Evaluation of compatible mortars to repair 19th century natural cement cast stone from the French Rhône-Alpes region

Avaliação de argamassas compatíveis com a reparação de pedra artificial moldada em cimento natural no século XIX, da região francesa de Rhône-Alpes

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Abstract

In France, natural cements were extensively produced in the middle of the 19th century. In the French Alps, due to their ochre color, these cements were massively used, notably to produce cast stone, to simulate natural freestone. A preliminary survey revealed an overall good state of preservation of the buildings of this period. Two kinds of decays mechanisms were however identified : erosion affecting the surface of the majority of the buildings, inducing a gradual disappearance of the initial "fake-stone aspect", and a spalling phenomenon often combined with salts crystallization, observed only on a few buildings. Today, due to a lack of appropriate repair materials, the rehabilitation of these buildings mainly consists in the use of gray Portland--cement-based-mortars combined with a painting finishing, which is not satisfactory considering the conservation deontology, as the original appearance is lost. Therefore, the aim of this project was to develop and to test compatible repair materials to restore the culture heritage of this region.

Based on the preliminary characterization of a set of representative ancient buildings, combined to a literature review, specifications concerning the composition and the main properties of repair materials, which could assure a compatibility with the ancient concrete of the region were established. Then, three Prompt-cement and one Portland-cement based mortars were selected, two of them being specifically formulated. Firstly, the appearance, the workability and the mechanical and physical properties of those mortars were characterized. Secondly, to evaluate the compatibility of the selected mortars with ancient concrete, Prompt-cement-based slabs were cast using a 19th century concrete formula, and were artificially eroded. After applying the 4 mortars on the slabs, visual observations and pull-out tests will be carried out before and after artificial aging. Finally, the repair mortar presenting the best performances will be tested on site in a monument of Grenoble.

Keywords

Cast stone; compatibility; erosion; natural cement; repair mortar.

Resumo

Em meados do século XIX, os cimentos naturais eram extensamente produzidos em França. Nos Alpes franceses, devido à sua cor ocre, estes cimentos eram largamente usados, sobretudo na produção de pedra moldada, para simular pedra natural. Um inquérito preliminar revelou que os edifícios deste período apresentavam, em geral, um bom estado de conservação. Dois tipos de mecanismos de degradação foram, no entanto, identificados: erosão, que afectava a maioria dos edifícios, induzindo um gradual desaparecimento do aspecto inicial de "pedra-falsa"; e um fenómeno de lascagem muitas vezes combinado com cristalização de sais, observado em apenas alguns dos edifícios. Hoje, devido à falta de materiais de reparação apropriados, a reabilitação destes edifícios consiste essencialmente na utilização de argamassas cinzentas baseadas em cimento Portland, combinadas com uma pintura de acabamento, solução que não é satisfatória do ponto de vista da deontologia da conservação, uma vez que se perde a aparência original. Assim, o objectivo deste projecto foi desenvolver e testar materiais de reparação compatíveis para o restauro do património cultural desta região.

Baseadas em caracterizações preliminares de um conjunto representativo de edifícios antigos, em combinação com uma revisão da literatura, foram estabelecidas especificações relativas à composição e principais propriedades dos materiais de reparação que assegurassem a compatibilidade com o antigo betão da região. Foram então seleccionadas três formulações baseadas em cimento natural e uma baseada em cimento Portland para testes, sendo que duas destas argamassas foram especificamente concebidas no âmbito do projecto. Em primeiro lugar, foram caracterizadas a aparência, a trabalhabilidade e as propriedades físicas e mecânicas destas argamassas. Em segundo lugar, para avaliar a compatibilidade entre as argamassas seleccionadas e o betão antigo, foram moldados painéis em cimento natural, de acordo com uma fórmula de betão do século XIX, que foram artificialmente erodidos. Após a aplicação das quatro argamassas nos painéis, serão conduzidos observação visual e testes de aderência por arrancamento, antes e após envelhecimento artificial. Finalmente, a argamassa de reparação que apresentar os melhores resultados será testada *in loco* num monumento de Grenoble.

Palavras-chave

Pedra artificial; compatibilidade; erosão; cimento natural; argamassa de reparação.

