DEVELOPMENT OF A GYPSUM-BASED GROUT FOR THE STABILISATION OF GYPSUM-BASED PLASTERS

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Abstract: Research on injection grouting for the stabilisation of delaminated wall paintings and historic plasters mostly focuses on grouts based on aerial or hydraulic lime and on earthen-based grouting. Materials for the stabilisation of delaminated gypsum-based plasters have never been fully studied, even if gypsum has been used as a constituent material of wall paintings since ancient times. Grout mixtures developed during this research were specifically designed for the stabilisation of the 11th-century gypsum-based wall paintings in the Ateni Sioni church in Georgia. Due to the gypsum sensitivity to water, it was important to reduce the water content of the grout; this was achieved by partially substituting water with an alternative liquid, i.e. ethanol. The grout mixture design involved laboratory testing to assess the working properties and some performance characteristics of the grouts. In addition to the regular tests, grouts were injected into replicas simulating the challenging horizontal delamination present in the vaults of the church. The research proposes gypsum as the binder for a grout together with the use of a water-reduced dispersion medium, aiming to stabilise delaminated gypsum-based plasters.

1. Introduction

1.1 Injection grouting

Wall paintings, defined as paintings executed on the bearing structure, may be composed of different layers: from the primary support to plaster layer(s), paint layer(s), varnish layer(s) and attachment(s). Lack of adhesion between plaster layers resulting in delamination is a widespread deterioration phenomenon in wall paintings and is defined as a separation between coherent plaster layers or between plaster and primary support. This often results in the formation of an empty space, a void between the delaminating layers. This unstable situation which can result in the loss of painted plaster, can be fixed with the direct intervention of grouting. Grouting aims to introduce in the delamination an adhesive material with bulking properties to re-establish adhesion [1]. Such intervention is one of the most challenging in wall paintings conservation since the problem is concealed and grouting is irreversible [2] (p. 472). Injection grouts are mixtures composed of binder(s), aggregates, and a liquid (suspension medium), which is typically water; additives may be added to the formulation [3]. Research on injection grouting for the stabilisation of delaminated wall paintings and historic plasters mostly focuses on hydraulic lime/lime-based grouts (among others, [3]; [1]; [4-7]) and/or earthen-based grouts [8, 9]. In the literature, such binders may be also used in combination (ex. earth-lime, [10]). Studies on historic gypsum-based plasters rather focus on their characterisation [11, 12] and the design of compatible repair plasters [13-15]. To the authors' best knowledge, there are no publications (in English or Italian) regarding gypsum as a binder for grouting of gypsum-based plasters where working properties and performance characteristics are systematically assessed. The properties of gypsum-based grouts have not been studied, even if gypsum is widely spread as an original material, and it has been used as a constituent material of wall paintings since ancient times [16, 17]. Since the grout introduced during the intervention becomes a non-extractable part of the stratigraphy, it is important to ensure compatibility and stability of the grout, as well as retreatability. The physico-chemical compatibility with the original materials and a physico-mechanical behavior close to the one of the original plaster are paramount: therefore, especially for relatively unexplored binders and extensive interventions on site, a systematic study evaluating the physico-mechanical properties of the injection grout in comparison to the original is necessary before undertaking the treatment.

1.2 Case study

The 7th-century Ateni Sioni church (Figure 1), located in Georgia, is one of the most significant religious sites in the country and is listed as an immovable cultural monument of national significance. The church is built with various types of tuff stone, which can be found at the site around the building (vitroclastic tuff containing analzim, yellowish tuff and green coarse grained tuffs which are high in quartzite) [18]. Beside its fine architecture, the 10th-century stone reliefs on the church exterior facades, the 7th-century aniconic decorations and the 11th-century wall paintings on the interior walls of the church are extremely important. The 11th-century painting's phase depicts stories of the New and Old Testament, including a large cycle of the life of the Virgin as well as numerous figures of saints and ornamental decorations [19] (Figure 1).

(**a**) (**b**)

Figure 1. (a) Ateni Sioni church, Georgia; view from the southeast. © Gvantsa Potskhishvili, 2015; (b) The 11th-century decoration phase; south apse, Ateni Sioni church, Georgia. © Gvantsa Potskhishvili, 2015.

