LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

INFLUENCE OF NANO-LIME AND NANO-SILICA CONSOLIDANTS IN THE DRYING KINETICS OF THREE POROUS BUILDING MATERIALS

RELATÓRIO 168/**2014 – DM/NBPC**

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Estudo realizado no âmbito do projeto de investigação DRYMASS (ref. PTDC/ECM/100553/2008) que é suportado por fundos nacionais através da Fundação para a Ciência e a Tecnologia (FCT) e do LNEC

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Título

INFLUENCE OF NANO-LIME AND NANO-SILICA CONSOLIDANTS IN THE DRYING KINETICS OF THREE POROUS BUILDING MATERIALS

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Abstract

In this report we describe an experimental study carried out at LNEC within the research project DRYMASS (ref. PTDC/ECM/100553/2008). The study was aimed at evaluating the possibility of increasing the drying rate of porous building materials by means of nano-treatments. It was justified by previous results of other authors that observed an apparently unexplainable increase in the evaporation rate of natural stone after application of nano-calcium hydroxide solutions as consolidating agents.

Two commercial treatments, consisting on alcoholic or aqueous suspensions of nano-lime or nano-silica, respectively, were tested on three porous building materials. The treatments are generally used for consolidation. The materials were a lime mortar and two natural stones (Ançã limestone and Bentheimer sandstone).

It was concluded that neither of the nano-treatments hinders drying. However, they were also not able to increase the drying kinetics of any of the three substrates.

Key words: nano-lime, nano sílica, drying, porous materials

Resumo

Neste relatório descreve-se um estudo experimental realizado no LNEC como parte do projeto de investigação DRYMASS (ref. PTDC/ECM/100553/2008). O estudo teve como objetivo avaliar a possibilidade de aumentar a taxa de secagem de materiais de construção porosos, através de nano-tratamentos. O trabalho foi justificado por resultados anteriores de outros autores, que observaram um aumento aparentemente inexplicável da taxa de evaporação de pedra natural, após a aplicação de soluções de nano hidróxido de cálcio como agentes de consolidação.

Dois tratamentos comerciais, que consistem em suspensões alcoólicas aquosas de nano-silica ou de nano-cal, respetivamente, foram testados em três materiais porosos de construção. Os tratamentos são geralmente utilizados para a consolidação. Os materiais foram uma argamassa de cal e duas pedras naturais (calcário de Ançã e arenito Bentheimer).

Concluiu-se que nenhum dos nano-tratamentos impede a secagem, no entanto, também não foram capazes de aumentar a cinética de secagem de qualquer dos três tipos de substratos.

Palavras-chave: nano-silica, nano-cal, secagem, materiais porosos

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1 | Introduction

Moisture is one of the main causes of degradation of the porous building materials that constitute our architectural heritage. In fact, in building conservation, most of the problems are related to the presence of water [1 Massari and Massari 1993], and their repair absorbs a significant fraction of the available resources. Elimination of the moisture present in old masonry is, indeed, not usually a straightforward undertaking. This happens because these constructions are usually based on thick solid walls, often very heterogeneous, built directly over the ground and made of porous hydrophilic materials. Another major reason is the presence of soluble salts, recurrent in historical buildings, which hinders drying and may give rise to hygroscopic phenomena.

In this report we describe an experimental study carried out at LNEC within the research project DRYMASS (ref. PTDC/ECM/100553/2008), which is aimed at evaluating the possibility of increasing the drying rate of porous building materials by means of nano-treatments. It builds on previous results achieved within the DRYMASS project, which showed that the drying kinetics of different substrate materials could be increased by the application of lime coatings [2 Brito and Diaz Gonçalves 2013] [3 Musacchi and Diaz Gonçalves 2013].

