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Article

Potential of Advanced Consolidants for the Application on Sandstone Rocks: A Comparative Study

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Abstract: To achieve efficient and durable consolidation of weathered sandstone, the selection of a suitable consolidant is essential. To reasonably assess the suitability of different formulations, it is fundamental to compare their performance as a consolidant within a substrate, which reliably models the properties of deteriorated material. As a test substrate, the sandstone from quarries in Mšené in central Bohemia was selected, for its developed porosity and relatively low mechanical strength. To obtain relevant comparison of their application potential, both commercial (Remmers KSE OH and Surfapore) and self-developed consolidants were included. To test the long-term stability of each consolidant, the stone was subjected to accelerated weathering. The characterization of texture properties was based on the physical sorption of nitrogen and krypton, mercury intrusion porosimetry and water uptake. While the mechanical properties in microscale were determined by nanoindentation, the mechanical strength in macroscale before and after consolidation was measured by drilling resistance. Both commercial exhibited good mechanical performance with reasonable durability. The performance of our developed samples was comparable or, in some cases, superior. Very interesting were the consolidants containing TiO_2 and ZnO nanoparticles, the former exhibiting comparable degree of consolidation and durability as commercial ones, with additional photocatalytic function, the latter unusually high increase in the mechanical strength, even after the weathering test. The diammonium hydrogen phosphate based consolidant showed exceptional durability in the weathering test, which makes it a promising product not only for carbonate but also sandstone materials.

Keywords: consolidation; sandstone; alkoxide consolidants; diammonium hydrogen phosphate; accelerated weathering; durability

1. Introduction

Alkoxysilanes have certainly been the most widely used stone consolidants over the past forty years [1]. Two compounds have been dominant: methytrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS). These compounds are hydrolyzed by water to form hydroxyalkoxysilanes, which then polymerize in a condensation reaction [2]. The water may come from the atmosphere or from the stone itself, or may be added as an ingredient. A solvent may be required in order to make the mixture miscible [1]. A catalyst is usually added in the form of an organo-tin or -lead. The hydrolysis and condensation reaction takes place after the treatment of stone, and resulting polymer gives the required strength to the stone.

A number of products are available that are based on TEOS and its oligomers. Their advantages are well known: the low viscosity, the ability to form silicon-oxygen-silicon (Si-O-Si) bonds [2]. The silicon-oxygen bonds are contained in many minerals, which contributes to the compatibility between alkoxysilanes and the stone. Owing to a low viscosity and high affinity to the minerals, the alkoxysilane consolidant easily penetrates within the porous system of the stone into a substantial depth [3]. Alkoxysilanes can function as a replacement binder in the stone for the original one, which was lost during weathering, leading to significant enhancement of the cohesion among the stone grains [2]. Silicon-oxygen bonds are quite stable and have good resistance to aging, which makes alkoxysilanes attractive for the outdoor use.

However, there are serious drawback concerning the application of TEOS as a consolidant, namely that the resulting silica gel shrinks and tends to develop cracks inside the stone due to the stress, caused by an increasing capillary force during aging and drying. This particular situation leads to brittle gel fragments that create a secondary capillary network in the stone, which can accelerate the rate of deterioration.

This issue has been of a major research interest in the stone consolidation applications. There are several commercial or noncommercial formulations developed to reduce the crack formation by a change of the catalyst [4,5], by adding oxidic nanoparticles (the so-called particle-modified consolidants, PMC) [3,6–11] or by incorporation of polydimethylsiloxane polymer (PDMS) [3,6–11]. Even if these "new" formulation have shown significant improvements, they are not optimal and exhibit considerable limitations, which is clearly due to the complexity of the treated stone objects.

To reasonably assess the suitability of different formulations, both commercial and noncommercial for application, it is fundamental to compare their performance as a xerogel itself and within a rock, which reliably models the properties of deteriorated material. To obtain valid outcomes, a combination of suitable physico-chemical techniques should be used and, importantly, also the effect of weathering should be included.

