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The Consolidation and Bonding of Water-Saturated Siliceous Stone With Lithium Silicate — A Preliminary Evaluation

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Abstract

The consolidation of siliceous stone has received a great deal of study and has become a conventional treatment requiring very little further research and site-specific evaluation. The literature on this topic is extensive and readily found across all languages. The backbone of siliceous stone consolidation has been the application of ethyl silicate. Considerations of water repellency lead to a more considered assessment to determine whether altering water flow will protect or damage the stone.

Stabilizing water-saturated stone presents a new set of criteria where water repellency and the water-repellent nature of ethyl silicate during application and cure render these methods redundant. This paper considers the specific consolidation and grouting requirements of water-saturated siliceous stone and discusses lithium silicate as a suitable water-compatible alternative to ethyl silicate. Evaluation has been carried out as a combination of laboratory and field evaluations.

Titre et Résumé

La consolidation et l’adhérence de pierre siliceuse saturée d’eau au moyen de silicate de lithium — Évaluation préliminaire

La consolidation de pierre siliceuse a fait l’objet de nombreuses études et elle fait maintenant partie des traitements classiques qui exigent très peu de travaux supplémentaires, que ce soit sous forme d’activités de recherche ou d’évaluation propre à un site particulier. Il existe un très grand nombre de publications, dans un vaste éventail de langues, qui traitent de ce sujet. L’élément clé du traitement de consolidation de pierre siliceuse a été jusqu’ici l’application de silicate d’éthyle. Une évaluation plus judicieuse des cas tient maintenant compte de l’hydrophobicité des matériaux utilisés, afin de déterminer si la modification de l’écoulement naturel de l’eau permet de mieux protéger la pierre ou, au contraire, peut l’endommager.

La stabilisation de la pierre saturée d’eau est caractérisée par un nouvel ensemble de critères, en vertu desquels la nature hydrophobe du silicate d’éthyle, lors de son application et de son durcissement, et l’hydrophobicité de l’objet traité rendent ces méthodes redondantes. Le présent article traite des exigences particulières relatives à la consolidation et à l’injection de coulis, dans le cas de pierre siliceuse saturée d’eau; il comporte aussi une discussion sur l’emploi de silicate de lithium comme matériau compatible avec l’eau pouvant adéquatement remplacer le silicate d’éthyle. Le projet d’évaluation a été réalisé en combinant des essais de laboratoire et de terrain.

Introduction

Ethyl silicate (tetra-ethyl ortho silicate, TEOS) has been widely used for the consolidation of siliceous stone (Munnikendam 1973; Charola 1994; Alonso 1992) and to a lesser extent lime-based materials (Pancella 1987; Saleh 1992). It replaces the earlier water-miscible potassium and sodium silicates (Nishiura 1988), considered unsuited to conservation through their release of salt forming cations.

Ethyl silicate is limited in wet surface applications due to its initial hydrophobic liquid state but more critically through the cure period that renders the treated area hydrophobic for up to 8 weeks. Water flowing through the rock during this gel phase may build sufficient pressure to cause stone failure.

Lithium silicate is a more recent variant of the water-miscible silicates, free of salt forming cations (lithium does not form known damaging salts) and thus providing an alternative to the water-incompatible ethyl silicate for both consolidation and grouting.

An aqueous treatment opens options in two directions. The first obvious benefit lies in the ability to apply the consolidant to water-saturated porous material without retarding moisture flow. The second option, discussed in more detail elsewhere (Thorn 2011) offers miscibility with limewater and other lime-based consolidants and grouts, providing an improved and compatible treatment for composite lime and silica-based plaster, fresco, and limestone.

Lithium silicate has been evaluated as a new chemical providing consolidative benefits similar to ethyl silicate (Buj and Gisbert), and in this paper compares the performance variables to the more established consolidant. Ethyl silicate has been studied and applied by the author to sandstone for over 25 years and provides a performance benchmark for the current evaluations. Factors such as penetration, surface alteration and the regaining of surface cohesion have been compared to ethyl silicate and assessed simply as achieving either better or lesser results in relation to this reference consolidant.

