



EFFECT OF PORE STRUCTURE ON CONCRETE DETERIORATION BY PHYSICAL SULPHATE ATTACK

Ahmed, R. Suleiman
Ph.D. Candidate, Western University, Canada

Moncef, Nehdi
Ph.D., P.Eng. Western University, Canada

ABSTRACT

Repeated crystallisation of salt minerals has been considered as the driving force for surface scaling of concrete exposed to physical sulphate attack. This damage is initiated when stresses induced by the internal pressure created via repeated salt crystallisation exceed the tensile strength of the concrete. The degree of such damage will depend mainly on the structure and connectivity of pores, which control the penetration of sulphates into the concrete. Several factors affect the pore structure including the concrete constituents, mixture proportions and the curing process. Therefore, in this paper, the effect of the pore structure on concrete deterioration by physical sulphate attack was investigated. Results show that the durability of concrete against physical sulphate attack can be controlled by tailoring the pore structure of the concrete surface.

Keywords: Physical; Sulphate attack; Pores; Scaling; Crystallisation.

1. INTRODUCTION

Despite the current knowledge and specifications on concrete deterioration due to sulphate attack, there are only limited information and studies regarding the damage of concrete due to physical sulphate attack. According to Haynes et al. (2008), in certain environmental conditions, physical sulphate attack can cause substantial damage of the concrete surface. This was reported in several field investigations for concrete structures around the world (Al-Amoudi, 2002; Hime et al. 2001; Novak and Colville, 1989; Yoshida et al. 2010). However, for decades, chemical sulphate attack on concrete was the main research interest, while physical sulphate attack has mainly been ignored (Haynes, 2008; Aye and Oguchi, 2011). It is only recently that researchers started to focus on the performance of concrete under physical sulphate attack. Nevertheless, there are contradictory views in the existing literature regarding concrete damage by physical sulphate attack. For instance, a field study by Irassar et al. (1995) reported that concrete with low permeability exhibited higher damage when exposed to an environment prone to physical sulphate attack than concrete with high permeability. It was suggested that concrete with fine pores, which can be achieved using a low w/c, is more vulnerable to damage due to physical sulphate attack (Hime 2003). Primarily, this concept was suggested based on the fact that stones with finer pores are more vulnerable to damage due to salt weathering or the so-called physical salt attack. However, laboratory investigation by Folliard and Sandberg (1994) showed that concrete made with w/c = 0.30 had better performance than concrete made with w/c = 0.50 under rapid salt crystallisation. Yet, a study by Nehdi and Hayek (2005) showed that concrete mortars with an intermediate w/c = 0.45 had an extensive efflorescence formation compared with w/c = 0.30 and w/c = 0.60. Therefore, more research is needed to investigate the main role of the concrete pore structure when exposed to physical sulphate attack.

Studies have shown that salt weathering can cause serious damage to rocks and stones based on their pore structures (Angeli et al. 2008; Scherer, 2004; Buj and Gisbert, 2010). Buj and Gisbert (2010) investigated fifteen samples of stones that are similar to those commonly used in the architectural heritage. They found that stones with low porosity and high amount of small pores with low connectivity are less vulnerable to damage than stones with high

porosity and higher average pore radius. Thus, the previous suggestion regarding the poor performance of concrete with low w/c ratio under physical sulphate attack is questionable. According to Wellman and Wilson (1965), rocks that contain large pores connected by micro-pores are more venerable to damage due to salt weathering. When a rock or a porous material is exposed to evaporation and its large and small pores are filled with a saturated salt solution, salt crystals will grow in the large pores at the expense of the smaller crystals in the small pores. This process will continue till damage occurs. The damage depends on the size of the small pores and the interfacial tension between the crystal face and its saturated solution compared with the strength of the rock (Wellman and Wilson, 1965). The current paper provides companion research data to that reported by Nehdi et al. (2014) and Suleiman et al. (2014) on concrete exposed to dual sulphate attack.

2. RESEARCH SIGNIFICANCE

Previous studies have shown that the susceptibility of stones and rocks exposed to salt weathering depends on their pore structure. Thus, factors that affect the concrete pore structure including the w/b ratio, binder type, and curing conditions were investigated under an environment prone to physical sulphate attack. The results of this study should explain the main role of these factors in concrete exposed to physical sulphate attack, which could allow to improve the durability design of concrete in sulphate environments.

