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Review

Current Trends in Stone Consolidation Research: An Overview and Discussion

B. Sena da Fonseca

Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal; bruno.fonseca@tecnico.ulisboa.pt

Abstract: This work aims to reveal the recent research trends in the consolidation of stone-built heritage and discuss the advantages and drawbacks of the options and strategies followed by researchers over the last 10 years. Peer-reviewed articles were used to build a database and analyze the details of the stone samples (chemical nature, type of voids, and condition), treatment protocols (application methods and consolidation products), and testing methods to assess the strengthening results of the treatments. In addition, the reported increments in the mechanical properties were also examined to reveal the strengthening capabilities of recent consolidation treatments. The statistical treatment of the results allowed pinpointing the stone varieties that need more frequent consolidation actions (limestone, biocalcarenite, and sandstone) and the aspects that make them more difficult and riskier. Other tendencies were discussed, for example, the predominant use of sound samples over decayed samples (61% vs. 39%) or the predominant use of alkoxysilanes (~46%) over other families of consolidants (e.g., nanolime, ~21%). The current consolidation treatments were found to improve stone strength; however, the most problematic issue in state-of-the-art is the difficulty of identifying high-risk situations of over-consolidation or poor distribution in depth because of either the lack of testing or limitations of the various assessment techniques.

Keywords: built heritage; decay; conservation; treatments; mechanical strength; strengthening capability; cohesion

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1. Introduction

The safeguarding of cultural heritage is an important challenge for today's society, as stated in the world policy guidelines for sustainable development [1]. Since stone has been one of the most used materials since antiquity and is thus present in numerous monuments and sites with cultural, historical, and artistic value, many researchers have focused their attention on stone decay phenomena as well as on their conservation. Within this context, stone consolidation plays an important role because it aims at avoiding the imminent and irreparable loss of deteriorating historic stone objects of cultural or artistic value. Ideally, it must restore the cohesion between particles of damaged stones and make them as durable as unweathered stones [2]. As a remedial conservation action, consolidation should be carried out when the object is in a fragile condition or when the current damaging processes will lead to its loss in a short period of time [3]. Unlike consolidation actions, the protection of stone materials is a preventive conservation action that is aimed at avoiding or minimizing future degradation or loss [3]. In practice, consolidants need to reach the underlying undamaged material to be effective—penetration depths of 15–20 mm are often needed [4,5]—while protective actions are required at the surface to avoid the ingress or retention of damaging agents such as water, biocolonization, graffiti, or staining/dirt.

In any case, conservation practice implies a respect for specific values, conservation principles, and a full understanding of the object and the characteristics of its materials. The need for intervention is determined through qualitative and quantitative analysis (direct observation, historical research, structural analysis, experiments, and tests) and no action should be undertaken without evaluating the benefits and possible harm to the heritage. The treated material should have mechanical, physical, chemical, and aesthetic compatibility with the untreated historic material [6,7]. Because stone consolidation deals with very delicate situations, such as highly carved surfaces losing their shape, it should only be performed after demonstrating that it is essential, indispensable, effective, and compatible.

The conservation intervention requirements allied with stone variability and specific technical issues make the stone consolidation practice extremely challenging and a field that deserves intensive investigation. Although many unresolved challenges are long-standing, the frequency of articles on stone consolidation published in peer-reviewed journals is increasing at a steady pace (Figure 1a), which implies a growing interest in the field.

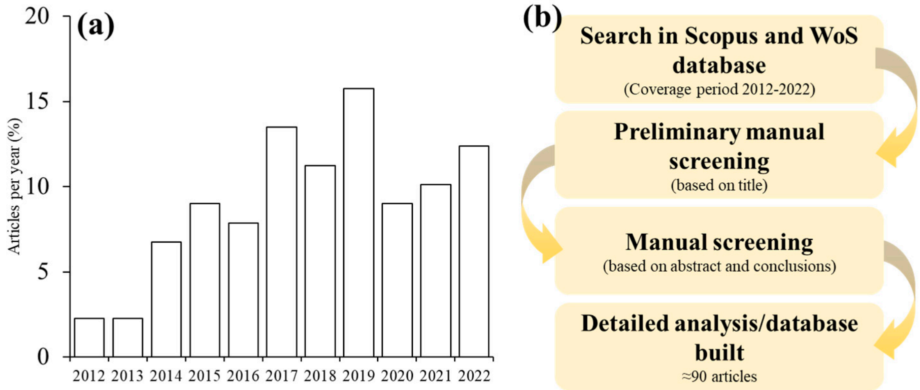

Figure 1. Evolution of the peer-reviewed articles published during 2012–2022 describing results of stone consolidation (only articles reporting strengthening effects) (**a**) and the methodology for building the database in this document (**b**).

Stone consolidation research has been based on two main types of studies, those studying new consolidants and their potential performance and those studying solutions for specific situations. Stone consolidants are constantly improving, and comprehensive reviews in this field addressed specific types of consolidants and focused on their chemical reactions, chemical variants, advantages and limitations, and potential performances in different stones, among other aspects. For example, stone consolidants based in alkoxysilanes [5,8], diammonium hydrogen phosphate [9], or nanolimes [10]. These analyses helped to identify gaps and problems in each family of consolidants and provided recommendations for further improvements. However, the gap between research and practice is being pointed out as a key problem of the field [11–13], something that requires a broader approach, including a critical analysis of the experimental methods and research strategies followed by researchers. The meaning and usefulness of research outcomes are determined by these options. Stone variety and damaging conditions (i), treatment specificities (consolidant family and application method) (ii), and the means to access the strengthening obtained (iii) vary from study to study.

Within this framework, this review discloses recent research trends in the consolidation of stone-built heritage to recognize the major issues and identify where the gaps between the reality of research and practice can be shortened.

Different ways to assess the potential efficacy of consolidation treatments have been adopted by researchers over the last 10 years. The overview and critical discussion of the advantages and drawbacks of the research strategies and experimental methods in this document aim at identifying research limitations and recommending areas that need further improvements.

2. Methods

2.1. Database Build

A number of scientific articles on the domain of stone consolidation were gathered and analyzed within the scope of current investigation according to the methodology described in Figure 1b [14–101]. The documents were selected for being peer-reviewed articles published in the last 10 years (2012–2022) and for being included in the Web of Science or Scopus databases. The ones that do not report strengthening values promoted by consolidation treatments were excluded. Valuable research was also published in conference proceedings; however, these documents are typically harder to obtain, may not be sufficiently detailed to build this database, and would make the topic too extensive and difficult to analyze. Therefore, they were not considered.

"Stone consolidation" was the main search term used, but the search was not limited to it. The articles were analyzed in different phases to extract all that were unrelated and build a list that fulfilled the aims of this study (see sequence in Figure 1b). A major challenge of this step was to exclude all the articles dealing with treatments whose aim was not consolidation as understood by conservation science or those dealing with multiple actions (e.g., consolidation and hydrophobicity). Several of the unrelated articles were not detected in the manual screenings using the titles or abstracts because of ambiguous terminology. This first step identified important issues that need to be improved in the field, which is the understanding of the concept behind consolidation actions (aims and how it should be assessed).

A database of key information obtained in the last 10 years of stone consolidation research was thus built by collecting the following information from each article: (i) stone variety, (ii) specificities of consolidation treatments, (iii) test methods used to assess the strengthening, and (iv) the strengthening promoted by the treatments.

Stone consolidation research also deals with other important aspects, such as the compatibility and durability of the consolidation treatments; however, the detailed analysis of these subjects was outside the scope of this manuscript.

