Assessment Of The Durability Of Two Natural Stones Intended For The Conservation Of The Historical Masonry Sea Wall In The Old Town of Acre

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1. Introduction

At December 2001 Meeting of the World Heritage Committee in Helsinki 31 new sites were inscribed on the World Heritage List. Among them is the Old City of Acre in Israel. The conservation of the Historical Masonry Sea Wall in the Old City of Acre demands implementation of the new materials compatible with those originally used in the structure. Natural kurkar (sandstone) is a main masonry material used in past in Israel, as well as in the Old City of Acre [1]. Thus, two natural stones were investigated from the durability point of view.

2. Historical, geographical and climatic background [1]

R. Gertwagen explains: “Acre with its port lies in a natural bay, the bay of Acre, in the north of the gulf of Haifa. The present fishing and yacht port is located to the south east of the town. A modern fisher-wharf, bordering the port along its southern side, extends from a modern restaurant, in the south-western end of the City, to the east and slightly to the south-east and turns to the north at its eastern tip. On its western side, the present port of Acre is bordered by restaurants and on its north-western side by a sea wall, built by Jazar Pasha in 1800-1801…

The position and planning of ports depend primarily on maritime conditions. A number of primary importance: protection against the prevailing storming winds, which could endanger navigation and anchorage in the port; adequate depth of water for the draft of the contemporary ships, and protection against the waves and sea currents, which could silt the port.

The prevailing winds along the Levantine coastline, during the whole year, are the north-north-western…

A special problem, unique to the bay of Acre, is the storms caused by the easterlies. These winds are common during and autumn and they can blow three days successively”.

3. Experimental

3.1 Materials

The laboratory experiments were done with two stones of the different origin:

- The first one was of the same kind as in the historical sea wall in Acre, i.e.: a grayish sandstone (kurkar stone) from local Israel quarry;
- The second stone was a crème limestone from Morocco’s quarry.

3.2 Tests

3.2.1 Mineralogical composition

- X-ray diffraction by CuKα rays.

  This is a qualitative analysis. It allows identifying the minerals in content more than 1-2% (by weight).

3.2.2 Physical properties

- Bulk density and total absorption – according ASTM C97 [2];
- Capillary absorption – according DIN 52617 [3]. The results of test were used for estimating of the absorption rate, i.e. a ratio of the amount of water absorbed during the different periods of time and the weight of the totally absorbed water;
- Evaporation test - This test was intended to find out the ability of the stones to return the absorbed water. Usually the rapid evaporation of the absorbed water is recommended in order to reduce the duration of the water entrainment in the stone and, thus, to diminish the possible corrosion of the stone. The test was described elsewhere [4]. The results of the test were used for estimating of the evaporation rate, i.e. a ratio of the amount of the evaporated water and the weight of water totally absorbed during the capillary absorption test.

Bulk density and total absorption of the un-weathered stones were measured. Capillary absorption and evaporation tests were carried out with the un-weathered, as well as the weathered stones.

The samples used for the tests were cubes of 70/70/70 mm in size.

3.2.3 Mechanical properties

- Compressive strength in the air-dry and the wet state.

  The measurements were carried out with the un-weathered, as well as the weathered stones according ASTM C170 [5]. The samples used for the tests were cubes of 50/50/50 mm in size.

3.2.4 Soundness

Two kinds of the accelerated weathering tests were done in the present investigation.

- Crystallization test with the sodium sulfate solution (14%) – according EN 12370 [6].
- This test was intended to study the stones' durability in the conditions of the offshore salinity. In the present investigation there were done up to 15 cycles of the crystallization test.
- Accelerated weathering under the impact of the ultra-violet (UV) radiation, wetting and drying (QUV test) - according the guidance of the American standard ASTM G53-95 [7].
- The test was intended to clarify the effect of the UV radiation (the most harmful component of the solar energy) on the durability of the stone. The stones were exposed to the cycles of radiation, wetting and drying during 1,000 hours. Each cycle included an exposure of the stones to the UV radiation during 8 hours and their wetting at temperature of 40ºC during 4 hours.