Grout success is similarly based on the ability to form a material with comparable or better cohesion than ethyl silicate grouts developed by the author from 1992 onwards, with similar material available commercially.

The grout design criteria follow those of the ethyl silicate grout (Thorn 2010) with the only new parameter being the application to moist surfaces.

Preliminary comparative use of sodium silicate revealed a problem with that material, apart from the very obvious salt formation, of being too strong rather than too weak. Ethyl silicate by contrast struggles to form a strongly cohesive and adhesive grout, particularly when injected into small closed voids by syringe.

Summary of Design Objectives

A stone consolidant should be readily available, affordable and simply applied under a range of weather conditions. The weathered zone should regain cohesion to a point where there is no further grain loss and this should be achieved to the depth of sound stone and beyond.

Much attention has been focussed on depth of penetration but this is a more critical issue for coatings and consolidants that alter vapour transport characteristics. Both ethyl and lithium silicates will penetrate adequately into the stone. The lithium silicate was evaluated with a specific wet stone in mind (volcanic tuff) and able to penetrate easily through a 90mm sample at a rate of $1mms^{-1}$.

An important consideration for stone consolidation is ongoing retreatment, which has often been an obstacle in reapplying synthetics. Ethyl silicate has been shown to be re-applicable without altering vapour permeability or creating rheological zones in the surface (Snethlage 2004).

The full design objectives for the grout have been described previously (Thorn 2010) building on earlier criteria (Bouineau 1982; Ferragni 1984; Peroni 1982). The unique requirements of the siliceous grout, extending beyond the previous criteria, are as follows:

1. The grout should not promote biological growth.
2. The grout should contain only stable and compatible components.
3. The colour must match its surroundings both in wet and dry conditions.
4. The material should be microscopically distinguishable from the stone.
5. The grout should be easily formulated on site.
6. The grout should be removable without threat to the original object.
7. The first treatment should not make subsequent treatments more difficult.
8. Tensile strength should be adequate to support the reattached stone spall through normal hydrothermal cycles experienced in outdoor conditions. (Thorn 2008)

Lithium Silicate for Consolidation

Lithium silicate improves upon earlier water-miscible potassium and sodium silicate by not releasing damaging salt forming cations (Buj and Gisbert), and has found application in the stabilization of concrete, as indicated by the commercial literature. Its high alkalinity (pH 10.8) is a desirable condition for reinforced concrete but presents issues when applied to siliceous rocks. The water miscibility of Lithium silicate has clear advantages when consolidating or grouting permanently wet rock, such as the surface illustrated in Figure 1. The formula for lithium silicate is shown in Figure 2.

Figure 1 Detail of a permanently water-saturated ignimbrite wall containing carved representations of canoes. Water flow and plant roots are causing delamination in many places.

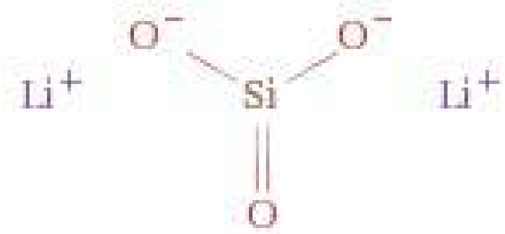

Figure 2 The structure of lithium silicate.

A water-dispersed treatment will readily mix with water and therefore not be adversely affected by it and will to some extent be carried to the depth of the water zone by osmotic mixing. This all sounds positive but in being water-miscible the consolidant can also be carried back to the surface where it precipitates in concentration. This redistribution of consolidant can result in a concentration gradient that leaves very little strengthening at depth and over-consolidation of the surface. It was established in preliminary trials that darkening of the tuff sample occurred at some point between 2.5 and 4.5% solids concentration with no way of predicting what concentration will be brought to the surface through evaporative accumulation.

