Sol-Gel Science and Cultural Heritage

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George Wheeler

This chapter is dedicated to Professor George W. Scherer of Princeton University, whom I first met at the Ultrastructure Processing of Advanced Ceramics conference in San Diego in 1987 – one of a series of conferences on sol-gel technologies organized by the late Donald Ulrich from 1984 to 1992. That meeting began a friendship and collaboration that has now spanned 30 years. Well known to sol-gel science, Professor Scherer also directed much of his prodigious intellect and energies to issues of cultural heritage preservation when he moved from industry to the university. Not only did he produce significant scholarship in understanding the deterioration and conservation of stone, and, mentored several in the next generation of scientists now pursuing similar subjects, he was and is generous with his time and knowledge in helping all of us to advance the field of science directed at cultural heritage preservation.

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G. Wheeler (✉)
Columbia University, New York, NY, USA
e-mail: gw2130@columbia.edu

Abstract

Building on the review of Bescher and Mackenize (Sol-gel materials for art conservation. In: Sakka S (ed) Handbook of sol-gel science, vol 3. Kluwer, Boston, pp 479–492, 2005) this chapter revisits the historical and current connection between sol-gel science and stone conservation and explores the fundamental question of the differences in performance of sol-gel derived stone consolidants on carbonate rocks such as limestones and marbles, and, silicate rocks such as sandstones and granites. The chapter then moves on to other cultural heritage materials such as glass and metals and updates the review of the literature with respect to research directed at their protection and conservation and concludes with expressing concern that little of this important work by scientists has placed new materials or methods of conservation into the hands of practicing conservators.

Introduction

In Chap. 22 of Volume 3 of the 2005 edition of *Sol-Gel Science and Technology* – "Sol-Gel Materials for Art Conservation" – authors Eric Bescher and J.D. Mackenzie provided both the necessary context and an excellent summary of much of the literature on the applications of sol-gel science to art conservation up to that point in time. In the intervening years sol-gel science has advanced, nanotechnologies have taken even stronger hold, and where we once referred to art and architecture, we now speak more generally of "cultural heritage." While it is not necessary to repeat Bescher and Mackenzie's literature summary, the historical connection between stone conservation and sol-gel science is both strong and long. For that reason, a refocusing on that history comprises a large portion of this chapter. What follows is a discussion and updating of other areas of conservation and preservation to which sol-gel science has been directed and may yet have significant impact.

Sol-Gel Science and Stone Conservation

Long before there was sol-gel science as we know it today, there was a vibrant and active science without the familiar epithet. While Brinker and Scherer's (1990) seminal, comprehensive, and eponymous work – *Sol-Gel Science* – may have securely imprinted the moniker for the larger scientific community, the term had been in common use among researchers for decades. Looking much further back in time, it could be argued that the science itself began as early as 1824 when J.J. Berzelius (1824) synthesized silicon tetrachloride ($SiCl_4$), a compound that would become an important building block for the silicone resin industry that much later flourished in both the United States and the Soviet Union. By combining silicon tetrachloride with ethanol, in 1846 J.J. von Ebelman (1846) synthesized an impure form of tetraethoxysilane (TEOS) containing mostly monomer and decreasing quantities of dimer, trimers, and oligomers, which is still known today as ethyl

silicate. (As a group, alkoxysilanes are referred to in the literature in number of ways: silicic ethers, silicon esters, silicic acid esters, ortho silicates, alkyl silicates, and, of course, alkoxysilanes. For tetraethoxysilane, the following names might be encountered: ethyl silicate, tetraethylorthosilicate, silicic acid ethyl ester, and, succumbing to the scientist's irrepressible compulsion to serial, alphabetic abbreviation – *T E O S*.) Anyone familiar with recent history of sol-gel science understands the continuing importance of TEOS to the field, but it might be surprising to learn that ethyl silicate entered the world of cultural heritage preservation only 15 years after its initial synthesis. In 1861 A.W. von Hofmann (Anon 1861) proposed ethyl silicate for the consolidation of the deteriorating Clipsham limestone used to construct the new Houses of Parliament in London. The original buildings were destroyed in a catastrophic fire in 1834, famously captured in two J.M.W. Turner's paintings *The Burning of the Houses of Lords and Commons* (1834–1835), and the new building was begun in 1840. It was somewhat of a scandal that the limestone was performing so poorly in such a short period of time and von Hofmann was called upon to address its condition.

Although there was little follow-up to von Hofmann's work at the time, it would be the foundation for an abiding interest in the use of ethyl silicate for restoring the physical properties of deteriorated stone in sculpture, monuments, and buildings. Along the way, in the latter part of the nineteenth century and the early part of the twentieth century, two other compounds were synthesized that became of interest to sol-gel science generally, and, stone conservation specifically – methyltrimethoxysilane (MTMOS) and methyltriethoxysilane (MTEOS; Ladenberg 1874).

