Igreja da Graça (1380), Santarém, Portugal

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

LNEC LABORATÓRIO NACIONAL DE ENGENHARIA CIVIL

Optical measurement of the alteration kinetics of porous building materials during salt crystallization

Teresa Diaz Gonçalves
Jessica Musacchi
Vânia Brito

Introduction

Salt crystallization tests

understand damage mechanisms
help avoid problems in practical conservation

Santa Cruz Monastery (1132-1223), Coimbra – courtesy of J Delgado Rodrigues

Introduction

Salt crystallization tests

Extreme conditions to obtain measurable changes in a short period of time:

- High temperature
  - ASTM; CEN; RILEM V.1a => oven drying at 105ºC
- Successive wet/dry cycles
  - ASTM; CEN; RILEM V.1a,V.1b,V.2 => several cycles

ASTM (2005) Standard test method for soundness of aggregates by use of sodium sulphate or magnesium sulphate. ASTM C88-05.

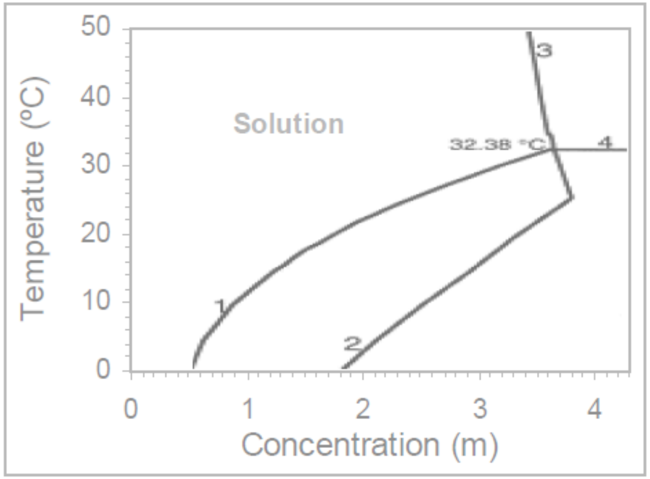
CEN (1999b) Natural stone test methods. Determination of resistance to salt crystallization. EN 12370

RILEM TC 25-PEM (1980) Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods, Materials and Structures 13, 233-235 (test V.1a), 235-237 (test V.1b) and 237-239 (test V.2).

Introduction

Salt crystallization tests

Sodium sulfate:



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2=solubility of the heptahydrate

3=solubility of thenardite

4=thenardite / mirabilite boundary

Solubility diagram of sodium sulfate: Adapted from Rodríguez-Navarro C, Doehne E, Sebastián E (2000) How does sodium sulfate crystallize? Implications for the decay and testing of building materials, Cement and Concrete Research 30, 1527-1534.

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Salt crystallization tests

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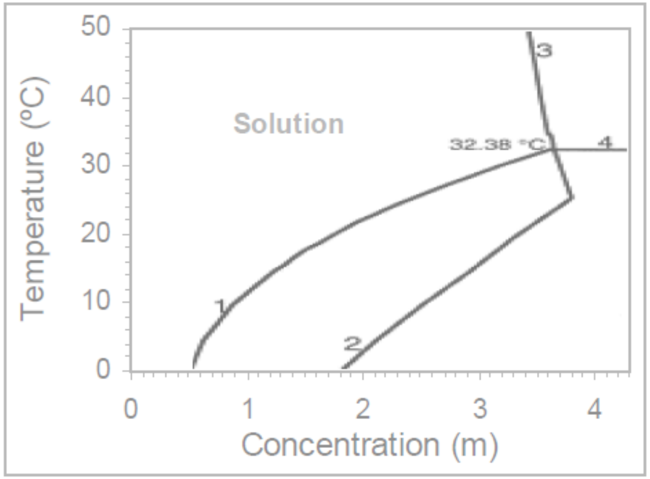

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Saline Minerals in Walls

Sulfates

Gypsum	$CaCO_4 \cdot 2H_2O$
Bassanite	$CaSO_4 \cdot 1/2\ H_2O$
Epsomite	$MgSO_4 \cdot 7H_2O$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Thenardite	Na_2SO_4
Arcanite	K_2SO_4
Astracanite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Picromerite	$K_2Mg(SO_4)_2 \cdot 6H_2O$
Syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$
Glaserite	$K_3Na(SO_4)_2$

Carbonates

Calcite	$CaCO_3$
Dolomite	$CaMg\ (CO_3)_2$
Magnesite	$MgCO_3$
Nesquehonite	$MgCO_3 \cdot 3H_2O$
Hydromagnesite	$Mg_5[OH(CO_3)_2]_2 \cdot 4H_2O$
Natron	$Na_2CO_3 \cdot 10H_2O$
Thermonatrite	$Na_2CO_3 \cdot H_2O$
Trona	$Na_3H(CO_3)_2 \cdot 2H_2O$
Kalicinite	$KHCO_3$

Nitrates

Nitrocalcite	$Ca(NO_3)_2 \cdot 4H_2O$
Nitromagnesite	$Mg(NO_3)_2 \cdot 6H_2O$
Nitronatrite	$NaNO_3$
Nitrokalite	KNO_3
Ammoniumnitrate	NH_4NO_3

Chlorides

Bischofite	$MgCl_2 \cdot 6H_2O$
Antarticite	$CaCl_2 \cdot 6H_2O$
Tachyhydrite	$CaMg_2Cl_6 \cdot 12H_2O$
Halite	$NaCl$
Sylvite	KCl

Solubility diagram of sodium sulfate: Adapted from Rodríguez-Navarro C, Doehne E, Sebastián E (2000) How does sodium sulfate crystallize? Implications for the decay and testing of building materials, Cement and Concrete Research 30, 1527-1534.

Arnold A (1982) Rising damp and saline minerals. In Fourth International Congress on the Deterioration and Preservation of Stone Objects, ed. K. L.Gauri and J. A.Gwinn. Louisville, Ky.: University of Louisville. 11–28.

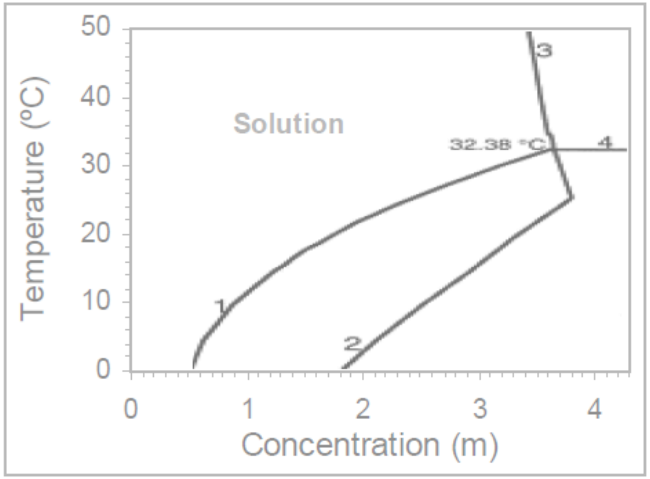
Introduction

Salt crystallization tests

Sodium sulfate:

three crystalline phases with different solubility

solubility is temperature-dependent



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high temperatures => temperature-induced crystallization [1]

successive wet/dry cycles => contact-induced crystallization [2]

[1] Doehne E, Selwitz C, Carson DM (2002) The damage mechanism of sodium sulfate in porous stone In Proc. SALTeXPERT Meeting, Prague. European Research on Cultural Heritage. State-of-the-Art Studies, Vol. 5, 2006, 127-160

[2] Chatterji S, Jensen AD (1989) Efflorescence and breakdown of building materials, Nordic Concrete Research 8, 56-61.

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Salt crystallization tests

Sodium sulfate:

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Massive decay patterns that hardly happen in constructions …

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Salt crystallization tests

Sodium sulfate:

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Massive decay patterns that hardly happen in constructions …

Can sodium sulfate be as much destructive in field conditions, where wet/dry cycles are slow and temperature variations smaller / less abrupt?

Methods - Crystallization test (single isothermal drying event)

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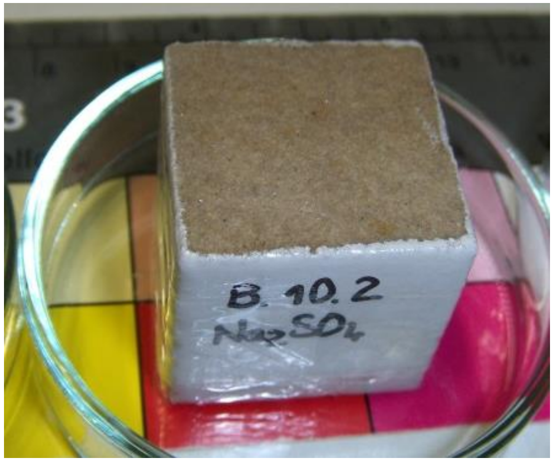
test specimens:
- cubes with 24 mm edge
- laterally sealed with epoxy

partial immersion during 3 days in:
- saturated Na_2SO_4 solution
- pure water (blank)

bottom-sealed

let dry at 20ºC and 50% RH

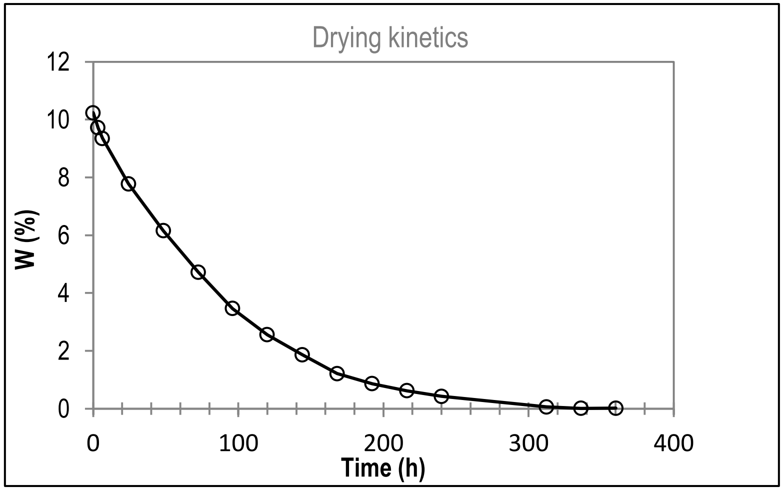


Methods - Crystallization test (single isothermal drying event)

1 - Evaporation curve

Objective: evaluate the drying kinetics

specimens periodically weighed

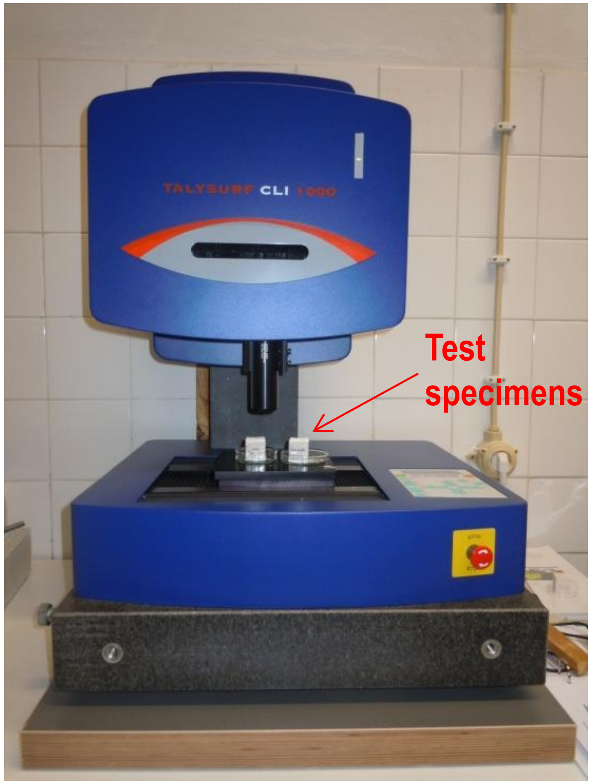


RILEM TC 25-PEM (1980) Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods, Materials and Structures 13, 204-207 (test II.5 "Evaporation curve")

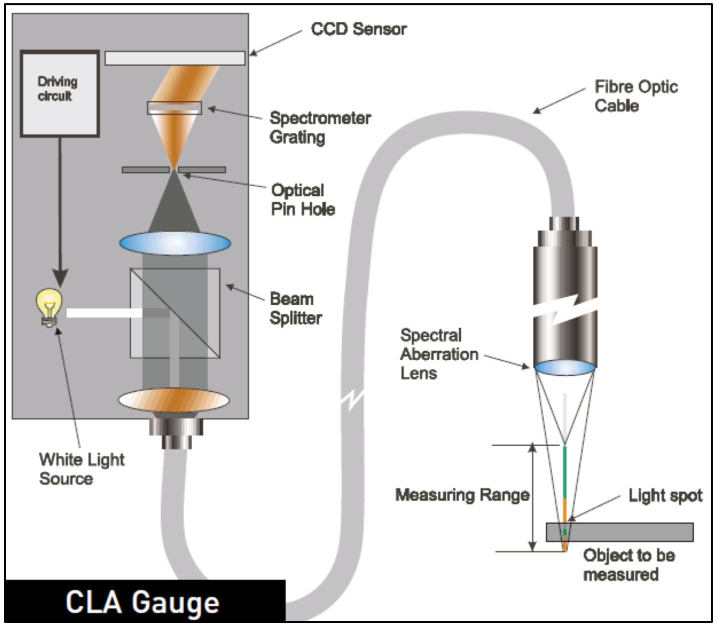
Methods - Crystallization test (single isothermal drying event)

