk of accelerated degradation or aesthetic changes. This Highlight attempts to correlate the action of consolidants with the stone through the tools of crystal engineering. It presents selected information on inorganic, organic, and multifunctional consolidants, and focuses on the possible mechanisms of the consolidating action through the “eyes” of the chemist/crystal engineer.

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### Introduction

Cultural heritage (CH) embraces tangible artifacts and intangible traditions. It is a vital component of human identity and a source of shared understanding across generations. While providing a link to the past, it fosters a sense of continuity and belonging while promoting cultural diversity and resilience in a rapidly changing world. Understanding and preserving CH enables citizens of the world to explore their roots, appreciate diverse perspectives, and contribute to a more inclusive and harmonious global society.

UNESCO categorizes CH into two main types: tangible and intangible.<sup>1</sup> Tangible cultural heritage is further classified into immovable (historical buildings, monuments, and archaeological sites) and movable categories (paintings, sculptures, furniture, and wall paintings). Nowadays, there is a growing interest in the development of different treatments for the conservation and protection of different invaluable assets of tangible cultural heritage. The preservation of CH is crucial because it protects our past, connects us to our roots, and shapes our future. It helps us understand our origins, our journey from the past to the present, and what values and traditions we can carry forward. By preserving tangible and intangible elements of our culture, we foster a sense of

identity and belonging within communities, promote intercultural dialogue, and contribute to a more vibrant and diverse world for future generations.

Consolidant materials are crucial for the long-term preservation of CH, especially for fragile or degraded structures. They help to reinforce and stabilize materials, preventing further damage from environmental factors or mechanical stresses. By filling voids and binding deteriorated particles together, consolidants can strengthen the structure of buildings, artifacts, and other CH objects, ensuring their survival for future generations.

A broad definition of a consolidant is this: it is a substance or material that is used to stabilize and strengthen deteriorating artifacts, structures, or artworks. It augments the cohesion of loose or friable materials, preventing or slowing down further damage, thus enabling the preservation of these valuable objects. The use of consolidants is common for the restoration of stone-based buildings and other stone artworks.<sup>2</sup> A consolidant contributes to establishing (or re-establishing) effective cohesion on weathered stones and adhesion between healthy and modified stone areas, but without causing any physicochemical or aesthetical alterations.<sup>3</sup> A consolidant can be inorganic,<sup>4</sup> organic,<sup>5</sup> hybrid,<sup>6</sup> or a blend of individual chemical species that may act synergistically.<sup>7</sup>

Highly desired attributes of a consolidant aimed towards stone deterioration include high penetration depth, chemical compatibility with the stone, and the ability to improve mechanical properties, while minimizing the risk of

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accelerated degradation or aesthetic changes. It should also be durable and resist further degradation.<sup>8</sup> Other features include cost-effectiveness, non-toxicity, and friendliness to the user/conservator. The above concepts are schematically displayed in Fig. 1.

This Highlight attempts to correlate the action of consolidants with the stone through the tools of crystal engineering. It presents selected information on inorganic, organic, and multifunctional consolidants,<sup>9–13</sup> providing further references for the interested reader, but focuses on the possible mechanisms of the consolidating action through the “eyes” of the chemist/crystal engineer.<sup>14–21</sup> To the best of our knowledge, this is the first attempt to relate crystal engineering concepts with the chemical consolidation field.

## Types of consolidants

### Inorganic consolidants

Inorganic materials have been considered as consolidants, mainly due to their compatibility with mineral substrates, their exceptional durability in outdoor environmental exposure, and their chemical stability. These materials typically act by precipitating a (usually) white, insoluble phase within the stone's pores or by reacting chemically with the substrate aiming to reproduce the stone's natural matrix and strengthen its structure. For example, silica-based consolidants are commonly used for sandstone, while calcium carbonate and barium carbonate are applied to limestone. However, empirical practice often reveals a critical oversight: the chemical compatibility between the consolidant and the stone is frequently overlooked.

