Salt weathering and ultrasonic pulse velocity: condition assessment of salt damaged porous limestone

N Rozgonyi-Boissinot, M A Khodabandeh, A Besharatinezhad and Á Török

Department of Engineering Geology and Geotechnics, Budapest University of Technology and Economics, Budapest, Hungary
torok.akos@emk.bme.hu

Abstract. Salt weathering is one of the crucial causes of building stone decay. For assessing the durability of stones against salt weathering, a standardised test procedure (EN 12370:2020 Determination of resistance to salt crystallisation) is used: the mass loss of the stone is measured during sodium sulphate crystallisation cycles. Porous, Miocene limestone test specimens collected from the Sóskút quarry (Hungary) were subjected to salt crystallisation cycles in laboratory conditions. The limestone with open porosities of up to 32 V% is composed of ooids, various types of bioclasts and other carbonate grains. Besides the classical measurements of mass changes, the ultrasonic pulse velocity was also recorded after each crystallisation cycle. The ultrasonic pulse velocity values of quarry stones and salt-laden porous limestone specimens were compared. The results indicate that when salt crystal clogs the pores, an increase in ultrasonic pulse velocity is observed. Additional salt crystallisation cycles reduce the pulse velocity. This negative shift in pulse velocities is linked to the opening of micro-cracks, indicating the damage of the studied limestone. Our tests have proved that ultrasonic pulse velocity testing device can detect salt crystallisation damage in a non-destructive way. Its application is recommended in the condition assessment of salt damaged stone heritage structures.

1. Introduction

The crystallisation of salts is one of the critical processes of weathering on stone-built monuments. Salt crystallisation can occur in a wide range of different environments like urban areas [1], deserts [2], forests, coastal areas, etc. This phenomenon has been observed under a vast range of relative humidity and temperature [3]. A clear understanding of the salt weathering process and critical parameters involving this phenomenon is demanded [4]. In recent years many studies regarding salt crystallisation and the main parameters affecting this phenomenon have been concluded [5-7]. According to Martinez et al. [5], salt mixture crystallisation is susceptible to temperature and relative humidity changes. Sato and Hattanji [6] investigated salt weathering of three types of rock (tuff, porous and dense sandstone) with sodium chloride, sodium sulphate, and magnesium sulphate under changing humidity conditions. The results showed that the most harmful salt is NaCl, but MgSO₄ also damaged all tested lithotypes. On the other hand, Na₂SO₄ had no effect on salt weathering in high humidity conditions.

Porosity is one of the most important parameters affecting rock behaviour during salt crystallisation. Compared with rocks with lower porosity, stones with high porosity are expected to undergo a high degree of decay [6-7].

An affordable and non-destructive technique for evaluating the physical and mechanical properties of rocks is determining ultrasonic waves propagation in rocks. It is increasingly used in geotechnical
engineering because this method is non-destructive and easy to implement [8]. The density and elasticity properties of the stone and the type of waves influence the velocity of ultrasonic waves. Two types of waves can be differentiated depending on the propagation mode and the arrival time of the wave: primary, compression or longitudinal wave (P wave) and secondary, transversal or shear wave (S wave). The manual determination of P wave arrival because of its high signal-to-noise ratio (SNR) is difficult. Determination of S wave is problematic because it is contaminated with P wave and manual picking of S wave arrival is challenging even for skilled engineers. One approach for estimating wave arrival was using the short-term average – long-term average (STA/LTA) ratio [9]. This method was used for P wave arrival identification and was dependent on variations in the signal's energy densities. However, evaluation of the signals with large amplitudes and low SNR were the limitations of this method [10]. To overcome the STA/LTA method’s limitation, modified energy ratio approach (MER) was developed based on STA/LTA. For data with a low SNR, the MER method provided more reliable results than the STA/LTA method. This approach successfully reduced the amplitude of the signal, which was one of the key factors in determining the first onset of the wave [10]. These procedures had the ability to determine P wave velocity precisely when the main signal was contaminated with low noises. But when the signal was highly contaminated with noises and for determining S wave velocity, these methods did not perform correctly. Benavente et al. [11] proposed an automatic algorithm to determine S and P waves’ first onset. Wavelet analysis was used to improve SNR. The output signal was filtered to attenuate the noises and reduce incoming pulses’ effect due to the reflection and diffraction.