2 - Optical profilometry

Objective: monitor the morphological alterations of the surface (very small changes…)



3D profilometer
(Talysurf® CLI1000, by byTaylor Hobson)



Non-contact white light gauge based on the principle of chromatic length aberration (CLA)

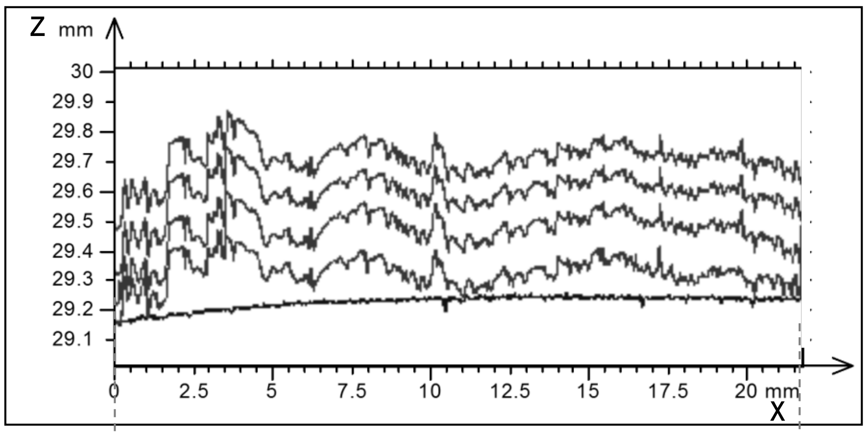
- vertical range = 3 mm
- vertical resolution = 100 nm
- lateral resolution = 5 µm

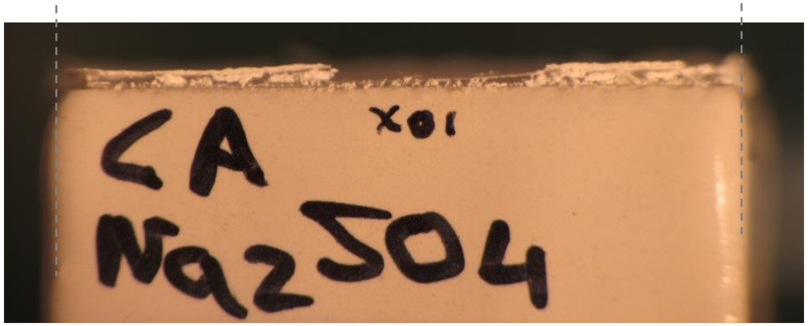
Methods - Crystallization test (single isothermal drying event)

2 - Optical profilometry

Objective: monitor the morphological alterations of the surface

- Profiles obtained every 3 hours: speed =2 mm/s; spacing = 5 µm



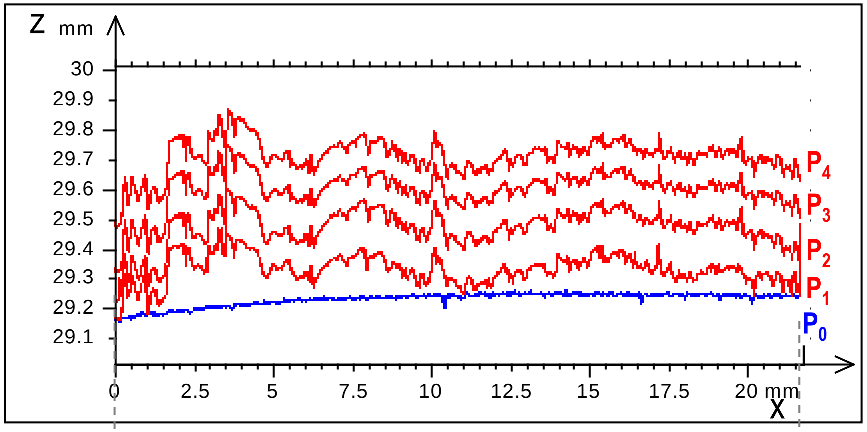


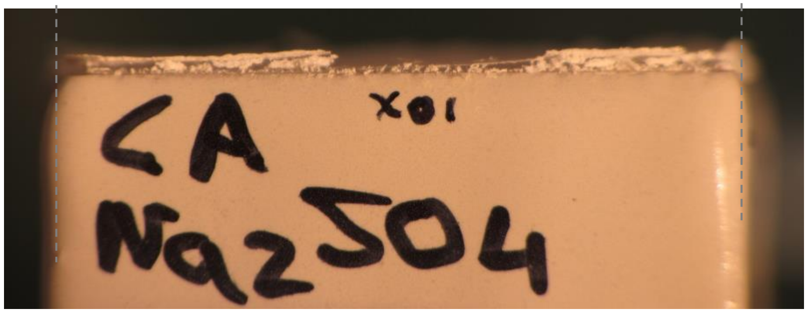
Methods - Crystallization test (single isothermal drying event)

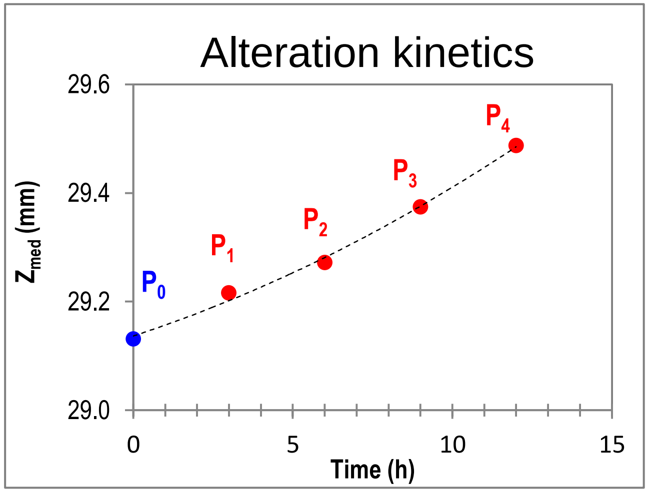
2 - Optical profilometry

Objective: monitor the morphological alterations of the surface

- Profiles obtained every 3 hours: speed =2 mm/s; spacing = 5 µm
- Alteration curve calculated: expresses the average lifting of the surface during the experiment





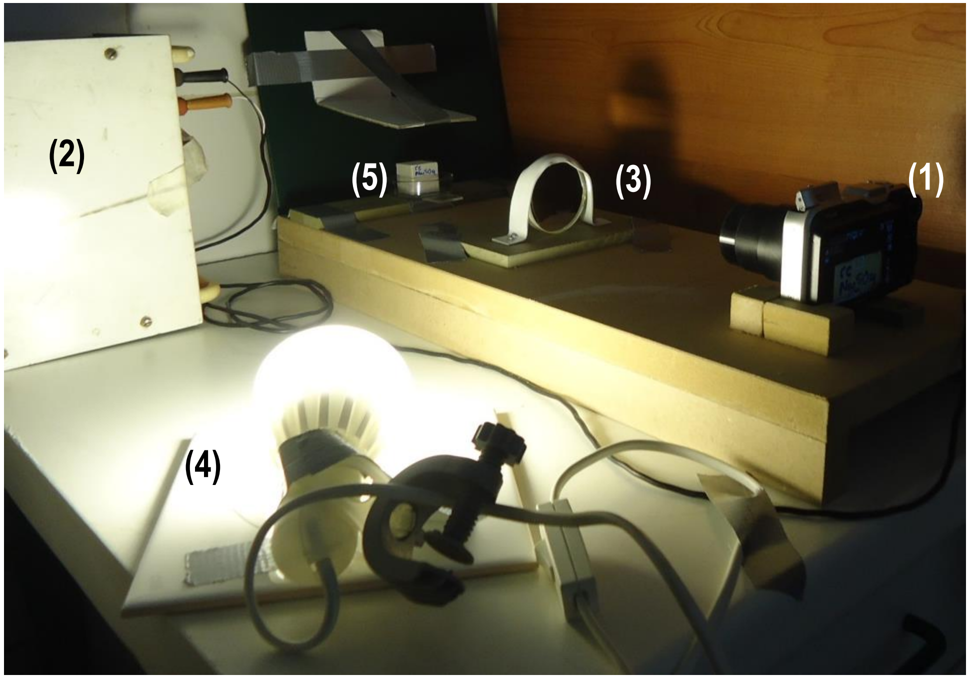


Alteration curve

Methods - Crystallization test (single isothermal drying event)

3 – Time-lapse photography

Objective: record the alteration process



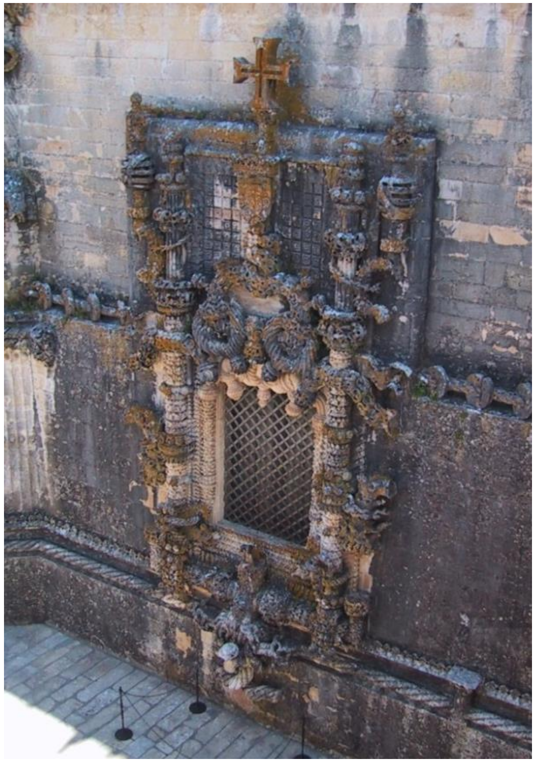
Set-up we used to film the specimens laterally

1) Camera with time-lapse software
2) Power supply
3) Lens
4) Light source
5) Test-specimen

Materials

Three natural stones relevant for cultural heritage

Ançã limestone (CA)



Christ Convent in Tomar, Portugal

Grey limestone (CC)

Portuguese pavement

Bentheimer sandstone (B)

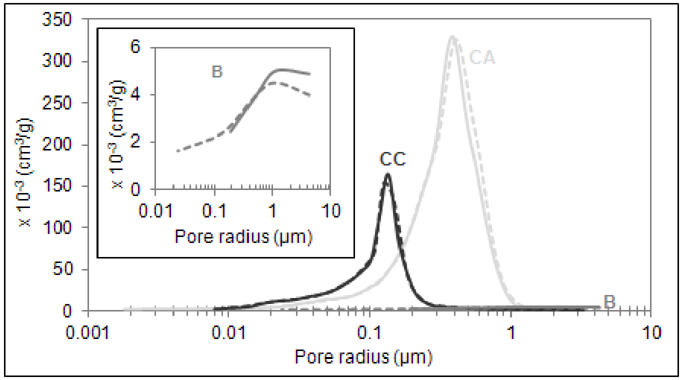
Nieuwe Kerk in Delft, The Netherlands

http://commons.wikimedia.org/

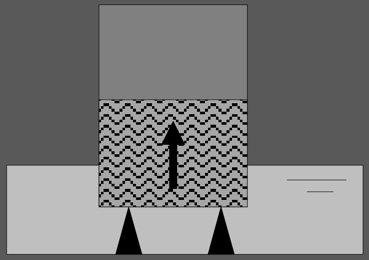
Materials

Three natural stones relevant for cultural heritage

		CA	CC	B
Capillary porosity (%V)		22.8	9.1	17.7
Pore radius (μm) – MIP modal value		0.35	0.13	20
Sorptivity - S x 10^6 (m/s$^{1/2}$)	pure water	166	20	305
	sat Na_2SO_4 sol	114	17	229



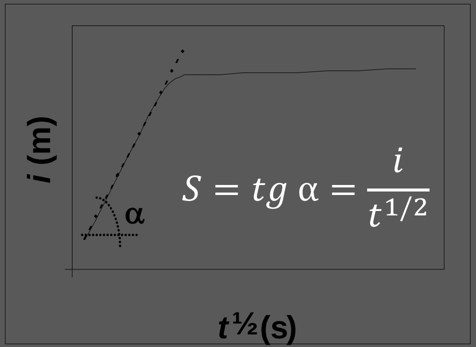
Sorptivity expresses the capability of a material to absorb and transmit liquids by capillarity:



