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CASE STUDY

Effects of acid–base solutions on some Turkish natural building stones: physico-mechanical and color changes

Engin Özdemir[1] · Fatih Kantarcı[2] · Didem Eren Sarıcı[1]

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Abstract

Natural stones are exposed to various physical, chemical and environmental interactions during service life. It is quite important to determine physico-mechanical properties of natural stones for specific applications. This paper presents an experimental study conducted to explore effect of acid and sulfate shocks on some physico-mechanical properties and color of natural stones. For this purpose, five different building stones used as marble (Malatya Beige, Ağrı Onyx, Adıyaman Crystal Emperador, Diyarbakır Black Pearl, Elazığ Rosso Levanto) were supplied from eastern region of Turkey. Point load strength, Schmidt hardness rebound, unit weight, porosity, water absorption and color measurements were conducted on provided natural stones. Additionally, mineralogical properties of natural stones were investigated with XRD and XRF analyses. Then, these natural stones were exposed to chemical shocks with 5% H_2SO_4 and Na_2SO_4 solutions for 0, 10, 20 and 30 cycles. Changes in Schmidt hardness, point load strength, porosity, dry weight and color after chemical shock cycles were investigated. Experimental results showed that Diyarbakır Black Pearl (DBP) and Malatya Beige natural stones might be used in aggressive H_2SO_4 and Na_2SO_4 environments for structural and ornamental purposes. After 30 cycles of H_2SO_4 and Na_2SO_4 shock, minimum decrease in point load values was obtained from DBP samples with 5.97% and 9.15%, respectively. Similarly, decrease in Schmidt harness values of DBP was minimum. Among natural stones exposed to H_2SO_4 and Na_2SO_4 shocks, AO sample that had the greatest strength loss was 17.36% and 9.68%, respectively.

Keywords Natural stones · Sulfate · Acid · Point load strength · Schmidt hardness rebound

Introduction

Natural stones have been used as construction material for hundreds of years worldwide, and they are subject to various climates, seasonal and atmospheric effects. These external effects can cause deterioration of marbles partially or completely. Marbles deteriorate more severely in urban environments. Weathering of marbles exposed to aggressive environments is a field of study in constant development. Predicting response of marbles to environmental weathering is a key factor for assessing a constructions life span [1–7]. Marketability of marbles is affected by many factors such as atmospheric pollution, natural geochemical and physical processes-slow dissolution by rain water, salt deposition, recrystallization, freeze-thawing cycles, spalling, climatic factors, air pollution, industrial pollutant, chemical contaminants, solar radiation, (notably acid rain), bio-deterioration and thermal effects. These effects cause changes in color, stains, efflorescence, material loss, porosity and loosening of rock cohesion. As a result, color change caused from chemical reactions during exposure to external effect has a priority for evaluation of decay. Weathering may cause chemical changes as oxidation or rain, producing a change in color of stones [6–15].

Accelerated durability tests and decay processes are conducted in order to avoid such decay. These tests provide valuable knowledge about degree of degradation, including surface properties such as changes of color and roughness [6, 8, 16, 17]. The commercial value of ornamental stones depends on color [18]. The degradation of stones is related to both internal parameters of rock such as porosity, texture and structure, as well as human and natural atmospheric factors [19–24]. Environmental effects such as acidic and

✉ Engin Özdemir
ozdemir.engin@inonu.edu.tr

[1] Department of Mining Engineering, İnönü University, Malatya, Turkey

[2] Department of Civil Engineering, İnönü University, Malatya, Turkey

alkaline solutions can deteriorate durability characteristics of natural building stones. The physical deterioration of marbles exposed to acidic environment is more severe than basic environment. Decay of natural stones exposed to acidic environments is also more prominent due to presence of hydrogen ions that accelerate corrosion [10, 25]. Acid conditions lead to both physical and chemical changes in marbles. The changes on marble surfaces can be observed up to a few millimeters deep. Acid solutions such as carbonic acid (CO_2H_2O), sulfuric acid (H_2SO_4), sulfurous acid (SO_2H_2O) and nitric acid (HNO_3) are main environmental effects that significantly destroy natural stones [9]. Sarıısık and Sarıısık (2011) investigated changes in unit weight by exposing natural stones having different water absorption and porosity to acidic environments. It was reported that as acid concentration increased, weight loss of natural stones having high porosity increased [10].

Another environmental factor affecting natural stones used for structural and ornamental purposes is salt crystallization [26]. The use of salt to de-icing in cold regions has increased salt damage that accelerates degradation of natural stones [27]. Especially porous rocks are more affected by salt crystallization due to their high water absorption ratios [6]. Sarıisik et al. (2010) investigated effect of sulfated water compounds on natural stones by exposing them to different sodium sulfate concentrations ($Na_2SO_410H_2O$) under laboratory conditions. For this purpose, they determined changes in their physico-mechanical properties by exposing two different natural stone samples to 5.0%, 1.0%, 0.5% and 0.2% sulfate decahydrate solution ($Na_2SO_410H_2O$). The salts that penetrate into natural stone cause voids in microstructure to grow over time and new cracks to form [28]. In Sarıisik and Sarıisik (2010), natural stones are exposed to various environmental factors throughout their lifetime and lose their initial strength over time. They stated that porosity, which is the most important factor affecting the magnitude of this loss, should be discussed in detail [29].