Interesting applications for nano-materials are being found within the conservation of cultural heritage. Nano-lime and nano-silica are two recent types of nano-products. They are presented as alcoholic or aqueous suspensions of nano-particles, respectively, and are generally used in consolidation treatments. Nano-limes are aimed at overcoming some of the limitations of traditional lime-based materials, such as the reduced penetration depth and the difficulty in achieving a complete carbonation, while maintaining their advantages [4 Daniele et al. 2008] [5 Vinardi et al. 2003] [6 Turriziani 1972]. Nano-silica has been reported to reduce the porosity of stone substrates which become more compact and, therefore, less susceptible to decay mechanisms related to the action of water [7 Zendri et al. 2007].

The current investigation evaluates the influence of nano-treatments based on nano-lime and nano-silica, respectively, on the drying of three porous building materials.

The inclusion of nano-treatments in the work of the Drymass project was justified by the recent results of Zornoza-Indart et al. [8 (2013)] who reported an unexplainable increase in the evaporation rate of natural stone after the application of nano-calcium hydroxide solutions as consolidating agent.

2 | Materials and Methods

2.1 General

The experimental program consisted on applying two different nano-solutions on one lime mortar and two natural stones (Ançã limestone and Bentheimer sandstone). The influence of the treatments on drying was then evaluated through the RILEM drying test [9 RILEM 1980] which was performed on treated and untreated specimens.

2.2 Substrates

The test specimens were small cubes with 25 mm x 25 mm x 25 mm.

The lime mortar was prepared following standard EN 1015-2 [10 CEN 1998]. Its molding and curing followed the procedure described by Gonçalves et al. [11 Gonçalves et al. 2012]. The Ançã limestone - a soft, and homogeneous white stone from Portugal - and the Bentheimer sandstone – a quartz-rich sandstone from Germany - were prepared by cutting of larger blocks. In Table 2.1 the capillary porosity of these substrate materials is shown, for characterization purposes.

Table 2.1 – Capillary porosity of the substrate materials (Brito and Diaz Gonçalves 2013)

Material	Capillary porosity (%)
Lime mortar	20.8
Ançã limestone	22.9
Bentheimer sandstone	17.7

All specimens were laterally sealed with an epoxy resin (Icosit K 101, from Sika) applied by brush in two crossed layers with an interval of around 24 h (Figure 2.1).

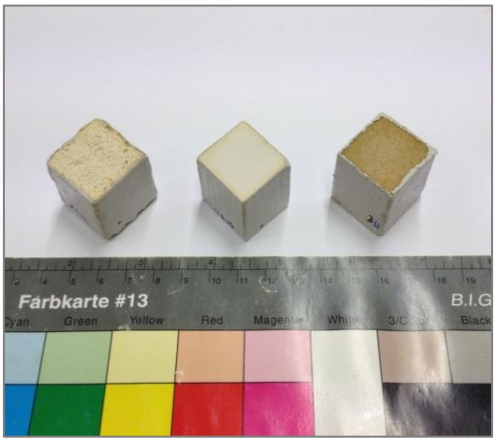

Figure 2.1 – Laterally sealed specimens: lime mortar, Ançã limestone and Bentheimer sandstone (from left to right)

2.3 Treatments

The following commercial products were selected for the work:

- CALOSIL – a colloidal solution of nano-calcium hydroxide in ethanol equal to that used by Zornoza-Indart et al. [8]
- NANO ESTEL – an aqueous colloidal solution of nano-silica

Both are ready-to-use products and, therefore, were not subjected to any preparation. Their main characteristics are described in Table 2.2. In Figure 2.2 is possible to observe their macroscopic appearance.

Table 2.2 – Identification and characteristics of the selected nano-solutions

Identification	Commercial ID	Description	Concentration (g/l)	Particle dimension (nm)	Colour
Nano-lime	CALOSIL E-25	3 | Colloidal dispersion of calcium hydroxide in ethanol	25	150 (average)	Not colored
Nano-silica	NANO ESTEL	Aqueous colloidal dispersion of nano-sized silica	300	20-40	Whitish

Figure 2.2 – Macroscopic appearance of the nano-solutions: nano-lime and nano-silica (from left to right)

3.1 Application and cure

Immediately before the application of the products, the surface of the specimens was brushed to remove any dust or other type of loose material. Then, the substrates were pre-wetted with pure water in order to allow a proper application. The application is facilitated due to the lower suction of the material and reduced friction of the paint brush on the wet surface.