The criteria of weathering used in the present study were the changes in the visual appearance, water absorption and evaporation ability of the stones before and after the tests, as well as the compressive strength of the stones after the crystallization test.

4. Results

4.1 Mineralogical Composition

The curves describing a mineralogical composition of the stones are shown in Fig. 1-2.

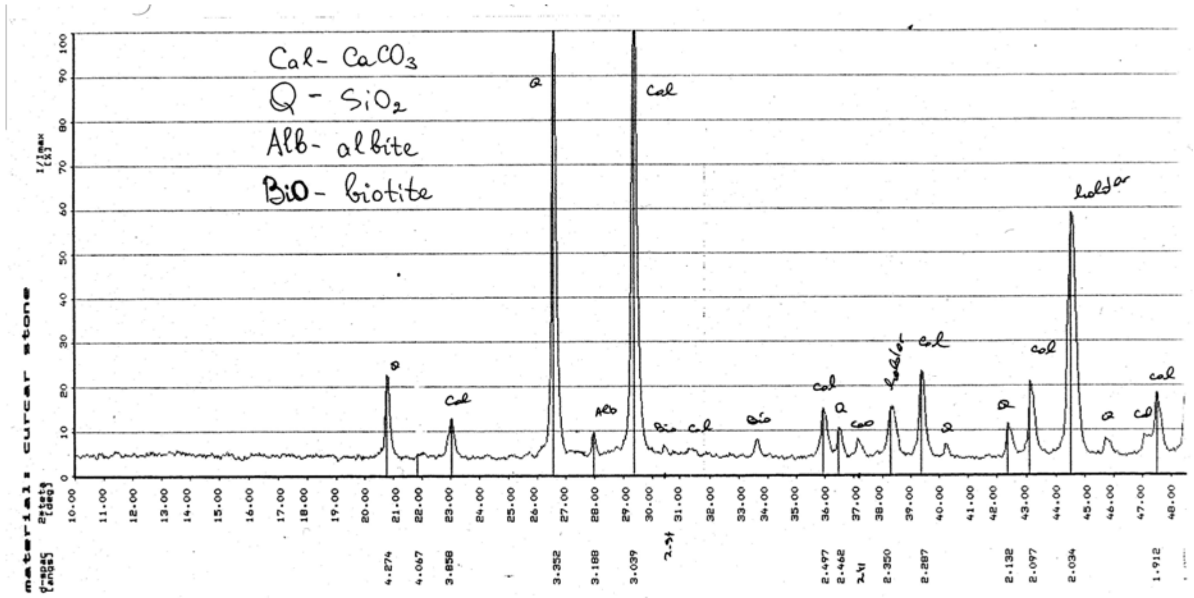


Fig. 1. X-ray diffraction of the grayish sandstone

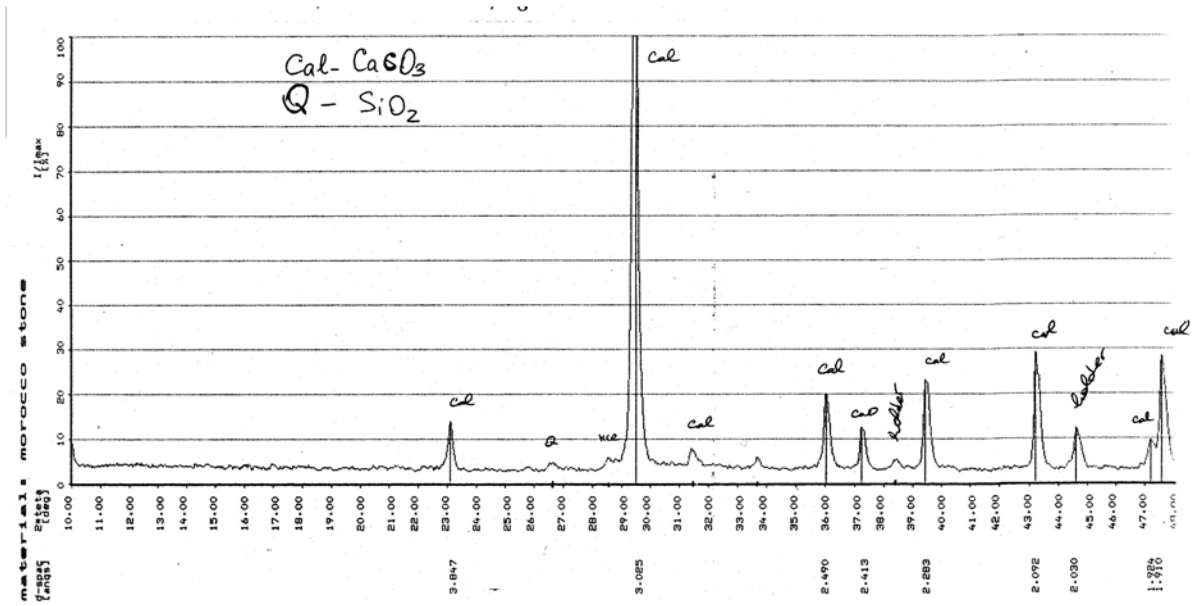


Fig. 2. X-ray diffraction of the crème limestone

The main minerals fond are:

- in the grayish sandstone – calcite, $CaCO_3$ and quartz, SiO_2. There were fond also the small amounts of sodium feldspar - albite, $NaAlSi_3O_8$; mica – biotite, $K(Fe,Mg)_3AlSi_3O_{10}$ and the traces of lime, CaO;
- in the crème limestone - calcite, $CaCO_3$. There were observed the rare traces of quartz, SiO_2; lime, CaO and silvite, KCl.

4.2 Physical and Mechanical Properties

The physical and mechanical properties of the un-weathered and weathered stones are shown in Table 1 and Fig. 3-5.

Table 1. Physical and mechanical properties of the stones: Israel crème sandstone and Morocco's grayish limestone

Stone	Bulk density, Kg per m^3	Total absorption, % of weight	Capillary absorption, % of weight	Capillary absorp. coefficient, kg per m² per hour^{½}	Compressive strength, MPa		
					Air-dry state	Wet State	Dry-to-wet Strength ratio
Grayish sandstone	2,004	10.4%	5.6%	1.2	27	23	0.85
Grayish sandstone - QUV test	-	-	7.0%	1.3	-	-	-
Grayish sandstone Crystallization test	Stone totally crumbled						
Crème limestone	2,029	10.5%	5.4%	1.1	16.5	10	0.60
Crème limestone QUV test	-	-	7.9%	1.4	-	-	-
Crème limestone Crystallization test	-	-	5.7%	3.4	20	-	-