It is important to determine behavior under different environmental conditions for long-term durability of historical artifacts and monuments built with natural stones [8]. Turkey possesses considerable natural stone reserves and high market potential with different color and texture qualities up to 650 types. The general purpose of this research is to evaluate effects of acidic and basic atmospheres on physico-mechanical and surface (color) of different stones. Thus, H_2SO_4 and Na_2SO_4 were used to create acidic (pH: 2.0–2.2) and basic (pH: 12.0–12.2) atmospheres under laboratory conditions. The samples were subjected to 5% H_2SO_4 and 5% Na_2SO_4 solutions for 0, 10, 20 and 30 cycles. The changes in Schmidt hardness rebound, point load strength, porosity, dry weight and color were investigated. As a result of experimental study, it was revealed that Diyarbakır Black Pearl (DBP) exhibited most resistant behavior against chemical shocks in terms of change in Schmidt hardness, point load strength, porosity and dry weight properties.

Materials and methods

Materials

This study investigates effects of sulfate and acid conditions on five natural stones, which are obtained from eastern of Turkey. The sample codes, commercial names and origins are given in Table 1. In order to determine physical properties (unit weight, water absorption, Mohs hardness) of natural stones, five samples were used for each rock with dimensions of 50 × 50 × 50 mm. For point load strength test, a total of 240 samples (30 × 40 × 40 mm), 48 for each natural stone, were used. Unit volume weight and porosity of natural stones are made to TS EN 1936, and water absorption TS EN 13,755 standards [30, 31]. Mohs hardness, which is resistance of a mineral to scratching, is determined according to TS 6809 [32]. The physical properties, XRD and XRF analysis of samples are given in Tables 2, 3 and 4.

Chemical shock cycles

Chemical shock cycles were performed with procedures suggested by TS EN 14,066, with minor modification [33]. The samples were immersed in solutions with different pH values instead of distilled water. The samples were kept in oven at 105 °C for 18 h and then immersed in two different chemical solutions for 6 h at room temperature. The pH values of 5% H_2SO_4 and 5% Na_2SO_4 chemical solutions were kept constant in range of 2–2.20 and 10–10.20, respectively. The chemical solutions were renewed so that pH values remained within this ranges. After every 10 cycles, point load strength, porosity, weight loss, Schmidt hammer hardness and color changes were determined and their arithmetic averages were calculated.

Table 1 Samples codes, commercial names and origins

Sample code	Commercial name	Location	Origin
ERL	Rosso Levanto	Elazig	Sedimantery
MB	Beige	Malatya	Sedimantery
AO	Onyx	Agri	Sedimantery
ACE	Crystal Emperador	Adiyaman	Sedimantery
DBP	Black Pearl	Diyarbakir	Sedimantery

Table 2 Physical properties of samples

	Natural unit weight (g/cm^3)	Saturated unit weight (g/cm^3)	Dry unit weight (g/cm^3)	Water absorption by weight (%)	Water absorption by volume (%)	Mohs hardness
ERL	2.71 ± 0.050	2.71 ± 0.060	2.70 ± 0.020	0.340 ± 0.210	0.91 ± 0.048	4
MB	2.69 ± 0.009	2.69 ± 0.010	2.69 ± 0.008	0.14 ± 0.037	0.40 ± 0.089	4
AO	2.69 ± 0.051	2.72 ± 0.040	2.69 ± 0.021	0.27 ± 0.098	0.73 ± 0.046	3
DBP	2.64 ± 0.071	2.64 ± 0.065	2.63 ± 0.023	0.209 ± 0.004	0.567 ± 0.05	4
ACE	2.63 ± 0.058	2.65 ± 0.043	2.63 ± 0.011	1.34 ± 0.148	3.55 ± 0.625	3–4

Table 3 XRF analysis of samples

Content	ERL (%)	MB (%)	AO (%)	DBP (%)	ACE (%)
SiO_2	23.19	0.51	0.21	1.35	0.07
CaO	20.71	54.12	49.21	52.39	33.22
Fe_2O_3	7.332	0.09	2.06	0.35	0.75
MgO	26.25	1.51	2.34	1.001	19.2
K_2O	< 0.0012	0.001	0.001	0.07	0.001
Al_2O_3	1.329	0.25	0.31	0.55	2.170
Na_2O	< 0.015	0.012	0.011	0.04	2.71
P_2O_5	0.3612	0.002	0.003	0.36	0.008
SrO	0.012	0.002	0.002	0.18	0.023
ZnO	0.004	0.002	0.003	0.01	0.340
Co_2O_3	0.023	–	0.0004	0.05	–
LOI	20.32	42.01	44.29	43.29	40.97

Experimental tests

Point load test

Point load test is an accepted test procedure used to determine mechanical properties of natural stones. This index can also be used to indirectly predict other mechanical properties of natural stones. The block point load test was carried out in accordance with ISRM procedures [34]. The 40 × 40 × 30 mm samples were used for tests. Tests were carried out at the end of 0, 10, 20, 30 cycles.

Porosity

Porosity was determined in accordance with TS EN 1936 standard [30]. Samples were kept in distilled water for 48 h. The saturated samples were weighed in air and water, dried in oven for 24 h at 105 °C. Afterward, the weights of samples were re-measured. The porosity is calculated using Eq. (1)

$$n = \frac{\left(m_{sat} - m_{dry}\right)}{\left(m_{sat} - m_{sub}\right)} \times 100 \tag{1}$$

where

n: porosity,
m_{sat}: weight of saturated samples,
m_{dry}: weight of dry samples,
m_{sub}: weight of saturated samples in submerged in water.

Percentage change by weight

The samples were washed with distilled water so that no particles remained on them and then kept in an oven at 105 ± 5 °C for 24 h until their mass stabilized. After drying process, samples were cooled at room temperature. Initial weights of samples were determined (m_1). Samples were shocked in 5% H_2SO_4 and 5% Na_2SO_4 solutions for 0, 10, 20, 30 cycles, and then, samples were dried for 24 h in an oven and cooled to room temperature, and final weight was determined (m_2). Change in dry weight is calculated by Eq. (2).

$$\Delta_W = \left[\left(m_1 - m_2\right) / m_1\right] * 100 \tag{2}$$

Δ_W = Change in dry weight, (%).
m_1 = Initial weight of samples.
m_2 = Final weight of samples.

