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Effect on Limestone of 15 Cycles of Immersion in Dead Sea Water

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Abstract: The standard BRE crystallization test using Dead Sea water (instead of hydrous sodium sulphate) has been applied on 10 limestone types. At the end of the 15th cycle, all the limestones have increased in weight. Most of the weight increase, being proportional to the porosity of limestone, occurred during the first five cycles. The 15 cycles of soaking and drying were not sufficient to cause any appreciable degradation of limestone. A longer period of exposure to the Dead Sea salts and factors other than merely soaking and drying may have been in effect in producing deterioration of tourist and industrial structures in the Dead Sea area. Effects of hydrous sodium sulphate and Dead Sea water on the studied limestones were found to be controlled by porosity. In low-porosity stones very little weight change has occurred, whereas, in high-porosity stones weight change was found to depend on the salt or salts used. This may be ascribed to the different behavior of single and mixed salts on one hand and the pore structure of the stone on the other.

Key words: Salt weathering, limestone, Dead Sea

INTRODUCTION

Tourist and industrial structures at the Dead Sea are highly deteriorated by the effect of saline water of the sea. Despite this fact, published literature on salt weathering of the Dead Sea is noticeably scarce (Masadeh, 2005). The present study is an attempt to study the effect of the Dead Sea water on the durability of limestone which is the most dominant construction material of Jordan. It is used in most stone buildings in the country. As well, it constitutes the majority of aggregates of concrete mixes.

The Dead Sea lies between Jordan and Israel. Its water is unique with salinity ten times the average salinity of normal seas. It also contains a number of salts different in their composition from any other sea water. The salts include:

Magnesium chloride 14.5% Sodium chloride 7.5% Calcium chloride 3.8% Potassium chloride 1.2% Magnesium bromide 0.5% Water 73%

MATERIALS AND METHODS

The geology of Jordanian building stones are summarized in Table 1 and the petrography of those selected for the present study is shown in Table 2 (Moh'd, 2003).

Twenty specimens representing ten building limestones were cut into 3-4 cm cubes and subjected to 15 cycles of immersion in the Dead Sea water and drying in an oven at 105°C. The same procedure of the crystallization test of the BRE (Ross and Butlin, 1989) was closely followed with the only difference being replacing sodium sulphate salt with the Dead Sea water. The weight, volume, density and porosity of the studied limestones are shown in Table 3. For details on porosity and related properties of Jordanian

Table 1: Stratigraphy of Cretaceous and early Tertiary rocks of Jordan

Series	Stage	Formation	Symbol	Description
	Eocene	Shallala/Ma'an*	SH/MNL	Chalk/Nummulitic limestone
Tertiary		Umm Rijam*	URC	Chalk, Chert, limestone
	Paleocene	Muwaqqar*	MCM	Chalk, marl, limestone concretions
	Maestrichtian	Al Hisa	AHP	Phosphorite, limestone, chert
Late	Sant./Camp.	Amman	ASL	Chert, limestone, dolomite
	Coniacian	Umm Ghudran	WG	Chalk
	Turonian	Wadi As Sir*	WSL	Limestone, dolomite
		Shuayb	S	Marl, nodular limestone
Cretaceous	Cenomanian	Hummar	H	Dolomite, limestone
		Fuhays	F	Marl, clayey
		Naur *	NL	Limestone, nodular, dolmite
Early Cretaceous		Kumub Sandstone	KS	

^{*} Units with good potential as sources of building stone

Table 2: Petrographic classification of Jordanian building limestones

Stone	Unit	Folk (1959, 1962)	Dunham (1962)	Fookes and Higginbottom (1975)
Ruweished	SH/MNL	Bioparite	Packstone	Bioclastic limestone
Turkish		Dolsparite	?	Dolomitic limestone
Hallabat	WSL	Biosparrudite	Packstone-grainstone	Bioclastic limestone
Izrit	MCM	Micrite	Mudstone-wackestone	Carbonate siltstone (chalk)
Ma'an	MNL	Biosparite	Packstone-grainstone	Bioclastic limestone
Karak	NL	Biosparite	Foss. packstone-grainstone	Bioclastic limestone
Sahrawi	MCM	Microsparite	mudstone	Fine-grained limestone
Yanahi Istafina Inha	WSL.	Peloidal micrite	Wackestone (with nackstone lenses)	Fine-orgined limestone

^{?:} classes not known in Folk's and/or Dunham's classifications

Table 3: Weight, volume, density and porosity of the studied limestones

	Weight	Volume	Density	Porosity
Dead Sea	(g)	(cm³)	(g cm ⁻³)	(%)
Hallabat	73.5	28.84	2.549	5.49
Sahrawi	65.2	27.91	2.336	13.38
Ma'an	71.2	27.71	2.569	5.20
Yanabi	75.5	28.37	2.661	1.81
Ishtafina	76.9	28.60	2.689	0.77
Izrit	62.6	26.40	2.404	11.29
Karak	75.6	29.46	2.567	5.28
Inba	84.6	32.67	2.59	4.43
Turkish	81.5	29.31	2.78	ND
Rweished	78.4	29.07	2.697	0.48

(limestones reference can be made to) Moh'd (2002 and 2003). Except for one slightly dolomitic limestone (Turkish), the rest of the studied carbonates are almost pure limestones. The porosity was calculated by using the dry density assuming that the grain density of limestone is 2.71 g cm⁻³ as follows:

Porosity% = $\{1-(dry density/grain density)\} \times 100$

RESULTS AND DISCUSSION

The weight increase at the end of 15 cycles of immersion (calculated as a percentage of the original weight) is shown diagrammatically in Fig. 1. It can be seen that most of change in weight occurred during the first 5 cycles of immersion. Figure 2 shows that the change in weight after 5 cycles of immersion plots nicely with the porosity of the studied limestones. This indicates that during the first five cycles of immersion and drying, most of salt crystallization takes place within the accessible pores in limestone. After that, it is believed that salt crystallizes within less accessible or isolated pores, as well as, on the faces of the studied cubes.