Various types of painted plasters have been identified in the Ateni Sioni church. Analyses of plaster fragments, thin and cross sections were performed at the University of Applied Sciences and Arts of Southern Switzerland (SUPSI) with Polarized Light Microscopy (PLM) and FT-IR (Fourier-Transform Infrared spectroscopy). Results showed that a thin layer (1 mm) of lime-based plaster containing particles of charcoal and probably red iron oxide was applied before the gypsum-based plaster, on the stone primary support. The most widely spread plaster type in the church is gypsum-based. It has been applied over the thin lime-based plaster, on the interior walls between the 7th-8th centuries [19]. The gypsum plaster does not contain aggregates and is usually applied in two layers, i.e. a thinner lower layer and a thicker upper layer reaching up to 1 cm of total thickness. The second most common plaster type in the church is a lime-based plaster with straw-like organic inclusions, usually present either in patches next to gypsum-based plaster or overlapping it. This plaster must have been applied between the 8th and 11th centuries [19]. The 11th-century wall paintings are painted using *a secco* technique on both the gypsum and the lime-based plasters. Another kind of lime-based plaster, mainly found in the pendentives, is characterised by high hair-like fiber content and organic inclusions, and most probably was applied between the 8th and 11th-centuries [19]. The church underwent several changes and restorations over the centuries and probably suffered from an early stage of problems of plaster adhesion. Starting from the middle of the 20th-century, a series of restoration works were undertaken on site due to the continuous water infiltration coming from the stone roof and due to the structural instability of the dome and the substructure. The stone roofing of the church was fully replaced between 1957 and 1970 with the same materials and construction technique. The roofing replacement seems to have continued every few years till 2005-2006, as the problems of water infiltration were still present [20]. Regarding the wall paintings, just brief notes can be found in the literature, which report restoration works [19]. The first note, dated to the 1930s, reports that the paintings were partially cleaned and “washed” by a Russian team of restorers. Later, in the 1950s, the paintings were cleaned and “safely fixed/stabilised” by the Georgian painter-restorers S. Abramishvili and K. Bakuradze [19]. Widespread delamination was found throughout the church and is documented in the condition assessment performed in 2012 by Prof. Francesca Piqué and Stefano Volta and in 2015 by Gvantsa Potskhishvili as part of her MA research work.

2. Definition of the problem and of the grouting performance criteria

The wall paintings condition assessment performed in the church showed the presence of large lacunas, of recent losses and of severe problems of lack of adhesion (i.e. delamination). In most of the cases, the delamination occurs between the stone and the plaster(s), i.e. the primary and the secondary supports. The most severely delaminated areas, being unstable, are located in the upper parts of the apses, on the horizontal and semi horizontal surfaces of the vaults and in the areas where there are joints between different plaster types (on horizontal, semi horizontal and vertical surfaces) (Figure 2). When not clearly visible, the delamination was located in the stratigraphy by tapping, and its severity assessed according to the vibration and the sound produced.

A thorough graphic and photographic documentation was produced to illustrate the extent and gravity of this precarious situation and the need for a stabilisation intervention. One of the possible interventions to be designed is that of grouting.

Figure 2. Delamination of the gypsum-based plaster; west apse, Ateni Sioni church, Georgia. © Francesca Piqué, 2012.

General performance criteria (such as physico-chemical stability, no introduction of soluble salts, etc.) are common to any conservation intervention [21]. Criteria which are specific to the type of intervention (e.g. grouting, consolidation, cleaning, etc.) are important for the design of the conservation treatment [21]. Working properties for grouting decorated surfaces should be sufficiently fluid to allow injection; in addition, minimal shrinkage upon hardening, mechanical strength similar or lower than that of the original materials, porosity and water vapour permeability similar to those of the original materials are necessary to ensure stability of the results over time [1]. Keeping in mind the criteria for any grouting intervention, *site-specific* performance criteria must then be defined case-by-case [21], and were indeed defined for the specific case at Ateni. The desired properties for the grouting intervention at Ateni were outlined, including working properties, i.e. short-term performance (during the intervention when the grout is in the fluid state), and performance characteristics, i.e. long-term performance (after the intervention and over time, when the grout is set and hardened) [21]. The site-specific working properties and performance characteristics of the grouts designed in this research were defined according to the composition of the original materials (gypsum plaster and stone support) and the specific condition on site, i.e. specifics of the delamination. Delamination between gypsum-based plaster occurred on horizontal, semi-horizontal or vertical surfaces. The void between the delaminated plaster and support in the vault could reach up to 5 cm. The severity of the delamination varied between unstable and dangerously unstable, with risk of loss of original material. Regarding injectability, since in the Ateni Sioni church access points need to be created in order to inject the grout, two size catheters to attach to the syringe for injection (one relatively narrow and the other larger in diameter, see Table 1) were tested, in order to design a versatile material, allowing flexibility on site and adapt the intervention to the different situations eventually found. The additional desired site-specific working properties and performance characteristics for the grout to be used in the Ateni Sioni church, including minimal water content because of the sensitivity to water of the original gypsum-based plaster, are described in Table. 1.

Table 1. Site-specific working properties (WP) and Performance characteristics (PC) of the grout to design for the Ateni SIoni Church**.**

Working Properties (WP)	**Performance Characteristics (PC)**
Good injectability: ability of the grout to easily pass through two catheters attached to the syringe (3.3 mm diameter and 4.7 mm diameter respectively)	Sufficient adhesion to both interfaces, primary stone support and gypsum plaster
Proper flow: ability of the grout to flow for a suitable distance in order to reach the edge of the delaminated area, vertically (on brick tiles and in replicas with gypsum plaster) and horizontally (in replicas with gypsum plaster)	Minimal dry density, especially for horizontal surfaces
Minimal water content: one of the most important requirements because of the sensitivity of gypsum-based plasters to water	Minimal hygral and thermal expansion and contraction
Good initial tackiness: to both interfaces, primary stone support and plaster, especially important for the delamination present on the horizontal surfaces	
Minimal wet density, especially for horizontal surfaces	
Reasonable hardening time: the grout should not start hardening during the intervention; however, relatively rapid hardening time is important to limit the period during which the wet grout is adding weight to the thin plaster layer, especially on horizontal surfaces and a support is necessary	