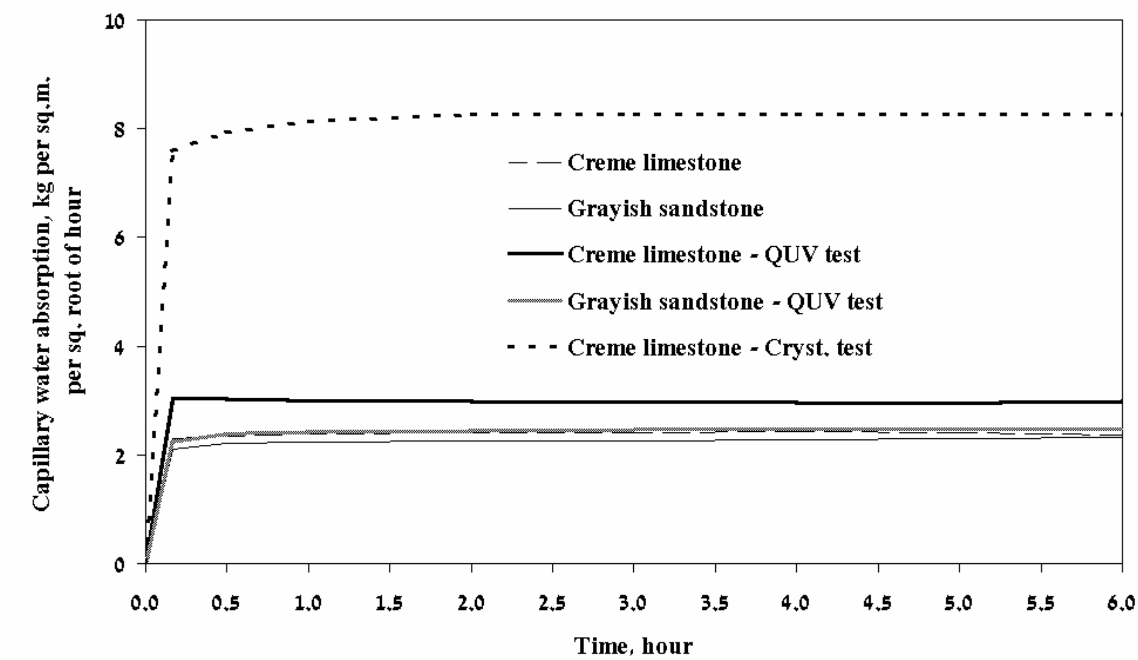
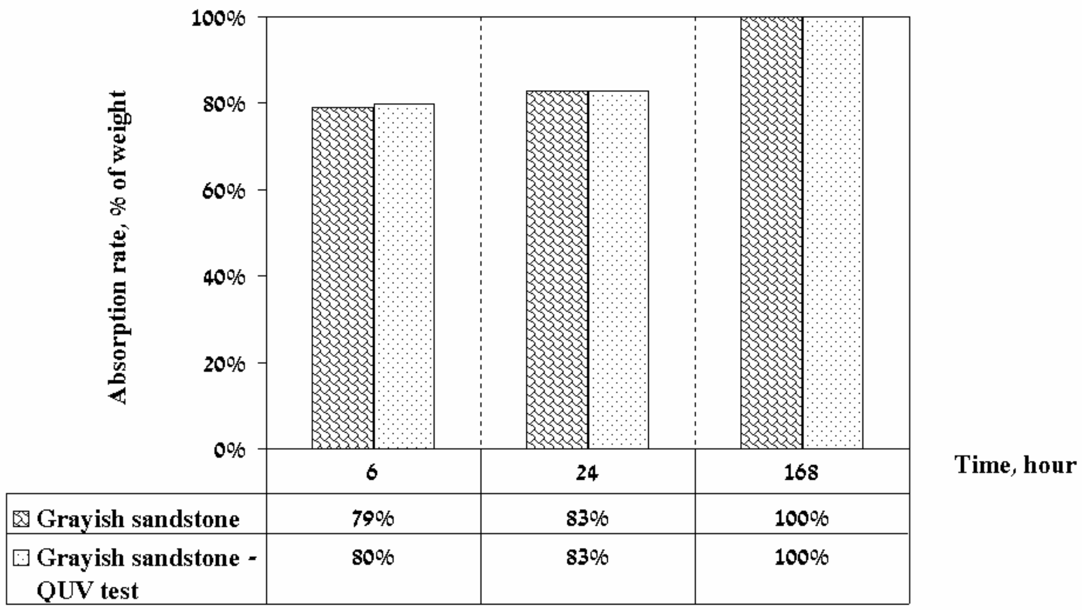