Therefore, in this study we selected two relevant commercial products with different composition, a series of self-developed PMC formulations and two phosphate-based consolidants. As a test substrate, the sandstone from quarries in Mšené in central Bohemia was selected, for its developed porosity and relatively low mechanical strength. Moreover, this rock was used a construction material for very important historical monuments, such as St. Vitus cathedral, the Charles bridge, the Old Town city-hall, several government buildings, all of them in Prague. For the determination of texture and mechanical properties both consolidant xerogels themselves and the sandstone treated with consolidants, in micro- and macroscale, sorption experiments in gas and liquid phase, nanoindentation and drilling resistance measurements were performed. Furthermore, the effect of weathering was included, using the accelerated weathering tests.

2. Materials and Methods

Materials

For the preparation of consolidants, five commercially available metal oxide nanoparticles were used, including Aeroxide® TiO2 P25 (Evonik Industries, Essen, Germany); Aerosil® SiO_2 200 Pharma, R805, R9200 (Evonik Industries, Essen, Germany) and NanoZnO (Bochemie, Bohumin, Czech Republic). Detailed characteristics of the nanoparticles are provided in reference [7]. Dynasylan 40 was obtained from Evonik Industries (Essen, Germany), isopropanol (IPA), dibutyltin dilaurate (DBTL), n-octylamine, all from Sigma-Aldrich (St. Louis, USA), $Ca(OH)_2$ (Penta, Prague, Czech Republic)

Used sandstone originates from quarries in Mšené, central Bohemia (Czech Republic). It is a white-greyish fine-grained sedimentary psamitic rock, dominantly containing quartz (95%) and muscovite and feldspar clasts as accessories. The matrix is formed by clay minerals (kaolinite, chlorite, illite) but its content is very low.

Preparation of the nanoparticle-modified consolidants

The self-developed alkoxide-based consolidants were prepared by adding the nanoparticles (3 % wt.) to Dynasylan®40 [7,10,11]. Afterwards, catalyst n-octylamine (0.18 % wt.) (Alfa Aesar) was added. The mixture obtained was diluted with isopropanol in the ratio 1:1. For the consolidant containing ZnO nanoparticles, a mixture of n-octylamine (0.18 % wt.) and dibutyltin dilaurate (1 %

wt.) was used because n-octylamine was not sufficient to achieve a formation of the gel. An overview of the consolidants is given in the Table 1, where in the designation of Samples the type of nanoparticles and catalyst used are given, e.g., SiGel-SiO_2-methyl-oa means that the consolidant contains methylated SiO_2 nanoparticles and n-octylamine catalyst.

The second type of self-developed consolidants included hydroxyapatite-based ones. An 2.0 M aqueous solution of diammonium hydrogen phosphate (DAP) were prepared by dissolving this salts in deionized water. This concentration (close to saturation at room temperature) was selected because the higher the DAP concentration, the more calcium phosphate phases are formed by the reaction with the calcium source.

The commercial consolidant KSE OH (Remmers) was used as reference. Compared to our developed consolidants, KSE OH contains only 25 % of solvents, while ours 50 %. According to the data sheet, this product should be suitable for the consolidation of weathered, friable natural stones, particularly sandstones, cast stone, renders and mortar. Another commercial consolidant SurfaPore FX WB was obtained from Nanophos SA (Lavrio, Greece). This innovative nano-material is suitable for enhancing the mechanical properties of worn building surfaces [12,13]. For testing, the consolidant xerogels aged two-month were used.

The consolidants were applied to stone by capillary suction; the stone specimens were partially immersed (3 mm depth) in the liquid products for 3 h. The application time was determined by measuring the evolution of the capillary fringe (mm) on the lateral surface of the specimens, being concluded that 3 h was the time necessary for the wet fringe of the majority of the consolidants to reach the top of the specimens (3 cm). The samples were weighed before and immediately after the application of the consolidant to calculate the uptake. In addition, they were re-weighed after complete drying (months after the consolidant application) to calculate the dry yield.

Methods

Textural properties of xerogels and rocks dried at 60 °C were determined by the analysis of adsorption isotherms of nitrogen or krypton at the boiling point of liquid nitrogen (ca 77 K). Before the adsorption experiment the samples were outgassed at 60 °C for 24 hours to ensure the complete cleaning of the surface. The experiments were carried out using a Micrometrics 3Flex volumetric adsorption unit. Because of the complex character of the samples' porosity the obtained isotherms were analyzed by a combination of several methods, especially the Broekhoff-de Boer t-plot and several variants of the NLDFT. The pore width is described using the IUPAC nomenclature, micropores, mesopores and macropores corresponding to the width of less than 2 nm, 2–50 nm and more than 50 nm, respectively.