Schmidt hardness

Schmidt hardness test has been increasingly used because of its simplicity, rapidity, non-destructiveness and portability [35]. Schmidt hardness was determined in accordance with ISRM (1978) at the end of 0, 10, 20 and 30 cycles [36]. Schmidt hammers are divided into 2 as L and N types when classified according to their impact energies. The impact energy of L type hammers is 0.735 Nm, and impact energy of N type Schmidt hammer is 2.207 Nm. However, when hardness

Table 4 XRD analysis of samples

Sample	ERL	MB	AO	DBP	ACE
Minerals	Calcite, Dolomite, Silica, Bentonite clay	Calcite	Calcite	Calcite	Calcite, Dolomite

testing is performed on core samples in laboratory, L type hammer is used instead of N type hammer. In this study, L type Schmidt hammer was used in experiments.

Color changes

The color change was assessed using Konica-Minolta color reader. In CIELAB system, color is quantified according to three chromatic coordinates: "*a*" parameter is red-green axis ($a<0$ green; $a>0$ red); "*b*" parameter is yellow-blue axis ($b<0$ blue; $b>0$ yellow) and L parameter represents lightness or luminosity ($L=100$ white; $L=0$ dark) [37]. The CIELAB coordinate system is given in Fig. 1 [15]. The total color differences (ΔE) are defining total color changes and determined in Eq. (3) [38].

$$\Delta E^*_{ab} = \sqrt{\left(\Delta L^{*2}\right) + \left(\Delta b^{*2}\right)} \qquad (3)$$

Result and discussion

Porosity, dry weight, Schmidt hardness and point load strength of samples after chemical shocks of 0, 10, 20 and 30 cycles are given as a whole in Table 5. Moreover, changes in these parameters after 30 cycles are also presented by percentage in Table 6. Then, findings are interpreted graphically in related title.

Color changes

After chemical shocks, color modifications occurred in all samples. At 30 cycles, color and lightness values of samples are given in Table 7. The total color differences after chemical shocks of samples are given in Table 8 and trends are given in Fig. 2.

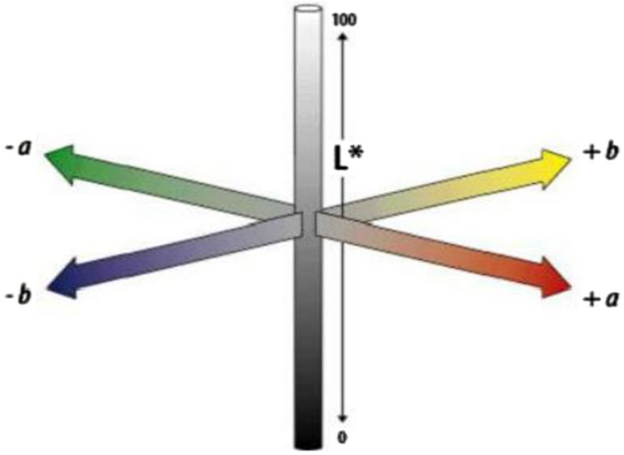


Fig. 1 CIELAB coordinate system

At the end of chemical shocks, color change was observed in all samples. H_2SO_4 shock led to more noticeable changes compared to Na_2SO_4. At 30 cycles, dark color samples (ERL, DBP and ACE) exhibited more evident color changes compared to MB and AO samples. The *L*, *a*, *b* are different in all samples. The most prominent color changes in terms of *L* occurred in ERL and DBP sample after chemical shocks. The glossiness of ERL and DBP showed higher increase compared to other samples. The color changes due to chemical shocks in case of lightness (*L*) are different in all samples. The remarkable differences occurred in ERL and DBP samples.

All samples have large redness. H_2SO_4 shock has positive effect on redness, except for ACE samples. Na_2SO_4 shock has negative effect on AO, ACE and ERL samples. In MB and DBP samples, Na_2SO_4 shock led to increase in redness. Except from DBP, all of samples had large yellowness. H_2SO_4 shock led to decrease in yellowness in ERL, AO, DBP samples. Na_2SO_4 led to increase in yellowness except for AO samples. When total color changes after H2SO4 and Na2SO4 cycles are examined, it is seen that the biggest change is in ERL (66.74%) and AO (50.64%), while the lowest change is in MB (17.39%) and ACE (16.39%) samples, respectively. Change in visual appearance of samples after chemical shocks of 30 cycles is also given in Table 9. When samples are examined, it is clearly seen that there was a significant decrease in surface glossiness of all samples. The glossiness of samples was not uniformly affected by chemical solutions after 30 cycles. In light-colored sample group (such as MB, AO and ACE), it was observed that a noticeable yellowing in color occurred after H_2SO_4 shock. In dark-colored sample group (such as ERL and DBP), there was lightening in color after chemical solutions.

Change in Schmidt hardness

Schmidt hardness changes of samples after chemical shocks are given in Figs. 3 and 4.