2.2. Database Structure

Although stone varieties can be grouped according to several criteria—genesis, texture, porosity, strength, etc.—this work grouped the stone varieties (i) according to 3 key criteria for stone consolidation:

- Chemical nature;
- Type of voids;
- Physical condition.

The rationales for grouping the data in these groups are discussed in Section 3.1.

On the treatment side (ii), the documents were analyzed considering two main aspects:

- Application protocol;
- Product family.

Regarding the application protocols found in the literature, the current manuscript addressed the application methods—immersion, brushing, spraying, poultice, etc.—and other relevant aspects, as specified in Table 1; however, this information was difficult to systematize as multiple situations are possible.

Table 1. Criteria used to analyze the experimental program of research articles regarding the stone sample characteristics (i) and the consolidation treatment details (ii).

<table>
<tr><td rowspan="7">(i) Stone samples</td><td colspan="2" rowspan="2">Chemical nature</td><td colspan="2">Carbonate (e.g., marble, limestone, biocalcarenite)</td></tr>
<tr><td colspan="2">Silicate (e.g., granite, sandstone, tuff)</td></tr>
<tr><td colspan="2" rowspan="2">Type of void</td><td colspan="2">Pore-shaped (e.g., limestone, biocalcarenite, sandstone, tuff)</td></tr>
<tr><td colspan="2">Fissure-shape (e.g., marble, granite)</td></tr>
<tr><td colspan="2" rowspan="3">Condition</td><td colspan="2">Sound (i.e., unweathered, unaged)</td></tr>
<tr><td colspan="2">Artificially aged (e.g., thermal action, freeze–thaw cycles, salt crystallization)</td></tr>
<tr><td colspan="2">Naturally aged</td></tr>
<tr><td rowspan="8">(ii) Consolidation treatment</td><td rowspan="3">Protocol</td><td rowspan="2">Application technique</td><td>Continuous fluid supply</td><td>Immersion, capillarity, poultice</td></tr>
<tr><td>Discontinuous fluid supply</td><td>Spray, brushing</td></tr>
<tr><td>Criteria</td><td colspan="2">Number of stokes, apparent saturation (time for film), soaking time, penetration depth, product consumed/absorbed, retreatment schedule, etc.</td></tr>
<tr><td colspan="2" rowspan="5">Product family</td><td>Si-based</td><td>Alkoxysilanes, silica nanoparticle suspensions, etc.</td></tr>
<tr><td>Inorganic products</td><td>Limewater, nanolime, diammonium hydrogen phosphate, calcium, barium hydroxide, ammonium, calcium oxalate, tartaric acid, nano-calcite suspensions, etc.</td></tr>
<tr><td colspan="2">Acrylic resins</td></tr>
<tr><td colspan="2">Epoxy resins</td></tr>
<tr><td colspan="2">Biomineralization</td></tr>
</table>

The organization of the most common consolidation products in this study was provided in [11] and divided the main families into the following groups: Si-based products, inorganic products, epoxy resins, acrylic resins, and biomineralization. This classification roughly divided consolidants by their chemical affinity; however, each group included consolidants with very different characteristics, appropriateness, and outcomes. Multiple active ingredients and mixtures were possible in each group, especially formulations prepared and tunned in the laboratory. Stone consolidants are constantly improving, and a comprehensive review of the families of consolidants most frequently used was outside the scope of this work. These can be found elsewhere: alkoxysilanes [5,8], diammonium hydrogen phosphate [9], and nanolimes [10].

Finally, the approaches used to assess the strengthening of the treatments (iii) were also analyzed with the aim of discussing the current trends and their suitability for each situation.

3. Results and Discussion

3.1. Stone Materials

3.1.1. Chemical Nature

Although all stone varieties decay and can present degradation forms eligible for consolidation, in recent years, research activity has been mainly focused on limestones, biocalcarenites, and sandstones (Figure 2a), which suggests that these require consolidation interventions more often and/or that their consolidation is somehow more challenging. While these stone varieties might be more vulnerable, research studies on many other stone varieties (marble, tuff, granite, dolostone, etc.), are also found in the literature (Figure 2a).

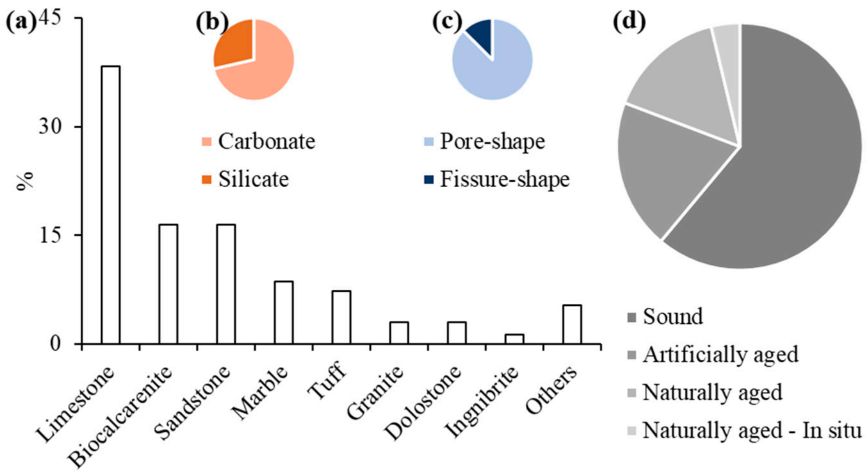

Figure 2. Distribution of stone varieties used in stone consolidation research according to lithotype (**a**), mineralogical nature (**b**), type of void shape (**c**), and condition (**d**).

The conservation field frequently divides stone materials according to their main chemical nature into silicate and carbonate stones. This separation is not justified based on their susceptibility to degradation but rather on their chemical affinity with the main groups of products. Si-based consolidants (alkoxysilanes, Si suspensions, etc.), are hypothetically more adequate for silicate stones, while most inorganic options (limewater, nanolime, DAP-based, etc.), or biomineralization are hypothetically more adequate for carbonate stones because of their chemical proximity. Therefore, this rough division is helpful when determining the family of products to be used in a given situation [11].

All lithotypes have specific problems but the consolidation of silicate stones (most sandstones, granite, tuff, etc.), has been less investigated than carbonate stones (limestones, biocalcarenites, marbles, dolostone, etc.) (Figure 2b). This likely occurs because their treatment is in general more effective and less problematic than that of carbonate stones. Si-based consolidants are theoretically more adequate for silicate stones such as sandstones or granites because of the hydroxyl-rich surfaces of the constituent minerals. On the other hand, this widely investigated family of consolidants has a poor affinity with carbonate stones such as marbles and limestones, something that has been discussed and studied for a long time [102–105]. These consolidants cannot establish adequate chemical bonds with carbonate minerals, and the properties of the consolidation material can be negatively affected by forming in an antagonistic chemical environment [8,106]. Current doubts about the application of these consolidants on carbonate varieties concern their medium/long-term behaviors [11].

Therefore, the literature on the consolidation of carbonate varieties prevails and addresses the tuning and improvement of Si-based formulations and the performance of inorganic options (limewater, nanolime, DAP-based, biomineralization, etc.), which are a priori more compatible, especially in the medium/long term.