3. EXPERIMENTAL PROGRAM

3.1 Materials and Specimen Preparation

Three groups of concrete mixtures with different w/b ratio (i.e. 0.30, 0.45, and 0.60) were tested. In each group, three binder types were used including ordinary portland cement (OPC), OPC with 25% class F fly ash (FA), OPC with 8% silica fume (SF), and OPC with 8% metakaolin (MK). The physical and chemical properties of the cement, mineral additives, and aggregates are summarized in Tables 1 and 2. The proportions of the concrete mixtures are provided in Table 3. For each of the concrete mixtures, standard cylinders 100×200 mm (4×8 in.) were cast according to ASTM C192 (Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory).

Table 1: Physical and chemical properties of various binders used in this study

Components /Property	Cement Type (10)	Silica Fume (SF)	Metakaolin (MK)	Fly ash (FA)
Silicon oxide (SiO ₂) (%)	19.6	95.3	52.2	43.39
Aluminum oxide (Al ₂ O ₃) (%)	4.8	0.2	41	22.1
Ferric oxide (Fe ₂ O ₃) (%)	3.3	0.1	1.8	7.7
Calcium oxide (CaO) (%)	61.50	0.49	-	15.63
Magnesium oxide (MgO) (%)	3.0	0.27	-	-
Sulfur trioxide (SO ₃) (%)	3.50	0.24	0.04	1.72
Loss on ignition (%)	1.90	1.99	1.1	1.17
Insoluble residue (%)	0.44	-	-	-
Equivalent alkalis (%)	0.7	-	-	-
Tricalcium silicate (C ₃ S) (%)	55	-	-	-
Dicalcium silicate (C ₂ S) (%)	15	-	-	-
Tricalcium aluminate (C ₃ A) (%)	7	-	-	-
Tetracalcium aluminoferrite (C ₄ AF) (%)	10	-	-	-
Blaine fineness (m ² /kg)	371	-	-	-
Autoclave expansion (%)	0.09	-	-	-
Compressive strength 28 days (MPa)	40.9	-	-	-
Specific gravity	3.15	2.58	2.20	2.50
Time of setting (min) Vicat Initial	104	-	-	-

Table 2: Physical and chemical properties of fine and coarse aggregates

Property	Coarse aggregate	Fine aggregate
Potential alkali reactivity (Mortar-bar method) (%)	0.05	-
Absorption (%)	1.11	1.09
Crushed particles (%)	68.00	-
Flat/elongated (%)	6.00	-
Micro-deval (A) (%)	11.00	17.00
Soundness (freeze-thaw) (%)	2.20	-
Soundness (MgSO ₄) (%)	3.90	-
Specific gravity (apparent) (%)	2.73	2.73
Specific gravity (dry) (%)	2.65	2.65
Specific gravity (SSD) (%)	2.68	2.68
Unit weight (kg/m ³)	1734	1512
Materials finer than 75- μ m (sieve # 200) (%)	0.90	2.10

Table 3: Proportion of tested concrete mixtures

Mixture #	Binder Type	Cement Content (kg/m ³)	Pozzolanic Content (kg/ m ³)	Aggregate Content (kg/m ³)		w/b	Super-plasticizer (ml/m ³)
				Coarse	Fine		
1	OPC	450	0.000	1110	804	0.30	2250
2	OPC + 25% FA	337.5	122.5		779	0.30	1600
3	OPC + 8% SF	414	36.00		791	0.30	3200
4	OPC + 8% MK	414	36.0		797	0.30	2900
5	OPC	400	0.000	1110	727	0.45	1570
6	OPC + 25% FA	300	100.0		705	0.45	900
7	OPC + 8% SF	368	32.00		715	0.45	2100
8	OPC + 8% MK	368	32.00		720	0.45	1850
9	OPC	350	0.000	1110	689	0.60	---
10	OPC + 25% FA	262	87.50		754	0.60	---
11	OPC + 8% SF	322	28.00		679	0.60	---
12	OPC + 8% MK	322	28.00		797	0.60	---

3.2 Curing Conditions

Concrete cylinders from each concrete mixture were cured for 28 days in a moist room at RH \geq 95% and T = 20°C [68°F] before exposure to the sulphate environment. The curing was carried out according to ASTM C511 (Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes). To investigate the curing effect, another identical group of cylinders from each mixture was exposed to the sulphate environment after 24 hours.