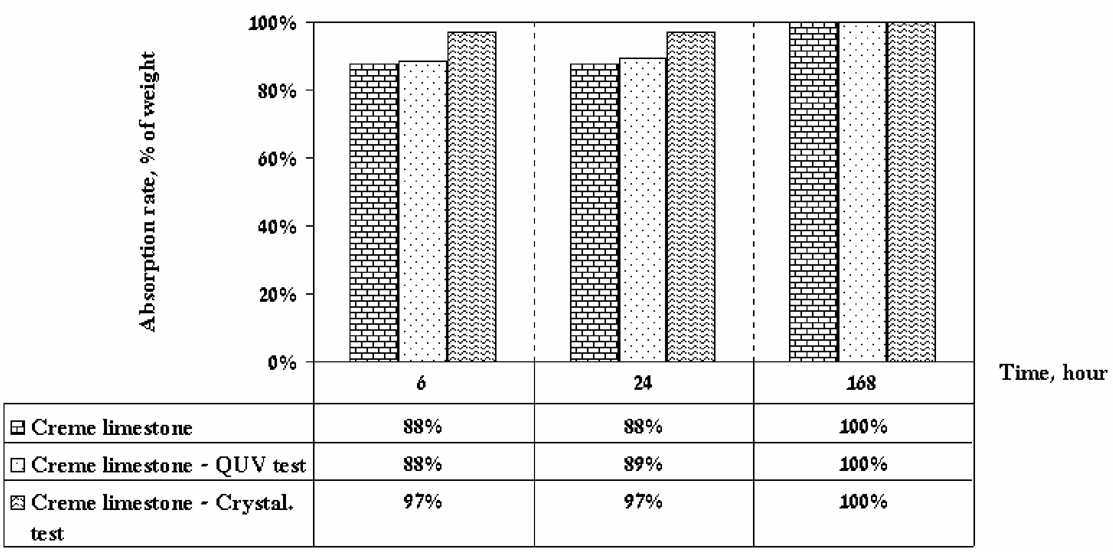