3.1.2. Voids Shape

There are multiple intrinsic features of stones that influence the behavior of consolidation treatments, e.g., porosity, pore size distribution, grain size, textural parameters, etc., and each lithotype has its own combination of factors. Nevertheless, the behavior of different consolidants and the most appropriate way to assess their strengthening capability depend on the physical shape of the stone voids, i.e., the contrast between fissure-shaped and pore-shaped voids is important not only in stone degradation phenomena but also in stone consolidation [107–109]. The first is characterized by elongated and narrow discontinuities that have extensions significantly larger in two directions, while the second is composed of voids having a more or less equidimensional shape [110].

Stones having fissure-shaped voids have low porosity and can absorb small amounts of consolidants, although they can penetrate fast and deeply, while stones having "pore-shaped" voids, such as limestones, sandstone, tuffs, or biocalcarenites, can absorb greater amounts of products, but under lower penetration rates [109].

Research on consolidation has mostly addressed pore-shaped stones (Figure 2c). Stone varieties with pore-shaped voids are found more often (limestones, biocalcarenites, sandstones, etc.), (Figure 2a) which indicates that their consolidation might be more difficult and riskier.

The consolidant should ideally accumulate on the connections between adjacent grains to prevent excessive pore clogging in pore-shaped stones, while in the case of fissure-shaped voids, it should establish bridges along the narrow fissures or act by particle lockage through a wedging effect [105,111]. Because of the smaller amounts absorbed and the original low porosity of fissured stones, the physical modifications caused by consolidation treatments have a lesser impact on the remaining properties than in the case of pore-shaped stones.

The characteristics of the pore space, namely, the void shape, has an important role in stone consolidation, perhaps more important than in any other conservation action. This was confirmed by the collected data and should be considered when detailing consolidation measures and when analyzing literature outcomes.

3.1.3. Lithotype Condition

The main target of consolidation treatments for decayed stones, artificially or naturally aged, is clear—re-establish the original cohesion of the stone—even if partial re-establishment might be sufficient and sometimes assumed as good in practice. However, sound stones have been the most frequent option to study stone consolidants (Figure 2d). The target when using sound stones is ambiguous since there is no reference for the strengthening value that "re-establishes" the stone cohesion, and the strengthening of the treatment might be less noticeable than when applied in decayed stones since the starting point is the resistance of the sound stone.

Although it is difficult to predict the actual behavior of a given treatment through preliminary tests on a sound stone, this allows us to assess whether or not it can strengthen the stone and to compare different products/treatments. In many cases, the use of sound stones is the most reasonable option, but the experimental process should be correctly adapted to the objective of the study, which must be clear to the researchers and consequently to the reader.

Even if sound stones are mostly used in consolidation research, studies carried out on aged stone samples obtained by artificial or natural processes treated in the laboratory or in situ are growing and make up a relevant percentage of the cases (≈40%).

Artificial Aging

The process of artificially aging samples does not necessarily need to reproduce natural processes but must cause a loss of stone cohesion and representative decay patterns. Therefore, these samples can be prepared by simulating natural processes or by using other procedures that can damage the stone according to their most typical patterns. The following damaging actions were found to be the most common in literature.

- **Thermal action:** Procedures using thermal effects to degrade the stone matrix are widespread in stone consolidation research. Generally, these exploit the differential thermal expansions of the minerals in polycrystalline stones such as granites or sandstones or the anisotropic thermal expansion of calcite/dolomite in monocrystalline stones such as marble. The differential responses of the minerals generate internal stresses in the stone matrix that cause the development of a network of fissures. Sugaring is a typical decay pattern in marbles and is carried out through artificially aging procedures based on thermal action. Experimental details should be mastered to avoid the development of large fissures that trigger the collapse of the samples and other degradation patterns that cannot be addressed by mass consolidation.

Researchers induce damage by the simple heating of samples, allowing them to cool down at a moderate rate, or by thermal shock through cooling down the samples quickly in water baths [81] or a water jet [67]. The latter also simulates the effect of cool water during the extinguishing of a fire.

Procedures without abrupt variations (thermal shock) and temperatures between 300–400 °C seem more adequate for marbles [19,75,78,84], while the minimum temperature for porous stones such as limestones, sandstones, or biocalcarenites is 400 °C [29–31,34,69,74,78,80] and desirable results might require more than one heating–cooling cycle [19,69,74,81] or a fast cooling [67,80].

- **Freeze–thaw cycles:** Although freezing and thawing are not the main concerns for stones from monuments in some areas, standard procedures for determining the resistance of stones to freezing and thawing have been adapted to affect the physical integrity of stone samples in order to study consolidants. Researchers have explored the good absorption capacity of some stones to load their pores with water that expands and generates internal stresses on the pore walls during the freezing phases. Samples submitted to freeze–thaw cycles underwent changes to their mechanical resistance because of microstructural damages. Depending on the stone's strength and porous characteristics, the major drawback of freeze–thaw cycles may be related to the long duration of the procedure. The ice crystallization pressure is more effective when damaging stones with pores within the 0.1–10 μm range than stones with pores of other size ranges [112].

A significant degradation degree is expected to occur with a reduced number of cycles in porous stones having well-connected pore systems and a portion of pores with specific sizes. Therefore, this strategy has proven useful for certain lithotypes such as porous limestones [92,113] and sandstones [38,101].

- **Salt crystallization:** A frequent cause of stone decay is the presence of salts and their pressure within the stone pore walls, which justifies per si its use to degrade stones for laboratory studies. Moreover, desalinization prior to consolidation treatments can follow several options in practice (poultices, electrochemical techniques, crystallization inhibitors, etc.), but none can guarantee the total removal of salts.

Nevertheless, this approach was not widespread in the literature, and only a few references were available in the last decade [42,81]. Similar to freeze–thaw artificial aging, standard procedures for determining the resistance of stones to salt crystallization have been adopted to prepare damaged (and contaminated) samples. The contamination is typically made by immersion in sodium sulfate solutions—one of the most damaging salts—and several immersion/drying cycles are involved. Depending on the conditions, the test can be too destructive and cause the loss of the samples [81,114]. As in the case of freeze–thaw cycles, it is important to establish the criteria for the required damage extent and adjust the protocols accordingly.

Because the effectiveness of this strategy also depends on the water absorption capacity of the stone and on the presence of pores of certain sizes, it is more adequate to degrade porous lithotypes having a relevant portion of pores smaller than 10 μm, such as some varieties of biocalcarenites [81] and limestones [42].

The artificial aging with salt crystallization imposes difficulties upon the study of consolidation treatments, namely, the excessive pore clogging and the poor efficacy of desalinization procedures [31,114]. This hinders the free penetration and distribution of the consolidants and eventually interferes with their normal chemical reactions. The consolidants also promote further salt mobilization, especially the water-borne consolidants.

Therefore, the option for salt-contaminated samples makes the analysis of consolidation treatments in the laboratory difficult because the presence of salts can limit the consolidation action of the products, trigger further loss of cohesion because of the dissolution of salts that act as a "binder", and facilitate the transport and re-crystallization of dissolved salts during the drying of the consolidant, which can act as an additional cycle [81].

Only a few research documents studying the behavior of the treatments in the presence of soluble salts were available [115], but they offer an important line of research for future exploration to close the gap between research and practice.

Other routes to artificially damaging stone materials for testing treatments have been sparsely used for specific evaluations. Attacking stone materials using acids or mechanical pre-stress are examples of these procedures. Acid nitric solutions can attack and dissolve stone minerals, which might threaten the integrity of stones [114], while sulfuric acid solutions attack stone minerals (carbonates) to form new instable ones such as gypsum. These must be stabilized or converted into a less soluble material through "consolidation" to avoid rapid dissolution and the attack of subsequent stone layers [55]. Mechanical pre-stress involves the development of microcracks through the application of a mechanical load below the typical failure load of the stone [99,114].

