LITHIUM SILICATE CONSOLIDATION OF WET STONE AND PLASTER

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Abstract

Lithium silicate has received some attention from the conservation profession as an alternative to ethyl silicate for the consolidation of siliceous stone. This interest has declined with increasingly difficult European supply in recent years.

Ethyl silicate has received considerable study both of its positive consolidative effects, and more recently, perhaps as a result of this success, a more critical assessment of its potential shortcomings. This paper assesses the performance of lithium silicate in relation to the better known and documented ethyl silicate, and in particular highlights its advantages when dealing with wet surfaces and those containing calcite and soluble salt.

One of the fundamental limitations of ethyl silicate is its incompatibility in high moisture environments. This is a two-fold limitation as not only does water cause the consolidant to react too quickly but also the treated surface remains highly hydrophobic for up to 8 weeks. Rapid reaction leads to very poor silica development and thus inferior binding, whereas prolonged water repellency can impede water flow out through the surface, leading to massive spalling.

Lithium silicate overcomes both problems forming lithium carbonate and calcium silicate in addition to the silica formation common to ethyl silicate. Not only can lithium silicate be applied in wet conditions but it overcomes some of the identified incompatibility issues encountered with silanes applied to calcitic substrates (Wheeler 2005). Recent trials in France have indicated that lithium silicate provides a beneficial consolidation for marble and is considered an ideal consolidant for lime and sand plasters, including fresco. Work is also being undertaken for the potential to consolidate clay painting supports that have previously been stabilized with colloidal silica (pers comm Anca Nicolaescu 2013).

Introduction

Lithium silicate is an aqueous dispersion of alkali silicate as illustrated in figure 1. It contains no hydrophobic groups and the reaction proceeds entirely in a hydrophilic environment, giving lithium silicate great potential as a consolidant for wet surfaces. This paper discusses the treatment issues associated with four sites, a volcanic tuff in New Zealand, a limestone cave in the Chatham Islands, a calcite consolidated dune sand in Western Australia and a fine grained conglomerate at Uluru in central Australia. Each of the four sites presents a

preservation typology that has been limiting for most other consolidation methods. The incompatibility between moisture and consolidant and that between calcite and silanes has been partially overcome with the current system.

Other benefits of lithium silicate ensure that it is worthy of consideration in many mainstream treatments where solutions already exist such as the more established use of ethyl silicate as a consolidant for siliceous stones. Lithium silicate matches the consolidative ability of ethyl silicate while its water miscibility and dilution ratios make it safer to use, more readily transportable, and less expensive.

Lithium silicate reaction

Lithium silicate has been trialed in many places over some years yet the literature on its consolidative abilities within the heritage field remains very sparse. For this reason it is difficult to refer to a depth of literature that reveals the full chemistry and behavior of the chemical. Lithium silicate has come into commercial favour largely as a substitute for sodium and potassium silicates in the stabilization of Portland cement concrete and hence, apart from its benefits over those homologues , the literature focusses on the performance and chemistry of alkali silicates in general without considering heritage requirements.

Lithium silicate is supplied as a 20-25% moderately viscous solution in water. The structural formula is presented in Figure 1 with the standard reaction sequence in equation 1 indicating that in addition to water, carbon dioxide is required. SiO_2 and $LiCO_3$ are the desired end products. The Li_2O allows the SiO_2 to remain in a stable liquid form.

Equation 1.

$$n\ SiO_2 \bullet Li_2O + k\ H_2O + i\ CO_2 \rightarrow n\ SiO_2 \cdot (1\text{-}i)\ Li_2O + i\ Li_2CO_3 + k\ H_2O$$

The formation of lithium carbonate is of interest in providing some compatibility with calcium present in the porous structure and hence improved consolidation for lime based heritage materials. More importantly the lithium silicate can react with CaO and CaOH among a suite of other polyvalent cations (Na Mg, etc.) to form insoluble of barely soluble silicates.

