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Original article

# In-situ study of the consolidation of wall paintings using commercial and newly developed consolidants

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ABSTRACT

This paper presents a comparison of consolidant effectiveness for a newly developed consolidant based on soluble calcium compound calcium acetoacetate and two nano-lime-based consolidants available on the market, i.e., CaLoSiL® E15 and Nanorestore®. Impressionist wall paintings made using the fresco technique in the Franciscan Church in Ljubljana were selected for *in-situ* studies. In order to monitor the colour differences and consolidation effectiveness before, and a few months after, the application of the consolidants, different non-destructive and micro-destructive methods were used. The colour differences were assessed visually and using spectrophotometry, while the consolidation effectiveness was monitored using three methods: the ultrasound velocity method, the surface hardness method and the DRMS method. We demonstrated the best recovery in terms of mechanical properties and with a negligible effect on the wall paintings' appearances after the treatment with the new consolidant. Both nano-lime-based consolidants show a less pronounced reinforcement in the mechanical strength – smaller increase in the drilling-resistance and the surface hardness. The formation of a white haze with the nano-lime consolidants led to a considerable change in the colours of the wall paintings.


## 1. Introduction

Wall paintings can undergo several degradation processes resulting in flaking of the paint layers, powdering, the formation of small blisters and loss of the artefact [1–3]. Over the past few decades a variety of materials have been used for the consolidation treatment of immovable art such as wall paintings. It is known that the use of compatible materials is preferable for the consolidation of artistic or historical substrates [2]. Due to its chemical compatibility, $Ca(OH)_2$ is one of the most compatible materials for the consolidation of carbonate-based works, such as a wall painting. But since the solubility of $Ca(OH)_2$ in water might be too low to allow an effective consolidation, the use of short-chain alcohols as dispersion media is preferred. The stability of alcohol dispersions is increased and the risk of forming a white haze is reduced. In addition, the use of nanoparticles of $Ca(OH)_2$ increases the surface area per unit volume, which leads to an enhanced reactivity to the external environment and penetration through the porous matrices [1]. Since the first development of $Ca(OH)_2$ particles in propanol in 1993 by Ferroni, numerous improvements have been made, two of them are available on the market under the trademarks Nanorestore® [4] and CaLoSiL® [5]. Overall, there are still many drawbacks to nano-lime-based consolidants, such as the use of a low concentration of $Ca(OH)_2$ (5–25 g/L), which means the need for many applications (10 and more), since a higher concentration could enhance the white haze and reduce the penetration into the substrate [1,2]. Furthermore, the use of solvents plays a major role, since the solvent should exhibit a not too high volatility, otherwise the penetration depth would be hampered. Additionally, the eco-toxicological impact should be considered due to the hazardous nature of the organic solvents employed [1]. In the frame of the HEROMAT project a new water-based solution of calcium acetoacetate for consolidating carbonate-based substrates was developed [6]. Because it is a water solution, greater penetration can be achieved. Moreover, due to the higher concentrations of calcium acetoacetate (up to 100 g/L), the number of applications can be much reduced, without any white haze on the treated surface. Finally, calcium acetoacetate is eco-toxicologically friendly, because harmless water is used as a solvent.

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The literature reports relatively few *on-site* applications of nanoparticle dispersions for wall paintings [2,3,7–13]. Although the assessment of the consolidation effectiveness for a wall painting is of great importance, almost all the reported studies for testing of consolidation effectiveness on wall paintings use only a visual assessment. There are few attempts to evaluate the consolidation effectiveness by instrumental methods. Natali et al. [8] were used water-absorption tests, spectrophotometry analyses and a Scotch-tape test to evaluate the consolidant's effectiveness. This methodology gives mainly information on consolidant effectiveness of a superficial layer. The water-absorption corresponds to its pore structure and therefore gives indirect information about porosity before and after consolidation [14]. Cohesion after the consolidant application is evaluated using the Scotch-tape test [8]. Morphology and carbonatization of consolidant is monitored using optical and scanning electron microscopy coupled with Fourier-transform infrared spectroscopy. Density and elastic properties of materials as well as consolidation effectiveness are studied by ultrasound velocity measurement [15]. Surface hardness test is carried out to measure the mechanical properties. Although the method suffers from limitations such as the impact of surface texture, weathering and moisture content, specimen dimensions, presence of dust and particles, on the final results [16,17], combining the method with other proposed approaches may give additional information about the consolidation process. Finally, DMRS provides the strength assessment in depth, with little intrusion, while other in-situ methods, such as surface hardness method and ultrasound velocity method, only manage to assess strength of a superficial layer. DRMS provides valuable information concerning mechanical properties, but since it is a micro-destructive method, the number of measurements is usually limited or in some cases not possible [18].