3. Materials and methods: Site-specific grout formulation

As stated, the most common type of plaster present in the Ateni Sioni church is a gypsum-based plaster. Although this type of plaster has been known as a support for wall paintings around the world since ancient times, the chemical and physical characteristics of gypsum and in particular its solubility in water [22] and the rapid hardening time are well-known potential limitations in the use of this material for building and/or decorative purposes [23, 24]. In the case of injection grouting, these issues can raise complications in terms of choice of materials for grout formulations and/or treatment methodology. If gypsum is chosen as the binder of the injection grout, its fast setting may be a hindrance for the implementation of the intervention, since the grout needs to remain fluid during the intervention and cannot harden too fast. This may be one of the reasons why other binders such as lime are generally used for the stabilisation of such plasters. In addition to this, generally it is common practice to use water as the suspension medium for injection grouts, which is problematic due to the water-sensitive original materials present [4], such as gypsum-based plaster. Gypsum is slightly water-soluble, even if its solubility is much lower than other soluble salts commonly found in building materials [25]. Therefore, since original materials at the Ateni Sioni church are water-sensitive, it was decided it was important to reduce the water content of the grout, partially substituting it with an alternative liquid, i.e. ethanol [4]. On the other hand, being gypsum the binder of the injection grout, water is necessary in the hydration reaction occurring during setting [25]. Stoichiometrically the minimum amount of water is indicated by the setting chemical reaction:

$CaSO_4 \cdot 0.5\ H_2O + 1.5\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O$.

The research focuses on developing a gypsum-based grout with a reduced amount of water, both to: i) reduce setting time of the grout with the use of gypsum (compared to a lime-based one) and use a material akin to the original ones, and ii) reduce solubility of the original material with the use of an alternative liquid beside water. The formulation of the grout proceeded in two stages: the first one focused on assessing the feasibility of the use of gypsum as the binder (*Stage 1*, Section 3.1 below), and the second one focused on refining the formulation (*Stage 2*, Section 3.2 below).

In the methodology for the formulation of a grout, the mix design and the testing of paramount properties must proceed in parallel to refine the formulation [5]. *Stage 1* aimed, through preliminary testing, to assess the feasibility of using grouts prepared with gypsum (on its own and in combination with lime), while lime was used as a control (see Section 3.1). Such preliminary testing involved the assessment of injectability, flow, shrinkage and adhesion, as these were judged as the fundamental working properties required, and helpful in guiding the grout design. Based on these results, the most promising three formulations were identified and then further refined during *Stage 2*, which led to the two final formulations (see Section 3.2). Such mixtures were further tested –beside injectability, flow and shrinkage– for expansion and bleeding, wet and dry density, hardening time, cohesion and adhesion into replicas. This multi-step formulation methodology is synthesized in Table 2; details of the different stages will be given in Section 3.1 and 3.2 below. Description of testing procedures and results will be fully reported in Section 4.

Table 2. Stages in the grout formulation.

Stage of formulation	Aim	Testing carried out	Mixture obtained
Stage 1	Feasibility of using gypsum or gypsum-lime as binder	**Preliminary testing of:** Injectability Flow Shrinkage Adhesion	Mix 1 (gypsum) Mix 2 (gypsum-lime) Mix 3 (lime)
Stage 2	Refining of the formulation to fulfil the site-specific performance criteria, particularly adhesion	**Full testing of:** Injectability Flow Expansion and bleeding Wet and dry density Shrinkage Hardening time Cohesion and adhesion (replicas)	Grout 1 (gypsum) Grout 2 (gypsum-lime)

3.1 *Stage 1* of formulation and testing

At the first stage of the grout mixture design, a wide range of materials (binder, fillers and suspension media) were considered according to their composition, properties and physico-chemical compatibility with original materials.

The following variables were considered in *Stage 1* of design and testing. Mixes which are the result of this first stage are then shown in Tab. 3.

- **Binder**: Gypsum was considered as the binder of the grout (Mix 1 in Table 3), due to the gypsum-based composition of the original plaster. It is important to underline that pure calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5\ H_2O$) without the presence of any additive (from LAGES, Lavorazione Gessi Speciali SPA, Italy) was used for this research; this is crucial, since commercial reactive calcium sulfate hemihydrate (gypsum hemihydrate) typically contains retarders and/or other additives to modify its properties and improve workability. Since the feasibility of the use of solely gypsum as the binder was still to verify and the authors wanted to assess the difference between gypsum and lime, two further binders were considered as well, i.e. 50% lime - 50% gypsum (Mix 2 in Table 3) and just lime (control, Mix 3 in Table 3). The choice of the binder for Mix 2 (and later Grout 2, see Section 3.2) was based on the well-known historical use of these two binders mixed in different proportions to obtain intermediate properties, e.g. addition of gypsum to speed up the setting time of lime-based mixtures (ex. in stucco technology) [26]. In addition to this, the first very thin (1 mm) plaster layer applied on the stone at the Ateni Sioni church is lime-based, so both lime and gypsum are present in the stratigraphy. The lime used in both cases was slaked lime putty (Grassello di Calce Candor, 48-months-aged, Italy) (ca. 50% $Ca(OH)_2$ and 50% H_2O), drained of the excess water, i.e. just the paste was used.