1D capillary suction
(RILEM 1980)

$$i = \frac{\Delta M}{A.\rho}$$

ΔM (kg) - cumulative mass of absorbed liquid
A (m^2) - area of the absorption surface
ρ (kg/m^3) - density of the liquid



Results and discussion

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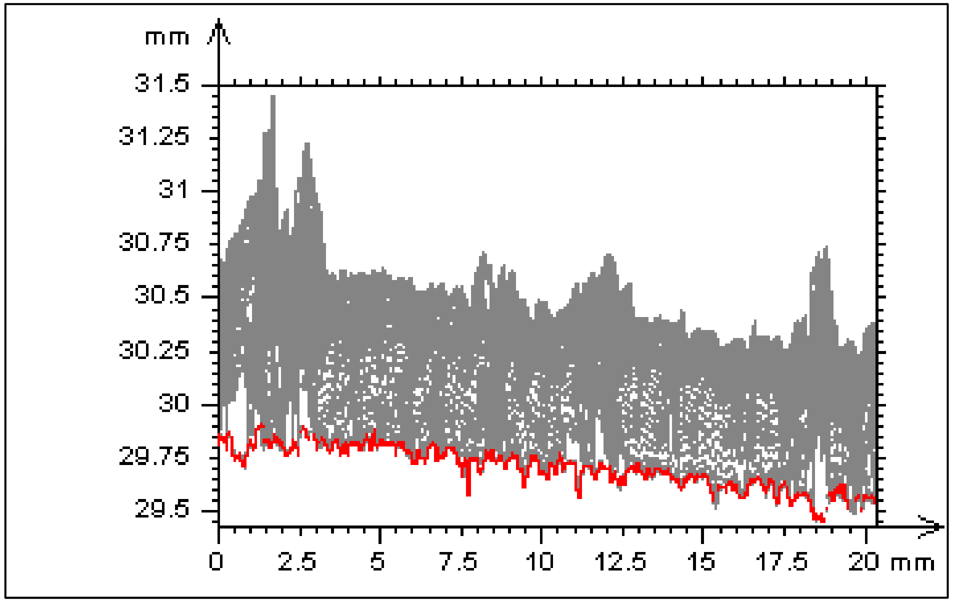
Bentheimer sandstone (B)

Surface alteration:
efflorescence

Results and discussion

Bentheimer sandstone (B)



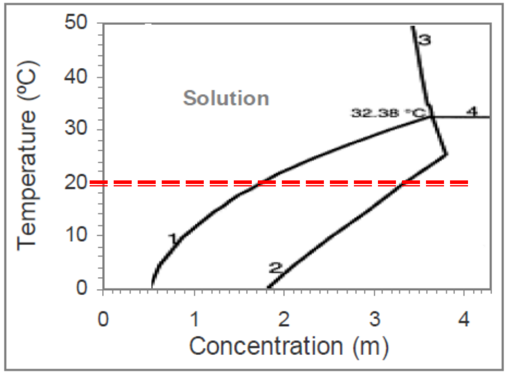
Non-contact profilometry: Profiles every 12 hours

Surface alteration: efflorescence

Results and discussion

Bentheimer sandstone (B)

Solubility phase diagram
(Rodriguez-Navarro *et al.* 2000)



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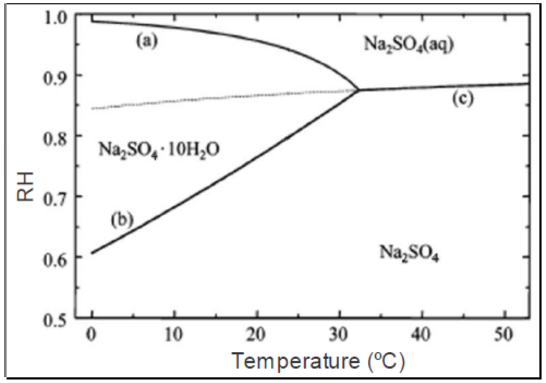

RH/T phase diagram
(Linnow *et al.* 2006)

(a) deliquescence-crystallization of mirabilite
(b) hydration-dehydration
(c) deliquescence-crystallization of thenardite
Light grey - metastable branch

Rodríguez-Navarro C, Doehne E, Sebastián E (2000) How does sodium sulfate crystallize? Implications for the decay and testing of building materials, Cement and Concrete Research 30, 1527-1534.

Linnow K, Zeunert A, Steiger M (2006) Investigation of sodium sulfate phase transitions in a porous material using humidity-and-temperature-controlled X-ray diffraction, Analytical Chemistry 78, 4683-4689.

Results and discussion

Bentheimer sandstone (B)

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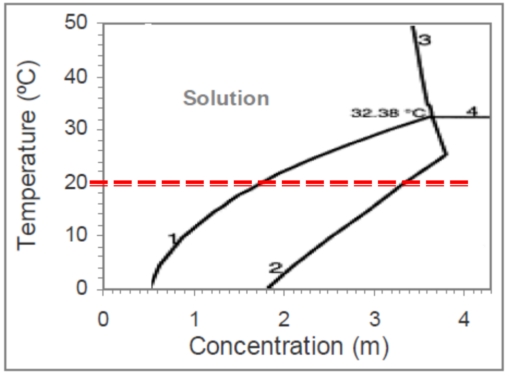

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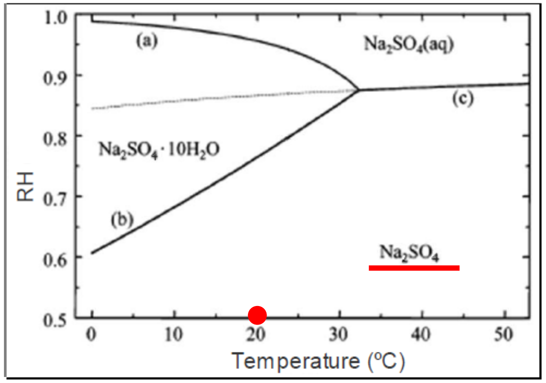

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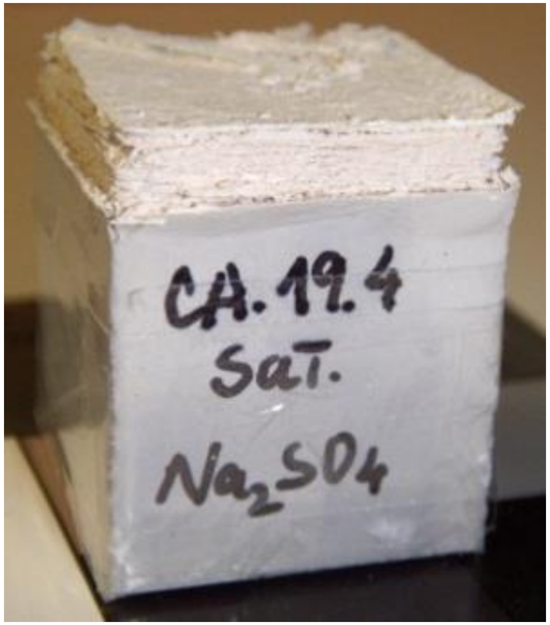
Results and discussion

Ançã limestone (CA)

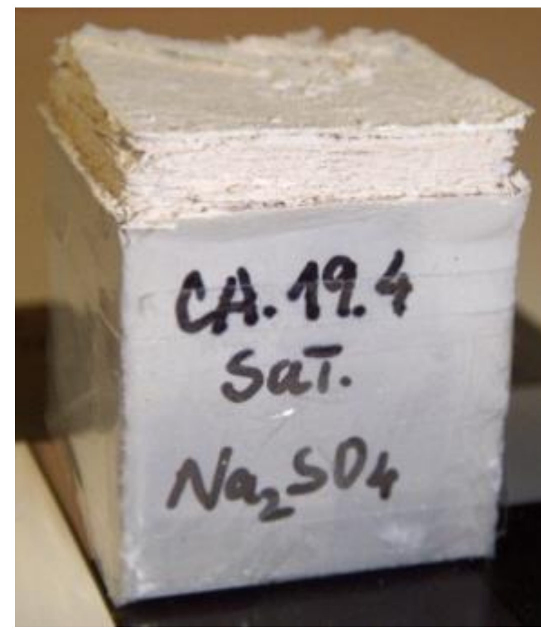


Surface alteration:
multi-layer delamination

Results and discussion

Ançã limestone (CA)

Columns at the cloister of Santa Cruz Monastery (1132-1223), Coimbra, Portugal, with delamination of Ançã limestone – courtesy of J Delgado Rodrigues



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Results and discussion

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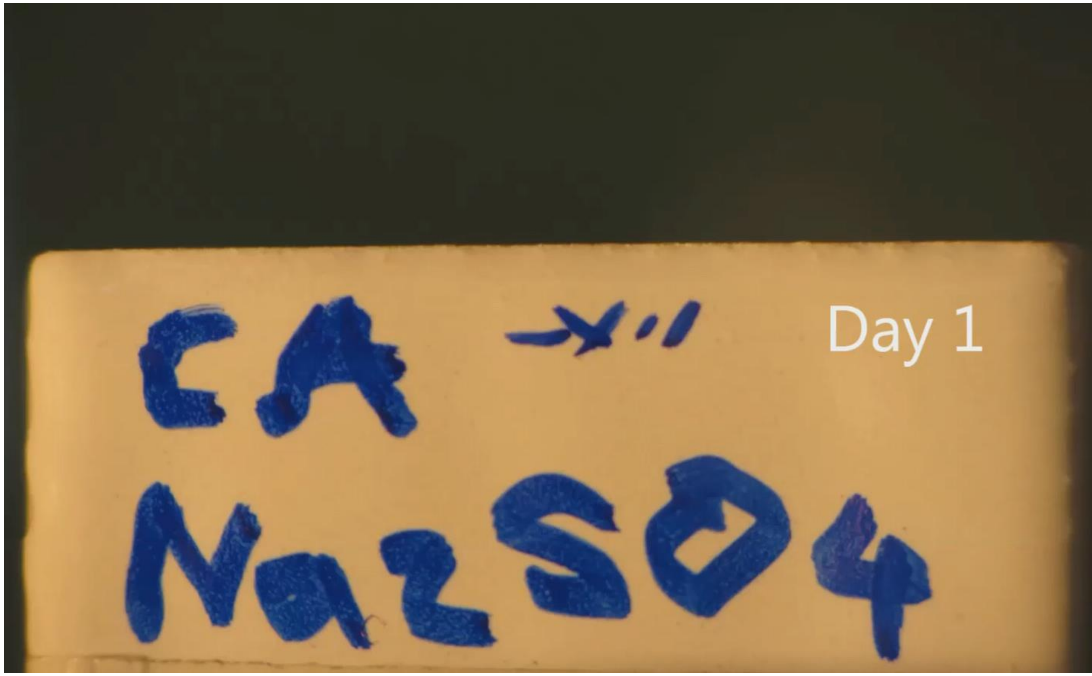

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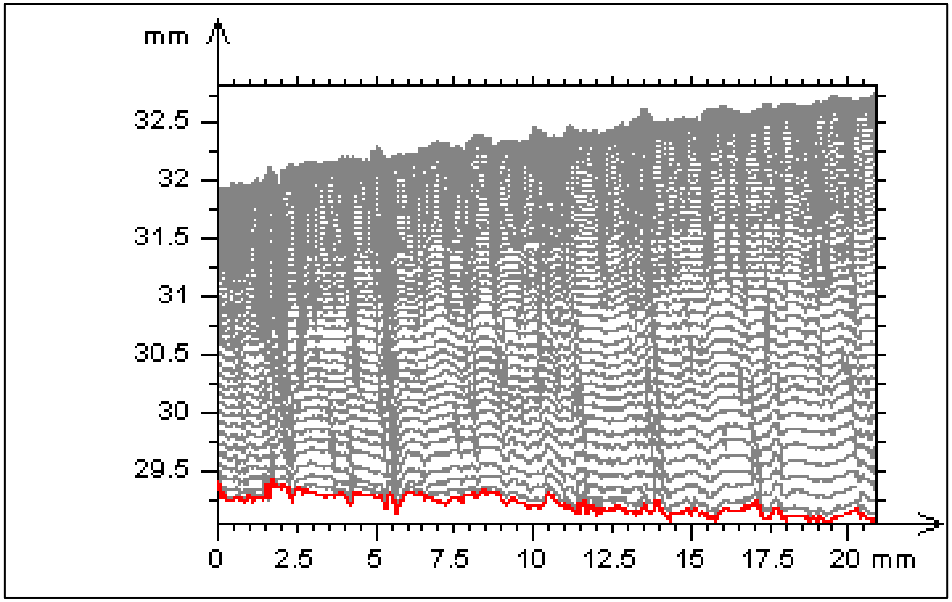
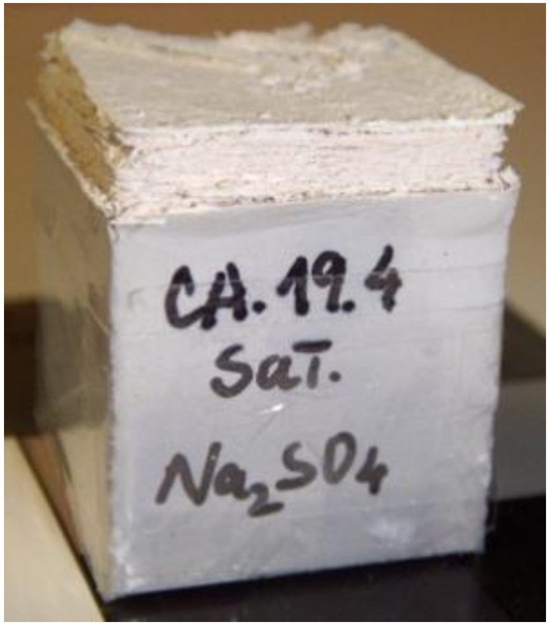