Table 1 Solubility of selected lithium salts in comparison with two calcium salts. (gmL^{-1})

Lithium species	formula	0ºC	10ºC	20ºC	30ºC	40ºC
Lithium acetate	**LiC$_2$H$_3$O$_2$**	**312**	**351**	**408**	**506**	**686**
Lithium bicarbonate	LiHCO$_3$			57.4		
Lithium carbonate	**Li$_2$CO$_3$**	**15.4**	**14.3**	**13.3**	**12.6**	**11.7**
Lithium chloride	LiCl	692	745	835	862	898
Lithium fluoride	LiF			2.7	1.35	
Lithium fluorosilicate	Li$_2$SiF$_6$.2H$_2$O			730		
Lithium formate	LiHCO$_2$	323	357	393	441	495
Lithium hydroxide	LiOH	127	127	128	129	130
Lithium nitrate	LiNO$_3$	534	608	701	1380	1520
Lithium oxalate	Li$_2$C$_2$O$_4$			80		
Lithium phosphate	Li$_3$PO$_4$			0.39		
Lithium selenide	Li$_2$Se			577		
Lithium selenite	Li$_2$SeO$_3$	250	233	215	196	179
Lithium sulphate	**Li$_2$SO$_4$**	**361**	**355**	**348**	**342**	**337**
Calcium carbonate	**Ca CO$_3$**			**0.006**		
Calcium sulphate	**CaSO$_4$.2H$_2$O**	**2.23**	**2.44**	**2.55**		
Sodium chloride	NaCl	356.5	357.2	358.9	360.9	363.7
Sodium silicate				150		

Table 1 shows lithium carbonate and most other lithium salts to be more highly soluble than calcite or gypsum; an issue to consider where the formed soluble minerals can migrate to the surface. This has been observed on a container of 22% lithium silicate that became increasingly milky with age. The supplier advised that this was a recently identified problem not observed in the 20% lithium variant. Lithium carbonate bloom can be removed with a 1% acetic acid wash however the aim is to have a treatment that requires no follow up adjustment. The colour stability of lithium grouts is equal to the very stable long-term colour achieved with ethyl silicate grouts and both are superior to those formed with sodium silicate (used for comparative properties), which displays a significant white bloom within days of cure. Short term colour matching is better with lithium silicate than almost any other grout as there is significantly less colour change between wet and dry appearance.

Previous discussions (Thorn 2010, 2011) have indicated the formation of an orange fringe in consolidated tuff and a dense brown film in grouts comprising 100% SiO$_2$. Lithium silicate has a high pH of between 10.8 (PQ literature) and 10.5 (confirmed) and it was found that lowering this to 8.3 (close to the equilibrium pH of calcite) avoided surface discolouration however there is some difficulty maintaining a solution below pH 10. The pH has been adjusted with acetic acid initially and then with phosphoric acid for reasons described further on.

The reaction in the presence of these acids is stable as indicated in equations 2 and 3.

Equation 2 acetic acid environment

$nSiO_2 \cdot Li_2O + k\ H_2O + 2\ H\ Ac \rightarrow nSiO_2 + 2\ LiAc + (k+1)\ H_2O$
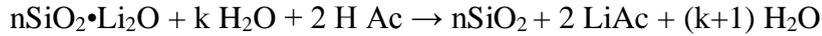
Equation 3 sulphuric acid environment

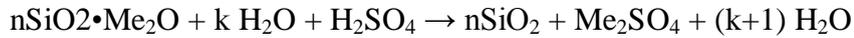$nSiO2 \cdot Me_2O + k\ H_2O + H_2SO_4 \rightarrow nSiO_2 + Me_2SO_4 + (k+1)\ H_2O$

Table 1 shows both acetate and sulphate to be highly soluble. The inclusion of an acetic acid buffer did not adversely affect the cohesive qualities of the grouts and this is seen to be an accurate assessment of the consolidative stability. Further refinement of the pH adjustment to avoid discolouration continues however it has only been observed in the PQ product and not in that supplied by Wollner.