The nano-treatments were applied in six layers with a paint brush. Between each layer, the operator waited for the complete absorption of the product in the material, which corresponded to a maximum interval of one hour, depending on the material. The application was carried out in a laboratory room with controlled environmental conditions (20ºC and 50% HR),

After the application of all the layers, the specimens were kept for 14 days in a laboratory room with controlled environmental conditions (20ºC and 50% HR). Afterwards, they spent 14 days in a carbonation chamber (23ºC, 60% RH and 5% CO_2), and finally another 2 days in the laboratory room for stabilization before the drying test. Figure 2.3 shows the specimens during their period in the laboratory room.

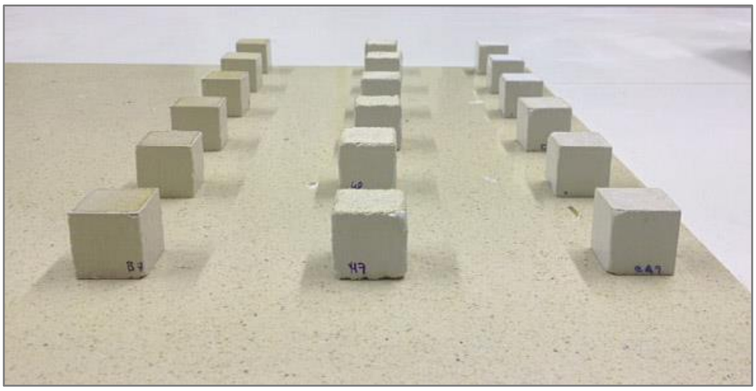

Figure 2.3 – Specimens curing in the laboratory

3.2 Drying test

The drying test was performed according to the RILEM procedure "evaporation curve" [10 RILEM 1980]. The specimens were left in partial immersion in pure water for 24 hours. During this period, the free-water level was kept approximately 2-3 mm above their bottom face (Figure 2.4). The specimens were afterwards removed from immersion, the excess water was quickly removed with a wet tissue and their bottom surfaces immediately sealed with polyethylene film.

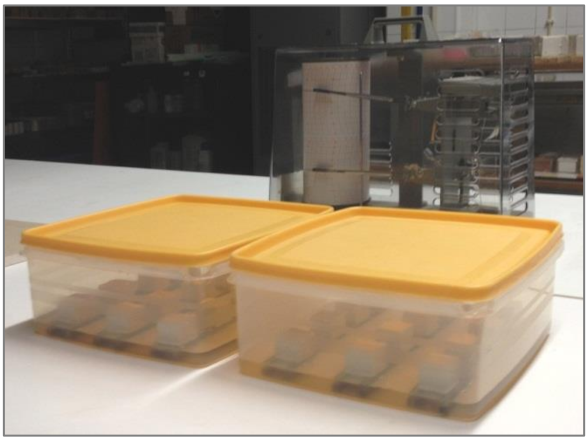

Figure 2.4 – Specimens in partial immersion

A total of 27 specimens was tested, including, for each type of substrate, three treated specimens of either nano-solution and three blank specimens without treatment.

Drying took place in the conditioned room at 20°C and 50% RH. The water evaporated through the top face of the specimens, which was the only one left unsealed. The loss of water was monitored by periodical weighing using an electronic balance with resolution of 0.001g. The total duration of the test was of approximately 70 h.

An evaporation curve was obtained for each specimen, where the initial straight line segment corresponds to drying stage I. As known, evaporative drying of porous materials has two main stages (see for example [11 Diaz Gonçalves et al. 2012]. During stage I, the moisture content is high, the drying rate constant and the drying front is located at the material surface. Stage II begins when, due to decrease of the moisture content in the material, the liquid flow to the surface becomes insufficient to compensate the evaporative demand. Therefore, the drying front recedes into the material and the drying rate decreases progressively.