In this study, the ultrasonic wave velocities (P and S waves) due to salt crystallisation in limestone samples were investigated. 15 and 50 salt cycles with sodium sulphate solution according to DIN EN 12370 were implemented. A Pundit (Portable Ultrasonic Non-destructive Digital Indicating Tester) instrument was used to determine the P wave velocity of samples before salt crystallisation and after each salt crystallisation cycle. Geotron (Consonic C2-GS Geotron Elektronik) instrument was used to determine P and S waves velocities on the samples after 15 and 50 salt crystallisation cycles and on samples without salt weathering.

2. Materials and methods

Highly porous limestone obtained from Sóskút (near to Budapest, Hungary) were tested. Nine cylindrical samples were prepared with diameter of 36-37 mm and height of 34-37 mm. The porosity of the studied specimens was between 24 and 32 V%. Moisture content, air dry and oven-dried densities were recorded prior to and after salt crystallisation tests (table 1). Samples SC15-2 and SC50-3 before salt crystallisation and after 15 and 50 cycles of salt crystallisation were presented (figure 1).

| Sample code | Salt cycles | Moisture (air dry) content (w%) | Density (air dry) (gr/cm3) | Density (dried) (gr/cm3) |
|-------------|-------------|---------------------------------|---------------------------|--------------------------|
| 1           | -           | 0.18                            | 1.559                     | 1.557                    |
| 2           | -           | 0.24                            | 1.480                     | 1.476                    |
| 3           | -           | 0.19                            | 1.737                     | 1.733                    |
| 4           | -           | 0.22                            | 1.539                     | 1.535                    |
| SC15-1      | 15          | 0.09                            | 1.526                     | 1.524                    |
| SC15-2      | 15          | 0.07                            | 1.541                     | 1.540                    |
| SC50-1      | 50          | 0.10                            | 1.505                     | 1.503                    |
| SC50-2      | 50          | 0.10                            | 1.551                     | 1.549                    |
| SC50-3      | 50          | 0.17                            | 1.811                     | 1.808                    |
Salt crystallisation tests were made according to the standard procedure of EN 12370. The samples were artificially weathered by complete immersion in a 14 w% sodium sulphate decahydrate solution (\(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}\)) and then dried in a ventilated oven. Each salt crystallisation cycle consisted of 2 hours of immersion in a 14 w% \(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}\) solution in 20 °C, followed by oven-drying. In the drying phase, the temperature was gradually raised until 105 °C in 10 hours, then kept there for 10 hours. It was followed by the cooling cycle that lasted for 2 hours at room temperature (20 °C). Before the next salt cycle, weight change and ultrasonic sound velocity were measured. Two samples were exposed for 15 salt crystallisation cycles, and three samples were submitted to 50 salt crystallisation cycles, while four samples were kept as reference (see table 1). Samples were not washed out in the water after salt crystallisation. Ultrasonic wave velocities of samples were measured by two instruments (Pundit and Geotron) (figure 2) after each salt crystallisation cycle. Test conditions for these two instruments were different (table 2).

**Table 2. Test conditions for Pundit and Geotron instruments**

| Instrument | Travel time | Wave form | Plasticine | Frequency | Result          |
|------------|-------------|-----------|------------|-----------|----------------|
| Pundit     | ✓           | -         | ✓          | 50 kHz    | P-wave         |
| Geotron    | ✓ ✓         | ✓         | -          | 80 kHz    | P and S waves |

Pundit (Portable Ultrasonic Non-destructive Digital Indicating Tester) is an easy to use equipment (figure 2a). The determination of P wave propagation time is automatic. The frequency of the transducers was 50 kHz. Plasticine was used as a coupling agent to fill the gap between transducers and the sample.