Laboratory evaluation

The performance of lithium silicate has been outlined by the author in recent times (Thorn 2010, 2011) and a summary of performance is given here. The evaluation has been based on the author's use of ethyl silicate as a consolidant since the 1980s together with development of ethyl silicate bound grouts from 1992.

Summarizing the ethyl silicate grout research (Thorn 2010) it has been found that they have limited tensile strength, in line with all mineral bound grouts, and do not quite achieve sufficient cohesive strength or adhesion to be the perfect filling and capping system. They have been developed to avoid the potentially damaging effects of lime grouts placed into sandstones where gypsum formation and biological staining are two significant side effects. Grouts developed by the author for sandstone have been implemented at more than 20 sites and their performance has been seen to be satisfactory in all situations other than where tensile strength is required. This includes situations where hydrothermal expansion of exposed stones generates greater forces than the gout can withstand. To this extent ethyl silicate gouts perform as well if not better than their lime equivalents without the undesirable consequences. More flexible ethyl silicate have been recommended (Leisen 2004) but the tensile forces generated in stone are too great for any mineral based system. (Thorn 2008)

Ethyl silicate consolidants have been found over three decades to perform very well on sandstone but the author has never used them for lime based supports due to known incompatibility (Wheeler 2005) despite the various references to its successful consolidation in this context (Mangum 1986, Grissom 1999).

The author's first application of ethyl silicate to sandstone was in 1987 and the monument has been inspected annually over the past ten years within a managed condition survey program. Stone that had been previously very granular remains firm after 25 years with some evidence of isolated grain dislodgement but not to a point where treatment is recommended.

In this study lithium silicate has been evaluated simply in terms of its ability to equal or better the performance of ethyl silicate in both consolidation and grout forming properties.

It can be said that in relation to ethyl silicate, lithium silicate-
- provides a stronger more cohesive grout
- achieves similar consolidative strength to 100% ethyl silicate at 20% dilution of supplied product (5% solids)
- is unaffected by highly water saturated stone with no evidence of reverse migration
- is less readily available but its dilution ratio makes it a cost effective option that can be shipped more freely due to its less explosive and toxic nature.

Lithium silicate presents some limitations, all of which have been overcome, including-
- Orange staining of consolidated tuff and pure silica grouts, overcome by lowering the pH or choosing the Wollner 20% product.
- Darkening of the surface begins to become evident at 20% loading, equal to the same darkening that ethyl silicate produces. 20% is the concentration at which effective consolidation is achieved but is overcome by applying two or more applications at 10% dilution.
- Lithium silicate binder at 20% dilution produces a cohesive grout but this lacks the workable tack of the ethyl silicate grouts relying on fumed silica to produce a biding gel. Increasing the concentration to 50% produces a tacky wet grout and this also provides a well bound cured grout with suitable water absorptive properties.
- In highly saline conditions the lithium silicate has produced significant white bloom.
- There is some degree of surface skin formation, which also implies depletion of binder at depth.

The four positive benefits have been expounded upon in earlier writings, however the slightly negative aspects warrant additional clarification.

It is unclear by what mechanism the tuff and pure silica grout components result in an orange rust like fringe in all of the test samples above a concentration of 1.25% in the PQ product. Nor can it currently be explained why lowering the pH avoids stain development or why the problem does not occur in the Wollner product. In the case of the tuff, staining developed in the laboratory but not in the identical stone in situ. The critical issue here is that such staining is possible and must be looked for during testing regimes.