Four tuff samples have been consolidated and the same consolidant made into a grout. The concentrations tested have been 4.6%, 2.3%, 1.15%, 0.58% and 0.29% lithium silicate.

Laboratory Evaluations

Water repellency

Laboratory consolidation of tuff with up to 4.6% lithium silicate resulted in all samples remaining water-absorbent from application onwards, with similar results achieved with three repeated 1.15% applications. The grout samples all allow ready water absorption.

Salt stability

A 0.58% concentration of lithium silicate was added to 1, 2 and 5% solutions of sodium chloride. No turbidity resulted from these additions. From this no incompatibility or adverse reaction from applying lithium silicate to saline porous materials was expected.

Typically 2% sodium chloride content in sandstone will be damaging with severe disruption above 5%. A 1.15% lithium silicate solution was applied to a moist saline surface at a test site at Uluru in central Australia. The results, while not being a controlled study for salt compatibility, produced an alarmingly white powdery precipitate (Figure 3). This was either rapidly reacted silicate material or precipitated salts mobilized by the water-based treatment. The white mass was readily dusted from the surface. Ethyl silicate had been applied the previous year to an adjacent and identically weathered surface with satisfactory results and with no evidence of white bloom. Sodium silicates applied in the 1990s also showed remnant white bloom.

In response to this observation a sample of tuff was saturated with halite and allowed to dry. The dry sample had halite crystals visible across the surface and a generally darkened appearance. A 1.15% lithium silicate solution, adjusted to a pH of 8.3, was applied to the surface. Early indications showed a substantial white crystalline mass forming within the dried edges of the sample indicating the formation of the white precipitate. It is therefore recommended that lithium silicate application to highly saline moist surfaces (Figure 4) requires prior desalination and certainly trial evaluation to assess bloom.

Figure 3 Test site at Uluru showing severe staining of lithium silicate applied to saline surface.

Figure 4 Identified need for consolidation in saline rock at Uluru. Desalination trials have preceded any discussion of consolidation. The areas to the top and right are darkened through water saturation with resultant spalling.

Ethanol miscibility

Ethanol was used at one of the sites, Te Ana a Maru (Figure 1), as an effective biocide following methods advocated by Ernfridsson (2009). Given that consolidation and biocidal control may become cyclical treatments there is logic in combining both into the one spray application across the site. Lithium silicate is however not sufficiently compatible at high ethanol doses to facilitate such a convenient treatment. Potassium silicate has known biocidal properties and current tests are evaluating this property for lithium silicate. It is considered that biocidal control will be required at Te Ana a Maru every 5 years and if this can be applied as a combined biocidal lithium silicate consolidant the long-term stability of the site can be better managed.

Consolidation trials

Lithium silicate was applied to tuff samples sawn into 20 mm thick slices of slightly variable surface area. The supplied product contains 23% lithium silicate solids in water. This was diluted to 4.6%, 2.3%, 1.15%, 0.58% and 0.29% solids content. Consolidation was evaluated by scratch resistance to a rotating wire passed across the surface. The depth of the abraded channel was compared to ethyl silicate consolidated surfaces.

All consolidant was introduced from the top of the sample and ceased when the bottom became visibly darkened. This is in contrast to other test methods that draw the liquid up by capillary attraction. The top down approach has been preferred for three reasons. Firstly it has been deemed important to apply the consolidant through the surface representing the outer application and evaporation surface to ensure there are no unforeseen variables overlooked by doing otherwise. Secondly, allowing the liquid to migrate downwards to the bottom of the sample and then stopping application ensures there is no extra loading that may concentrate lithium silicate at the evaporation front if prolonged absorption is allowed. The third advantage was in being able to saturate some of the test samples by drawing water into them from below while consolidating in the opposite direction to water flow.

Application into one block from the side face confirmed the same absorption velocity in both orientations.

Two aspects were evaluated using the top down application method - depth of penetration and consolidative effect.