The results of the drying test were analysed in terms of the stage I drying rate, which expresses the loss of mass per unit area as function of time, and is given by the slope of the first straight line segment of the evaporation curve (see Appendix A).

4 | Results and Discussion

4.1 Macroscopic observation

In conservation, the respect for the aesthetical characteristics and uniqueness of the historic material is a very important aspect. Therefore, a macroscopic observation of the changes induced by the applied nano-solutions was carried out during the application and curing phases. The aspect of the surface after application was recorded, in order to being able to compare it with the situation before treatment (Figure 2.1) and thereby detect possible colour changes or any other anomalies (Figure 4.1).

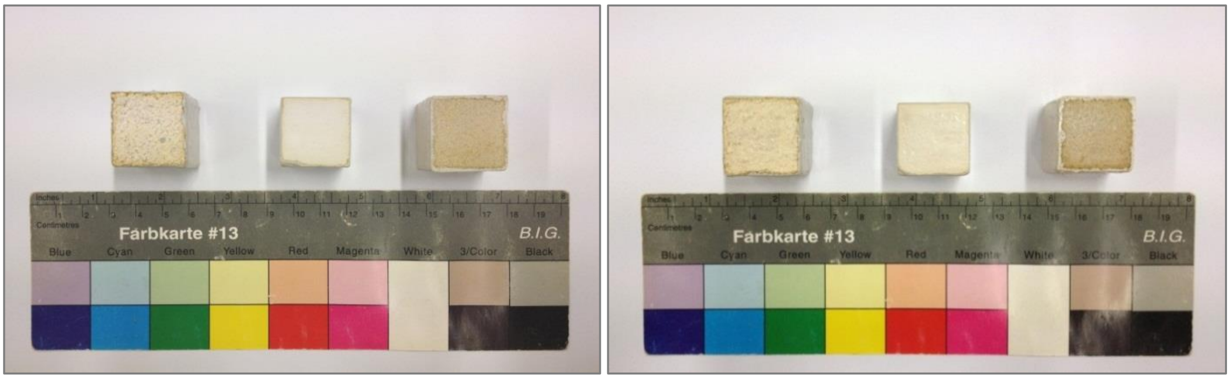

Figure 4.1 – Macroscopic appearance of the specimens after application of the treatments: nano-lime (left) and nano-silica (right)

As seen, after the application of the nano-lime, the surface of the three types of substrate became whitish. This is most likely due to the deposition of calcium hydroxide particles after the evaporation of the alcohol. These particles covered the surface and then converted into calcium carbonate by reaction with the atmospheric carbon dioxide. Aesthetical changes were also noticed after the application of nano-silica. In this case, the surface of the specimens became shinier, especially in the case of the lime mortar.

4.2 Drying test

Figure 4.2 depicts the stage I drying rates obtained for each treated and untreated substrate material. This drying rate corresponds to the slope of the first straight line segment of the evaporation curve (Appendix A).

As seen in Figure 4.2, no significant alterations in the drying rate of the three tested materials are noticed in association with the application of nano-lime or nano-silica. It can be therefore concluded that neither of the nano-solutions hinders drying. However, they are also not able to increase the drying kinetics of any of the three substrates.

Comparing the present results with those of Zornoza-Indart et al. [8], we cannot confirm therefore the previous results of these authors. In that case, the use of the nano-lime gave rise to an increase in the drying rate of the treated stone. It is possible that this is due to the fact that a different stone, a calcarenite, was used in that work. This means that the effect of the nano-lime may be different according to the type of stone.