Inorganic consolidants often fall short due to several interrelated issues. The most challenging and well-determined problem in the literature is their poor penetration, as they can form a fragile, superficial crust rather than penetrating deeply into the stone. In addition,

inorganic materials can produce harmful soluble salts as by-products, they may induce undesirable crystal growth, and they often fail to effectively bind stone particles.<sup>22</sup>

For several years alkoxy silane-based consolidants, most commonly those derived from tetraethoxysilane (TEOS), have served as the foundation of stone consolidation efforts.<sup>23</sup> These products typically contain alkoxy silanes with three or four alkoxy groups. After application, they hydrolyse and condense directly within the stone's pore structure, forming a continuous, three-dimensional silica network (Si–O–Si) that significantly enhances cohesion in porous substrates. These systems offer notable advantages, including their low viscosity which promotes deep penetration into the stone's pore network. Furthermore, they exhibit strong chemical and thermal stability due to the strong Si–O–Si bonds. Their application is convenient and user-friendly, and can be retreated later if needed, while having minimal impact on stone's appearance and moisture dynamics. Finally, the by-products of sol-gel polymerization—primarily water or ethanol—are generally harmless in the context of stone treatment.

Although alkoxy silane consolidants perform effectively in siliceous stones like sandstone, they face serious limitations when applied to carbonate stones such as porous limestone. The presence of calcium carbonate in these substrates delays hydrolysis and condensation reactions often preventing proper gel formation and resulting in weak chemical bonding. In marble, some mechanical stability may be achieved by consolidants wedging into cracks, but this is ineffective in fine-grained carbonate stones with pore-shaped voids, where deeper integration is lacking. Even when gelation occurs, the resulting gel tends to crack and shrink during drying due to capillary stresses, compromising durability. Additionally, slow polymerization can leave the material mechanically weak for extended periods and may negatively affect the stone's pore structure and moisture behaviour over time.

To address these shortcomings, several specialized commercial formulations have been introduced. Elasticized variants like KSE 300 E® and ESTEL 1100® incorporate flexible molecular segments to produce a more flexible silica gel and significantly reduce brittleness and crack formation. Meanwhile, formulations such as KSE 300 HV® are engineered with specific adhesion-promoting agents targeted at carbonate substrates.<sup>24</sup>

Recent investigations have explored ammonium phosphate, particularly diammonium hydrogen phosphate (DAP), as an innovative consolidant for lime- and cement-based mortars. By reacting the calcium-rich substrate with aqueous solutions of ammonium phosphate, calcium phosphates (CaPs) can be formed inside the stone pores. These newly formed CaP minerals bond more effectively with aggregate particles, significantly enhancing the mechanical properties. The DAP treatment has shown high mechanical effectiveness on all substrates, thus resulting in the most effective consolidant on marble and limestone. Across all



Fig. 1 Attributes that an ideal consolidant must possess.



formulations tested, the ammonium phosphate treatment consistently improved mechanical resilience without substantially altering the pore structure or adversely impacting water transport properties. Compared to other treatments, DAP has the advantage of being effective after just a few days, instead of weeks, without significantly altering the pore system and the water transport properties of mortar. In addition, the colour change was always below the visibility limit of the human eye and alterations in pore size distribution and water transport properties were minor. The DAP treatment also showed remarkable durability, since all the DAP-treated substrates were able to reach the end of the accelerated durability test (130 freezing–thawing cycles for marble and limestone, 28 for mortar) basically without any weight loss. Finally, the DAP treatment can be accounted for low global warming impact.<sup>25,26</sup>

Calcium hydroxide is a classic consolidant for limestone.<sup>27</sup> Typically applied as an aqueous solution/dispersion, commonly referred to as limewater, it reacts with carbon dioxide in the air to form calcium carbonate on the stone surface, although carbonation occurs only near the surface. A dense layer of calcite forms quickly, which in turn blocks further CO<sub>2</sub> diffusion and prevents deeper consolidation. Unfortunately, this surface carbonate is inherently weak and prone to sulphation in polluted environments, which produces the much more soluble calcium sulphate (gypsum) and diminishes long-term durability. Although many conservators consider limewater harmless, they acknowledge its effects are superficial without repeated treatments.

Nanolime dispersions – colloidal Ca(OH)<sub>2</sub> nanoparticles suspended in alcohol – offer a modern improvement.<sup>28</sup> Nanolime can penetrate into deeper pores of carbonate stones, while avoiding the formation of a blocking surface crust. Several studies have shown that nanolime treatments improved drilling resistance and reduced water uptake in several stone types. Thicker slaked lime pastes—made by mixing quicklime with water to form layers of pure Ca(OH)<sub>2</sub>—have been evaluated on small-scale stone objects such as statues at Wells Cathedral (Somerset, England). These methods produced observable consolidation after weeks, although such approaches are applicable mainly on small objects.

