Freeze-thaw decay in sedimentary rocks: a laboratory study with CT under controlled ambient conditions

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Abstract

This study presents an experimental X-ray micro-CT study of the freeze-thaw processes in limestone under controlled ambient conditions. The processes weres studied with time-lapse micro-CT and dynamic micro-CT, using the Environmental X-ray CT (EMCT) at the Centre for X-ray Tomography of the Ghent University (www.ugct.ugent.be). The EMCT is a gantry-based system on which full µCT scans were aquired in approximately 80 s. A custom made freezing cell was used for freezing experiments to -15 °C with 9 mm diameter samples.

The experimental data show that the observed decay is strongly related to the local water saturation and to the rock texture, i.e. pore size distribution. The decay is expressed by the fracture development in limestone due to ice crystallization. These fractures show a dynamic response to the imposed freeze-thaw cycles. Ice wedging occurs upon the moment of ice crystallization, which is indicated by the release of latent heat. During subsequent thawing, the fractures close. The timing indicates that ice crystallization alone is sufficient to instigate fracturing. Assumptions based on the ice crystallization theory allow to calculate the theoretical pore sizes where ice crystallization occurred. This shows that in these experiments, water crystallizes in the nanometric pores, thus under transient conditions. The existence of such pores were validated with other techniques such as SEM and were linked to the rock features observed with CT.

Introduction

Freeze-thaw processes play an important role in the physical weathering of porous rocks in cold and humid environments (e.g. Ruedrich and Siegesmund, 2007; Matsuoka and Murton, 2008). In the built environment, freeze-thaw deterioration threatens the aesthetic properties of monuments and artwork in our cultural heritage and it can cause actual danger by affecting the structural integrety of building materials. Therefore, it is important to assess the susceptibility of building stones to prolonged freezing and freeze-thaw cycling. This is typically done by normalised freeze-thaw testing. Nevertheless, the extrapolation from laboratory tests to natural conditions is not always easy (Ingham, 2005), and therefore the historical performance is an important criterium as well as are field measurements of freeze-thaw processes (Hall, 2006; Thomachot *et al.*, 2005; McAllister *et al.*, 2013).

To improve the interpretation of macro-scale laboratory experiments, it is important to study the processes involved on the micro-scale (Hall and André, 2003). X-ray CT lends itself as good tool to study the micro-scale effects of freeze-thaw processes. Hence, since the development of laboratory micro-CT, different studies of freeze-thaw processes have been done using micro-CT (Ruiz de Argandona *et al*, 1999; Dewanckele *et al.*, 2013). As these studies focus on the resulting micro-structural effect of freeze-thaw decay on rocks, we focus on the real-time processes of freezing and thawing in porous, sedimentary rocks. Therefore, we perform dynamic imaging of samples under ambient freeze-thaw cycling, with a gantry-based X-ray CT system capable of acquiring full micro-CT scans in the time order of a minute.

The cause for freeze-thaw decay is the stress induced by the crystallization of ice within the pore network (Scherer, 1999; Steiger, 2005), where the freezing point is depressed for capillary water according to the Kelvin equation (e.g. Ruedrich *et al.*, 2011). The main precondition for freeze-thaw decay is that the macroscopic stress induced by ice crystallization pressure exceeds rock strength, fixed by a strength-controlling flaw. Hence whether or not building stones will experience freeze-thaw decay depends on their intrinsic properties and the environmental conditions to which they are subjected. In these experiments, we focus on the spatial pore size distribution of the samples, local water saturation and freezing temperature.

Methods

X-ray micro-CT was performed at the Centre for X-ray Tomography of the Ghent University (UGCT; www.ugct.ugent.be; Masschaele *et al.*, 2007) using two custom-built laboratory micro-CT scanners: HECTOR (Masschaele *et al*., 2013) and EMCT (Dierick *et al.*, 2014). HECTOR was used to obtain high resolution (< 10 µm) images of reference samples or subsamples from laboratory freeze-thaw experiments.