There was not significant decrease in Schmidt hardness values of DBP and MB samples. After H_2SO_4 and Na_2SO_4 shock cycles, there is a decrease of 4.33–2.5% in DBP sample and 6.68–3.23% in MB sample, respectively. However, there was a noticeable decrease in Schmidt hardness values of ERL, AO and ACE samples after immersion in H_2SO_4 and Na_2SO_4 solutions. After H_2SO_4 and Na_2SO_4 shock cycles, there is a decrease of 17.36–9.68% in AO sample, 14.11–7.07% in ACE sample, and 11.02–5.63% in ERL sample, respectively. This decrease may be associated with increase in porosity of ERL, AO and ACE samples. Additionally, water absorption by weight and by volume of ERL, AO and ACE samples is higher and point load

Table 5 Porosity, dry weight, Schmidt hardness and point load strength of samples

	Cycles		ERL	MB	AO	ACE	DBP
Porosity, (%)	0	H_2SO_4	1.70	0.32	0.72	1.58	0.50
		Na_2SO_4	1.70	0.32	0.72	1.58	0.50
	10	H_2SO_4	3.05	1.39	1.77	3.40	1.14
		Na_2SO_4	1.73	0.33	0.73	1.64	0.52
	20	H_2SO_4	3.94	1.90	3.25	4.67	1.77
		Na_2SO_4	1.88	0.35	0.75	1.71	0.53
	30	H_2SO_4	5.00	2.44	5.06	5.51	2.27
		Na_2SO_4	1.91	0.39	0.81	1.74	0.56
Dry weight, (gr)	0	H_2SO_4	134.46	128.30	133.59	149.42	134.15
		Na_2SO_4	136.66	130.93	131.60	132.16	134.14
	10	H_2SO_4	134.12	127.68	132.75	148.40	133.85
		Na_2SO_4	136.65	130.93	131.49	132.12	134.14
	20	H_2SO_4	133.01	127.43	131.97	147.33	133.49
		Na_2SO_4	136.39	130.89	131.47	131.90	134.13
	30	H_2SO_4	132.43	127.19	130.85	146.77	133.00
		Na_2SO_4	136.296	130.823	131.413	131.66	134.103
Schmidt hardness	0	H_2SO_4	35.40	43.40	31.10	41.10	43.90
		Na_2SO_4	35.50	43.40	31.00	41.00	44.00
	10	H_2SO_4	34.10	42.50	28.90	39.00	43.20
		Na_2SO_4	35.00	43.00	30.10	40.20	43.70
	20	H_2SO_4	32.80	41.80	27.80	37.20	42.70
		Na_2SO_4	34.10	42.40	29.20	39.30	43.30
	30	H_2SO_4	31.50	40.50	25.70	35.30	42.00
		Na_2SO_4	33.50	42.00	28.00	38.10	42.90
Point load strength, (MPa)	0	H_2SO_4	5.87	7.85	3.62	7.05	8.01
		Na_2SO_4	5.87	7.87	3.63	7.06	8.02
	10	H_2SO_4	5.49	7.51	3.22	6.31	7.88
		Na_2SO_4	5.70	7.62	3.27	6.77	7.97
	20	H_2SO_4	5.02	7.09	3.00	6.00	7.49
		Na_2SO_4	5.39	7.33	3.15	6.14	7.66
	30	H_2SO_4	4.79	6.88	2.73	5.59	7.27
		Na_2SO_4	5.15	7.25	3.05	6.00	7.54

Table 6 Changes in porosity, dry weight, Schmidt hardness, point load strength at 30 cycles

Changes, (%)		ERL*	MB*	AO*	ACE*	DBP*
Porosity	H_2SO_4	+194.98	+670.88	+605.43	+247.79	+351.68
	Na_2SO_4	+12.85	+20.56	+13.21	+9.72	+11.46
Dry weight	H_2SO_4	−1.51	−0.87	−2.05	−1.78	−0.86
	Na_2SO_4	−0.27	−0.08	−0.14	−0.38	−0.03
Schmidt hardness	H_2SO_4	−11.01	−6.68	−17.36	−14.11	−4.32
	Na_2SO_4	−5.63	−3.22	−9.67	−7.07	−2.5
Point load strength	H_2SO_4	−18.44	−12.39	−24.71	−20.69	−9.15
	Na_2SO_4	−12.22	−7.92	−15.95	−15.01	−5.97

*Increase (+), decrease (−) compared to unexposed sample

strength values are low. Similarly, Taghipour et al. (2015) investigated durability of limestones obtained from Dariyan and Ilam formations against acid solutions and stated that Dariyan limestone showed lower Schmidt hammer rebound values than Ilam limestone due to lower strength properties and durability [39]. Figure 5 shows decrease in Schmidt hardness by percentage.

Table 7 Color and lightness values of samples at 30 cycles

Sample	*L*	*A*	*b*
ERL (reference)	60.00	2.20	2.40
ERL (H_2SO_4)	36.60	5.42	3.70
ERL (Na_2SO_4)	45.50	2.10	2.07
MB (reference)	74.86	0.75	14.7
MB (H_2SO_4)	79.76	1.13	12.23
MB (Na_2SO_4)	70.76	1.60	11.46
AO (reference)	70.47	2.67	11.85
AO (H_2SO_4)	76.96	3.70	14.06
AO (Na_2SO_4)	78.45	1.50	6.00
ACE (reference)	57.47	8.43	17.33
ACE (H_2SO_4)	57.80	7.30	11.90
ACE (Na_2SO_4)	59.10	7.90	14.53
DBP (reference)	27.16	1.35	−1.05
DBP (H_2SO_4)	37.53	2.80	−1.35
DBP (Na_2SO_4)	35.30	3.23	−1.00

Table 8 Changes of *L*, *a*, *b*, *E* values after chemical shocks

Sample	ΔL	Δa	Δb	ΔE
ERL (H_2SO_4)	39.00	−146.00	−54.16	66.74
ERL (Na_2SO_4)	24.16	4.54	13.75	27.79
MB (H_2SO_4)	6.27	−50.67	16.23	17.39
MB (Na_2SO_4)	5.47	−113.30	22.04	22.70
AO (H_2SO_4)	−9.20	−38.57	−18.64	20.78
AO (Na_2SO_4)	−11.32	43.82	−49.36	50.64
ACE (H_2SO_4)	0.57	13.40	31.33	31.33
ACE (Na_2SO_4)	−2.83	6.28	16.15	16.39
DBP (H_2SO_4)	−38.18	−107.40	−28.57	47.68
DBP (Na_2SO_4)	−29.97	−139.25	4.76	30.34

Change in porosity

The porosity values of samples after chemical shocks of 0, 10, 20 and 30 cycles are given in Figs. 6 and 7.