Non-contact profilometry: Profiles every 3 hours



Surface alteration:
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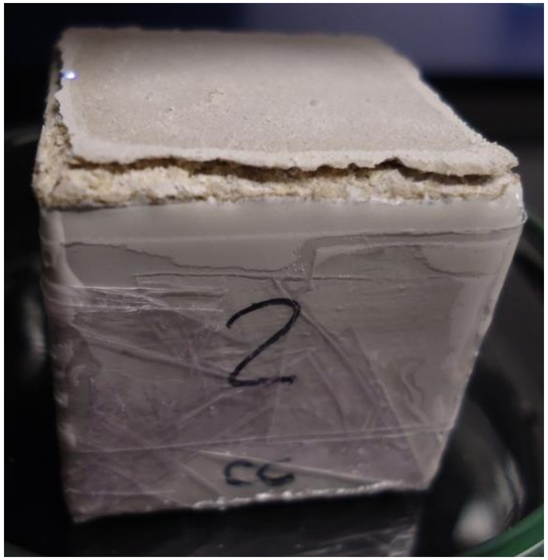
Results and discussion

Grey limestone (CC)



Surface alteration:
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Results and discussion

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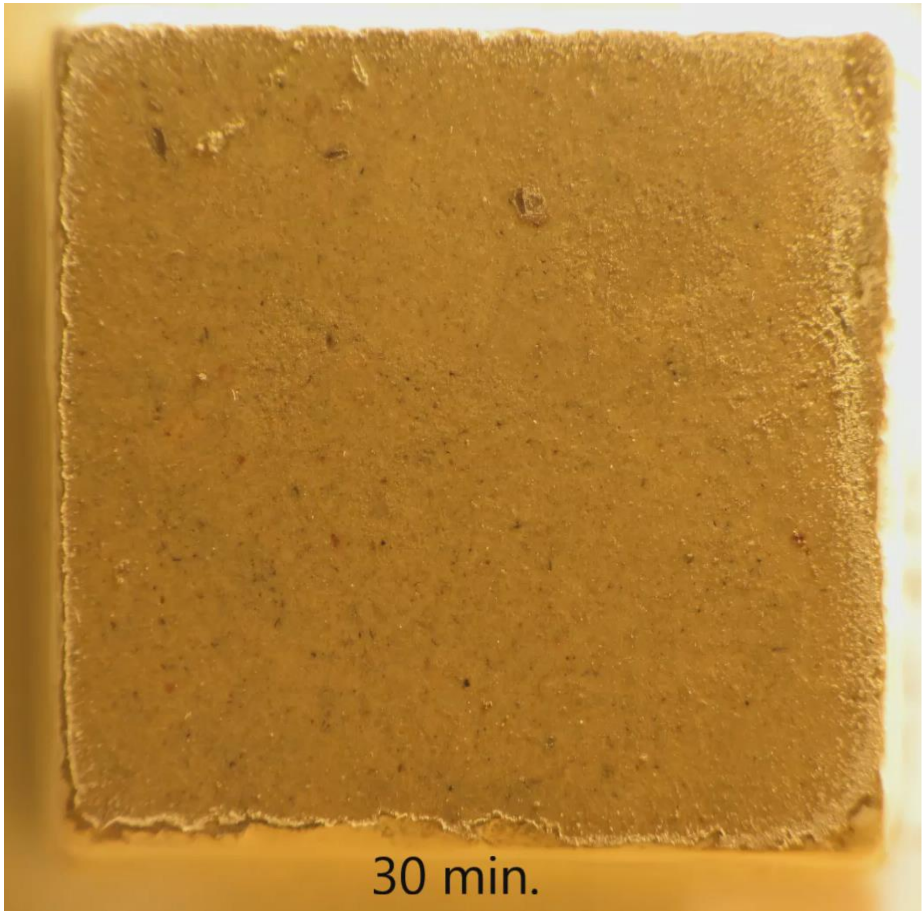

Surface alteration:
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Results and discussion

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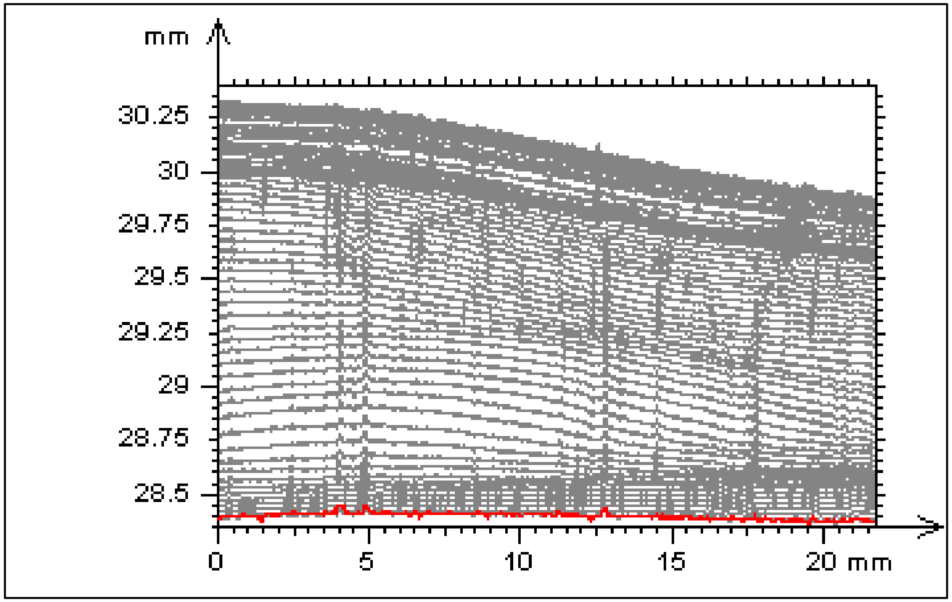
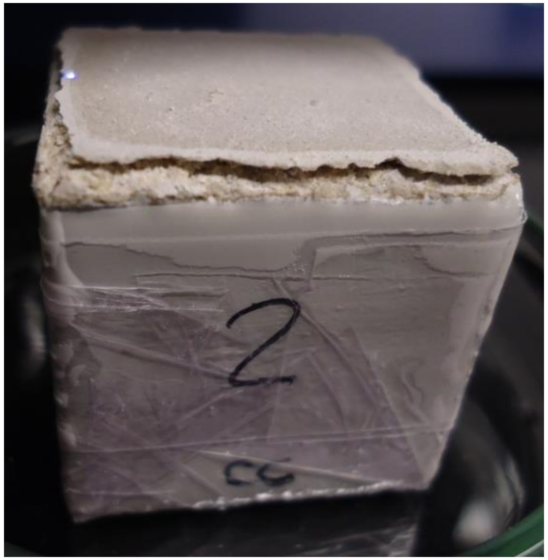