The pore size distribution and the total open porosity were determined by mercury intrusion porosimetry using the Quantachrome Poremaster PM-60-13 instrument, working in the pressure range corresponding to pore sizes from several nanometers to about 200 μm. The mercury parameters were as follows: 480 erg cm^{-2} for the surface tension and 140° for the contact angle. Sample size was about 1 cm^3.

In the measurement of the water uptake by capillary suction, the stone specimens were partially immersed (3 mm depth) in water for 3 h and the amount of soaked water was determined by weighing [14].

The mechanical properties in microscale level were tested using Hysitron TI 750L Ubi nanoindentation instrument. A three-sided pyramidal diamond Berkovich indenter and the Oliver-Pharr method were used to get the elastic modulus and hardness. Each sample was scanned by in-situ Scanning Probe Microscopy (SPM) imaging to select a suitable place for experimental testing with minimum roughness. Maximum load was Pmax = 1.0 mN, load was increased linearly for 5 s to reach maximum, which was held for 2 s and then full unloading was achieved within 5 s. The samples to be measured were embedded in resin, after 24 hours they were grinded with SiC paper (up to grit #2000) and polished. Finally, the surfaces were cleaned by sonication. The distance between the indents and the total test area were 1 μm and 25 μm^2, respectively. Because of the embedding in resin and porosity of samples, single indents were performed to distinguish the resin from the gel in pores.

The location of single indents was selected with the aid of optical microscope and for each sandstone sample, at least 30 indents were carried out.

The mechanical properties in macroscale level were determined by a Drilling Resistant Measuring System (DRMS, from SINT Technology, Calenzano, Italy) [15]. The blocks of the sandstone 3 × 3 × 3 cm in size were drilled drill bits of 4.8 mm in diameter at a rotation speed of 300 rpm and a penetration rate of 30 mm min^{-1}.

Accelerated weathering

Determination of material degradation mechanisms due to water, moisture, humidity, heat, illumination. Accelerated weathering and light stability tester are widely used for research and development, quality control and material certification. Q-Sun Xenon Test Chamber reproduce the full spectrum of sunlight, including ultraviolet, visible light and infrared. The simulating test was done according to ASTM G 155-05a Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials (2005). This test include irradiation with xenon light at increased temperature of 47°C combine with water spray for one hour, as summarized in Table 2.

3. Results and Discussion

3.1. Characterization of the used rock substrate

The porous sandstone used displayed characteristics typical to those of deteriorated sandstone. For instance, mercury intrusion porosimetry showed that the material had a high open porosity of ca. 30 % and a pore radius of ca. 9 µm. Our adsorption experiments, in which both nitrogen and krypton were used as sorbates (at the boiling point of liquid nitrogen), produced similar surface areas of ca. 0.5 m^2 g^{-1}, which did not significantly differ from that determined by mercury intrusion porosimetry. The mechanical performance of the sandstone was determined by three different methods: drilling resistance (9.7 N), compressive strength (28.0 MPa) and bending strength (1.3 MPa) measurements. These low mechanical properties confirmed the suitability of our porous material for use in studying the consolidation of deteriorated sandstone.

3.2. Characterization of the consolidant xerogels

Effect of catalyst and added nanoparticles on xerogels texture properties

A sol-gel process was used to transform liquid consolidants into solid xerogels, whose properties were determined by an extensive adsorption study, the results of which are summarized in Table 3.

The addition of nanoparticles to the sols whose gelation was catalyzed by dibutyltin dilaurate did not lead to the formation of mesoporosity in corresponding xerogels. This might be due to formation of a narrow corona around the nanoparticles, the corona itself being identified as a micropore. In fact, an increase of about 20% in micropore volume was observed. The surface properties of the added particles, their hydrophilicity for a surface covered with hydroxyl groups and hydrophobicity for a surface covered with methyl or octyl groups, did not affect the character of porosity. Therefore, it can be assumed that there was no formation of chemical bonds between the particle surface and the surrounding gel because if chemical bonds were formed, there would be a difference.

Table 1. Overview of the composition of self-prepared and commercial consolidants.