Fig. 3. Initial capillary absorption of the un-weathered and weathered stones

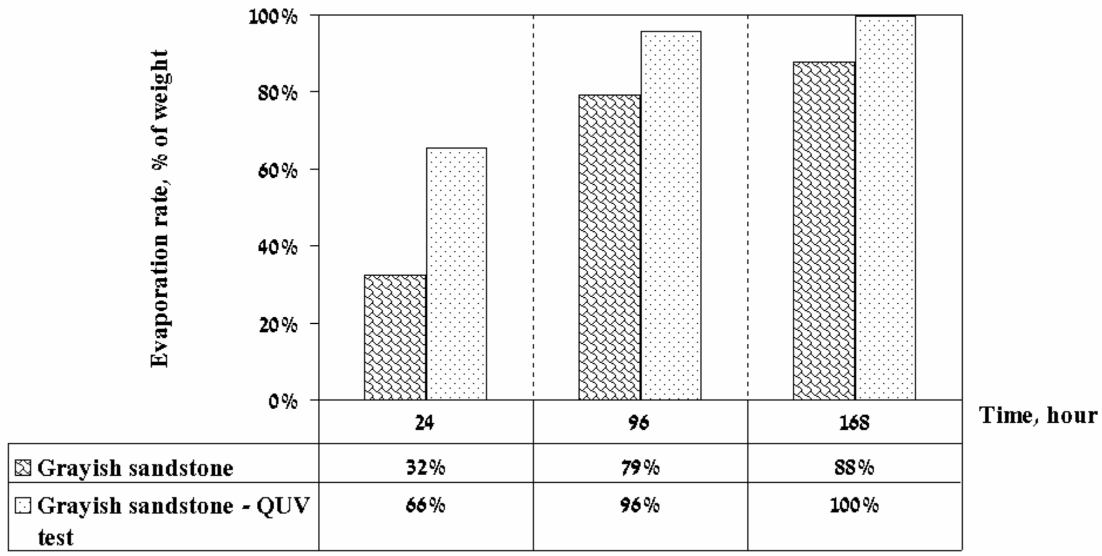


a)