When porosity changes are examined, there are changes depending on pH value of chemical and cycle's number. However, Na_2SO_4 shock does not lead to serious changes in porosity. There is a significant increase in porosity of samples (especially ERL, AO and ACE) immersed in H_2SO_4 solution. Transition of chemical solutions into samples caused expansion of pores and existing of new pores. As a result of experimental and statistical studies on similar rock types, it was observed that the strength decreased as porosity increased [40]. In this study, it was determined that porosity increased and point load strength decreased as pH value decreased.

Change in dry weight

Increase in porosity and water absorption capacity of samples is most important parameters affecting decay rate and weight loss. Dry weight losses by percentage of samples at the end of 30 cycles are shown in Fig. 8. Chemical shocks led to a decrease in dry weight of all samples. The dry weight was not uniformly affected by chemical shocks. Samples exposed to H_2SO_4 shock exhibited higher decrease in dry weight than Na_2SO_4. After H_2SO_4 and Na_2SO_4 shock, minimum dry weight loss occurred in DBP samples with 0.86% and 0.03%, respectively. Similarly, DBP samples are more durable than others in terms of Schmidt hammer hardness and point load test values. ERL, AO and ACE samples exposed to chemical shock showed higher decrease in dry weight. After H_2SO_4 and Na_2SO_4 shock cycles, there is a decrease of 2.05–0.14% in AO

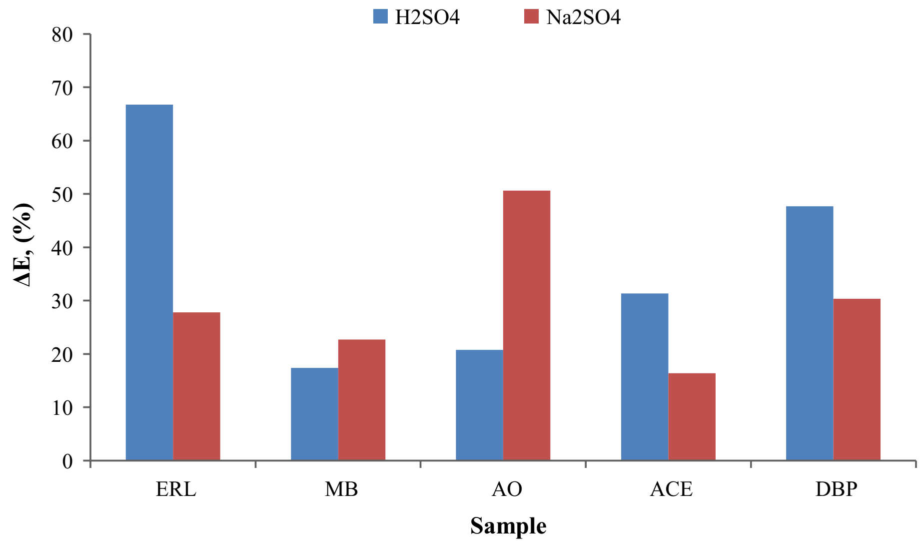
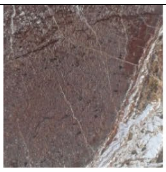
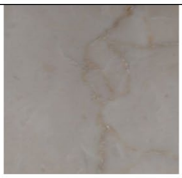


Fig. 2 Total color differences at 30 cycles

Table 9 Change in visual appearance of samples at 30 cycles

Samples	Reference	After H_2SO_4 shock	After Na_2SO_4 shock
ERL			
MB			
AO			
ACE			
DBP			