Source	**Sample**	**Consolidating agent**	**Solvent**	**Catalyst**	**Additive**
IPC [1]	SiGel-d	50% oligomeric TEOS	50% IPA [2]	dibutyltin dilaurate	–
IPC	SiGel SiO_2-d	50% oligomeric TEOS	50% IPA	dibutyltin dilaurate	SiO_2
IPC	SiGel SiO_2-octyl-d	50% oligomeric TEOS	50% IPA	dibutyltin dilaurate	SiO_2-octyl
IPC	SiGel-oa	50% oligomeric TEOS	50% IPA	n-octylamine	–
IPC	SiGel SiO_2-oa	50% oligomeric TEOS	50% IPA	n-octylamine	SiO_2
IPC	SiGel SiO_2-octyl-oa	50% oligomeric TEOS	50% IPA	n-octylamine	SiO_2-octyl
IPC	SiGel SiO_2-methyl-oa	50% oligomeric TEOS	50% IPA	n-octylamine	SiO_2-methyl
IPC	SiGel TiO_2-oa	50% oligomeric TEOS	50% IPA	n-octylamine	TiO_2
IPC	SiGel ZnO-oa/d	50% oligomeric TEOS	50% IPA	n-octylamine+ dibutyltin dilaurate	ZnO
IPC	HAP	23% DAP	77% H_2O	–	$Ca(OH)_2$
Remmers	KSE OH	75% oligomeric TEOS	25% MEK	dibutyltin dilaurate	–
NanoPhos SA	SP FX	20% TEOS	80% IPA	n-octylamine	CaC_2O_4

[1] IPC = J. Heyrovsky Institute of Physical Chemistry; [2] IPA = isopropyl alcohol; [3] DAP = diammonium hydrogen phosphate.

Table 2. Parameters of the accelerated weathering testing.

Steps	**Exposure period / min**	**Irradiance**[1] **/ W m^{-2}**	**Black standard temperature / °C**	**Chamber temperature / °C**	**Relative humidity / %**
1. light	40	0.55	70 (±2)	47 (±2)	50 (±5)
2. light and spray	20	0.55	70 (±2)	47 (±2)	50 (±5)
3. light	60	0.55	70 (±2)	47 (±2)	50 (±5)
4.dark and spray	60	0.00	38 (±2)	38 (±2)	95 (±5)

[1] Wavelength of 340 nm.

Table 3. Textural properties of the xerogels determined by sorption measurements.

Xerogel	**Micropore volume / cm^3 g^{-1}**	**Mesopore volume / cm^3 g^{-1}**	**BET surface area** [1]**/ m^2 g^{-1}**	**Pore width / nm**	**Total porosity** [2]**/ %**
SiGel-d	0.15	0.00	*	0.8	25
SiGel-oa	0.00	0.23	198	5.0	34
SiGel-SiO_2-oa	0.00	0.24	187	6.6	35
SiGel-SiO_2-methyl-oa,	0.00	0.26	223	5.6	39
SiGel-SiO_2-octyl-oa,	0.00	0.24	209	5.4	35
SiGel-TiO_2-oa	0.00	0.22	207	5.0	33
SiGel-ZnO-oa/d	0.14	0.17	55	1.9; 4–5	41
KSE OH	0.06	0.27	379	1.9; 4–5	38
SP FX	0.00	0.01	12	2–4	2

[1] BET equation is not applicable in narrow micropores.

[2] Total porosity was calculated from the total pore volume.

When an organic amine, a substance with a higher basicity than dibutyltin dilaurate but a lower basicity than inorganic bases (e.g. ammonia or hydroxides of alkaline metals), was used as the catalyst, important changes in porosity occurred [5]. The formation of micropores was substantially suppressed and a considerable amount of mesopores were formed, their width achieving 5 nm depending on the type and concentration of organic amine used. Due to the structure of their molecules, some primary amines with a longer alkyl chain (such as octyl or dodecylamine) might function as non-ionic surfactants that reduce the surface tension.

The texture of SiGel-ZnO-d/oa was more complex, exhibiting both micro- and mesoporosity, due to the combination of both dibutyltin dilaurate and organic amine catalysts. The commercial KSE OH consolidant exhibited similar texture properties, but SP FX was practically non-porous.

Thus, to suppress the formation of micropores, which have a negative effect on the cracking of gels due to their high capillary pressure [2] and to induce the formation of advantageous, substantially wider mesopores, an organic amine is preferable as a catalyst [5].