- **Fillers**: Several fillers were selected for the preliminary testing, depending on their chemical composition (reactive with lime vs. inert), particle size and morphology. Aggregates reactive with lime (while no chemical reaction with gypsum occurs) included pumice (from CTS, Italy) in different granulometry (<90 µm, <140 µm, <240 µm, <280 µm), Pozzolana Romana Gialla Micronizzata (<63 µm) (from Opificio Bio Aedilitia, Italy), Scotchlite K1® (sodalime borosilicate glass, reactive with lime [4]; from 3M, <120 µm according to the technical data sheet). Quartz sand (from Taiana, Switzerland, 100-250 µm), inert, was also considered. Scotchlite K1®, round, hollow and non-porous, helps to improve injectability in grouts [9, 5, 27] and aids in obtaining mixtures with low density; the other aggregates tend to have an angular shape, helping packing geometry and therefore cohesion. Pumice 0-140 µm (1 pt/V) coupled with Scotchlite K1® (3 pt/V) was chosen as the best fillers combination (see Tab. 3), giving good injectability and minimal/no shrinkage. The other types of fillers coupled with Scotchlite K1® were discarded for the following reasons:

    1. Mixes tended to segregate when Quartz sand and/or Pozzolana were added (with all three binders);
    2. Flow got dramatically worse when Pumice 0-90 µm was added (with all three binders): mixes tended to segregate and material to accumulate at the bottom of the drip during the flow test, giving an inhomogeneous drip;
    3. The amount of suspension medium required to obtain a fluid grout with proper injectability and flow was higher when Pumice 0-240 µm or Pumice 0-280 µm were added to the mixes compared to mixes with Pumice 0-140 µm, and in case of Pumice 0-280 µm material tended to accumulate at the bottom of the drip during the flow test, giving an inhomogeneous drip.

    Furthermore, it was assessed that the amount of Scotchlite K1® has a significant impact on the properties of the grout: 2 pt/V was the minimum amount necessary in order to have sufficient flow and medium/low shrinkage of the mix. The mix with 2 pt/V Scotchlite K1® was compared with mixes with 2.5 pt/V and 3 pt/V Scotchlite K1®; the most satisfactory results were obtained for the mixes with 3 pt/V Scotchlite K1®, in terms of fluidity and minimal/no shrinkage.

- **Suspension medium**: Solubility bench tests were carried out on a fragment of original plaster from the Ateni Sioni church: water vs. solutions with a different proportions of water : ethyl alcohol. These were added drop by drop on the original plaster, and its hardness was verified gently pressing it with a metal spatula and assessing the indents left on the surface. Bench tests confirmed that the original gypsum-based plaster is sensitive to water, even the first few drops. However, results also showed that the gypsum plaster is very stable and seems not to soften/visibly solubilize (from a macroscopic assessment) with a solution of 50% water - 50% ethyl alcohol. In this case, pressure with the spatula did not leave any indents on the surface. In order to further reduce the water amount, also solutions with water - alcohol 40%-60% and 30%-70% were tested in the grout design, thinking that, considering the potential (high) amount of grout injected on site, lowering further the amount of water would have been advantageous. However, no promising results were obtained compared to the solution water-alcohol 50% - 50%. Mixes with water - alcohol 40%-60% and 30%-70%, in fact, tended to significantly shrink and even collapse in the moulds. Therefore, the 50%-50% solution was chosen as the grout suspension medium. It was calculated that the amount of water in the gypsum grout was amply sufficient for the hydration reaction to fully occur. On the other hand, for the lime-based grouts, previous research has proved that lime carbonation and hydraulic reactions (lime + pumice) can occur also with a reduced water content (here amply in the minimum amount) and in presence of ethanol [4].

After this first formulation round (*Stage 1*) where injectability, flow and shrinkage were assessed, three preliminary formulations (see Tab. 3) were chosen, in which the only variable is the binder; the rest of the components remain constant for all the formulations (in terms of typology, proportion and amount).

Table 3. Preliminary formulations of the grouts.