Non-contact profilometry: Profiles every 6 hours

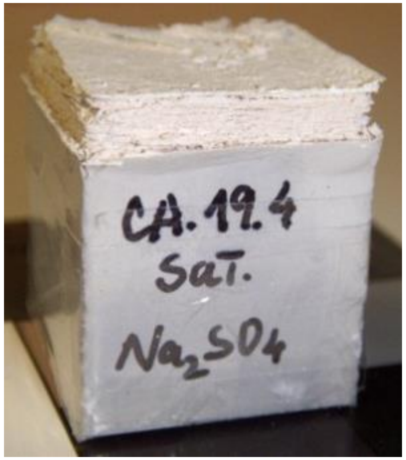


Surface alteration:
uni-layer delamination

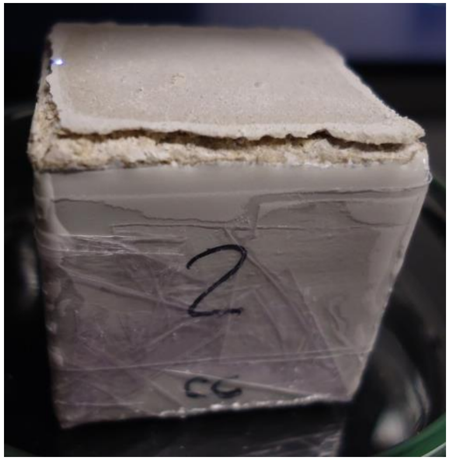
Results and discussion

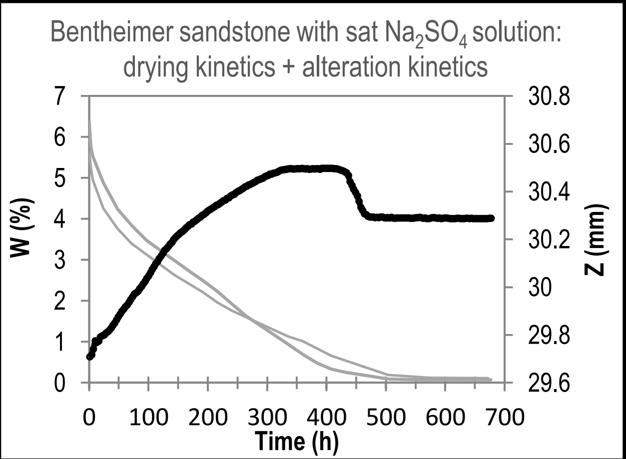
Bentheimer sandstone
efflorescence

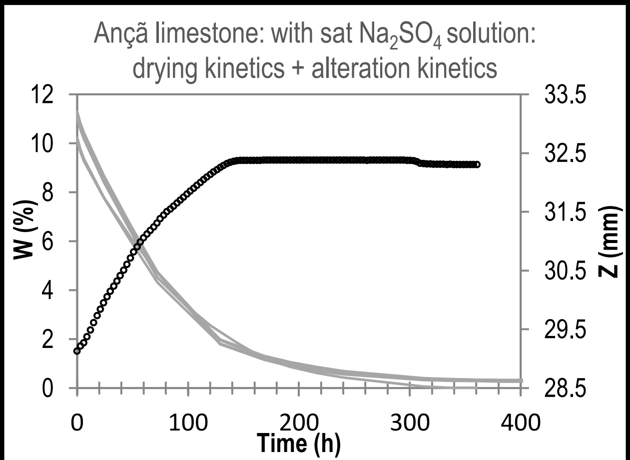
Ançã limestone
multi-layer delamination

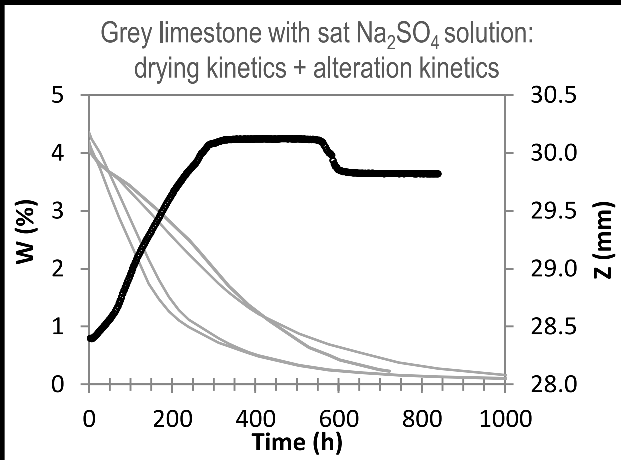


Grey limestone
uni-layer delamination









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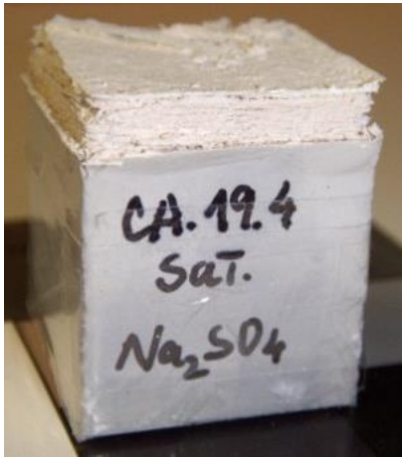
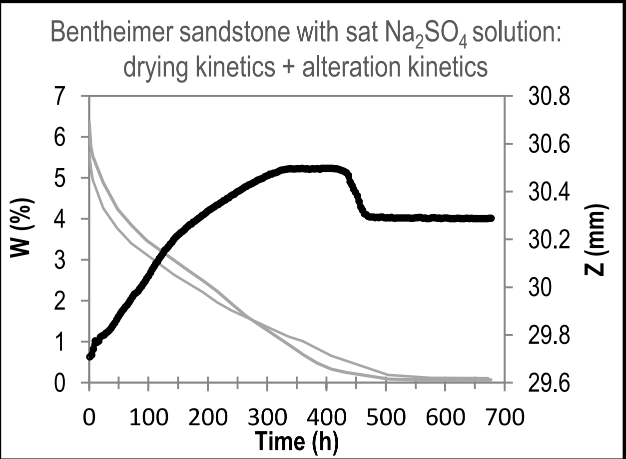
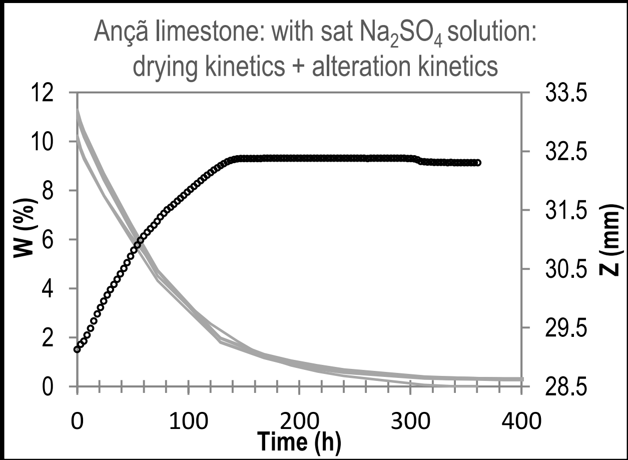
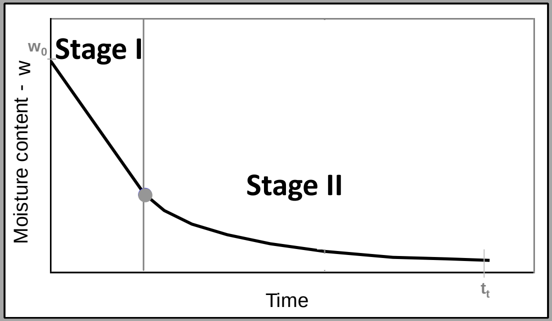


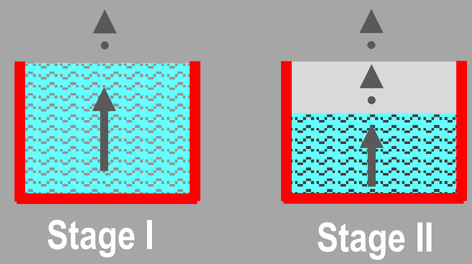




Drying of porous materials with pure water



Typical drying kinetics curve
Stage I => straight line



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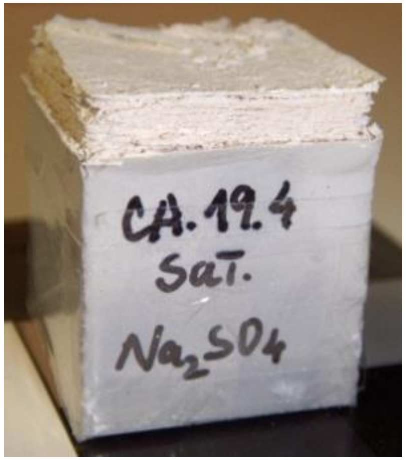
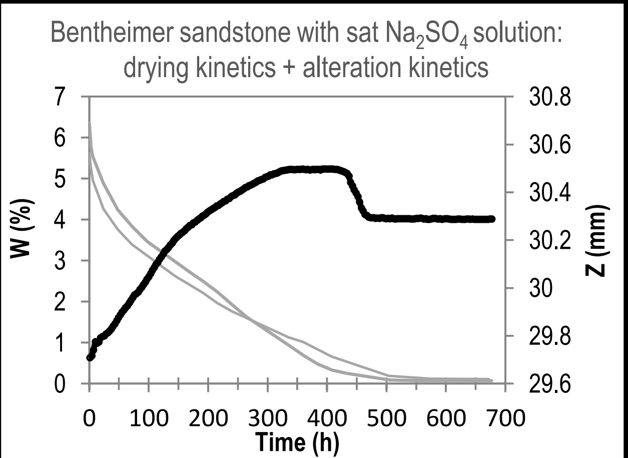
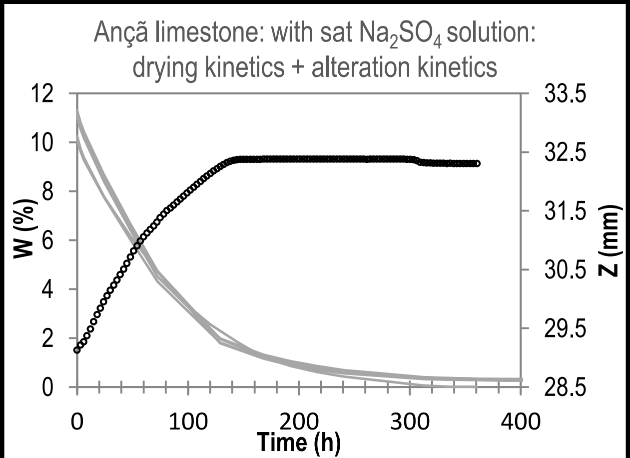
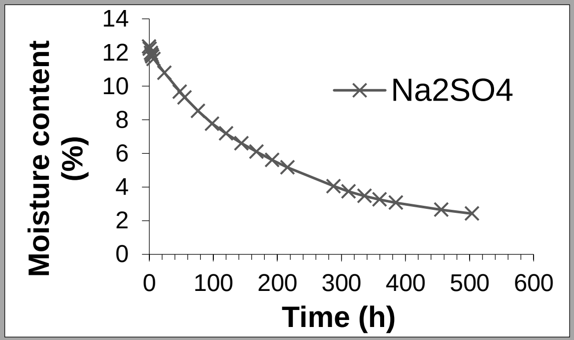


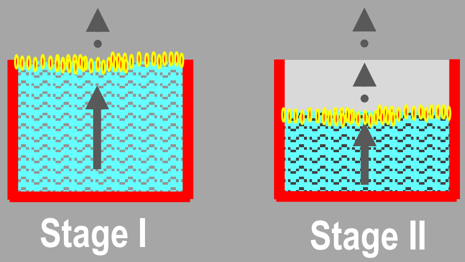




Drying of porous materials with salt solutions

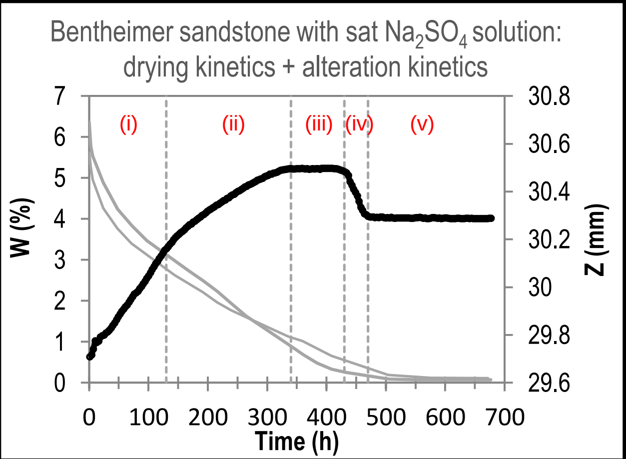


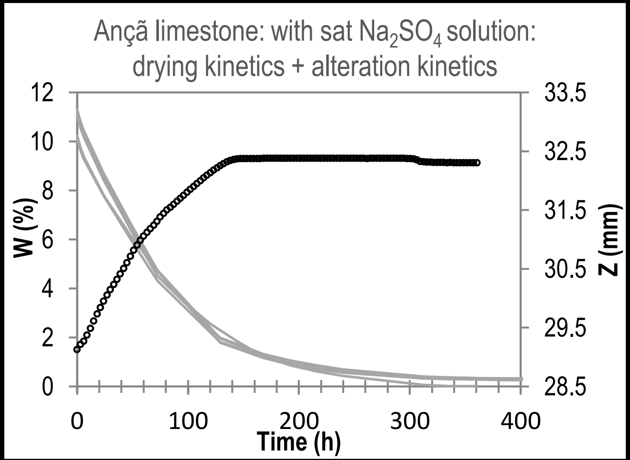
Example of a drying curve
slower drying + irregularities

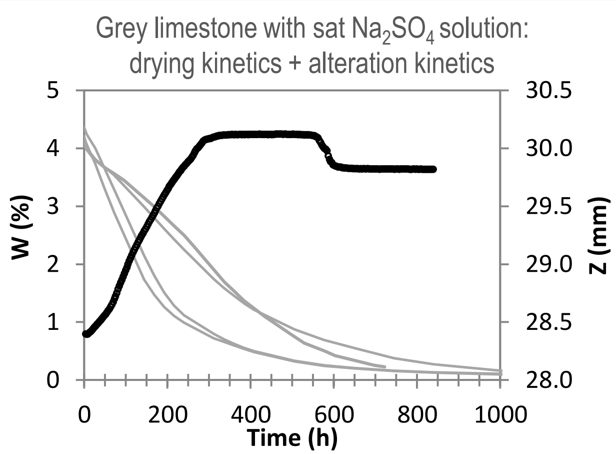


Results and discussion

Bentheimer sandstone
efflorescence



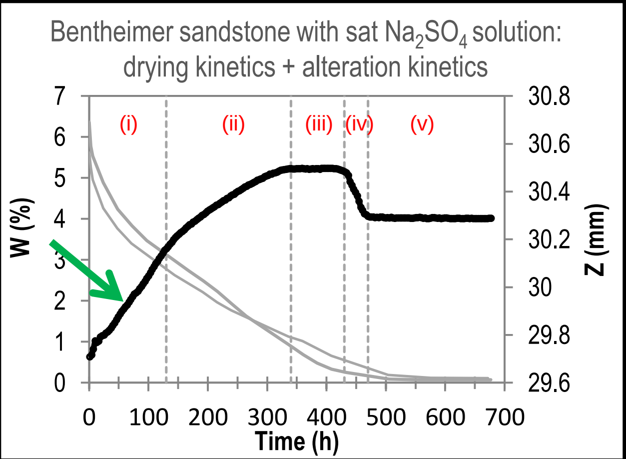


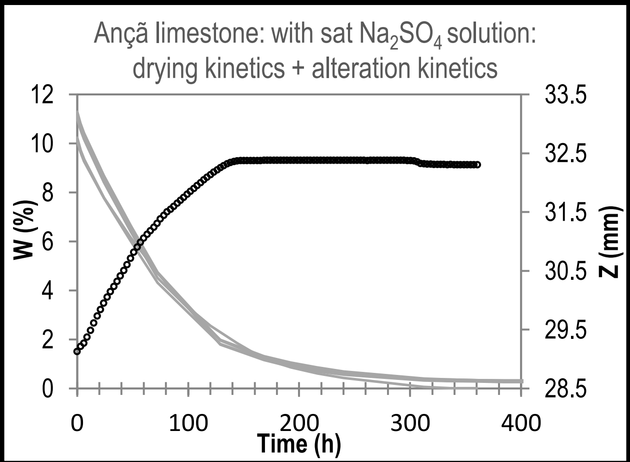


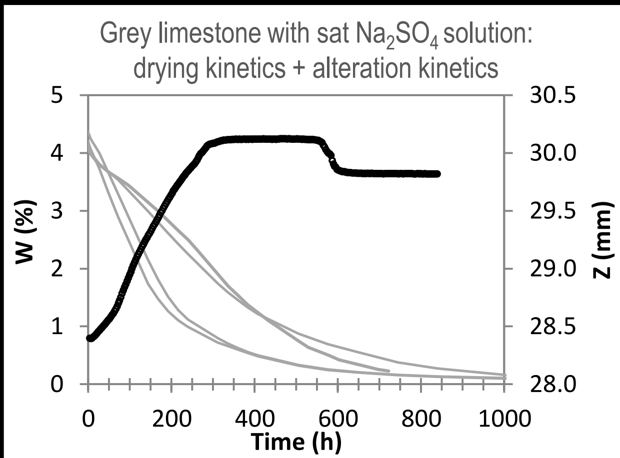
Bentheimer sandstone efflorescence

Results and discussion

i. Efflorescence grows at constant rate (surface is saturated)