Natural Aging

The condition and specificities of naturally decayed stones are a result of a combination of factors, namely, the lithotype and its inherent variability and multiple degradation phenomena. Research on consolidation treatments using naturally aged stones can be performed in the laboratory using naturally aged samples or in situ by testing specific zones. Even if some lithotypes are more vulnerable than others, all can degrade and might require conservation interventions, even the most durable ones. Consequently, the literature reporting consolidation treatments of naturally aged stones addressed a vast variety of lithotypes. Naturally aged samples, limestones [49,59,63,70,82,97], marbles [19,43,75,84,85], biocalcarenites [32,33,58,90], sandstone [22,59,82], chert [40], chalk [28], and tuff [21] are examples, while from testing areas on monuments, marbles [75,85], biocalcarenite [47,80], marlstone [45], granite [25] and limestone [20] are examples.

Naturally aged samples are usually prepared from samples collected from bigger or movable objects exposed to natural conditions that were taken to the laboratory. The treatment is performed under controlled conditions, avoiding the difficulties imposed in situ, which has several advantages: it is possible to control the moisture content of the stone before the treatment and position the surface to be treated more conveniently (e.g., horizontally); resort to application methods that are difficult to execute in situ (e.g., total or partial immersion); allow more control of the environmental conditions during and after the treatments, and make it possible to carry out a more complete study on the behavior of the treatment as more tests are available.

However, stone samples obtained by core extraction or loosened pieces from stone objects with cultural significance need to be well justified and are only acceptable when there is already a familiarity with the treatment, i.e., at a late phase of the studies. The same applies to the treatment trials in situ, which should only be carried out after an extensive experimental campaign and screening process to reduce the risk of failure.

The availability of samples/testing surfaces is limited, and they tend to be heterogeneous, which complicates result interpretation in comparative terms, and systematic studies on the differences among multiple treatment procedures and/or consolidants are not possible. In fact, most investigations start with representative samples (sound or artificially aged) to determine the best application procedures/consolidants for a given situation prior to the studies on naturally aged samples/testing areas of monuments [84,116].

3.2. Treatments

3.2.1. Application Methods

Brushing was the most used application method in consolidation research (≈40% of the cases, Figure 3) probably because it is the most straightforward and practical option for common situations. Consequently, research studies have tended to adopt this application method, which is also considered the default method in the conservation [11] to approximate laboratory tests and trials to reality.

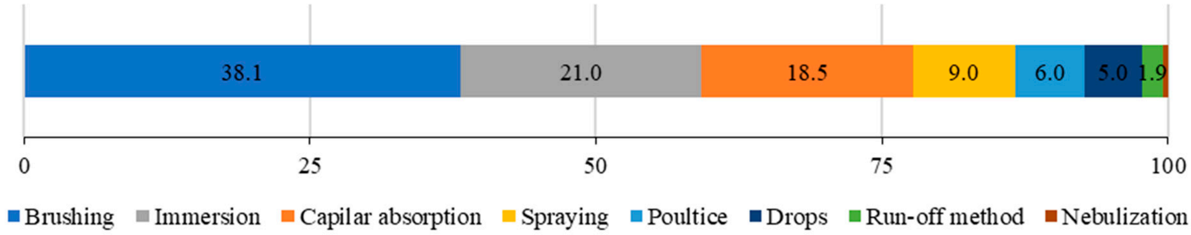

Figure 3. Distribution of the application methods used in stone consolidation research.

Capillary absorption and immersion (at ambient pressure) were also techniques frequently adopted in stone consolidation research, not because they are practical methods for built heritage but because both can produce reproducible results. They are thus suitable for studying consolidants in the laboratory and allow fair comparisons. Additionally, both are valid techniques for small and movable stone objects.

On the other hand, when large areas must be covered, spraying is a useful alternative. Based on this advantage, 9% of the treatments reported by the articles used this method to apply stone consolidants (Figure 3). However, the need to treat large areas such as entire facades is more frequent when dealing with protective treatments; therefore, protective products are more often applied by spraying than consolidants.

Poultices were utilized for salt removal and cleaning [117] and also produced satisfactory results in stone consolidation as good penetration depths are obtained, causing significant improvements in mechanical strength [31,78,118]. For certain consolidants, they provide particularly good results on marbles when compared to other techniques [78]. In recent years, the use of diammonium hydrogen phosphate-based consolidants has been explored [31,43,45,75,78,85] because they can also extract the unreacted DAP during the drying phase, in line with the mechanisms used for desalinization [31]. Other consolidants, such as ammonium oxalate [85,118] or alkoxysilanes [21], were applied by poultice in stone substrates; however, they were applied less regularly than the previously addressed methods.

Nebulization was much less frequently used in stone consolidation research (Figure 3) because it is hard to reproduce, is not precise, and complicates the penetration of the consolidants owing to excessive evaporation of solvents [11,58,119].

Run-off and drops were popular among conservators since they allow a much more targeted application than the previous examples. Moreover, they avoid direct contact with stone surfaces, which can be important when stone surfaces are in a very fragile condition [11,119]. Nevertheless, these methods were rarely used in consolidation research.

The application methods were divided into those supplying a continuous fluid flow, such as immersion, poultice, or capillary absorption, and those supplying a discontinuous flow, such as brushing or spraying. Although the methods supplying a discontinuous flow can favor the superficial accumulation of the consolidant and the formation of a superficial hard crust, there were many practical examples indicating that this was not the rule [30]. The occurrence of this superficial overconcentration of consolidant was reported for acrylics when applied by brushing, while for epoxy consolidants, for example, it was mainly reported for immersion, a method that supplies a continuous flow [4]. Alkoxysilanes can also be distributed homogeneously in depth when applied by discontinuous methods [30].

Certain porous varieties have a tendency to concentrate the product near the surface for poultice or capillary absorption applications because they can supply high amounts of products, which facilitates reverse migration [109]. In these cases, post-application measures to prevent or delay evaporation, such as isolating the stone surface, can avoid or reduce this effect.

Therefore, general rules about the consequences of a given application method were hard to establish since they depend on a complex combination of variables.

3.2.2. Consolidants

In conservation, it is good practice to choose the chemical affinity as the first selection criterion of the consolidant for a given stone [11]. Analogously, efforts to develop and test new consolidants should consider the characteristics of the targeted stones and use them as the main design conditioning factors. However, this did not always occur, which caused unexpected successes but also numerous failures. However, the outcomes cannot be merely explained by a supposed good chemical affinity or lack thereof.

Chemicals and compounds of different natures were used over time to consolidate and protect different varieties of stones. An aqueous solution of calcium hydroxide ($Ca(OH)_2$)—limewater—is one of the longest lasting options for limestones, with which they have very good affinity [2]. In the 1940s and 1950s, new synthetic organic polymers such as acrylics, epoxies, and polyesters were first used in many consolidation treatments, whereas alkoxysilanes and barium hydroxide were developed during the 1960s [120]. Several failures, especially on porous carbonate varieties because of their low mechanical resistance and chemical specificities, fostered the search for more adequate solutions and originated new research lines. A different approach to preserving carbonate stones, based on bacterial biomineralization, began in the 1990s [121], and scientific investigations on nanolime or tartaric acid started in the 2000s [10,122]. Around 2010, the use of diammonium hydrogen phosphate (DAP) to consolidate stones by means of hydroxyapatite and other calcium phosphates was proposed [9]. Other alternatives, such as ammonium oxalate [55,123], nanoparticles dispersed in aqueous colloidal suspensions (or zirconia [80] calcite [69], silicon dioxide [80], titanium [50]), and lithium silicate [91,124] were sparsely explored.