For Geotron measurements, UP-SW transducers were used (figure 2b) with 80kHz frequency. UP-SW transducers propagate ultrasonic waves to determine elastic material parameters. These transducers facilitate the determination of the arrival of the S wave because the longitudinal waves are highly attenuated. P and S wave velocities were measured five times on the same sample prior to and

**Figure 1. Photos of porous limestone samples a) sample SC15-2 before salt crystallisation (diameter =37.01 mm) b) sample SC15-2 after 15 cycles of salt crystallisation c) sample SC50-3 before salt crystallisation (diameter =36.81 mm) d) sample SC50-3 after 50 cycles of salt crystallisation**
after the salt crystallisation cycles. For the identification of the first onset of P wave and S wave, the selected amplitudes were 50mV and 2V, respectively. The results were evaluated manually by Lighthouse Software (Geotron). The waveforms were determined with the software.

**Figure 2.** Ultrasonic sound testing devices: a) Pundit instrument (Portable Ultrasonic Non-destructive Digital Indicating Tester); b) Consonic C2-GS Geotron Elektronik instrument.

P wave velocity was detected automatically based on the first onset of P wave arrival (figure 3a). The signal was not filtered since it is possible to clearly define the arrival of P waves (green dashed line on figure 3a). For the determination of the first onset of S wave Benavente et al. [11] proposed applying a band-pass filter to reduce the effect of P wave background signal. A band-pass filter passes frequencies with specific ranges and attenuates frequencies outside this range [12].

**Figure 3.** Graphs for sample SC15-2 a) Wave graph with amplitude=50mV b) FFT graph with band-pass range c) Wave graph with Amplitude=2V before and after filtering (the green dashed lines on ‘a graph’ and ‘c graph’ show the first onset of the P and S wave, respectively).
For the selection of the band range, the Fast Fourier Transform (FFT) graph from the original wave was used. The Fast Fourier Transform (FFT) is a mathematical procedure for translating a signal from the time domain to the frequency domain (figure 3b). The conversion of the original wave to the frequency domain reveals how the amplitude varies with frequency. With the help of the FFT graph, the S wave frequency can be selected: the frequency of the highest peak of the amplitudes is the frequency of the S wave. The frequency band range of ±3000 Hz of the maximum amplitude was selected. Based on this frequency, the position of the band was calculated. The original signal with amplitude 2V (blue curve in figure 3) and its filtered signal with the band-pass filter (red curve) was identified for each measurement.

3. Results and Discussion
The weight of samples increased up to 4 salt crystallisation cycles (figure 4). After four cycles, an abrupt loss of weight was observed, and then a slower rate was recorded. The smallest amount of weight loss was 6w%, while the most significant loss was over 15w% (figure 4).

![Figure 4. Weight changes of samples after salt crystallisation cycles: a) 50 cycles and b) enlarged graph up to 15 salt crystallisation cycles (sample codes are given in table 1)](image)