3.3 Environmental Exposure Conditions

All concrete cylinders were partially immersed in a 5% sodium sulphate solution and placed inside a walk-in environmental chamber with cycling temperature and RH. Cycles consist of one week at temperature = 20°C [68°F] and RH = 82% followed by one week at temperature = 40°C [104°F] and RH = 31%.

3.4 Visual Inspection

Concrete cylinders were visually inspected for up to six months of sulphate exposure. The visual rating of concrete surface damage was rated according to the rating system proposed by Malhotra et al. (1987). In this system, concrete can be rated on a scale of ten based on its surface scaling and mass change as shown in **Table 4**.

Table 4: Visual rating system for damaged concrete (Adapted from Malhotra et al. 1987)

Rating Grade	Rating Description
0	Less than 15% of surface aggregates are exposed
1	More than 15% of surface aggregates are exposed
2	50% of surface aggregates immediately below the surface are exposed
3	80% of surface aggregates are exposed
4	Surface aggregates are exposed over 20% of their perimeter
5	90% of the surface aggregates are exposed over one half of their perimeter
6	95% of volume of specimen remaining
7	80% of volume of specimen remaining
8	60% of volume of specimen remaining
9	20% of volume of specimen remaining
10	Specimen disintegrated

3.5 Mass Loss

Concrete cylinders from each mixture were transferred to the exposure condition after measuring their initial mass using a balance with an accuracy of 0.01 g [0.00035 oz.]. Before measuring their initial mass, all concrete cylinders were air-dried in the laboratory at temperature = 23°C [73.4 °F] and RH = 70% until constant mass was reached. The mass loss was calculated according to the following equation:

$$[1] \quad \text{Mass loss at } (t) = \frac{M_i - M_t}{M_i} \times 100$$

Where; (t) is the time, M_i is the initial mass of the cylinder; M_t is the mass of the cylinder at time (t) .

4. RESULTS AND DISCUSSION

4.1 Visual Inspection

Figure 1 shows salt crystals on concrete surface. During the first week, salt precipitation (efflorescence) appeared above the solution level (5% of sodium sulphate) on the drying surface of the concrete cylinders when exposed to a temperature of 20°C [68°F] and RH of 82%. According to previous studies (Thaulow and Sahu, 2004; Haynes et al. 2008), this exposure condition can lead to mirabilite formation. In the second week, the exposure was altered to a temperature = 40°C [104°F] and RH = 31%, a condition conducive to thenardite formation. It was observed that the volume of the precipitated salt on the concrete surface decreased compared to that in the first exposure. This is due to the conversion of mirabilite to thenardite, which results in a volume reduction of about 314% according to Tsui et al. (2003).

Table 5 reports the visual rating for concrete cylinders after six months of exposure to physical sulphate attack. Scaling of concrete surfaces started to appear above the sulphate solution level approximately a month after the exposure (4 cycles of wetting and drying). The exposure was continued for up to six months (24 cycles of wetting and drying) and all concrete cylinders were inspected to diagnose the level of damage.



Figure 1: Salt crystals on concrete surface

Figure 2 illustrates the damage above the solution level for the cured concrete cylinders made with $w/b = 0.60$. Higher surface scaling above the solution level was found in the cured concrete specimens incorporating pozzolanic minerals compared to that of the specimens made with 100% OPC at a $w/b = 0.60$. Figures 3 and 4 show the cured concrete cylinders made with $w/b = 0.45$ and 0.30 after six months of physical sulphate exposure. Concrete cylinders having a $w/b = 0.45$ achieved similar results to that of cylinders made with $w/b = 0.60$, but with significantly less damage. For the cured concrete cylinders with $w/b = 0.30$, no surface scaling was detected after six months of sulphate exposure. For the non-cured concrete cylinders, an increase in damage was observed in comparison to their cured counterparts.