The research on Si-based products has been predominant in the last 10 years (Figure 4a). Interestingly, these products—more specifically, the ones based on alkoxysilanes—were still among the most developed and investigated despite the growth of new families of consolidants. The perseverance of alkoxysilanes in the search for new and improved consolidants is supported by their versatility, which has promoted research studies and captivated researchers. Alkoxysilane blends may integrate different functionalities, such as waterproof, biocide, or self-cleaning properties; however, documents addressing multiple functionalities were excluded from this survey; otherwise, the predominance of alkoxysilanes over other families of products would be even more categorical.

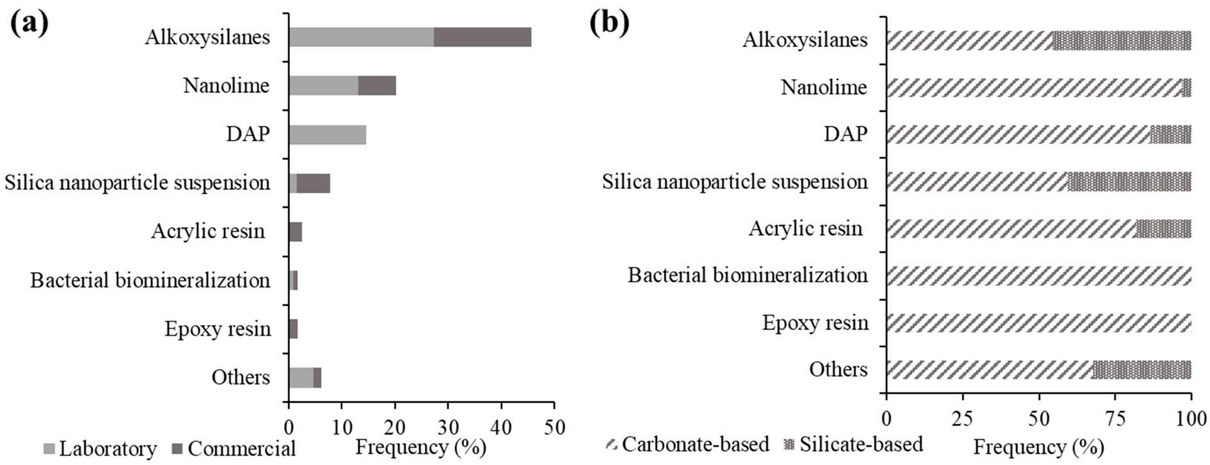

Figure 4. Distribution of the most used families of consolidants in stone consolidation research (**a**) and percentages according to the stone's chemical nature (**b**).

Relevant properties in consolidants can be tunned (dry residue, viscosity, morphology, stiffness, etc.), by managing reactional parameters and/or by the incorporation of diverse organic components such as organically modified silanes and silane formulations loaded with nanoparticles of several natures.

Advances in sol–gel chemistry have been boosted by other research fields because of their widespread application, something that has encouraged the development of more interesting formulations for stone consolidation as well.

A significant portion of the investigated articles dealt with simple alkoxysilane-based products—"ethyl-silicates"—(Figure 4a, dark gray) that are well established in the market and easily available. Therefore, alkoxysilanes were studied with different scopes as solutions for specific situations (e.g., [22,79,87]); as application procedures (e.g., [14,23,29]); and for comparison with new consolidants, whether they were based on alkoxysilanes or not (e.g., [21,24,25,33,89]).

It was interesting to note that Si-based consolidants, including alkoxysilane-based consolidants and silica nanoparticle suspensions, were applied and widely studied on carbonate varieties (Figure 4b). Nevertheless, the scientific community was also focused on alternative and theoretically more compatible solutions with carbonate substrates. Indeed, nanolime and diammonium hydrogen phosphate-based consolidants—two inorganic options with some affinity with carbonates—were also families of products frequently researched (Figure 4a).

The principles and action mechanisms of nanolime have several similarities with limewater and share the same theoretical high compatibility with carbonate stones. In addition to carrying calcium hydroxide ions, as in limewater, the nanolime consolidants can transport calcium hydroxide particles in the nanometer range (50–300 nm [125]) into the pore structure of the stone. These products are generally able to penetrate deeply in most porous stones, but the partial back-migration of nanolime particles with the solvent toward the drying surface is a major concern [126]. It is possible to manage the rate of evaporation according to the environmental conditions and the characteristics of the stone by changing the solvent in order to obtain improved results in relation to this aspect [127,128]. Research activity was further focused on mastering the conditions and procedures that enhance the strengthening potential in depth [10,95]. This consolidant is chemically compatible with carbonate varieties since calcium carbonate is the main constituent in both. Therefore, nanolimes were investigated mostly for carbonate stones (Figure 4b), mainly limestones but also marbles.

Another consolidation option, the third most investigated one (Figure 4a), was DAP, which reacts with calcite from stone (or Ca ions from other sources) to generate hydroxyapatite and/or other metastable calcium phosphate phases. In recent decades numerous concentrations of DAP in aqueous solutions and the incorporation of other reagents, such as calcium chloride and ethanol in different amounts, were investigated to optimize DAP treatments [129,130]. This type of treatment is also beneficial in terms of compatibility with carbonate stones, especially because of the similarity between calcite and hydroxyapatite in their crystal symmetry and lattice spacing [26].

Other solutions under the umbrella of inorganic products were rarely investigated in recent years—6% of the cases (Figure 4a)—and included suspensions of nanoparticles of several natures (e.g., nano-calcite [69,100], nano-zirconia [80,98], or nano-strontium [23]) and ammonium and calcium oxalates [28,55,85].

Bacterial mineralization is an option to consolidate carbonate stones since the consolidation material (mainly calcium carbonate [20,131]) is produced by bacteria in situ. The bacteria can be inoculated into the stone or the relevant microbial community resident on the stone can be active [132]. These solutions favor the precipitation of consolidation material on large pores because of bacteria size [133]; nevertheless, relevant consolidation actions in depth can be achieved under specific circumstances [134]. Advances in this field are occurring at a slow pace since the approach is technically complex and requires multidisciplinary teams, and there is a restricted number of specialists. The availability of scientific documents on this process was limited when compared to other families of consolidants.

Acrylic and epoxy-based products were two of the most researched and applied families of chemicals in the past; however, little attention has been paid to these consolidants in the last few years (Figure 4a). Their poor reputation is mainly due to incompatibility issues [102,135] and has hindered the interest of researchers, although their unique high strengthening capacity can be useful for specific situations, such as load-bearing elements with ongoing mass loss [11].