The gestation period from von Hofmann's prescient suggestion and exploration into the use of ethyl silicate as a *stone consolidant* – as it is typically referred to in the conservation community – was almost 60 years. The most significant follow-up came in the 1920s when Arthur Pillans Laurie, a Scottish chemist who applied his scientific knowledge to both technical art history and to developing, testing, and evaluating materials and methods for the conservation of objects of art and archaeology, secured at least five patents for stone consolidants – all based on ethyl silicate (Laurie 1923, 1924, 1925, 1926a, b). Also significantly, Laurie would be the first to observe the difference in the nature of gel formed from ethyl silicate in sandstone as compared to limestone. In the 1924 United States Patent Application entitled "Preservation of Stone" he stated, "The solution may be applied to sandstone. . ., and, the silicic ester hydrolyzes to form hydrated silica that cements stone particles together. . .Alkaline conditions before and after hydrolysis produce a soft gelatinous precipitate that is useless as cement. . ." Calcareous stones such as limestone and marble, which comprise primarily calcite (calcium carbonate), are indeed mildly alkaline compared to silicate rocks such as sandstone and granite – the pH of mineral surfaces is sometimes referred to as "abrasion pH" (Stevens and Carron 1948).

Laurie's work generated a renewed interest in ethyl silicate as a stone consolidant and by the 1930s it became a focus of study at the prominent United Kingdom research center – the Building Research Station. A leader in the study of the conservation of stone at the time and for decades to follow was R.J. Schaffer, whose 1932 book, *The Weathering of Natural Building Stone*, remains reprinted

and relevant today. Against the trend of other contemporary researchers and those working in the ensuing decades, Schaffer opined that ethyl silicate "had no protective effect" on stone. The decades covering the 1930s to the 1960s were populated with over 50 publications directly related to the use of alkoxysilanes for cultural heritage applications, mostly for stone conservation (Wheeler 2005; Grissom and Weiss 1981), and the shift to an expanded use of ethyl silicate as a stone consolidant occurred at the end of this period. The era of consistent and widespread use of alkoxysilanes for the consolidation of stone began with the development and patenting of products by Wacker-Chemie (Bosch et al. 1973, 1976), which also occurred at this time. Although the patents mapped out a terrain large enough to encompass the development of a wider range of products, the two commercial formulations that most clearly stem from this work are the now classic Wacker OH and H. These products are still in use today, over 40 years later, and they and their analogs are by far the most commonly used stone consolidants.

What has propelled the more-than-century-and-half interest in alkoxysilanes for the consolidation of stone and where is that interest resonant and dissonant with the more common applications found in sol-gel science? The two properties most often cited are: the low viscosity of their monomers and oligomers, and, their fundamental ability to form siloxane bonds. Low viscosities – MTMOS and TEOS monomers have viscosities of 0.3750 and 0.7180 mPa·s respectively – make for mobile liquids that can invade and permeate stone's intergranular network – a functionality essential to successful consolidation. Typical sol-gel applications produce macro or semi-macro bodies, and, while low viscosity is not anathema to these applications, in many cases it is not essential. Commonly attractive to both sol-gel and stone consolidation applications is the stability – thermal, oxidative, and ultraviolet – of the siloxane bonds that result from the polymerization of alkoxysilanes. Like myriad silicate minerals comprising the earth's crust, gels formed from alkoxysilanes have little tendency to discolor through breakdown and reconfiguration of the bond network – also an essential property for application to irreplaceable objects of cultural heritage as well as optical applications for sol-gel derived materials. A property less often cited as useful for penetration into the pore system of stone is low surface tension, which most alkoxysilanes and their polymers also possess – on the order of 20 dynes/cm. The lack of attraction between molecules of these compounds prevents them from "beading up" on mineral surfaces and allows them to pass into even small pores in stone, in strong contrast to water molecules with a surface tension of approximately 80 dynes/cm.

Returning to the consolidants Wacker H and OH (OH stands for *ohne hydrophobie* or without hydrophobing properties), Wacker-Chemie took a page from book of silicone chemistry in developing and formulating their signature consolidants. Unlike more familiar sol-gel formulations, which typically rely on added water, acid or base catalysts, and co-solvents such as low molecular weight alcohols to provide homogeneous mixtures, Wacker employed the same metal carboxylate catalysts commonly used to cure RTV silicone rubber – compounds such as dibutyltindilaurate. The "beauty" of this catalyst is that it dissolves in ethyl silicate without co-solvents and is neutral with respect to pH, and, therefore, cannot

damage acid sensitive limestones and marbles, or base sensitive sandstones or any other stone made up mainly of silicate minerals. In addition, and, in contrast to more typical laboratory-based sol-gel applications, once the gel has formed inside the porous network of stone, there is usually little or no opportunity for postprocessing such as heating or applying a vacuum to extract catalysts or excess solvents.