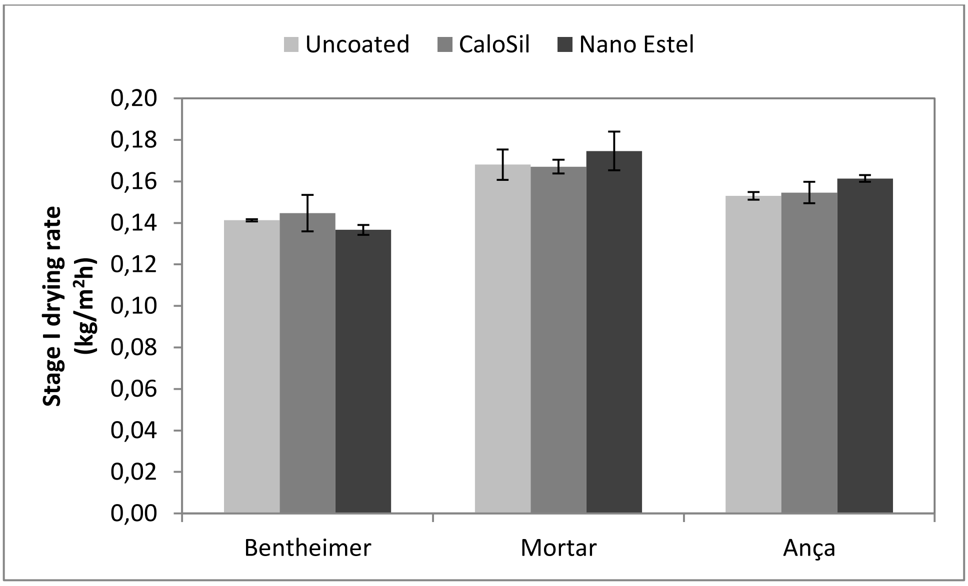

Figure 4.2 – Stage I drying rate of all applied products

Despite that an acceleration of the drying rate was not observed, a deceleration was also not observed. Our results are therefore a positive indication about the compatibility, in relation to the presence of water, of nano-lime and nano-sílica consolidation treatments. Indeed, hindering of the drying rate of the substrate is a problem in consolidation treatments, which was not observed here.

5 | Conclusions

It can be concluded from this work that the tested nano-lime and nano silica treatments are probably compatible, in relation to the presence of water, with the tested substrate materials (Ançã limestone, Bentheimer sandstone and lime mortar) which are representative of many of those found in our cultural heritage. Indeed, the treatments did not hinder the evaporation from those building materials during drying, maintaining their drying rate unchanged. However, the same cannot be said in relation to the aesthetical aspects: the nano-lime gave a whitish tone to the surfaces and the nano-silica gave them some shine. It should also be noted that this study did not evaluate the effectiveness of these products as consolidants.

In relation to the main objective of the work, it can be concluded that the tested nano-treatments are not able to increase the drying kinetics of any of the three substrates, at least under the chosen conditions. Therefore, the previous results of Zornoza-Indart et al. [8 (2013] are not confirmed.