Mechanical properties of the xerogels in microscale

First, the elastic character of the xerogels was confirmed by the frequency sweep - constant force measurements, which showed that their storage modulus did not depend on the frequency (see Figure 1a).

The mechanical properties in microscale of the xerogel were determined by a nanoindentation testing. From the stress-strain curve, the contact stiffness and reduced elastic modulus, representing the Young's modulus of elasticity and indentation hardness, respectively, were obtained. The example of the nanoindentation curves is shown in Figure 1b.

The catalyst used decisively affected the mechanical performance of the xerogels (Table 4). Both reference xerogels SiGel-d and KSE OH, for which organometallic catalyst was used, exhibited much higher hardness than those catalyzed by n-octylamine. The indentation hardness correlated with the Young’s modulus and the contact depth. The shape of nanoindentation curves for the harder xerogels exhibited the character of glass-like deformation, while that for softer xerogels was polymer-like. The difference in the mechanical properties is probably due to the compact structure containing only narrow micropores of the xerogels catalyzed by organometallic compounds. The xerogels prepared using n-octylamine catalyst showed lower values of both mechanical parameters, which is connected with their more open mesoporous structure.

Generally, the hardness and elasticity were depth dependent (Figure 1c,d), those of the outermost surface layers being higher compared to the bulk, probably due to the faster hydrolysis and condensation of the ethylsilicate species within the surface layers of the xerogel block. However, from the consolidation viewpoint, the consolidation should be homogeneous within the stone profile. This feature was reasonably fulfilled using our consolidants, better than with the commercial ones. The storage modules determined by this method are in agreement with those in Figure 1a.

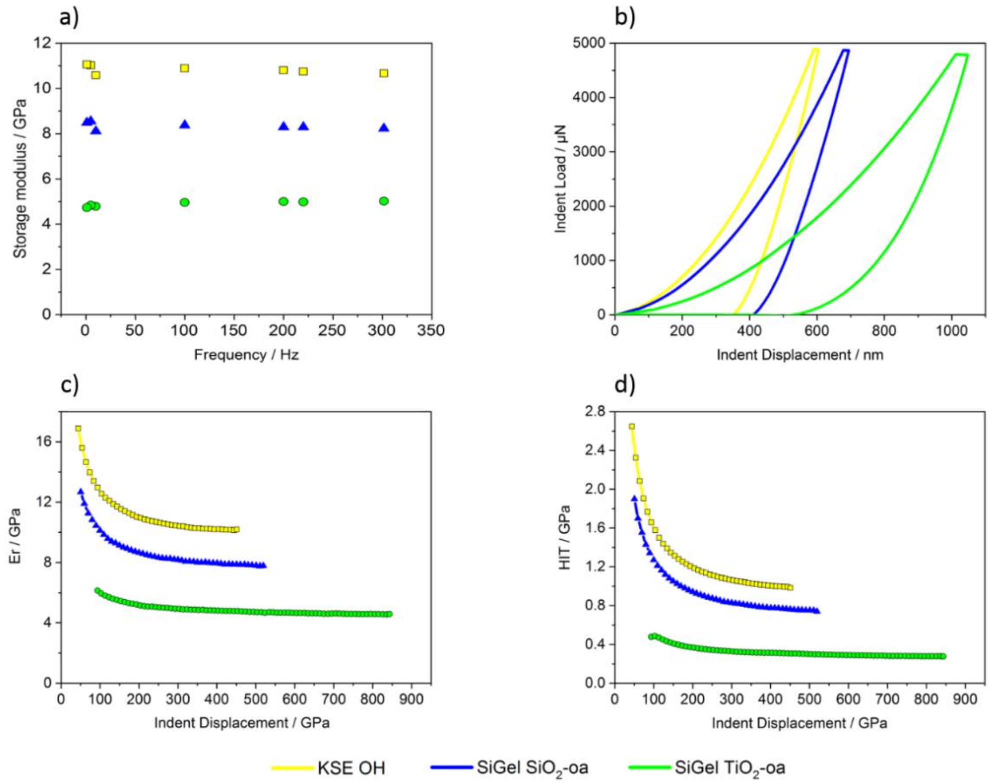

Figure 1. Mechanical properties of the xerogel in microscale level. a) Variation of storage modulus with the sweep frequency; b) load-displacement curves; c) Dependence of Young´s modulus (c) and hardness (d) on indent displacement.