The Wacker endeavor spawned a wider industry interest in ethyl silicate consolidants. In the 1970s and 1980s new-but-similar products were developed and came on the market. In Germany, T. Goldschmidt and Keimfarben competed with Wacker for market share of stone consolidants from nearly the beginning. The products Tegovakon V and T (Goldschmidt) were the equivalents of Wacker's OH and H as were Keim's Silex OH and H. All employed tin catalysts and added solvents to reduce viscosity. Solvents included mineral spirits, acetone, methylethylketone, and alcohols. In France, Rhone-Poulenc formulated three products in the 1970s: RC70, RC80, and RC90. RC70 was the OH analog with white spirits as a solvent (a mostly nonaromatic hydrocarbon solvent) and an organotin siloxane catalyst. RC80 and RC90 were the hydrophobic versions using methyl- and methylphenylsilicones respectively as the water repellent component. In Japan, COLCOAT produced the OH equivalent SS-101, and, in the United States, ProSoCo parroted the Wacker products with *Conservare* OH and H. By the 1990s, in response to environmental concerns, all existing consolidants in this group were reduced to "solventless" versions out of choice or in order to comply with volatile organic components (VOC) standards, and tagged "100" to the existing name, e.g., *Conservare* OH100, Keim Silex OH100, and for the originator, Wacker SILRES OH100.

From early on in the explorations and use of alkoxysilanes such as ethyl silicate for the consolidation of stone, the influence of stone type – in particular mineralogy and texture – became of concern. Starting with mineralogy, the rock kingdom is often divided into carbonate rocks such as limestones and marbles, and, silicate rocks such as sandstones, granites, and gneisses. Rocks or stones (see Thorson 2004 for rock vs. stone) most frequently the focus of consolidation have been the sedimentary varieties – limestones and sandstones – as they generally have a greater tendency to deterioration due to their higher porosities. Limestones consist primarily of the mineral calcite ($CaCO_3$) (and less often dolomite – $(Ca,Mg)(CO_3)_2$) with a much wider array of accessory minerals. As stated above, Laurie was the first to note the differences in the gels formed in contact with limestones as compared to quartz-rich sandstones – soft and "clumpy" with the former and hard and "glassy" with the latter. This difference was more closely explored by Charola et al. (1984) and Danehey et al. (1992). Charola demonstrated that fine calcite powders (approximately 200 mesh) – a surrogate for highly deteriorated limestone – were poorly consolidated by methyltrimethoxysilane (MTMOS), while similarly fine powders of quartz formed tough monoliths. In this context it should be pointed out that it was no coincidence that secondary name attached to the original Wacker OH product was *sandstein verfestiger* or *festiger* – sandstone strengthening agent. The name acknowledged past research – Laurie's observations about the difference in the nature of the gel formed in contact with limestone and sandstone – and, common

logic – silicate polymers would be more compatible with silicate minerals than carbonate minerals. However, given their tendency to deteriorate, it would not take long before practitioners to begin to apply OH to limestones and marbles, and, several stone types other than sandstone. By the 1980s, either as a marketing ploy or an acceptance of the reality of use, the qualifying name for Wacker's consolidants would be dropped.

Moving from powders to rocks, Wheeler et al. (1991b) applied neat MTMOS to cylindrical samples of limestone and a quartz-rich sandstone, and, in the first hour after application most of the MTMOS in the limestone evaporated. The sandstone, on the other hand, retains 24% of the alkoxysilane from 2 h and on to gelation and beyond. The near absence of the consolidant in limestone appears to be confirmed by mechanical testing performed 8 weeks later: the sandstone exhibits an 85% increase in modulus of rupture (MOR) and the limestone only 11%. Using ^{29}Si NMR, Danehey et al. demonstrated that the polymerization of MTMOS (in solution with water and methanol) is significantly reduced in the presence of calcite and that it is specifically the condensation reaction that is hindered. Recalling that the calcite is mildly alkaline, with an abrasion pH of approximately 9 in contact with water, the *slowing* of the condensation reaction is in sharp contrast with the acceleration of condensation produced by base catalysis reported in the sol-gel science literature. Clearly, more needs to be understood about the reactions of alkoxysilanes in contact with calcite and related rocks such as limestone and marble.

In unpublished work following the model of Charola et al. (1984), the author applied neat MTMOS dropwise to powdered quartz and calcite in small Nalgene containers until the powders were saturated. The containers were weighed periodically over the next few weeks. For the quartz powders the mass of MTMOS-derived gel stabilized at 28% w/w and the powder was fully consolidated. The calcite powder remained unconsolidated with little gel deposited from the MTMOS. Over the next 2 months the calcite powder was treated repeatedly with MTMOS until the mass return was the same as for quartz, but the calcite powder remained unconsolidated, confirming that consolidation is not simply a matter of depositing enough treatment material.