Depth of penetration

The objective, as with ethyl silicate consolidation, was simply to replace lost binding material and thus return the altered surface more closely to its initial unweathered state, compatible with the mechanical properties of the underlying parent rock.

Initial tests indicated that absorption into tuff was very high with little difference between ethyl silicate, lithium silicate and pure water. The only real difference was that induced by the two aqueous systems, not readily absorbed initially due to their high surface tension. Pre-wetting the surface with ethanol allowed the water-based systems to be rapidly absorbed.

The rate of absorption was in the order of 1mm/sec to a depth of 20 mm with the greatest consolidation depth of 95 mm reached in less than three minutes. Penetration was timed through blocks of varying thickness with the time recorded when the opposite face became visibly wet.

It is unlikely such depths can be achieved in sandstone and not certain whether the consolidant will achieve these results in a more water-saturated tuff. Buj and Gisbert (link cited) applied lithium silicate at 50% dilution (10% solids) with modest penetration into sandstones. The current work has indicated that 50% is unnecessarily concentrated and this may affect the published penetration results. What is clear from both studies is that lithium silicate will penetrate as well or better than ethyl silicate, which has broadly accepted penetration properties.

Colour stability

One of the absolute requirements of a consolidation treatment is that it must leave the surface visibly unaltered from the untreated rock appearance.

All of the lithium silicate treatments up to 2.3% left the surface appearance unaltered, whereas 4.6% concentration darkens the tuff substrate to the same level as ethyl silicate. Acceptable darkening is defined here as the level caused by ethyl silicate consolidation.

Early testing produced a very noticeable brown surface on the grout and an orange fringe around the consolidated tuff at concentrations above 0.29%. Repeat applications of the 0.29% concentration produced the same stain after one or two more applications. The stain appears to be an evaporation stain, as seen in figure 5.

Figure 5. Deep brown staining of a 10% grout sample (left) and orange fringe development on tuff consolidated with 4 applications of 1.25% lithium silicate.

The high pH of lithium silicate was considered the cause of stain development. Adjusting to pH 8.3 eliminated the stains and all treatments have remained colour stable with no evidence of the orange fringe returning. pH was adjusted with acetic acid, chosen as the least damaging in terms of potential salt formation. It is not expected that acetic acid buffered to pH 8.3 will damage stone directly and that acetate salts are less damaging than chlorides, nitrates and sulphates.

Lithium Silicate Grouts

Water-miscible silicates produce higher strength grouts than those achieved with ethyl silicate and this is also true of lithium silicate to the extent that while it is weaker than potassium or sodium silicate (both of which form overly hard grouts), a 4.6% dilution will result in a far more cohesive and durable grout than that achieved with 100% ethyl silicate binder.

Grout development using lithium silicate binder proved straight forward, given the many years devoted to developing an almost satisfactory ethyl silicate grout (Thorn 2010). A 4.6% lithium silicate binder produces a stronger more cohesive grout than the 100% ethyl silicate system, based on surface abrasion assessment. Particle size distribution is still considered an essential rheological factor and for this fumed silica and the equally critical 1-100 micron quartz fraction are specified quite precisely (Thorn 2010). Lithium silicate grouts are not as tacky and hence workable as ethyl silicate but their application into wet surfaces on wet days gives them greater flexibility.

Results and Discussion

Strengthening of the surface is the primary requirement with the testing program. All other tests are ancillary to this single objective.

To summarize the results, all concentrations from 2.3% and below did not produce the same surface durability as the 100% ethyl silicate sample. The 4.6% single application of lithium silicate equalled the strength of the ethyl silicate sample with a similar degree of slightly perceptible darkening, a temporary situation for ethyl silicate but seemingly more permanent for lithium silicate. The 2.3% sample on the other hand did not give a very satisfactory consolidation, with unacceptably high grain loss. It is believed that the degree of darkening observed with the 4.6% lithium silicate would be acceptable if the treatment is applied uniformly to the whole rear wall thus avoiding obvious treatment tide lines. A two or three staged 2.3% application can achieve the desired durable surface with no colour change and is obviously the preferred approach.