Strontium and barium hydroxides function similarly to calcium hydroxide, reacting with atmospheric CO<sub>2</sub> to yield their respective carbonates.<sup>29</sup> A key advantage is that their sulphation products, SrSO<sub>4</sub> or BaSO<sub>4</sub>, are very insoluble, thus improving resistance in sulphur-polluted environments compared to calcium-based treatments. However, aqueous application tends to generate dense surface crusts with shallow penetration, which frequently exfoliate due to crystal mismatch or growth stresses. Experimental approaches using controlled, *in situ* precipitation—such as dissolving Ba(OH)<sub>2</sub> with urea to slow carbonate formation—have been studied for more stable consolidation, but remain largely experimental and not yet validated for long-term effects.

## Organic consolidants

Acrylic-based resins have found widespread use in stone conservation, in particular acrylic resins dissolved in organic solvents, such as Paraloid B72 (a.k.a. Acryloid B72). They promote a substantial enhancement in stone strength, in spite of the fact that they are able to consolidate only a thin outer stone layer. Although the epoxy resins promote a higher increase in mechanical strength than silanes or acrylic consolidants, they present certain issues that raise concerns about the lack of reversibility, unacceptable colour changes, and high viscosity. They are generally transparent and colourless, and exhibit good resistance to atmospheric agents, but are prone to degradation in the presence of water, especially in acidic or alkaline conditions. Lastly, suitable methods of application are not well established.<sup>30</sup> The acrylic consolidant Paraloid B72 is an ethyl-methacrylate/methylacrylate copolymer (manufacturer Röhm and Haas), is compatible with several solvents (*e.g.*, toluene, xylene and acetone) and has a long history in the CH conservation field.<sup>31</sup> Despite their sensitivity to photo-oxidative weathering, treatments based on acrylic resins have been used for stone consolidation for decades, because of their efficiency in bonding together calcite grains, while providing water-repellent properties as well.<sup>32</sup>

Epoxy resins are commonly supplied in the form of oligomers dissolved in a suitable solvent (necessary to reduce the high viscosity). The size of the stone pores is a critical parameter. Large pores allow more consolidant to infiltrate. Small stone pores may seriously limit the use of preformed polymers. This is why it is preferable to allow monomers to infiltrate into the stone interior and then to polymerise.<sup>33</sup> A cycloaliphatic epoxy resin, EP 2101 (produced by EUROSTAC) is available in the form of a solution (25% in toluene/isopropanol).<sup>34</sup> Epoxy resins in general, despite featuring strong bonds and high mechanical resistance, have poor resistance to atmospheric agents and are prone to yellowing, due to exposure to UV radiation.

A non-polymeric treatment based on ammonium oxalate was developed in the '90s.<sup>35</sup> The use of a water-soluble oxalate induces the formation of calcium oxalate. The advantage of this approach is that the artificially formed calcium oxalate is completely colourless, in contrast to the spontaneously formed calcium oxalate in natural patinas, which appears in various colours (from light yellow to amber, to black) due to incorporation of atmospheric particulate matter.

## Dual consolidants

The first application of alkoxy silanes functionalized appropriately with organic moieties to consolidate carbonate stones goes back to the early '90s. Four trimethoxysilane-bearing consolidants functionalized with adhesion promoting groups (amine, diamine, acrylic, and epoxy) were evaluated for the consolidation of carbonate stones. Promising



consolidation efficiency was reported, and significant improvements on the rupture modulus were noted for limestones treated with amino-trimethoxysilanes, despite the unacceptable colour alterations.<sup>36</sup> More recently, the presence of the amine functional group was further exploited as an adhesion promoter by using the amino functionalized alkoxy silanes 3-aminopropyltriethoxysilane (APTES) and N1-(3-trimethoxysilylpropyl)diethylene-triamine (SiDETA). These were used either mixed with conventional alkoxy silane formulations or by carbonate substrate functionalization as a primer for subsequent treatments. A formulation containing polyethylene glycol (PEG) was also used to induce low cracking tendency and enhanced adhesion (due to the presence of SiDETA).<sup>37</sup> The beneficial effects of amine-functionalized silanes (APTES) were independently confirmed in consolidation efforts in porous limestone based on DRMS measurements, see Fig. 2.<sup>38</sup>

A common problem with alkoxy silane consolidants is that they allow the formation of cracks. Hence, the development of hybrid alkoxy silane-based consolidants is a viable solution to crack-free products. The use of hydroxyl-terminated polydimethylsiloxane (PDMS-OH) is a common approach, as it can induce xerogel rigidity acting as an “elastic bridge” to produce modified networks.<sup>40</sup> An additional effect of the formulations containing PDMS-OH is that they offer surface hydrophobicity due to the non-polar nature of the PDMS-OH polymeric chains.