Overcoming evaporative loss can be addressed by means other than such repeated applications as described above. First, lower vapor pressure monomers such as tetraethoxysilane (TEOS) can be used. Second, monomers can be partially hydrolyzed and condensed to create a range of low molecular weight oligomers. Third, catalysts can be incorporated that increase the rate of reaction and thereby reduce the time it takes for the solid gel to form. From its inception Wacker OH employed all three of these strategies. Limestone and sandstone samples similarly treated with OH also returned similar percentages of gels (30% w/w and 36% respectively). Nonetheless, despite similar deposits of gel, the percentage increases in modulus of rupture (MOR) of the two stones before-and-after treatment are quite different: a 60% increase in MOR for limestone and a 240% increase for sandstone.

If similar amounts of gel are deposited in sandstone and limestone for the typical catalyzed formulations used by conservators, and, the strength increases are quite different, are the gels themselves quite different? To address this question, solid state

^{29}Si NMR was performed on gels derived from OH in the presence of calcite, quartz, and with no minerals added (Wheeler et al. 1991b). The spectra were essentially identical and demonstrated that for these *catalyzed* formulations, the minerals have little influence on the bond distribution in the gel. If the gels from catalyzed TEOS formulations in contact with different minerals are nearly identical, and the amounts deposited are similar, how are the large differences in modulus of rupture for consolidated limestone and sandstone explained?

One possible explanation investigated by Elfving and Jäglid (1992) is that bonding may occur between specific minerals and alkoxysilanes. They employed minerals commonly found in granite, sandstone, limestone, and marble such as quartz, feldspars (albite and microcline), micas (biotite and muscovite), calcite, and gypsum (i.e., the latter being most common alteration product of calcite in contact with sulfuric acid rain or SO_2 dry deposition). By using *trimethyl*methoxy- and *trimethyl*ethoxysilane they limited the reaction products to monomers and nonreactive dimers. The reaction of the alkoxysilane takes place in the presence of each mineral in the form of a powder. After the reaction, excess liquid is removed by filtration and the powders evacuated. Evacuation further removes excess starting materials – water, monomer, and solvent – and reaction products not attached to mineral surfaces – hydrolyzed monomers, dimer, and alcohol (methanol for the methoxysilane and ethanol for the ethoxysilane). Analysis of the treated mineral powders by infrared spectroscopy determines if the alkoxysilane has attached to the mineral surface by detection of C-H bonds from the methyl groups attached to silicon.

In examining spectra for the silicate minerals, quartz, albite, muscovite, calcite, and gypsum reacted with trimethylmethoxysilane, there was strong evidence for condensation reactions between the alkoxysilane and quartz and feldspars, surprisingly less for micas with their abundant OH bonds, and virtually no evidence of condensation with calcite and gypsum. The conclusion is that limited but detectable condensation reactions occur between alkoxysilanes and silicate minerals but no such reactions occur with calcite. Similar to what is seen in fiber-reinforced composites, where coupling agents are used to produce bonding between glass fibers and organic resins, the strength of the composite is increased by that bonding. Analogously, bonding between the alkoxysilane gel and mineral surface in stone produces a stronger "composite" system.

We can summarize what has been covered so far concerning the interactions of alkoxysilanes with some sandstones and limestones or their primary mineral constituents – quartz and calcite:

- The condensation reaction of uncatalyzed solutions of MTMOS, water, and methanol is slower in the presence of calcite. The reduced rate of condensation allows large amounts of MTMOS to evaporate. Only a slight reduction in the rate of condensation is seen with quartz. With neat MTMOS, evaporation is significant in the presence of calcite powder or a purely calcitic limestone, an effect not noted with quartz powder or a quartz-rich sandstone. It is therefore likely that with neat MTMOS in contact with calcite the rate of condensation is reduced in

a manner and degree similar to solutions of water, MTMOS, and methanol. Neither effect – reduction in the rate of condensation or significant evaporation – has been noted for catalyzed, partially polymerized TEOS solutions such as Wacker OH.

- Gels formed from solutions of MTMOS, water, and methanol in the presence of a calcitic limestone are initially weaker and less coherent than gels from the same solutions in contact with quartz powders or quartz-rich sandstones. In contrast, solid state ^{29}Si NMR shows that gels derived from OH have nearly the same bond distribution in contact with quartz and calcite powders, which suggests that the gels are similar with this catalyzed formulation and independent of the stone type with which they are in contact.
- Bonds form between alkoxysilanes such as trimethylmethoxysilane and silicate mineral substrates such as quartz, feldspars, and to a lesser degree, micas. These bonds are absent with calcite powder.
- Fine quartz powders are strongly consolidated with neat MTMOS. Fine calcite powders remain *un*consolidated.
- Some quartz-rich sandstones exhibit substantially higher *increases* in modulus of rupture than some purely calcitic limestones.