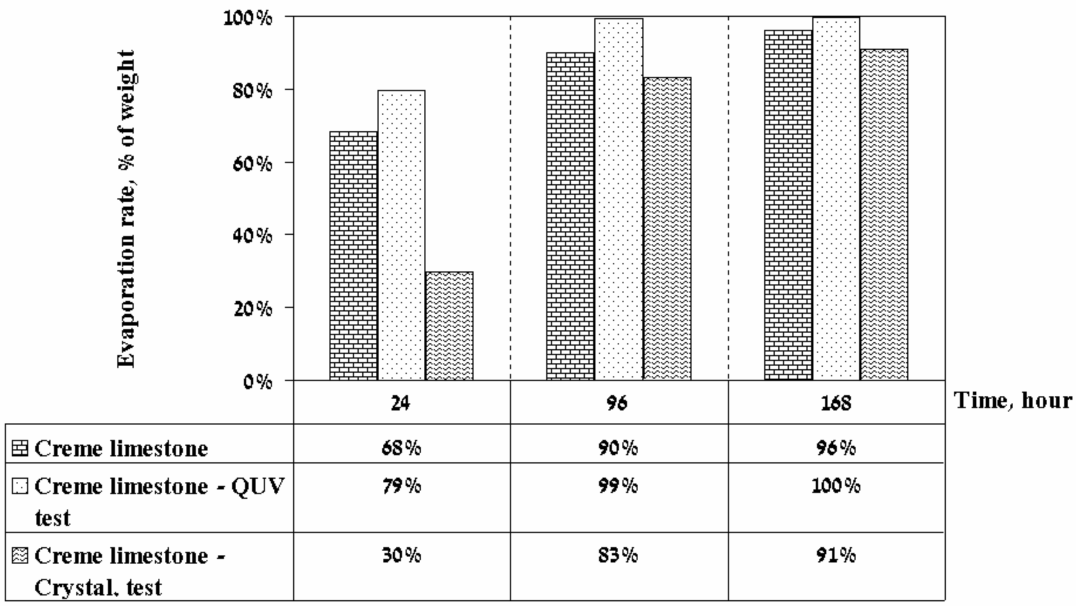


b)

<u>Fig. 4.</u> Capillary absorption rate: a) Grayish sandstone; b) Crème limestone



a)



b)

Fig. 5. Water evaporation rate: a) Grayish sandstone; b) Crème limestone

4.3 Soundness

4.3.1 Crystallization test

The visual observations of the stones before and after the test are given in Fig. 6-7

The efflorescence phenomenon was observed in the investigated stones after the test. The deterioration of the grayish sandstone was much more obvious than that of the crème limestone. Crumbling of the sandstone began after 2 cycles of the test. In spite of it, the limestone crumbled slightly only after 9 cycles.

4.3.2 QUV test

There weren't fond any differences in the appearance of the stones before and after the test.

a)

b)

Fig. 6. Visual observations of the grayish sandstone before (a) and after (b) the crystallization test

a)

b)

Fig. 7. Visual observations of the crème limestone before (a) and after (b) the crystallization test

5. Discussion

5.1 Mineralogical Composition

Calcite, $CaCO_3$ is a main mineral in the both investigated stones. It has a very brittle fracture producing small, conchoidal fragments once the tenacious limit has been exceeded. (Conchoidal - fractures developed in brittle materials characterized by smoothly curving surfaces. Tenacity is the resistance that a mineral offers to breaking, crushing, bending, cutting, or other acts of destruction) [8].

Quartz, SiO_2 is a second main mineral in the grayish sandstone. It has a conchoidal fracture.

Calcite and quartz are crystallized in the same trigonal crystal system.

Albite, $NaAlSi_3O_8$ has a blocky texture and uneven fracture, i.e. flat surfaces fractured in an uneven pattern. Albite is crystallized in triclinic crystal system.

Biotite, $K(Fe,Mg)_3AlSi_3O_{10}$ has micaceous texture, i.e. a platy texture with "flexible" plates, and uneven fracture. Biotite is crystallized in monoclinic crystal system.

The results of X-ray diffraction let conclude the more homogeneous composition of the crème limestone. In spite of it the grayish sandstone is obviously non-homogeny material by his mineralogical composition.