3.3. Assessing the Strengthening

3.3.1. Introductory Remarks

The penetration and presence of consolidation material within the stone pores are not synonymous with good consolidation action; therefore, it is necessary to guarantee an effective increment of cohesion, something that can be assessed by a single or a combination of test methods. The available test methods that quantify the strengthening capability of a certain treatment provide information with varying degrees of detail, as described as follows:

- Test methods that provide information essentially on **bulk** properties include compression tests, triaxial compressive tests, bending tests, splitting tests, ultrasonic pulse velocity with standard transducers, or dynamic elastic modulus. Most can provide overall information related to the strengthening caused by the treatment; however, information about the strength distribution along the treated depth is scarce or inexistent. Unless the entire volume of the object can be equally consolidated [2], which is very rare in practice, such bulk measurements are unsuitable, considering the heterogeneous character of the treated region [2,136,137]. Moreover, cases of subtle consolidation and/or superficial consolidation, as are sometimes needed, might not be properly quantified or detected by these tests.
- Test methods that provide information about **superficial** properties, such as the hardness test and peeling test, are usually non-destructive and provide information about the strengthening at a very superficial level. These can be informative when the objective is to stabilize stone surfaces, particularly in situ. The surface of stone objects has the most relevant artistic and architectural value; however, the quantification of the strengthening achieved of the most superficial thin layer of material might not be sufficient to explain the success of the consolidation action or predict the behavior of the whole stone object. Premature loss of the supposedly preserved hardened superficial layer of stone is frequent.
- Test methods that offer **thorough (continuous)** information, such as drilling resistance, register the evolution of strength from the surface up to a few centimeters in depth. The continuous data along the stone depth allow us to understand how the strengthening varies along the whole thickness of the consolidated stone and quantify the maximum consolidation depth.
- The **thorough approach (discontinuous)** provides information about the thickness that was consolidated and how the consolidation action varies in depth in a discontinuous way using bulk and superficial testing methods, or both. Examples of this approach were as follows: (a) Gauri et al. [136] resorted to the hardness evolution along cores of untreated and treated marble; (b) Remzova et al. [36] cut thin slices (3 mm) from sandstone samples and determined the bending strength of each one to obtain strengthening profiles in depth; and (c) Ferreira Pinto and Delgado Rodrigues [14], Sena da Fonseca et al. [84], among others [108,138], carried out ultrasound velocity measurements using exponential transducers along stone sample sides to draw profiles of the internal cohesion of crystalline stones.
- Discontinuous information along the treated depth can be obtained by following these or similar approaches.

Understanding the consolidation action in depth is not a new concern [2,137] and should have two major purposes: (i) to assess the penetration capacity of the product to reach the sound stone and "anchor" the treated degraded portion of stone to the sound one [137]; (ii) to guarantee adequate properties to the treated stone to avoid marked differences between the sound and treated material, which might cause the accumulation of moisture and salts behind the treated layer and delamination because of different hygro-thermal properties [2]. Relevant parameters that play an important role in the distribution of the consolidation action in depth are viscosity, surface tension, rate of formation/precipitation of consolidating material, method/condition of application, and rate of solvent evaporation.

Therefore, test methods or approaches that can assess the consolidation effect in detail are key, not only to assess the strengthening but also to provide important indications about compatibility issues.

Apart from the tests fitting the abovementioned categories, different artificial aging procedures are used to compare the behavior of untreated and treated stones [23,27,28,40,93]. Some assume these durability tests to be the best approach to assessing the success of consolidation treatments in terms of efficacy [23,37]; however, the results are very hard to interpret. The outcomes of these tests depend on several factors that include the durability of the consolidation effect, compatibility of the consolidant with the stone, and properties of the stone [2].

3.3.2. Most Used Test Methods and Approaches

Table 2 presents the test methods that were most often applied during the last 10 years to assess the strengthening capability of consolidation treatments and the frequency of their use. Some of the tests can provide a good dataset for the consolidation action, while others need to be combined to properly describe the impact of consolidation treatment.

Table 2. Distribution of the test methods used to assess the strengthening in stone consolidation research.

Test Method	Frequency (%)
Drilling resistance	19.7
Ultrasonic pulse velocity	17.9
Peel test	15.6
Hardness tests	14.1
Dynamic elastic modulus	9.8
Bending tests	9.4
Compression tests	4.9
Splitting tensile test	3.6
Abrasion test	1.5
Point load test	1.5
Young Modulus	1.1
Slake durability	0.4
Triaxial compressive tests	0.4

Drilling resistance measurements were made available in the early 2000s and have become the most used parameter to study consolidation treatments (Table 2), especially in stones containing pore-shaped voids [139], Figure 5c. The drilling resistance measurement allows an understanding of the behavior of the consolidants in depth, but it has other advantages, such as being micro-destructive, requiring a reduced amount of material, and allowing in situ performance [140,141].

The number of studies resorting to drilling resistance as a unique assessment test (Figure 5b) indicated that it is perhaps the most complete and informative technique. Nevertheless, it has some technical limitations: interpretation of drilling profiles in crystalline stones is hard, results from different drilling conditions are not comparable, possible dust accumulation in the drill hole [142], pre-drilling might be required but is hard to implement in situ, or drill bit wear [143].

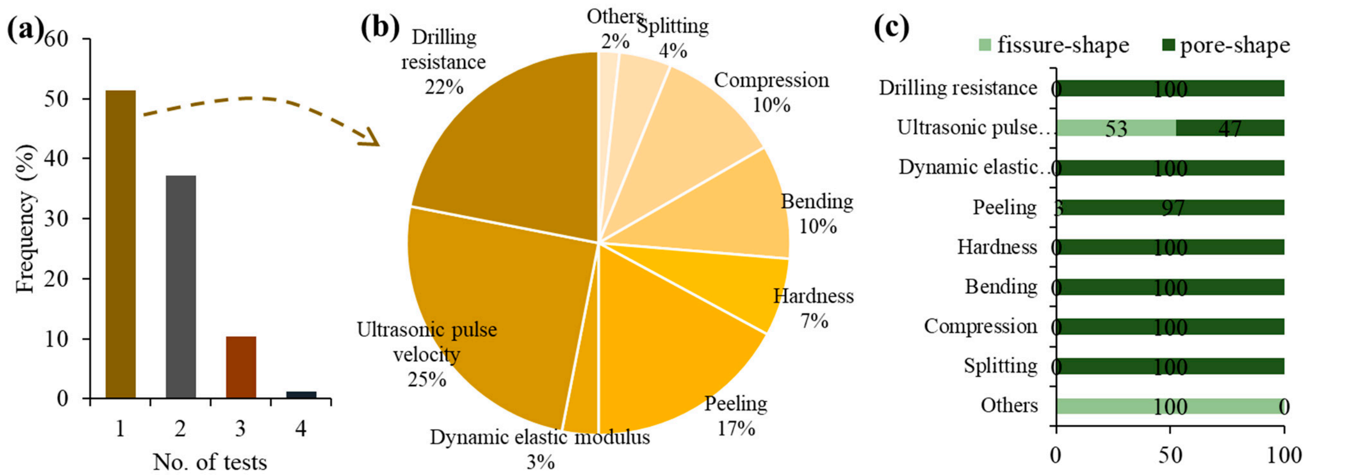

Figure 5. Distribution of the number of tests used to assess the strengthening effect of stone consolidants (**a**), distribution of the tests used when only one is employed (**b**), characteristics of the stones in relation to the types of voids when only one test is employed (**c**).

Ultrasonic pulse velocity was the second most used technique (first if considering the dynamic elastic modulus) (Table 2). It can detect and quantify possible alterations to treated stones from the presence of consolidating materials in the stone pore spaces. In fact, this method is considered one of the best options to evaluate the consolidation action in stones having fissure-shape voids, but it is not as suitable for stones containing pore-shape voids [108]. This is because the fissures are thin and have long discontinuities, which forces the ultrasound waves to cross them, and a significant decrease in their velocity is common. Thus, the presence of consolidation material filling the fissures triggers a significant increase in the ultrasound velocity. In contrast, in stones with a pore-shaped space, the ultrasound waves tend to pass through the stone matrix, avoiding the voids, and as a result, the consolidating material within the stone pores has a reduced influence on the ultrasound velocity [144]. Nevertheless, ultrasonic pulse velocity was frequently used to assess the strengthening ability of consolidation treatments applied on pore-shaped stones as the main assessment technique (Figure 5c), which may have caused inaccurate conclusions about their behavior when a poor or incipient consolidation action was achieved.