Acknowledgments

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APPENDIX

Appendix A: Stage I drying rate

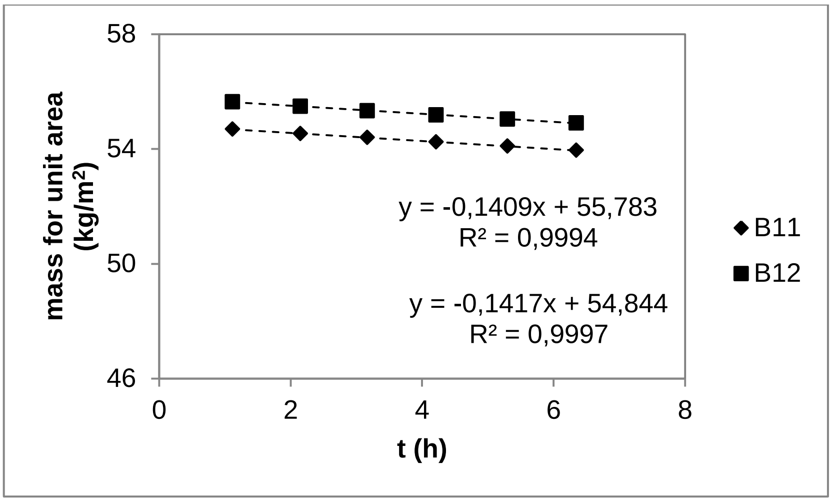

Figure A.1 – Untreated Bentheimer

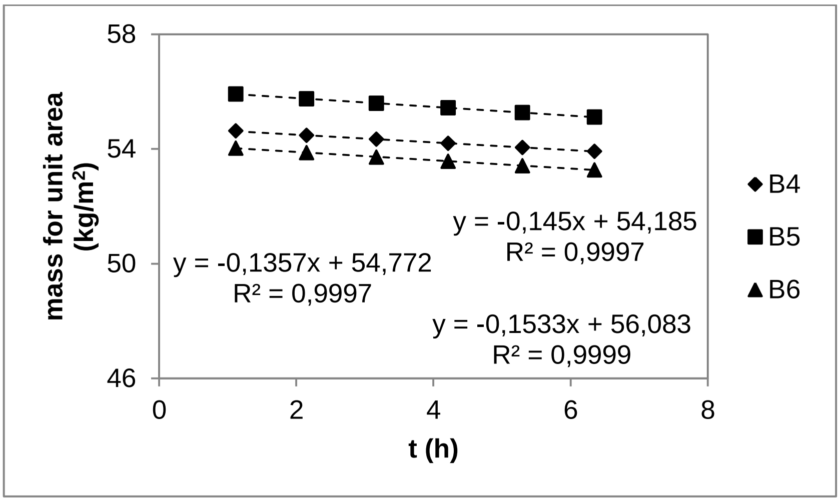

Figure A.2 – Bentheimer treated with nano-lime

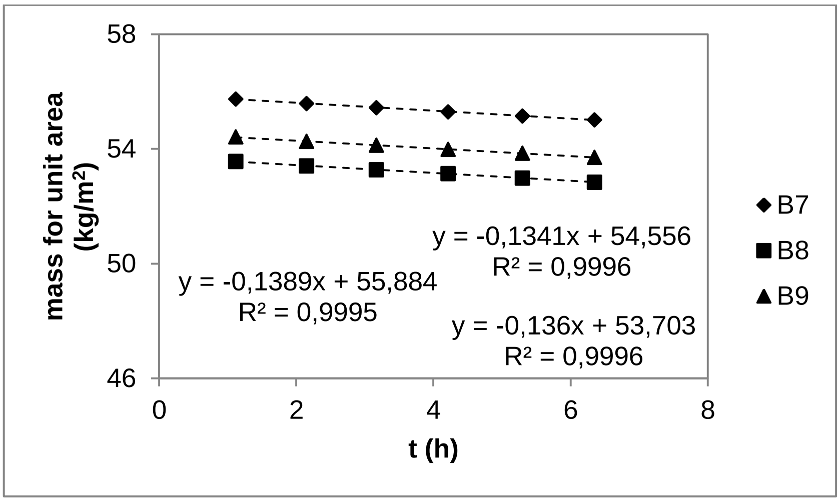