Often single application treatments limit the amount of consolidant that can be applied. The reference consolidant ethyl silicate has been applied routinely as 4 to 5 passes over a 2 day period. This ensures that all consolidant remains in its liquid state before reacting into the gelled phase. Occasionally a five pass ethyl silicate treatment resulted in slightly darker surfaces to the degree seen in the 4.6% lithium silicate samples. In other ethyl silicate treatments stones have been consolidated in a two pass system and reconsolidated up to three times over several years.

The implications for lithium silicate are that by applying lower loadings and allowing them to fully form into the final product the pores are open to receive further liquid that retracts back to a less filled surface. Snethlage (2004) has confirmed that repeat ethyl silicate consolidation does not lead to case hardening or other rheological problems and nor does it lead to darkening of the surface. Lithium silicate does not go through a hydrophobic gel phase so can be absorbed into the substrate at any time after the previous application.

Based on current knowledge it is recommended that a 2-3% solution of lithium silicate be applied to the surface in three passes with the third treatment subject to assessment of the first two and potentially several years after. Ongoing re-treatment will be subject to assessment.

Conclusion

Lithium silicate has proven itself capable of consolidating wet stone and forming suitably strong grouts for reattachment. It has been adjusted to eliminate some application problems and solutions have been found to treat difficult situations such as highly saline surfaces. Being an aqueous dispersion gives a slight advantage in terms of transportation and general user safety and the dilution ratios necessary to achieve comparable consolidative effect, result in a cheaper alternative to ethyl silicate. The following benefits can be summarized;

- Low solids loadings can achieve same surface strengthening as ethyl silicate.
- Can be applied into wet surfaces that would react the ethyl silicate too quickly.
- Free of chemical diluents.
- Water dispersion provides safer transport and application.
- Effective low dilution ratios mean a cheaper product than ethyl silicate.
- Can make a stronger grout than the best achieved with ethyl silicate binders.
- Does not release salt forming ions such as those abundantly present in sodium and potassium silicates.

References

Alonso, F.J., J. Ordaz, A. Perez, and R.M. Esbert. "Laboratory study of a treated dolostone subjected to thermal cycles". pp. 745-752 in *Preprints of the 7th International Congress on Deterioration and Conservation of Stone*. 1992.

Bouineau, A., et J. Rocard. "Reinforcement des maçonneries pour injections de coulis dans la region nord-est de la France". pp 165-184 in *ICCROM Symposium - Mortars, Cements and Grouts used in the Conservation of Historic Buildings*. ICCROM Rome, 1982.

Buj, O. and J. Gisbert. "Evaluation of three consolidants on Miocene sandstone from the Ebro basin." http://crcodiletest.jsn-server4.com/publicaciones/34.pdf, accessed 16-09-2011.

Charola, A.E., R.. Koestler, and G. Lombardi (editors). *Lavas and volcanic tuffs; Proceedings of the International meeting, Easter Island, Chile.* ICCROM*,* 1994.

Ernfridsson, E. Personal communication while assessing results of treatments in Tanum, Sweden, 2009.

Ferragni, D., M. Forti, J. Malliet, P. Mora, J.M. Teutonico, and G. Torraca. "Injection grouting of mural paintings and mosaics." pp. 110-116 in *Adhesives and Consolidants.* International Institute for the Conservation of Historic and Artistic Works, 1984.

Munnikendam, R.A. "A new system for the consolidation of fragile stone". *Studies in Conservation* 18, 2. (1973) 95-96.

Nishiura, T., and L. Zuixiong "Experimental study on the consolidation of fragile porous stone with potassium silicate for the conservation of cave temples in China". pp. 108-112 in *Conservation of Far Eastern Art*. International Institute for the Conservation of Historic and Artistic Works. (1988)

Pancella, R., V. Furlan, F. Girardet, et M. Stahli. "Conservation de la fresque de Hans Erni au musee d'ethnographie de Neuchatel-Suisse: etudes preliminaires". pp.771-778 in *Preprints of the 8th Triennial Meeting of the International Council of Museums Conservation Committee,* 1987.