Introduction

The most ancient concretes encountered in France date back to the middle of the 19th century. They were produced in the Rhône-Alpes region, and notably used to cast concrete blocks or quite complex ornaments, which were aiming at imitating the color and the texture of natural stone. One of their specificity is an ochre color, varying from light brown to red. Even if this cultural heritage is on the whole quite well preserved, an erosion phenomenon affects the majority of the surfaces, leading to a gradual disappearance of the concrete skin, detrimental to the initial "natural stone aspect". As the color and the composition of these concretes are very specific, there is a lack of suitable repairing mortars. Therefore, the aim of this study was to develop and to test compatible mortars to restore these erosion facies frequently encountered.

Problematics [1-2]

The natural cements from the department of Isère in the Alps were obtained by the extraction of an argillaceous limestone which was crushed and cooked in vertical furnaces similar to those used for lime manufacture. Between the middle of 19th and the beginning of the 20th century, these natural cements were produced in large amounts and used in both the industrial (water pipelines…) and the construction fields.

Preliminary survey

In a preliminary survey, more than 60 buildings using natural cements were listed in the French department of Isère. Houses and apartment buildings constituted the majority of them, but a significant proportion of churches was also identified (Figure 1).

Decay

The majority of the inspected buildings were quite well preserved. Nevertheless, two kinds of damages were identified:

- an erosion phenomenon (Figure 2), which was affecting the surface of the majority of the buildings, leading to a progressive elimination of the concrete skin and to the appearing of the coarser aggregates. Consequently, the original aspect of the concrete blocks imitating freestones is progressively lost, and a gradual degradation of the details of the sculptures is generally noticed;
- and a spalling phenomenon, which was observed only on a few buildings and which was sometimes associated with black crusts or white efflorescences.

Rehabilitation techniques

In order to rehabilitate those buildings, gray Portland cement-based mortars, combined with a yellow or

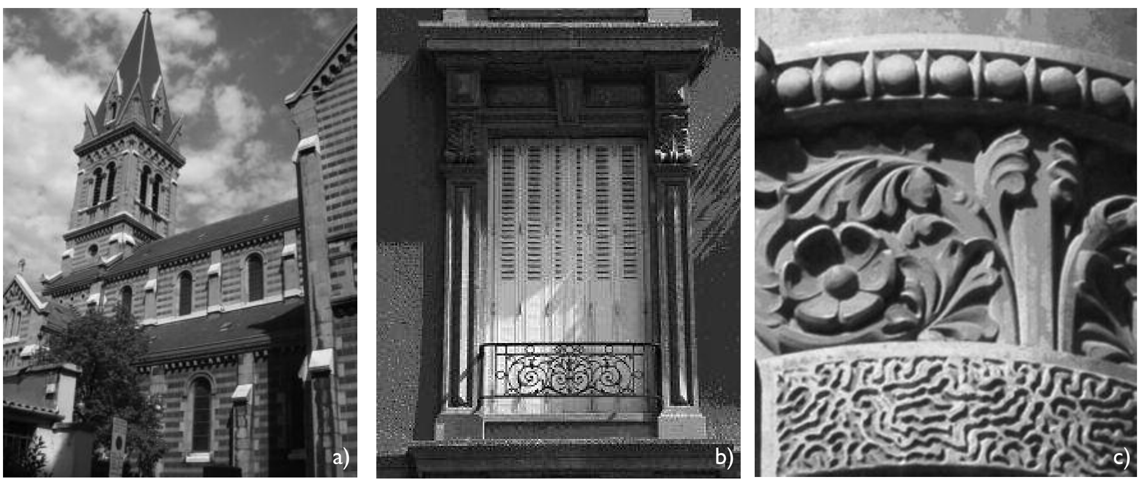

Fig. 1 Examples of natural cement applications in the French city of Grenoble: a) concrete blocks; b) window frame; c) façade ornament.

Fig. 2 Examples of erosion phenomenon observed either on sculptures (a), or on concrete blocks (b) in the city of Grenoble.

brownish painting as finishing, are generally used (Figure 3). In some cases, painting is even directly applied on the ancient concrete, without preliminary application of a surfacing mortar.

With such rehabilitation techniques, the initial mineral texture and the numerous ochre shades encountered, which are very specific and which make those fake stones look so real, are lost. Moreover, as the composition of the natural cements of the French Alps region is very distinct of that of Portland cements, incompatibilities might occur.

However, no alternative repair mortar, more adapted (physico-chemically, mechanically and aesthetically compatible) to these ancient concretes, is available, and the specific problem of erosion is tricky to treat as the layer to be re-surfaced is very thin (generally less than 1 cm).