The incorporation of *n*-octylamine as a templating agent for the growth of the silica network was proposed as another solution to the cracking issue. *N*-Octylamine can form micelles (under appropriate conditions) acting as templates for the condensation of silanol, see Fig. 3. The gradual growth of the silica network on the *n*-octylamine micelles creates pores in the consolidant similar to those formed by nanoparticles. This approach causes the coarsening of the gel pores, which reduces the pressure on the silica matrix during the drying stage.<sup>41,42</sup>



Fig. 2 Comparative drilling resistance measurements of untreated and treated porous carbonate. The treatments were consolidant formulations containing TEOS only, and TEOS + SiDETA. Reproduced from ref. 39 with permission from Springer Nature BV, copyright 2018.



Fig. 3 Schematic representation of the proposed mechanism for the silica network build-up by using *n*-octylamine. Created by the authors.

A dual function consolidant was developed by our group for gypsum stones that is based on a molecule that possesses two phosphonate groups and an alkoxy-silane group. The consolidant 3-(trihydroxysilyl)propylamino-diphosphonate (TRIPADIPHOS) is considered as a multifunctional one because it possesses a self-condensable (after hydrolysis) trihydroxysilyl  $[-Si(OH)_3]$  moiety and two phosphonate groups. TRIPADIPHOS showed excellent gypsum consolidation features and was much more efficient (per unit concentration) than all other tested consolidants (commercial TEOS, RC-70 and RC-90). Its action was ascribed to its better gypsum anchoring ability *via* surface Ca-complexation. Selected compressive strength studies were performed on gypsum samples treated with the phosphorus-based consolidants and corroborate the findings from DRMS. Fig. 4 shows schematically its mode of action.<sup>43</sup>

The term “ormosil” refers to organically modified silica or organically modified silicate, a class of materials that have favourable properties, such as optical transparency and rich surface chemistry.<sup>44</sup> Ormosils can serve as an ideal nanoplatform for the assembly of “multimodal” nanoparticles for consolidation purposes. They are produced by adding silane reagents to a silica gel during the sol-gel process.<sup>45</sup>





Fig. 4 Conceptual correlation of the structural/functional features of TRIPADIPHOS with its efficacy as a gypsum consolidant. Reproduced from ref. 43 with permission from the authors and the American Chemical Society, copyright 2024. This publication is licensed under CC-BY 4.0.

A hydrophobic crack-free nanomaterial was reported with application to stone restoration. An ormosil consolidant was synthesized by the co-condensation of TEOS and PDMS in the presence of *n*-octylamine.<sup>46</sup> The effectiveness of the synthesized material as a combined consolidant and hydrophobic agent was evaluated on biocalcareous sandstone used commonly in monument construction in southwest Spain. An increase in the mechanical resistance of the stone was reported, while the creation of a hydrophobic coating was observed, based on the high contact angles measured. No adverse effects on the treated stone were observed. Ormosils with hydrophobic surface features have been synthesised, see Fig. 5.<sup>47</sup> The interested reader can resort to more extensive literature works available on the subject of hybrid consolidants.<sup>48</sup>

### Bacterial consolidants

Bacterial  $\text{CaCO}_3$  mineralization is a natural process. It is widespread among various bacterial organisms and can occur



Fig. 5 Example of the synthesis of a hydrophobic ormosil. Reproduced from ref. 47 with permission from the Royal Society of Chemistry, copyright 2014.

in various environments. Recently, it was proposed as a new and environmentally friendly tool in the conservation of calcareous stones encountered in ornamental and monumental objects. The goal is to exploit treatments based on bacteria-mediated mineralization, thus providing a robust and coherent  $\text{CaCO}_3$  layer on the surface of a deteriorated stone. This protective film can offer prophylaxis against water and chemical ingress and can consolidate the interior of the compromised structure. An advantage of this strategy is that a mineral salt is bacterially produced that is similar to the calcareous stone substrate and mimics the natural process of stone formation. In this section we will briefly discuss the mechanisms of bacterial mineralization and review the current strategies *via* this approach to enhance stone reinforcement.<sup>49</sup>

Bacterial mineralization is principally governed by four important physicochemical factors. These are: (a) the  $\text{Ca}^{2+}$  ion concentration, (b) the dissolved inorganic carbon concentration (*i.e.*,  $\text{HCO}_3^-/\text{CO}_3^{2-}$ ), (c) the solution pH, and (d) the nucleation sites on the surface. The key changes driven by the bacteria are the increase of the dissolved inorganic carbon concentration and the pH increase.<sup>50</sup> Hence, when these events occur in the presence of  $\text{Ca}^{2+}$  ions, supersaturation takes place, producing  $\text{CaCO}_3$ .