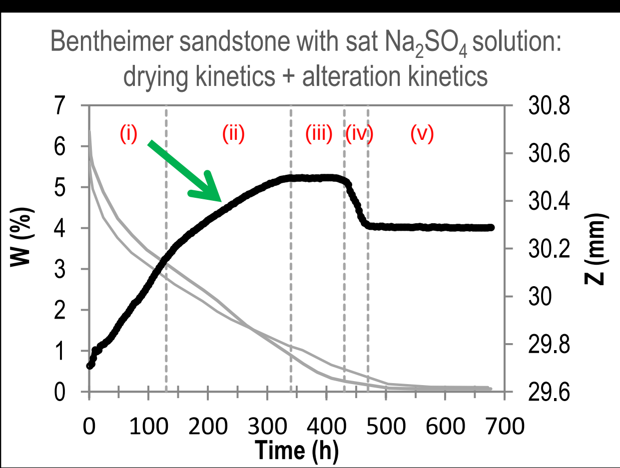


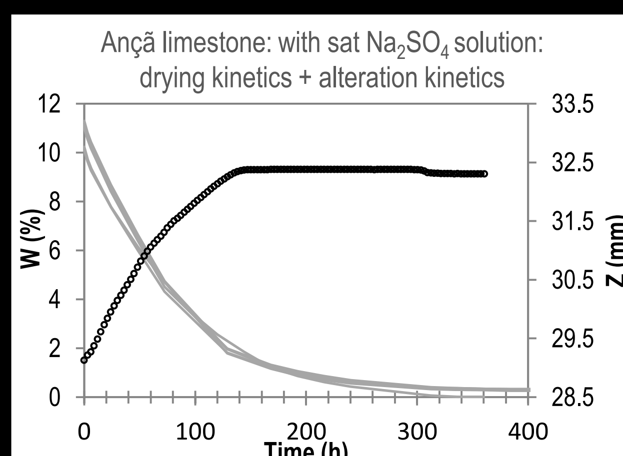


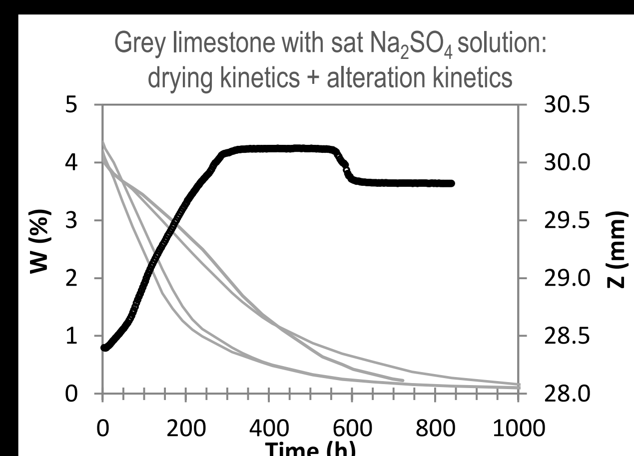
Results and discussion

Bentheimer sandstone
efflorescence

i. Efflorescence grows at constant rate (surface is saturated)
ii. Efflorescence grows at decreasing rate (liquid continuity to the surface progressively reduced)







Results and discussion

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Efflorescence growth stops
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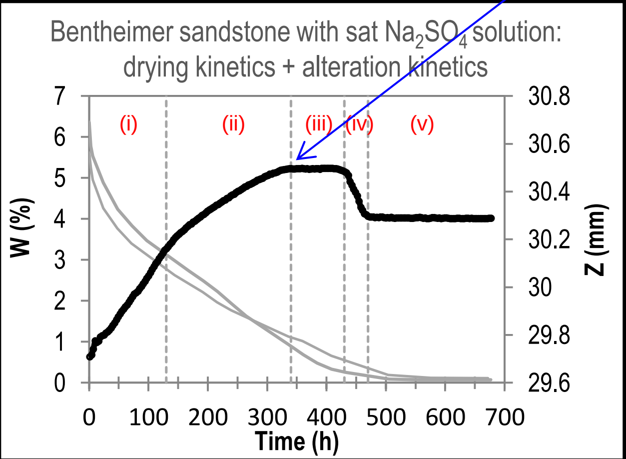

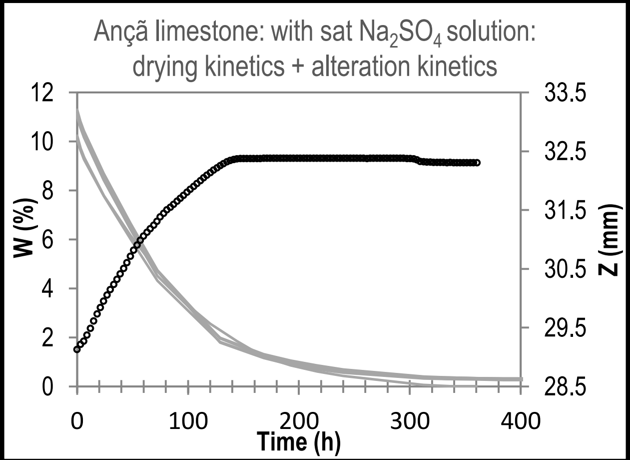

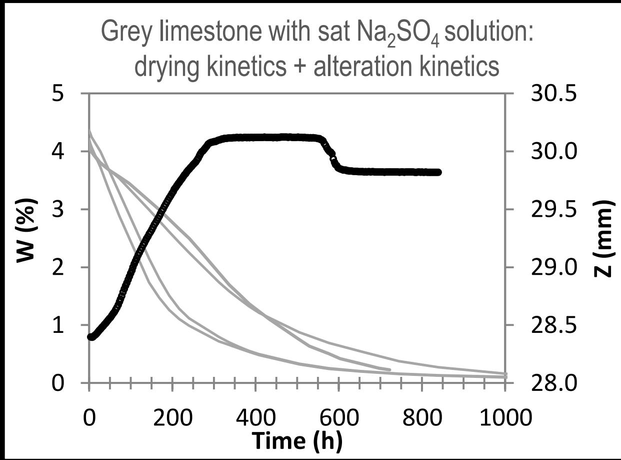

FCT Fundação para a Ciência e a Tecnologia
LNEC LABORATÓRIO NACIONAL DE ENGENHARIA CIVIL

Results and discussion

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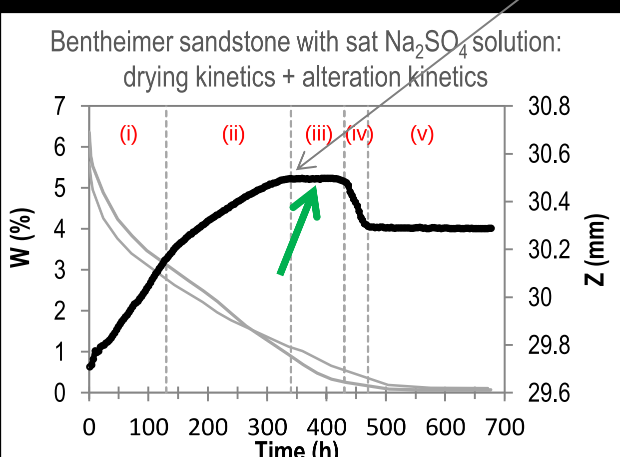

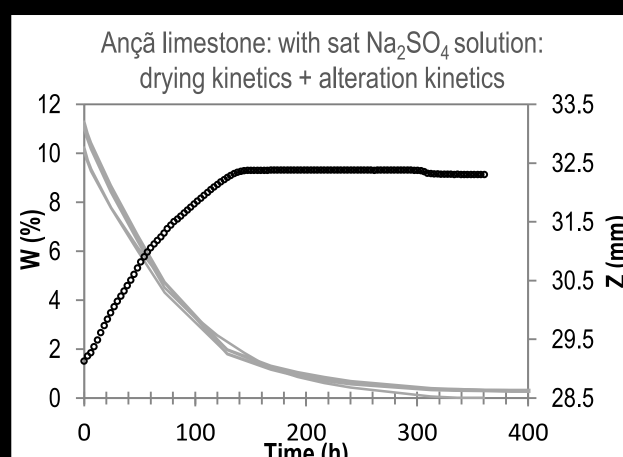

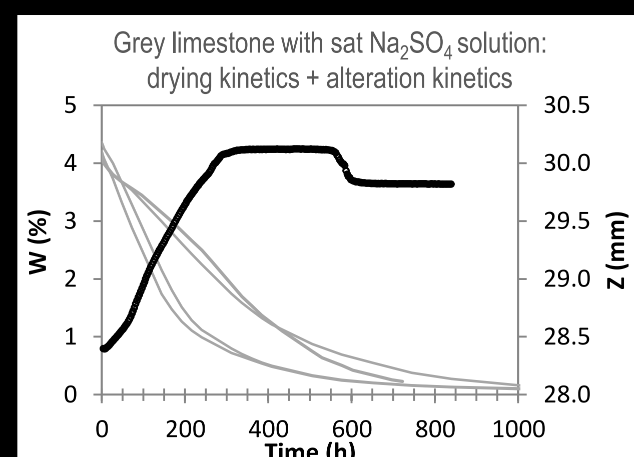

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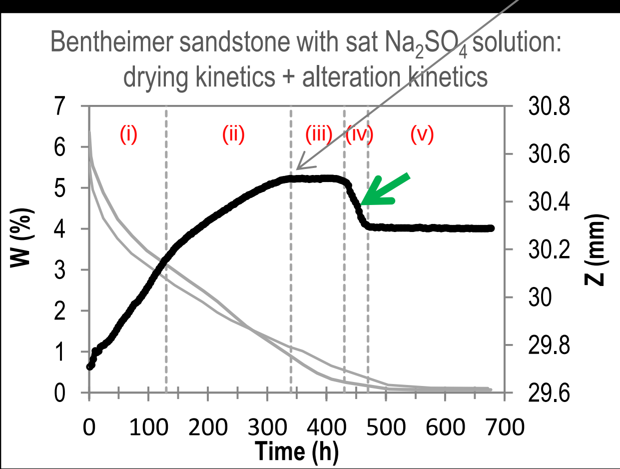

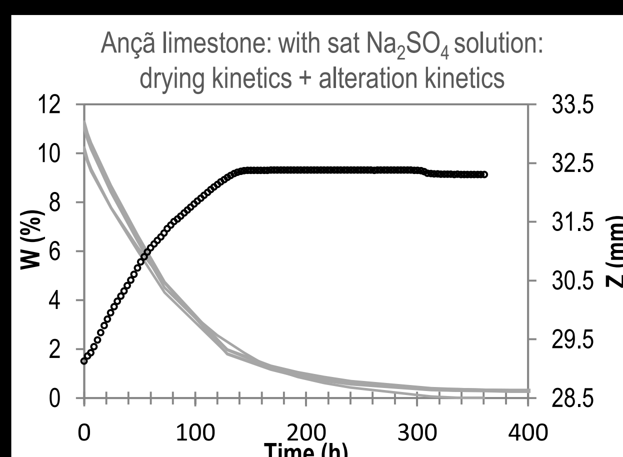

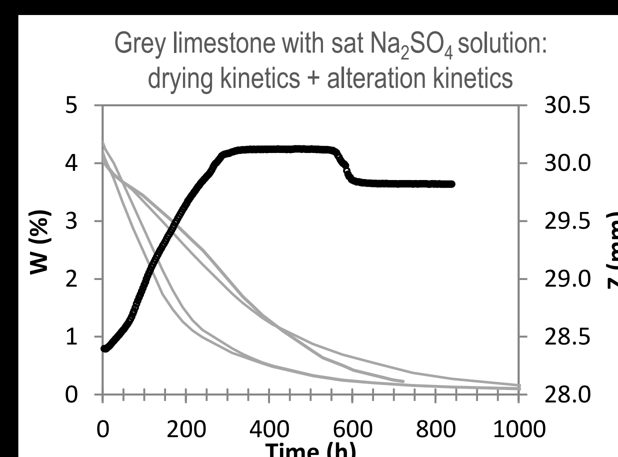

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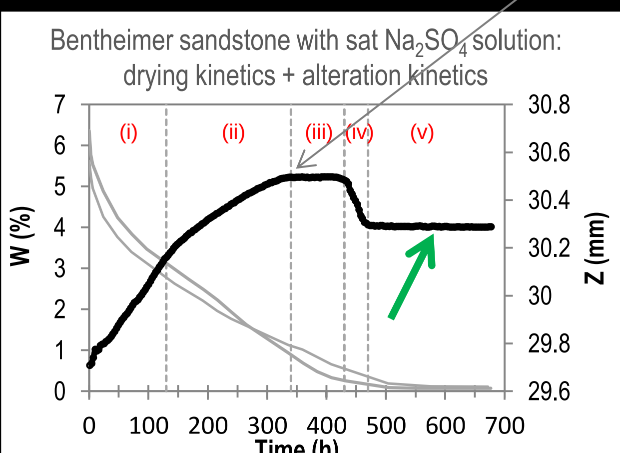
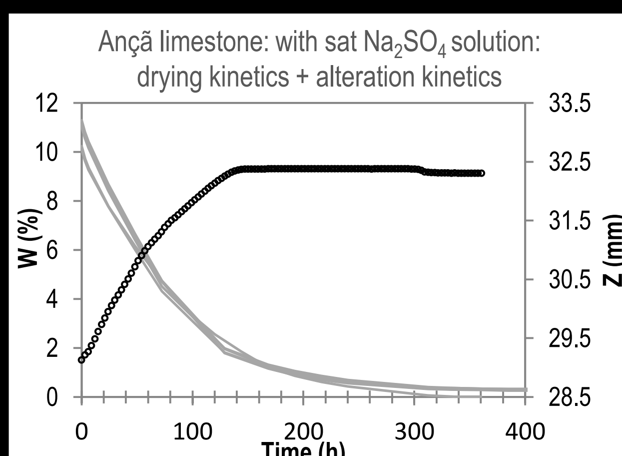
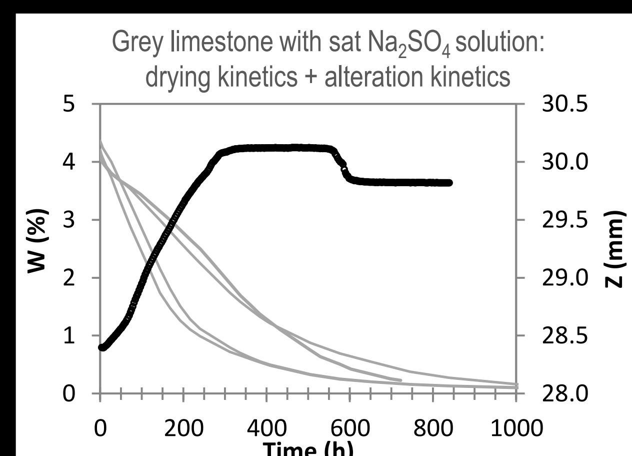
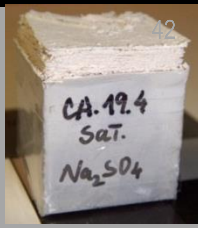