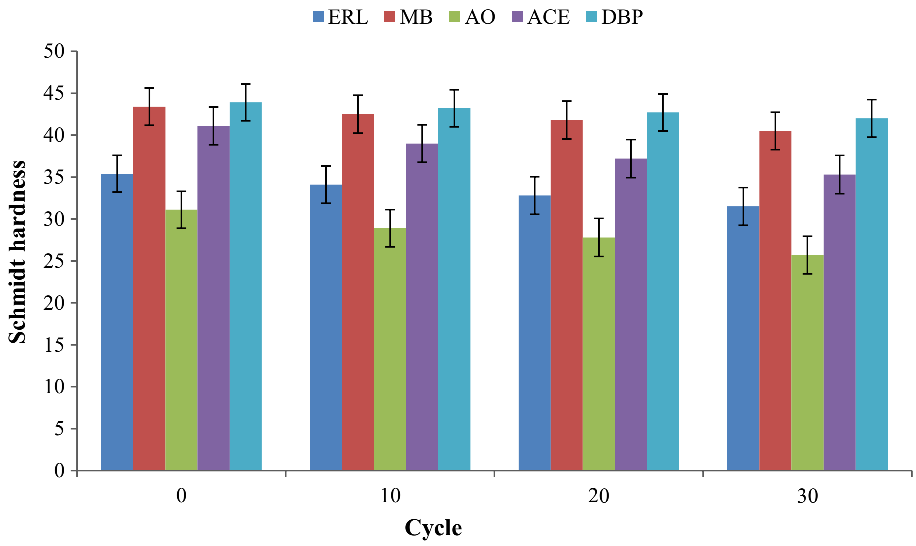


Fig. 3 Schmidt hardness values of samples after H_2SO_4 shock

Fig. 4 Schmidt hardness values of samples after Na_2SO_4 shock

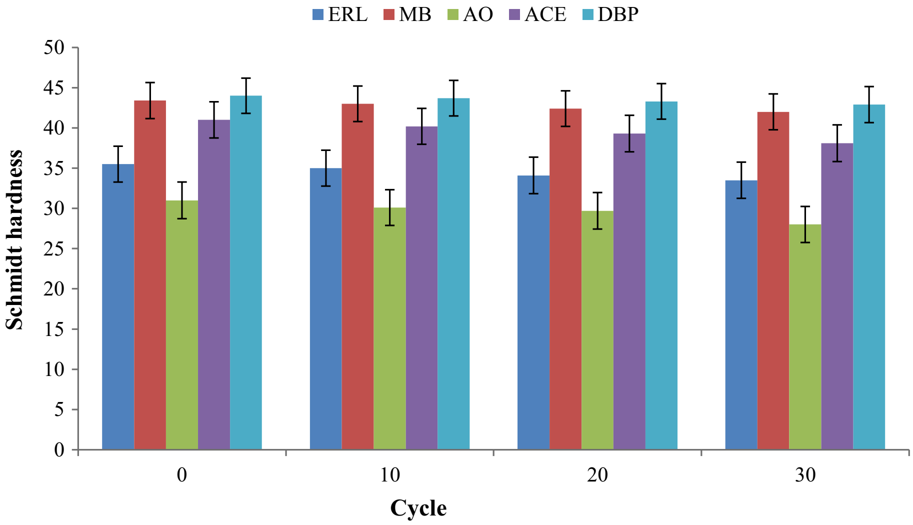


Fig. 5 Decrease in Schmidt hardness at 30 cycles

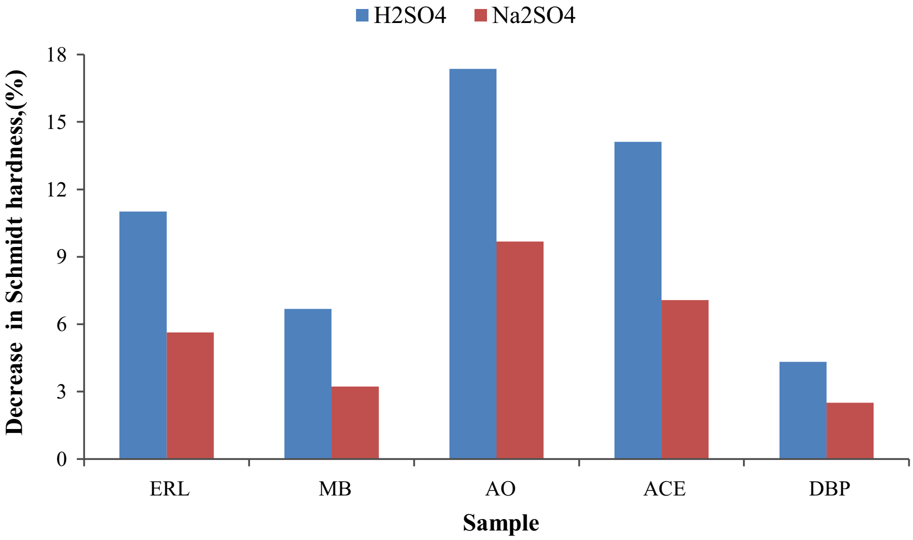
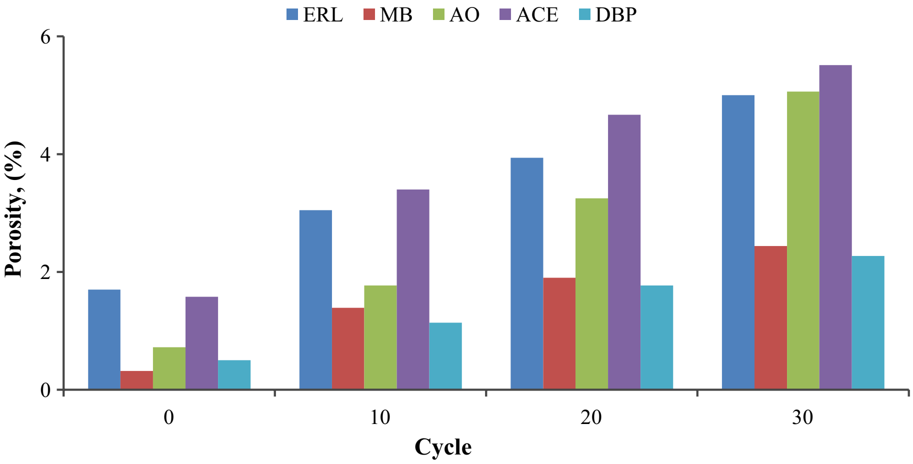


Fig. 6 The porosity values of samples after H_2SO_4 shock



sample, 1.78–0.38% in ACE sample, and 1.51–0.27% in ERL sample, respectively. This may be because ERL, AO and ACE samples have higher porosity and water absorption capacity.