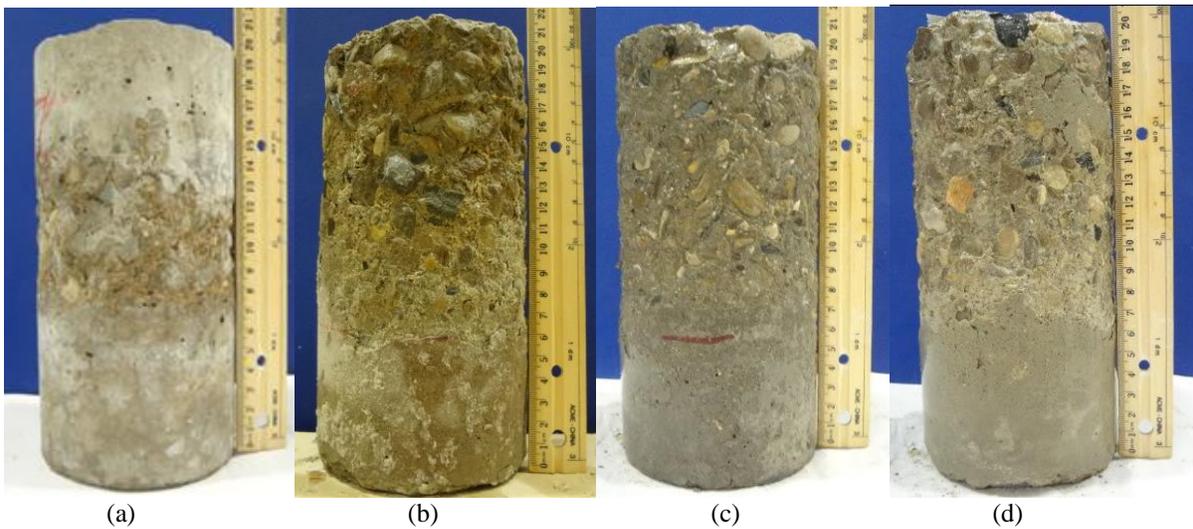


Figure 2: Cured concrete cylinders made with $w/b = 0.60$ after six months of physical sulphate exposure: (a) concrete made with OPC, (b) OPC + 25 % FA, (c) OPC + 8 % SF, and (d) OPC + 8% MK.

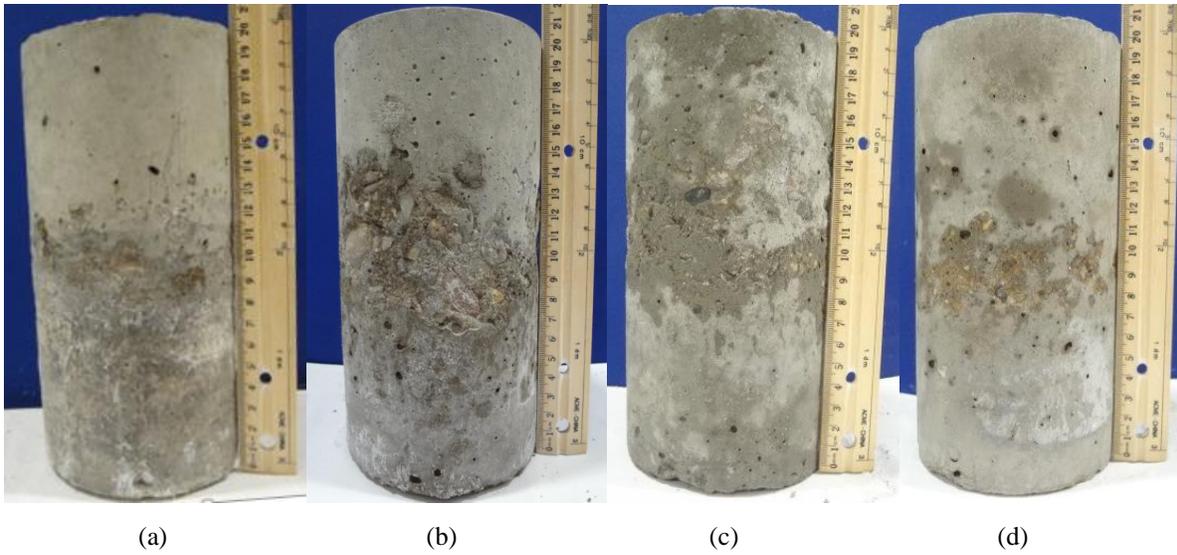


Figure 3: Cured concrete cylinders made with $w/b = 0.45$ after six months of physical sulphate exposure: (a) concrete made with OPC, (b) OPC + 25 % FA, (c) OPC + 8 % SF, and (d) OPC + 8% MK.