Mix	**Mix 1 (Gypsum)**			**Mix 2 (Gypsum & Slaked lime)**			**Mix 3 (Slaked lime)**		
Components	**pt/V**	**Vol. (mL)**	**Weight (g)**	**pt/V**	**Vol. (mL)**	**Weight (g)**	**pt/V**	**Vol. (mL)**	**Weight (g)**
Gypsum hemihydrate	1	100	86	0.5	50	44	-	-	-
Slaked lime	-	-	-	0.5	50	76	1	100	150
Pumice 0-140 µ	1	100	81	1	100	81	1	100	81
Scotchlite K1®	3	300	20	3	300	20	3	300	20
Water –Alcohol 50%-50%	2.2	220	195	2.2	220	195	2.2	220	195

Adhesion of such selected grouts was then assessed in the laboratory onto the two materials lacking adhesion in the Church of Ateni: gypsum plaster and tuff stone. To assess the adhesion to the plaster, a gypsum plaster prepared in the laboratory was applied on a brick tile and a boundary was placed around the tile itself; fluid grout was poured on the plaster and allowed to harden for 10 days. 50 mm diameter circular incisions were carved from the surface down to the brick. Metal plugs were glued on such incisions and pulled off with a dynamometer to measure the force needed for the failure to occur. To assess the adhesion of the grout to the tuff stone support, cylindrical plastic moulds 50mm diameter x 20mm height leant on the stone were filled with fluid grout (Figure 3). After 10 days of hardening, metal plugs were glued to the surface of the grout cylinders and then pulled off with a dynamometer. It was found that the adhesion properties of the gypsum-based grouts (Mix 1 and 2) were not satisfactory, as in both cases the failure occurred between the grout and the stone support/gypsum plaster with a minimal force applied. Therefore the formulations needed to be refined (*Stage 2*, Section 3.2), since a good adhesion to both interfaces (plaster and stone), in fact, is one the most important requirement for a grout, and crucial in the case of the Ateni Sioni Church.

Figure 3. Assessment of the adhesion of the grout to the tuff stone support. © Gvantsa Potskhishvili, 2015.

3.2 *Stage 2* of formulation and testing

Since in *Stage 1* of preliminary testing it was found that the adhesion of the gypsum grouts was not satisfactory, introduction of an additive was necessary to improve adhesion, particularly considering the delamination occurring on horizontal surfaces, where gravity has an important role and the grout needs to support the overlaying stratigraphy.

A literature review [3, 28-31] showed that two main categories of materials could be considered when looking at additives to improve adhesion for grouts: natural and/or synthetic. One of the most used synthetic material for this purpose is known to be an acrylic dispersion in water, PRIMAL® [30, 31], however the actual references detailing its use are limited. One of the earliest cited use of PRIMAL® AC-33 as an additive for grouts is for the *in situ* reattachment of earthen plasters in Peru, 1975-1977 [31] (p. 53). Nowadays, the most widely used acrylic dispersions for consolidation and adhesion interventions are PRIMAL® CM 330 (previously E330S) and PRIMAL® B60A ER. These products, according to the corresponding technical data sheets, have very similar properties, especially in terms of solid content (CM 330: 46.5-47.5%; B60A: 46-47%), pH (CM 330: 9.5-10.5; B60A: 9.4-9.9), appearance and minimal film formation temperature (CM 330: 10°C; B60A: 9°C). For the given research, it was decided to test PRIMAL® B60A, as its use seems to be better documented as an additive for grouts in previous studies [30, 31]. A minimum amount of acrylic was added in order to minimally alter the porosity and water transport properties of the hardened mixtures, yet obtaining adequate adhesion.

Table 4 shows the final formulations of the two grouts chosen for a possible implementation on site, subject to further testing (fully reported in Section 4). Mix 3 (just lime-based) was excluded from the further testing, since the objective of this research was to assess gypsum-based grouts to be potentially used on site and gypsum-based mixtures were preferred for a matter of chemical compatibility with the original plaster. Mix 3, in fact, is lime-based and it was originally included in the preliminary testing as a control rather than a grout developed for *in situ* use. The final Grout 1 and Grout 2 shown in Table 4 have different binder, i.e. gypsum in case of Grout 1 and gypsum-slaked lime in case of Grout 2. The amount of pumice is slightly higher in Grout 2 with gypsum-lime, because a higher amount of aggregate was necessary to obtain no shrinkage (Grout 1 with gypsum had already no shrinkage). On the other hand, the addition of Primal required a slight increase in solution in Grout 1 to obtain suitable injectability and flow: the reasons for this, the interaction acrylic-gypsum and its influence on the rheology of the mix should be further investigated and were beyond the scope of the present research. In Grout 2, on the other hand, slaked lime putty was used, which already contains 50% water and can aid in working properties [32, 33], including injectability and flow. The purpose was not to directly compare these two grouts to understand the influence of the single variables, since the change in more than one variable for practical purposes impedes such comparison. These modifications to the grouts were made to ensure their satisfactory working properties and performance characteristics, in order to design mixes to be used effectively on site.

Table 4. Final formulations of the grouts.