Fig. 7 The porosity values of samples after Na_2SO_4 shock

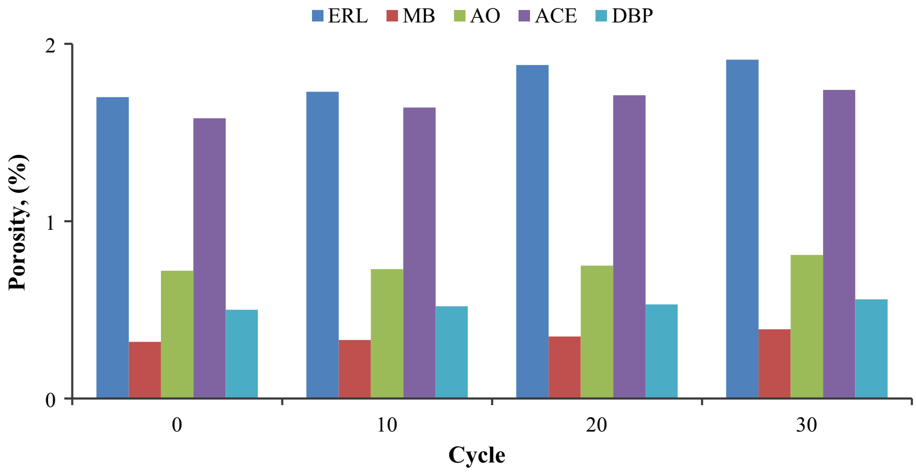


Fig. 8 Decrease in dry weight at 30 cycles

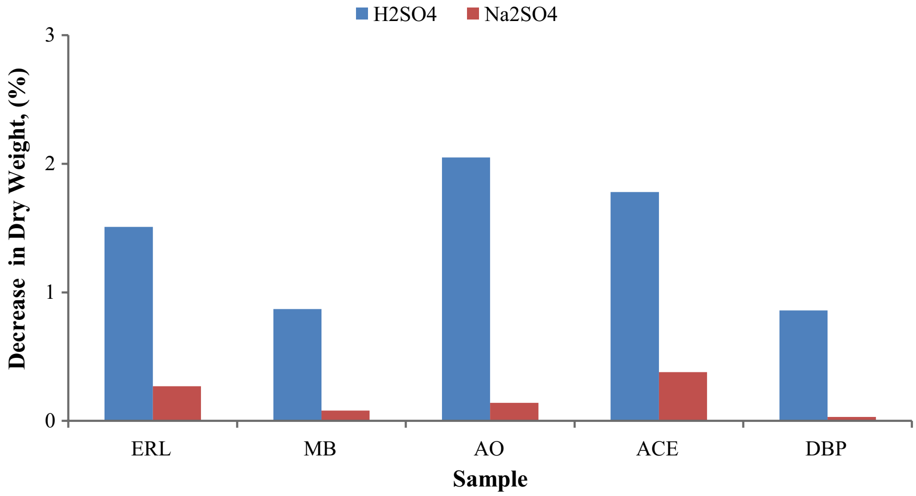
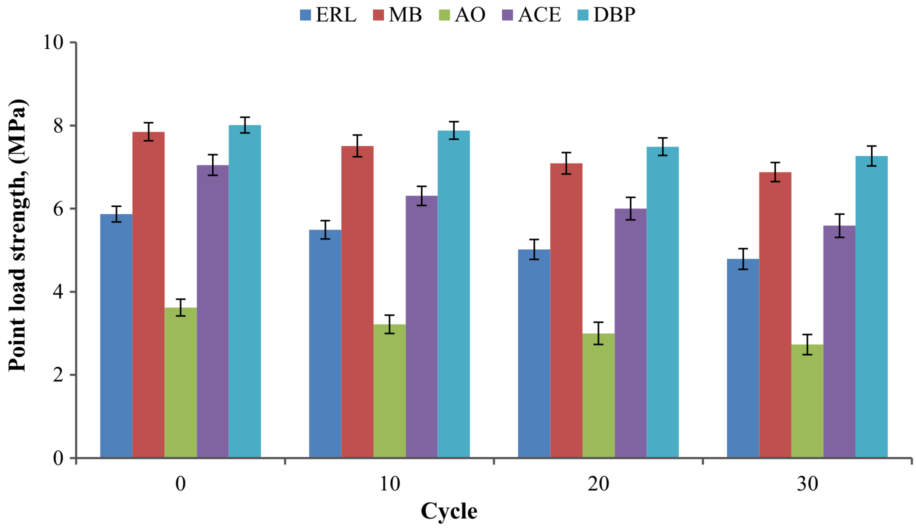


Fig. 9 Point load strength values of samples after H_2SO_4 shock



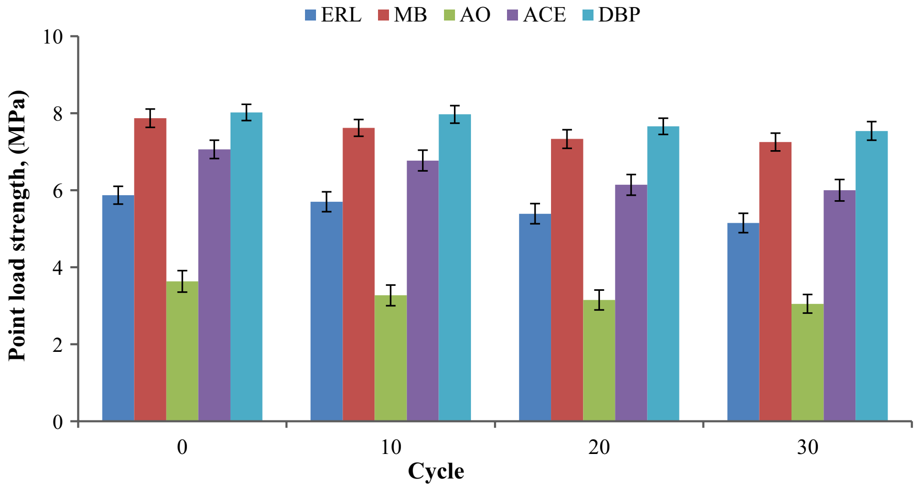


Fig. 10 Point load strength values of samples after Na_2SO_4 shock

Change in point load strength

The point load strength values of samples after chemical shocks are given in Figs. 9 and 10.