Results and discussion

Ançã limestone
multi-layer delamination



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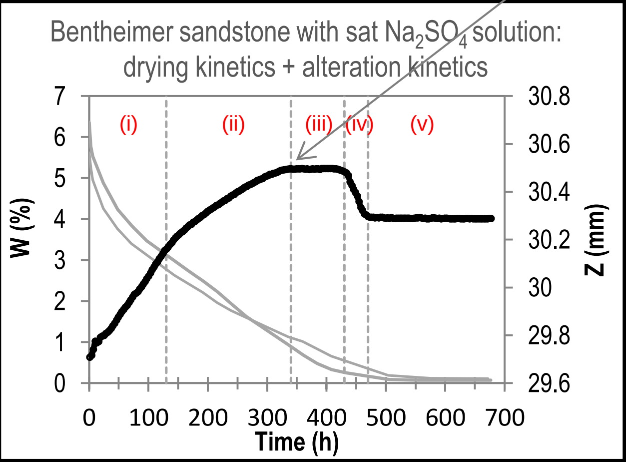

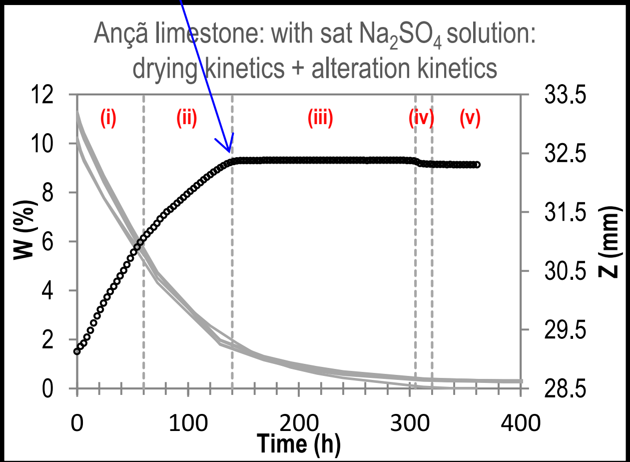

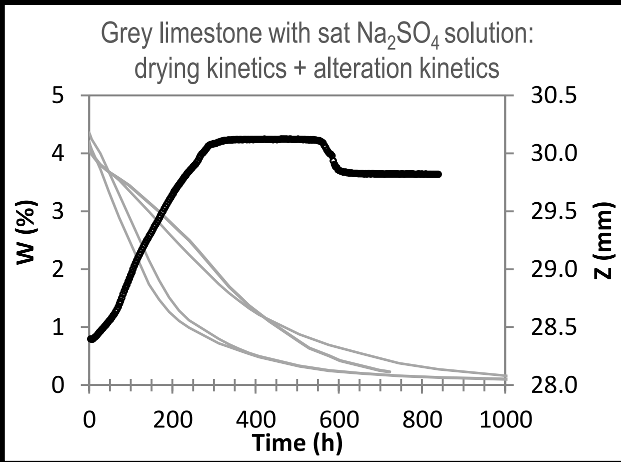

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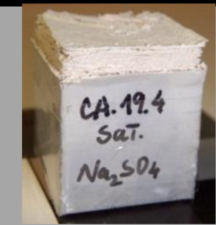

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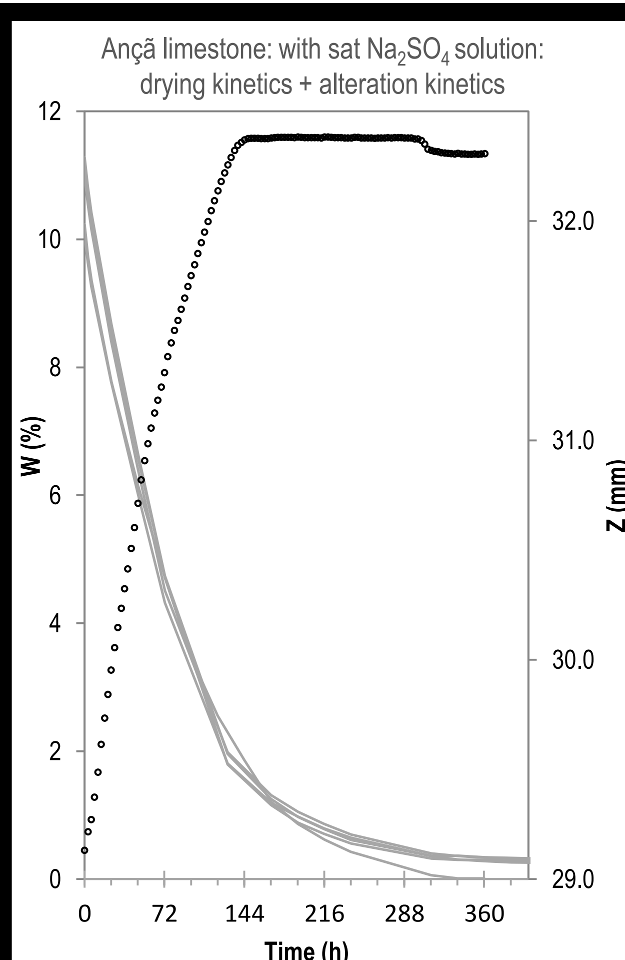

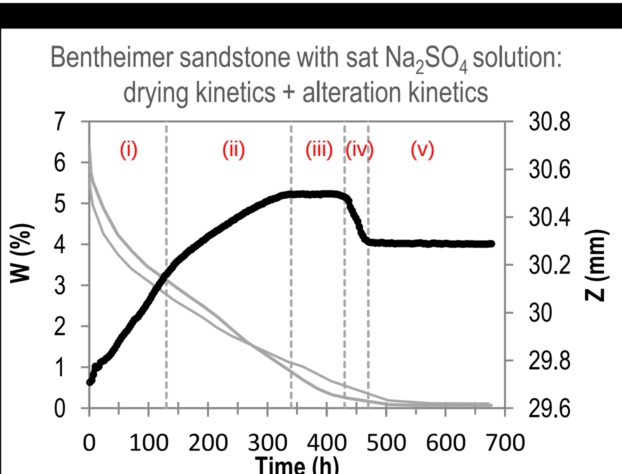

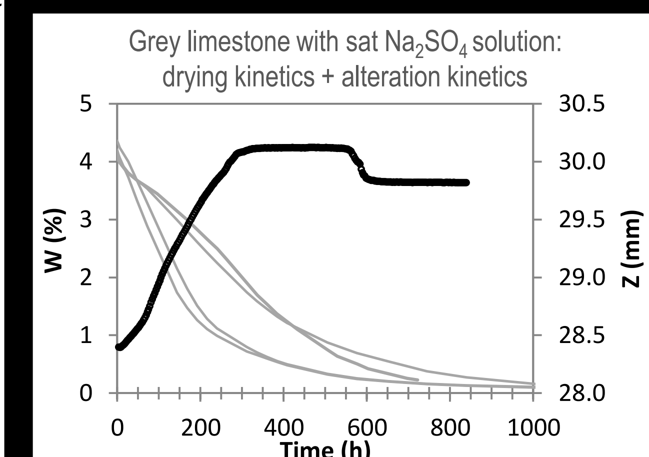

Results and discussion

Grey limestone
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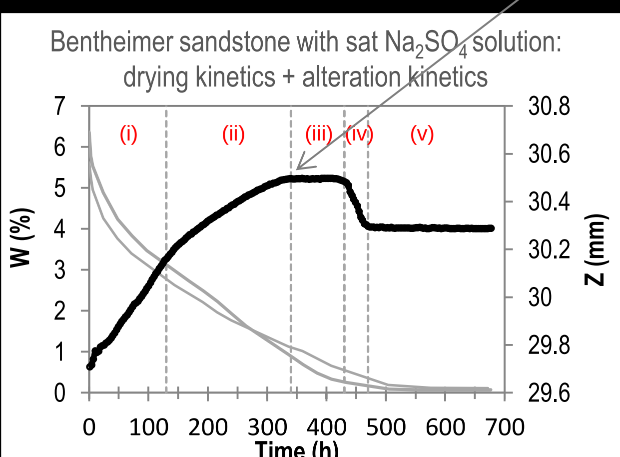

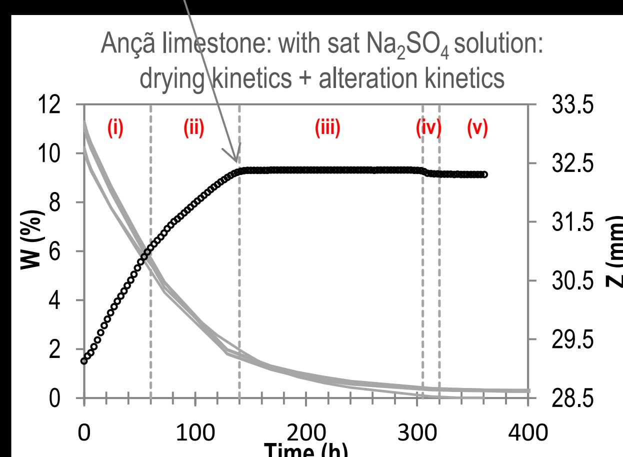

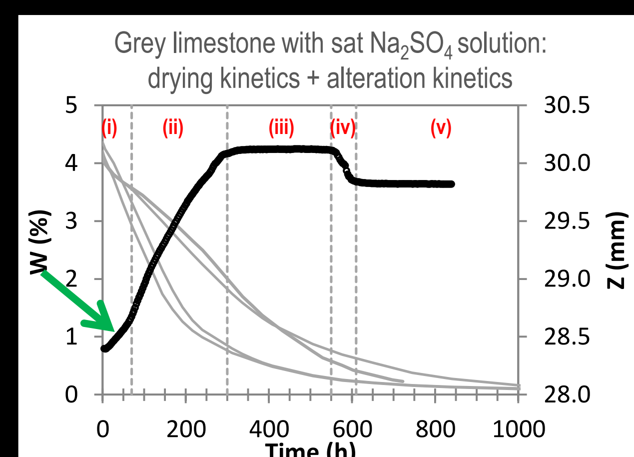

Results and discussion

Grey limestone
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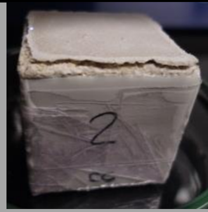