Therefore, based on the analysis of the composition and properties of several ancient concretes of this region, the aim of this study was to formulate and to test natural cement-based repair mortars to restore eroded surfaces and to compare their performances to that of the Portland cement-based mortar currently used.

Requirements

Ancient concrete preliminary characterization [1-2]

In order to characterize these specific ancient concretes, several samples were collected on 4 representative buildings erected between 1873 and 1889, either from concrete blocks or from ornaments. Then their main properties were evaluated (Table 1).

Fig. 3 A yellowish or brownish painting is generally applied on the ancient concrete, with (a) or without (b) preliminary application of a Portland-cement-based surfacing mortar.

Table 1 Main characteristics of the concrete sampled.

Type of element	Density (kg/m^3)	Water porosity (%)	E dynamic (GPa)	Cement content (kg/m^3)	Sulfates content* (%)	Alkali content* (kg/m^3)
Concrete blocks	2253 ± 73	16.0 ± 1.8	31.6 ± 2.1	397 ± 63	4 ± 0.3	4.4 ± 1.3
Ornaments	1978 ± 105	25.9 ± 3.7	27 ± 3.7	780**	3.20**	3.92**

*Both sulfates and alkali contents are expressed by weight of cement.
** As only one sample was characterized, no standard deviation could be evaluated.

It is to be noticed that the concrete blocks showed the presence of very coarse aggregates (river shingles), whereas the microstructure of the ornamental elements had more to do with a mortar.

For all the buildings, quite high alkali and sulfates contents were measured not only on the surface but also deeper in the concrete. This indicates that their presence was linked to the composition of these natural cements and was not due to an external pollutant. SEM observations confirmed the high sulfates contents as many Ettringite crystals were generally observed, but also smaller amounts of Gypsum, Syngenite and Thenardite crystallizations.

Repairing mortars requirements [3-7]

As quite high alkali contents were measured in the ancient concretes to be restored, the use of alkali reactive (even if just potentially) aggregates had to be avoided. The aggregates size had also to be adapted to the quite small thickness of the eroded concrete to be repaired.

Concerning the binder, as a consequence of the high sulfate contents observed in the ancient concrete to be restored, to ensure a good compatibility, the cement to be used had to show a good sulfate resistance.

To ensure the durability of the restoration and to avoid further decay of the ancient concrete, the properties of the repair mortars had to be adapted to those of the ancient support, in terms of transfer properties (water vapor permeability higher than that of the support…) or mechanical performances (modulus of elasticity equal or higher than that of the support…).

But the mortars had also to be able to resist to the main stresses that repair mortars usually face (low shrinkage, high tensile strength…).

Finally, to fit with the esthetical requirements, cements able to produce an ochre color or mineral pigments had to be used.

Repair mortar selection

Based on the requirements previously established, two mortars were specifically formulated and two others were selected among the repairing mortars available on the market (Table 2).

It is to be noted that in France, in the Alps region, there is a natural cement (so called Prompt cement), still produced using the 19th century industrial process, and which composition is very close to the one of the cements encountered on the ancient concrete preliminarily characterized. Therefore this Prompt cement was used in the composition of the 2 specific formulations and in one of the ready-to-use mortar. The fourth mortar selected was a Portland cement-based one containing fibers, currently used for rehabilitation operations.

Table 2 Repairing mortars selected.

Mortar reference	Cement type	Mortar type	Comments
1	Prompt cement	Ready-to-use	Available on the market
2	Prompt cement	Ready-to-use	Specially formulated
3	Prompt cement	"On site" mortar	Specially formulated, for skilled operator
4	Portland cement	Ready-to-use	Available on the market

Table 3 Formula of concrete tested.

Components	Type	Mixture
Aggregate (from the Alps region)	4/20 mm rolled or 5/20 mm	0.8 m^3 →1200 kg/m^3 [8]
		1 m^3 →1500 kg/m^3 [9]
Sand (from the Alps region)	0/8 mm or 0/3 mm	0.4 m^3 →560 kg/m^3 [8]
		0.3 m^3 →420 kg/m^3 [9]
Cement	Prompt cement	400 kg/m^3
Water	Ratio W/C= 0.4	160 kg/m^3
Retarding agent		2.24 kg/m^3
Deactivation Product		0.2 to 0.25/m^2

Testing protocol and samples manufacture

First the intrinsic properties of the 4 selected mortars were characterized, through shrinkage, water porosity, water vapor permeability, dynamic modulus of elasticity, bending and compressive strength measurements.