There was decrease in point load values of all samples in both H_2SO_4 and Na_2SO_4 solutions. Decrease in point load values of samples immersed in H_2SO_4 solution was more than ones immersed in Na_2SO_4. Similarly, Sharma et al. (2007) revealed that physico-mechanical properties of sample were adversely affected by an acidic and alkaline watery environment. The reduction recorded in physico-mechanical properties was lower in an alkaline environment, compared to an acidic environment. In acidic environment, greater decrease in strength is due to fact that a higher concentration of hydrogen ions accelerates rate of abrasion [10, 25]. After 30 cycles, minimum decrease in point load values was obtained from DBP samples with 5.97% and 9.15%, respectively. Similarly, decrease in Schmidt harness values of DBP was minimum. It is known that there is a general relation between rock strength and porosity [40–42]. Smaller porosity results in greater rock strength [43]. DBP was most resistant after chemical shocks in terms of change in Schmidt hardness, point load strength, porosity and dry weight properties. However, ERL, AO and ACE samples were weaker against H_2SO_4 and Na_2SO_4 conditions. Decrease in point load strength by percentage at the end of 30 cycles is shown in Fig. 11. After H_2SO_4 and Na_2SO_4 shock cycles, there is a decrease of 24.72–15.96% in AO sample, 20.69–15.02% in ACE sample, and 18.45–12.22% in ERL sample, respectively. Both point load and Schmidt hardness values are inversely related to porosity. It was observed that point load and Schmidt hardness values decreased with increasing porosity.

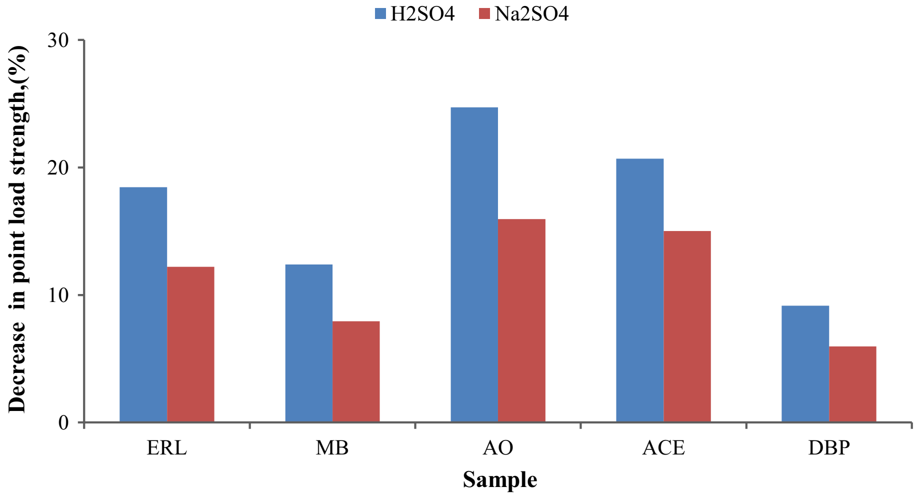


Fig. 11 Decrease in point load strength at 30 cycles

Conclusion

Natural stones are exposed to various atmospheric effects during their service life, and their strength properties decrease over time. This paper presents an experimental study conducted to explore some physico-mechanical properties of five different samples after exposed to Na_2SO_4 and H_2SO_4 shocks up to 30 cycles. The following conclusions are drawn from this study:

- H_2SO_4 shock led to more noticeable color changes compared to Na_2SO_4. The glossiness of ERL and DBP showed higher increase compared to other samples. H_2SO_4 shock has positive effect on redness, except for ACE samples. H_2SO_4 shock led to decrease in yellowness in ERL, AO, DBP samples. In dark-colored sample group (such as ERL and DBP), there was lightening in color after chemical solutions. When total color changes (ΔE) are examined, the greatest change after H_2SO_4 cycle is seen in ERL sample with 66.74%, while the greatest change after Na_2SO_4 cycle is in AO sample with 50.64%.
- There was not significant decrease in Schmidt hardness values of DBP and MB samples. After H_2SO_4 and Na_2SO_4 shock cycles, a percent loss was obtained in DBP sample of 4.33–2.5% and in MB sample of 6.68–3.23%, respectively.
- There are changes in porosity values depending on pH value of chemical and number of cycles. However, it was observed that Na_2SO_4 shock did not cause serious changes in porosity.
- There were parallel decreases in weight losses due to increase in porosity and water absorption capacity of samples. Considering percent weight losses, the greatest loss after H_2SO_4 cycle is seen in AO sample with 2.5%, while the greatest loss after Na_2SO_4 cycle is in ACE sample with 0.38%.
- Point load strength test is one of the most important methods used to determine indirectly compressive and tensile strength values of rocks. In this study, point load strength was performed as a mechanical parameter. There was decrease in point load strength of all samples in both H_2SO_4 and Na_2SO_4 solutions. After 30 cycles, minimum decrease in point load strength was obtained from DBP samples with 5.97% and 9.15%, respectively.

DBP and MB samples may be preferred in Na_2SO_4 and H_2SO_4 environments when used for structural and ornamental purposes. However, ERL, AO and ACE samples are not suitable for such aggressive environments because of its high porosity and water absorption capacity. Additionally, it will be beneficial to investigate effect of different acidic and alkaline environments (acid rain related attack and dissolution, salt crystallization, and freeze–thaw cycles, etc.) on physico-mechanical properties of samples obtained from different rock types with different porosity and water absorption capacity.

Declarations

Conflict of interest The authors declare that they have no confict of interest.

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