Bacterial surfaces are also important in  $\text{CaCO}_3$  mineralization. Cell walls serve as sites for  $\text{Ca}^{2+}$  ion absorption and as templates for heterogeneous nucleation and crystal growth.<sup>51</sup> Certain biomacromolecules may act as templates on the cell wall. They can also augment mineral formation in their “free” state, as part of the extracellular matrix, and not firmly attached to, or embedded in the cell wall.

During the past decades, bacterial mineralization-based approaches have been studied as alternative consolidation treatments for calcareous stones.<sup>52</sup> The advantage of such treatments is that a mineral forms *in situ* inside the stone pores that is similar in nature to the substrate being consolidated. According to the state-of-the-art in this field, there are three principal strategies to treat stone monuments with this technology. These are based on the application of (a) live cultures of certain bacterial strains, (b) bacterial culture media, and (c) selected components of bacterial cells.



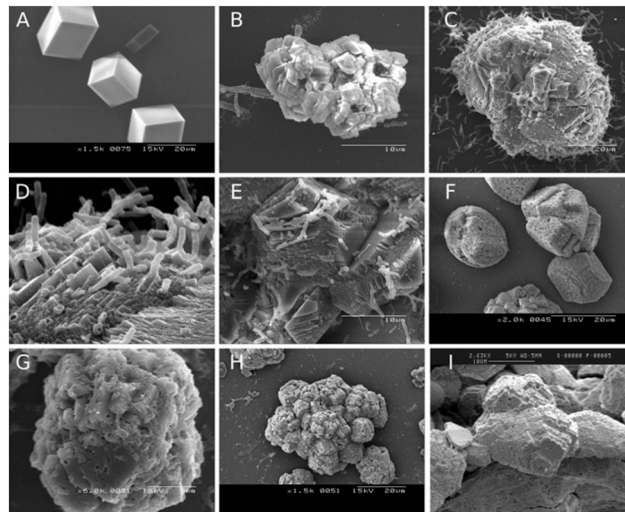
Historically, the first conservation application of bacterial mineralization on cultural heritage stones appeared in 1990 and was coined as “Calcite Bioconcept” technology.<sup>53</sup> The inventors sprayed cultures of selected bio-calcifying bacterial strains on the stone surface, while supplying a suitable growth medium. Subsequently, a new, few  $\mu\text{m}$  thick calcareous coating layer (biocalcin) composed of encrusted bacteria and  $\text{CaCO}_3$  formed on the surface. Laboratory work showed that *Bacillus cereus* showed the best performance among the tested bacteria and was selected for field applications. According to the field results, the deposition of biocalcin occurred inside stone pores, and no aesthetic changes were recorded.<sup>54</sup> Attempts to improve the process in the laboratory led to similar results.<sup>55</sup>

Later, the calcifying microorganism *Myxococcus xanthus* was tested on quarry calcarenite, which is a Gram-negative, non-pathogenic soil bacterium. The researchers managed to see improvements in the laboratory and in field trials.<sup>56</sup> They observed the formation of a coherent carbonate cement of calcite grains in the pores down to a depth  $\geq 500 \mu\text{m}$  (Fig. 6). This layer was thicker than that of biocalcin.

In an alternative strategy, the ability of bacterial dead cells (*Bacillus subtilis* strain 168) to precipitate  $\text{CaCO}_3$  was tested



**Fig. 6** SEM photomicrographs of treated sterile quarry calcarenite immersed in sterile culture media: (a) M-3, (b) M-3P, and (c) CC; sterile quarry calcarenite immersed in *Myxococcus xanthus*-inoculated culture media: (d) M-3, (e) M-3P, and (f) CC; non-sterile quarry calcarenite immersed in sterile culture media: (g) M-3, (h) M-3P, and (i) CC; and non-sterile quarry calcarenite immersed in *Myxococcus xanthus*-inoculated culture media: (j) M-3, (k) M-3P, and (l) CC. Legend:  $\text{cc}_{\text{spar}}$ : sparite;  $\text{cc}_{\text{mic}}$ : micrite; cbc: calcified bacterial cells;  $\text{cc}_{\text{new}}$ : newly formed bacterial calcite rhombohedra;  $\text{cc}_{\text{sph}}$ : bacterial carbonate (vaterite) spherulites; EPS: exopolymeric substances. Reproduced from ref. 56 with permission from Elsevier, copyright 2008.