Mix	**Grout 1 (Gypsum)**			**Grout 2 (Gypsum & Slaked lime)**		
Components	**pt/V**	**Vol. (mL)**	**Weight (g)**	**pt/V**	**Vol. (mL)**	**Weight (g)**
Gypsum hemihydrate	1	100	86	0.5	50	44
Slaked lime	-	-	-	0.5	50	76
Pumice 0-140 µ	1	100	81	1.2	120	104
Scotchlite K1®	3	300	20	3	300	20
Primal B60A (47%)	0.02	2	2.05	0.02	2	2.05

Water -Alcohol 50%-50%	2.4	240	210	2.2	220	195

4. Testing program and results

As seen in Section 3, this research involved firstly testing of basic properties (such as injectability, flow and shrinkage) in parallel to the design of mixtures, to then move to a more thorough assessment of working properties (in the fluid state) and performance characteristics (in the hardened state) of the final grouts. This included injection into replicas simulating the horizontal delamination present in the ceilings and vaults of the church. The laboratory testing procedures adopted are described below and results are summarised in Table 5.

Injectability

Injectability of the grouts was assessed by evaluating the ability of a grout to pass through a syringe and/or through a syringe with a catheter attached to it, when approximately the same pressure is applied on the syphon by hand (adapted from [5]). A 60 mL syringe with two different catheters (diameters 3.3 mm and 4.7 mm) was used for the test. 30 mL grout was placed in the syringe and injected, firstly through the syringe and after through the syringe plus catheter. This procedure was performed at least three times for each syringe/catheter setting for each grout. According to how many mL of grout was passing through in a set amount of time (5 seconds), the grout was assessed as ‘easy’ (>20 mL), ‘medium’ (10-20 mL) or ‘difficult’ (<10 mL) to inject. Both grouts showed an ‘easy’ injectability through the tip of the syringe and the 4.7 mm catheter, and ‘medium’ injectability through the 3.3 mm catheter.

Flow

A brick tile (tuff would have replicated better site conditions, but it was not available) with vertical grooves was positioned vertically, and 10 mL grout was injected from the top to let it flow through the vertical channels present on the tile (adapted from [34] (p. 75)) (Figure 4). Approximately the same pressure on the syphon was applied each time to have as similar testing conditions as possible. Distance and time of flow were recorded, and the homogeneity and body of the drip were observed and evaluated (Figure 4). The test was repeated at least 10 times for each grout. The average flow distance (cm) and the average time taken for the grout to flow (s) were recorded, and the flow rate (cm/s) was calculated. Grout 2 (50% gypsum-50% lime) showed a longer flow distance and higher flow rate compared to Grout 1 (gypsum-based). Both produced a homogeneous drip with a good body.

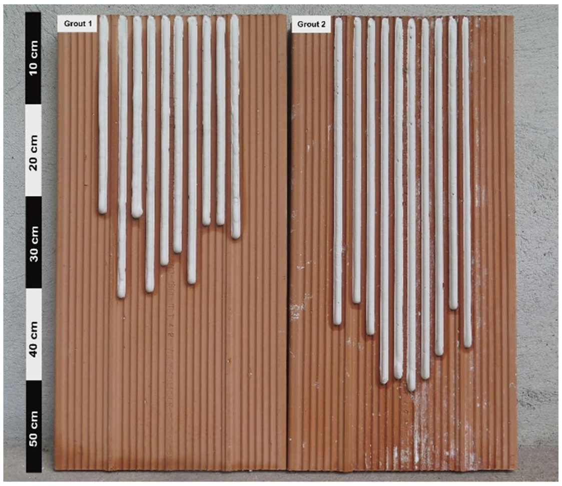


Figure 4. Grout 1 and Grout 2 injected in the vertical channels incised in the brick tile. © Gvantsa Potskhishvili, 2016.

Expansion and bleeding

In this research, the standard test (ASTM C940-10) to measure expansion and bleeding was modified using a smaller amount of grout (30 mL instead of 800 mL). The test was carried out in plastic syringes without the syphon, and the tip of the syringe was blocked with a tape; the syringe was fixed in a vertical position so that it was stable. 30 mL of grout was placed in the syringe and the top of the syringe was covered with cling film to impede evaporation. The grout in the syringe was observed every 10 minutes for one hour, to assess if expansion and/or bleeding occurred. The two grouts showed neither expansion nor bleeding.

Wet and dry density

Density (wet and dry) of the grouts was calculated with the formula density=mass/volume (g/cm^3). Wet density is the density of the freshly prepared grout; dry density is the density of the hardened grout. To assess wet and dry density of the grouts, 30 mL of freshly prepared grout was placed in a Petri dish and weighed over time till the weight did not vary more than 0.01 g in three consecutive daily readings (adapted from [5]). Grout 1 and 2 showed similar wet and dry density, Grout 1 (gypsum-based) having a slightly lower wet density and Grout 2 (50% gypsum- 50% lime) having a slightly lower dry density.

Shrinkage

The shrinkage was qualitatively assessed with a porous support. 30 mL of freshly prepared grout was placed into a gypsum plaster cup (adapted from [34] (p. 83)), previously pre-wetted with 5 mL of water: alcohol 1:1 solution, and the system was covered with a gypsum plaster disc to reproduce a real case, in which the grout hardens in a pocket and it is not directly exposed to air [5]. After hardening, the surface was firstly observed to detect cracks and/or shrinkage close to the plaster cup walls, and the grout was then gently excavated with a spatula close to the walls, in order to observe the shrinkage in depth [5]. Both grouts showed no shrinkage, neither at the surface nor in depth.