Figure A.3 – Bentheimer treated with nano-silica

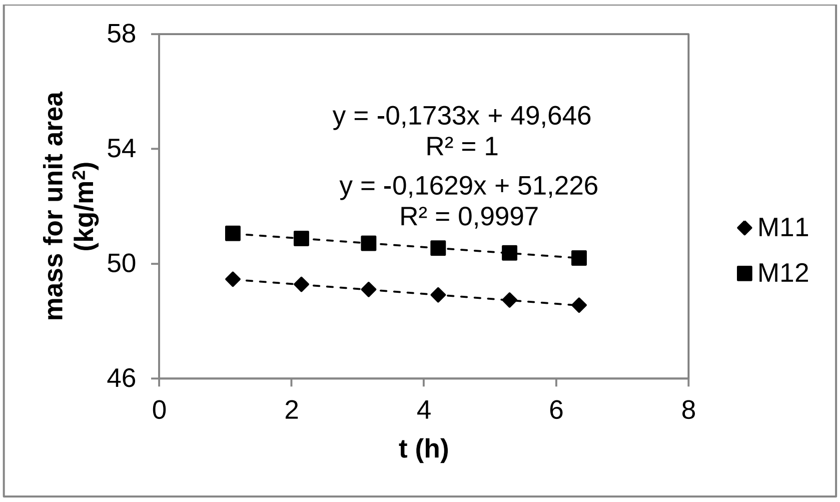

Figure A.4 – Untreated lime mortar

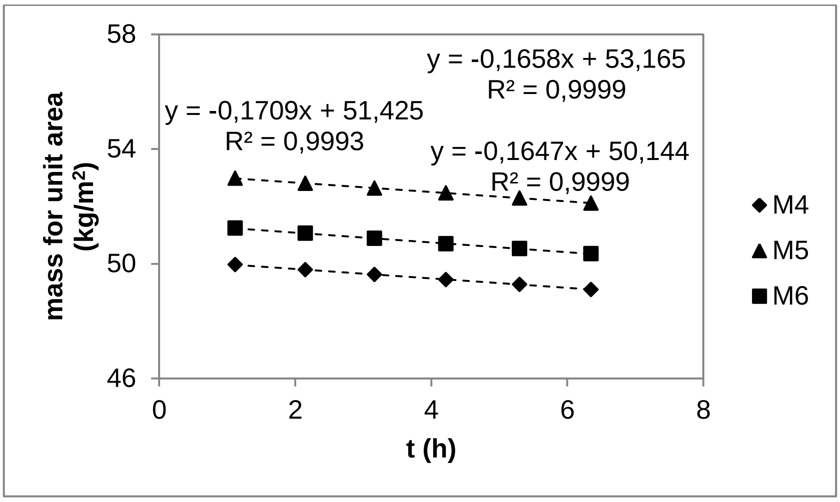

Figure A.5 –Lime mortar treated with nano-lime

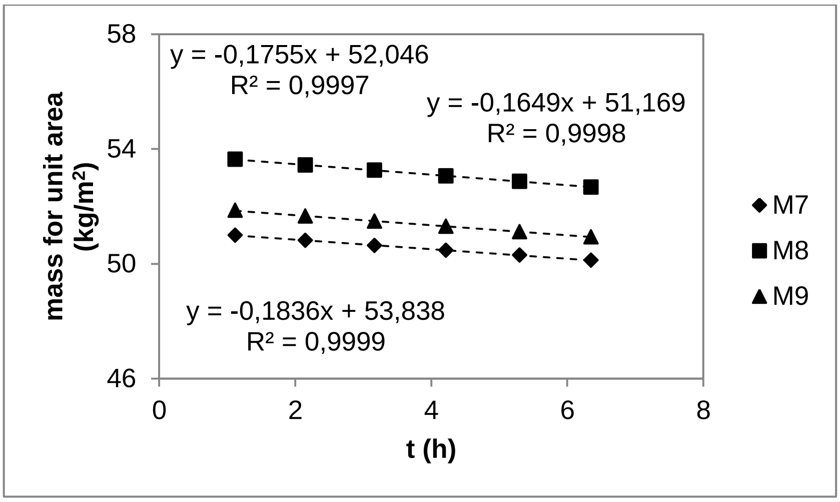

Figure A.6 –Lime mortar treated with nano-silica