Table 4. Mechanical properties of the xerogels determined by nanoindentation.

Xerogel	Young’s modulus / GPa	Hardness / GPa	Contact depth / nm
SiGel-d	7.74±0.52	1.04±0.09	182.21±9.35
SiGel-oa	4.49±0.14	0.41±0.02	297.88±6.50
SiGel-SiO_2-methyl-oa	3.83±0.06	0.45±0.01	285.80±4.43
SiGel-TiO_2-oa	4.72±0.03	0.33±0.00	349.96±2.10
KSE OH	11.44±0.25	1.32±0.05	175.75±4.34

Accelerated weathering of xerogels

The test showed that the durability of the xerogels substantially depended on the nanoparticles used as additives. The cohesion of weathered xerogels prepared using different nanoparticles, the formulation being otherwise the same, considerably differed (Figure 2). The SiGel-SiO_2-methyl-oa xerogel exhibited excellent stability, while SiGel-SiO_2-oa and SiGel-ZnO-oa/d performed much worse. The sorption measurements showed that after the accelerated weathering test, the structure of the tested xerogels significantly changed. The structure of SiGel-SiO_2-methyl-oa and SiGel-SiO_2-octyl-oa xerogel was more stable, however, a decrease of surface area and pore volume was observed. This process is similar to the Oswald ripening, during which destruction of narrow pores and formation of rigid structure occur. The structure of SiGel-SiO_2-oa significantly disintegrated, thus, the surface area increased. Xerogel SiGel-ZnO-oa/d is anomalous due to sedimentation of the ZnO nanoparticles during the sol-gel process, which fundamentally affected the structure of the material. Therefore, high increase of the surface area and pore volume was observed. Compare to macroscopic material block, for a thin layer form in narrow pores of the rock, it can be expected that this process will be less pronounced. Thus, it does not mean that ZnO nanoparticles are unsuitable as additives for consolidants.

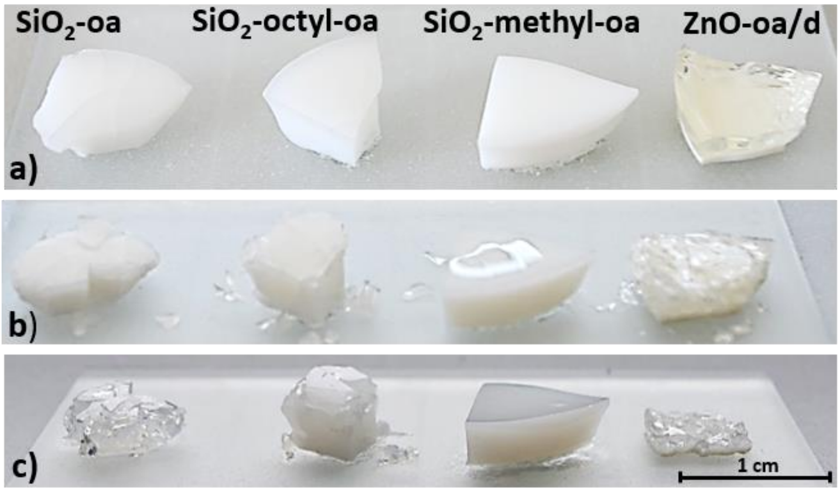

Figure 2. Effect of weathering on the consistency of the xerogels. a) fresh; b) after one WAT cycle; c) after two WAT cycles.

3.3. *Application of the consolidants on the sandstone*

Uptake of the consolidants

When applied on the sandstone, the uptake of all the tested consolidants by the capillary suction was similar of about 10% (Table 5). However, their dry matter yield differed substantially.

For octylamine-catalyzed SiGel consolidants it was in a narrow range of about 4–5%. For the commercial sample SP FX this yield was only 1.1%, which roughly corresponds to the lower content of TEOS in this consolidant (see Table 1). For the other commercial product KSE OH, which contains higher percentage of oligomeric TEOS (75%) than the SiGel samples (50%), the yield was surprisingly only 2.7%. The reasons for such a low value may be the different solvent used, the presence of nanoparticles, and, especially, the catalyst, which controls the rate of hydrolysis and polycondensation. The insufficient rate of these processes may lead to a loss of the active species (alkoxide) by faster evaporation.