The P wave velocity increased during the first 12-15 cycles (figure 5). It is attributed to pore-clogging by salts, reduction of porosity and coeval increase in density. This result partly contradicts that of Barone et al. [13]. In their study, the effects of salt crystallisation on the physical and mechanical properties of natural building stones were analysed. They concluded that with increasing salt crystallisation cycles, the porosity increased and consequently, ultrasonic velocity decreased. After 12-15 cycles, the trend was changed, and a steady decrease of P wave velocities was measured until the 50 cycles. The P-wave velocity increased the most by 20% after 15 cycles. The P-wave velocity loss after 50 cycles has a range of 7% to 12.45%.
A comparison between the results of Pundit and Geotron instruments was presented in Table 3. The Pundit and Geotron instrument results showed that the average P wave velocities after 15 cycles of salt crystallisation were increased. However, after 50 salt crystallisation cycles, the P wave velocity was decreased even compared to the initial values of non-weathered samples. The average P wave velocities recorded by Pundit of non-weathered samples, the samples after 15 cycles, and the samples after 50 cycles were 2.701, 2.937 and 2.407 km/s, respectively. Similarly, for the Geotron instrument, the average P wave velocities were 2.726, 2.971 and 2.414 km/s for non-weathered samples, for the samples after 15 cycles and after 50 cycles, respectively. The differences in P wave velocities of the two instruments were around 5%. The average S wave velocities for non-weathered samples, the samples after 15 cycles, and 50 cycles were 1.325, 1.442 and 1.450 km/s, respectively. Consequently, S wave velocity showed an increasing trend from non-weathered samples to 50 salt cycles. The S wave velocity tendency after the different number of salt cycles is not the same the P wave tended. Generally, the standard deviation for the results of the Geotron instrument was increasing after salt crystallisation cycles, and for Pundit was decreasing.

Table 3. P and S wave velocities of samples with the standard deviations (std)

| Sample code | Salt crystallisation cycle | P wave velocity (km/s) | S wave velocity (km/s) |
|-------------|----------------------------|------------------------|------------------------|
|             |                           | Pundit (Std. dev)      | Geotron (Std. dev)     | Filter (±3000 Hz) (Std. dev) |
| 1           | -                         | 2.675 (0.063)          | 2.696 (0.057)          | 1.383 (0.073)                |
| 2           | -                         | 2.544 (0.058)          | 2.583 (0.044)          | 1.234 (0.063)                |
| 3           | -                         | 3.254 (0.042)          | 3.296 (0.102)          | 1.393 (0.094)                |
| 4           | -                         | 2.330 (0.062)          | 2.329 (0.050)          | 1.288 (0.110)                |
| SC15-1      | 15                        | 3.019 (0.073)          | 3.056 (0.088)          | 1.371 (0.350)                |
| SC15-2      | 15                        | 2.854 (0.043)          | 2.886 (0.075)          | 1.513 (0.220)                |
| SC50-1      | 50                        | 2.298 (0.043)          | 2.267 (0.126)          | 1.365 (0.230)                |
| SC50-2      | 50                        | 2.560 (0.049)          | 2.630 (0.141)          | 1.476 (0.162)                |
| SC50-3      | 50                        | 2.362 (0.027)          | 2.345 (0.073)          | 1.510 (0.064)                |

Figure 5. The changes in P wave velocity after the salt crystallisation cycles (sample codes are given in table 1)
The P wave velocity of samples increased after 15 salt crystallisation cycles, and it decreased with additional salt crystallisation cycles. But, this is not a parallel trend to the weight change of the samples. There was good consistency between the results of Pundit and Geotron instruments. The differences in the measured values of P wave velocity were, on average, around 5%. The measured differences are larger after salt crystallisation cycles. S wave velocity of samples was increased after salt crystallisation cycles. This linked to the fact, that salts were not washed out from samples. The clogging of pores and the reduction of porosity always associated with an increase in strength [14] or density [15].

4. Conclusions
1- P wave velocity increases after 15 salt crystallisation cycles by up to 20%, but an additional salt cycle causes loss in P wave velocity to compare with P wave velocity before the salt crystallisation process by 12%.
2- The results showed that the weight of samples increased slightly until four cycles, then it decreased rapidly until the end of salt crystallisation cycles. This weight loss can be as high as 16%.
3- The P wave velocity increase does not show a parallel trend to the weight changes of the samples because it shows some increase up to 15 cycles, while the weight loss starts after 4 cycles.
4- Shear wave velocity shows an increase up to 50 cycles, because the salt has not been washed out from samples.