Hardening time

The hardening time of the grouts was measured by assessing it with the Vicat needle apparatus. The Vicat needle apparatus is typically used to measure the "setting time" of cement-based mortars (standard UNI-EN 196-3); just the bell-shaped needle (to assess the setting end) was here considered. Different definitions of hardening and setting are used in conservation and in materials technology [35] and in this research, the conservation definitions are considered. 30 mL of freshly prepared grout was placed in a gypsum plaster cup (previously pre-wetted with 5 mL of water: alcohol solution 1:1); measurements were taken approximately every 10 minutes, observing the depth of penetration of the Vicat bell-shaped needle and the mark left by it. Grouts were considered hardened when only the central point of the bell-shaped Vicat needle was marked on the surface of the specimen after the measurement. The time the grouts took to harden was recorded. Grout 1 (gypsum-based) hardened in 1 hour, while Grout 2 (50% gypsum- 50% lime) hardened in 2 hours and a half.

Cohesion and Adhesion

The specific system was designed to assess the cohesion and adhesion of grouts as well as their bulking property/filling capacity in replicas simulating a delamination between a tile (fired brick; tuff would have replicated better site conditions, but it was not available) and a gypsum-based plaster. For this purpose, replicas were prepared as follows: a layer of gypsum-based plaster was placed into a concave mould simulating the delamination profile (approximately 3 cm thick in the deepest point); holes were carved in the plaster as access points for the injection to be performed later. Once the plaster was dry, it was removed from the mould and attached to the brick tile using the same gypsum-based plaster, so that a pocket was left between the support and the concave layer of plaster. Injection of a freshly prepared grout into the replica was performed through the hole(s) with a syringe and a catheter attached to it (diameter of the catheter 4.7 mm).

The testing procedure included:

- Pre-wetting of the internal surface of the void with a solution of water and ethyl alcohol (1:1);

- Injection of the grout into replicas positioned vertically and horizontally respectively; replicas were positioned horizontally (support facing up and plaster facing down as in a ceiling) to imitate delamination of the plaster present on the semi-horizontal and horizontal surfaces in the church (Figure 5);

- Monitoring of the intervention with an infrared thermography (IRT) imaging technique (AGEMA Thermovision 570 camera). Thermo Images were taken at the beginning, before the intervention, after the pre-wetting, immediately after the injection and 30, 60 and 120 minutes after the injection. The image taken after one hour from the injection showed that the surface was almost evenly homogenous in terms of temperature;

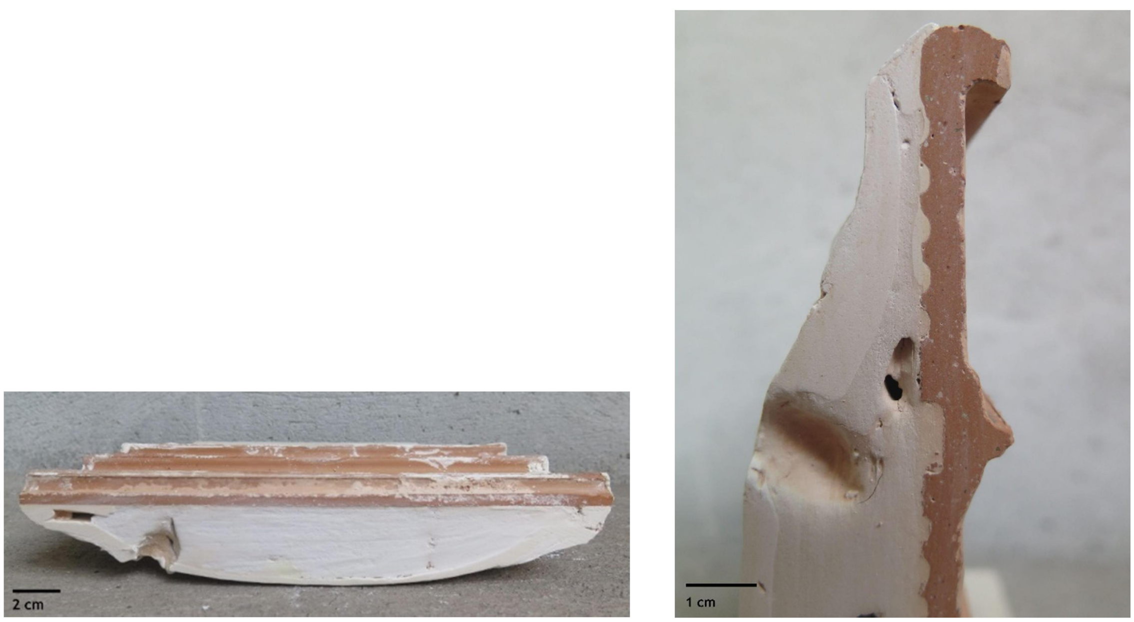
- Letting the grouts harden for two weeks in the laboratory with relative humidity ~70% and temperature ~23°C;

• Cutting the replicas and observing their cross-sections to assess cohesion of the grout, adhesion and bulking properties.