**Fig. 7** SEM micrographs of calcite crystals produced by *Bacillus subtilis* dead cells and BCF. (A) Crystals formed in the control solution ( $\text{CaCl}_2$ ). (B–E) Crystal development by *Bacillus subtilis* dead cells from day 1 to day 4. (D and E) Bacterial body-induced crystal growth. (F–I) Calcite crystals induced by BCF. Reproduced from ref. 57 with permission from Elsevier, copyright 2014.

in a solution assay containing  $\text{Ca}^{2+}$  and carbonate ions. Dead cells were able to induce calcite formation exclusively (Fig. 7). Bacterial cell fractions, obtained with different fractionation methods, were then tested in the precipitation assay. A bacterial cell fraction containing the cell wall, called BCF, induced calcite formation (Fig. 7).<sup>57</sup>

A new method based on the bioconsolidation capacity of carbonatogenic bacteria for historical gypsum plasters was reported and compared with conventional consolidation treatments (Fig. 8). Improved results were obtained using the bioconsolidation treatment based on the application of M-3P



**Fig. 8** TEM images of bacterial vaterite. (A) General view of bacterial vaterite spherulites forming micrometer sized aggregates. (B) Detail of a vaterite structure showing its internal mesostructure. Reproduced from ref. 58 with permission from Elsevier, copyright 2014.



culture medium to activate the carbonatogenic microbiota present in the plasters. The bacteria produced calcium carbonate biocement composed of vaterite embedded in an organic matrix, providing high mechanical resistance. The depth of consolidation achieved by this biotreatment (up to 2 cm) does not cause any aesthetic alterations in the treated material.<sup>58</sup> The interested reader can resort to more extensive literature works available on the subject.<sup>59</sup>

## Mineral-consolidant interactions

The intimate interaction of a consolidant (organic, inorganic or hybrid) with the mineral surface to be consolidated largely governs its consolidating efficiency. The subject of molecular interactions of various species (either small molecules or polymers) with a mineral (inorganic) surface is of interest in several scientific and technical fields, such as crystal growth (and its control), dispersion, surface attachment, surface complexation, *etc.*<sup>60</sup> The consolidation field has a lot to gain from these fields along the lines of how such interactions are studied, enforced or modified. Below, some representative cases will be discussed that involve mineral-molecule and/or mineral-ion (mostly anion) interactions and are “borrowed” from the crystal growth field.

Molecular dynamics (MD) simulations were used to explore how widely used phosphonate-based molecules adsorb onto calcite surfaces. MD simulations reveal that phosphonate-based scale inhibitors predominantly adsorbed as hydrated outer-sphere surface complexes within the Stern double layer. Meanwhile, the carboxylate-based molecules formed both inner- and outer-sphere surface complexes with higher adsorption than phosphonate-based ones. The four compounds depicted were three phosphonate-based (ATMP, amino-tris(methylenephosphonic acid), EDTMP, ethylenediamine-tetrakis(methylenephosphonic acid), and HDTMP, hexamethylenediamine-tetrakis(methylenephosphonic acid) and one carboxylate-based (DTPA, diethylenetriamine-pentaacetic acid). The results showed that the phosphonate moiety significantly outperformed carboxylate in binding to both calcite and barite. The number of phosphonate groups and their degree of protonation were identified as key factors



Fig. 9 Simulation of the calcite-ATMP interaction confined in a calcite nanopore in the reservoir water. Reproduced from ref. 61 with permission from the American Chemical Society, copyright 2025.

influencing their interactions with metal cations, which in turn affected the aggregation and adsorption capacity.<sup>61</sup> Fig. 9 shows the interaction of ATMP with the calcite surface.