Superficial test methods, namely, peeling tests and hardness tests, were also well-established tests in stone consolidation research (Table 2). Peel tests provide direct information about the superficial cohesion of stone. This cohesion is normally quantified by the amount of material retained on an adhesive tape that is attached and removed from the testing surface. The peeling test is recognized as extremely useful for practitioners since it is easily used in situ and provides quantitative information that allows comparing situations before/after treatment and monitors the treatments over time [145]. However, its applicability is sometimes overestimated and the results are often non-reproducible and inaccurate [146]. Critical fluctuations in the results may arise because of the operator (attaching pressure and the speed of detachment), adhesive tape characteristics (e.g., flexural stiffness), and roughness of the surface [146,147]. Other limitations are the lack of information about excessive superficial strengthening that may cause incompatibility issues and the absence of information regarding the strengthening in depth.

Hardness tests included those based on rebound techniques [79,148–151], mainly the Leeb method, and those based on indentation techniques (durometers) that include the Vickers hardness tester [89,152,153], Martens sclerometer [14], and Shore durometers of different types [154]. Results reported in the literature regarding the superficial hardness of consolidated stones were hardly comparable since they included different types of methods and hardness scales. All types of tests are relatively simple to perform, can be carried out in situ, and are not as destructive. However, the rebound techniques have limited application since they are not accurate for small alterations in the stone's superficial hardness and can induce destructive effects on soft stones.

As mentioned before, the information is limited to the surface and must be complemented by other tests, capable of providing information in depth. Nevertheless, there remain cases that used one of these two tests as a single source of information about the strengthening capability (Figure 5b).

The most used traditional tests for the mechanical characterization of materials, such as compression or bending tests, were employed to study the strength increments due to consolidation actions [155,156], but because of their limitations and the development of more complete tests, these are now seldomly used to evaluate the efficacy of stone consolidants, see Table 2. The same is true for destructive tests, such as splitting tests used to indirectly determine the tensile strength, which were also employed by a small fraction of the researchers. Depending on how these mechanical tests are performed, they might only provide rough indications about the consolidation action [80,87,157]. These tend to present high scattering on brittle materials and the inhomogeneity of natural stone complicates their interpretation. A large number of samples is required to obtain a solid dataset [4,156]. In fact, the results from these tests should be considered with caution, especially the ones from compression and splitting tests, because the volume of the samples is under tension, and in most situations the samples are not fully and equally consolidated. An increase in tension could be hard to interpret, since it might be due to the over-consolidation of a thin superficial layer or to a slight, but homogeneous, consolidation of the integral volume of the sample. Compression and splitting tests do not have the required accuracy to determine this. Because of the limitations of these tests and the establishment of more complete tests, they are now less frequently used to evaluate the strengthening ability of stone consolidants (Table 2).

As reported in Figure 5a, only a single technique was used to assess the strengthening of consolidation treatments in more than 50%, drilling resistance and ultrasonic pulse velocity being the most used test methods in this case (Figure 5b). However, there was still a significant portion of studies using bulk and superficial techniques alone (hardness, peeling, and compression tests), which do not allow a complete understanding of the consolidation action. Complementary methods are important not only to quantify the distribution of the increase in strengthening in depth but also to enable a detailed analysis of the alterations to evaluate if they meet the diverse requirements that should be considered when dealing with the selection process for a real application.

3.3.3. Criteria to Analyze the Strengthening Effect of Consolidation Treatments

Conceptually, a consolidation treatment is applied on decayed stones with loss of cohesion—typically occurring from the stone surface to its interior—and aims at restoring its original sound condition as schematically represented in Figure 6a.

Recommendations for thresholds of the mechanical properties used to assess the suitability of consolidation treatments varied. Early proposals recommended that the compressive strength of the treated portion of stone should be at least 10% over the compressive strength of the sound stone, and thus, the minimum objective of a consolidation treatment should be the total reestablishment of strength plus 10% of this value, as represented in Figure 6b [2,137]. However, the high incompatibility risks of an excessive strengthening effect (over-consolidation), or even a full reestablishment of the integrity in some circumstances, were subsequently highlighted [158]. Instead of establishing minimum thresholds for acceptable performances, later documents proposed maximum thresholds to reduce the risks of these type of treatments. Sasse [4] recommended that the bending strength of the treated stone should always be inferior to three times the bending strength of the sound stone, as represented in Figure 6c, while Delgado Rodrigues, and Grossi [159] suggested that the mechanical properties of the treated stone, in terms of bending strength, compressive strength, drilling resistance, or modulus of elasticity should not exceed the value of sound stone by more than 25%, preferentially below 10% (Figure 6d).

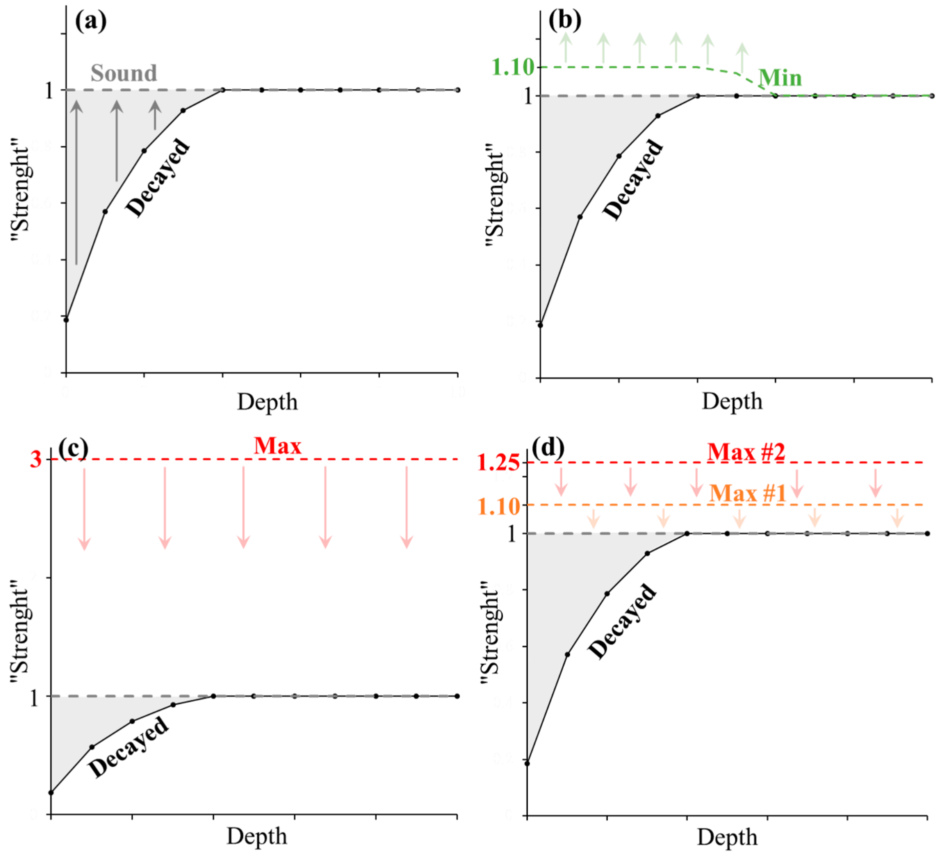

Figure 6. Different recommendations for adequate consolidation actions illustrated by schematic "strength" profiles: (**a**) restoration of the original strength; (**b**) treated portion of stone has at least 10% more strength than sound stone [137]; (**c**) maximum consolidation is 3 times the strength of sound stone [4]; (**d**) consolidation should not exceed the value of sound stone by more than 25%, preferentially below 10% [159].