Peroni, S., C. Tersigni, G. Torraca, S. Cerea, M. Forti, F. Guidobaldi, P. Rossi-Doria, A. de Rege, D. Picchi, F.J. Pietrafitta, and G. Benedetti. "Lime-based mortars for the repair of ancient masonry and possible substitutes." pp. 63-100 in *ICCROM Symposium - Mortars, Cements and Grouts used in the Conservation of Historic Buildings*, 1982.

Saleh, S.A., F. Helmi, M. Kamal, and A.F.E. El-Banna "Consolidation study of limestone: Sphinx, Giza, Egypt". pp. 791-800 in *Preprints of the7th International Congress on Deterioration and Conservation of Stone,* 1992.

Snethlage, R. "Re-treating sandstone with ethyl silicates – is there a risk of over strengthening the surface." pp. 283-289 in *Preprints of the 10th International Congress on Deterioration and Conservation of Stone*, 2004.

Thorn, A. "Mechanical response of a Tasmanian sandstone to heat and moisture." pp. 949-956 in *Preprints of the International Council of Museums Conservation Committee 15th Triennial Conference*, 2008.

Thorn, A. "Two siliceous grouts for the preservation of stone". pp. 1199-1208 in *Proceedings of the 2nd conference and of the Final Workshop of RILEM TC203-RHM: Pro 78; Historic Mortars,* 2010.

Thorn, A. "Preliminary evaluation of lithium silicate for consolidation and grouting of stone in wet locations". in *Wall Paintings in Crypts, Grottoes and Catacombs. Strategies for the Conservation of Coated Surfaces in Damp Environments*. ICOMOS Germany, 2011, in press.

Materials and Suppliers

Ethyl silicate, Stone Strengthener OH, supplied by Wacker Chemicals, Melbourne Australia

Lithium silicate, Lithisil 25, PQ Corporation, Valley Forge Pennsylvania, USA.

Author Biographies and Contact Information

Andrew Thorn is a conservator working for ARTCARE in Melbourne, Australia. He specializes in the conservation of mural paintings and stone monuments, with a particular focus on the preservation of rock paintings. While essentially a hands-on conservator, Andrew pursues a better understanding of deterioration through environmental and materials analysis and compliments field observations with laboratory development of conservation methods and materials. He has developed products as diverse as filling media for easel paintings and microtome mounting resins to meet specific client needs. The ongoing search for a perfect grout for exposed sandstone and siliceous rocks has remained a main objective since the early 1990s. Andrew is currently Coordinator of the International Council of Museums – Committee for Conservation (ICOM-CC) Working Group on Murals, Stone, and Rock Art and administrator of the professional Facebook page "In Situ Preservation."

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Andrew Thorn est un restaurateur au service d'ARTCARE à Melbourne, en Australie. Il est spécialiste de la restauration des peintures murales et des monuments de pierre, et possède des compétences plus pointues encore en préservation des peintures rupestres. Bien qu'il exerce la restauration dans un contexte avant tout pratique et concret, M. Thorn approfondit sa compréhension de la détérioration en procédant à des analyses des conditions ambiantes et des matériaux et précise ses observations sur le terrain en perfectionnant les méthodes et les matériaux de restauration en laboratoire. Il a mis au point des produits aussi diversifiés que des agents de remplissage pour les tableaux de chevalet et des résines de montage des coupes au microtome permettant de répondre aux besoins particuliers d'un client. La quête incessante du coulis parfait pour le grès nu et les roches silicieuses n'a jamais perdu de son importance depuis le début des années 1990. M. Thorn est actuellement coordinateur du groupe de travail sur les murales, les œuvres de pierre et l'art rupestre du Comité pour la conservation du Conseil international des musées (ICOM-CC) et l'administrateur de la page Facebook « In Situ Preservation ».

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