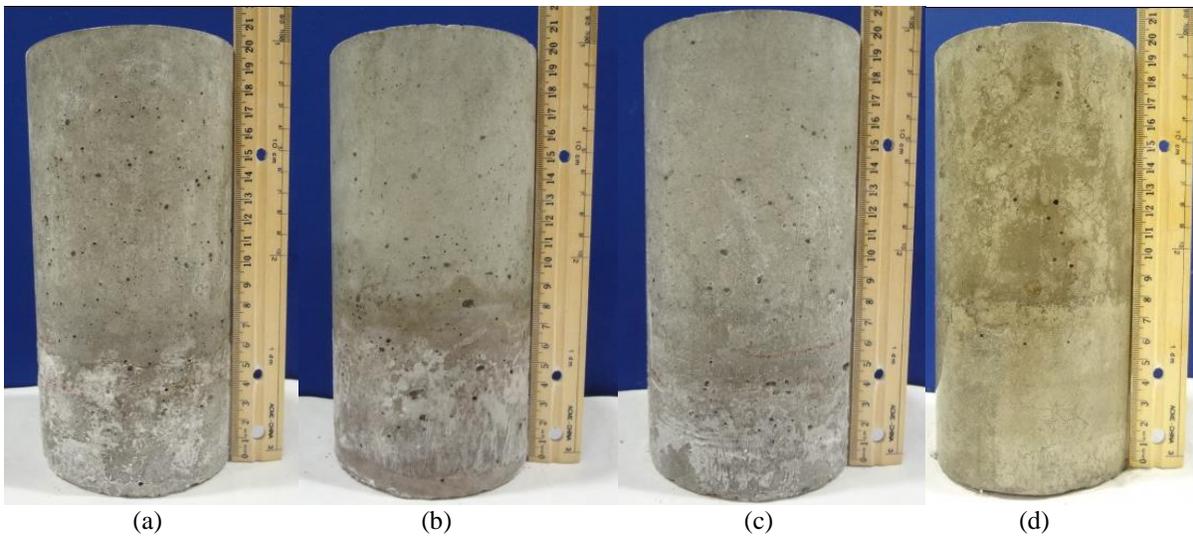


Figure 4: Cured concrete cylinders made with $w/b = 0.30$ after six months of physical sulphate exposure: (a) concrete with OPC, (b) OPC + 25% FA, (c) OPC + 8% SF, and (d) OPC + 8% MK.

Table 5: Visual rating for concrete cylinders after six months of exposure to physical sulphate attack

	w/c = 0.60	w/c = 0.60*	w/c = 0.45	w/c = 0.45*	w/c = 0.30	w/c = 0.30*
OPC	2.20	3.80	0.65	0.95	0	0
OPC + 25% FA	5.80	7.50	2.25	2.85	0	0
OPC + 8% SF	5.00	6.25	1.20	1.55	0	0
OPC + 8% MK	5.50	6.95	1.35	1.80	0	0

*Non-cured

4.2 Mass Loss

The mass loss was observed for all concrete cylinders that were partially immersed in the sodium sulphate solution and exposed to cyclic temperature and RH. **Figure 5** shows the mass loss after 6 months of exposure to physical sulphate attack. During the first month, concrete cylinders gained mass due to water absorption, particularly for those with higher w/b. For example, cured concrete cylinders with w/b = 0.60 gained higher mass than the cured cylinders made with w/b = 0.45 and w/b = 0.30, respectively. In addition, at the same w/b ratio, 100% OPC concrete cylinders gained higher mass than that of samples incorporating pozzolanic minerals. For the non-cured concrete cylinders, the mass gain was higher than the cured concrete cylinders. Approximately one month later, concrete cylinders started to lose mass. Higher mass loss was observed for the non-cured concrete cylinders than for their cured counterparts. The highest mass loss was detected for those concrete cylinders made with w/b = 0.60 and incorporating pozzolanic minerals. A similar trend was observed for concrete cylinders made with w/b = 0.45 but with less mass loss. However, all concrete cylinders made with w/b = 0.30 did not exhibit any mass loss.