Then, their compatibility with an ancient concrete is planed to be assessed by pull-out tests before and after artificial aging.

To proceed to these tests, 20 slabs (50×50×8 cm^3) were cast. Several formula extracted from documents dating back to the end of 19th century or the beginning 20th were tested (Table 3), using Prompt-cement as a binder. The final formula consists in a mix of 1600 kg/m^3 of coarse aggregates, 540 kg/m^3 of sand (both coming from the French Alps region), 400 kg/m^3 of Prompt-cement and 190 kg/m^3 of water (corresponding to a 0.47 W/C ratio).

Considering its quick setting, a retarding agent was added to the formula, and small batches were prepared (1 batch for 2 slabs), using a concrete mixer. After 28 days, the density and the compressive strength of this "Prompt-concrete" were measured on samples kept in water according to the French standard NF EN 12390-3. The density measured (2350±100 kg/m^3) is very close to results obtained on the ancient concrete blocks (2253 kg/m^3, Table 1), and a quite low compressive strength was evaluated (13±1.8 MPa).

To reproduce a surface similar to the erosion facies the more commonly encountered, 2 deactivation products were tested (Figure 4). The best results were obtained with the product inducing the higher depth of deactivation. It was then pulverized on the 20 slabs surfaces just after their casting.

After manufacturing, the slabs were kept 28 days in a room at 20 °C and 95 % RH and dried in the open air.

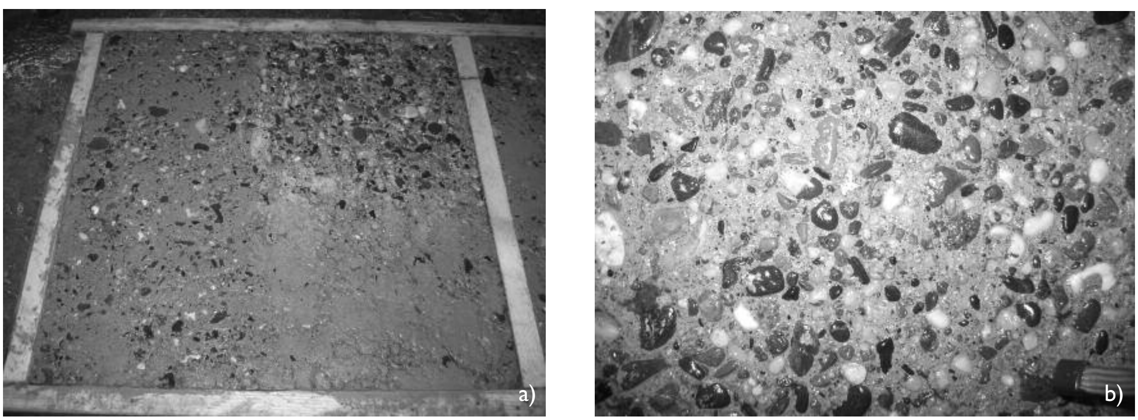

Fig. 4 To reproduce the eroded facies encountered on the ancient concrete to be restored, two deactivation products were tested, inducing 2 depths of deactivation (a) and (b).

Then the 4 selected mortars were applied (4 slabs per mortar). It is to be noticed that mortar 1 was very fluid and led to immediate shrinkage cracks, whereas mortar 4, which is dark gray, was sticking to the tools and therefore was quite hard to apply.

First results

Shrinkage

Shrinkage measurements (Figure 5) were performed according to the French standard NFP15-433, 28 days, 3 months and 6 months after the manufacture of the samples (4×4×16 cm^3 prisms), stored at 20 °C and 50 % RH.

The highest shrinkage was observed with mortar 1 (up to 0.17 % after 6 months), which was the mortar that led to immediate cracking during the preparation of the slabs for the compatibility tests. The best results were obtained with mortars 2 and 3, for which shrinkage were quite low and stable with time. Finally, surprisingly, mortar 4, which contains fibers in order to limit the shrinkage phenomenon, shows values higher than mortars 2 and 3.

It is to be noticed that in order to provide a good resistance to shrinkage cracking, several shrinkage thresholds are encountered in the literature: 0.04 % after 28 days [7] and 0.1 % after 1 year [5]. But, for the four tested mortars, the shrinkage values measured exceed the 28 days threshold.