Buffering with mineral and carboxylic acids has been considered and equations 2 and 3 show the formation of stable compounds from both buffers. Table 1 indicates however that the resultant lithium species are significantly more soluble than the lithium carbonate formed through carbon dioxide interaction. Lithium carbonate is 5 times more soluble than gypsum whereas the sulphate and acetate are 140 and 160 times more soluble respectively, a similar solubility to halite (Table 1). Given that gypsum is considered a mobile mineral in stone it

must be anticipated that some lithium salts will migrate to the surface in time. Lithium carbonate has been noticed on in situ trials and over the course of 6 months has been seen to wash from the surface. Phosphoric acid additions have produced more durable grouts in water immersion tests where samples containing 0% and 1% H_3PO_4 were formulated and cured under identical conditions the immersed in water for 24 hours. The 0% sample powdered whereas the 1% sample remained unaffected.

Colour change through saturation of the surface is an unacceptable alteration. Lithium silicate at 20% dilution has been considered an equivalent consolidative benefit to that provided by ethyl silicate. It has been found that 20% lithium silicate darkens the surface to the same degree as ethyl silicate. Such darkening may be acceptable when an overall treatment is applied and the resultant colour change is not perceptible and within acceptable colour shift parameters. The ideal result is to have no colour change at all.

Two applications of 10% lithium silicate will achieve the same result and if applied with complete drying between, more than two applications can be applied without darkening. One critical advantage of lithium silicate in wet conditions is that there is no accelerated reaction in the presence of moisture, whereas high moisture can lead to a white crystalline surface with ethyl silicate treatments.

Using higher concentrations of lithium silicate, up to 50% dilution (10-12% solids) provides a very cohesive siliceous grout with no adverse properties and current testing at 100% produces a suitably porous but possibly over strong material. Saturation of the original surface is not an issue as grouts are formulated to match their surroundings and the issues relating to the treatment of original material do not apply.

Stability in halite solutions in the laboratory showed a stable solution at up to 5% halite. Field tests at a wet saline site at Uluru in central Australia, where the erosion mechanism is driven largely by very high halite concentrations, revealed substantial crystal formation on the surface. Replication of this by applying lithium silicate to a halite impregnated sample resulted in a less pronounced but similar crystal formation. This crystal development has not been analyzed to date, other than to observe that it is not substantially water soluble and mirrors a similar remnant bloom present on earlier consolidation trials carried out by others in the mid-1980s using sodium silicate.

It is quite possible that sodium silicate has formed in this situation following the reaction in Equation 4 where a more complex compound is formed, again of moderate solubility (Table 1.)

Equation 4
$$\Xi\,Si - O\text{-} + Li_2\text{+} + \text{-}O - Si\,\Xi \rightarrow \Xi\,Si - O\text{-}\,Li_2\text{+}\,\text{-}O - Si\,\Xi$$
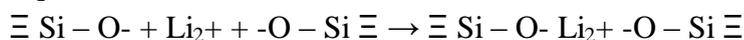
The main issue here is that the compound formed sits heavily on the surface and provides no effective consolidation. The solution to a problem like this is to extract the soluble salts from the stone prior to treatment, thus providing a low salinity consolidation zone. Depending on the moisture content it may also be necessary to accelerate the reaction with the addition of stabilized silica sols, however earlier work by the author in desalination of highly saline sandstone caverns showed that salts could be kept at low levels in natural rock shelters for up to 12 months. There is much further work required in this facet of the development.

Lithium silicate for the treatment of lime rich materials.

One of the most interesting properties of lithium silicate is its compatibility with calcium and CO_2, both of which readily participate in crystal forming reactions. To test the efficacy of lithium silicate a series of grouts has been formulated using a natural limestone with the addition of calcium hydroxide (commercial hydrated lime) and calcium carbonate powders. These two additions have been added at 10% by weight to the limestone to compare the curing properties of CaOH. As determined for the siliceous stone testing, the ability to form grouts is seen as a reasonable indicator of consolidative properties.

Two critical observations were made, despite 20% lithium silicate forming a cloudy solution when added to saturated CaOH in water.