Dynamic X-ray micro-CT experiments were performed with EMCT, using cylindrical samples of 9 mm diameter. The samples were water-saturated by atmospheric imbibition for 24h. Subsequently, they were subjected to ambient freeze-thaw cyling from 20°C -15 °C using a custom made freezing stage (De Schryver *et al.*, 2015). The sampled were scanned in the middle of each freezing and thawing phase. Moreover, continuous scanning was performed for 24 minutes during the cooling phase, resulting in 14400 projections of 100 ms exposure time over 18 full-360° rotations. The X-ray tube was operated at a tube voltage of 65 kV and a power of 14.3W. The reconstructed voxel resolution was around 20 µm.

Laboratory freeze-thaw cycling was performed according to the European Standard EN 12371 (2010) on 40 mm edge cubic samples with 6h of freezing at -12°C, followed by 6h of thawing while immersed in water of 20 °C.

A Zeiss Axioscope with camera was used for petrographical description of uncovered 30 µm thin sections stained with Alizarine Red-S. Scanning electron microscopy (SEM) was done with a FEIT Quanta 200F on gold-coated samples. Petrophysical properties were determined according to the appropriate European Standards.

The experiments were performed on different sedimentary rocks, used as building materials in Belgium. Here we focus on some results of a porous miliolid limestone from the Paris basin, which are more thoroughly discussed in De Kock *et al.*, 2015 and some preliminary results of a sandy limestone, Lede stone, and an oolitic limestone Massangis, whos properties were discussed in De Kock *et al.*, 2013.

Results and discussion

Micro-CT allows to visualize the micro-scale freeze-thaw decay of the porous samples. The freeze-thaw cycling results in the development of fractures within the sample (Figure 1). This is the result of ice wedging, a process where the ice crystals push the fracture surfaces apart. The development of the fractures is strongly related to the rocks' fabric. More specifically, they develop within the planes of discoidal forams, which are microfossils. It was already shown by Dewanckele *et al.* (2013) that these act as flaws. Capillary rise experiments show that these forams acts as preferential water uptake paths. Therefore it is assumed that the water saturation is relatively high in the volume fraction of the rock around these forams during freezing, increasing the volume that can be affected by freezing. Hence, there seems to be a clear link between local saturation and freeze-thaw decay.

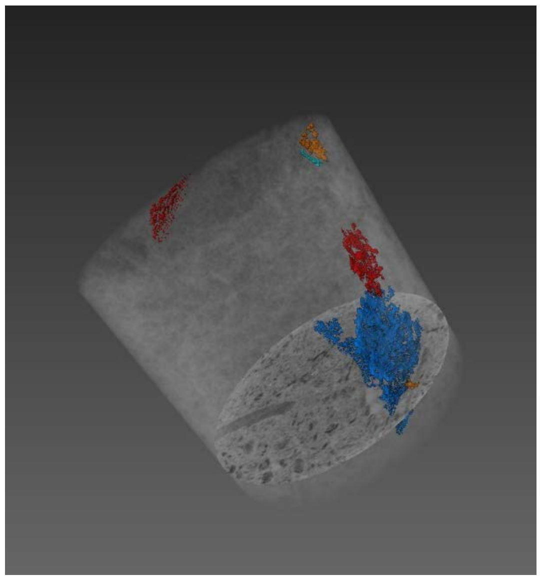

Fig. 1. *Fractures segmented (in colour) within the bulk volume (transparent) and one reference slice (opaque). Sample diameter is 9 mm.*

Figure 2 shows the development and growth of the fracture in size in function of the freeze-thaw cycles. During the second cycle, it can be seen that a fracture develops, which cannot be segmented due to the partial volume effect. From the 3rd freeze-thaw cycle, however, the fracture is large enough to be segmented and this enables that its volume can be analysed. First of all, it can be seen that the fracture opens during freezing en closes during subsequent thawing. This is in favour of the ice crystallisation theory as discussed in the introduction. After successive freeze-thaw cycling, there is a progressive opening of the fracture, allowing to observe fracture propagation. After the 4th cycle, the fracture does not close entirely and there is residual strain. Finally, the crack size also stagnates in the last cycles, illustrating that the facture volume accommodates the ice crystallization.