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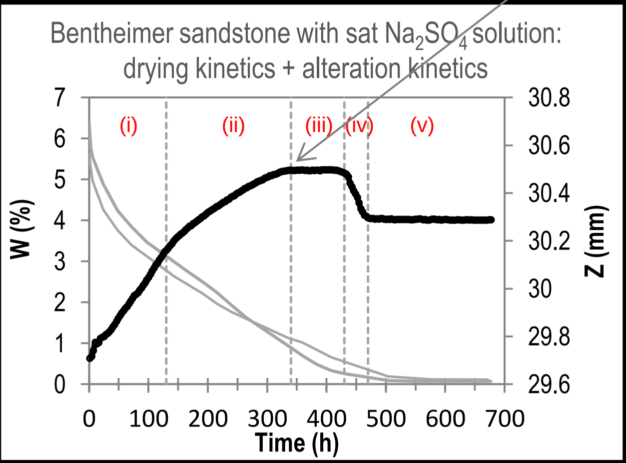
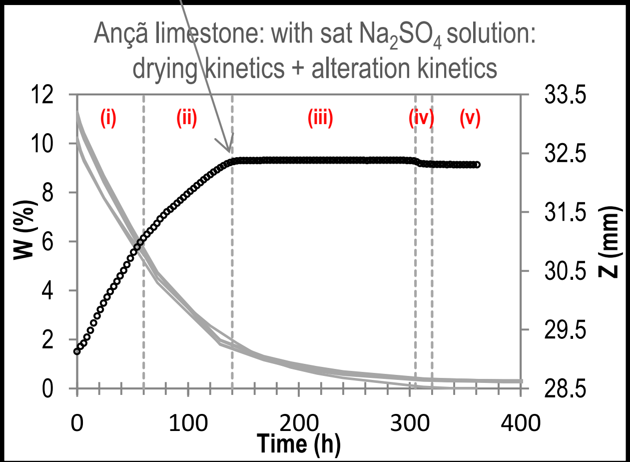
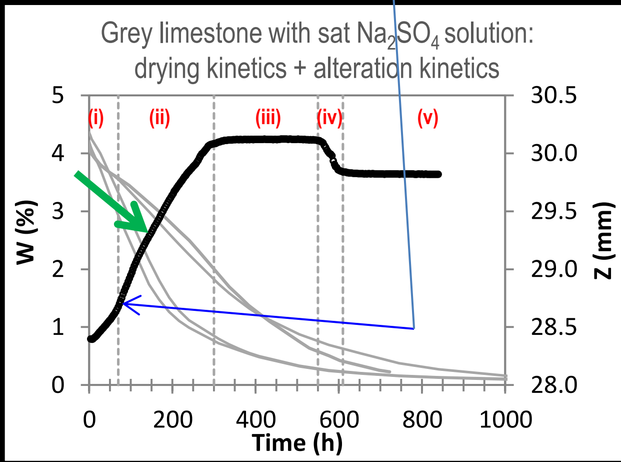
Detachment of the surface layer







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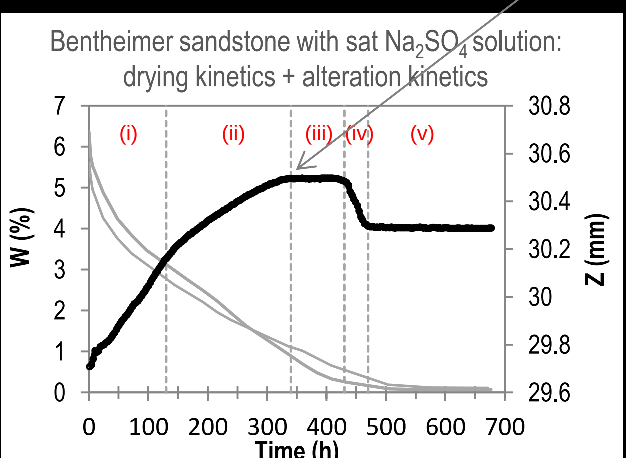

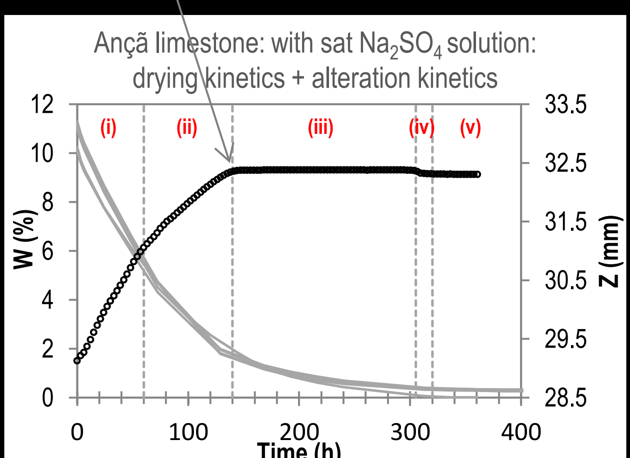

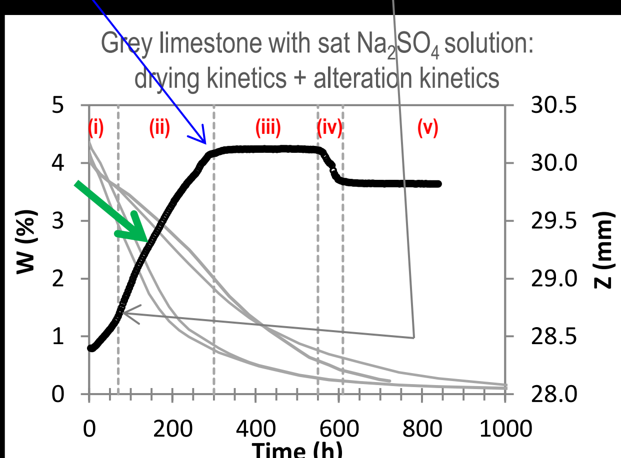

Conclusions

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Diaz Gonçalves T and Brito V (in press) Alteration kinetics of natural stones due to sodium sulphate crystallization: can reality match experimental simulations? Environmental Earth Sciences. DOI:10.1007/s12665-014-3085-0

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- New method:
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Conclusions

- Can sodium sulfate be as much destructive in field conditions? **Yes**
- Delamination pattern: does not require wet/dry cycles
- New method:
  - The optical profiling technique is appropriate to monitor salt decay
  - Alteration kinetics curves are useful to:
    - complement the information provided by gravimetric drying curves
    - understand salt decay mechanisms and behaviours

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Acknowledgements

This work was performed under the research project DRYMASS (ref. PTDC/ECM/100553/2008) which is supported by national funds through the Fundação para a Ciência e a Tecnologia (FCT) and the Laboratório Nacional de Engenharia Civil (LNEC)

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Sílvia Pereira
José Delgado Rodrigues
Luís Nunes
José Costa
Veerle Cnudde
Timo G. Nijland
Manuel Francisco Pereira

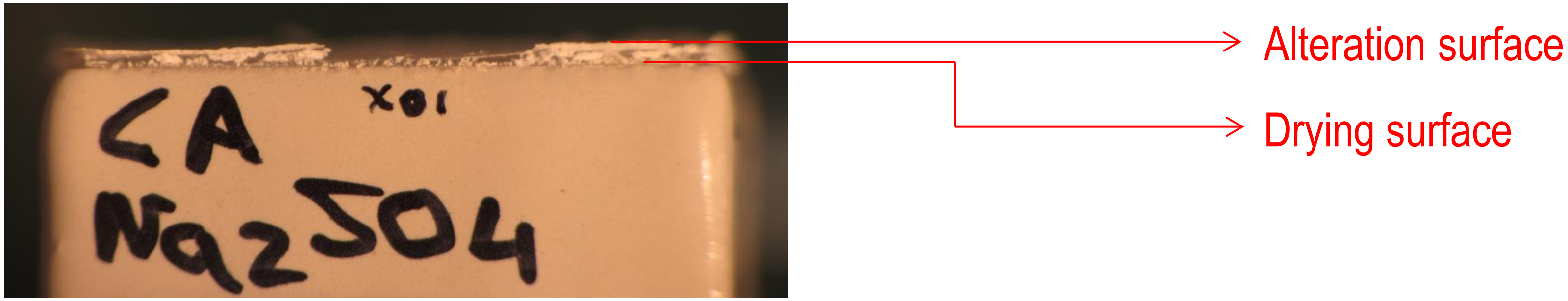
Thank you!

Methods - Crystallization test (single isothermal drying event)

2 - Optical profilometry

Objective: monitor the morphological alterations of the surface

- Profiles obtained every 3 hours: speed =2 mm/s; spacing = 5 µm
- Alteration curve calculated: expresses the average lifting of the surface during the experiment



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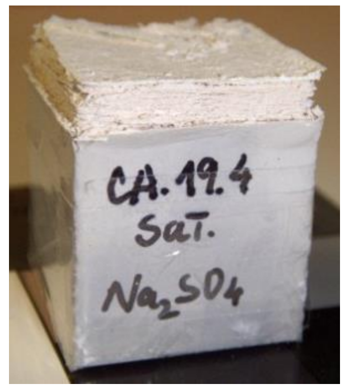

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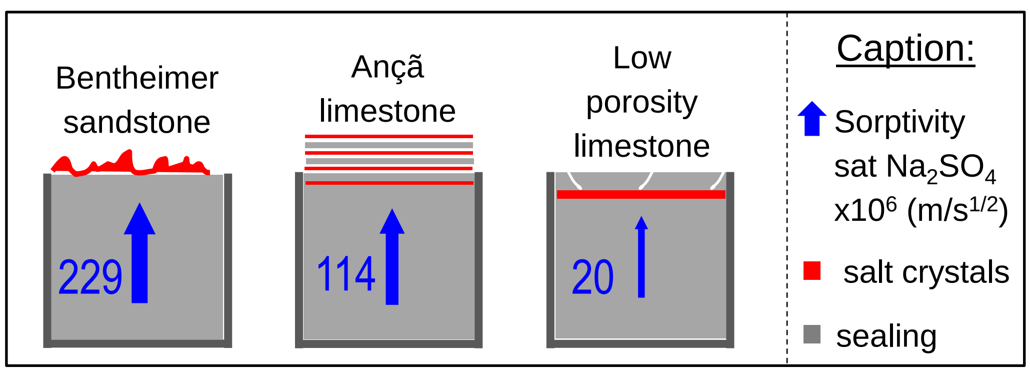

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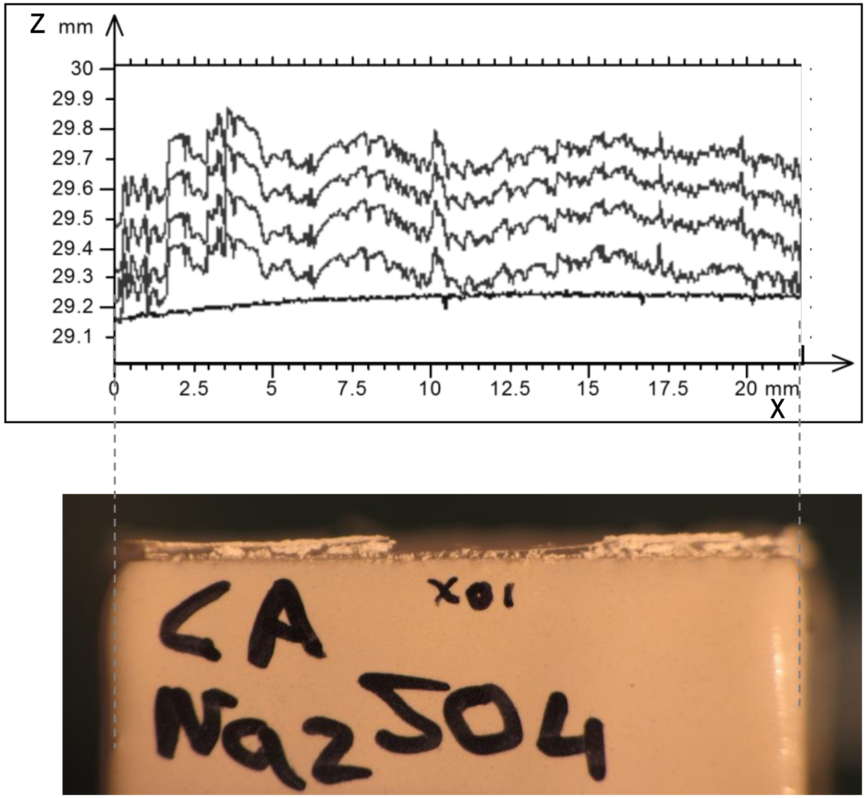

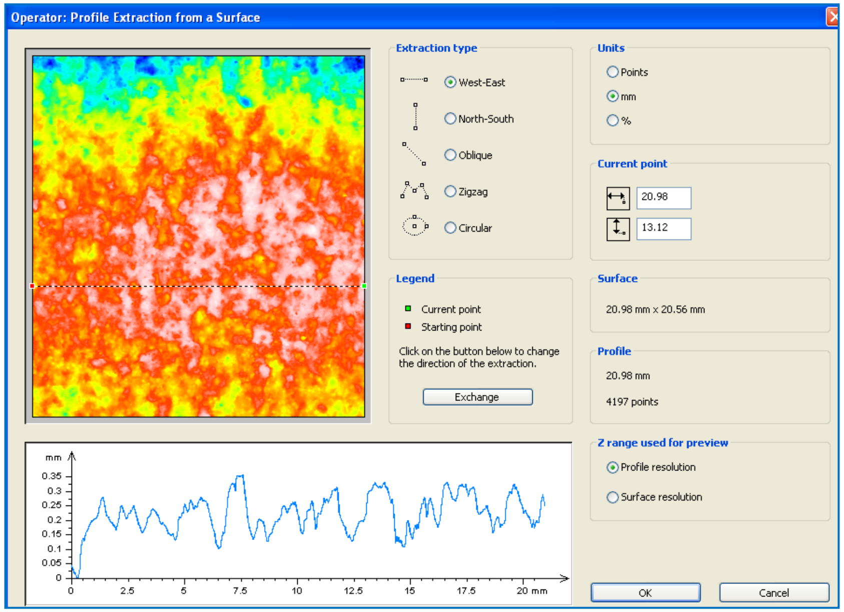

Profile extraction