Long *et al.* examined the scale inhibition behaviour of a composite agent comprising PESA (PESA = polyepoxysuccinic acid) and CMC-Na (CMC-Na = sodium carboxymethyl cellulose) in several process environments using the static scale inhibition technique. Furthermore, using Material Studio software, MD simulations of the scale inhibition process were carried out to assess the binding energies of the used molecules on the surfaces of calcite (104) and calcite (110). The MD simulations provided further insights into the composite agent mechanism of calcite scale inhibition. The calculations indicated that the composite PESA-CMC exhibited greater binding energy compared to the CMC-Na, PESA, and the calcite surface, suggesting that the PESA-CMC composite was the most effective in calcite inhibition (Fig. 10).<sup>62</sup>

Interactions of various phosphonates (as osteoporosis drugs) with calcium phosphate mineral surfaces (present in bones) were also studied.<sup>63</sup> Differences in bone mineral binding affinities of clinically utilized bisphosphonates (BPs) have been described with a decreasing rank order of zoledronate > alendronate > risedronate > etidronate. This may lead to differences in bone uptake and release. A computer-aided 3-D analysis of nitrogen (N)-containing BPs was conducted to explain these differences. Once a low energy conformation of each BP was oriented in a tridentate binding mode on the trigonal prismatic column of calcium atoms in hydroxyapatite (HAP), the N side chain conformations of the BPs were examined for their interaction with the [001] surface. The 4-amino group of alendronate can form a strong N-H...O hydrogen bond (132°, N...O distance 2.7 Å) to the labile -OH oxygen on HAP. The corresponding ring N of zoledronate can only form a weaker electrostatic interaction with this labile -OH site. However, it can form an additional strong hydrogen bond



Fig. 10 The calcite (104, upper) and (110, lower) surfaces: (i) CMC-Na adsorption, (ii) PESA adsorption, and (iii) composite CMC-PESA adsorption structures. Reproduced from ref. 62 with permission from Elsevier, copyright 2024.



to a bifurcated network, between two oxygen atoms coordinated to a calcium in a neighbouring column of trigonal prismatic calcium centres including a  $132^\circ$  angle and a  $2.7 \text{ \AA}$   $\text{N}\cdots\text{O}$  distance, explaining its high affinity. In the case of risedronate, steric hindrance of the pyridyl ring prevents its N from forming hydrogen bonds in either direction and it may only form weaker electrostatic interactions, such as at the labile  $-\text{OH}$  ( $102^\circ$ ,  $\text{N}\cdots\text{O}$  distance  $3.0 \text{ \AA}$ ) This affords weaker affinity compared to alendronate and zoledronate, but produces higher affinity than etidronate (containing no N functional group).

Molecular modelling was used to interpret the effect of two structurally similar molecules EDTMP and EDTA (the former being a tetra-phosphonate, while the latter is a tetracarboxylate) on the crystal growth of barium sulphate.<sup>64</sup> The replacement energy was found to correlate with the degree of inhibition as determined from conductivity experiments. It was also possible to predict the preferred barium sulphate face for additive adsorption. For EDTMP, the energetically favoured adsorption configurations were those where the phosphonate groups occupied vacant sulphate lattice sites, while for EDTA it was generally not possible for all four carboxylate groups to lie within the surface and so surface Ba–O interactions (Ba comes from barite, O from the organic molecule) became important. Whether in the surface or above it, the number of Ba–O interactions were important in making adsorption of the modifier energetically favourable.

A phosphonate macrocycle (1,7-dioxo-4,10-diaza-12-crown-4-*N,N*-dimethylenephosphonate), according to computer simulations, should recognize and bind to all the important crystal growth faces of barium sulphate.<sup>65</sup> Subsequent crystallization experiments clearly showed that all faces were modified by the formation of spherical single crystals, thus showing the viability of the novel design strategy (Fig. 11), *i.e.*, the application of a universal crystal-face blocking agent. Such an approach should prove invaluable as a general protocol for the design of not only new crystal growth inhibitors, but of novel heterogeneous systems and materials.

Molecular modelling techniques were used to investigate the interaction of alkyldiphosphonate molecular anions with the surfaces of barium sulphate. It was shown that the most stable sites are on the (100) and (011) surfaces with the fully deprotonated  $-\text{PO}_3^{2-}$  groups of the diphosphonates replacing surface sulphate ions. These results were compared with experimental observations. Analysis of the calculated energies demonstrated that the overall binding energy represented a subtle balance between the internal energy of the diphosphonate and the binding energy of the distorted diphosphonate in the site.<sup>66</sup>

The adsorption of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC, a well-known mineral scale inhibitor) on calcite surfaces (110), (102), (104), (113), and (202) was studied by molecular simulations.<sup>67</sup> The phosphonic and carboxylic acid functional groups energetically interacted with the faces and



Fig. 11 Binding of 1,7-dioxo-4,10-diaza-12-crown-4-*N,N*-dimethylenephosphonate on the crystallographic faces of barium sulphate, together with relative energies for each conformation. Reproduced from ref. 65 with permission from the American Chemical Society, copyright 2000.

preferentially occupied the carbonate ion sites by chemisorption, which is in agreement with the critical pH experiments. The strength of adsorption followed the order of  $(110) > (113) > (102) > (202) > (104)$ . The binding energy gradually decreased with increasing temperature. The relationship between the critical pH and the adsorbed  $\text{PBTC}^{2-}$  configuration indicated that the adsorbed configuration played an important role in inhibition efficiency (Fig. 12).