Another interesting question of mineralogy and the performance of alkoxysilane consolidants on stone is the influence of clay minerals. Clays form from the degradation of feldspars and, due to their fine particle size typically deposit intergranularly or in concentrated layers with quartz and feldspars in sandstones, and, with calcite fossils or fine micrite in coastal marine environments to produce impure limestones. (Clays are a group of minerals with a range of compositions and structures, and, to a geologist, are also a particle size designation: clays are <0.002 mm; silt, 0.002–0.06 mm; and sand, 0.06–2 mm). Clay-bearing stones are often more in need of consolidation due to their greater tendency to deteriorate because the interposed clay particles interfere with other more stable cementing materials and processes. It might appear that clays with their abundant OH groups offer receptive surfaces for condensation reactions with alkoxysilanes. (This applies to phyllosilicates more generally, which is a group of minerals with sheet-like or platy structures and comprises over 50 minerals but is dominated in rocks by clays and micas). Nonetheless, the conservation literature reports quite mixed data on the influence of clays in the consolidation of sandstones and limestones. Sattler and Snethlage (1988) state that clay-cemented sandstones exhibit only half the strength increases of silica-cemented sandstones when each is treated with ethyl silicate. In contrast to these results, Thickett et al. (2000) obtained 140% increases in crushing strength for an 80/20 mixture of sepiolite and palygorskite treated with Wacker OH and SEM images showed conformal films of OH gel similar to those found on sandstone for a sepiolite-containing limestone. Grissom et al. (1999) showed that lime plaster containing from 9% to 15% smectite clay (the authors indicate it is probably montmorillonite) had 355% increase in tensile strength when treated with *Conservare* OH, and, again, SEM revealed conformal films of OH-derived gel. BRETHANE, the catalyzed MTMOS-based consolidant, created at tough monolith

from a well-mixed combination (10% w/w) of fine powders of illite clay and calcite but gives little consolidation to calcite by itself. Caselli and Kagi (1995) treated samples of a quartz sandstone with an (unspecified) clay-rich matrix using Wacker OH, Wacker H, and BRETHANE. In compressive strength tests, treated and dry samples were about 100% stronger than those untreated and dry. In wet conditions treated samples were 150% stronger than untreated samples. (For this stone, untreated wet samples are about half the strength of untreated dry samples.)

It is difficult to draw definitive conclusions from the data and information on clay minerals presented above. Tentatively, it can be said that when clays are present in limestones they improve the performance of consolidation with alkoxysilanes when measured by most mechanical tests. Conversely, clays appear to reduce that performance on sandstones. The clays mentioned here are not all of the same structure: sepiolite and palygorskite, illite, montmorillonite, and kaolin are from different clay groups. These structures may have an influence on their ability to be consolidated but how those structures influence consolidation, not only cannot be determined from the current stone conservation literature but also offers an important opportunity for fundamental research into the interaction of alkoxysilanes with clay minerals.

Although the main body of literature on the consolidation of stone has been directed at sandstones and limestones, other stone types have been treated with alkoxysilanes. For volcanic rocks Tabasso et al. (1994) showed a 100% increase in compressive strength and 57% increase in ultrasonic velocity for a pyroclastic tuff treated with Tegovakon V. These stones are often characterized by high porosity and low mechanical strength. Useche (1994) studied a volcanic tuff and found that treatments of Wacker H and OH brought about 66–296% increases in compressive strength depending dilution, contact time with the consolidants, and number of applications. For plutonic rocks, Costa and Rodrigues (1996) made an extensive study of the conservation of granites. Treatment of granite with ethyl silicate yielded bending strength increases similar to sandstone (>170%) and a 74% increase in ultrasonic velocity. Treatments have also been carried out with *Conservare* OH on scoria, schist, and calc-schist, and Jerome et al. (1998) carried out treatments also on a calc-schist.

Without question, the most important other stone type that has been consolidated with alkoxysilanes is marble. Marbles – so frequently used for sculpture, monuments, and buildings – are characterized by high carbonate content, most often calcite, and, to a lesser degree dolomite. They also contain a wide variety of accessory minerals: phyllosilicates such as micas and chlorites, chain silicates such as tremolite, and nonsilicates such as pyrite. Given the dominant carbonate mineralogy it would be expected that alkoxysilanes perform on marble as they do on purely calcitic limestones, i.e., yielding relatively low strength increases, and this is generally confirmed by laboratory testing. (It is surprising to note how little mechanical testing of treated marble can be found in the literature (Rohatsch et al. 2000). Recent work by the author on highly deteriorated Carrara marble found that significant strength increases could be obtained with range of ethyl silicate consolidants but that after several cycles of changes in temperature and humidity, almost all of the

strength increases were lost. One exception to complete loss of strength was obtained with Funcosil 500STE).