The measurements after 1 year are not yet performed. But considering the slight constant increase of shrinkage observed for each mortar, only mortar 2 and 3 will probably fulfill the shrinkage requirement after 1 year.

Water porosity

The porosity considered was the accessible to water porosity. It corresponds to the ratio of the total volume of open pores respect to the apparent volume.

The measurement, according to the French AFPC--AFREM recommendation, consists in a series of weighing. Thus, after impregnation of water under vacuum, the sample is weighed in water a first time (M_{water}). Then, the sample, being still water impregnated, is weighed in the air (M_{air}). Finally, the sample is dried (until its weight reaches a constant value) and weighed a last time (M_{dry}).

From these values, the accessible to water porosity is calculated according to equation 1.

$$WaterPorosity = \frac{M_{air} - M_{dry}}{M_{air} - M_{water}} * 100 \qquad \textit{(Equation 1)}$$

For the 4 selected mortars, water porosity was evaluated 28 days, 3 months and 6 months after the manufacture of the samples (4×4×16 cm^3 prisms), stored at 20 °C and 95 % RH.

The results are quite scattered (Figure 6), mortar 4 being the less porous (less than 15 %), and mortar 1 being excessively porous (more than 40 %). It is to be noticed that the water porosity of mortar 2 seriously decreases upon time.

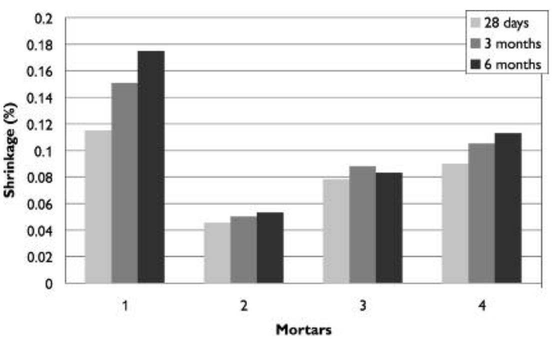

Fig. 5 Shrinkage measured after 28 days, 3 months and 6 months.

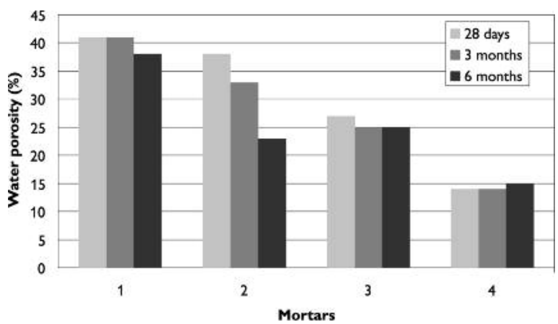

Fig. 6 Water porosity measured after 28 days, 3 months and 6 months.

Water vapor permeability

Water vapor permeability was measured according to the NF EN 1015-19 standard.

The test is performed on discs of mortar (ϕ11 cm × 1 cm) classically cured (95 % RH, 20 °C). The wax sealed discs are placed on a cup, in which the water vapor pressure is kept constant (93.2 % RH, at 20 °C), using a saturated solution of KNO_3. Then the cups are placed in a temperature controlled environment with a water vapor pressure lower than the one in the cup. Usually, a 55 % RH at 20°C environment is selected (maintained using $MgNO_3$).

The results (Table 4) reveal a quite high water vapor permeability for mortar 2, and on the contrary a very low permeability for mortar 4, incompatible with the needs of water vapor evacuation of ancient masonries.

Bending and compressive strength

The measurement of bending and compressive strengths were performed according to the French standard NF EN 1986-1, on prisms (4×4×16 cm^3), 28 days, 3 months and 6 months after their manufacture and storage at 20 °C, 95 % RH.
The results (Figure 7 and Figure 8) evidence very low performances for mortar 2, even if they increase with time. On the contrary, the Portland cement-based mortar (mortar 4) presents much higher bending and compressive strength than the 3 other Prompt-cement-based mortars.