The interaction of carboxymethyl dextran (CMD) with calcite surfaces was studied *via* quantum mechanical calculations and MD simulations.<sup>68</sup> Specifically, the interactions between the functional groups of CMD and calcite (104), (110), and (1–10) surfaces in aqueous solution were modelled at different degrees of polymerization (DP) of CMD (2, 4, 6, 8, and 10, respectively), see (Fig. 13).





Fig. 12 Most suitable configurations and preferential adsorption sites of  $\text{PBTC}^{2-}$  ions on calcite surfaces. Reproduced from ref. 67 with permission from Elsevier, copyright 2016.

The adsorption configuration, radial distribution function, deformation energy, binding energy, and relative concentration distribution of water molecules near the surface of calcite were calculated. The results showed that the carboxyl functional groups in CMD were strongly electronegative and able to form strong chemisorption bonds with  $\text{Ca}^{2+}$  ions on the calcite surface. Furthermore, as the DP increased, the binding energy and the peak value of the radial distribution function increased, indicating an increase in the probability and strength of adsorption of CMD on the calcite surface (Fig. 13).

The interactions between four carboxylate-containing polymers, polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), oxidized starch (OS), and carboxymethyl cellulose (CMC) with the surfaces of  $\text{CaCO}_3(110)$ ,  $\text{CaCO}_3(104)$ ,  $\text{CaSO}_4(020)$  were investigated by molecular dynamics simulations and density functional theory calculations.<sup>69</sup> The results indicated that the binding energy of the polymer onto the surface of  $\text{CaCO}_3(110)$ ,  $\text{CaCO}_3(104)$ , and  $\text{CaSO}_4(020)$  follows the ranking: PESA > PASP > OS > CMC (Fig. 14).



Fig. 13 Adsorption configuration of CMD on calcite surfaces: upper, (101) plane; middle, (110) plane; lower, (1-10) plane. Reproduced from ref. 68 with permission from Elsevier, copyright 2023.



Fig. 14 Geometry optimization of polymer-calcite interaction systems with water. Reproduced from ref. 69 with permission from Elsevier, copyright 2021.

## Conclusions/perspectives

The field of consolidation of CH is a truly interdisciplinary area where several scientific and technical sectors meet. Consolidants, either inorganic, organic, hybrid or biochemically produced, are chemical compounds whose particular properties are exploited in the framework of CH preservation.

A chemical consolidant must possess certain attributes for successful application. Among the physicochemical features, the most prominent is its affinity for the stone/material to be consolidated. This is ensured by the presence of suitable chemical moieties on the consolidant backbone. Examples of such chemical groups include carbonate, sulphate and phosphate (for inorganic consolidants) and phosphonate and carboxylate (for organic consolidants).

Other significant practical aspects also need to be considered: maintenance of the aesthetics of the stone, lack of cracks, penetration depth, absence of brittleness, allowance for the stone to “breathe”, and absence of undesirable and harmful by-products.

Apart from the practical aspects of consolidant application in the field, it is equally important to set a solid basis of the chemistry and crystal engineering behind the phenomenology of the consolidation process. This starts from the molecular level, particularly with the intimate interactions of a consolidant (either organic, inorganic or hybrid) with the mineral surface to be consolidated. Importantly, such interactions principally govern consolidation efficiency. This is the area where crystal engineering strategies can be most useful, as outlined in the previous sections of this Highlight.



Chemical consolidants and proper consolidation approaches are integral parts of the preservation of CH artefacts. There exist numerous opportunities for development and improvement, as this area is a truly interdisciplinary field of research, bringing together expertise from inorganic/organic/polymer/physical chemistry, materials science, computational science, engineering and archaeology.

## Author contributions

Stefania Liakaki-Stavropoulou: writing – original draft, writing – review & editing. Konstantinos D. Demadis: conceptualization, writing – original draft, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this Highlight.

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