In any case, the reestablishment of the integrity should not jeopardize the long-term stability of the stone and modest increments with controlled incompatibility risks are currently considered the most suitable options [160]. In fact, minor increments have been seen as a better and safer contribution to preserving stone objects than excessive increments, as in most circumstances it is only necessary to avoid the loss of stone grains rather than increase the load-bearing capacity of the stone [158], and the need of a future re-treatment should always be preferable to the high risk of losing the treated surface because of over-consolidation.

In order to understand the trends in terms of the strengthening capabilities of recent consolidation treatments, regardless of their chemical family, the strengthening values were converted into percentages (in relation to the initial values of the untreated stones, whether sound or aged). In the case of drilling resistance profiles, the considered value was the average resistance in depth. Simple statistics were used to characterize the results, which were grouped in terms of assessment techniques (Figure 7).

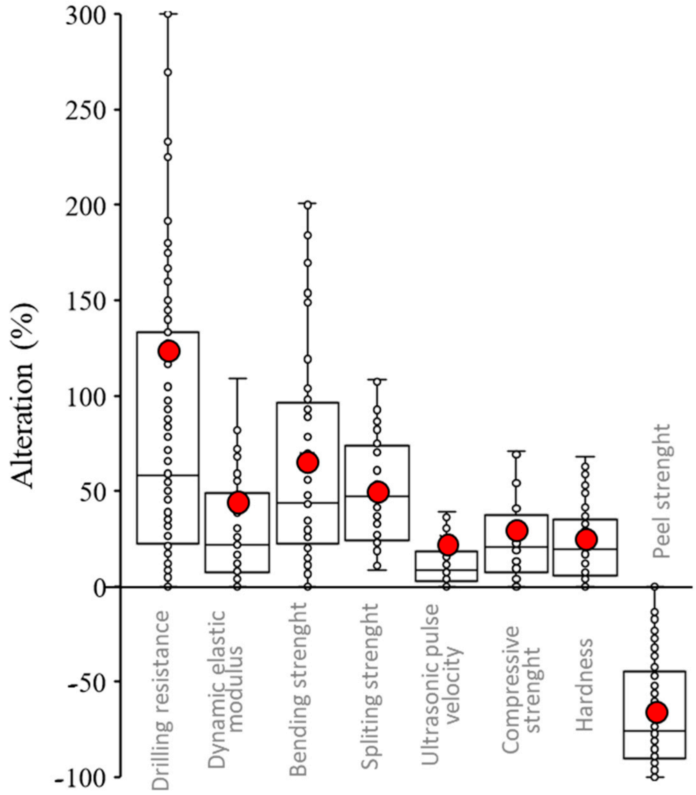

Figure 7. Statistics on the strengthening values (alteration) reported by the articles included in the database for the consolidation treatments. The data are grouped according to the assessment techniques used. (Lower limit: 1st quartile; upper limit: 3rd quartile; black line: media; red dot: average; outliers not represented).

The alterations promoted by the treatments varied between nonexistent (0%) and more than 250%. The results depicted diverse levels of alteration, as expected, since different stone materials, treatments, and products were involved, from cases of failure due to the absence of any consolidation to cases of failure due to over-consolidation.

The results of the peel test have a different scale (0 to −100%) as the nonexistence of detached material is the final target. In this case, scattered results were obtained although ~75% of the cases were able to reduce 50% or more of the amount of detached material.

It was possible to distinguish different scales and ranges of alteration in the properties. Hardness and compression tests were suggested to be less sensitive tests to analyze consolidation action as the range of values provided by them was globally lower than the remaining ones, which was expected in view of what was discussed in Section 3.2.2. Therefore, the outcomes of these test methods required detailed interpretations, and maximum threshold values as percentages should be carefully utilized as compatibility problems might be underestimated. A wide range of values was obtained by authors using drilling resistance, which reinforced its capacity to distinguish minor differences between treatments, at least on soft stones.

The results highlighted the risks of selected consolidation treatments based on generic thresholds. For instance, a treatment that caused an increase of 50% in drilling resistance might appear similar to a treatment that caused an increase of 50% in compressive strength; however, the actual strengthening was very different, as demonstrated by the different magnitudes in Figure 7. Therefore, a direct comparison of the increments of different mechanical properties of stones may not be suitable and percentage recommendations for minimum, maximum, or optimal resistance gains should be handled with care.

4. Conclusions

This article analyzed and discussed recent practices in stone consolidation research over the last 10 years. The following findings emerged from this work.

The context, aim, and scope of research documents are frequently hard to identify or too ambitious, which does not contribute to the scientific progress of the field. Establishing targets with narrow scopes, because of the particularities of each situation, is not unusual and should be assumed by the authors. Actual contributions to the state-of-the-art require coordination among all experimental conditions.

The selection of stone samples for research works is highly conditioned by their presence in heritage but also by the need for consolidation. Limestones, biocalcarenites, sandstones, and marbles are the most addressed stones. Carbonate-based varieties prevail over silicate-based varieties and pore-shaped stones prevail over fissure-shaped stones. These research trends pinpoint the stone varieties that require consolidation interventions more often and the characteristics that make consolidation actions more difficult and riskier.

Most research is carried out on sound stone samples; however, an increasing percentage of decayed stone samples has been used, either artificially or naturally decayed. Stone samples are frequently damaged by simple artificial thermal procedures, although clastic/porous varieties can require higher temperatures, more heating–cooling cycles, or faster cooling stages than crystalline varieties. The effect of salt crystallization has been poorly explored because it has various drawbacks. However, studying the behavior of treatments in the presence of soluble salts was identified as an important research line in the future.

Brushing is the most used application method since it is straightforward, while alkoxysilanes are the most researched family of consolidants. The scientific community is still focused on improving and studying alkoxysilane-based consolidants, which are used in both silicate and carbonate stones, which are less compatible. There is still room to promote significant improvements and expand the capabilities of nanolime and DAP consolidants.

The results suggested that drilling resistance is a suitable option for most stones containing pore-shape voids. In stones having fissure-shaped voids, ultrasonic pulse velocity prevails and is adequate to evaluate the consolidation action, especially if measurements along stone depth are taken. Even though it does not have the sensitivity to describe alterations in stones having pore-shaped voids, it is still widely used. Alternative test methods in these cases are recommended.

There are many studies based solely on techniques that do not provide a complete picture of the consolidation effect (e.g., hardness, peeling, bending, and compression tests). These must be complemented with information about the distribution of the increment of resistance in depth. In fact, the main problem in stone consolidation is not the lack of strengthening the capacity of the treatments. The most frequent problem seems to be over-consolidation, in which the strength of the treated stone is significantly higher than that of the untreated part. This happens more easily on low strength stones.

Although the thresholds reported in the literature for stone strengthening do not solve the existing difficulties of consolidation treatments, they can be useful if their scope and domain of application are clearly defined, and the specificities of each assessment technique are considered. For example, drilling resistance is much more accurate and informative than, for example, compressive strength or hardness. Using the same thresholds and criteria to analyze the strength increments obtained by both techniques is not recommended.

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