All mentioned methods, with exception of DRMS method, give information of the physical and mechanical properties of the surface of the tested cultural heritage object, while DRMS method provides the strength assessment in the depth of the material. Unlike water-absorption test and Scotch-tape test, methods such as DRMS, ultrasound velocity measurement and surface hardness test are known in the literature to have a strong relationship with compressive strength [19–23], which has been traditionally regarded as the sole relevant structural material property. Combination of non- and micro-destructive techniques are necessary to obtain reliable result related to cohesional properties [24], therefore combination of methods such as DRMS, USV and SH method seems like a good attempt/idea to evaluate consolidant efficiency. In this work, we use a range of methods, which, in combination, give a new insight into the effectiveness of three selected consolidants on real case study.

## 2. Research aim

The aim of this work was to study the effectiveness of the consolidant for the newly developed consolidant CFW (calcium acetoacetate), developed in the scope of the HEROMAT project [25], compared to two different nano-lime-based consolidants (CaLoSiL® E15 and Nanorestore®) on frescoes painted between 1935 and 1936 in the vault of the presbytery in the Franciscan Church of the Annunciation in Ljubljana, Slovenia.

Due to the lack of an assessment of the consolidant's effectiveness (physical and mechanical properties before and after the treatment) in real situations in the literature, we firstly perform a number of in-situ studies of the consolidant's effectiveness and assess the methodology. Different non-destructive and micro-destructive methods were used to assess consolidant's effectiveness before as well as 1 and 3 months after the consolidant's application.

## 3. Experimental

### 3.1. Test field

For the purpose of the study, a test field was created on the wall paintings in the vault of the presbytery of the Franciscan Church, where conservation restoration intervention began in 2014. The valuable wall paintings were painted by impressionist Matej Sternen in 1935 and 1936, in the fresco technique, with details in the secco technique. As part of the conservation-restoration work we decided to test the consolidant's effectiveness for the three selected consolidants.

The measurements locations for each method were marked and are shown in Fig. 1. For each consolidant three test fields were selected. Each test field was 60–73 cm long and 20 cm wide (Fig. 1). To determine any colour difference, three similar colours (light red, dark red and grey) were chosen on each test field and are shown as numbers (1–3). The pigments of the chosen paint layer are as follows: carbon-based black mixed with red and yellow ochre was used for the grey colour, red ochre mixed with carbon-based black and ultramarine blue for the light red colour and red ochre mixed with carbon-based black for the dark red colour. The paint layer is followed by a fine lime mortar layer (intonaco) with a thickness of approximately 4 mm and a coarse lime mortar layer (arriccio). The composition of both layers is similar: the aggregate consists of coarse grains of dolomite, which prevails, while limestone and quartz grains are present in minor amounts. The difference is in the grain size, which is up to 1.5 mm for intonaco and 2.6 mm for arriccio. For measuring the ultrasound velocity, a grid with letters (a–f) was designed, where the sound from one point (transmitter) to another point (receiver) was measured. The selected distance points were: a–b, c–d, e–f and b–f. Surface hardness measurements were performed on the same measuring location as the spectrophotometry measurements (numbers 1–3). The measurement locations for the drilling-resistance of each field are shown with arrows. During the 3-months monitoring period, the relative

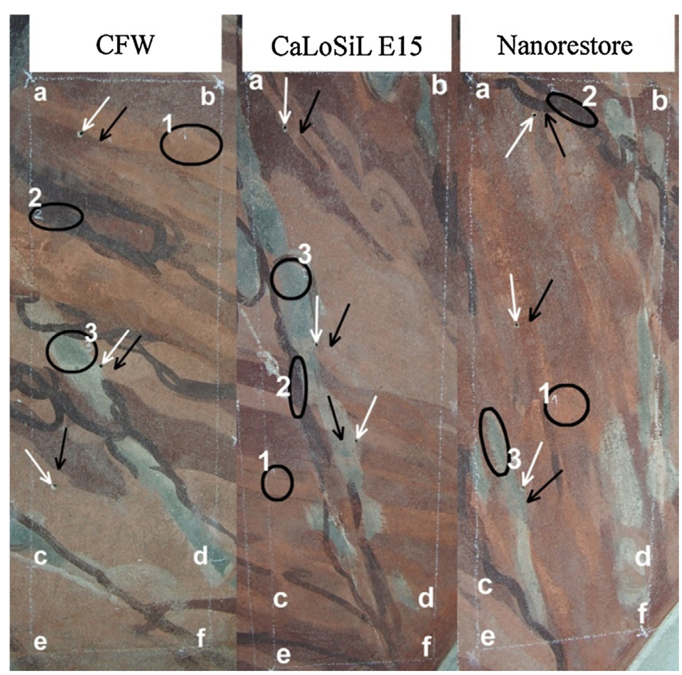


**Fig. 1.** Test field used for the consolidation and measurement locations: a: spectrophotometry and surface hardness (marked with numbers: 1: light red, 2: dark red and 3: grey); b: ultrasound velocity (marked with letters: a–b, c–d, e–f and b–f); c: drilling resistance (marked with arrows: white arrows before and black arrows 3 months after consolidation).

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