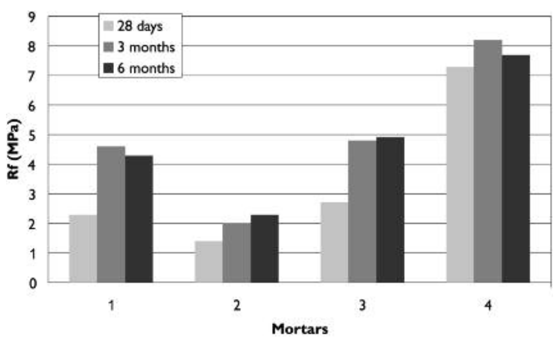

Fig. 7 Bending strength measured after 28 days, 3 months and 6 months.

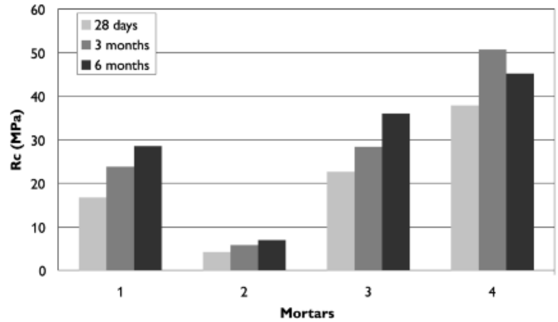

Fig. 8 Compressive strength measured after 28 days, 3 months and 6 months.

Dynamic modulus of elasticity

Ultra-sound wave velocities of propagation were measured on the samples. Then the dynamic modulus of elasticity were calculated according to equation 2; E being the dynamic modulus of elasticity (Pa), ν being the Poisson coefficient (generally ν = 0.2), ρ being the density of the concrete (kg/m^3) and ν_m being the sound velocity (m/s).

$$E = \frac{(1+\nu)(1-2\nu)}{(1-\nu)} \rho \nu_m^2 \qquad \textit{(Equation 2)}$$

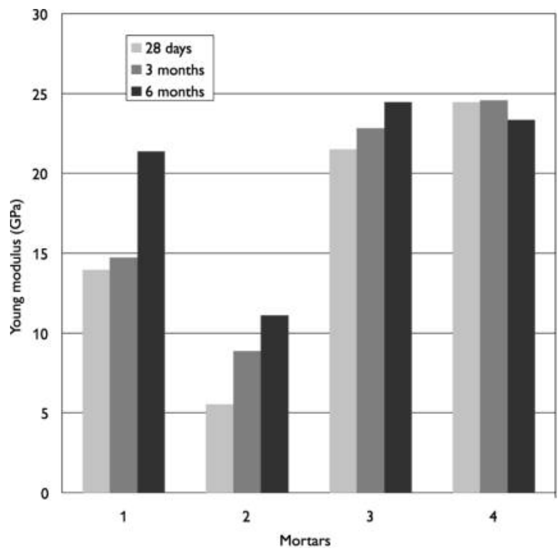

Fig. 9 Dynamic modulus of elasticity calculated after 28 days, 3 months and 6 months.

Whatever the mortar, the resulting dynamic modulus of elasticity (Figure 9) are lower than 27 GPa, which is the lowest value measured on the ancient concretes, on ornament. No incompatibility was therefore evidenced.

Conclusion

The purpose of this study was to develop and to test repair mortars compatible with the ancient concrete encountered in the French Rhône-Alpes region, which are affected by an erosion phenomenon. Those ancient concretes, which are characterized by an ochre color and which were used to cast either concrete blocks or complex ornaments, are very specific of the concrete production of the end of the 19th century in France. Therefore, they constitute a valuable cultural heritage to be preserved.

After a first characterization of the properties of a set of representative ancient buildings, 4 mortars were selected, 2 being specifically formulated. Then, based on ancient recipes encountered on the literature of the 19th century, a Prompt-cement-based concrete was developed. Concrete slabs were then cast using this formula, and artificially eroded in order to perform compatibility tests.

On the same time, the intrinsic properties of the 4 selected mortars were characterized, and the first results already revealed unsuitable performances or incompatibilities.

Thus, mortar 1 shows a clearly too high shrinkage. As a consequence, an almost instantaneous shrinkage cracking was observed when it was applied on the artificially eroded concrete slabs.

Mortar 4, which is Portland-cement-based is clearly too water vapor impermeable which might be incompatible with an ancient masonry. Its mechanical performances are also much higher than the 3 Prompt-cement--based mortars.

But the 1 year tests and the compatibility tests to be performed on the slabs before and after artificial aging, might evidence clearer compatibility or incompatibility.

In order to improve the possible comparison with the ancient concrete sample group, complementary characterization of the Prompt-cement-based concrete is also scheduled.

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