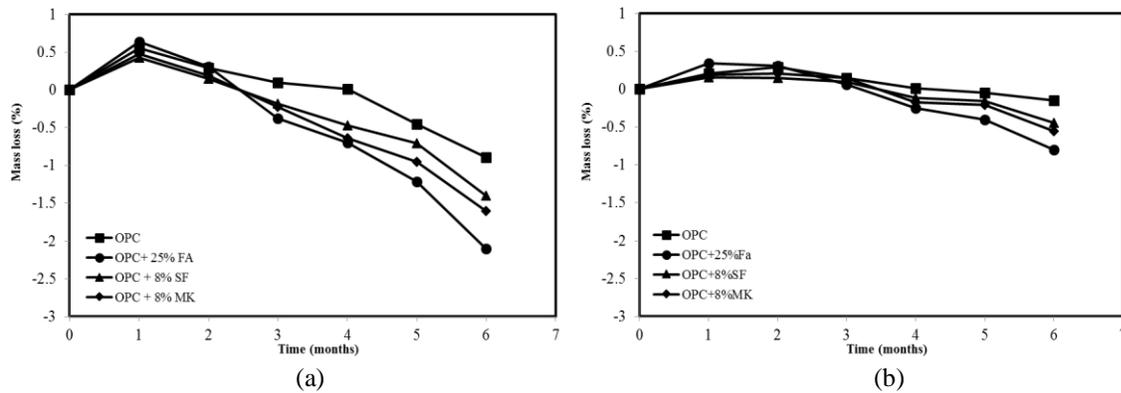


Figure 5: (a) Mass loss for cured concrete cylinders made with w/b = 0.60, (b) Mass loss for cured concrete cylinders made with w/b = 0.45.

After six months, the portion of all concrete cylinders immersed into the sodium sulphate solution was found mostly intact. This finding indicates that the mass loss occurred due to damage of the concrete surface above the solution level. Since the concrete surface above the solution level was exposed to evaporation, supersaturation of the sodium sulphate solution can be reached. Therefore, crystals can grow from the supersaturated solution and generate high tensile stress, leading to damage and mass loss of the concrete above the solution level. In addition, high crystallisation pressure can be achieved through cycling the temperature and RH, resulting in accelerated damage.

Results indicate that the vulnerability of concrete to damage due to physical sulphate attack depends on the pore structure, which is similar to natural stones or rocks. Using pozzolanic minerals in concrete exposed to physical sulphate attack was found to escalate the surface scaling. This finding can be related to the fact that pozzolanic minerals refine the concrete pore structure and increase the volume of pores with smaller diameters. Since pores with smaller diameter tend to increase the capillary rise on the concrete surface, a larger amount of solution will be exposed to evaporation, leading to a higher supersaturation. Thus, salt crystals will grow and apply higher pressure, resulting in larger surface scaling and increased mass loss of the concrete. In case of increasing the w/b, the volume of the pores and their connectivity can be increased, leading to higher capillary rise and increased salt growth on the concrete surface. Therefore, more damage can occur as shown in this study. In addition, it was found that curing the concrete for 28 days led to less surface scaling. This finding can be attributed to the fact that curing the concrete increases the solid volume of the concrete (Mehta and Monteiro, 2006), leading to a decrease in the total volume of the pores and their connectivity.

5. CONCLUSIONS

In this paper, the durability of concrete exposed to an environment prone to physical sulphate attack was investigated. Several conclusions can be drawn based on the results:

- The performance of concrete exposed to physical sulphate attack depends on the concrete's pore structure rather than its chemical composition.
- Reducing the w/b ratio improved the durability of concrete under physical sulphate attack. This can be explained by the fact that reducing the w/b ratio reduces the total volume of the pores and their connectivity, resulting in less capillary rise and surface scaling.
- Moist curing the concrete for 28-days before exposure to physical sulphate attack reduced the damage.
- Partially replacing the ordinary portland cement with pozzolanic minerals escalated the damage from physical sulphate attack since pozzolanic minerals refine the concrete pore structure, leading to higher capillary rise and more surface area for evaporation.