There is a marked strength in the cured limestone grouts containing calcium hydroxide, supporting the literature stating that CaOH reacts with lithium silicate to form calcium silicates, as indicated in equation 4. Grouts containing calcium carbonate in the same proportions form a weaker grout and take considerably longer to cure. Consolidation into lime plasters shows increased cohesion however it is not expected that old plasters or calcitic rocks will have calcium in the hydroxide state. The turbidity of the lithium silicate lime water solutions foreshadows consolidation problems, however these are overcome if the lithium silicate is applied first, followed by limewater. The low miscibility of lithium silicate in ethanol (cloudy at 30% ethanol) also indicates that there are limitations to water reduction as in the "nano-lime" approach, however there are several ways of introducing CaOH into the matrix.

Lithium bound limestone grouts used commercial hydrated lime and in this situation no incompatibility was observed. This is perhaps due to the dry state of the CaOH compared to the turbid limewater results.

Application sites driving the research

Several sites have been identified as beneficiaries of the lithium silicate consolidation and grouting system. All are currently included in research to establish the performance properties of lithium silicate.

Te Ana a Maru, New Zealand

Te Ana a Maru is a rock shelter of high cultural significance, containing carvings into a naturally formed volcanic tuff (ignimbrite) wall. The site and its environmental conditions have been previously described (thorn 4, 5) and the key limitation here is that the carved wall is more or less permanently wet. The ceiling above, formed of a slightly denser tuff, drips water directly through the rock face during slight showers and there is almost no day in the year when the surface is not high in pore water. All surfaces support prolific biological growth with many species ranging from algae to ferns present. As part of a larger responsibility to protect the cultural surface, a series of laboratory and field trials have been conducted to strengthen the surface. The site is almost permanently sheltered but at one end where sunlight strikes the surface for part of every day a noticeable silica film has strengthened the surface. This thin consolidated film itself becomes prone to exfoliation, as do most of the more stable protected parts of the shelter. The vegetation is considered undesirable due to mechanical root damage from the higher plants. Less obvious is the fact that dissolved minerals seen precipitating on the rock surface in the more light-exposed locations cannot do so where the biota covers the surface. In these locations evaporation is from the outer surface of the biota and not the rock itself.

Milyeannup, Western Australia

Milyeannup is a site comprised of a series of cultural markings carved into a lime bound dune sand pavement of approximately 400mm thickness, lying within an ephemeral swamp subject to regular water inundation. Dissolution analysis of the rock has indicated a ratio –

Soil, organic	0.029gm	2%
Quartz	0.246gm	25%
Carbonate	0.727gm	73%

The carbonate was deposited around the quartz rather than being discrete grains, indicating a calcrete type precipitation, which is believed to be no older than 16,000 years. The almost 3:1 ratio of lime to sand suggests that this has been predominantly a deposition of micro-faunal remains living in the swamp, incorporating lesser amounts of blown sand from the coastal dunes 500 metres away.

No analysis has been carried out on the surface alterations at this stage but there is evidence of dissolution and alteration, suggestive of gypsum formation forming fringes around natural water holding depressions in the upper surface. There is a need to strengthen the surface and an aqueous spray application has been proposed. Chemicals suited to this include limewater, ammonium oxalate, particularly for its ability to insolubilize gypsum, and lithium silicate.

The site also requires reattachment of some areas using grouts. Given the fact that the pavement can be submerged at regular intervals it is necessary to have a grout that will remain stable in these conditions. Lime grouts are not considered to meet this criteria.

Te Ana a Nunuku, Chatham Islands

Te Ana a Nunuku is a limestone dissolution cavern with motifs carved onto the outer entrance surface. The limestone has been deposited under the sea but displays no evidence of salt erosion. The limestone is coarse and friable, vulnerable to both granular erosion and mechanical damage.