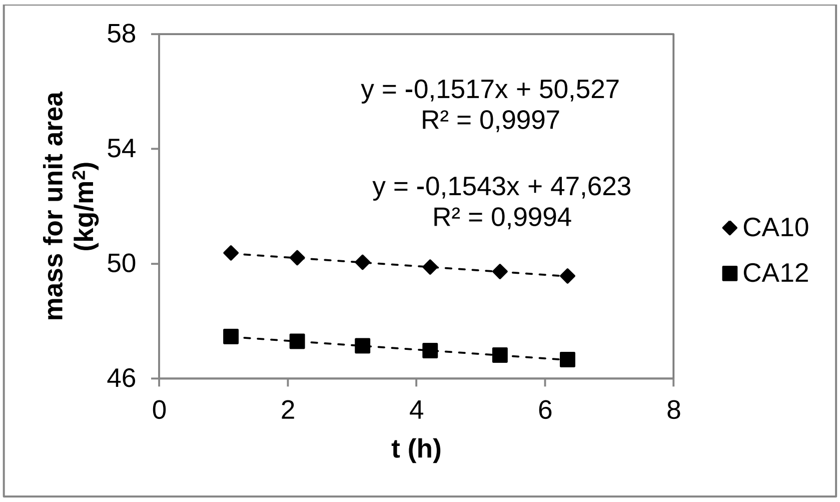

Figure A.7 – Untreated Ançã limestone

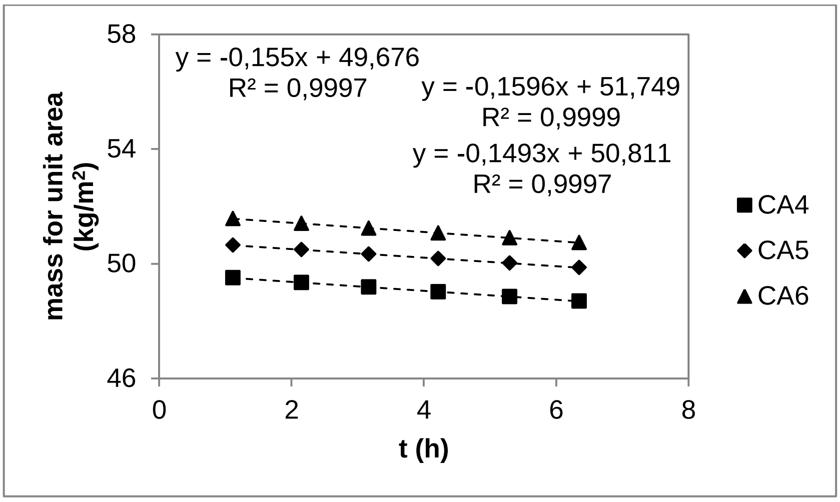

Figure A.8 – Ançã limestone limestone treated with nano-lime

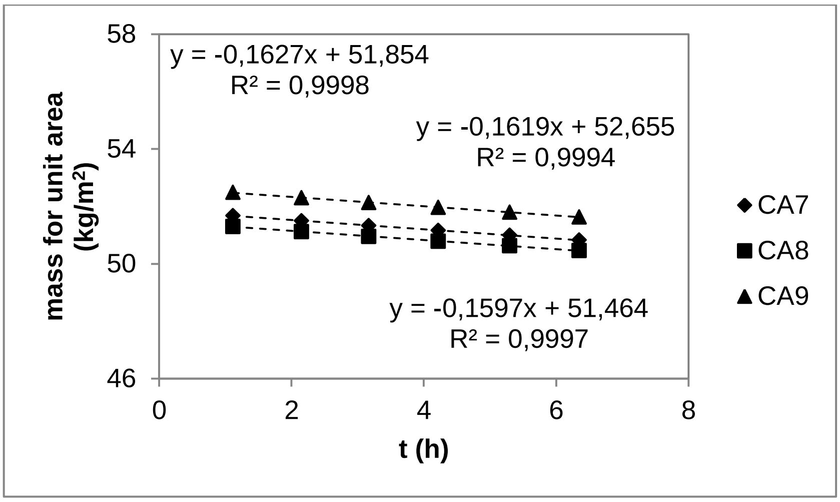

Figure A.9 – Ançã limestone limestone treated with nano-silica