The question which should be asked now is that why no deterioration of limestone has been noticed in the studied samples whereas the stone and concrete structures in the Dead Sea area are highly affected by salt deterioration. Our discussion will concentrate on the potash plant area. It is believed that factors other than just saturation and drying of salt contribute towards the deterioration there. These factors can be subdivided into two types internal and external. External factors mean here factors related to the natural environment before the potash and allied industries have been introduced in

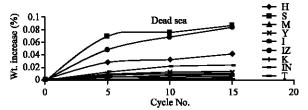


Fig. 1: Change of weight (as a percentage of the original weight) with the progress of crystallization

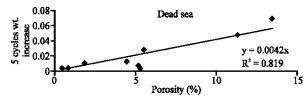


Fig. 2: Weight increase after 5 cycles of immersion and drying versus porosity

the area whereas internal factors are more related to potash production and associated processes. It is quite clear that it is impossible in the testing program to include all the parameters (internal and external) affecting the area. It is also evident that the time factor is quite different in the testing program (restricted to 15 cycles) from that occurring in the field with some concrete buildings and structures date back to 1970's.

As outlined by Charola (2000), seldom can the deterioration of porous materials be attributed to the presence of only one salt. In general, two or more salts are found to be present and this the case of the Dead Sea. The simultaneous presence of two salts affects their behavior in solution and, in particular, their individual solubility. If the salts have an ion in common, such as sodium chloride or sodium sulfate, solubility of both will decrease. Again, the solubility of the less-soluble salt, sodium sulfate, will be affected more than that of the more soluble one. However, not all salts behave in this way; for example, the solubility of potassium nitrate increases in the presence of other nitrates (Steiger and Dannecker, 1995).

A solution of a mixture of salts will not have a single equilibrium RH at a given temperature but will show a range of such humidities (Price and Brimblecombe, 1994). This range will not necessarily fall between the levels of

Table 4: Change of crystallization weight loss of Jordanian and Britishx

Stones with it	uniber of cyc	105		
Stone type	Loss (%)	Loss (%)	Loss (%)	Ratio
Jordanian limestones	5 cycles	10 cycles	15 cycles	10/15 cycles
Hayyan	-0.40	2.15	8.54	0.25
Hatem	-0.45	3.87	23.73	0.16
Izrit	3.04	31.36	53.41	0.59
Sahrawi	-0.34	2.27	5.28	0.43
Hallabat	-0.34	1.97	4.33	0.45
British limestones				
M	8.46	35.62	53.06	0.66
CDO	1.49	17.85	29.63	0.60
CD	-0.22	10.22	21.45	0.48
MP	11.62	40.45	61.85	0.65

Table 5: Crysta	allization weight los	s in low porosity rocks	s and Tafih stone
	Loss (%)	Loss (%)	Loss (%)
	5 cycles	10 cycles	15 cycles
Ballas	-0.055	-0.065	+0.140
Yanabi	-0.051	-0.061	-0.030
Travertine	-0.047	-0.039	+0.010
Karak	-0.061	-0.059	0.070
Jazeirah	-0.116	-0.173	-0.180
Sat'h	-0.065	-0.11	+0.140
<u>Tafih</u>	-0.439	-0.891	-0.950

the equilibrium RH of the individual salts and can even be broader, as is the case for the mixture of potassium chloride and sodium chloride: the equilibrium RH ranges from close to 85 to 72.4%, while equilibrium RH for the individual salts is 84.3 and 75.3%, respectively (Steiger and Dannecker, 1995) Further details about the model used to calculate the behavior of multiple salt systems can be found in Price and Brimblecombe (1994), Steiger and Zeunert (1996) and Steiger et al. (1998).

The other question which should also be asked is why the Jordanian stones have been deteriorated to different degrees when subjected to the standard BRE crystallization test (Table 4 and 5). It is evident that the crystallization pressure of hydrous sodium sulphate salt used in the standard test is much higher than those of the Dead Sea water. This may also indicate the different behavior of the same salt when crystallization occurs in an open space such as salt pans and a restricted system as it is the case within the pores of a rock.

CONCLUSIONS

It can be concluded from the present work that the response of the stone set after exposure to 15 cycles of immersion and drying is similar in the low porosity (and consequently low permeability) stones in both the Dead Sea water and hydrous sodium sulphate. High porosity stones, however, show a marked difference in the two brines. This can be ascribed to the effect of the mixture of salts combined with the effect of the common ion (chlorine) in the case of the Dead Sea.

The combination of the effects of internal and external factors mentioned in the text combined with sufficient time may offer a good explanation for the degradation observed in the Dead Sea area.

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