5.2 Well-known Tendencies of Minerals Weathering

The mineralogical composition could be used as 'a coarse sieve' for the durability assessment of the investigated stone.

The offshore weathering of **calcite** leads to the formation of gypsum crust. Calcium dissolves from carbonate rocks and tends to form the sulfate gypsum.

Salts are the most powerful weathering agent. Sodium sulfate is the most efficient factor in rock disintegration. Salts from sea spray as halite, NaCl, as well as gypsum, $CaSO_4 \cdot 2H_2O$, and magnesium sulfate, $MgSO_4 \cdot 6H_2O$ can form white rims at the surface as efflorescence, at the open ends of the capillaries or just beneath the surface as subflorescence. The crystallization pressure of salts could achieve 200 – 2,000 atmosphere [9] causing a stone crumbling.

"**Quartz** sandstones consist of crystalline sand grains and a usually finer grained to amorphous silica cement; this results in differential solubility that can lead to crumbling of the host rock and migration of silica in solution toward the surface, leading to case hardening and to the formation of thin surface flakes and shells" [9].

Natural weathering processes can lead to the transformation of micas and feldspars into secondary crystalline and amorphous products. In wet, acid conditions **feldspar** weathering causes to the formation of secondary clay minerals such as authigenic kaolinite, $Al_4(OH)_8[Si_4O_{10}]$, [Blum]. In a CO2 + H2O rich atmosphere the idealized ctoichiometry of the kaolisation reaction for **albite** may be written as follows [???]:

$$4Na[AlSi_3O_8] + 4H_2O + 2CO_2 \leftrightarrow Al_4(OH)_8[SiO_{10}] + 2\ Na_2CO_3 + 8SiO_2$$

In [11] was fond that SO_2-enriched urban atmosphere strongly promoted the above weathering process. SO_2 plays a dual role promoting both sulfate precipitation and kaolinisation of feldspar.

Weathering of **biotite** can lead to the formation of vermiculite, $(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4(H_2O)$ or montmorillonite, $Na_{0.5}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2 \cdot n(H_2O)$. The important stage of biotite's weathering is oxidation of iron ions: $Fe^{2+} \rightarrow Fe^{3+}$. The further step is transfer of iron ions from the inner structure into the mineral surface and formation of iron hydroxides. As result of these processes color of rocks containing biotite is changing from grayish-green to swarthy-brown [12]. Thus, the rust spots and veins could appear in the stone.

5.3 Physical And Mechanical Properties Of The Un-Weathered Stones

The investigated grayish sandstone and crème limestone are very similar in bulk density, total and capillary water absorption. But they distinctly differ in their evaporation ability, compressive strength and wet-to-dry ratio of modulus of rupture.

According DIN 52617 [3] materials with a capillary absorption coefficient of 0.5 – 2.0 kg per m^2 per $hour^{½}$ are materials with the inhibited water absorption ('wasserhemmende Baustoffe"). The total absorption of stones is an indication of their open porosity, whereas the capillary pores cause the capillary absorption. The results of the total and capillary water absorption let suggest that the capillary pores makes up just more than a half of the open porosity in the investigated stones. There are a lot of the large pores and caverns in the stones. These pores and caverns are clearly visible to the unaided eye (see Fig. 6-7).

It was fond that the both stones absorbed the most of water in the first 6 hours of their contact with moisture.

The grayish limestone evaporated the capillary water slower than the crème limestone. Hence, the finer capillary pores could be suggested in the grayish sandstone. As was previously emphasized the rapid evaporation of the absorbed water is recommended in order to reduce the duration of the water entrainment in the stone and, thus, to diminish the possible corrosion of material.

Therefore, there is a larger risk to the grayish sandstone being more susceptible to the destruction by the offshore hazards, which are penetrating with moisture.

Compressive strength of the grayish sandstone is much bigger than of the crème limestone. The strength reducing of the compressive strength is strongly obvious in the wet crème limestone.