Another marked difference between the octylamine-catalyzed SiGel consolidants and the reference KSE OH was in the water uptake. That of the former group of consolidants was smaller by an order of magnitude. The explanation for the smaller uptake by SiGel consolidants seems to be their higher hydrophobicity caused by the use of amine catalyst. The high water uptake of SP FX and HAP consolidants approaching that of the untreated rock is clearly due to a rather low dry matter yield.

Table 5. Sandstone uptake by capillary suction.

Sandstone treatment	Consolidant uptake / % (w/w)	Dry matter yield / % (w/w)	Water uptake / % (w/w)
Untreated	–	–	11.60
SiGel-oa	10.1	4.0	0.09
SiGel-SiO_2-oa	8.0	4.3	0.06
SiGel-SiO_2-methyl-oa	10.3	4.2	0.12
SiGel-SiO_2-octyl-oa	9.2	4.8	0.12
SiGel-TiO_2-oa	10.1	4.8	0.11
SiGel-ZnO-oa/d	10.2	3.7	0.32
HAP	13.9	0.24	9.8
HAP+$Ca(OH)_2$	10.8	0.31	9.8
KSE OH	10.6	2.7	2.3
SP FX	9.6	1.1	9.5

Mechanical testing in microscale

The direct determination of the location of the consolidant xerogel within the porous system of the sandstone and measuring of its mechanical properties was carried out by the nanoindentation. The consolidant was applied on the stone by brushing. To localize the consolidant, a series of indents (applied stress of 1 mN) were performed to identify a xerogel deformation pattern. The contact depth for the mineral grains in the sandstone, SiGel-d consolidant and a soft epoxy resin was ca. 100, 180 and 500 nm, respectively.

On the stone, the SiGel-d xerogel formed a thin layer, which corresponded to the Young´s modulus and hardness of 11.40 GPa and 0.93 GPa, respectively. Furthermore, the xerogel penetrated through the porous system and was detected in the lowest point of 700 µm, in which the Young´s modulus and hardness was 10.97 and 0.74 GPa, respectively. For the SiGel-oa, the xerogel was not observed on the sandstone surface. First deposits of the xerogel were located in the depth of 250 µm. For this xerogel, the contact depth was ca. 300 nm, which was higher compared to SiGel-d. The probable explanation is the better penetration of the SiGel-oa consolidant and the higher compliance of the xerogel formed due to the presence of wider mesopores in comparison with the narrower micropores of the SiGel-d xerogel.

Compared to the pristine SiGel-oa and SiGel-d xerogels, their counterparts localized in the pores of the stone exhibited a roughly two-fold increase in the Young´s modulus. This difference may be due to a confinement effect of the pore walls [16–20], which may increase the Young´s modulus owing to the wrapping of the gel by hard stone material . For the hardness, however, no such increase was observed. This observation implies that the microstructure of the xerogel was not influenced by the presence of pore walls, which is a reasonable conclusion provided there was no formation of the chemical bonds between the gel and the surface of the pore walls.

Mechanical testing in macroscale

Due to the treatment with octylamine-catalyzed SiGel consolidants, there is a systematic decrease in the surface area (Table 6), which is in agreement with smooth and uncracked character of the xerogels. Sample SiGel ZnO-oa/d exhibited an anomalous behaviour with a ten-fold increase in the surface area and formation of a microporosity. The surface of KSE OH treated sample is comparable with the untreated sample even if it should decrease due to the filling of pores, especially of the finer ones. The reasonable explanation is a cracking of the xerogel inside the pores, which created an additional surface area. The performance of the SP FX consolidant characterized by an increase in the surface area and formation of micropores is comparable with the SiGel ZnO-oa/d. With DAP consolidants, there was only limited decrease in the surface area which is in agreement with the very low dry matter yield for this samples.

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Table 6. Properties of sandstone treated with various consolidants weathered by 50 cycles.