Given the poor or only modest performance of these consolidants on calcite powders and purely calcitic limestone described earlier in the chapter, how do we explain the frequent use of alkoxysilanes on marble? Two factors are relevant in this discussion: (1) the most common form of deterioration of marble is granular disintegration, often referred to as "sugaring," and (2) unlike most sedimentary rocks, marble consists of relatively large grains in nearly direct contact, i.e., there is no intergranular matrix or cementing material. Consequently, the porosity of marble, even decayed marble, is low, and the shape of the intergranular spaces is sheet-like: large in two dimensions and small in the third dimension. Similar to other calcitic rocks, the liquid consolidant that enters these spaces does not create an adherent gel but the gel does significantly fill the space and prevent loose grains from moving and being dislodged, i.e., the process is more one of stabilization rather than consolidation.

Given the brittleness of alkoxysilane-derived gels and their tendency to shrink and crack during the process of going from mobile liquid to glassy solid, how large are the gaps that can be bridged by such materials? Wendler postulated that such gels could not bridge gaps greater than 50 μm, even for minerals such as quartz that are receptive to consolidation with alkoxysilanes. The work of Charola et al. (1984) cited earlier is relevant. They attempted to consolidate two grain sizes of quartz – "fine" quartz at approximately 75 μm and "coarse" quartz at approximately 400 μm. The former was well consolidated and the latter was not. We can approximate the intergranular spaces for these quartz powders: for a collection of spherical particles all in contact with each other, the gap between particles is approximately 0.3 times the diameter of the particles, i.e., about 40 μm for "fine" quartz and 120 μm for "coarse" quartz. In line with Wendler's prediction, the fine quartz forms a monolith with MTMOS and the coarse quartz is poorly consolidated.

Later Development in Sol-Gel Science and Stone Conservation

As was stated at the beginning of this chapter von Hofmann first suggested using ethyl silicate to consolidate deteriorated stone in 1861. Perhaps somewhat surprisingly, partially polymerized tetraethoxysilane is still the foundational ingredient of most commercial products to this day. Two generally recognized drawbacks of consolidants based on ethyl silicate are: (1) the inability to bond to calcite, and (2) the tendency for gels to crack during shrinkage and drying due to their brittleness.

Two strategies have been explored to address the bonding to calcite. Weiss et al. (2000) chemically altered the mineral's surface to make it more receptive to ethyl silicate. Calcite by itself contains few hydroxyl groups for alkoxysilanes to condense with. They designed a treatment to create a hydroxyl-rich surface by reacting calcite with ammonium hydrogen tartrate in a pH-balance solution commercially known as HCT – Hydroxy Conversion Treatment. Ammonium tartrate reacts with calcite to form calcium tartrate.

The newly formed calcium tartrate can condense with alkoxysilanes to create Si-O-C linkages that bind the gel to the calcite. The hydrolytic stability of these Si-O-C bonds is not known. In theory they can be hydrolyzed and therewith separate the gel from the mineral substrate. The tartrate group is large and itself hindered by its attachment to the calcite substrate. These factors would make hydrolysis difficult.

Field testing of HCT is still rather limited, but laboratory tests have shown some promising results. For example, cleaved pieces of Iceland spar – a very pure and transparent form of calcite – that have been treated with HCT followed by *Conservare* OH create a monolithic "sandwich" that remains intact even after several months of immersion in water, and, the gel remains adhered to the Iceland spar even after the "sandwich" is split open. Similar pieces of spar treated with *Conservation* OH neither form monoliths nor is the gel attached to the substrate.

Another approach that has been advanced to create linkages across the interface between calcite and alkoxysilane-derived gels is to employ alkoxysilane coupling agents. These coupling agents are compounds that have hydrolyzable alkoxy groups (usually three such groups) attached to the central silicon atom and a fourth group attached to silicon with an unhydrolyzable Si-C bond. Coupling agents are fundamental to improving the strength of composite materials that comprise inorganic fillers surrounded by organic resins. In the fabrication of a composite material made, for example, of glass fibers and epoxy resin, the two different functional groups on the alkoxysilane coupling agent offer separate compatibility with the fibers and the resin. Alkoxy groups provide silanols to link with similar groups on the glass fibers and the organic group (a.k.a "R" group) links with the epoxy resin. The resulting material is much stronger than its equivalent without the coupling agent. Wheeler et al. (1991a, 1992, 2000) used a similar approach to improve the performance of alkoxysilane consolidants on marble and limestone. In this case, the inorganic substrate or "filler" is the stone (calcite) and the resin is the alkoxysilane consolidant. They reasoned that "R" groups could be found that were compatible with or bond to calcite and that the hydrolyzed alkoxy groups on the coupling agent would form silanols to condense with the alkoxysilane consolidant. Coupling agents have been tested both as primers followed by TEOS-based consolidants, and, as integral blends in these same consolidants. Marked improvements in modulus of rupture – up to 153% over and above treatments without couplings agents – were noted. In recent years, the German company Remmers formulated consolidants using ethyl silicate and aminopropyltrimethoxysilane as the coupling agent under the name Funcosil 300 V. Laboratory work and field testing has been performed by Pinto and Delgado Rodrigues (2008, 2012) and show similar improvements when evaluated using drill resistance measurements. They also showed that high levels of consolidation can occur at limited depth with on these materials – not an optimal result.