Wet-to-dry strength ratio could be used as ‘a crude immediate indicator’ of the stone’s durability [8]:

- wet-to-dry strength ratio of 0.8-1.0 indicates an excellent durability;
- 0.7 – 0.8 – good to excellent durability;
- 0.6 – 0.7 – fair to poor durability;
- 0.5 – 0.6 – poor durability;
- less than 0.5 – very bad durability (too much clay).

Thus, from this point of view the grayish sandstone looks much more durable than the crème limestone. But this classification doesn’t care about the chemical and mineralogical composition of stone, as well as the evaporation ability that are critical factors regarding the durability. Hence, ‘fine tuning’ considering soundness should be done.

5.4 Physical And Mechanical Properties Of The Weathered Stones

The results in Table 1 and Fig. 1-2 obviously show a negligible increase in the capillary absorption of the investigated stone after QUV test. The capillary absorption rate didn’t change after QUV test. The evaporation rate is obviously accelerated as a result of QUV test. Thus, it could be concluded that the ultra-violet radiation and cyclic wetting and drying almost had no effect on the durability of the investigated stones. The investigated stones are the porous materials. Therefore, it could be supposed that their thermal expansion was also negligible.

The crystallization test strongly affected the investigated stones, especially the grayish sandstone. This stone strongly deteriorated as a result of sodium sulfate crystallization. Crumbling of the grayish sandstone began at the most early stages of the test. Probable, the non-homogenous mineralogical composition of the grayish sandstone and destruction of the secondary minerals caused the accelerated degradation of the stone.

The crème limestone was obviously more durable in the conditions of sulfate ‘attack’. There were not observed any signs of crumbling in the stone up to the ninth cycle.

Crystallization test strongly affected the capillary absorption and water evaporation ability of the crème limestone. The capillary absorption coefficient of the stone is trebled after the test. The capillary absorption rate is accelerated after the test, whereas the evaporation ability strongly dropped. Probably, sodium sulfate crystals that precipitated in the pores of the stone promoted the water absorption and strongly confined the moisture in the pores of the stone.

The compressive strength of the air-dry crème limestone increased after the crystallization test as a result of pore reinforcing by the precipitated salt. The weathered crème limestone was much more stronger than the weathered grayish sandstone that crumbled in fingers.

As the open porosity of the investigated stones is the same, and the grayish sandstone crumbled after 2 cycles, whereas the crème limestone – after 9 cycles, it could be suggested that the life cycle of the crème limestone is several time longer than the grayish sandstone.

Therefore, it could be suggested that the crème limestone is more durable stone than the grayish sandstone. This is in spite of the classification based on the dry-to-wet strength ratio.

6. Conclusions

The assessment of the durability of two different stones was done in order to choose a right material for conservation of the historical masonry sea wall in the Old City of Acre.

The physical properties of the stones were almost the same, whereas their mineralogical composition and compressive strength were different. The first stone was Israel grayish sandstone. The same kind of stone is used in the historical wall. There is not any evidence that the investigated grayish sandstone was quarried in the same quarry as a historical one.

The second stone was Morocco's crème limestone. The compressive strength of this stone is obviously less than that of the grayish sandstone, as well as wet-to-dry ratio.

It was fond that the UV radiation and cyclic wetting and drying didn't affect the durability of the investigated stones.

In spite of the QUV test the crystallization test had a strong impact on the stones' soundness. The grayish sandstone was almost not durable in the contact with sulfates. The crème limestone demonstrated the better durability in the contact with the typical hazards of Acre offshore zone, i.e. an elevated temperature, moisture and salinity. Hence, the longer life cycle could be supposed for the crème limestone in the direct contact with seawater and wetting-and-drying cycles.

In the conditions of the cyclic exposure of the stones to the UV radiation, wetting and drying without any contact with seawater the grayish sandstone and the crème limestone are durable in the same manner. Thus, the decision regarding a chose of the right stone should be done from the aspects of the strength.

7. References

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