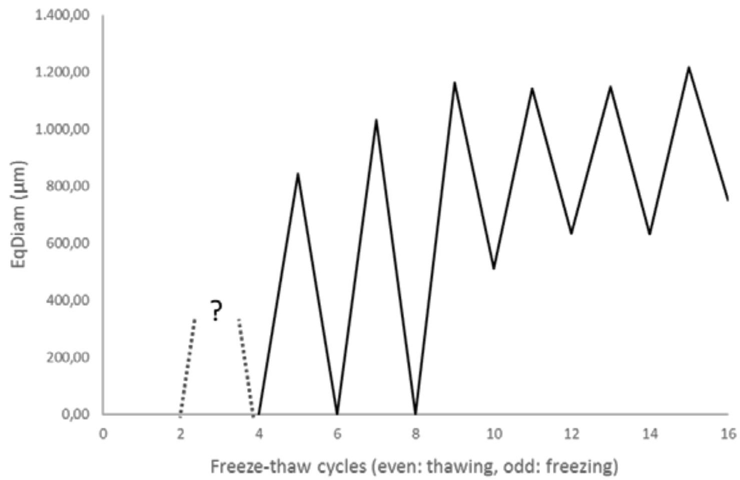

Fig. 2. *Size of a fracture expressed as equivalent diameter in function of successive freeze-thaw cycles.*

During cooling a temperature exotherm, considered as a proxy for ice crystallization, was recorded at a temperature of -9.7°C. According to the Kelvin equation for freezing point depression, this corresponds to crystallisation in pores smaller than 20 nm. As it is thermodynamical more favorable to crystallize within larger pores (Everett, 1961), crystallization in these experiments occurs under transient conditions. Most likely, this is related to the probability of having a nucleation site within such a small sample (Sun and Scherer, 2010). Figure 3 consists of a SEM image showing the presence of such small pores within the tests of these forams. The susceptibility of this sample to freeze-thaw decay is thus related to a combination of larger pores as the foram's test chambers which have a higher capillary suction velocity resulting in higher local water saturation, with nanometric pores from the test itself that provide a higher probability of nucleation sites.

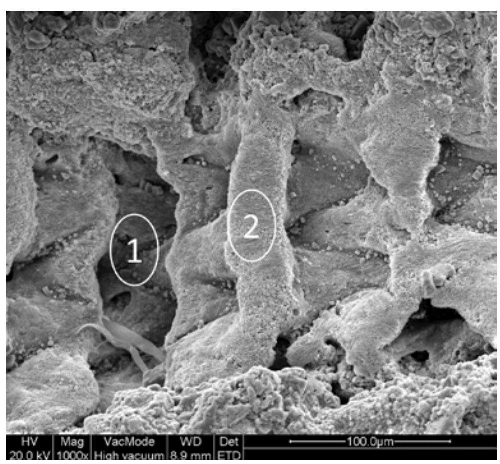

Fig. 3. *SEM image of part of the foram's test, with larger interparticular micrometer pores (1) and nanometric pores in the test (2).*

In addition, continuous scanning allows to visualise the dynamics in the sample during freezing. It can be seen that the fracturing is abrupt and coincides perfectly in time with the occurrence of the exotherm. This validates the ice crystallization theory as mechanism for freeze-thaw decay in these experiments.

Preliminary results of experiments with other stones also illustrate the relation of freeze-thaw fractures with the rock's fabric, more specifically with the fabrics that promote a high local saturation degree.

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