Increased tourist visitation has led to a protective shelter above the site but this too is leading to further damage. The conservator has proposed a strengthening campaign to give the limestone surface sufficient strength to withstand occasional flowing moisture. This is in combination with other water diversion strategies that will require the use of compatible grouts. Detachments across the surface also justify consolidation and grouting.

Of the chemical treatments, the ammonium oxalate consolidation pathway does not have an equivalent grouting option and the main consideration is to what extent the site can be treated with lime, lithium silicate, or a combination of both.

Uluru, central Australia

Uluru is a large conglomerate inselberg with over 100 painted sites around its base. The conglomerate is the result of rapid erosion of granites washing into a highly saline inland sea. The resultant rock is high in soluble salts and easily disrupted due to poor cementing between the large angular grains including, quartz, feldspars and biotite, the oxidation of which gives the rock its distinct red colour. Lithium silicate has been tested in a non-cultural cavern 6 metres above the ground plain, in a wet saline erosion area. Ethyl silicate had previously been tested at the same site and follows earlier attempts by others to stabilize the rock using commercial products.

The challenge at Uluru is to find a consolidant that is adhesive enough to bridge between the large angular aggregates and at the same time able to cope with the highly saline conditions. Despite being one of the driest regions on earth, percolating water plays a significant role in current weathering mechanisms. The majority of painted shelters are formed through on-going percolation of saline waters from rain water trapped in large basins on top of the rock.

Conclusion - Matching treatments to site limitations

The sites outlined above present a combination of conditions that limit the effective use of established methods. High moisture, salt and calcite preclude the effective use of ethyl silicate, while gypsum formation suggests that calcium based systems provide a short-lived solution.

Ammonium oxalate has the advantage of being able to stabilize sulphated calcium material (Matteini 2008) but requires a complimentary grout system. It has been identified as the ideal consolidant at Milyeannup where the site may be subjected to further inundation. Applying calcite in this situation would seem to be a futile treatment. Lithium silicate is able to provide a grouting solution that does not depend on the formation of calcite to achieve a cohesive grout. The seasonal nature of the swamp ensures that grouts can be applied and cured while the rock and surrounding soil are at their driest.

Lithium silicate as a consolidant offers advantages over oxalate and the CaOH approaches,

namely its reactivity to the diverse mineral components and impurities of the treated material. It has not been proved in the laboratory yet but field observations at Uluru indicate a potential for lithium silicate to react with halite to form sodium silicates with reduced water solubility (Table 1). This is not considered a major advantage, however the ability to consolidate in the presence of soluble salt is a major advantage. This is somewhat conflicted by the fact that application at Uluru to a substantially halite contaminated surface resulted in a highly visible white crystalline surface.

Desalination to the desired treatment depth will allow lithium silicate to form in a less reactive environment, especially at the surface. Desalination studies of similarly high surface halite in sandstone rock shelters shows that the surface remains salt free for at least 12 months after desalination.

In conclusion it has been determined through laboratory and field evaluations that lithium silicate can successfully consolidate both sandstone and limestone and has shown similar benefits on lime plasters. Current work includes its application to painted clay supports for paintings in Sikkim and Ladakh where silica dispersions have been tested in the past.

Lithium silicate has the benefit over ethyl silicate in being able to be applied into wet surfaces, and those containing calcite, clays and salts with improved results. In combination with ammonium oxalate a system for consolidation, grouting and gypsum stabilization has been established.

Product suppliers

Ethyl silicate

Wacker Chemie, worldwide distribution

Lithium silicate

PQ Corporation 300 Lindenwood Drive Valleybrooke Corporate Center, Malvern, PA 19355-17 www.pqcorp.com/pc/NorthAmerica/Products/LithiumSilicates.aspx
Wöllner GmbH & Co. KG, Wöllnerstraße 26,D-67065 Ludwigshafen
www.woellner.de/en/index.php?nid=64
Ammonium oxalate Alpha Chemicals Pty Ltd 18 INMAN ROAD, CROMER, NSW 2099
www.alphachemicals.com.au

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