The second major problem associated with alkoxysilane consolidants – and equally well known from the sol-gel literature – is their brittleness and the related tendency to crack with drying and shrinkage. Wendler (1996) and Wendler et al. (1991) chose to address this problem by making the gel itself more compliant by introducing segments of linear siloxanes that linked up with the larger silicate

networks of the gel. Both the gel and the consolidated stone are less brittle and there is a less abrupt transition between deteriorated stone that has been consolidated and undeteriorated/unconsolidated stone that lay below the surface. This smoother transition leaves treated stone less susceptible to contour scaling. These ideas have been incorporated into a line of products also by Remmers and known as Funcosil 300E and Funcosil 500E.

Researchers in George Scherer's group (Yang et al. 1998; Escalante et al. 2000, 2002; Aggelakopoulou et al. 2002; Miliani et al. 2007) at Princeton University took a different approach to gel shrinkage and cracking. They noted that drying shrinkage is controlled by a competition between the capillary pressure that drives contraction and the elastic modulus of the gel that resists contraction. Their approach involved adding small particles (~ 2 μm) in silica sols. The addition of the particles increased the moduli and pore sizes and the resulting gels experience reduced shrinkage and little cracking. Scherer has continued to work on the development of these systems, which may hold promise for consolidating highly porous stone. Once again, by staying close to discoveries communicated in the stone conservation literature, Remmers developed a product (Funcosil 500STE) based on the work of Scherer's group.

Since Remmers introduced Funcosil 300E, 300V, and 500 STE, there has been little or no change in products being offered or used for practical conservation work from the field of sol-gel science. In fact, of all of the several manufacturers and suppliers of ethyl silicate-based consolidants, the versions that mimic Wacker's original OH formulation (minus the added solvents) are still the go-to-choices for practicing conservators. Nonetheless, scientists working in the area of sol-gel continue to develop and evaluate new materials for stone conservation.

Recent work in stone conservation of related materials like mortar, plaster, and concrete has focused on consolidants, and, in developing improved hydrophobic or self-cleaning surface treatments. The emergence of nanotechnologies has impacted and influenced these efforts. Emblematic is the work of Bergamonte et al. (2014), who evaluated the performance of sol-gel-derived nano-silica solutions on a highly porous and relatively weak limestone known as a calcarenite – a limestone composed mostly of detrital, sand-sized grains of calcite. For similarly carbonate-rich rocks and for porous volcanic rocks such as tuffs and trachytes, new approaches being explored are the serial application of nano-lime and either nano-silica solutions or commercial ethyl silicate consolidants similar to OH. For plasters, Formia et al. tested organic-inorganic hybrids using TEOS as precursor along with a cycloaliphatic epoxy resin and a polysiloxane-epoxy formulation, and, for concrete, Barberena-Fernandez et al. (2013) applied and evaluated an OH-style ethyl silicate consolidant with nano-lime solutions. Finally, Mirabelli et al. (2013) and Illescas and Mosquera (2013) have created hydrophobic coatings by blending polymethylsiloxanes with oligomeric silica sols.

One of the most important and frequently executed conservation activities on outdoor sculptures, monuments, and buildings is cleaning. Many of these objects are fabricated in stone, brick, terra cotta, cast stone, and concrete. The need for cleaning

is predicated on the prevalence of soiling, and, like consolidation, the mechanisms of soiling are different for carbonate materials like marble, limestone, and related materials like cast stone and concrete, as opposed to silicate materials like granite, sandstone, gneiss, as well as brick and terra cotta: carbonate surfaces soil where they remain dry and silicate surfaces soil where they are wet. Preventing or minimizing soiling has been a significant area of research unrelated to cultural heritage objects, in part, due to savings associated with fewer episodes of maintenance cleaning. Typical of so much of cultural heritage conservation research is the testing and redirecting of existing commercial products on materials of art and architecture, and, research and development of useful products to limit or prevent soiling has determined that the anatase form of titanium dioxide is highly effective on some surfaces. Self-cleaning or anti-soiling titania coatings were synthesized using sol-gel methods and directly applied to limestone and travertine and evaluated in a series of papers by Quagliarini et al. (2012a, b, 2013) and Munafo et al. (2015) and found good compatibility with the stone substrates and efficiency in anti-soiling activity. Similarly, Kapridaki and Maravelaki-Kalaitzaki (2013) used a SiO_2-TiO_2 coating derived from a mixture of tetraethoxysilane (TEOS) and titanium isopropoxide (TIP) incorporating a hydroxyl-terminated polydimethylsiloxane (PDMS). No work has been found that has been carried out on the performance of sol-gel anti-soiling coatings on silicate substrates.