Sandstone treatment	**BET area fresh [1] / $m^2 g^{-1}$**	**BET area aged [2] / $m^2 g^{-1}$**	**DRMS fresh [3] / N**	**DRMS aged [4] / N**	**Δ DRMS [5] / %**
Untreated	0.56	-	9.7 ± 0.5	3.2 ± 0.2	−67
SiGel-oa	0.05	5.90	11.6±0.8	9.2±1.2	−21
SiGel SiO_2-oa	0.05	16.77	15.5± 0.8	12.1± 0.8	−22
SiGel SiO_2-octyl-oa	0.15	8.41	10.5±0.7	4.0±1.0	−62
SiGel SiO_2-methyl-oa	0.06	7.42	17.3±1.9	12.7±1.0	−27
SiGel TiO_2-oa	0.02	0.17	23.3 ± 2.5	18.1 ± 1.4	−22
SiGel ZnO-oa/d	5.10 *	10.60 *	54.9 ± 1.7	60.9 ± 2.2	+11
KSE OH	0.46	2.54	25.2 ± 1.4	18.5 ± 1.5	−27
SP FX	2.10 *	3.00	22.7 ± 1.6	16.4 ± 1.4	−28
HAP	0.23	0.42	18.5 ± 1.3	18.1 ± 1.6	−2
HAP+$Ca(OH)_2$	0.23	0.73	17.8 ± 1.4	17.6 ±1.5	−1

* Samples containing micropores; [1] BET surface area before weathering; [2] BET surface area after weathering; [3] Drilling resistance force before weathering; [4] Drilling resistance force after weathering; [5] Change in the Drilling resistance force due to weathering

Compared to the untreated sandstone, the drilling resistance for the treated samples increased (Table 6). However, this increase depended substantially on the consolidant used.

For the consolidant SiGel-oa without nanoparticles, only very limited increase in the force was observed. However, importantly, the stone retained its cohesion after weathering, as the resistance force decreased only by 21%. Concerning the SiGels containing SiO_2 nanoparticles, some effect of their surface modification was observed. The surface coating with octyl-groups decreased the resistance force in comparison with other two types of particles. Moreover, SiGel SiO_2-octyl-oa exhibited low durability. The reason is probably the practically complete coverage of the SiO_2 particles with octyl-groups. The performance of SiGel containing TiO_2 nanoparticles was slightly better that of both commercial products, exhibiting higher durability. Interestingly, the SiGel containing ZnO nanoparticles, catalyzed by both amine and organometallic compounds, exhibited exceptionally high resistance force, even after the weathering treatment. This performance might be due to the unusual micro-mesoporous texture of the xerogel and the solubility of ZnO nanoparticles. A reaction between the zinc ions and the xerogel formed ion the course of the sol-gel process. Similar reactions can be expected during the process of accelerated weathering. Finally, both HAP samples exhibited a reasonable degree of the consolidation and excellent durability.

The BET surface areas measured after the weathering treatment partially correlated with the resistance force. Samples with small surface area after the weathering treatment (less than 1 $m^2 g^{-1}$), i.e., SiGel TiO_2-oa, HAP and HAP+$Ca(OH)_2$, exhibited high durability. The large surface area of SiGel-oa sample and those containing SiO_2 nanoparticles correlates with their lower durability, with the exception of SiGel SiO_2-oa. SiGel ZnO-oa/d exhibited unusual surface areas, which might be connected with the structure changes as suggested above.

4. Conclusions

We showed that both self-developed and commercial samples exhibited good mechanical performance in the consolidation of porous sandstone with reasonable durability. The performance of our samples was comparable to that of commercial ones or, in some cases, superior. Very interesting potential exhibited the alkoxide consolidant containing TiO_2 nanoparticles, providing a very good consolidating performance with high durability. Moreover, due to the content of TiO_2 nanoparticles a very desirable self-cleaning property can be expected. The performance of consolidant containing ZnO nanoparticles and catalyzed by a mixture of amine and organometallic compounds was exceptional, exhibiting unusually high strength and durability. Furthermore, an additional biocide function due to the presence of ZnO particles can be reasonably anticipated. Finally, the diammonium hydrogen phosphate-based materials proved their important potential as high-performance consolidants of not only carbonate materials, for which they were originally developed, but of sandstones as well. As confirmed by only low increase in the BET surface area after weathering, these consolidants formed a thin compact layer covering the inner surface of the stone. Clearly, this layer survived the weathering treatment without any formation of cracks. This universality of their performance is highly interesting from the application point of view as it simplifies their application, especially in case of problematic calcareous sandstones or sandy limestones.

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