5. References
[1] Török Á, Rozgonyi N 2004 Morphology and mineralogy of weathering crusts on highly porous oolitic limestones, a case study from Budapest Env. Geol. 46 333–349. https://doi.org/10.1007/s00254-004-1036-x
[2] Smith BJ, Warke PA, McGreevy JP, Kane HL 2005 Salt-weathering simulations under hot desert conditions: Geomorphology 67 211–22. https://doi.org/10.1016/j.geomorph.2004.03.015
[3] Sun Q, Zhang Y 2019 Combined effects of salt, cyclic wetting and drying cycles on the physical and mechanical properties of sandstone. Eng Geol. 248 70–79. https://doi.org/10.1016/j.enggeo.2018.11.009
[4] Çelik MY, Aygün A 2019 The effect of salt crystallisation on degradation of volcanic building stones by sodium sulfates and sodium chlorides. Bull. Eng. Geol. Environ. 78 3509–3529. https://doi.org/10.1007/s10066-018-1354-y
[5] Martínez-Martínez J, Torrero E, Sanz D and Navarro, V 2020 Salt crystallization dynamics in indoor environments: Stone weathering in the Muñoz Chapel of the Cathedral of Santa María (Cuenca, central Spain). J. Cultur. Herit. https://doi.org/10.1016/j.culher.2020.09.011
[6] Sato M and Hattanji T 2018 A laboratory experiment on salt weathering by humidity change: salt damage induced by deliquescence and hydration. Prog. Earth. Planet. Sci. 5(1) 1-10. https://doi.org/10.1186/s40645-018-0241-2
[7] Akin M and Ozsan A 2011 Evaluation of the long-term durability of yellow travertine using accelerated weathering tests. Bull. Eng. Geol. Environ. 70 101–114. https://doi.org/10.1007/s10064-010-0287-x
[8] Sharma PK and Singh TN 2008 A correlation between P-wave velocity, impact strength index, slake durability index and uniaxial compressive strength: Bull. Eng. Geol. Environ. 67 17–22. https://doi.org/10.1007/s10064-007-0109-y
[9] Withers M, Aster R, Young C, Beiriger J, Harris M, Moore S and Trujillo J 1998 A comparison of select trigger algorithms for automated global seismic phase and event detection. Bull. Seism. Soc. Amer. 88(1) 95-106.
[10] Lee M, Byun J, Kim D, Choi J and Kim M 2017 Improved modified energy ratio method using a multi-window approach for accurate arrival picking. J. Appl. Geophys. 139 117–130. https://doi.org/10.1016/j.jappgeo.2017.02.019
[11] Benavente D, Galiana-Merino JJ, Pla C, Martinez-Martinez J and Crespo-Jimenez D 2020 Automatic detection and characterisation of the first P-and S-wave pulse in rocks using
ultrasonic transmission method. Eng. Geol. 266 105474. https://doi.org/10.1016/j.enggeo.2020.105474

[12] MATLAB 2019. 9.7.0.1190202 (R2019b). Natick, Massachusetts: The MathWorks Inc.

[13] Barone G, Mazzoleni P, Pappalardo G and Raneri S 2015 Microtextural and microstructural influence on the changes of physical and mechanical proprieties related to salts crystallisation weathering in natural building stones. The example of Sabucina stone (Sicily). Const. Build. Mater. 95 355-365. https://doi.org/10.1016/j.conbuildmat.2015.07.131

[14] Vasanelli E, Micelli F, Colangiuli D, Calia A, Aiello MA 2020 A non-destructive testing method for masonry by using UPV and cross validation procedure. Mater. Struct. 53 134. https://doi.org/10.1617/s11527-020-01568-8

[15] Benavente D, García del Cura MA, Bernabéu A, Ordóñez S 2001 Quantification of salt weathering in porous stones using an experimental continuous partial immersion method. Eng. Geol. 59 (3-4) 313-325, https://doi.org/10.1016/S0013-7952(01)00020-5.