REFERENCES

- Al-Amoudi, O. S. B. 2002. Attack on Plain And Blended Cement Exposed to Aggressive Sulfate Environment. *Cement and Concrete Composites*, 2 (3): 305-316.
- Angeli, M. Benavente, D. Bigas, J. Menendez, B. Hebert, R. and David, C. 2008. Modification of the Porous Network by Salt Crystallization in Experimentally Weathered Sedimentary Stones. *Materials and Structures*, 41 (6): 1091-1108.
- ASTM C192. 2012. Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory. *American Society for Testing and Materials*, West Conshohocken, PA.
- ASTM C511. 2009. Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes. *American Society for Testing and Materials*, West Conshohocken, PA.
- Aye, T. and Oguchi, C. T. 2011. Resistance of Plain and Blended Cement Mortars Exposed to Severe Sulfate Attacks. *Construction and Building Materials*, 25 (6): 2988-2996.
- Buj, O. and Gisbert, J. 2010. Influence of Pore Morphology on the Durability of Sedimentary Building Stones from Aragon (Spain) Subjected to Standard Salt Decay Tests. *Environment Health Science*, 61 (7): 1327-1336.
- Folliard, K. J. and Sandberg, P. 1994. Mechanisms of Concrete Deterioration by Sodium Sulfate Crystallization. V.M. Malhotra (Ed.), *3rd CANMET/ACI International conference on durability of concrete*, Nice, France (SP-145), American Concrete Institute, Detroit, MI. 933-945
- Haynes, H. O'Neill, R. Neff, M. and Mehta, P. K. 2008. Salt Weathering Distress on Concrete Exposed to Sodium Sulfate Environment. *ACI Materials Journal*, 105 (1): 35-43.
- Hime, W. G. 2003. Chemists Should Be Studying Chemical Attack On Concrete. *Concrete International*, 25 (4): 82-84.
- Hime, W. G. Martinek, R. A. Backus, L. A. and Marusin, S. L. 2001. Salt Hydration Distress. *Concrete International*, 23 (10): 43-50.
- Irassar, E. F. Di Maio, A. and Batic, O. R. 1995. Sulfate Attack on Concrete with Mineral Admixtures. *Cement and Concrete Research*, 26 (1): 113-123.
- Malhotra, V. M. Carette, G. and Bremner, T. 1987. Durability of Concrete Containing Supplementary Cementing Materials in Marine Environment. *ACI Special Publication*, 100: 1227-1258.

- Nehdi, M. and Hayek, M. 2005. Behavior of Blended Cement Mortars Exposed to Sulfate Solutions Cycling in Relative Humidity. *Cement and Concrete Research*, 35 (4): 731-742.
- Nehdi, M. Suleiman, A. R. and Soliman, A. M. 2014. Investigation of Concrete Exposed to Dual Sulfate Attack. *Cement and Concrete Research*, 64: 42-53.
- Novak, G. K. and Colville, A. A. 1989. Efflorescent Mineral Assemblages Associated With Cracked and Degraded Residential Concrete Foundations in Southern California. *Cement and Concrete Research*, 19 (1): 1-6.
- Scherer, G. W. 2004. Stress from Crystallization of Salt. *Cement and Concrete Research*, 34 (9): 1613-1624.
- Suleiman, A. R. Soliman, A. M. and Nehdi, M. 2014. Effect of Surface Treatment on Durability of Concrete Exposed to Physical Sulfate Attack. *Construction and Building Materials*, 73: 674-681.
- Thaulow, N. and Sahu, S. 2004. Mechanism of Concrete Deterioration Due to Salt Crystallization. *Materials Characterization*, 53 (2-4): 123-127.
- Tsui, N. Flatt, R. J. and Scherer, G. W. 2003. Crystallization Damage by Sodium Sulfate. *Journal of Cultural Heritage*, 4 (2): 109-115.
- Wellman, H. W. and Wilson, A. T. 1965. Salt Weathering, a Neglected Geological Erosive Agent in Coastal and Arid Environments. *Nature*, 205: 1097-1098.
- Yoshida, N. Matsunami, Y. Nagayama, M. and Sakai, E. 2010. Salt Weathering in Residential Concrete Foundation Exposed to Sulfate-Bearing Ground. *Journal of Advanced Concrete Technology*, 8 (2): 121-134.