Sol-Gel Science and Other Cultural Heritage Materials

The consolidation of stone has long been the main application of sol-gel science to objects of cultural heritage – as we have seen, going back to the middle of the nineteenth century. More recently, sol-gel scientists and conservation scientists interested in sol-gel materials and processes have turned their attention to other materials. By far the greatest attention has been on materials for the preservation of stained glass, in part, due to the logical compatibility between silica sols and the silicate networks of glasses.

J.D. Mackenzie and then graduate student Mary Colby were early explorers in this area through a research contract from the Getty Conservation Institute. This work resulted in a project summary document for the GCI and publication in the 1988 Materials Issues in Art and Archaeology proceeding of the symposium in Reno, NV (Colby et al. 1988). At the time, other sol-gel scientists picked up this thread, particularly Helmut Schmidt, Dieter Fuchs, and Hannelore Römich at the Fraunhofer-Institut für Silicatforschung in Wurzburg, Germany, looking at ORMOSILS and ORMOCERS for protection of historic glass. More recently further studies on the use of TEOS-based silica sols for the protection of older cultural heritage glass have been conducted by dal Bianco and Bertoncello (2008); dal Bianco et al. (2008) and Monti et al. (2008) tested another compound – perhydro-polysilazanes – that ultimately also conduces to silica. Both de Ferri et al. (2013) and Carmona et al. (2006) formulated organo-functionalized alkoxysilanes with TEOS sols for protective coatings older glasses. They are generally transparent, colorless

water repellent, compatible with glass, and do not generate corrosion products or color changes upon aging. Finally, Carmona et al. (2006, 2009) used both functionalized alkoxysilanes in TEOS sols, mixed sols of TEOS and zirconium alkoxides, or silicon-zirconium alkoxides for the consolidation of paint on historic glass.

The last area of the application of sol-gel science to cultural heritage materials to discuss is metals. A good deal of the research on this subject is directed at protecting contemporary or new installations of metal objects to deter corrosion (see review article by Figueira et al. 2015), but applications to historic objects have also being explored. Bescher and Mackenzie's (2003) work using ORMOSILS – epoxy-functionalized trimethoxysilanes and methyltrimethoxysilane sols – for brass and bronze and cited in the 2005 version of this chapter has remained a model for subsequent work as was Pilz and Römich's (1997) epoxy-functionalized ORMOCER also for outdoor bronzes. Kiele et al. (2014, 2015) applied TEOS sols modified with trimethylchlorosilane or hexamethyldisilazane on both copper alloys and steel alloys and found good protection again corrosion. Similarly, Zucchi (2013) tested 3-mercaptotrimethoxysilylpropane using different methods of deposition for the protection of bronzes and the modified sol produced good efficiency against corrosion. Finally, Barranco et al. (2010) used ZrO_2-SiO_2 along with diethyldimethoxysilane or methylacryloxypropyltrimethoxysilane with tetra-alkoxysilane sols to make electrochemically active surfaces for the protection of painted metal surfaces.

Conclusions

All of this recent work should be applauded and encouraged. It is nonetheless somewhat sobering that despite significant research by scientists, none of these efforts has yet to lead to products adopted and applied with confidence by practicing conservators since the original development of ethyl silicate consolidants for stone and refinements to these products in recent decades. In fact, these consolidants remain the only commercial sol-gel derived products for the conservation of cultural heritage commonly used by conservators. In most areas of cultural heritage conservation the trajectory of adopting new materials is to take products created for other industries and apply them to objects of art, archaeology, and architecture. Typical examples would be the development of the Paraloid series of thermoplastic acrylic resins (B44, B48N, B67, B72, A11) as coatings in the 1940s and 1950s. They were not developed for conservation applications but because of their relative stability were soon adopted *by conservators* for such applications. Scientists quickly followed in evaluating the performance of the Paraloids. The fundamental point is that it is quite rare for a material to be developed explicitly for a conservation application – Wacker-Chemie's stone consolidants remain almost unique in this regard. It can easily be seen from the perspective of commerce, there is no significant incentive for developing products specifically for cultural heritage applications because the volume and frequency of use is so small. However, perhaps the reason

that the scientists highlighted in this chapter have invested their energies into conserving materials of cultural heritage is the value of that heritage itself to all of us, now and in the future. . .is that not incentive enough?

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