Neither Grout 1 nor Grout 2 showed shrinkage: the adhesion to both the support and the plaster was very good, and no cracks were observed. The grouts resulted well cohesive and filled all the gap, showing excellent bulking properties (Figure 6).

(**a**) (**b**)

Figure 5. Injecting the grout into the replica positioned horizontally (a) and vertically (b). © Gvantsa Potskhishvili, 2016.



(**a**) (**b**)

Figure 6. (a) Cross-section of the replica; Grout 1 has been injected into the replica positioned horizontally. © Gvantsa Potskhishvili, 2016; (b) Cross-section of the replica; Grout 1 has been injected into the replica positioned vertically. © Gvantsa Potskhishvili, 2016.

Table 5. Summary of the working properties testing results.

Grout	Injectability			Flow			Density		Shrinkage	Hardening
	Syringe 60 mL	Syringe & catheter ø4.7 mm	Syringe & catheter ø3.3 mm	Average time (sec.)	Average distance (cm)	Flow rate(cm/s)	Wet *(g/cm^3)*	Dry *(g/cm^3)*	In replicas	(Hour)
Grout 1 (Gypsum hemihydrate)	Easy	Easy	Medium	12	26	2.1	0.86	0.44	No	~ 1 hour
Grout 2 (Gypsum hemihydrate & Slaked lime)	Easy	Easy	Medium	9	35	3.8	0.89	0.42	No	~ 2 hours 30 min

5. Discussion and Conclusions

The objective of this research was to develop an injection grout(s) to address the severe delamination of the plaster afflicting the 11th century wall paintings in the Ateni Sioni church in Georgia. The focus was to produce a material compatible with the original gypsum- and lime-based plasters of the church and suitable for the type of deterioration encountered. Two grouts (one gypsum-based and one gypsum-lime-based) with a composition similar to that of the original materials (lime and gypsum-plasters and the tuff stone primary support) were developed following a thorough testing procedure and according to the set site-specific requirements. Bench tests revealed that the original gypsum-based plaster is susceptible to water and therefore grouts with a reduced water content were developed. To achieve this, water in the suspension medium of the grout was partially substituted by ethyl alcohol. Based on numerous bench tests it was concluded that a 50% water- 50% ethyl alcohol solution does not seem to damage the original plaster and gives the best results in terms of grout properties. At the same time, the amount of water present is sufficient for the chemical reactions to occur [25, 4] and produces a well-cohesive grout. Due to the unsatisfactory adhesion property of the initially formulated *Mix 1* and *Mix 2* (*Stage 1*), it was necessary to consider the addition of a synthetic adhesive (*Stage 2*). Tests demonstrated that the addition of an acrylic water dispersion, Primal B60A, 0.4-0.5% in weight on the overall mixture, significantly improved the adhesion of both the formulations. Overall, *Grout 1*, gypsum-based*,* showed to have satisfactory injectability and flow. No expansion and no bleeding were detected. It showed similar wet and dry densities compared to the other grout, gypsum-lime-based, tested in this research. Such grout showed excellent ability to fill voids of different thicknesses without shrinking (results obtained through replica test) as well as good adhesion to both the interfaces in the replicas (gypsum and brick tile) and good internal cohesion. *Grout 1* also proved to have an appropriate hardening time (1 hour) to be used for *in situ* implementation, long enough for the grout to be comfortably used, and quick enough to stabilise the delamination rapidly (not having the wet grout loading the stratigraphy of the ceiling for too long). *Grout 2*, gypsum-lime based, similarly to *Grout 1*, showed satisfactory injectability and flow properties. *Grout 2* has longer flow distance and higher flow rate compared to *Grout 1*, which could be advantageous in case of a ceiling/vault delamination where the grout needs to travel horizontally. No expansion and no bleeding were detected. In terms of density, *Grout 2* showed similar results to Grout 1. Also in this case, the grout had satisfactory results in filling the gaps of different thicknesses, as well as good adhesion to both the interfaces in the replicas, and good cohesion. The hardening time, as expected, was longer than the one of the gypsum-grout. The fact that hardening time is longer leads to the wet weight of the grout to be borne by the original materials in stratigraphy for longer, and this may be a problem for thick horizontal unstable delamination. The results obtained for Grout 1 (gypsum-based) proved that gypsum, in combination with fillers (Pumice and glass microspheres), an adhesive (Primal B60A) and a suspension medium (water: ethyl alcohol), has satisfactory working properties and performance characteristics for the *in situ* implementation of the grout. Furthermore, a second grout formulation (*Grout 2*) with 50% gypsum and 50% slaked lime used as the binder (also in combination with fillers Pumice and glass microspheres, and small amounts of adhesive -Primal B60A- and a suspension medium -water: ethyl alcohol) showed equally satisfactory results, and can be also further implemented *in situ,* according to the need of the particular areas. For example, Grout 2 may be a better option for less critical areas which require, though, a better flow of the grout (ex. horizontal delamination not dangerously unstable where the grout needs to travel far), while, Grout 1 with a faster hardening time may be preferable for dangerously unstable areas requiring a faster stabilisation.

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